Environmental Measurement Symposium

"Protecting Human Health Through Environmental Measurement and Monitoring"

PROCEEDINGS

San Antonio, Texas
August 5 – 9, 2013

Symposium Sponsors





Agilent Technologies







PerkinElmer®
For the Better

Thank you
to all the volunteers who donate their time to make the Symposium a success!

NEMC

Conference Chair
Lara Phelps, USEPA OSA

Symposium Organizer
Jerry Parr, The NELAC Institute

Program Chair
Earl Hansen, The NELAC Institute

Program Manager
Ilona Taunton, The NELAC Institute

Steering Committee
Dan Hautman, USEPA OW
Joe Konschnik, Restek Corporation
Judy Morgan, Environmental Science Corporation

Session Chairs
Kesavalu Bagawandoss, Accutest Laboratories
Robert Benz, BTLIMS Ltd.
Mark Bruce, TestAmerica, Inc.
Scot Cocanour, Promium
Nancy Copeland, Environmental Express, Inc.
Andy Eaton, Eurofins Eaton Analytical
Michael Flournoy, Microbac
Deb Gaynor, Phoenix Chemistry Services
Zoe Grosser, Horizon Technology
Reza Karimi, Battelle Memorial Institute
Kory Kelly, Phenomenex
David Kennedy, Phenomenex
Kitty Kong, Chevron Energy Technology Company
Joe Konschnik, Restek Corporation
William Lipps, OI Analytical / Xylem, Inc.
George Lucier, Battelle Memorial Institute
Ray Martrano, Seewald Laboratories
Pat McIsaac, TestAmerica, Inc.
Marlene Moore, Advanced Systems
Stu Nagourney, New Jersey DEP
Jeff Pritt, USEPA Region 7
Joe Romano, Waters Corporation
Patsy Root, IDDEX Laboratories
Matt Sica, ACLASS
David Speis, QC Laboratories, Inc.
David Thal, Environmental Standards
Kim Watson, Stone Environmental
Nicola Watson, Markes International
Lem Walker, USEPA OW
Robert Wyeth

The NELAC Institute

Board of Directors
Jordan Adelson, US Navy
Joe Aiello, New Jersey DEP
Aaren Alger, Pennsylvania DEP
Steve Arms, Florida DOH
Brenda Bettencourt, USEPA Region 9
Brooke Connor, US Geological Survey
George Detsis, US Department of Energy
Judith Duncan, Oklahoma DEQ (retired)
Zonetta English, Louisville and Jefferson County
Jack Farrell, Analytical Excellence
Keith Greenaway, ACLASS
Sharon Mertens, City of Milwaukee
Judy Morgan, Environmental Science Corporation
Patsy Root, IDEXX Laboratories
Matt Sica, ACLASS
Scott Siders, Illinois EPA
Alfredo Sotomayor, Wisconsin DNR
Dave Speis, QC Laboratories
Elizabeth Turner, North Texas Municipal Water District
Susan Wyatt, Minnesota DOH

Committee Chairs
Aaren Alger, Pennsylvania DEP
Steve Arms, Florida DOH
Justin Brown, Environmental Monitoring and Technology
Richard Burrows, TestAmerica, Inc.
Robin Cook, City of Daytona Beach
Jeff Flowers, Flowers Laboratories
Maria Friedman, TestAmerica, Inc.
John Kuhn
Paul Junio, Northern Lake Service
Stacie Metzler, Hampton Roads Sanitation District
Mitzi Miller, Dade Moeller, Inc.
Judy Morgan, Environmental Science Corporation
Bob Shannon, QRS
Alfredo Sotomayor, Wisconsin DNR
Kim Watson, Stone Environmental
Robert Wyeth

TNI Staff
Jerry Parr, Executive Director
Lynn Bradley, Program Administrator
Carol Batterton, Program Administrator
William Daystrom, IT Administrator
Dan Hickman, Database Administrator
Joel Holtz, Exhibit Coordinator
Ken Jackson, Program Administrator
Kay Parr, Meeting Planner
Suzanne Rachmaninoff, Meeting Support
Ilona Taunton, Program Administrator

NEMC 2013

CONFERENCE HIGHLIGHTS

The 29th Annual National Environmental Monitoring Conference (NEMC) was held this year at the Hyatt Regency, San Antonio TX from August 5 – 9, 2013, in conjunction with the Forum on Laboratory Accreditation Conference. This year's symposium theme was ***"Protecting Human Health through Environmental Measurement and Monitoring"***. Some of the week's highlights included:

- A special half-day session providing perspectives on shale gas exploration;
- Over 175 technical presentations and posters on a variety of cutting-edge environmental monitoring issues;
- Meeting of The NELAC Institute (TNI) Committees to further TNI efforts on environmental laboratory accreditation, proficiency testing, and accreditation of field sampling and measurement organizations;
- An exhibit program showcasing the latest innovations in environmental monitoring;
- Three technical training courses on a variety of topics;
- Three special keynote presentations on topics of general interest; and
- An open meeting of the U.S. Environmental Protection Agency's Environmental Laboratory Advisory Board.

NEMC is the largest conference focused on environmental measurements in North America and is co-sponsored by The NELAC Institute (TNI) and the U.S. Environmental Protection Agency (USEPA). The technical program is organized by a committee of environmental experts to bring together a balance of technical and policy topics that are of interest to all. The conference was initiated in 1985 as part of EPA's efforts to foster a partnership among the Agency, the regulated community, the public, state regulatory agencies, and the other members of the monitoring community.

NEMC 2013 PROCEEDINGS

TABLE OF CONTENTS

SECTION **PAGE #**

1. KEYNOTE & LUNCH PRESENTATIONS 16

Linking Low-Dose Exposure of Environmental Contaminants to Health Effects (presentation) 17
Dr. Linda Birnbaum; National Institute of Environmental Health Sciences (NIEHS)

Changing the Paradigm of Air Pollution Monitoring… Opportunities and Challenges (presentation) 28
David Shelow; EPA OAQPS, et al

EPA's Scientific Integrity Policy (presentation) 40
Anand Mudambi; USEPA, Office of the Science Advisor

2. ACADEMIC RESEARCH TOPICS IN ENVIRONMENTAL MEASUREMENT AND MONITORING 52

Fully Automated On-line SPE Coupled to LC MS/MS for Rapid, Sensitive, and Simultaneous Analysis of Multiple PPCPs in Water (abstract; presentation) 53
Tarun Anumol, Sheher Mohsin, Sylvain Merel, Shane A. Snyder; University of Arizona Department of Chemical & Environmental Engineering

Agricultural Air Quality: Measurements, Monitoring, and Modeling (abstract, presentation) 74
Viney P. Aneja; North Carolina State University Department of Marine, Earth, and Atmospheric Sciences

Early Engagement of University Undergraduate Students in Environmental Monitoring (abstract, presentation) 97
B.H. Kiepper, C.W. Ritz; University of Georgia Department of Poultry Science

Low Impact Design as a Supportive Measure for Non Point Source Management (abstract, presentation) 116
Afamia Elnakat; UTSA Texas Sustainable Energy Research Institute

3. CONTAMINATED SEDIMENTS 129

Considerations for Grain Size Analysis of Sediment (abstract, presentation) 130
Christine Mott Frans; EcoChem, Inc.

Asbestos in Soil - Assessing Risk (abstract, presentation) 144
Ed Cahill; EMSL Analytical, Inc.

Passive Sampling for Sediment Pore-Water (abstract, presentation) 174
James Whetzel; Amplified Geochemical Imaging, LLC

Extraction of Total and Methyl Mercury from a DGT (abstract, presentation) 188
Ray Shock; TestAmerica

Analysis of Semi-Volatile Compounds in Marine Sediment by GC/MS-MS *(abstract, presentation)* 199
Gregory Perez; City of Tacoma Environmental Services Laboratory

4. FIELD MEASUREMENTS, SENSORS, AND IN-SITU MONITORING 224

Micro-AirCore: Spatial Mapping of Atmospheric Species (abstract, presentation) 225
Kristin Favela, Pieter Tans, Tom Jaeckle, William Williamson; Southwest Research Institute

Considerations for the Collection of Solid Samples for Volatile Organic Analysis in an Arctic Environment: Frozen Cores and More (abstract, presentation) 239
Lester J. Dupes, Rock J. Vitale, Steven J. Lennon, Joseph P. Kraycik; Environmental Standards

Maximizing the Value of Existing Monitoring Technologies: Stream Temperature and Dissolved Oxygen as Best Case Examples (abstract, presentation) 249
Bob Rose; USEPA Office of Water

NEMC 2013 PROCEEDINGS
TABLE OF CONTENTS cont.

SECTION **PAGE #**

In-Situ Simultaneous Monitoring of Water Stage and Water Quality Using Fiber Optic Sensors (abstract, presentation) 260
Dr. Ying Huang; North Dakota State University Civil Engineering Department

Accelerated Remediation at a Region 1 Residential Clean-up Site Using PHILIS On-site Analytical Laboratories *(abstract, presentation)* 272
Lawrence Kaelin, Erica Canzler, and Michael Nalipinski; USEPA Region 1 OSC
Julie Capri and Alex Bleich; CSC-Dynamac Corp

Comparison of Field Operations Guidelines with NEFAP (abstract, presentation) 286
Marlene Moore; Advanced Systems Inc.

5. HISTORY OF ENVIRONMENTAL MONITORING 297

Pre- and Early EPA Monitoring (abstract, presentation) 298
Lawrence H. Keith

And They Said It Couldn't Be Done: A Brief History of Environmental Water Monitoring (abstract, presentation) 316
William Telliard; USEPA (retired)

History of the EPA Solid Waste Methods Program (SW-846) (abstract, presentation) 334
David Friedman

The Evolution of Instrumentation for Environmental Monitoring (abstract, presentation) 344
David C. Kennedy; Phenomenex

The Evolution of Quality Assurance & Quality Control in Environmental Laboratories (abstract, presentation) 357
David Speis; QC Laboratories

History and Future of Laboratory Accreditation (abstract, presentation) 369
Jerry Parr; The NELAC Institute

6. MONITORING PESTICIDES IN THE ENVIRONMENT: PAST, PRESENT, AND FUTURE 388

A Study of Cross-Industry Pesticide Analysis in the US and Abroad (abstract, presentation) 389
Kory Kelly; Phenomenex

Collaborative Opportunities for Analytical Method Development (abstract, presentation) 400
Lara Phelps; U.S. EPA Office of the Science Advisor

SDWA Perspective on Pesticide Monitoring (abstract, presentation) 413
Andrew Eaton; Eurofins Eaton Analytical Inc.

Monitoring Pesticides in the Environment: Past, Present and Future (abstract, presentation) 427
Shen-yi Yang; U.S. EPA Office of Resource Conservation and Recovery

Pesticide Analysis: Now and in the Future? (abstract, presentation) 433
Robert Wyeth

Changes in Technical Innovation and Customer Expectations Associated with the Use of LC-MS to Solve Challenges Encountered whilst Ensuring Food and Environmental Safety (abstract, presentation) 447
Simon Hird; The Food and Environment Research Agency

The Analysis of Environmental Pesticides in Asia (abstract, presentation) 475
Kory Kelly; Phenomenex

NEMC 2013 PROCEEDINGS
TABLE OF CONTENTS cont.

SECTION **PAGE #**

The FDA Perspective (abstract, presentation) 488
Chris A. Sack; Food and Drug Administration

Environmental Monitoring: Where Will Technology Be in 10 Years? (abstract, presentation) 509
Paul Winkler; AB Sciex

7. TOPICS IN SHALE GAS EXPLORATION 521

Challenges of Managing Water in the Marcellus Play (abstract, presentation) 522
Nick Inkenhaus; Range Resources

Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania (abstract, presentation) 534
Shahla Farhat; GSI Environmental Inc.

Quality and Legal Issues Associated with Unconventional Drilling (abstract, presentation) 547
David A. Gratson, Rock J. Vitale; Environmental Standards
Brian J. Clark; Buchanan Ingersoll & Rooney PC

Environmental Forensic Investigation of Hydraulic Fracturing Fluids Used in Shale Gas Wells in the Eastern United States *(abstract, presentation)* 564
Frank L. Dorman, Jessica Westland, Nathaniel Girer; Penn State University

A Survey of Telemetry-Enabled Sensors for Onsite Characterization of Flowback Water from Hydraulic Fracturing (abstract, presentation) 589
Sayan Chakraborti, MRI Global, et al

Baseline and Impact Monitoring for Shale Gas Exploration Constituents (abstract, presentation) 601
Andrew Pawlisz; Conestoga-Rovers & Associates

Challenges in Microbial Assays of Produced Waters (abstract, presentation) 613
Keith McLeroy; Schlumberger

Applied Ion Analysis of Various Water Matrices in Hydraulic Fracturing Process (abstract, presentation) 623
Jay Gandhi; Metrohm USA

8. MODELING, MAPPING, AND GEOSPATIAL TOOLS 654

Pre-Serve Mapping Tool to Help Protect Endangered Plant Species (abstract, presentation) 655
David J. Healy; Stone Environmental Inc.

Detection of Melt Pond from Aerial Photos through Object-Based Image Classification Scheme (abstract, presentation) 660
Xin Miao, Missouri State University Department of Geography, Geology and Planning, et al

California Pesticide Use Reporting and Mapping Tool (abstract, presentation) 675
David Healy; Stone Environmental Inc.

9. SPOTLIGHT ON METHOD 8270 INSTRUMENTATION 680

Agilent GC/MS Hardware, Software, and Consumables Optimized for the Analysis of US EPA Method 8270 (abstract, presentation) 681
Fred Feyerherm; GCMS Applications

NEMC 2013 PROCEEDINGS

TABLE OF CONTENTS cont.

SECTION **PAGE #**

Meeting Requirements for USEPA Method 8270 Using a Highly Sensitive, Robust, and Easy-to-Use GC/MS (abstract, presentation) 694
Ed George; Bruker Corporation

Optimizing EPA Method 8270: PerkinElmer Clarus SQ8 Gas Chromatograph/Mass Spectrometer (GC/MS)… Meeting the Challenges and Optimizing Results and Profitability (abstract, presentation) 714
Lee Marotta; PerkinElmer

USEPA Methods 8270D and 8260C on a Single GCMS without Changing Columns (abstract, presentation) 733
Laura Chambers, Richard Whitney, Clifford Taylor; Shimadzu Scientific Instruments, Inc.

From Helium to Hydrogen: GC-MS Case Study on SVOCs in Water (abstract, presentation) 747
Dwain Cardona; Thermo Fisher Scientific

10. AIR METHODS/MONITORING: COMPLIANCE MONITORING AND REGULATORY ISSUES 775

USEPA's Technology Innovation Network: Evaluating Pilot Projects on Air Sensors and Monitoring (abstract, presentation) 776
Anand Mudambi, Martha Otto, Matt Hoagland; USEPA

Environmental Protection Agency's National Radiation Air Monitoring Network (presentation) 786
Daniel Askren; National Analytical Radiation Environmental Laboratory

Evolution of Ozone Precursor Measuring and the PAMs Project from 1992 to Present (abstract, presentation) 804
Lee Marotta; PerkinElmer

A Comparison of Various Design and Operational Approaches to Site Remediation Perimeter Air Monitoring Programs (abstract, presentation) 825
Melissa Wellman; AECom

The Stationary Source Audit Sample Program Central Database (abstract, presentation) 836
Maria Friedman

Implementation Experience with ASTM D7036: What Emission Testing Firms, Accreditation Bodies, Regulators, and the Regulatory Community Need to Know (abstract, presentation) 849
David L. Elam, Jr.; Summa Consultants Inc./Stack Testing Accreditation Council, Inc.

Method 0023A: A Healthier PBMS Alternative Know (abstract, presentation) 863
Yves Tondeur, SGS Analytical Perspective, et al

11. CURRENT TOPICS IN MICROBIOLOGY 879

Method Development for Detection of Biothreat Agents from Environmental Samples (abstract, presentation) 880
Tonya Nichols; US EPA

Predicting Water Quality at Ohio Beaches Using qPCR (abstract, presentation) 894
Mark Citriglia; Northeast Ohio Regional Sewer District

Approaches to the Detection of Fecal Coliforms (abstract, presentation) 908
Colin Fricker; CRF Consulting Ltd.

OMG…. I got a finding! Now what? (abstract, presentation) 916
Robin Cook; City of Daytona Beach EML

What Are the Critical Elements in the Microbiology Laboratory? (abstract, presentation) 932
Margo E. Hunt

NEMC 2013 PROCEEDINGS
TABLE OF CONTENTS cont.

SECTION **PAGE #**

Auditing Laboratories for Cryptosporidium and Giardia (abstract, presentation) 955
Debra Waller; NJDEP – Office of Quality Assurance

Improvement to Method 1623 to Detect Cryptosporidium and Giardia (abstract, presentation) 965
Leah Villegas; CB&I Federal Services

12. LEGAL DEFENSIBILITY OF DATA 981

Legal Defensibility Is an Oxymoron (abstract, presentation) 982
Jerry Parr; Catalyst Information Resources

Data Management: Ensuring Our Data Is Ethical and Legally Defensible (abstract, presentation) 997
JoAnn Boyd; Southwest Research Institute

The Data User's Guide to Producing Legally Defensible Environmental Data (abstract, presentation) 1021
Christina Hiegel; Trihydro Corporation

Enabling Data Defensibility and Laboratory Productivity Using a Laboratory Execution System (abstract, presentation) 1038
Kathy Smith; The Narragansett Bay Commission

The Other Half of Your Lab Result (abstract, presentation) 1057
Bryan Vining; SGS Analytical Perspectives

How to Choose a Laboratory that Will Meet Your Data Assessment and Testing Needs? (abstract, presentation) 1072
Kim Watson; Stone Environmental, Inc.

Data Validation, Usability and Defensibility (abstract, presentation) 1085
Kesavalu Bagawandoss; Accutest Laboratories

13. AIR METHODS/MONITORING: MONITORING, METHODS, AND TECHNOLOGY 1095

Alternate Method 25Z for Accurate VOC Emission Measurements (abstract, presentation) 1096
Charles Simon; VOC Reporting, Inc.

Recent Developments in SO3 Source Emission Testing Methods (abstract, presentation) 1110
David Ostaszewski; O'Brien and Gere

Seasonal Variability of Nitro-PAHs and PAHs in Ambient Air Samples Taken Close to a Major Highway in Toronto, Canada (abstract, presentation) 1120
Shawn Heier; Maxxam

Mil-53(Al) as a Sorbent for Large Volume Air-Sampler for Chemical Warfare Agents (abstract, presentation) 1133
Bill Williamson; Southwest Research Institute

Evaluation of an Automated Continuous Air Sampling System for Vapor Intrusion (abstract, presentation) 1145
Kyle Hunt; Signature Science

Mobile Monitoring to Locate and Quantify Open Source Emission Plumes (abstract, presentation) 1155
Chatten Cowherd; MRI Global

On-Site Real-Time Air Monitoring for Chemical Emergencies (abstract, presentation) 1170
Dominic Lortie; Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ)

NEMC 2013 PROCEEDINGS

TABLE OF CONTENTS cont.

SECTION **PAGE #**

14. FORENSIC CHEMISTRY 1194

Fingerprinting of Crude Oil Spill Sources (abstract, presentation) 1195
Kesavalu Bagawandoss; Accutest Laboratories

The Added Value of Utilizing Stable Isotopes in Environmental Forensics (abstract, presentation) 1213
Paul Philp, Tomasz Kuder and Jon Allen; University of Oklahoma School of Geology and Geophysics

Analysis of Alkyl PAHs, Geochemical Biomarkers for Fingerprinting Petroleum Products (abstract, presentation) 1235
Charles Neslund; Eurofins Lancaster Laboratories

Dominguez Channel: A Petroleum Spill in Pipeline Alley (abstract, presentation) 1254
Alan Jeffrey; DPRA/Zymax Forensics

Isotopic Forensic Techniques for Methane Source Descrimination (abstract, presentation) 1270
Julie K. Sueker, George H. Cramer; ARCADIS

Extraction of Contaminant Source Information from Site Investigation Data *(abstract, presentation)* 1291
Jun Lu; AECom

15. OPERATIONAL AND ADVOCACY ISSUES IMPACTING THE ENVIRONMENTAL LABORATORY INDUSTRY .. 1300

Third Party NELAP Accreditation -- The Time Has Arrived (abstract, presentation) 1301
Bruce Godfrey; Curtis & Tompkins Laboratories

Public/Private Partnerships to Improve Environmental Monitoring and Compliance (abstract, presentation) 1312
JoAnn Slavin; H2M Labs

Tools for Managing an Environmental Laboratory Program (abstract, presentation) 1324
John Phillips, Ford Motor Company and Jim Tomalia, Enovis, Inc.

The Effect of Method Flexibility on Efficiency Improvements, Waste Reduction, and Supplies Conservation (abstract, presentation) 1350
J.D Gentry; ESC Lab Sciences

A New GC/MS System Designed for Helium Carrier Gas Conservation (abstract, presentation) 1365
Dale Walker; Agilent Technologies

Acrolein, Acrylontrile, Styrene, and Vinyl Chloride; Acid Reactive Compounds or Not? (abstract, presentation) 1385
Stephen Zeiner; Environmental Standards

Document Control and Document Archival Procedures (abstract, presentation) 1402
Catherine Katsikis; Laboratory Data Consultants FL, Inc.

16. ADVANCES IN SAMPLE PREPARATION AND CLEAN-UP 1423

Productivity Enhancements in Microwave Assisted Extractions (EPA Method 3546) of Semi Volatile Organic Compounds (SVOCs) from Environmental Samples (abstract, presentation) 1424
Sumedh Phatak; Milestone Inc.

Simultaneous Extraction of PAHs and PCBs from Tissue and Soil Samples Using a New Accelerated Solvent Extraction (ASE) Procedure (abstract, presentation) 1438
Richard Jack; Thermo Fisher Scientific

SECTION **PAGE #**

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) Extraction Approach and Comprehensive Two - Dimensional Gas Chromatography of Persistent Organic Pollutants in Human Breast Milk (Advances in Sample Preparation and Clean-up) (abstract, presentation) 1456
Christopher Rattray; Restek

How Solid Phase Chemistries Are Enabling Broader Adoption of SPE in Environmental Applications (abstract, presentation) 1475
Kory Kelly; Phenomenex

Recent Advances in Solid Phase Extraction for the Determination of a Full Range of Organic Compounds from Challenging Samples (abstract, presentation) 1488
David Gallagher; Horizon Technology

Rapid Concentration of Pathogens in Liquid Samples (abstract, presentation) 1508
Ann Packingham; InnovaPrep

17. ANALYSIS OF METALLIC SPECIES AND ORGANOMETALLICS 1525

Evaluation of Preservation and Holding Time Requirements for Hexavalent Chromium to Meet Data Quality Objectives for a Logistically Challenged Site (abstract, presentation) 1526
Ruth Forman; Environmental Standards, Inc.

Cr(VI) Extraction Method for COPR-Contaminated Soils (presentation) 1540
Stuart J. Nagourney, Retired; NJ Department of Environmental Protection

Application of Selenium Speciation Analysis to Elucidate Limitations with Accepted Total Selenium Methods (abstract, presentation) 1553
Russell Gerads; Applied Speciation and Consulting

Elemental Speciation as Essential Part of Formulating Exposure Assessments that Support Risk Estimates (abstract, presentation) 1570
Jack Creed; USEPA, Office of Research and Development

Multifaceted Approach to Arsenic Speciation Analysis of Plant and Animal Tissue (abstract, presentation) 1579
Russell Gerads; Applied Speciation and Consulting

Advances in Interference Removal for Accurate Arsenic Analysis in Food and Beverages (abstract, presentation) 1592
Steven Wilbur; Agilent Technologies

18. COLLABORATIVE EFFORTS TO IMPROVE ENVIRONMENTAL MONITORING 1614

Automated In-line Digestion and Analysis of Total Phosphorous (TP) and Total Nitrogen (TN) in Environmental Water Samples (abstract, presentation) 1615
William Lipps; OI Analytical

Simplified Method for the Determination of Total Kjeldahl Nitrogen in Water and Wastewater (abstract, presentation) 1644
Cary Jackson; Hach Company

Proposed Updates to the 40CFR Part 136 MDL Procedure (abstract, presentation) 1656
Richard Burrows; TestAmerica

Collaborative Efforts for Creating a Robust Trace Metals Analytical Procedure for Flue Gas Desulfurization Wastewater by ICP-M (abstract, presentation) 1670
Stan Smith and Ewa Pruszkowski; PerkinElmer, Inc.

SECTION PAGE #

Expanded Clarification of Oil and Grease in Part 136 (abstract, presentation) 1684
Joseph Stefkovich; Xenosep Technologies

CWA and Degradation Product Analysis for Matrix-Specific Environmental Samples (abstract, presentation) 1697
Stuart Willison; USEPA, National Homeland Security Research Center

19. DATA MANAGEMENT 1712

Optimized Data Review and Management Tools (abstract, presentation) 1713
Nazy Abousaeedi; DatAssess Offering, CDC and Michael S. Johnson; USEPA HQ

Reconciling EPA Approved Methods in a Database (abstract, presentation) 1727
Daniel Hickman; The NELAC Institute

Understanding End-Users' Approaches to Ensuring the Quality of Environmental Data (abstract, presentation) 1748
Christina Hiegel; Trihydro Corporation

Web-based Chain of Custody Service & LIMS Integration (abstract, presentation) 1759
Scot Cocanour; Promium

Managing Environmental Monitoring Information in Cloud (abstract, presentation) 1766
Neno Duplan; Locus Technologies

Making Informed Decisions through LIMS Data Exploration and Visualization (abstract, presentation) 1792
John Nobles; PerkinElmer, Inc.

20. AIR METHODS/MONITORING: INDOOR AIR QUALITY AND VAPOR INTRUSION 1815

The Use of "Green" Thermal Techniques to Simplify Analyses for the Protection of Human Health (abstract, presentation) 1816
Ben Peters; CDS Analytical

Calibration of Adsorbent Based Passive Vapor Samplers for Concentration Reporting in Air, Soil Gas, and Water for Vapor Intrusion Investigations (abstract, presentation) 1836
James Whetzel, et al; Amplified Geochemical Imaging, LLC

New Hampshire Mold Task Force Standard of Care (abstract, presentation) 1855
Guy Sylvester; Absolute Resource Associates

Analysis of Particulate and Vapor Phase Semi-Volatile Organic Compounds in Indoor Air Using Thermal Desorption Gas Chromatography-Mass Spectrometry (abstract, presentation) 1877
Heidi Hayes, et al; Eurofins Air Toxics, Inc.

Developing a National Standard for Health Based Emissions (abstract, presentation) 1890
Jessica Evans, NSF International and Scott Steady, UL Environment

Developing ASTM Standards for Test Specimen Preparation and Measuring Emissions of Volatile and Semi-Volatile Organic Compounds (VOCs and SVOCs) from Spray Polyurethane Foam (SPF) Insulation Products (abstract, presentation) 1900
John Sebroski; Bayer MaterialScience, LLC

NEMC 2013 PROCEEDINGS
TABLE OF CONTENTS cont.

SECTION **PAGE #**

21. LABORATORY ACCREDITATION 1913

When You Cannot Travel to Conduct a Required TNI Audit, What Are Your Options? (abstract, presentation) 1914
Stuart J. Nagourney, Retired; NJ Department of Environmental Protection

The Benefits of a Public/Private Partnership on Laboratory Accreditation (abstract, presentation) 1924
Chris Gunning; A2LA Environmental Services

An Independently Prepared Second Source Lot Reference Material – Where Did This Come From and What Does It Really Mean? (abstract, presentation) 1935
Joseph Konschnik; RESTEK Corporation

Development of a PT National Average (abstract, presentation) 1952
Matthew Sica; ANSI-ASW National Accreditation Board

Difficulties Encountered in Gaining Acceptance of Newly Approved Methodology (abstract, presentation) 1965
William Lipps; OI Analytical

Laboratory Ethics: An Auditor's Perspective (abstract, presentation) 1973
Gary Yakub; Environmental Standards, Inc.

22. TOPICS IN DRINKING WATER 1982

Coconut Charcoal Solid Phase Extraction - Large Volume Splitless Injection - GC-MS for Analysis of Dioxane, Tetrahydrofuran, Nitrosamines, Ethylene Dibromide, Trichloropropane, Dibromochloropropane, Chlorinated Solvents, and Disinfection Byproducts in Drinking Water: The Possibility for a Single Comprehensive Method (abstract, presentation) 1983
Christopher Rattray; RESTEK Corporation

Water and Wastewater Analysis Following Catastrophic Events (abstract, presentation) 2008
Matthew Magnuson; USEPA, Office of Research and Development

Screening Environmental Samples for a Diverse Range of Compound Classes and Structures with Accurate Mass LC-MS and an Integrated Scientific Information System (abstract, presentation) 2024
Kenneth Rosnack; Waters Corporation

Simultaneous Determination of Paraquat and Diquat in Environmental Water Samples by HPLC-MS/MS (abstract, presentation) 2047
Richard Jack; ThermoFisher Scientific

Update in the Development of a Drinking Water Method for the Measurement of Select Organic Contaminants in Drinking Water Using Hydrophilic-Modified Polymeric SPE and GC/MS (abstract, presentation) 2059
Paul Grimmett; USEPA, Office of Research and Development

Ultra-Sensitive Detection of Pharmaceutical and Personal Care Products (PPCPs) in Water with an Integrated On-Line Extraction-UHPLC-MS/MS System (abstract, presentation) 2072
Helen Sun; Bruker Corporation

23. POSTER PRESENTATIONS 2087

A Convenient Alternative for Low Level VOC Sampling (abstract) 2088
Linda Coyne, C. Kuhlman

An Inert Flow Path GC: A Vital New Tool for Trace Environmental Analyses (abstract) 2089
Fred Feyerherm; Agilent Technologies

NEMC 2013 PROCEEDINGS
TABLE OF CONTENTS cont.

SECTION **PAGE #**

Application of Incremental Sampling Methodology to Sediments (abstract, presentation) 2090
Mark Bruce; TestAmerica

Combining Hyperspectral Imaging and LIDAR – New Chances in Environmental Monitoring (abstract) 2094
Toralf Meyer

Determination of 4-Nonylphenol in Biosolids and Biosolids-Applied Soil using SpeedExtractor and GS/MS/MS (abstract) 2095
William Ickes

Development of a State Wastewater Laboratory Certification Program (abstract, presentation) 2096
Franklin Hall

Fully Automating Environmental Analyses Using Inline Autodilution (abstract) 2099
Paul Field

High Throughput Analysis of Hydraulic Fracturing Waste Water (abstract, presentation) 2100
Michael Sgroi

How Much Can a 15m X 0.25mm X 0.10µm GC Column Be Trimmed for Maintenance Before the BDE 49 and 71 Resolution Requirements Are No Longer Met for EPA Method 1614 (abstract) 2103
Christopher Rattray; Restek

Kentucky's Approach to Defining EPA's "Most Sensitive Method" for NPDES Permits (abstract, presentation) 2104
Patrick Garrity

Quantitative and Qualitative Extraction and Determination of Cyanide in Soils and Sediments (abstract, presentation) 2107
William Lipps; OI Analytical

Sinkhole Hazard Assessment Based on In-Situ Monitoring Soil Strain Using BOTDR, TDR, and GPR Techniques (abstract) 2111
Yongli Gao

Summer Surface Albedo Evolution of Arctic Sea Ice –A Case Study from Ice Stations during 4th CHINARE in 2010 (abstract, presentation) 2112
Wentao Xia

SW-846: What You Need to Know (abstract, presentation) 2115
Amy Dahl

Performance of Method 8270 Using Hydrogen Carrier Gas on Bruker SCION GC-MS (abstract) 2117
Ed George; Bruker Corporation

Analysis of PCB Arochlors Utilizing GC Tandem Mass Spectrometry (abstract, presentation) 2118
Dale Walker; Agilent Technologies

Comparison of US EPA 245.7 to ISO 17852 and ISO 12846 Using CVAAS and CVAFS (abstract) 2122
David Clarke

Complete Determination of Acids, Bases, and Neutrals in Water Using Mixed-Mode Solid Phase Extraction for EPA Method 8270 (abstract) 2123
Xiaoyan Wang

Data Quality Screening Using Trend Charts (abstract, presentation) 2124
Roseanne Sakamoto

TABLE OF CONTENTS cont.

SECTION **PAGE #**

Evaluation of a Device for Preparing Calibrated Air Sampling Tubes That Mimics Real Air Sampling Conditions (abstract) 2127
Katherine Stenerson

Evaluation of an Automated Air Sampling System: LESS™ (abstract) 2128
Kyle Hunt; Signature Science LLC

Extraction Methods Versus Phenol Recoveries in a Single-Blind Performance Evaluation Study (abstract, presentation) 2129
Amanda Cover, Environmental Standards

ISO 17025 Accreditation of U.S. National Guard Weapons of Mass Destruction—Civil Support Team Mobile Laboratories (abstract) 2134
Molly Isbell

Reduced Volume Technology: Modernization of Collection & Preparation Techniques in Extractable Organic Analyses (abstract, presentation) 2135
Judith Morgan

Study of Snow Cover Dynamics in Upstream Area of Heihe River Using Time Series MODIS Data (2002–2012) (abstract) 2136
Yunbo Bi

Using Automated Sample Prep to Streamline Laboratory Accreditation (abstract) 2137
Philip Bassignani

Volatiles in Air: Active vs Passive (abstract) 2138
Elizabeth Winger; Calscience Environmental Laboratories, Inc.

24. BIOGRAPHIES 2139

SECTION 1

KEYNOTE AND LUNCH PRESENTATIONS

NIH National Institute of Environmental Health Sciences

Linking Low Dose Exposure of Environmental Chemicals to Health Effects

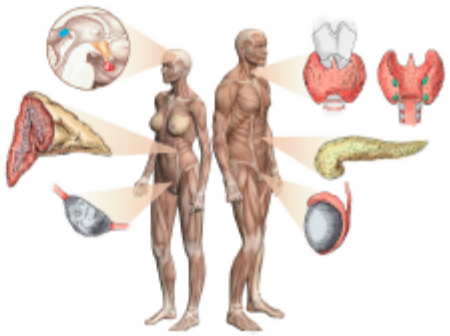
National Environmental Monitoring Conference
San Antonio, TX
6 August 2013

Linda S. Birnbaum, Ph.D., D.A.B.T., A.T.S.
Director
National Institute of Environmental Health Sciences and
National Toxicology Program

NIH National Institute of Environmental Health Sciences

The Endocrine System

- Extremely complex
- Many controls, interacting parts
- Multiple points of regulation for finely-tuned responses
- Sensitive to perturbations
- Naturally operates at low doses

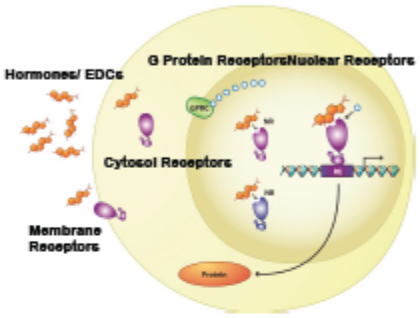


NIH National Institute of Environmental Health Sciences

Hormones and Endocrine Disrupting Chemicals (EDCs)

Endocrine Disruptor: *an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations.* (WHO 2002)

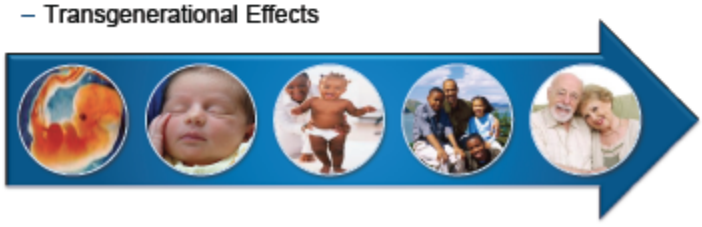
- Highly specific receptor interactions
- Saturation, desensitization
- Cofactor abundance
- Non-specific interactions
- Tissue specific
- Developmentally specific
- Signaling cross-talk



NIH National Institute of Environmental Health Sciences

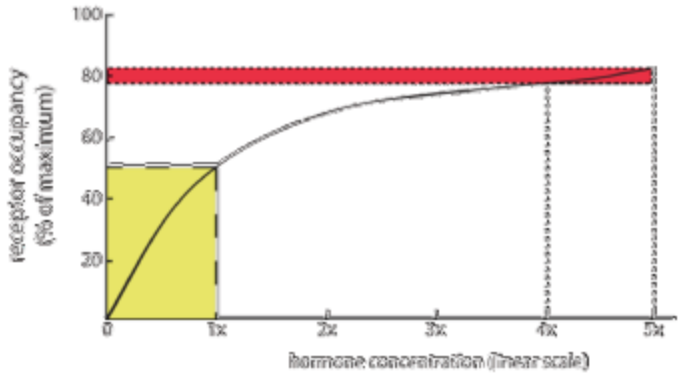
Timing of Exposure is Critical

- Development at each stage in life is fully under the control of hormones
- Changes that occur during development irreversible
- Changes may not be visible early in life, but they will have long-lasting implications
  - DOHaD
  - Epigenetic reprogramming
  - Transgenerational Effects



NIH National Institute of Environmental Health Sciences

Hormones: Small changes can have Big Effects



Vandenberg *et al.* Endo Reviews 2012

NIH National Institute of Environmental Health Sciences

Hormones Act at Very Low Levels

- ***Tiny*** amounts of hormones have profound effects on development and health (ppb-ppt)
- As a result, EDCs have major effects at low doses

Measured adult blood levels of hormones and EDCs

free testosterone (men): 0.04-0.244 ng/ml

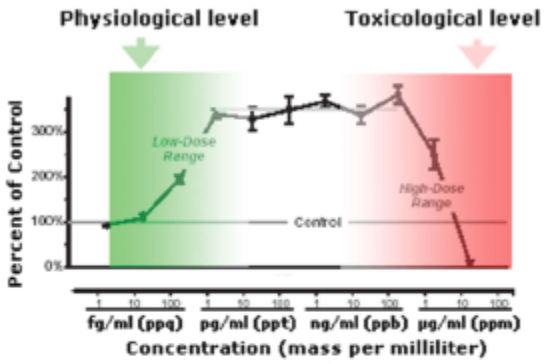
free estradiol (women): 0.05-0.250 ng/ml

PCB180: 0.6 ng/ml

MEP (phthalate): 150-180 ng/ml

NIH National Institute of Environmental Health Sciences

Are toxicologists working in too high of a dose range?



Welshons et al. 2003

NIH National Institute of Environmental Health Sciences

Defining Low Dose

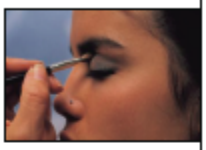
- In 2001, the NTP reviewed the low dose EDC literature. "**Low Dose Effects**" were defined as any biological changes
  - In the range of typical human exposure
  - At doses below the toxicological NOEL
- "**Low Dose Effects**" have also been defined as
  - Changes at doses below the toxicological LOAEL
  - Changes occurring at administered doses that produce blood concentrations measured in humans



NIH National Institute of Environmental Health Sciences

Studies Suggest a need to Revisit the "Low Dose Hypothesis"

- EDCs have effects, especially on reproduction and development, at low doses
- Traditional "high-dose" toxicity studies are not adequate to assess adverse effects from these hormonally active agents
- Effects observed in exposed animals are occurring at doses similar to human exposures (i.e., at doses that are thought to be safe)

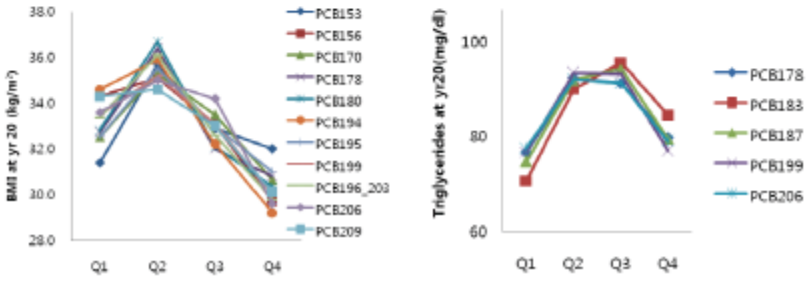





NIH National Institute of Environmental Health Sciences

Low Doses Examples in Humans

Exposure to POPs at low doses may contribute to development of obesity, dyslipidemia, and insulin resistance, common precursors of type 2 diabetes.

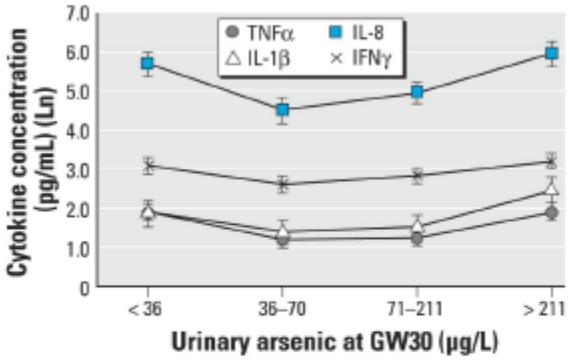


D.K. Lee et al. 2011

NIH National Institute of Environmental Health Sciences

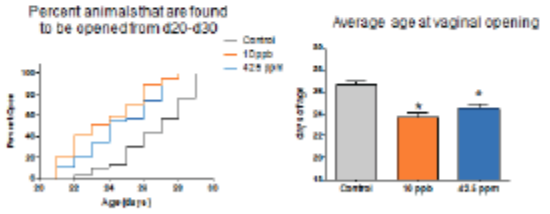
Low Doses Examples in Humans

Arsenic exposure during pregnancy enhances placental inflammatory responses reduce placental T cells, and alter cord blood cytokines.

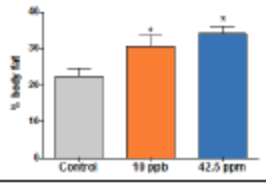


NIH National Institute of Environmental Health Sciences

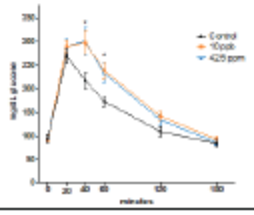
In utero exposure to arsenic results in early vaginal opening



Body fat content is increased after in utero arsenic exposure



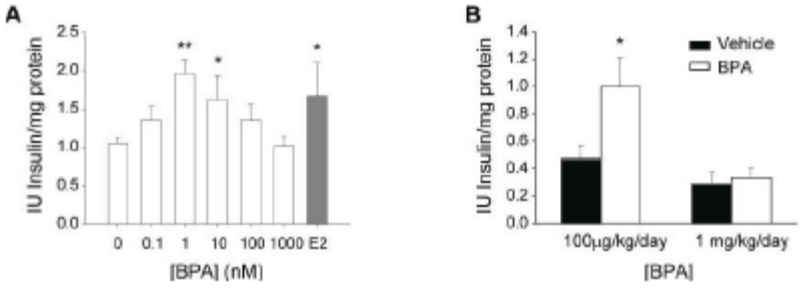
Females exposed to arsenic in utero develop glucose intolerance



Yao and Rodriquez (Pers.Comm.)

NIH National Institute of Environmental Health Sciences

Low Doses of BPA Increase Pancreatic Insulin



In vitro: Insulin content of islet cells treated with BPA for 24 hours.

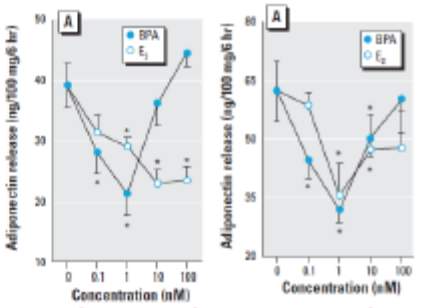
In vivo: Insulin content of islet cells iisolated from mice treated with BPA or vehicle for 4 days..

Alonso-Magdalena, et al., 2006

NIH National Institute of Environmental Health Sciences

Suppression of Adiponectin by BPA and E2 in Human Adipose Explants

- No specific explanation for non-linear dose response
- Non-classical ERs implicated
  - ICI had no effect or suppressed adiponectin
  - BPA and E2 equipotent in suppressing adiponectin
  - Proposed GPR30 and ERRγ involvement



"Typical" dose response by explants from one patient; mean of 6 determinations

"Typical" dose response by explants from one patient; mean of 6 determinations

Hugo et al., 2006

NIH National Institute of Environmental Health Sciences

Joint Low Dose Research Program on BPA

CLARITY-BPA (2011-2015)

FDA Food and Drug Administration
NCTR National Center for Toxicological Research

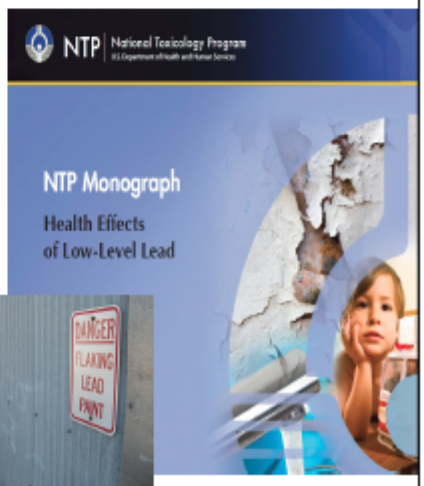
- Consortium Linking Academic and Regulatory Insights on BPA Toxicity
- GLP-compliant study of BPA toxicity in rats
  - Includes developmental exposure
  - ***Broad dose range: 2.5 – 25,000 µg/kg bw/day***
  - 2 doses reference estrogen
- NIEHS, NTP and FDA involved in planning, studying specific disease endpoints

National Toxicology Program

NIH National Institute of Environmental Health Sciences

Low-dose effects go beyond the endocrine system





NIH National Institute of Environmental Health Sciences

Minimal Body or Liver Weight Effects at Low Doses of PFOA

		Control	0.01 mg/kg	0.1 mg/kg	1.0 mg/kg
PND 1	Total Body (g)	1.82 ± 0.11	1.69 ± 0.06	1.77 ± 0.23	1.72 ± 0.06
	Whole Liver (g)	0.079 ± 0.005	0.059 ± 0.004	0.079 ± 0.020	0.095 ± 0.009
	Relative Liver (g)	0.043	0.035	0.045	0.055*
PND 4	Total Body (g)	3.43 ± 0.33	3.39 ± 0.111	-	3.52 ± 0.189
	Whole Liver (g)	0.123 ± 0.005	0.122 ± 0.007	-	0.183 ± 0.016*
	Relative Liver (g)	0.037	0.036	-	0.052*
PND 7	Total Body (g)	6.07 ± 0.24	5.86 ± 0.21	5.87 ± 0.35	5.62 ± 0.23
	Whole Liver (g)	0.218 ± 0.012	0.219 ± 0.015	0.211 ± 0.015	0.286 ± 0.001*
	Relative Liver (g)	0.036	0.037	0.036	0.051*
PND 14	Total Body (g)	11.37 ± 0.55	10.62 ± 0.59	10.60 ± 0.45	11.46 ± 0.51
	Whole Liver (g)	0.449 ± 0.035	0.401 ± 0.036	0.435 ± 0.028	0.551 ± 0.022*
	Relative Liver (g)	0.040	0.038	0.041	0.048*
PND 21	Total Body (g)	16.84 ± 0.72	15.84 ± 0.42	14.55 ± 0.25	15.99 ± 0.49
	Whole Liver (g)	0.887 ± 0.040	0.813 ± 0.031	0.772 ± 0.021	0.904 ± 0.023
	Relative Liver (g)	0.053	0.052	0.053	0.057



NIH National Institute of Environmental Health Sciences

Examples of Low-Dose Effects in Humans

- **Phthalates:** neurobehavior, adult fertility, metabolic syndrome, anogenital distance
- **PBDEs:** thyroid hormone levels, neurodevelopment, autism
- **BPA:** metabolic syndrome, infertility, neurodevelopment
- **DDT:** body weight, cancer, neurodevelopment, oxidative stress
- **Chlorpyrifos:** neurodevelopment, behavior, asthma

NIH National Institute of Environmental Health Sciences

Low Dose Context and Implications

- Different mechanisms and different biological processes occur at different doses
- Timing of exposure is critical. Exposure during development is not comparable to adults
- Phenotypes are often due to the combination of different mechanisms
- Dose responses are different between individuals and populations
- Many animal studies are done in human exposure ranges
- Low dose exposures need to be integrated into RA

NIH National Institute of Environmental Health Sciences

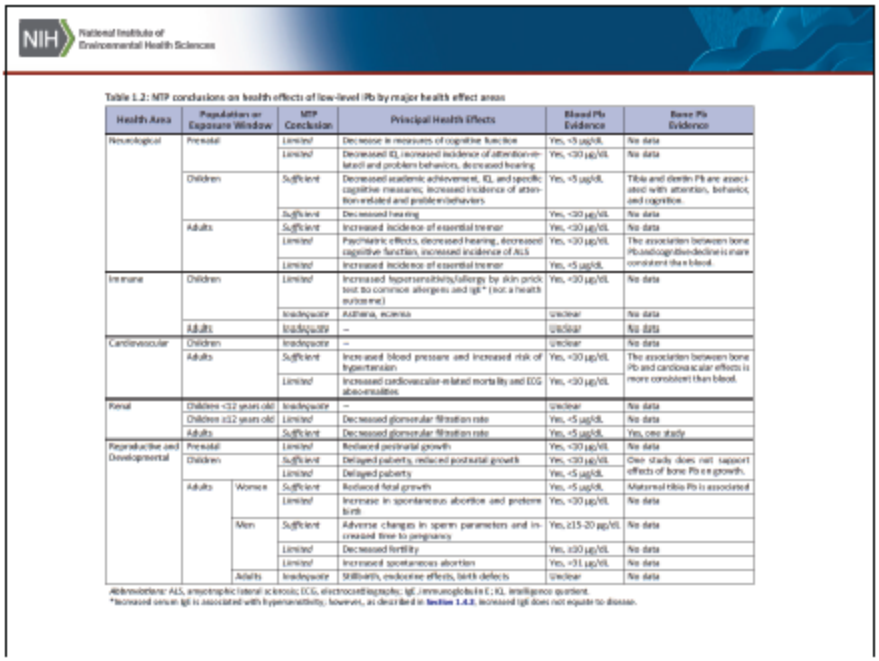
Thank you!

NIH National Institute of Environmental Health Sciences

National Toxicology Program

http://www.niehs.nih.gov





National Institute of Environmental Health Sciences

Table 1.2: NTP conclusions on health effects of low-level Pb by major health effect areas

Health Area	Population or Exposure Window		NTP Conclusion	Principal Health Effects	Blood Pb Evidence	Bone Pb Evidence
Neurological	Prenatal		Limited	Decrease in measures of cognitive function	Yes, <5 µg/dL	No data
			Limited	Decreased IQ, increased incidence of attention-related and problem behaviors, decreased hearing	Yes, <10 µg/dL	No data
	Children		Sufficient	Decreased academic achievement, IQ, and specific cognitive measures; increased incidence of attention-related and problem behaviors	Yes, <5 µg/dL	Tibia and dentin Pb are associated with attention, behavior, and cognition.
			Sufficient	Decreased hearing	Yes, <10 µg/dL	No data
	Adults		Sufficient	Increased incidence of essential tremor	Yes, <10 µg/dL	No data
			Limited	Psychiatric effects, decreased hearing, decreased cognitive function, increased incidence of ALS	Yes, <10 µg/dL	The association between bone Pb and cognitive decline is more consistent than blood.
			Limited	Increased incidence of essential tremor	Yes, <5 µg/dL	
Immune	Children		Limited	Increased hypersensitivity/allergy by skin prick test to common allergens and IgE* (not a health outcome)	Yes, <10 µg/dL	No data
			Inadequate	Asthma, eczema	Unclear	No data
	Adults		Inadequate	--	Unclear	No data
Cardiovascular	Children		Inadequate	--	Unclear	No data
	Adults		Sufficient	Increased blood pressure and increased risk of hypertension	Yes, <10 µg/dL	The association between bone Pb and cardiovascular effects is more consistent than blood.
			Limited	Increased cardiovascular-related mortality and ECG abnormalities	Yes, <10 µg/dL	
Renal	Children <12 years old		Inadequate	--	Unclear	No data
	Children ≥12 years old		Limited	Decreased glomerular filtration rate	Yes, <5 µg/dL	No data
	Adults		Sufficient	Decreased glomerular filtration rate	Yes, <5 µg/dL	Yes, one study
Reproductive and Developmental	Prenatal		Limited	Reduced postnatal growth	Yes, <10 µg/dL	No data
	Children		Sufficient	Delayed puberty, reduced postnatal growth	Yes, <10 µg/dL	One study does not support effects of bone Pb on growth.
			Limited	Delayed puberty	Yes, <5 µg/dL	
	Adults	Women	Sufficient	Reduced fetal growth	Yes, <5 µg/dL	Maternal tibia Pb is associated
			Limited	Increase in spontaneous abortion and preterm birth	Yes, <10 µg/dL	No data
		Men	Sufficient	Adverse changes in sperm parameters and increased time to pregnancy	Yes, ≥15-20 µg/dL	No data
			Limited	Decreased fertility	Yes, ≥10 µg/dL	No data
			Limited	Increased spontaneous abortion	Yes, >31 µg/dL	No data
		Adults	Inadequate	Stillbirth, endocrine effects, birth defects	Unclear	No data

Abbreviations: ALS, amyotrophic lateral sclerosis; ECG, electrocardiography; IgE, immunoglobulin E; IQ, intelligence quotient.
*Increased serum IgE is associated with hypersensitivity; however, as described in Section 1.4.3, increased IgE does not equate to disease.





Changing the Paradigm of Air Pollution Monitoring….Opportunities and Challenges

Presented by David Shelow (EPA OAQPS)
Emily Snyder, Tim Watkins, Eben Thoma, Gayle Hagler, Ron Williams – EPA ORD, and variety of other contributors.

A technology shift is under way……..

Technology advances are supporting a shift toward new ways of measuring and communicating air quality information

- Smartphone / tablet generation
- Miniaturization of sensors
- Lower-cost components
- Easy to use
- Crowd-funding supporting DIY innovation

e.g., fitbit activity tracker





e.g., Arduino microprocessor



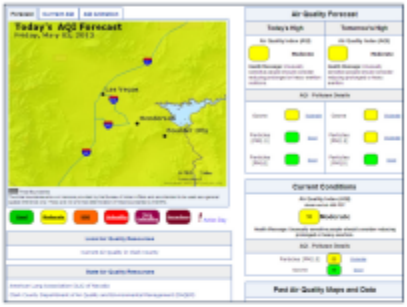


e.g., Kickstarter

2

And a cultural shift is under way

Where we are today: government-provided data, AQI on broad time and spatial scales

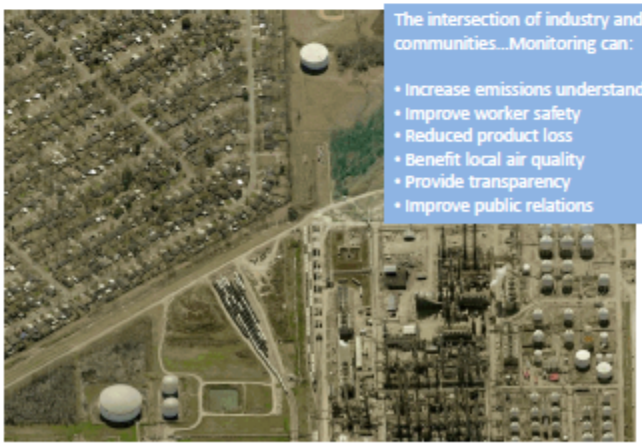


Public demand for more personalized information – what about *my* exposure, *my* neighborhood, *my* child??



3

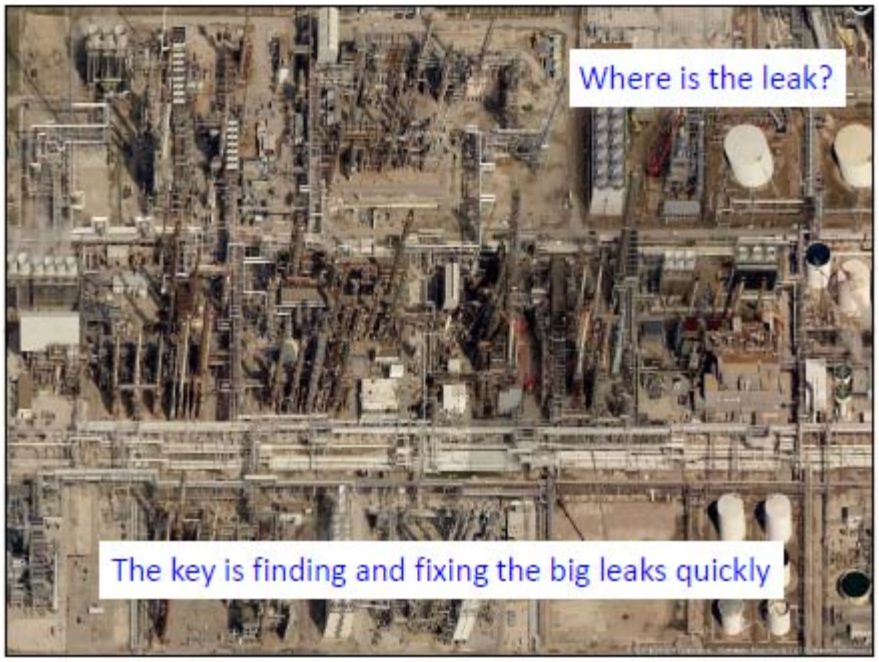
Imagine a different air monitoring landscape…



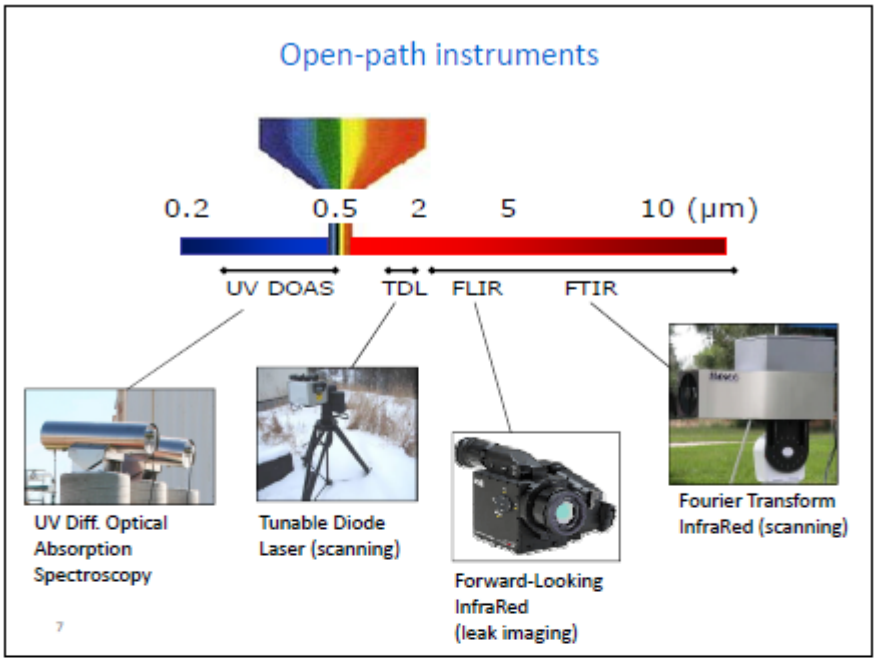
The intersection of industry and communities…Monitoring can:

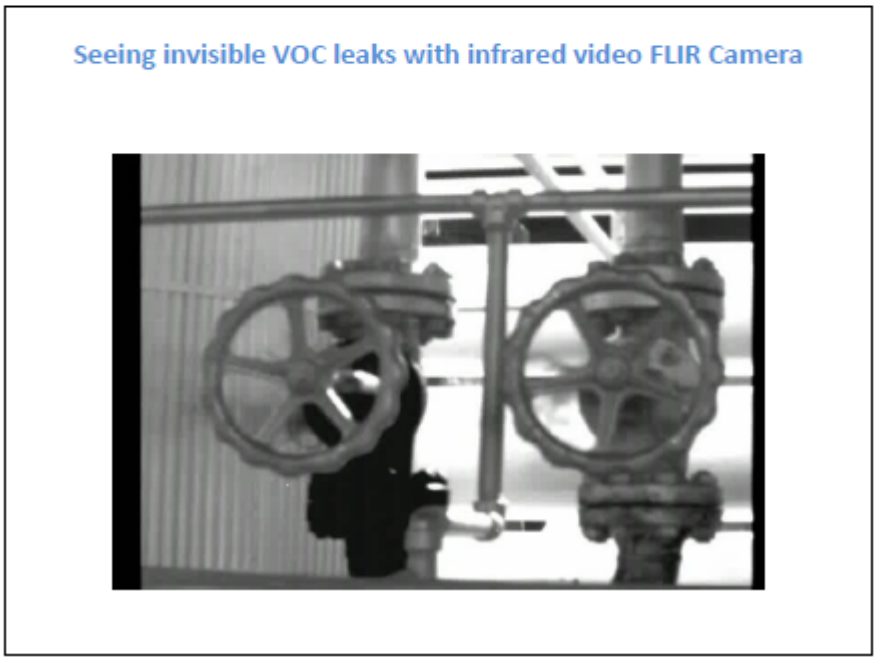
- Increase emissions understanding
- Improve worker safety
- Reduced product loss
- Benefit local air quality
- Provide transparency
- Improve public relations

Neighborhood next to industry…….

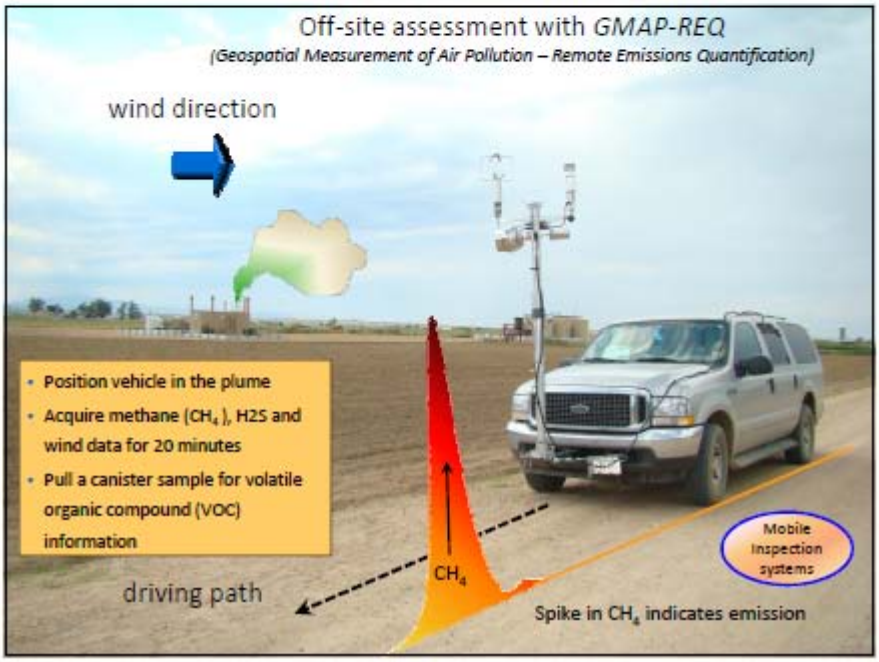

Where is the leak?
The key is finding and fixing the big leaks quickly


Open-path fenceline systems to detect emissions and direct quick response LDAR
Open-path optical systems
Wind

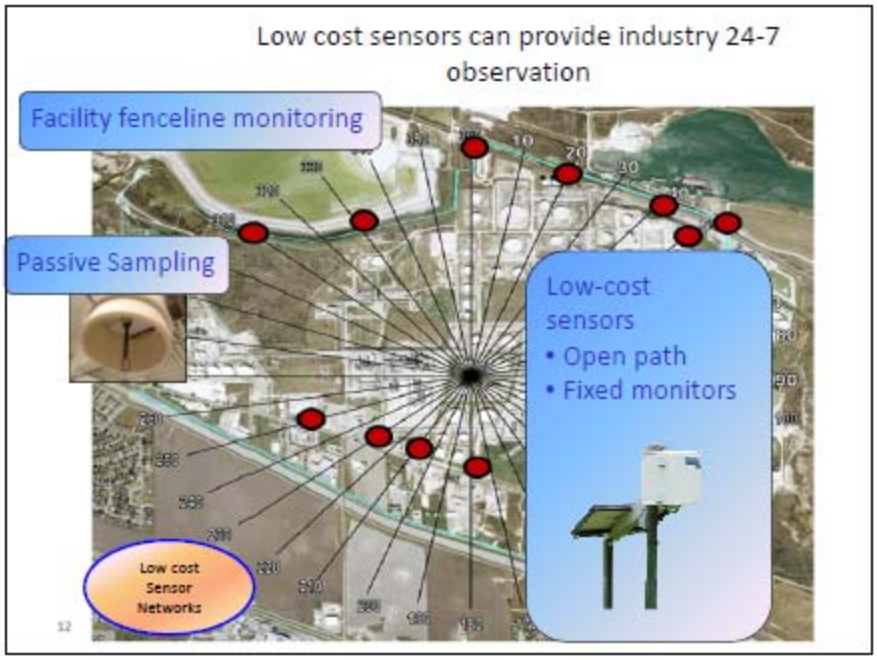

Open-path instruments
0.2
0.5
2
5
10 (µm)
UV DOAS
TDL
FLIR
FTIR
UV Diff. Optical Absorption Spectroscopy
Tunable Diode Laser (scanning)
Forward-Looking InfraRed (leak imaging)
Fourier Transform InfraRed (scanning)
7


Seeing invisible VOC leaks with infrared video FLIR Camera


Periodic mobile inspection to look for emissions and provide transparency.
(Think of automated systems in facility vehicles)
Mobile Inspection systems
Wind


Off-site assessment with GMAP-REQ
(Geospatial Measurement of Air Pollution – Remote Emissions Quantification)
wind direction
Position vehicle in the plume
Acquire methane (CH_4), H2S and wind data for 20 minutes
Pull a canister sample for volatile organic compound (VOC) information
driving path
CH_4
Mobile Inspection systems
Spike in CH_4 indicates emission


Emerging low cost sensors provide a variety of new solutions for 24-7 coverage
Fenceline with passive and active sensors
In-plant sensor networks
Wind
Low cost Sensor Networks
11


Low cost sensors can provide industry 24-7 observation
Facility fenceline monitoring
Passive Sampling
Low-cost sensors
• Open path
• Fixed monitors
Low cost Sensor Networks
12


Emerging low cost sensors provide a variety of new solutions for 24-7 coverage
Fenceline with passive and active sensors
In-plant sensor networks
Community monitoring lower cost systems
Low cost Sensor Networks
Wind


Fixed location sensors examples
Aqmesh.com: AQ electrochemical sensors
Prototype PID sensor package (pres. temp. , RH., VOC)

Fixed location sensors examples



Fixed Sensor Specifications

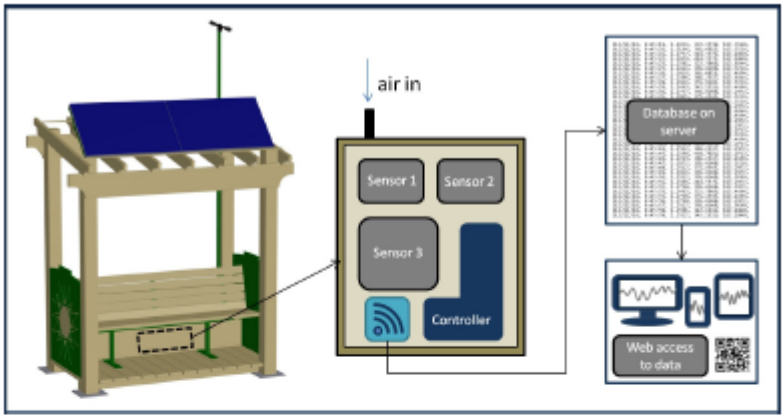
SENSOR *	RANGE (@0°C 1 ATM)	PRECISION	LOW DETECTION LIMIT	RESOLUTION	BACKGROUND NOISE	ACCURACY	RESPONSE (T90)
CARBON MONOXIDE (CO)	0-100 mg/m³ 0-80 ppm	< 2% f.s.	0.1 mg/m3	0.1 mg/m³	0.1 % f.s.	+/- 0.5 mg/m³	< 3 sec.
NITROGEN DIOXIDE (NO_2)	0-500 µg/m³ 0-400 ppb	< 2% f.s.	0.1 µg/m3	0.1 µg/m³	0.1 % f.s.	+/- 10 µg/m³	< 3 sec.
OZONE (O_3)	20-500 µg/m³ 10-200 ppb	< 10% f.s.	10 µg/m3	1.0 µg/m³	0.1 % f.s.	+/- 10 µg/m³	< 3 sec.
BENZENE (C_6H_6)	0-100 µg/m³ 0-30 ppb	< 2% f.s.	0.1 µg/m3	0.1 µg/m³	0.1 % f.s.	+/- 1 µg/m³	< 3 sec.
NITROGEN OXIDES (NOX)	0-800 µg/m3 0-500 ppb	< 2% f.s.	0.1 µg/m3	0.1 µg/m3	0.1 % f.s.	+/- 10 µg/m3	< 3 sec.
METHANE (CH_4)	0-300 µg/m³ 0-400 ppb	< 2% f.s.	0.1 µg/m3	1 µg/m³	0.1 % f.s.	+/- 10 µg/m³	< 3 sec.
OPERATIVE CONDITIONS	Temperature: -20°C to 50°C Relative Humidity: 5 to 95% (non condensating)			ZERO/SPAN DRIFT		< 2.5% / 6 months < 2.5% / 3 months (for O_3)	

* OTHER SENSORS AVAILABLE ON REQUEST

UniTec
Innovation in Analysis

UNITEC srl
VIA C. COLOMBO, 37/E
44100 FERRARA (ITALY)
TEL. +39 0532 751123
FAX +39 0532 738537
WWW.UNITEC-SRL.COM
INFO@UNITEC-SRL.COM

Village Green Project design



17

Let's take it another step forward...citizen monitoring/crowdsourcing

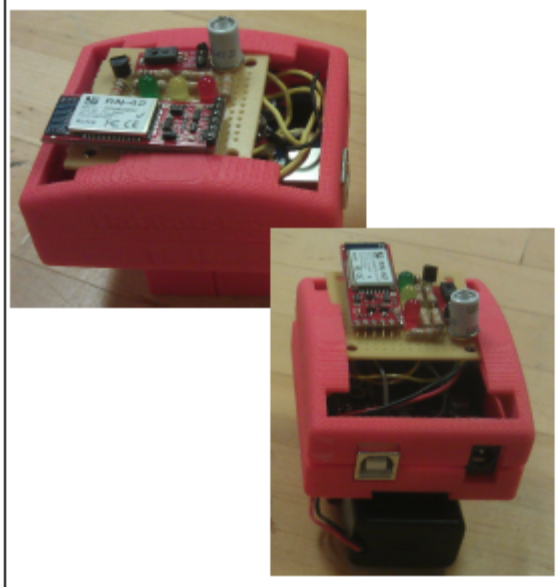


Michael Heimbinder, Habitat Map, Brooklyn NY

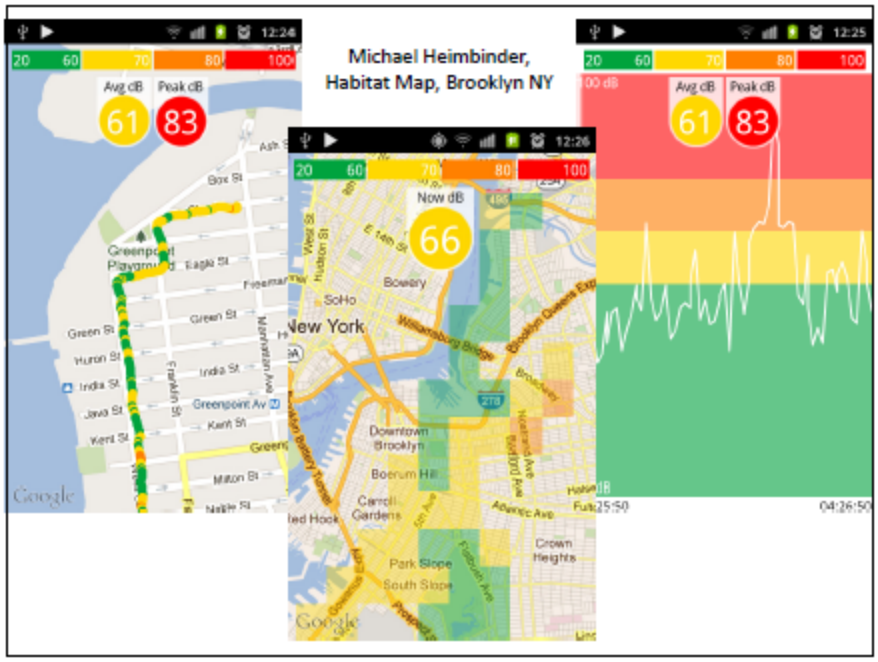
AIR CASTING

Share Your Air!

Michael Heimbinder, Habitat Map, Brooklyn NY

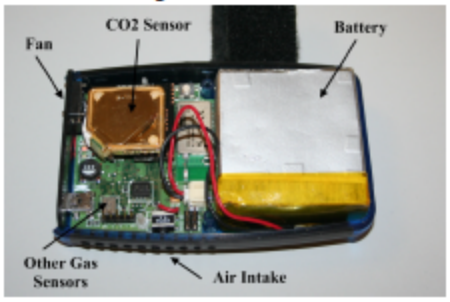






M-Pod Components

Mike Hannigan – Univ. of Colorado



Sensor	Gas Measured	Technology
e2v, MICS-2614	Ozone	Metal Oxide Semiconductor
ELT, S100	Carbon Dioxide	Non-Dispersive Infrared
e2v, MICS-5526	Carbon Monoxide, and VOC	Metal Oxide Semiconductor
e2v, MICS-4514	Carbon Monoxide, VOC, and Nitrogen Dioxide	Metal Oxide Semiconductor
Sensirion, SHT21	Temperature, and Humidity	Digital Humidity and Temperature Sensors

How big is it?



EPA's Scientific Integrity Policy

Anand Mudambi
USEPA

August 7, 2013
NEMC
San Antonio, Texas

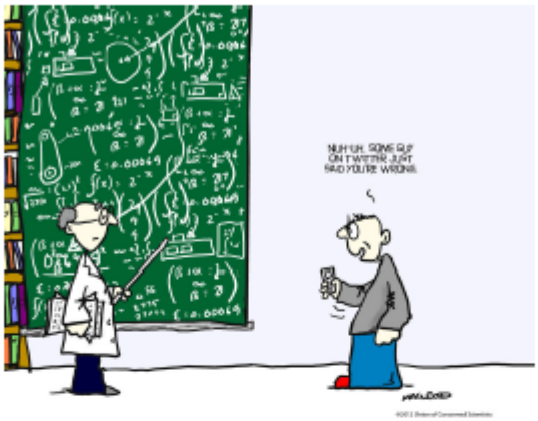
1

DISCLAIMER

- NOTE: Reference herein to any specific commercial product, process, or service by trademark, manufacturer, or otherwise, does not imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

2

Science in the World Today



"Nuh-Uh. Some guy on Twitter said you' re wrong." 3

From: Union of Concerned Scientists

Outline

- Background
- Developing EPA' s Scientific Integrity Policy
- Policy: Sections and Highlights
- Policy: Implementation

4

Background

March 2009: Presidential Memorandum on Scientific Integrity (SI) sent to Heads of Executive Departments and Agencies

- Requested the OSTP* Director Dr. Holdren develop recommendations to guarantee SI throughout the Executive Branch within 120 days.

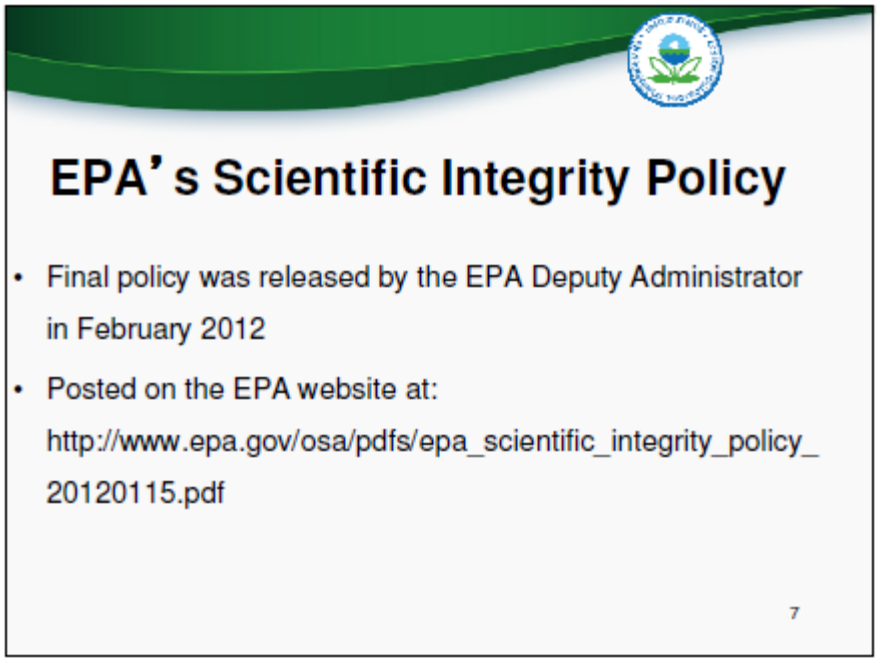
*White House Office of Science and Technology Policy

5

EPA Scientific Integrity Policy Development

- In May 2011, Dr. Holdren requested Agencies and Departments to submit their draft SI policies to OSTP within 90 days
- EPA established a workgroup of senior officials to develop a Draft SI policy
- In August 2011, EPA submitted it's Draft SI Policy to OSTP and also posted it for public comment

6


EPA's Scientific Integrity Policy
• Final policy was released by the EPA Deputy Administrator in February 2012
• Posted on the EPA website at: http://www.epa.gov/osa/pdfs/epa_scientific_integrity_policy_20120115.pdf
7


EPA's Scientific Integrity Policy cont'd
• Applies to all EPA employees including political appointees
• Reemphasizes EPA's Principles of Scientific Integrity
• Established an Agency Scientific Integrity Official to champion SI across EPA
8

EPA Scientific Integrity Policy – Its Great!

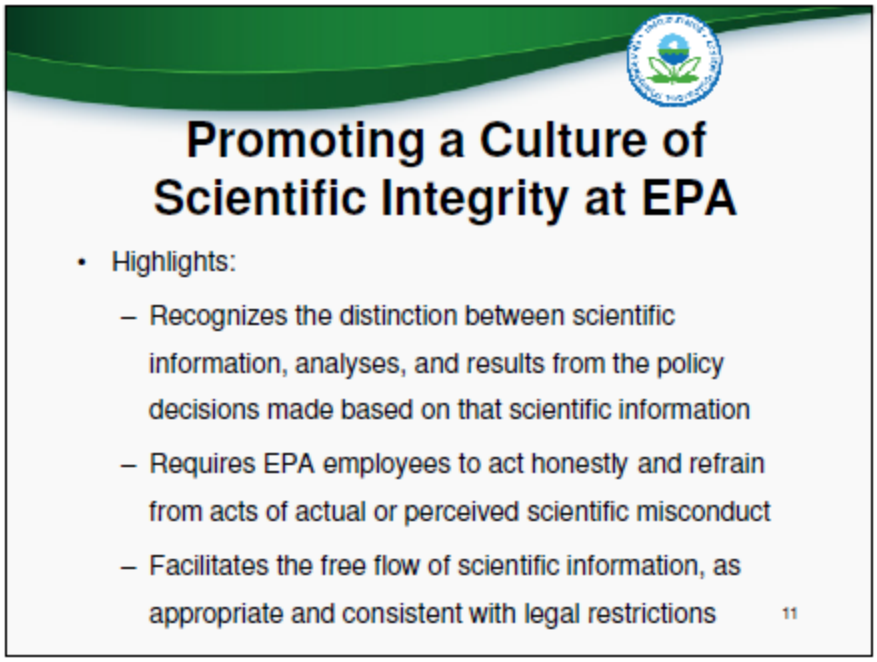
- The Union of Concerned Scientists (a non- profit advocacy group) reviewed scientific integrity policies from 22 Federal Agencies
- EPA's SI Policy was among the top 6 as one that "Actively Promotes and Supports a Culture of Scientific Integrity".

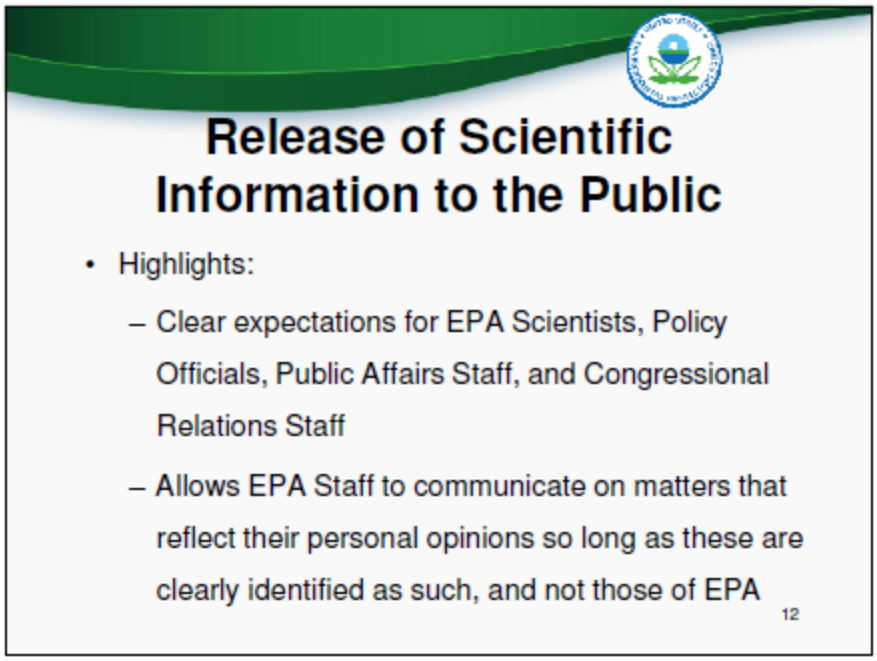
9

EPA's Scientific Integrity Policy: Main Areas

- Promoting a culture of SI at EPA
- Release of scientific information to the public
- Use of federal advisory committees and peer review
- Professional development of government scientists and engineers
- An Agencywide Scientific Integrity Committee

10


Promoting a Culture of Scientific Integrity at EPA
• Highlights:
– Recognizes the distinction between scientific information, analyses, and results from the policy decisions made based on that scientific information
– Requires EPA employees to act honestly and refrain from acts of actual or perceived scientific misconduct
– Facilitates the free flow of scientific information, as appropriate and consistent with legal restrictions
11


Release of Scientific Information to the Public
• Highlights:
– Clear expectations for EPA Scientists, Policy Officials, Public Affairs Staff, and Congressional Relations Staff
– Allows EPA Staff to communicate on matters that reflect their personal opinions so long as these are clearly identified as such, and not those of EPA
12

Possible Communications without a Scientific Integrity Policy



"We've made your environmental report greener. It now uses 50% less paper."

"We' ve made your environmental report greener. It now uses 50% less paper."

From: Union of Concerned Scientists

13

Use of Federal Advisory Committees and Peer Review

- Gives direction regarding recruitment of FACA committee members (consistent with GSA and White House guidance)
- Reaffirms EPA's Peer Review Policy and use of EPA's *Peer Review Handbook* to assure that EPA's scientific products undergo appropriate peer review by qualified experts

14

Professional Development of Government Scientists and Engineers

- The Policy
  - Encourages publication and presentation of research findings
  - Allows Agency scientists and engineers to serve on editorial boards of professional & scholarly journals and participate in professional societies
  - Encourages Agency scientists to obtain appropriate training to keep their scientific qualifications current

15

EPA's Scientific Integrity Committee (ScIC)

- The Policy also outlines the following for the ScIC:
  - Roles and Responsibilities
  - Training
  - Annual Reporting

16


Scientific Integrity Committee:
Roles and Responsibilities
• Charged with implementing, reviewing, and revising as needed, the SI Policy
• Providing leadership for the Agency on SI
• Providing an Annual Report on SI
17


Scientific Integrity
Implementation at EPA
18

Scientific Integrity Committee

- Meets regularly to discuss SI Implementation issues
- These include:
  - Addressing Scientific Integrity Allegations
  - Developing framework for clearance procedures for Agency scientific products
  - Developing an Annual Report

19

Annual Review

- EPA held a listening session on June 25 with the following partners concerning the SI Policy
  - Federal and Non-Federal partners
  - EPA Union Representatives
  - Senior Managers from EPA Programs and Regions
- Input from this session will be included in the Annual Report
- Annual Review Process still under development

20

Scientific Integrity Training

- ScIC is overseeing development and implementation of training on the SI Policy
- Accredited EPA laboratories already provide annual Laboratory Ethics and Data Integrity training to scientists and engineers who generate scientific data

21

What Could Happen Without Scientific Integrity Policies

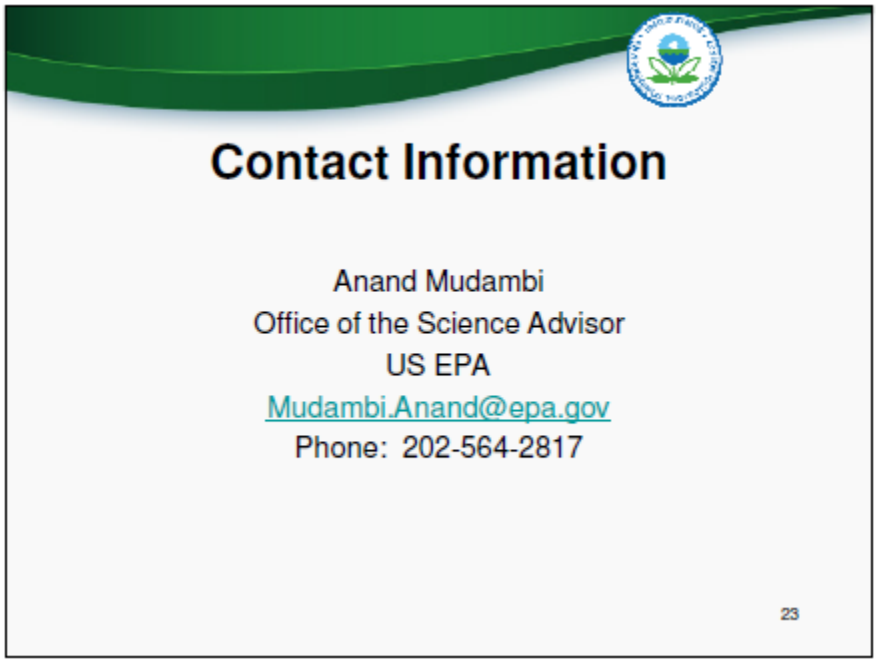
From: Union of Concerned Scientists



You'd think the FDA would notice this kind of thing.

"You' d think the FDA would notice this kind of thing."

22


Contact Information
Anand Mudambi
Office of the Science Advisor
US EPA
Mudambi.Anand@epa.gov
Phone: 202-564-2817
23

SECTION 2

ACADEMIC RESEARCH TOPICS IN ENVIRONMENTAL MEASUREMENT AND MONITORING

Fully Automated On-line SPE Coupled to LC MS/MS for Rapid, Sensitive, and Simultaneous Analysis of Multiple PPCPs in Water

Tarun Anumol, Sheher Mohsin, Sylvain Merel, Shane A. Snyder
University of Arizona
Department of Chemical & Environmental Engineering

Abstract

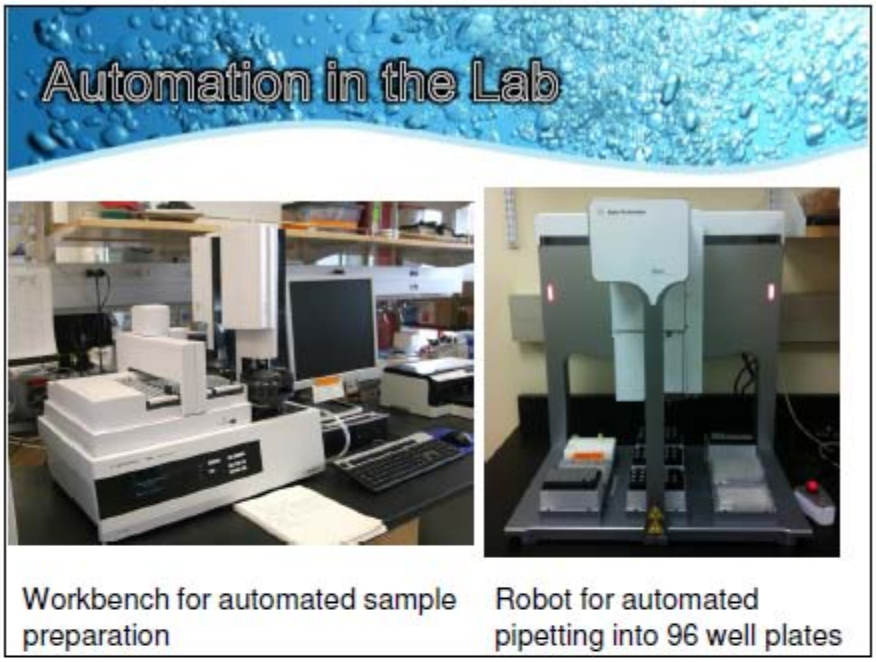
With the presence of Pharmaceuticals and Personal Care Products (PPCPs) in water now reported frequently and the synergistic effects of low doses largely unknown, the need for sensitive and rapid analytical measurement of these compounds is paramount. The traditional method to achieve low detection limits has been to use off-line concentration techniques like solid-phase extraction (SPE) or continuous liquid-liquid extraction (CLLE). This method requires large sample volume, is time consuming and labor-intensive. With the increasing sensitivity of new analytical instruments, Large Volume Injection (LVI) has been mooted as a possible solution; this technique though adversely affects the life of an analytical column while failing to remove possible interference in the matrix due to a lack of sample clean-up. Trace enrichment or on-line SPE eliminates all these difficulties while providing sample clean-up and reduces interferences which LVI cannot do. Further, it can be completely automated to reduce labor while increasing reproducibility of results. In this study, a single automated analytical method for the analysis of over 25 PPCPs (both in ESI- and ESI+) using on-line SPE coupled to a tandem mass spectrometer will be shown. Critical parameters like sample loading volume, extraction cartridge material and elution solvents will also be discussed. The results were compared to off-line SPE which showed comparable results while offering significant time, labor and solvent savings. Further, the online method significantly reduced ion suppression in complex matrixes compared to off-line SPEand LVI. The method was also run on several different water matrixes including surface water, ground water and wastewater, always producing accurate and reproducible results.


Fully Automated Online SPE coupled to LC/MS/MS for Rapid, Sensitive and Simultaneous Analysis of PPCPs in Water
NEMC
San Antonio, TX
Tarun Anumol[1]
Sheher Mohsin[2]
Sylvain Merel[1]
Shane A. Snyder[1]
[1]Chemical & Environmental Engineering, BIO5 Institute, University of Arizona, Tucson, AZ, USA
[2]Agilent Technologies Inc., Schaumburg, IL, USA

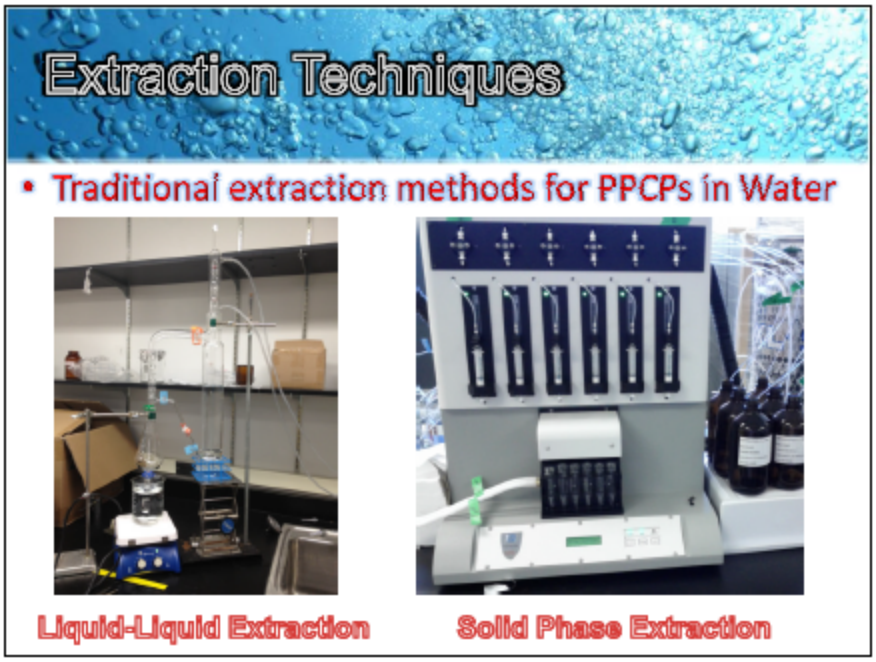

ARMED WITH
URINE
DETECTION
DEVICE (UDD)
EMU

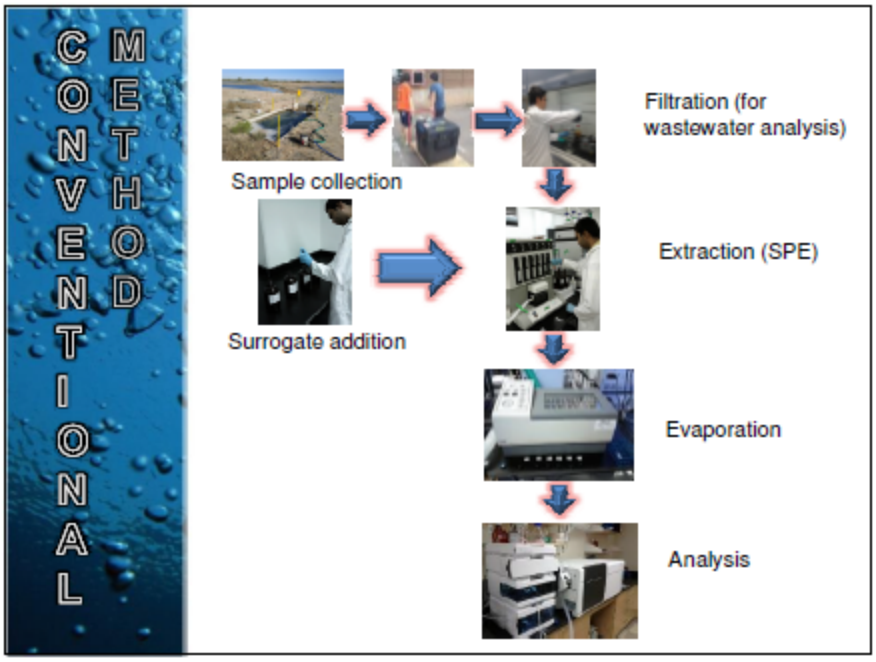

Media Coverage
Pharmaceuticals lurking in U.S. drinking water
AP probe found traces of meds in water supplies of 41 million Americans
Painkillers found in drinking water of 15 Ontario cities, study reports
Study: India's Water Contains Highest Levels of Pharmaceuticals in World
Published January 26, 2009 / Associated Press
The Washington Post
Six years later, gender-bending fish in our water supply remain a mystery
£30bn bill to purify water system after toxic impact of contraceptive pill
Drug firms oppose an EU call for controls on potent chemicals that have been blamed for the gender mutation of freshwater fish
theguardian
271M Lbs Of Pharmaceuticals In Our Water


Au.to.ma.tion
"the technique of making an apparatus, a process, or a system operate automatically"
Past
Present
Future ?


Automation in the Lab
Workbench for automated sample preparation
Robot for automated pipetting into 96 well plates

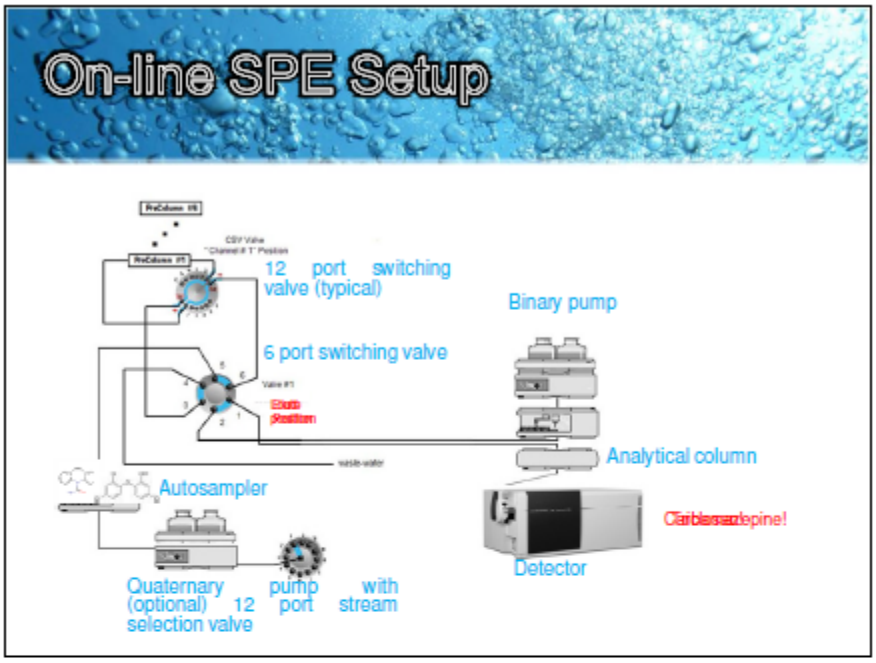

Automation in the Lab
Credit: Agilent technologies

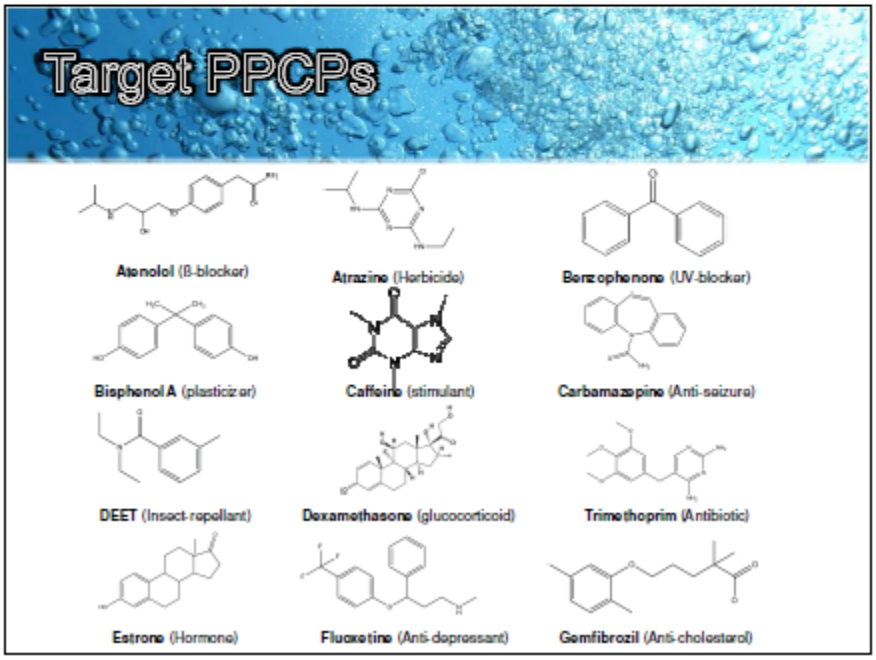

Extraction Techniques
• Traditional extraction methods for PPCPs in Water
Liquid-Liquid Extraction
Solid Phase Extraction

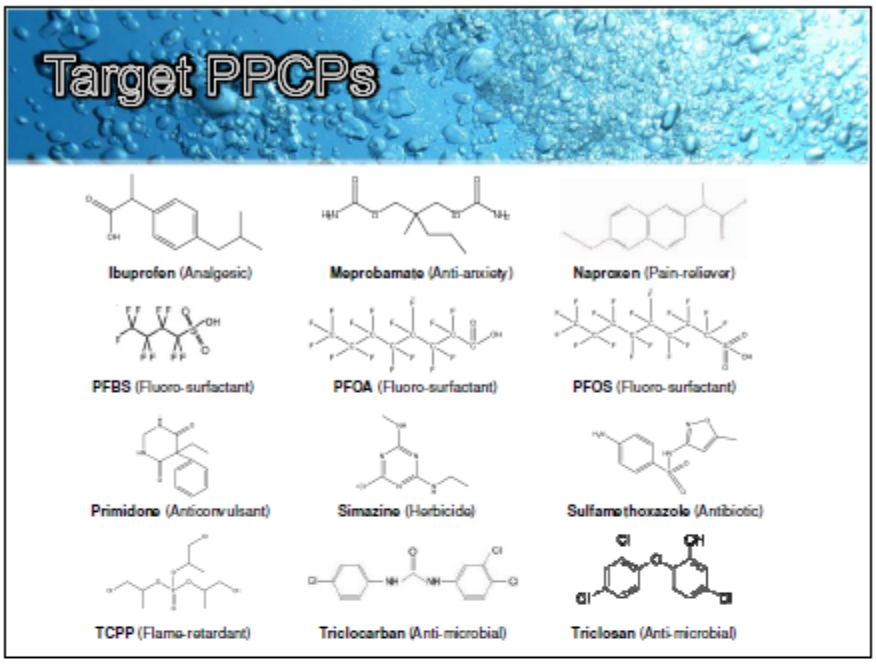

CONVENTIONAL METHOD
Sample collection
Surrogate addition
Filtration (for wastewater analysis)
Extraction (SPE)
Evaporation
Analysis

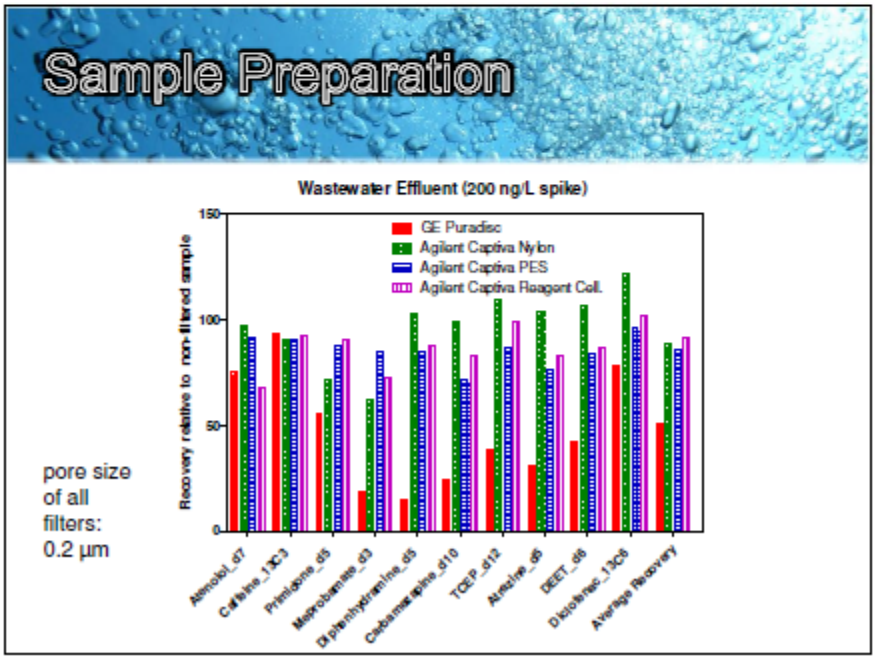

Sample Volume

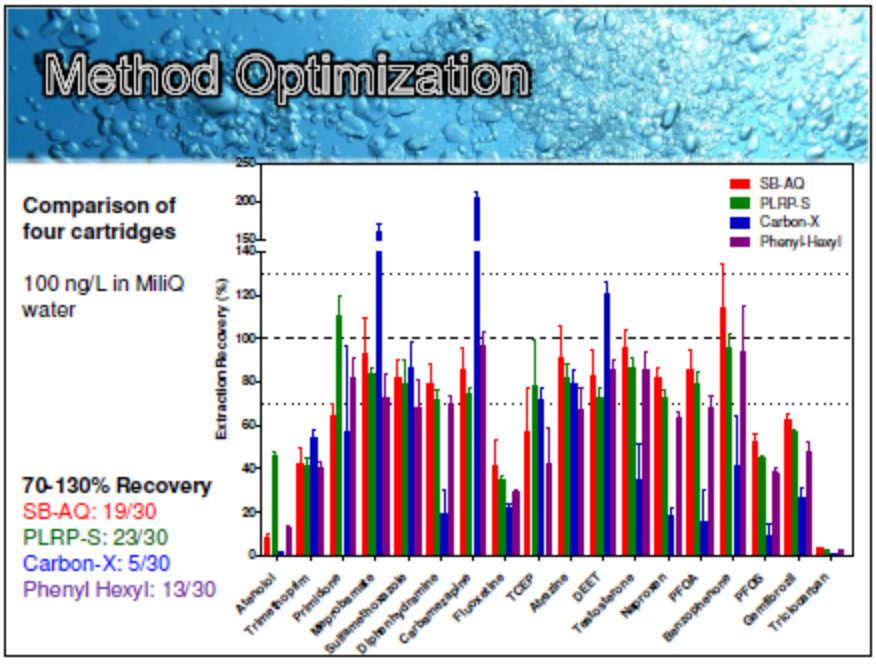

Instrument Setup
Credit: Agilent Technologies
for gradient

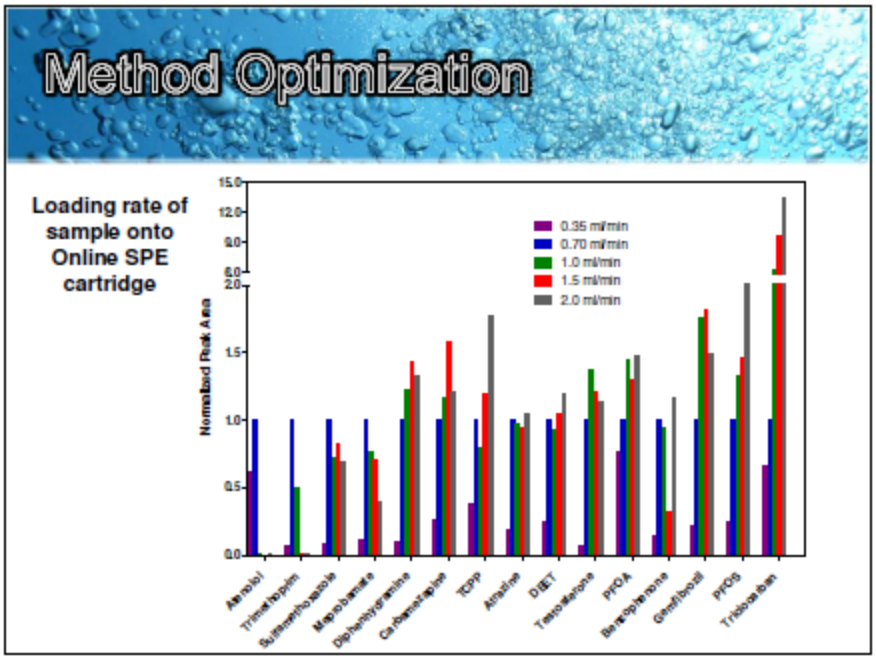

On-line SPE Setup
12 port switching valve (typical)
6 port switching valve
Autosampler
Quaternary pump (optional) 12 port selection valve
with stream
Binary pump
Analytical column
Detector

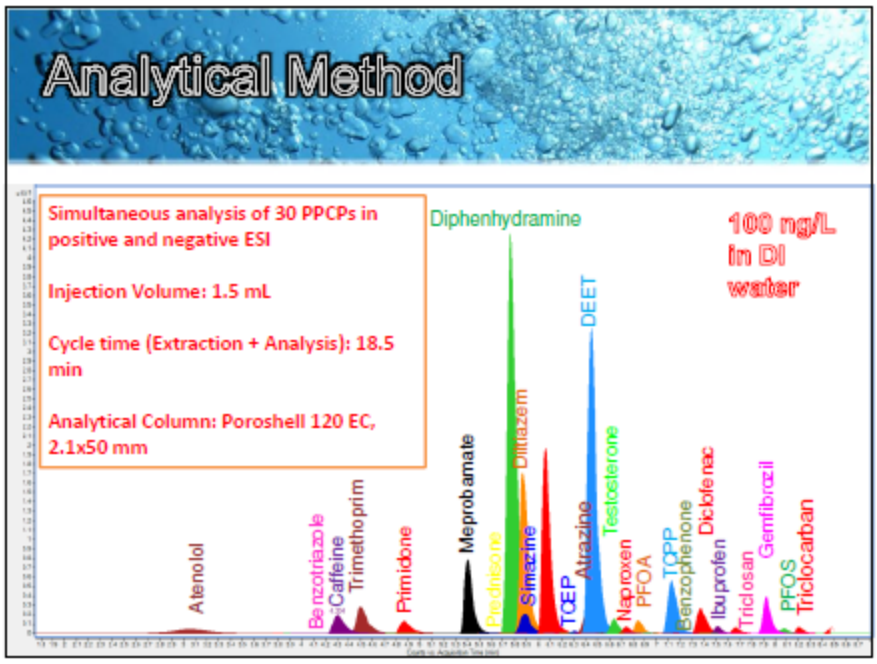

Target PPCPs
Atenolol (ß-blocker)
Atrazine (Herbicide)
Benzophenone (UV-blocker)
Bisphenol A (plasticizer)
Caffeine (stimulant)
Carbamazepine (Anti-seizure)
DEET (Insect-repellant)
Dexamethasone (glucocorticoid)
Trimethoprim (Antibiotic)
Estrone (Hormone)
Fluoxetine (Anti-depressant)
Gemfibrozil (Anti-cholesterol)


Target PPCPs
Ibuprofen (Analgesic)
Meprobamate (Anti-anxiety)
Naproxen (Pain-reliever)
PFBS (Fluoro-surfactant)
PFOA (Fluoro-surfactant)
PFOS (Fluoro-surfactant)
Primidone (Anticonvulsant)
Simazine (Herbicide)
Sulfamethoxazole (Antibiotic)
TCPP (Flame-retardant)
Triclocarban (Anti-microbial)
Triclosan (Anti-microbial)


Sample Preparation
Wastewater Effluent (200 ng/L spike)
GE Puradisc
Agilent Captiva Nylon
Agilent Captiva PES
Agilent Captiva Reagent Cell.
Recovery relative to non-filtered sample
150
100
50
0
pore size of all filters: 0.2 µm
Atenolol_d7
Caffeine_13C3
Primidone_d5
Meprobamate_d3
Diphenhydramine_d5
Carbamazepine_d10
TCEP_d12
Atrazine_d5
DEET_d6
Diclofenac_13C6
Average Recovery

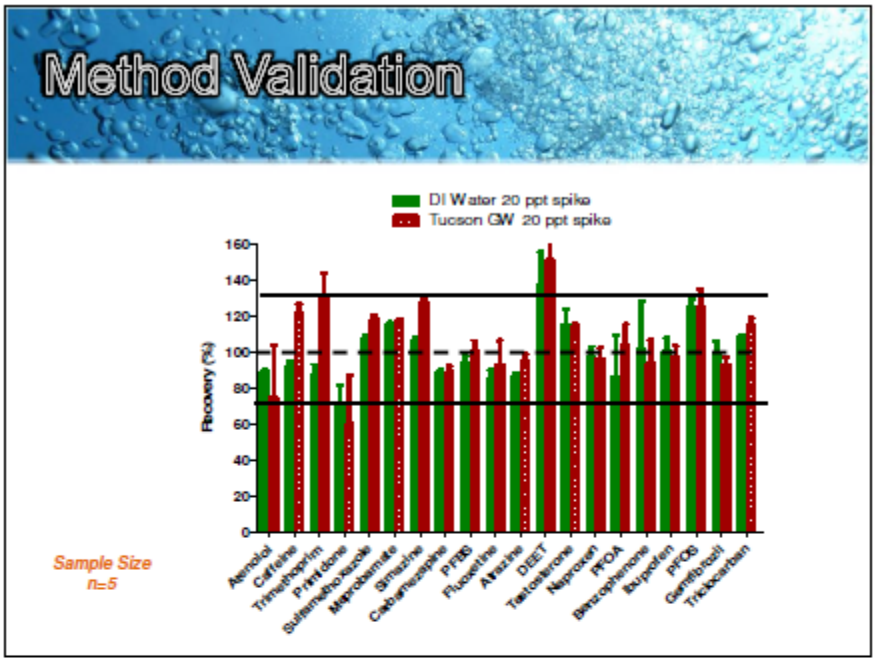

Method Optimization
Comparison of four cartridges
100 ng/L in MiliQ water
70-130% Recovery
SB-AQ: 19/30
PLRP-S: 23/30
Carbon-X: 5/30
Phenyl Hexyl: 13/30
Extraction Recovery (%)
SB-AQ
PLRP-S
Carbon-X
Phenyl-Hexyl
Atenolol
Trimethoprim
Primidone
Mepivacaine
Sulfamethoxazole
Diphenhydramine
Carbamazepine
Fluoxetine
TCEP
Atrazine
DEET
Testosterone
Naproxen
PFOA
Benzophenone
PFOS
Gemfibrozil
Triclocarban

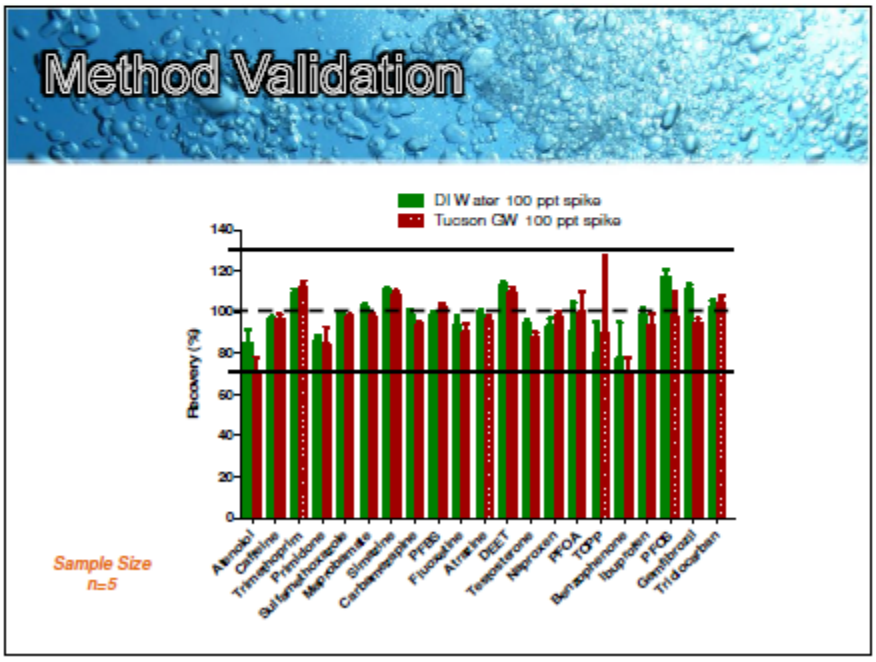

Method Optimization
Loading rate of sample onto Online SPE cartridge
Normalized Peak Area
0.35 ml/min
0.70 ml/min
1.0 ml/min
1.5 ml/min
2.0 ml/min
Atenolol
Trimethoprim
Sulfamethoxazole
Mepivacaine
Diphenhydramine
Carbamazepine
TCPP
Atrazine
DEET
Testosterone
PFOA
Benzophenone
Gemfibrozil
PFOS
Triclocarban

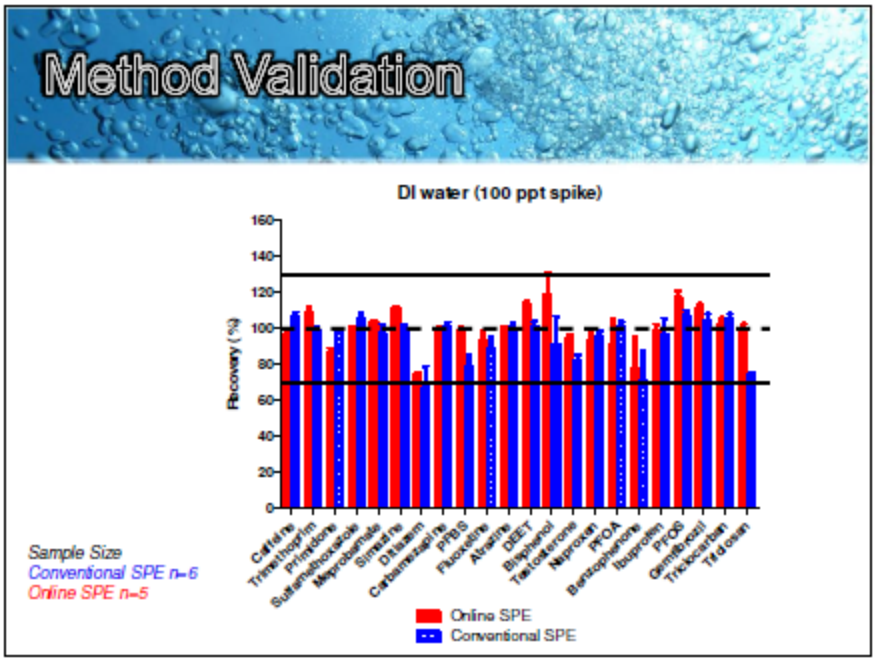


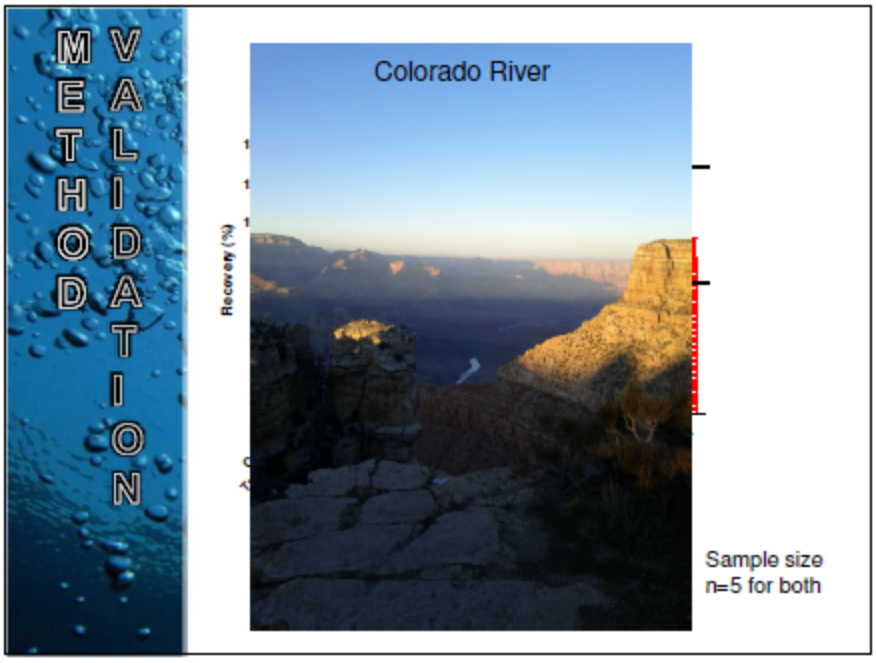
METHOD PERFORMANCE

Analyte	MRL (ng/L)	Analyte	MRL (ng/L)
Atenolol	10	*Gemfibrozil*	1.5
Atrazine	5	*Ibuprofen*	10
Benzophenone	15	*Meprobamate*	0.5
Bisphenol A	10	*Naproxen*	10
Caffeine	0.5	PFBS	10
Carbamazepine	2.5	*PFOA*	10
DEET	0.1	*PFOS*	5
Dexamethasone	10	*Primidone*	15
Diphenhydramine	1	*Diltiazem*	0.5
Estrone	20	Simazine	1.5
Fluoxetine	10	*Sulfamethoxazole*	2.5
Trimethoprim	5	*Triclocarban*	1
TCPP	0.5	*Triclosan*	5

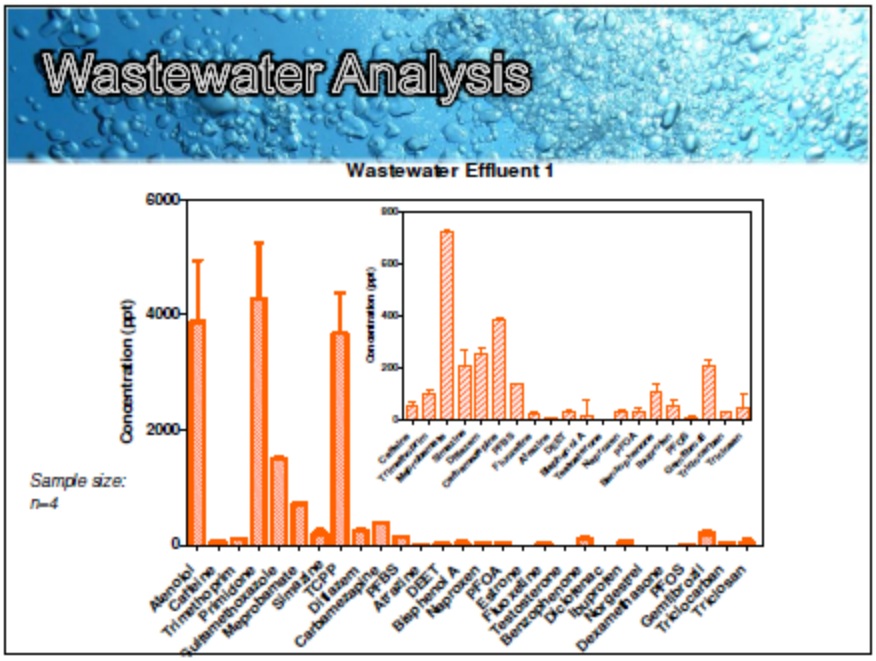

Method Validation
DI Water 20 ppt spike
Tucson GW 20 ppt spike
Recovery (%)
0
20
40
60
80
100
120
140
160
Atenolol
Caffeine
Trimethoprim
Primidone
Sulfamethoxazole
Meprobamate
Simazine
Carbamazepine
PFBS
Fluoxetine
Atrazine
DEET
Testosterone
Naproxen
PFOA
Benzophenone
Ibuprofen
PFOS
Gemfibrozil
Tricloscarban
Sample Size
n=5

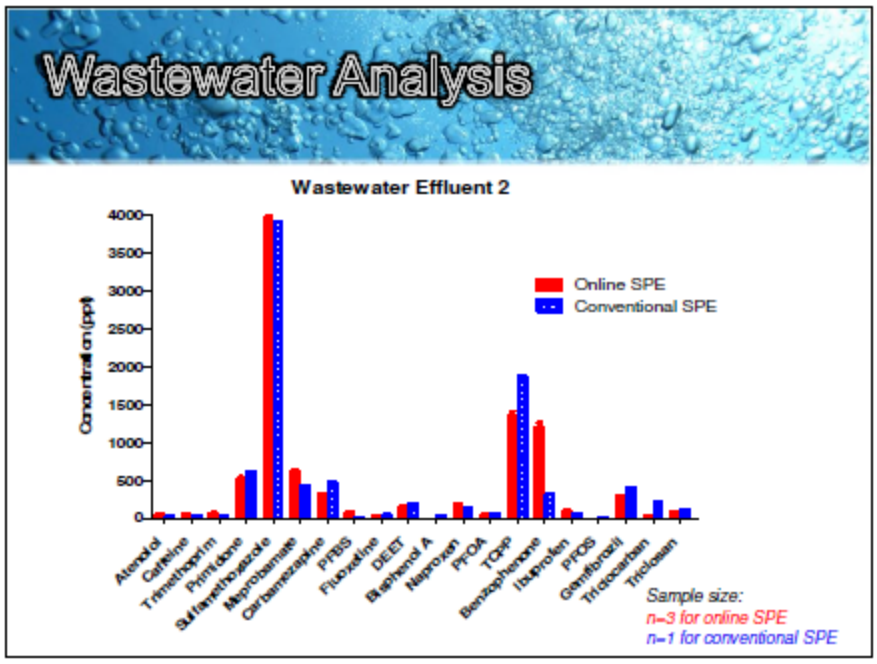

Method Validation
DI Water 100 ppt spike
Tucson GW 100 ppt spike
Recovery (%)
0
20
40
60
80
100
120
140
Atenolol
Caffeine
Trimethoprim
Primidone
Sulfamethoxazole
Meprobamate
Simazine
Carbamazepine
PFBS
Fluoxetine
Atrazine
DEET
Testosterone
Naproxen
PFOA
TCPP
Benzophenone
Ibuprofen
PFOS
Gemfibrozil
Tricloscarban
Sample Size
n=5

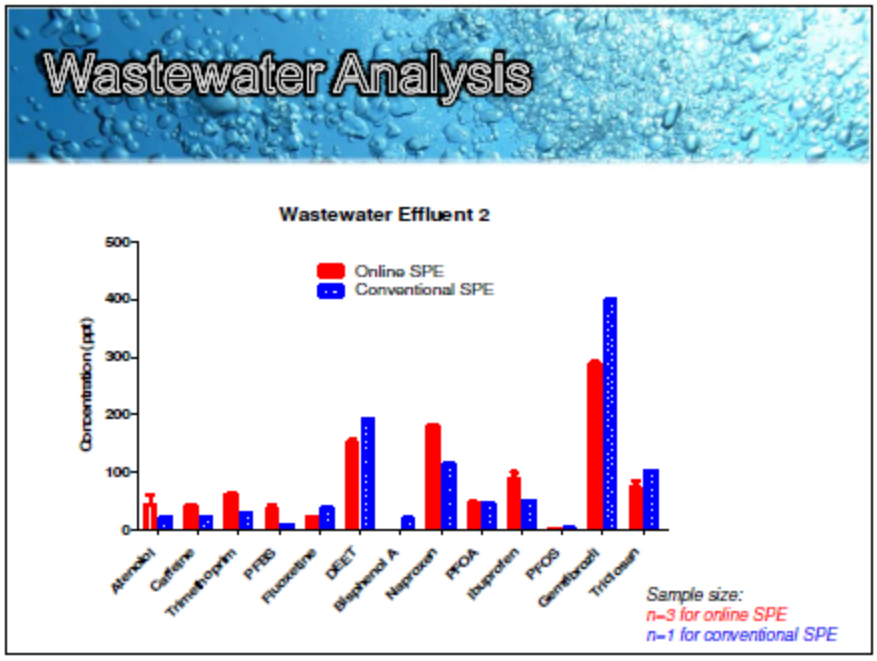

Method Validation
DI water (100 ppt spike)
Recovery (%)
160
140
120
100
80
60
40
20
0
Caffeine
Trimethoprim
Primidone
Sulfamethoxazole
Meprobamate
Simazine
Diltiazem
Carbamazapine
PFBS
Fluoxetine
Atrazine
DEET
Bisphenol
Testosterone
Naproxen
PFOA
Benzophenone
Ibuprofen
PFOS
Gemfibrozil
Triclocarban
Triclosan
Online SPE
Conventional SPE
Sample Size
Conventional SPE n=6
Online SPE n=5

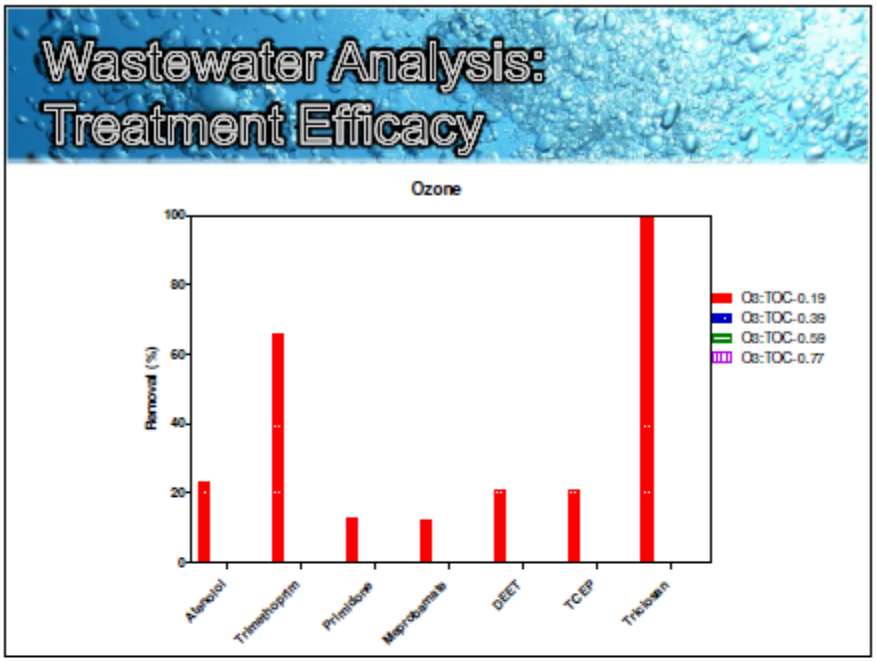

METHOD VALIDATION
Colorado River
Recovery (%)
Sample size
n=5 for both

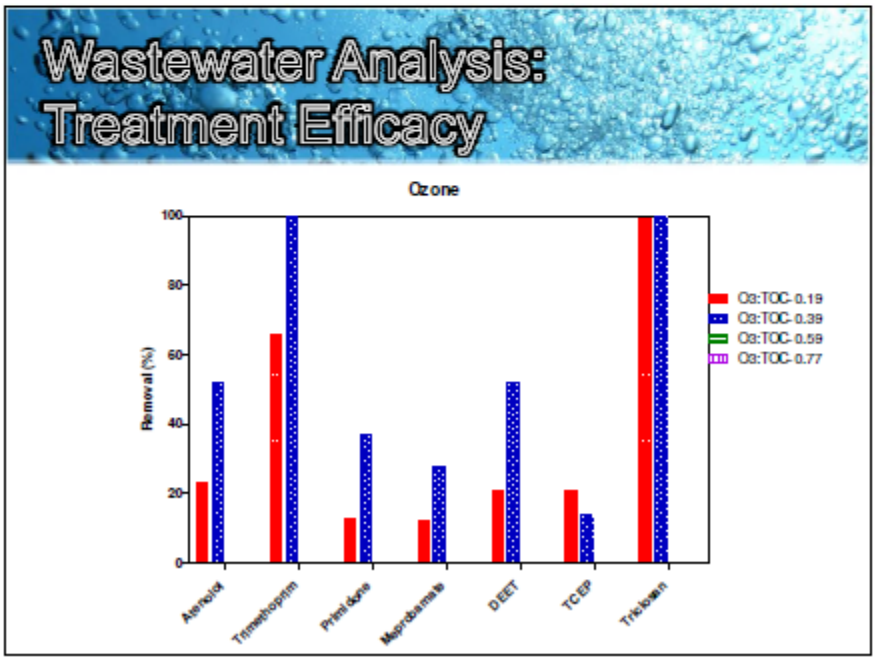

Wastewater Analysis

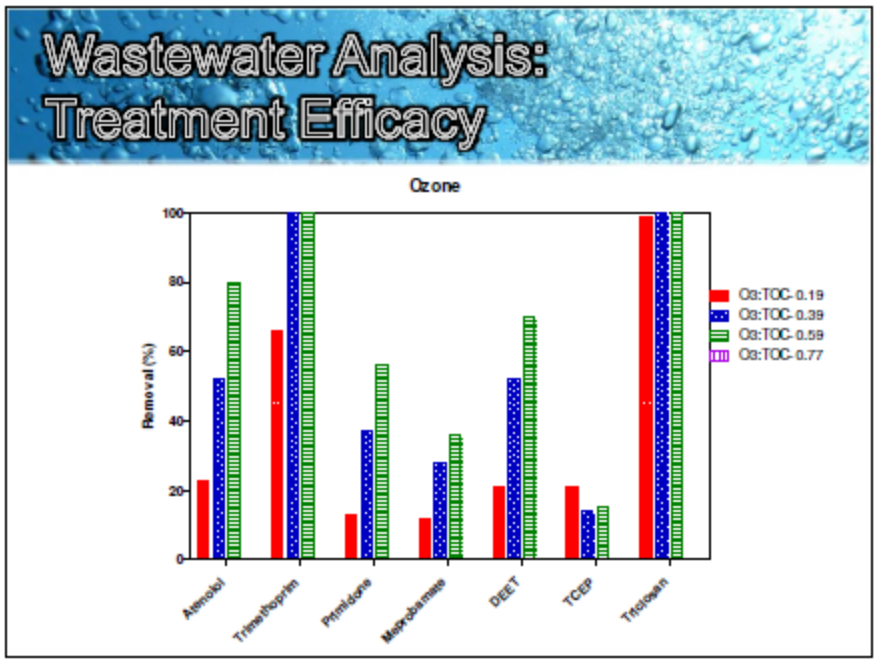

Wastewater Analysis
Wastewater Effluent 1
Concentration (ppt)
6000
4000
2000
0
Sample size:
n=4
Atenolol
Caffeine
Trimethoprim
Primidone
Sulfamethoxazole
Meprobamate
Simazine
TCPP
Diltiazem
Carbamazepine
PFBS
Atrazine
DEET
Bisphenol A
Naproxen
PFOA
Estrone
Fluoxetine
Testosterone
Benzophenone
Diclofenac
Ibuprofen
Norgestrel
Dexamethasone
PFOS
Gemfibrozil
Triclocarban
Triclosan

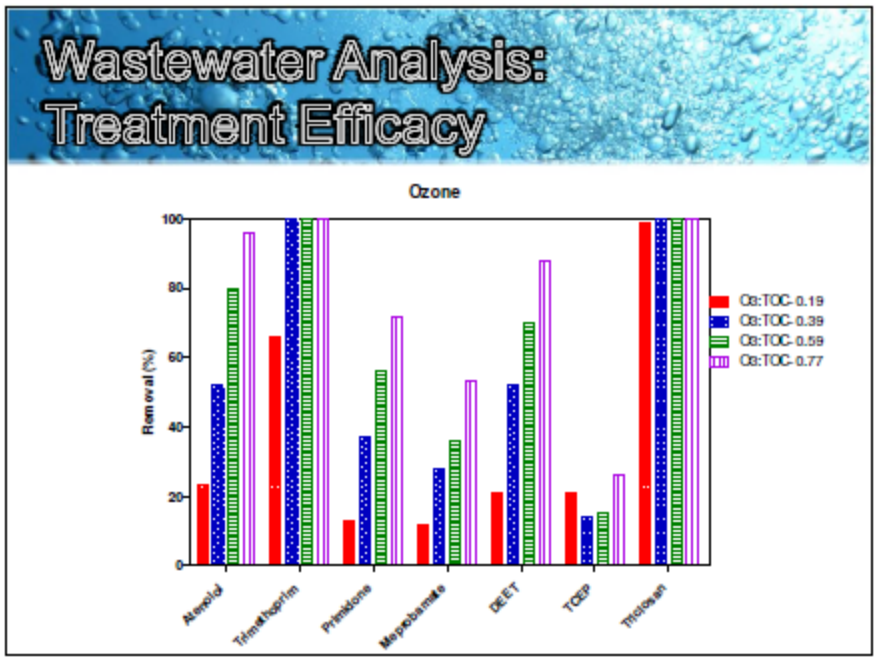

Wastewater Analysis
Wastewater Effluent 2
Concentration (ppt)
4000
3500
3000
2500
2000
1500
1000
500
0
Online SPE
Conventional SPE
Atenolol
Caffeine
Trimethoprim
Primidone
Sulfamethoxazole
Meprobamate
Carbamazepine
PFBS
Fluoxetine
DEET
Bisphenol A
Naproxen
PFOA
TCPP
Benzophenone
Ibuprofen
PFOS
Gemfibrozil
Tricloscarban
Triclosan
Sample size:
n=3 for online SPE
n=1 for conventional SPE


Wastewater Analysis
Wastewater Effluent 2
Concentration (ppt)
500
400
300
200
100
0
Online SPE
Conventional SPE
Atenolol
Caffeine
Trimethoprim
PFBS
Fluoxetine
DEET
Bisphenol A
Naproxen
PFOA
Ibuprofen
PFOS
Gemfibrozil
Triclosan
Sample size:
n=3 for online SPE
n=1 for conventional SPE


Wastewater Analysis:
Treatment Efficacy
Ozone
Removal (%)
100
80
60
40
20
0
Atenolol
Trimethoprim
Primidone
Meprobamate
DEET
TCEP
Triclosan
O3:TOC-0.19
O3:TOC-0.39
O3:TOC-0.59
O3:TOC-0.77


Wastewater Analysis:
Treatment Efficacy
Ozone
Removal (%)
100
80
60
40
20
0
Atenolol
Trimethoprim
Primidone
Meprobamate
DEET
TCEP
Triclosan
O3:TOC-0.19
O3:TOC-0.39
O3:TOC-0.59
O3:TOC-0.77


Wastewater Analysis:
Treatment Efficacy
Ozone
Removal (%)
100
80
60
40
20
0
Atenolol
Trimethoprim
Primidone
Meprobamate
DEET
TCEP
Triclosan
O3:TOC- 0.19
O3:TOC- 0.39
O3:TOC- 0.59
O3:TOC- 0.77


Wastewater Analysis:
Treatment Efficacy
Ozone
Removal (%)
100
80
60
40
20
0
Atenolol
Trimethoprim
Primidone
Meprobamate
DEET
TCEP
Triclosan
O3:TOC- 0.19
O3:TOC- 0.39
O3:TOC- 0.59
O3:TOC- 0.77

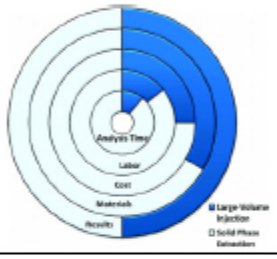
Direct Injection

- Direct injection of a large sample volume
- >10% of analytical column void volume
  - ✓ Typically 50-100 µL into a 2.1x50 mm UHPLC column
  - ✓ Void volume~ 220 µL
- Generally pre-treatment involves filtering of samples (~ 0.2 µm filter for UHPLC analysis) or centrifugation

Is SPE Necessary for Environmental Analysis? A Quantitative Comparison of Matrix Effects from Large-Volume Injection and Solid Phase Extraction Based Methods

Will J. Backe[†] and Jennifer A. Field[†,‡]

Backe & Field, ES &T (2012)



MRL COMPARISON

Analyte	Online SPE MRL	LVI MRL	Analyte	Online SPE MRL	LVI MRL
Dexamethasone	10	-	*Primido*		-
Estrone	20	-	Simazi		-
Fluoxetine	10	-	*Sulfametho*		75
Trimethoprim	5	75	*Triclocar*		75
TCPP	0.5	-	*Triclos*		500

Concentration: ppt (ng/L)

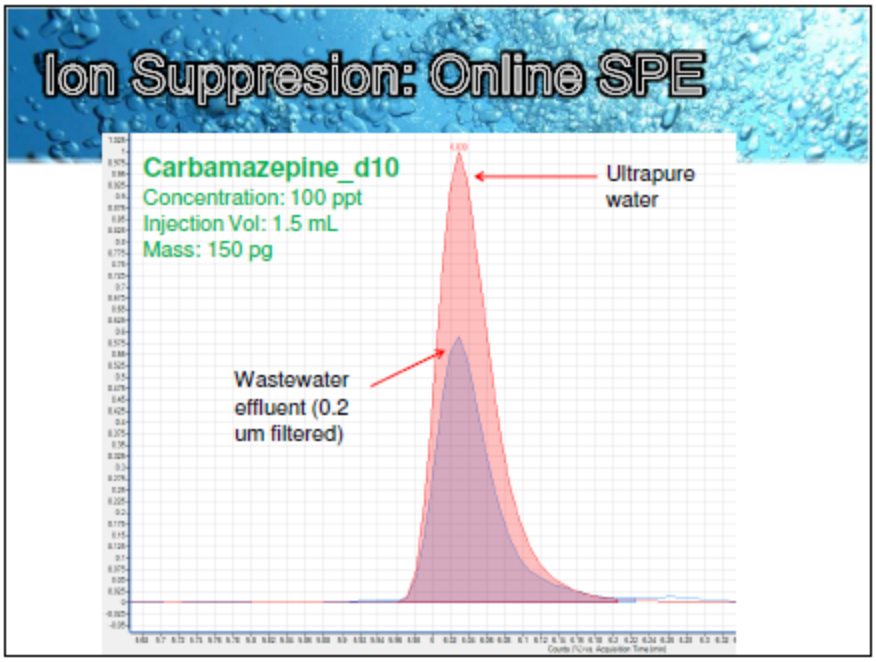
Direct Aqueous Analysis of Pharmaceuticals in Water at ppt Levels by LC/MS/MS with the Agilent 6490 Triple Quadrupole LC/MS System with Ion Funnel Technology

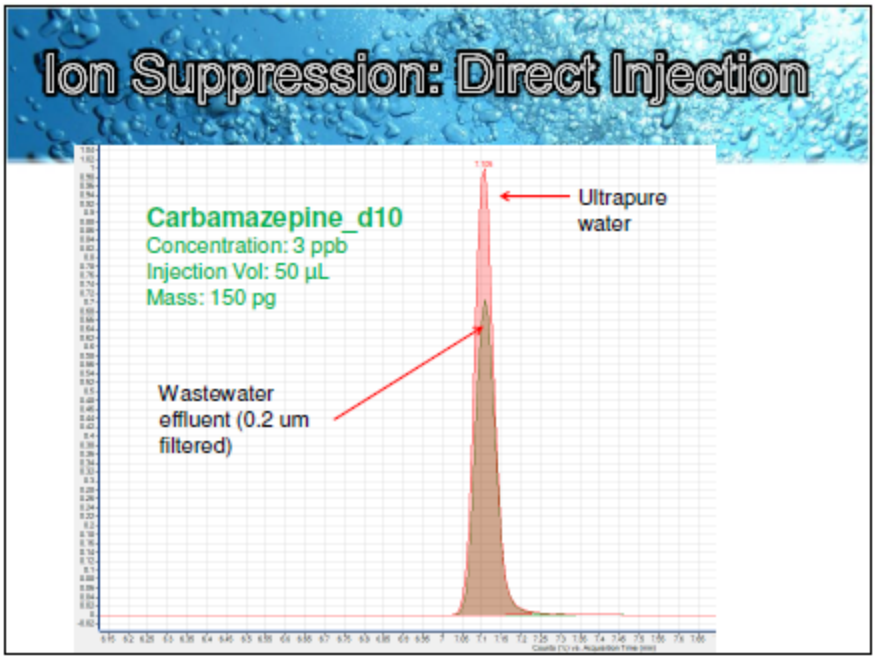
Application Note

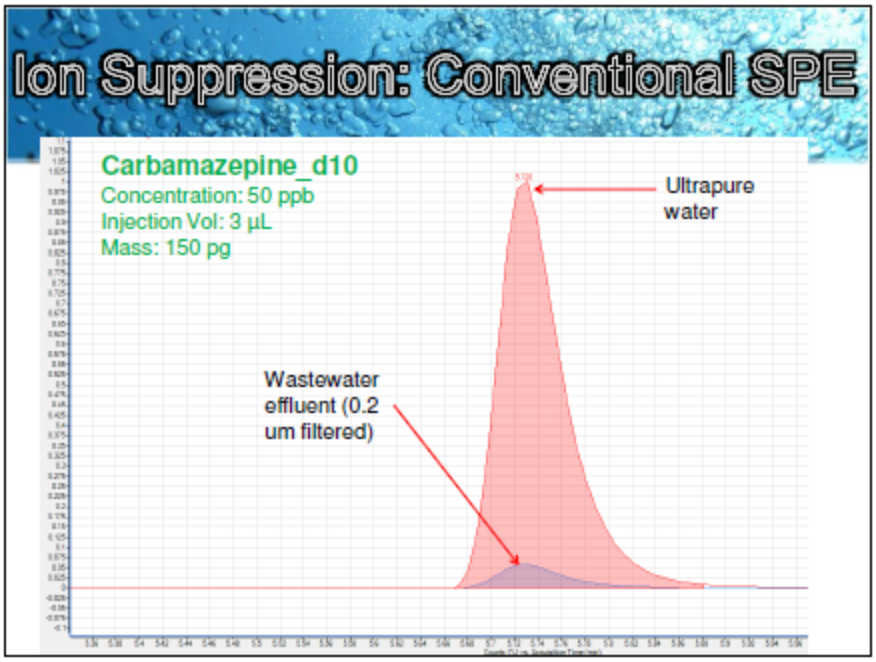
Authors

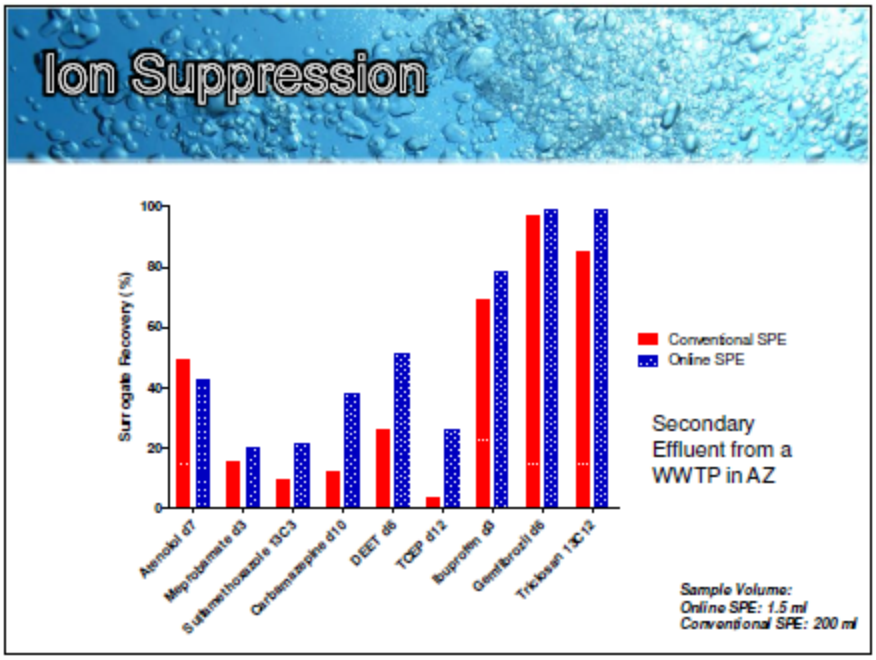
Imma Ferrer, E. Michael Thurman
Center for Environmental Mass Spectrometry
Dept of Environmental Engineering
University of Colorado
Boulder, Colorado 80309

Michael Flanagan
Agilent Technologies Inc.
Santa Clara, CA


Ion Suppresion: Online SPE
Carbamazepine_d10
Concentration: 100 ppt
Injection Vol: 1.5 mL
Mass: 150 pg
Ultrapure water
Wastewater effluent (0.2 um filtered)


Ion Suppression: Direct Injection
Carbamazepine_d10
Concentration: 3 ppb
Injection Vol: 50 µL
Mass: 150 pg
Ultrapure water
Wastewater effluent (0.2 um filtered)


Ion Suppression: Conventional SPE
Carbamazepine_d10
Concentration: 50 ppb
Injection Vol: 3 µL
Mass: 150 pg
Ultrapure water
Wastewater effluent (0.2 um filtered)


Ion Suppression
Surrogate Recovery (%)
100
80
60
40
20
0
Conventional SPE
Online SPE
Secondary Effluent from a WWTP in AZ
Sample Volume:
Online SPE: 1.5 ml
Conventional SPE: 200 ml

Comparison of 3 Methods

Parameter	Conventional SPE	Online SPE	LVI
Labor	*	***	***
Solvent Use	*	***	***
Materials Cost	*	**	***
Detection Limits	***	**1/2	*
Ion Suppression	*	**1/2	**1/2
Volume of sample	*	***	***
Total Cycle Time	*	***	***

* Least favorable ** Moderately favorable *** Optimal

Conclusions

- Online SPE allows sensitive analysis of trace organics in water while allowing significant time and labor savings.
- Method has been proven to be robust in several different water matrixes.
- Online SPE is significantly less affected by ion suppression compared with conventional offline extraction techniques.
- LVI is currently not sensitive enough to attain desired MRLs but offers promise with rapid increase in sensitivity of newer mass spectrometers.
- Use of online SPE with accurate mass detectors (ToF & Q-ToF) could allow for real-time analysis of trace unknowns in water.


Acknowledgements
ARIZONA
SNYDER RESEARCH GROUP
PIONEERING RESEARCH REGARDING DETECTION, TREATMENT, AND HEALTH RELEVANCE OF ENVIRONMENTAL CONTAMINANTS
BIO5 Institute
Agilent Technologies
Esp. Joe Weitzel & Sheher Mohsin
Visit Us: snyderlab.arizona.edu
ARIZONA

Agricultural Air Quality: Measurements, Monitoring, and Modeling

Viney P. Aneja
North Carolina State University
Department of Marine, Earth, and Atmospheric Sciences

Abstract

Emissions of gases and particulate matter from agricultural operations can impact human and ecological health and can contribute to global atmospheric greenhouse gas accumulation. As farmers respond to increasing demands for food, feed, fiber, and fuel, the potential environmental and health risks increase. Agricultural air quality is an important emerging area of environmental science, which offers significant challenges to many aspects of policy and regulatory authorities. Improvements are needed in measurements, modeling, emission controls, and farm operation management, apart from socio-economic aspects of food production. Controlling emissions of gases and particulate matter from agriculture is notoriously difficult as this sector affects the most basic need of humans, i.e. food, and policies combine an inadequately known science covering a very disparate range of activities in a complex industry with social and political overlays. Moreover, agricultural emissions derive from both area and point sources. Given the serious concerns raised regarding the amount and the impacts of agricultural air emissions, ways must be found to make real progress in reducing these environmental impacts.

Agricultural emissions produce significant local and regional impacts, such as odor, Particulate Matter (PM) exposure, eutrophication, acidification, and exposure to toxics, and pathogens. Agricultural emissions also contribute to the global problems caused by greenhouse gas emissions. Agricultural emissions are variable in space and time and in how they interact within the various processes and media effected. Most important in the US are ammonia (where agriculture accounts for ~90% of total emissions), reduced sulfur (unquantified), PM2.5 (~16%), PM10 (~18%), methane (29%), nitrous oxide (72%); and odor and emissions of pathogens (both unquantified). Agriculture also consumes fossil fuels for fertilizer production and farm operations, thus emitting carbon dioxide (CO2), oxides of nitrogen (NOx), sulfur oxides (SOx) and particulates. Current research priorities include the quantification of point and non-point sources, the biosphere-atmosphere exchange of ammonia, reduced sulfur compounds, volatile organic compounds, greenhouse gases, odor and pathogens, the quantification of landscape processes, and the primary and secondary emissions of PM. Although European policymakers have made progress in controlling these emissions, regulations in the United States remain inadequate.

AGRICULTURAL AIR QUALITY:
Measurements, Monitoring, and Modeling

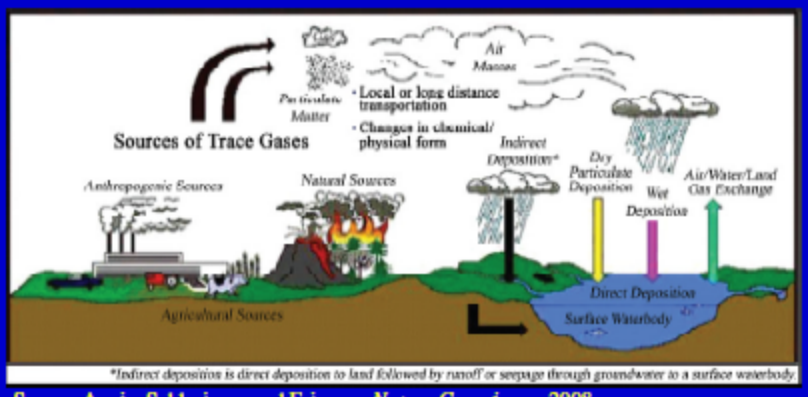
Viney P. Aneja
Department of Marine, Earth, and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695-8208, U.S.A.
http://www.meas.ncsu.edu/airquality



2013 Environmental Measurement Symposium
San Antonio, Texas
August 5, 2013.

NC STATE UNIVERSITY

Emission, Transport, Transformation, and Deposition of Trace Gases



Source: Aneja, Schlesinger and Erisman, *Nature Geoscience*, 2008.

U.S. Agricultural 2012 Preliminary Revenues

- Confined Animal Feeding Operations (CAFOs) Livestock receipts: ~$172 billion
- Crop receipts: ~$220 billion

Source: http://www.ers.usda.gov/data-products/farm-income-and-wealth-statistics.aspx#.UXWZEoKcHF8

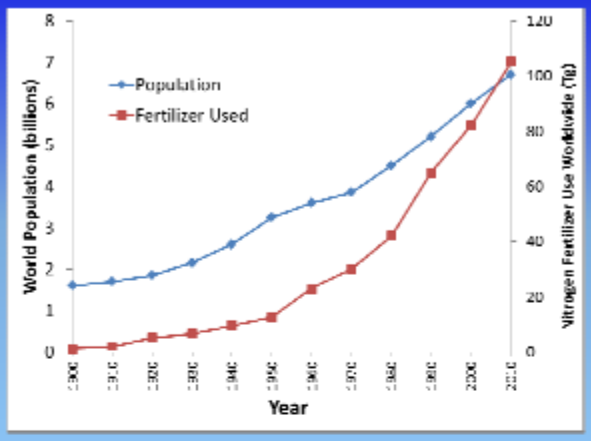
Intensification of Agriculture







Population increase and use of nitrogen fertilizer from 1900 to 2010

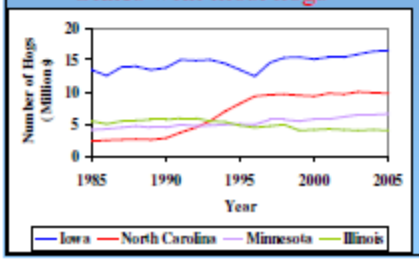


Source: Anja et al., *Atmospheric Environment*, 2008.
International Fertilizer Industry Association

National Hog Farming Trends

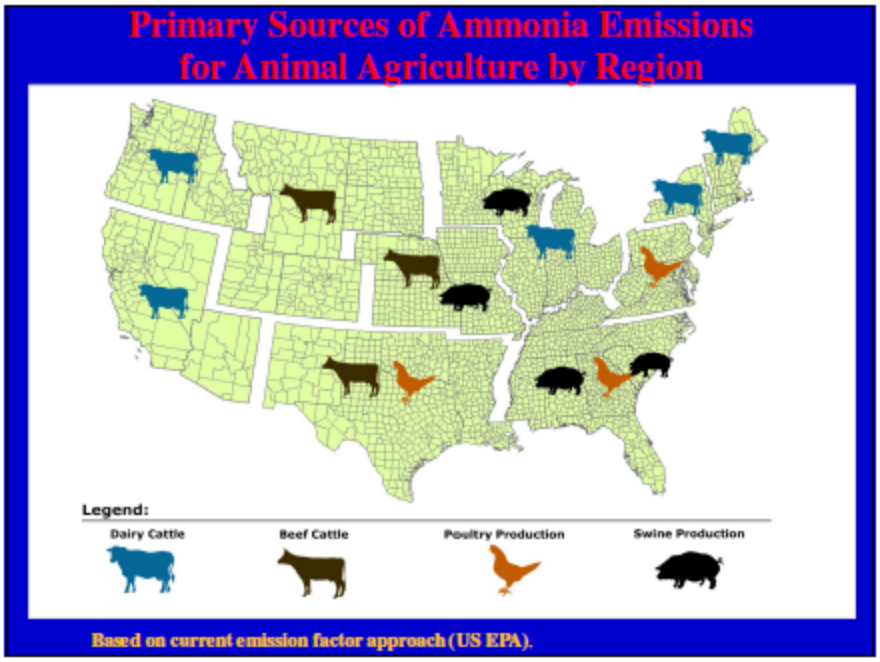


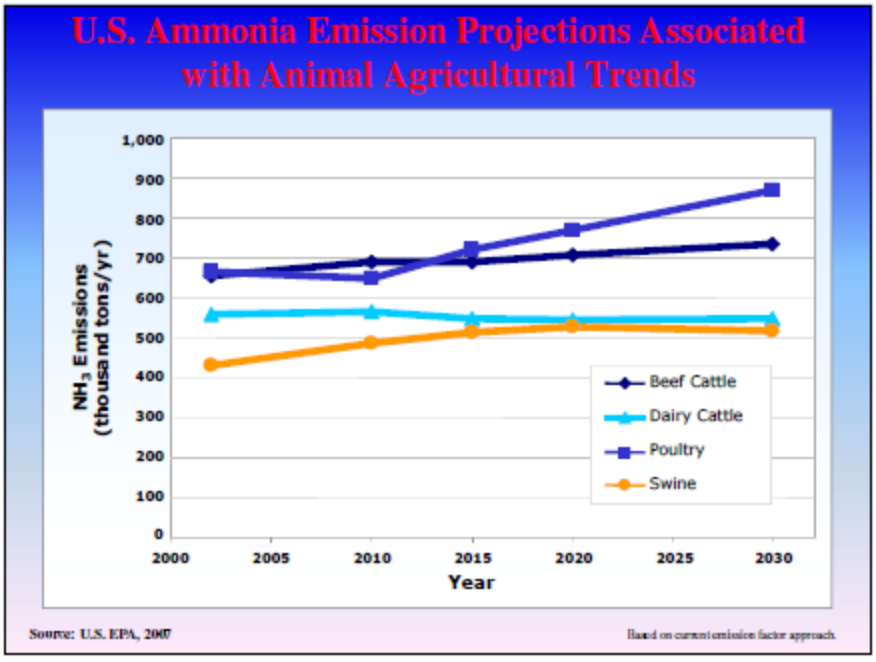
States with most hogs



Changes in Production Facilities

1992	2005
Hog Population	
58.2 million	61.3 million
Animals in Facilities > 2000 Head	
29%	79%


Primary Sources of Ammonia Emissions for Animal Agriculture by Region
Legend:
Dairy Cattle
Beef Cattle
Poultry Production
Swine Production
Based on current emission factor approach (US EPA).


U.S. Ammonia Emission Projections Associated with Animal Agricultural Trends
NH3 Emissions (thousand tons/yr)
1,000
900
800
700
600
500
400
300
200
100
0
2000
2005
2010
2015
2020
2025
2030
Year
Beef Cattle
Dairy Cattle
Poultry
Swine
Source: U.S. EPA, 2007
Based on current emission factor approach.

National Research Council, 2002

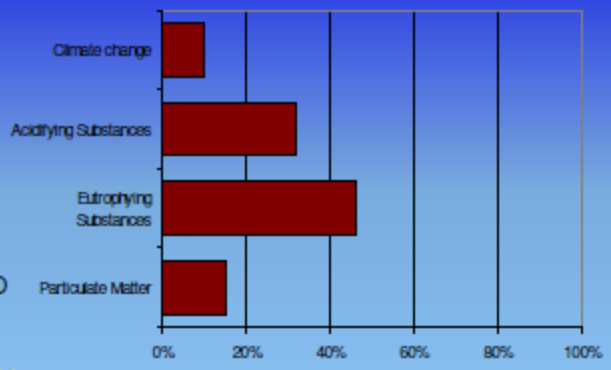
Report "The Scientific Basis for Estimating Emissions from Animal Feeding Operations"

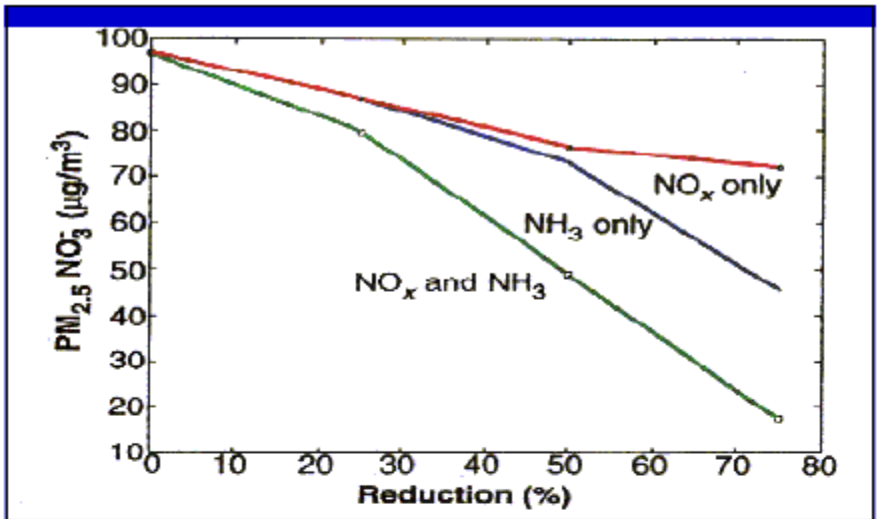
- **"The stakes in this issue are large. More and more livestock are raised for at least part of their lives in AFO's in response to economic factors that encourage further concentration. The impacts on the air in surrounding areas have grown to a point where further actions to mitigate them appear likely."**
- **"EPA may use information from this project in determining how it will approach regulating both air and water quality impacts of AFOs. Substantial emissions of nitrogen (N), sulfate (S), carbon (C), particulate matter (PM), and other substances from AFOs do occur and cannot be ignored."**

Agriculture and air quality: emissions and issues

Direct:
- NH_3
- CH_4
- N_2O
- PM
- VOCs
- Odour
- Pesticides
- SO_2, H_2S, NO
- CO_2

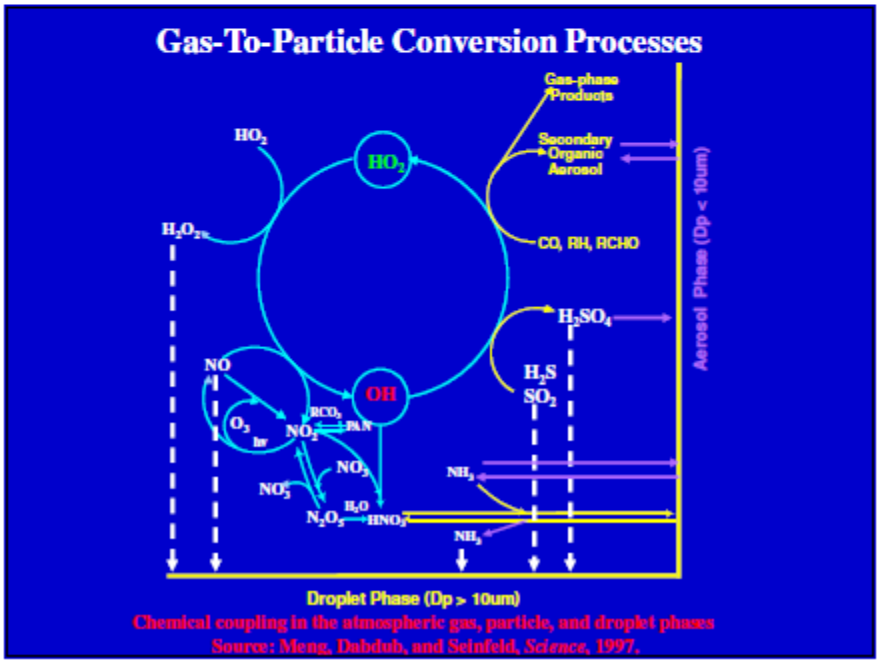
Indirect:
- Secondary PM
- CO_2 sequestration and loss (managed soils)
- Indirect N_2O (N deposition)





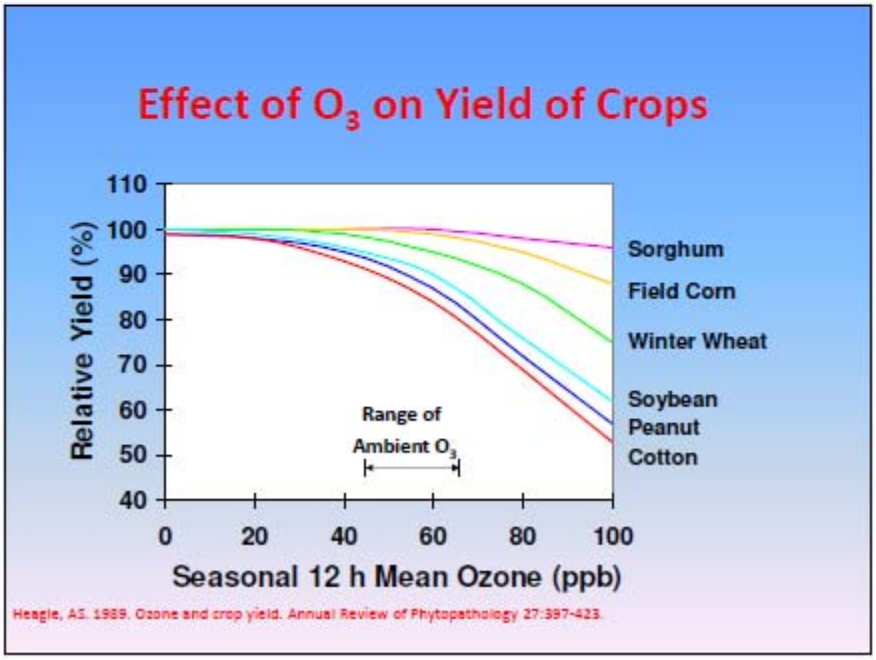
Peak 1-hour average $PM_{2.5}$ nitrate levels achieved at Riverside, California, on 28 August, 1987 as dependent on the degree of emissions reduction from the base conditions of the episode.

(Source: Meng, Dabdub, and Seinfeld, *SCIENCE*, 1997)



Chemical coupling in the atmospheric gas, particle, and droplet phases
Source: Meng, Dabdub, and Seinfeld, *Science*, 1997.


Ozone influences on plant-soil interactions in a soybean-wheat no-till system
Open Top Chambers
FL Booker. 2009. USDA-ARS Plant Science Research, Raleigh, NC USA


Effect of O_3 on Yield of Crops
Relative Yield (%)
110
100
90
80
70
60
50
40
0
20
40
60
80
100
Seasonal 12 h Mean Ozone (ppb)
Range of
Ambient O_3
Sorghum
Field Corn
Winter Wheat
Soybean
Peanut
Cotton
Heagle, AS. 1989. Ozone and crop yield. Annual Review of Phytopathology 27:397-423.

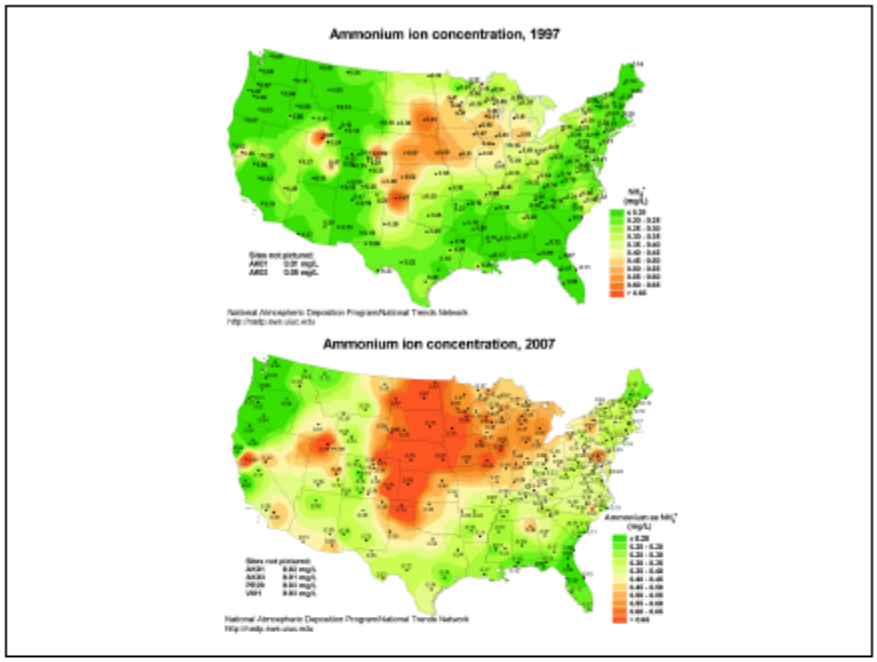
U.S. Agricultural Emissions

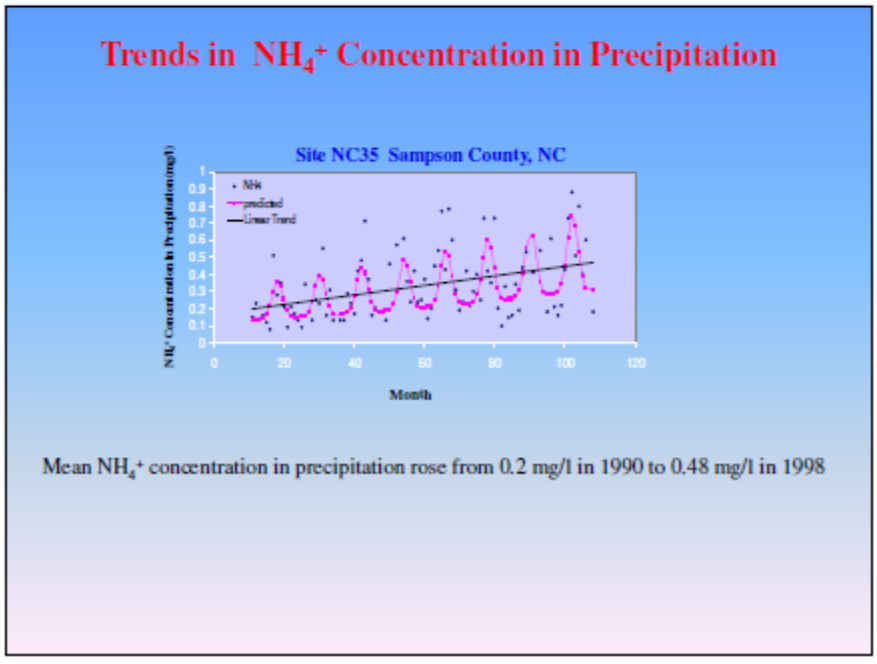
• Ammonia	~ 80%
• Reduced Sulfur	unquantified
• $PM_{2.5}$	~ 16%
• PM_{10}	~ 18%
• Methane	~ 29%
• Nitrous Oxide	~ 72%
• Odor	unquantified
• Pathogens	unquantified

Source: Aneja, Schlesinger, and Erisman, *ES&T*, 2009.

Impacts of Enhanced Ammonia on the Environment

- Particulate matter (PM) formation
- Visibility degradation
- Nitrogen enrichment and eutrophication in aquatic ecosystems
- Impact on crop and forest production
- Impact on ground water quality
- Impact on biodiversity
- Odors and odorants
- Changes in rainfall chemistry


Ammonium ion concentration, 1997
Ammonium ion concentration, 2007


Trends in NH4+ Concentration in Precipitation
Site NC35 Sampson County, NC
NH4 predicted
Linear Trend
NH4+ Concentration in Precipitation (mg/l)
Month
Mean NH4+ concentration in precipitation rose from 0.2 mg/l in 1990 to 0.48 mg/l in 1998

U.S. Air Pollutant Emission Estimates

(million tons/yr)

	CO	NOx	$PM_{2.5}$	PM_{10}	SO_2	VOC	Pb	NH_3
1970	197.3	26.9	2.3 (1990)	12.2	31.2	33.7	0.221	1.9
2005	89	19	2	2	15	16	0.003	2.6
Percent Change	-55%	-29%	-13%	-84%	-52%	-53%	-99%	+27%

Source: http://www.epa.gov/airtrends/econ-emissions.html

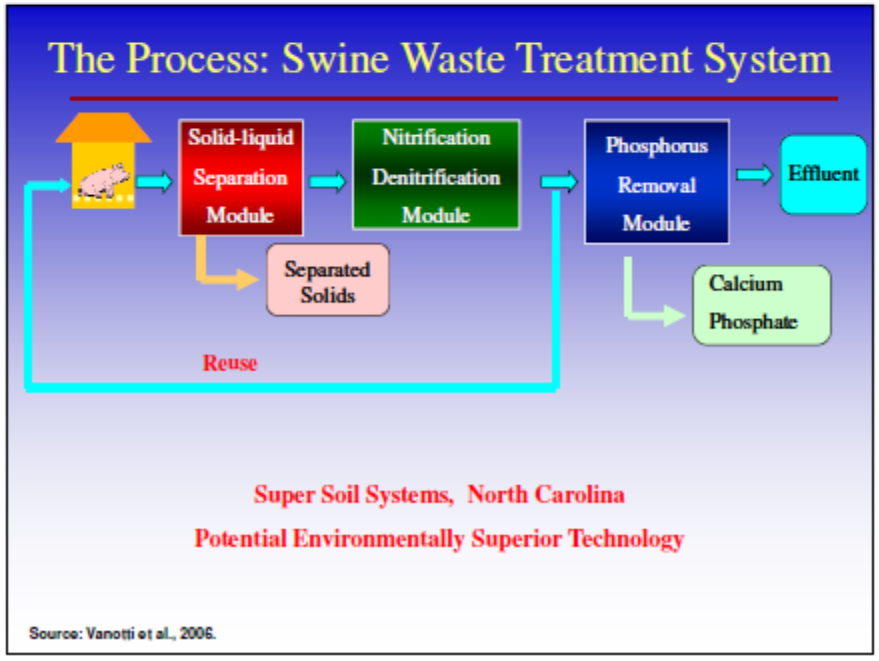
U.S. and Europe Air Pollutant Emission Estimates

(million tons/yr)

	CO	NOx	$PM_{2.5}$	PM_{10}	SO_2	VOC	Pb	NH_3
1970	197.3	26.9	2.3 (1990)	12.2	31.2	33.7	0.221	1.9
2005	89	19	2	2	15	16	0.003	2.6
Percent Change (U.S.)	**-55%**	**-29%**	**-13%**	**-84%**	**-52%**	**-53%**	**-99%**	**+27%**
Percent Change (Europe)	-54%	-34%		-83%	-76%	-43%	-99%	-22%

Source: http://www.epa.gov/airtrends/econ-emissions.html


Europe NH_3 Abatement Measures
Manure processing
Emission poor housing systems
Mineral accounting
• Maximum manure application per land use
• Decrease of N in concentrates: lowering urea concentration in milk
• Housing cattle at night
• No slurry application in winter
• Good agricultural practice
Slurry injection
Coverage of storage facilities


The Process: Swine Waste Treatment System
Solid-liquid Separation Module
Nitrification Denitrification Module
Phosphorus Removal Module
Effluent
Separated Solids
Calcium Phosphate
Reuse
Super Soil Systems, North Carolina
Potential Environmentally Superior Technology
Source: Vanotti et al., 2006.

Methods to Quantify Agricultural Emissions

- Emission factors
- Process based modeling
- Emission based on inverse modeling
- Remote sensing

Commercial Hog Farm in North Carolina, US

Sampling Sites



Trace Gas Flux Micrometeorological Experiment



Dynamic Flow-Through Chamber System



Estimating Agricultural NH_3 Emissions (Emission Factor Approach)

Emission Rate (kg NH_3 $year^{-1}$) =

*Activity Data (animal population) * Emission Factor (kg NH_3 $animal^{-1}$ $year^{-1}$)*

- **Activity Data: U.S. Census of Agriculture for 2012 at county-level**
- Beef and Dairy Cattle
- Hogs and Pigs
- Chickens
- Broilers
- Turkeys
- Horses
- Sheep
- Fertilizer Application (AAPFCO)

U.S. Ammonia Emission Factors for Animal and Crop Agriculture

Animal Agriculture Emission factor (kg-NH_3/animal/ yr)		
Animal	Battye, Aneja, & Roelle, 2003[1]	U.S. EPA: Battye et al., 1994[3]
Dairy cow	28	40
Beef cow	10.2	27 (steers)
Sow	16.4	16
Finishing pig	6.4	7
Laying hen	0.31	0.31
Broiler	0.28	0.17
Sheep	1.34	3.4
Horses	8.0	12
Crop Agriculture Emission factor (kg NH_3/Mg N)		
Fertilizer	Aneja et al., 2003[2]	U.S. EPA: Battye et al., 1994[3]
N-P-K	48	48
Nitrogen solutions	30	30
Ammonium phosphates	48	48
Anhydrous NH_3	12	12
Urea	182	182
Ammonium nitrate	25	25
Other straight nitrogen	30	30
Ammonium sulfate	97	97
Aqua NH_3	12	12
Ammonium thiosulfate	30	30

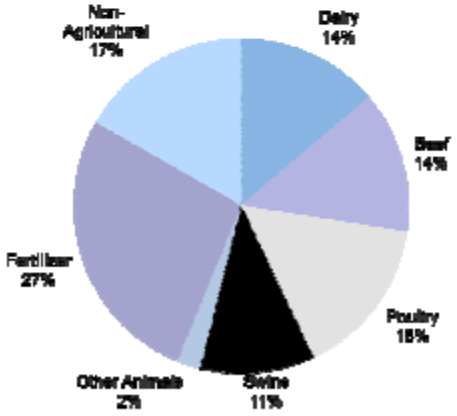
GLOBAL SOURCES OF TROPOSPHERIC AMMONIA

1.	Fossil Fuel Combustion	2 Tg N/Yr
2.	Soil-Biogenic Emissions	
	Cultivated Land	10 Tg N/Yr
	Undisturbed Soils	10 Tg N/Yr
3.	Domestic Animal Waste	32 Tg N/Yr
4.	Human Excretion	4 Tg N/Yr
5.	Biomass Burning	5 Tg N/Yr
6.	Seas and Oceans	13 Tg N/Yr
	Total Global Ammonia Emissions	~75 Tg N/Yr

Volcanic emissions ?

(Source: Schlesinger & Hartley, 1992)

U.S. Ammonia Emission Estimates (2008)

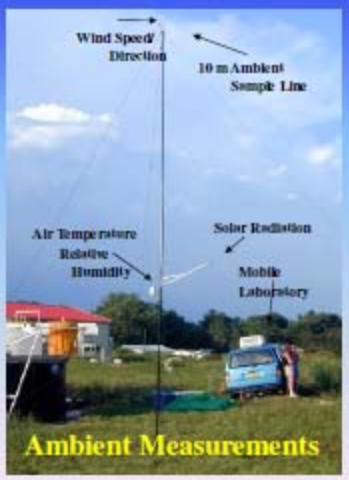


Total emissions: ~4 Tg/yr

Source: U.S. EPA 2008 National Emissions Inventory

On-Site Measurement Locations







Seasonal Lagoon Flux

$\mu g\ m^{-2}\ min^{-1}$

Season	Mean[a]	Minimum	Maximum
NH_3-N Flux			
Fall 2004	1634 (505)	1110	3305
Winter 2005	1290 (246)	867	2027
Spring 2005	2495 (465)	1565	3216
Summer 2005	4294[b]	3864	NA
H_2S Flux			
Fall 2004	0.3 (0.1)	0.0	0.8
Winter 2005	~0.0 (0.2)	0.0	1.2
Spring 2005	0.5 (1.0)	0.1	7.1
Summer 2005	5.3 (3.2)	0.8	13.3

NH_3-N flux = (14/17) NH_3 flux

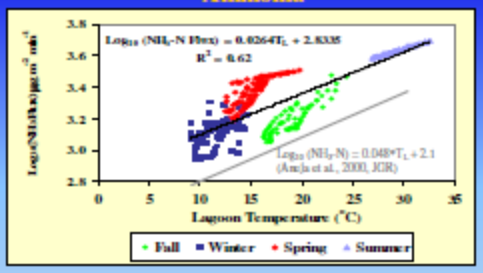
[a] Numbers in parenthesis represent one standard deviation

[b] NH_3 concentration was above maximum range on the ammonia analyzer. Maximum flux values are unknown.

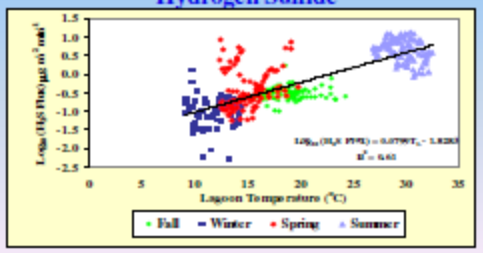
Source: Blunden and Aneja, *Atmospheric Environment*, 2008.

Flux vs Lagoon Temperature

Ammonia



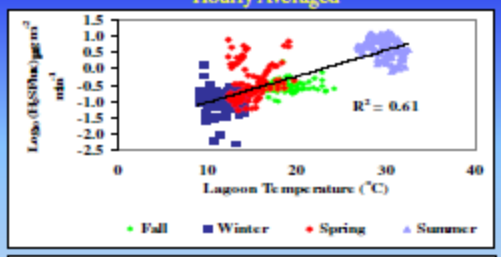
Hydrogen Sulfide

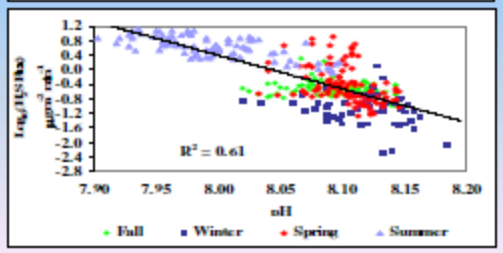


Source: Blunden and Aneja, *Atmospheric Environment*, 2008.

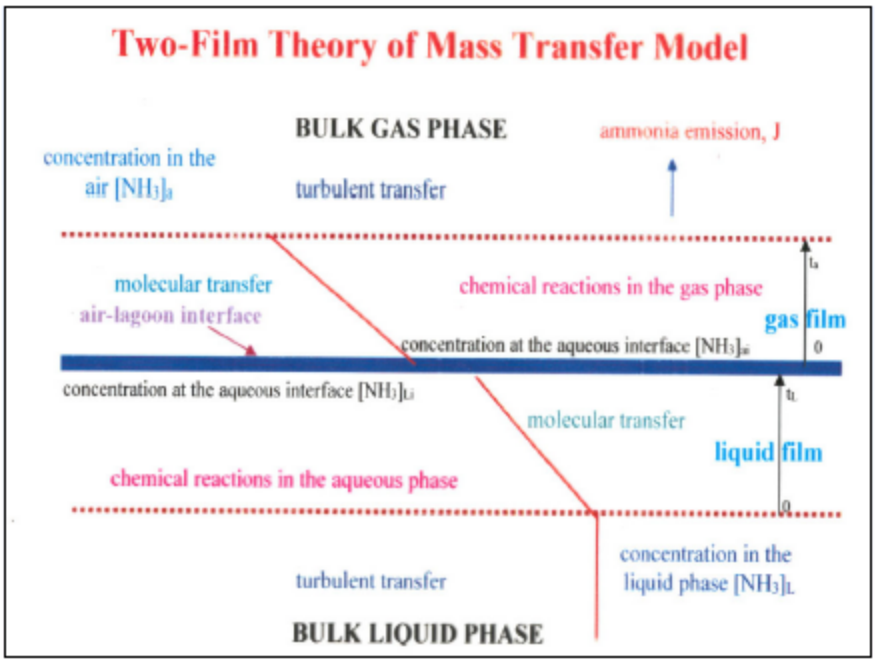
H_2S Flux vs Lagoon Parameters

Hourly Averaged





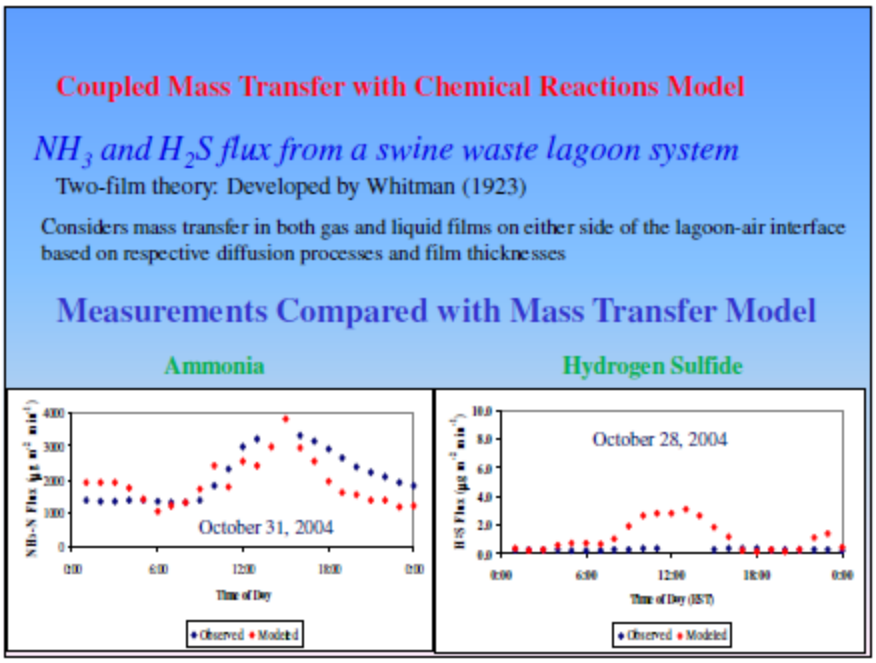
Source: Blunden and Aneja, *Atmospheric Environment*, 2008.

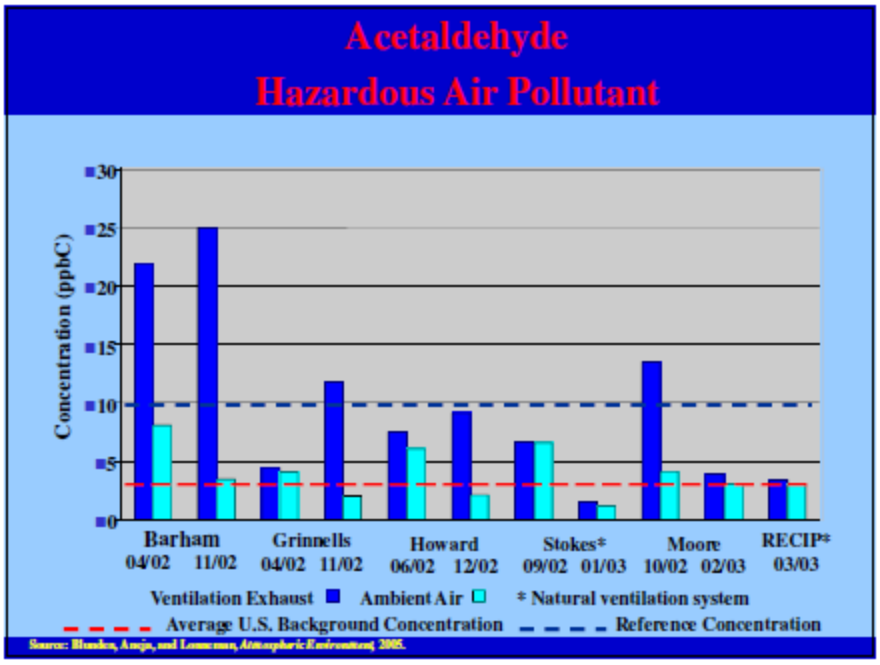


Basic Difussion Equation

$$D\left(\frac{d^2C(z)}{dz^2}\right) = K_r \times C(z)$$

- C(z) Ammonia concentration at the height of z in the films (m)
- D Molecular diffusion coefficient of ammonia in the phases
- z Vertical direction height (m)
- K_r 1st order reaction rate constant of ammonia in the phases


Coupled Mass Transfer with Chemical Reactions Model
NH_3 and H_2S flux from a swine waste lagoon system
Two-film theory: Developed by Whitman (1923)
Considers mass transfer in both gas and liquid films on either side of the lagoon-air interface based on respective diffusion processes and film thicknesses
Measurements Compared with Mass Transfer Model
Ammonia
Hydrogen Sulfide
October 31, 2004
October 28, 2004
Time of Day
Observed
Modeled


Acetaldehyde
Hazardous Air Pollutant
Concentration (ppbC)
30
25
20
15
10
5
0
Barham 04/02 11/02
Grinnells 04/02 11/02
Howard 06/02 12/02
Stokes* 09/02 01/03
Moore 10/02 02/03
RECIP* 03/03
Ventilation Exhaust
Ambient Air
* Natural ventilation system
Average U.S. Background Concentration
Reference Concentration

Summary and Conclusions

- Main issues: quantification of diffuse sources, atmosphere-biosphere exchange and primary and secondary PM
- Improved Nitrogen, Sulfur, Carbon, GHGs, gaseous emission inventory
- Application of Best Management Practices
- Development of Environmentally Superior Technologies
- Development of national network monitoring system for atmospheric gas concentrations and emissions from agricultural areas, and subsequent deposition

Summary and Conclusions

- Emission factors approach
  - Easy to use, but results may have uncertainty
- Process based and inverse modeling approach
  - Complex but results have less uncertainty
- Remote sensing approach
  - Emerging area of gaseous and PM emission analysis

Challenges for the Community

- What are the potential health effects from exposures to ambient levels of NH_3?
- Is there long range atmospheric transport?
- Are current air monitoring methods sufficient for NH_3 measurement?
- Vertical bi-directional transport of ammonia ?
- Are current air quality modeling techniques sufficient for analyzing the N cycle, including NH_3?
- Is it prudent to regulate NH_3 and NO_X or should we focus on the total N cycle?
- How do we optimize and evaluate the impacts of reductions of the various forms of N and of other air pollutants?
- Are control technologies for agricultural sources available? Are they feasible?
- What are the proven methods (BMPs) and their associated costs for reducing NH_3 from agricultural sources?
- **Need for a network to monitor emissions from agricultural sources.**

Acknowledgements

- NCSU Air Quality Research Group
- U.S. Department Of Agriculture – National Research Initiative, Contract No. 2004-35112-14253
- Phosphate Potash Institute, The Fertilizer Institute
- The National Science Foundation
- The Kenan Institute
- Animal and Poultry Waste Management Center / Smithfield Foods


AGRICULTURAL AIR QUALITY:
Measurements, Monitoring, and Modeling
Viney P. Aneja
Department of Marine, Earth, and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695-8208, U.S.A.
http://www.meas.ncsu.edu/airquality
San Antonio, Texas
August 5, 2013
NC STATE UNIVERSITY

Early Engagement of University Undergraduate Students in Environmental Monitoring

B.H. Kiepper, C.W. Ritz
University of Georgia
Department of Poultry Science

Abstract

In 2010 the University System of Georgia, in an effort to increase retention rates of freshman students across the state, established a series of early student-faculty engagement goals. In response, the University of Georgia, in Athens, created the "First-Year Odyssey" seminar program. All freshman students at UGA are required to complete a 1-credit hour seminar during one semester of their first year on campus. The goals of the FYO seminar are to introduce first-year students to the importance of learning and academics in the academic culture of the University, to give first-year students an opportunity for meaningful dialogue with a faculty member to encourage positive, sustained student-faculty interactions, and to introduce first-year students to the instruction, research, public service and international missions of the University and how they relate to teaching and learning in and outside the classroom. To maximize student-faculty engagement, class size is limited to 15 students. This paper will discuss the development of the UGA FYO seminar entitled "Environmental Monitoring: How Scientist use Water, Air and Soil to Learn about the World around Us". The seminar uses a combination of field environmental sampling events coupled with laboratory tours and analytical exercises to not only meet FYO seminar goals, but to also engage university freshman students into the field of environmental monitoring. The seminar has been taught during three semesters to a total of 45 freshman students. Seminar marketing, curriculum development and lessons learned will be discussed.

Early Engagement of University Undergraduate Students in Environmental Monitoring

B.H. Kiepper and C.W. Ritz
Department of Poultry Science
University of Georgia
Athens, GA



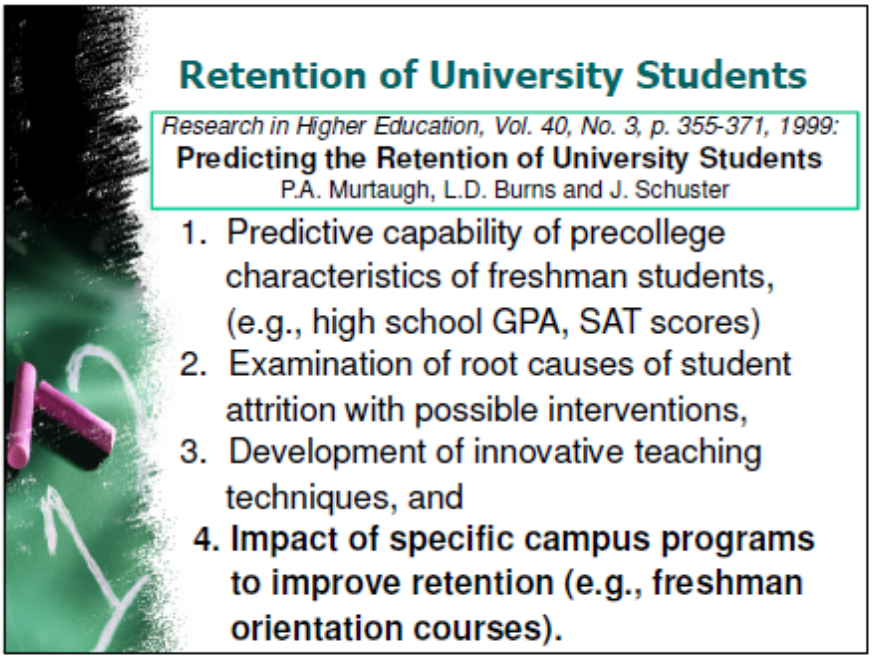


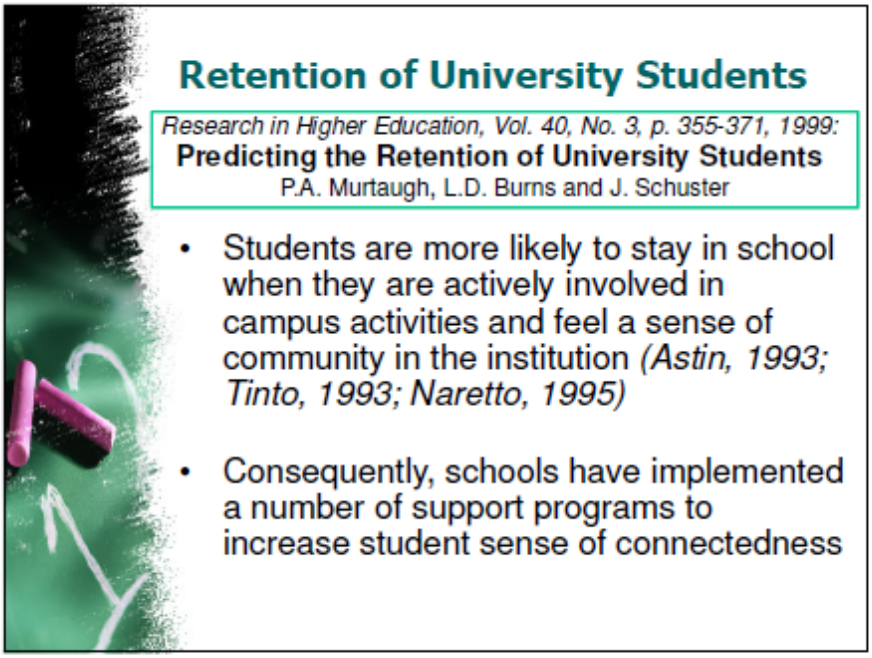
Retention of University Students

Research in Higher Education, Vol. 40, No. 3, p. 355-371, 1999:
Predicting the Retention of University Students
P.A. Murtaugh, L.D. Burns and J. Schuster

- Retention of students at colleges and universities has long been a concern for educators
- Published research on student retention has focused on multiple themes:




Retention of University Students
Research in Higher Education, Vol. 40, No. 3, p. 355-371, 1999:
Predicting the Retention of University Students
P.A. Murtaugh, L.D. Burns and J. Schuster
1. Predictive capability of precollege characteristics of freshman students, (e.g., high school GPA, SAT scores)
2. Examination of root causes of student attrition with possible interventions,
3. Development of innovative teaching techniques, and
4. Impact of specific campus programs to improve retention (e.g., freshman orientation courses).


Retention of University Students
Research in Higher Education, Vol. 40, No. 3, p. 355-371, 1999:
Predicting the Retention of University Students
P.A. Murtaugh, L.D. Burns and J. Schuster
• Students are more likely to stay in school when they are actively involved in campus activities and feel a sense of community in the institution (Astin, 1993; Tinto, 1993; Naretto, 1995)
• Consequently, schools have implemented a number of support programs to increase student sense of connectedness

Retention of University Students

Research in Higher Education, Vol. 40, No. 3, p. 355-371, 1999:
Predicting the Retention of University Students
P.A. Murtaugh, L.D. Burns and J. Schuster

- Greatest attrition occurs between freshman and sophomore years
- Thus, retention programs tend to focus on first-year students

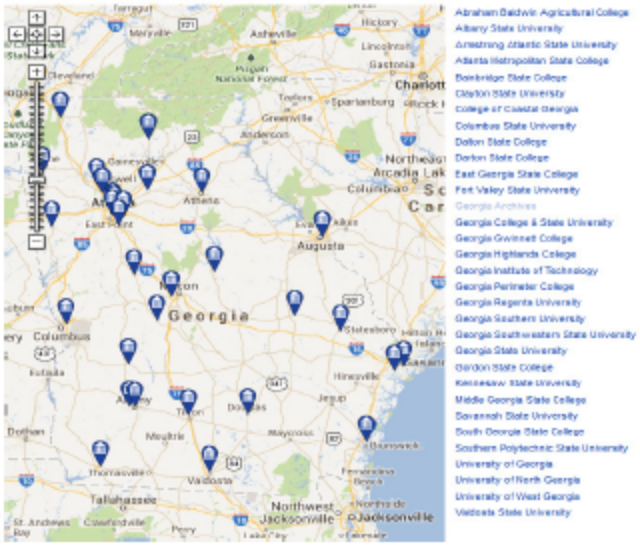


University System of Georgia

In 2010, the University System of Georgia, in an effort to increase retention rates of freshman students across the state, established a series of early student-faculty engagement goals



University System of Georgia



University of Georgia, Athens, GA

- **Founded:** January 27, 1785, by the Georgia General Assembly
- UGA is the first state-chartered university in America
- **18 Schools and Colleges:** Agricultural and Environmental Sciences, Arts and Sciences, Business, Ecology, Education, Environment and Design, Family and Consumer Sciences, Forest Resources, Graduate School, Journalism and Mass Communication, Law, Pharmacy, Public Health, Public and International Affairs, Social Work, Veterinary Medicine, the GRU/UGA Medical Partnership, and Engineering

University of Georgia, Athens, GA

- **Enrollment – Fall Semester 2012:**
  Undergraduate: 26,215
  Graduate/Professional: 8,260
  Total: 34,475
- **2012 Freshmen: 4,970 total**

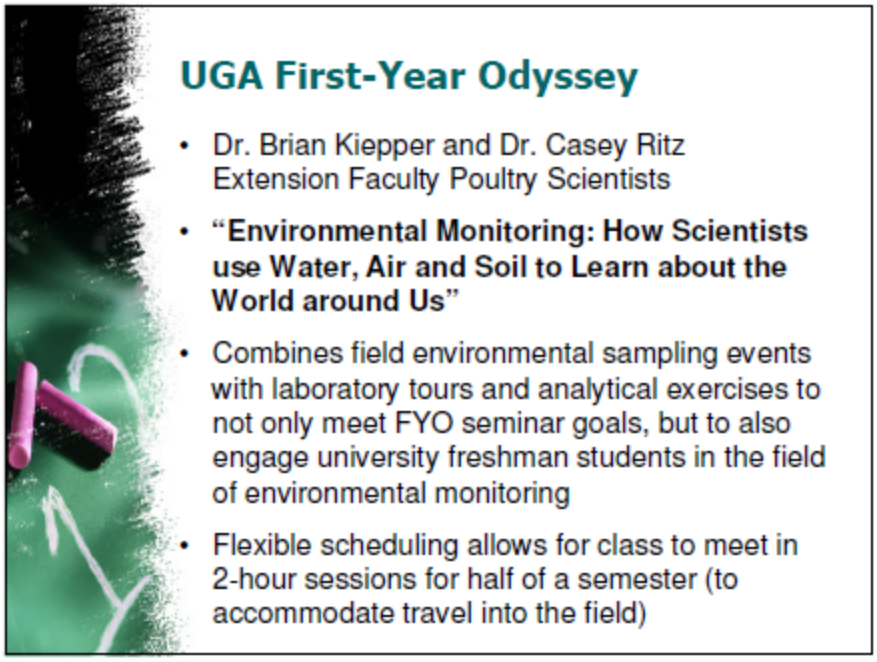


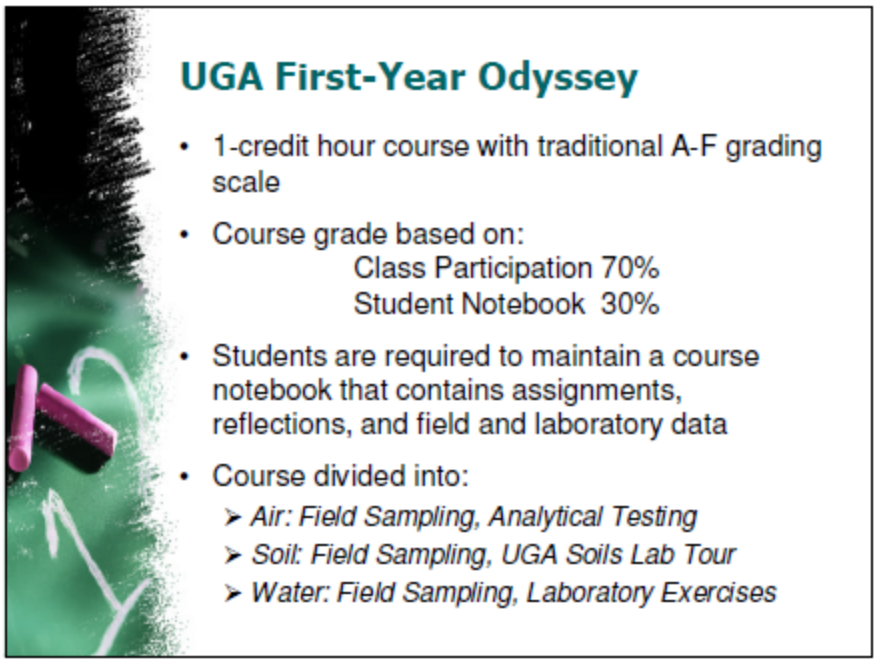
University of Georgia

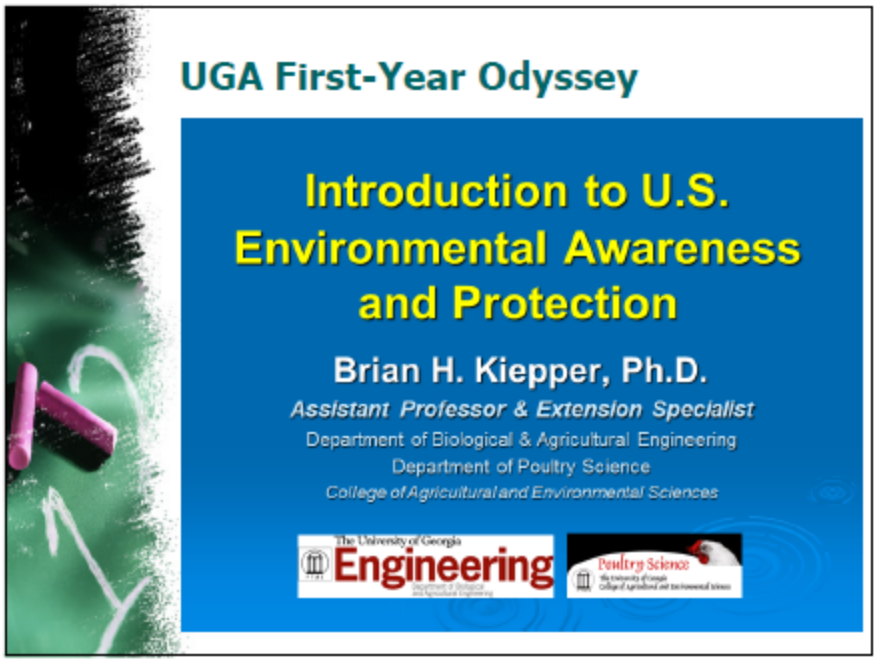
- Created the "**First-Year Odyssey**" seminar program
- All freshman students at UGA are required to complete a **1-credit hour seminar** during one semester of their first year on campus
- To maximize student-faculty engagement, class size is limited to 15 students
- Faculty receive additional compensation for teaching a seminar and co-teaching is encouraged




University of Georgia
FIRST-YEAR ODYSSEY
ABOUT
SEMINARS
EVENTS
FAQ
CONTACT
HOME
for FACULTY
ENGAGE
IN A SMALL CLASS SETTING
SEMINAR #
Scientists Behaving Badly: Hoaxes, Charlatans and Frauds in Science and Medicine
ATTENTION
EVENTS


UGA First-Year Odyssey
• Dr. Brian Kiepper and Dr. Casey Ritz Extension Faculty Poultry Scientists
• "Environmental Monitoring: How Scientists use Water, Air and Soil to Learn about the World around Us"
• Combines field environmental sampling events with laboratory tours and analytical exercises to not only meet FYO seminar goals, but to also engage university freshman students in the field of environmental monitoring
• Flexible scheduling allows for class to meet in 2-hour sessions for half of a semester (to accommodate travel into the field)


UGA First-Year Odyssey
• 1-credit hour course with traditional A-F grading scale
• Course grade based on:
Class Participation 70%
Student Notebook 30%
• Students are required to maintain a course notebook that contains assignments, reflections, and field and laboratory data
• Course divided into:
➢ Air: Field Sampling, Analytical Testing
➢ Soil: Field Sampling, UGA Soils Lab Tour
➢ Water: Field Sampling, Laboratory Exercises


UGA First-Year Odyssey
Introduction to U.S. Environmental Awareness and Protection
Brian H. Kiepper, Ph.D.
Assistant Professor & Extension Specialist
Department of Biological & Agricultural Engineering
Department of Poultry Science
College of Agricultural and Environmental Sciences
The University of Georgia
Engineering
Poultry Science

Environmental Monitoring: AIR



Air Sampling

- University of Georgia, **Poultry Research Farm**, Athens, GA



Air Sampling

- **Instrument**: Boreal Laser GasFinder
  boreal-laser.com, Calgary, Canada

BOREAL LASER GasFinder2

Marketed as a fully portable, open path, single gas monitor providing one second response and a broad dynamic range. Compact, light and can be set up and operating in less than five minutes



Air Sampling

Schematic Representation



boreal-laser.com
Calgary, Canada
info@boreal-laser.com
Phone 1.403.452.5173

©Boreal Laser Inc 10/2010

Standard: HF, NH_3, H_2, S, CH, CO_2, HCN
Custom: HCl, CO, C_2, H_2, H_2O


Air Sampling


Air Sampling


Air Sampling


Air Sampling

Environmental Monitoring: SOIL

- Soil Sampling Field Exercise, University of Georgia, College of Engineering, **Bioconversion Center**, Athens, GA



Soil Sampling




UGA Composting


Environmental Monitoring: SOIL
• University of Georgia, State Soil, Feed & Water Laboratory, Athens, GA


Environmental Monitoring: SOIL


Environmental Monitoring: SOIL

Environmental Monitoring: WATER

- Athens/Clarke County Government, **Oconee River Greenway**, Athens, GA



Water Sampling

- Athens/Clarke County Government, **Oconee River Greenway**, Athens, GA



Water Sampling

- **Equipment:** Van Dorn Water Sampler

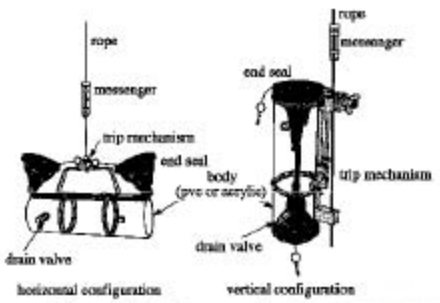


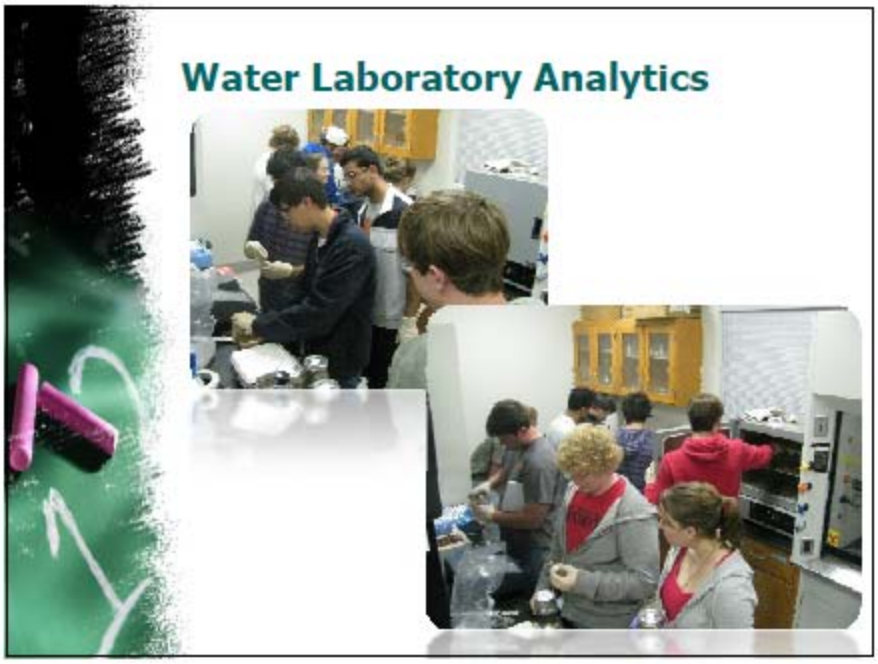
Figure 1. Van Dorn sampler



Water Sampling




Water Laboratory Analytics


Water Laboratory Analytics


Questions?

Low Impact Design as a Supportive Measure for Non Point Source Management

Afamia Elnakat
UTSA Texas Sustainable Energy Research Institute

Abstract

Increased drought periods in areas like south central Texas and around the nation have resulted in degraded parched soils. The hard surface soils and improved impervious cover from development followed by off seasonal rainstorms result in flash floods. Flash floods significantly increased levels of sedimentation runoff and sewer overflows. Monitoring non point sources continues to challenge the environmental industry and policymakers. Preventative measure to non point sources runoff discharge is becoming more possible with Low Impact Design (LID). LID can be utilized to mimic predevelopment hydrology to reduce sedimentation. This presentation will highlight the benefits and limitations of LID measures to include aesthetic function and public and cross-disciplinary acceptance.

UTSA | TexasSustainableEnergy RESEARCH INSTITUTE

Low Impact Design as a Supportive Measure for Non Point Source Management

Afamia Elnakat, Ph.D., R.E.M.

Associate Professor of Research



Overview

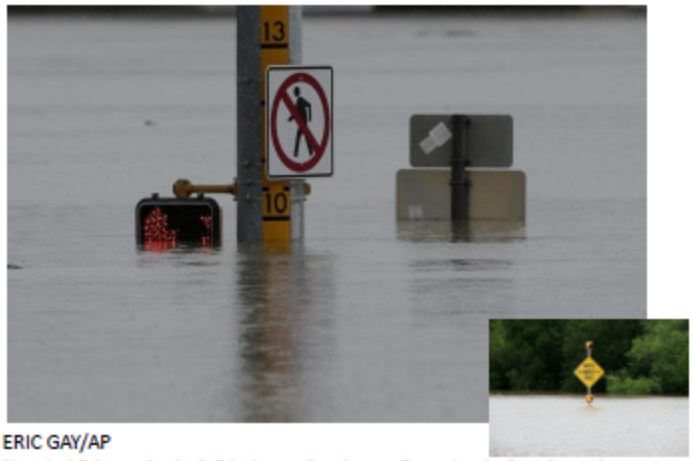
- **Problem Statement**
  - Increased drought periods in areas like south central Texas and around the nation have resulted in degraded parched soils.
    - The hard surface soils
    - Improved impervious cover from development
    - Off seasonal rainstorms and extreme weather patterns







Floods hit San Antonio, Texas, with nearly 10 feet of water; at least 2 dead
THE ASSOCIATED PRESS - SUNDAY, MAY 26, 2013, 9:34 AM



ERIC GAY/AP
Nearly 10 feet of rain fell in just a few hours Saturday in San Antonio

Objective

- **Problem Statement**
  - Monitoring non point sources continues to challenge the environmental industry and policymakers.

Can We Use LID as a Supportive Measure?

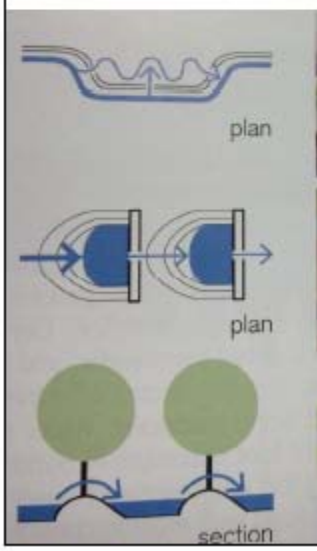
  - This presentation will highlight:
    - The benefits and limitations of LID measures
    - Include aesthetic function
    - Public and cross-disciplinary acceptance

What is LID

Low Impact Development | Low Impact Urban Design | Stormwater Management

Ecological Engineering of Stormwater Management!!

What is LID





curb
street curbs typically line street edges; however, they can be cut and shaped to allow for water passage into a LID facility *Curb Alternatives* pp. 96-97



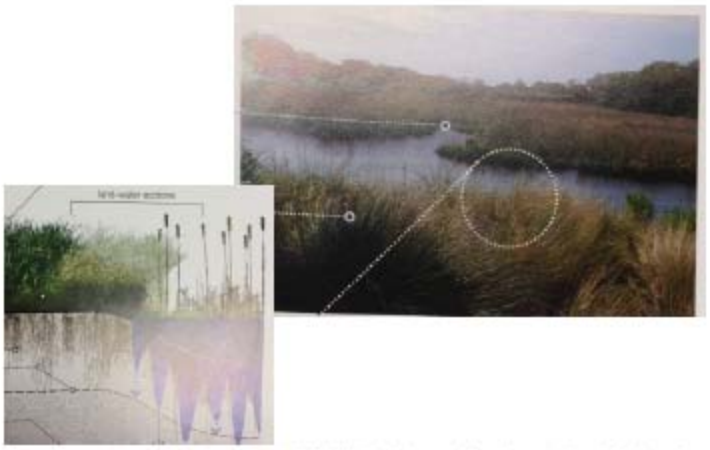
check dam
small dams constructed across a ditch or swale to slow and temporarily hold water during larger storm events



tree mound
trees planted on mounds within a swale, bioswale, or ditch can act as natural check dams, attenuating stormwater flow

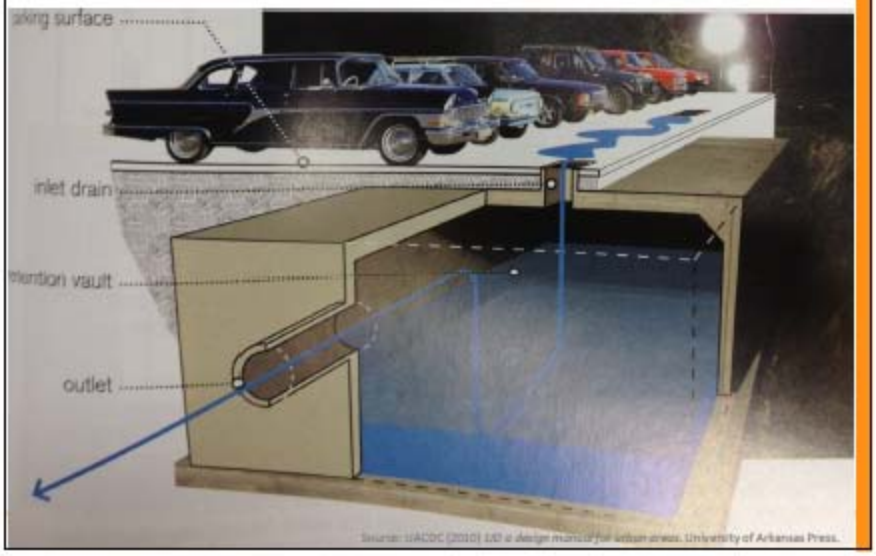
Source: UACDC (2010) *LID a design manual for urban areas*. University of Arkansas Press.

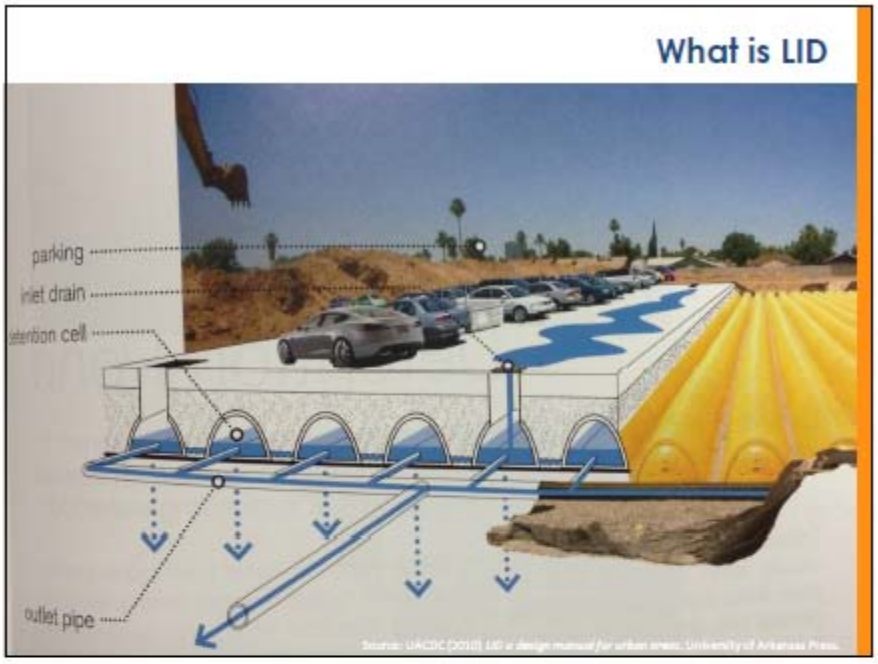
What is LID

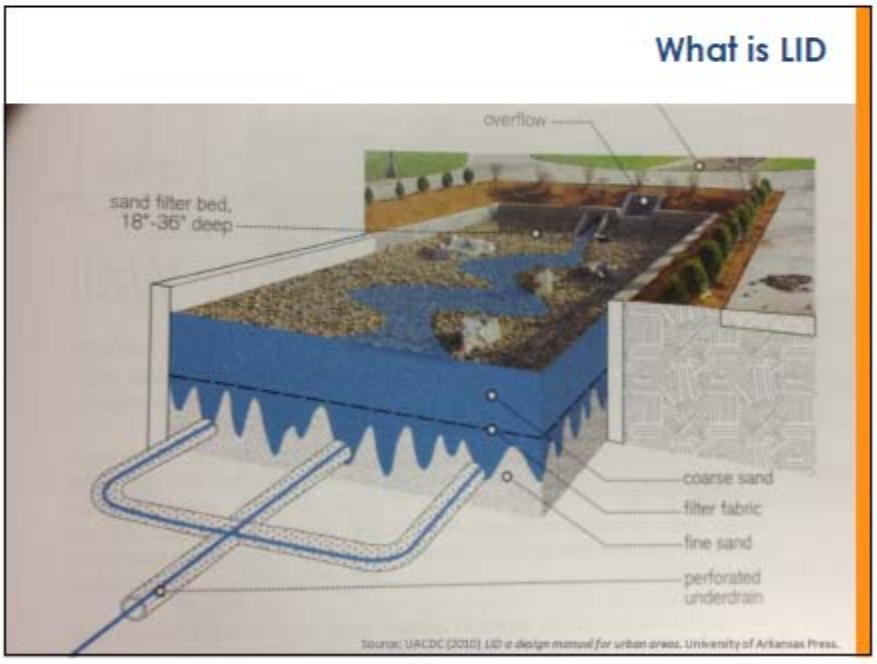


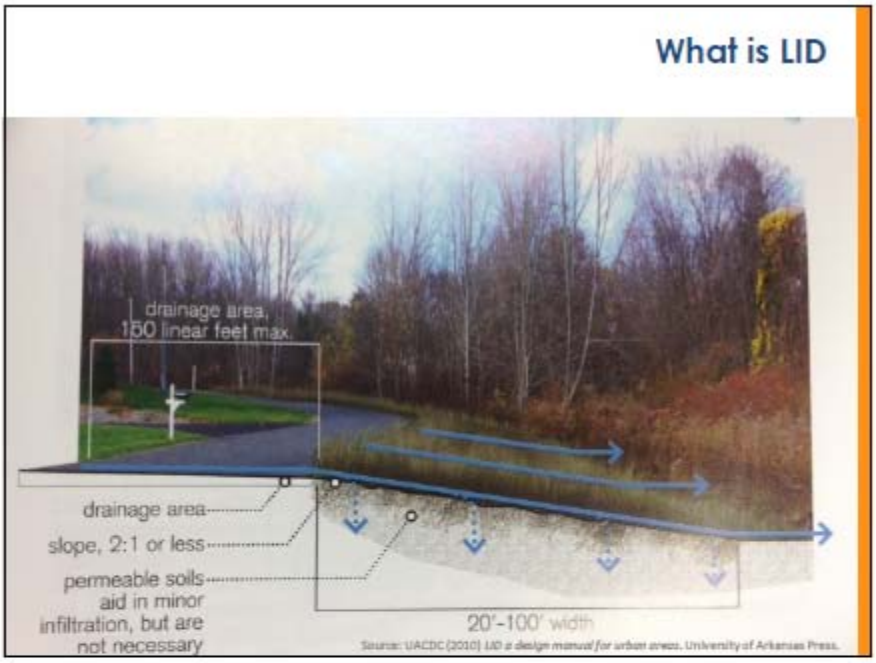
Source: UACDC (2010) *LID a design manual for urban areas*. University of Arkansas Press.

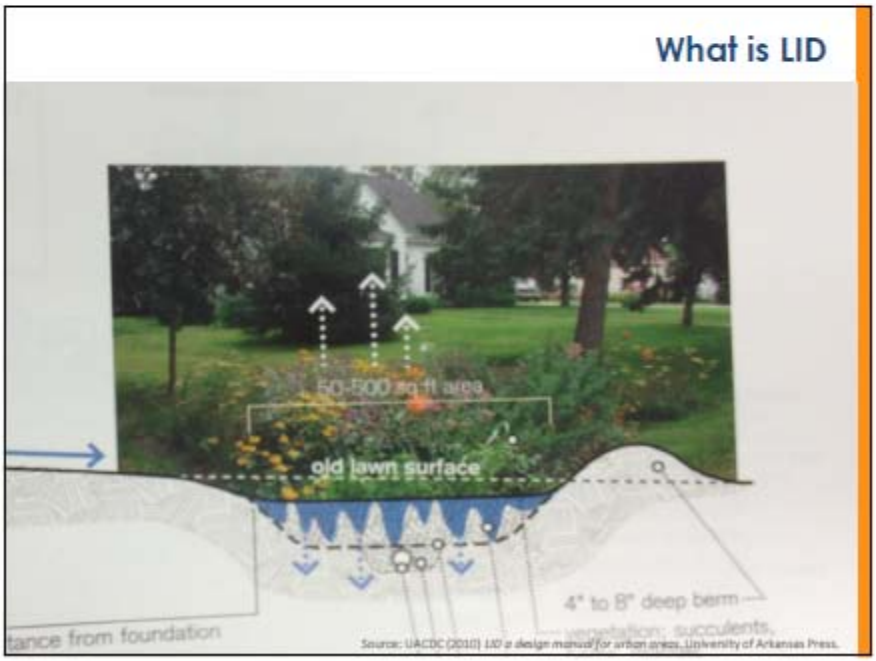
What is LID

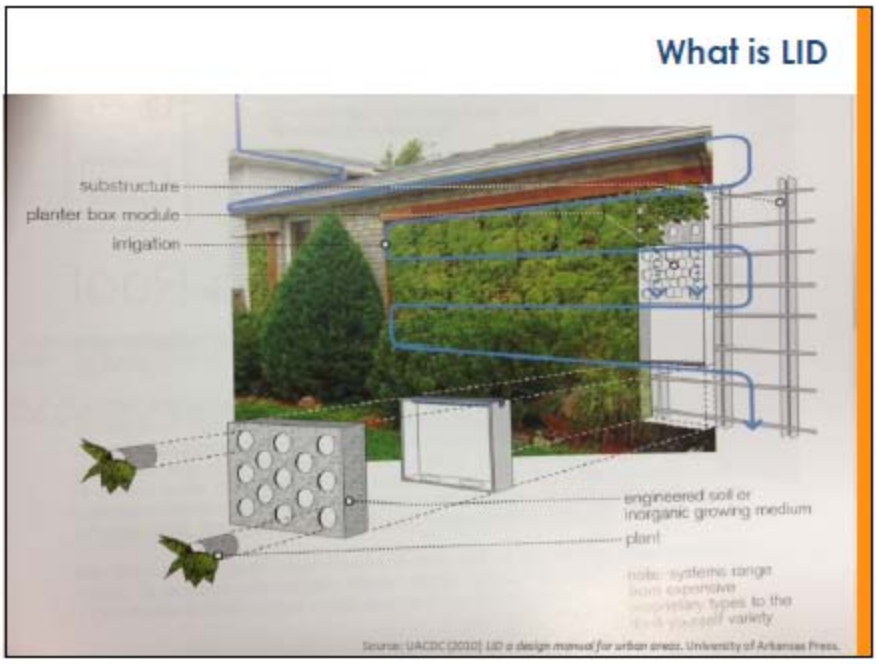


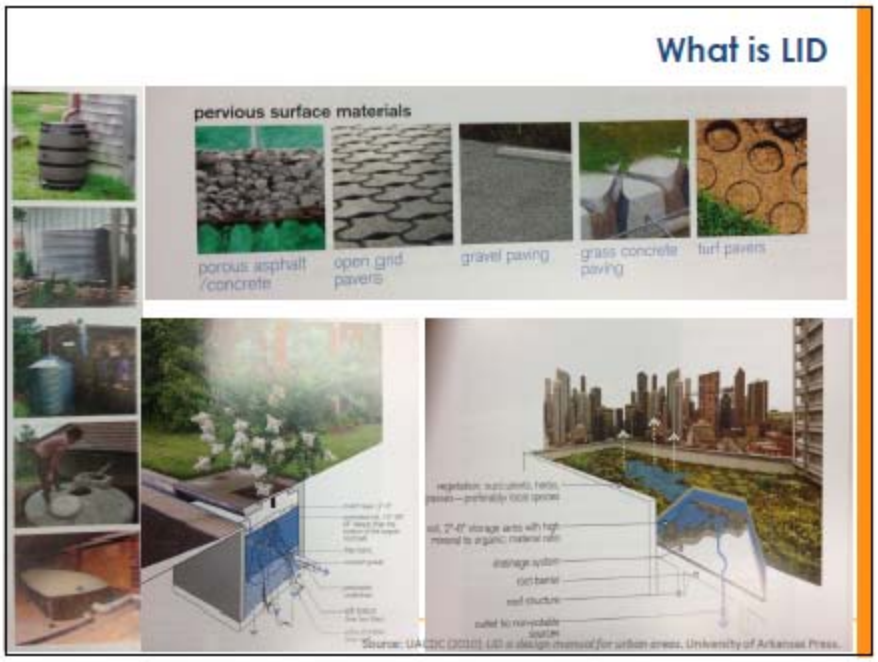

What is LID
parking
inlet drain
retention cell
outlet pipe


What is LID
overflow
sand filter bed,
18"-36" deep
coarse sand
filter fabric
fine sand
perforated
underdrain


What is LID
drainage area,
150 linear feet max.
drainage area
slope, 2:1 or less
permeable soils
aid in minor
infiltration, but are
not necessary
20'-100' width
Source: UACDC (2010) LID a design manual for urban areas. University of Arkansas Press.


What is LID
50-500 sq ft area
old lawn surface
4" to 8" deep berm
vegetation: succulents,
tance from foundation
Source: UACDC (2010) LID a design manual for urban areas. University of Arkansas Press.


What is LID
substructure
planter box module
irrigation
engineered soil or
inorganic growing medium
plant


What is LID
pervious surface materials
porous asphalt
/concrete
open grid
pavers
gravel paving
grass concrete
paving
turf pavers

LID Goals

- **Mimic pre-development hydrology**
- **Soft engineering into hard engineering**
  - Vegetated treatment networks
  - Best Management Practices (BMPs)
- **BMPs that manage stormwater runoff close to it's source**
  - Infiltrate
  - Filter
  - Store
  - Evaporate

~~Conventional Design~~
~~Pipe & Conveyance Infrastructure~~
~~Channeling Runoff in Distances~~
~~Overloading our WW Treatment Plants~~

Pros of LID

- **Reduce Stormwater Impact**
  - Reducing peak rate volume
  - Reducing runoff
- **Providing water quality treatment**
  - Settling
  - Filtration
  - Sorption

Quantity

Quality

Pros of LID

- **Reduce Infrastructure Cost**
  - Narrower streets
  - Absence of curbs/gutters/pipelines/concrete boxes
  - LID Landscaping can mature to equal market
- **Extend Lifetime of Existing Infrastructure**
  - Barely passing grade
  - Sewer Overflows
- **Alleviate Environmental Impacts**
  - Hazards of flooding
  - Pollutant loads entering streams
  - Reduce impervious cover: runoff, air quality, aesthetics, habitat, noise buffer

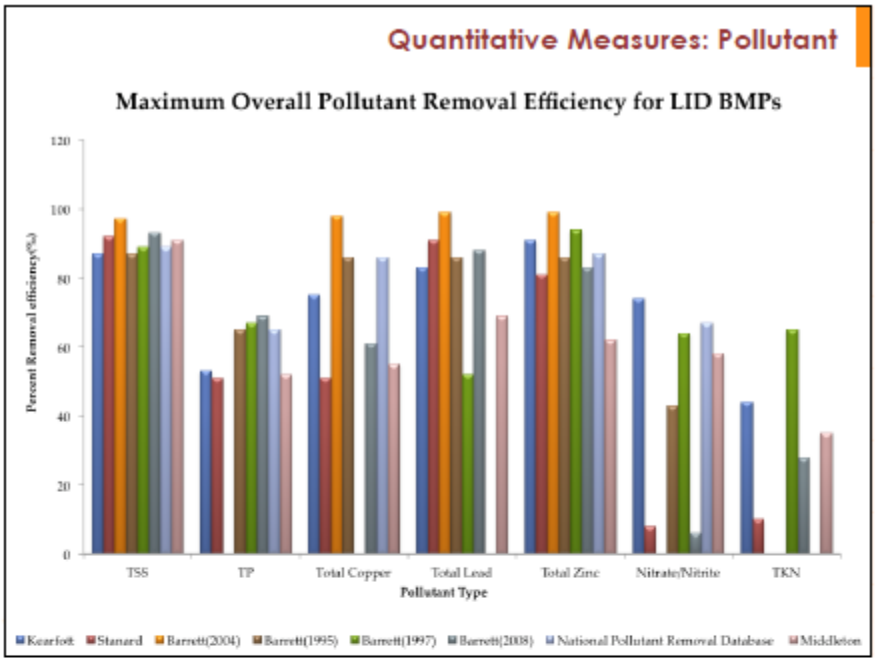


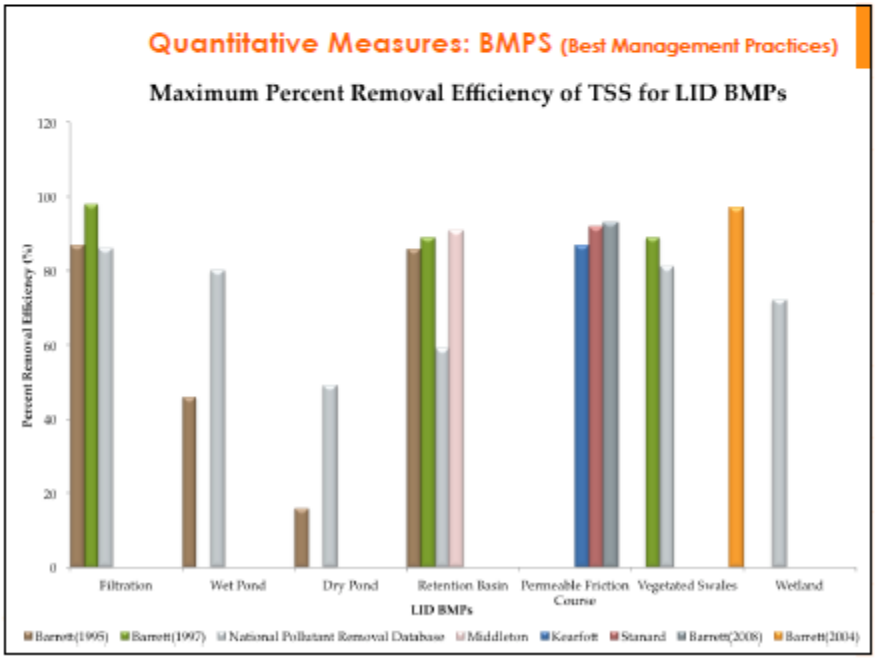
Cons of LID

- **Many LID Design Concepts Restricted by Zoning & Development Codes**
  - Minimum street width for buses, emergency, garbage and other utility vehicles
  - Lack of confidence from city personnel and developers
- **Public Health Concerns**
  - Water ponding and harboring mosquito
  - Ice formation

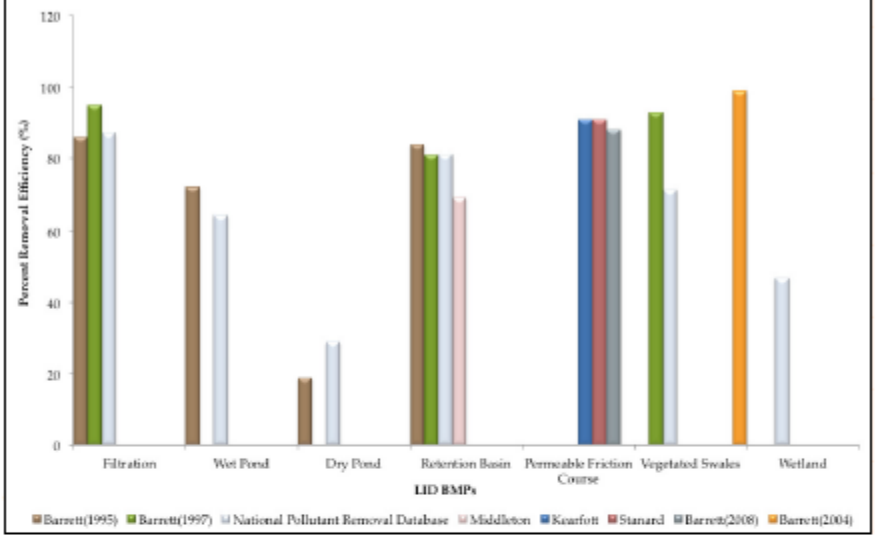


- **Will Require Maintenance**
  - Not a Con because conventional infrastructure requires maintenance
  - Incorporated into HOAs and easements


Quantitative Measures: Pollutant
Maximum Overall Pollutant Removal Efficiency for LID BMPs
Percent Removal efficiency(%)
120
100
80
60
40
20
0
TSS
TP
Total Copper
Total Lead
Total Zinc
Nitrate/Nitrite
TKN
Pollutant Type
Kearfott
Stanard
Barrett(2004)
Barrett(1995)
Barrett(1997)
Barrett(2008)
National Pollutant Removal Database
Middleton


Quantitative Measures: BMPS (Best Management Practices)
Maximum Percent Removal Efficiency of TSS for LID BMPs
Percent Removal Efficiency (%)
120
100
80
60
40
20
0
Filtration
Wet Pond
Dry Pond
Retention Basin
Permeable Friction Course
Vegetated Swales
Wetland
LID BMPs
Barrett(1995)
Barrett(1997)
National Pollutant Removal Database
Middleton
Kearfott
Stanard
Barrett(2008)
Barrett(2004)

Quantitative Measures: BMPS (Best Management Practices)



Conclusions

- **Way of thinking** ***incorporated to development codes*** **and** ***engineering design.***
- **Offer up an environmentally friendly approach, more sustainable approach to** ***managing impervious cover.***
- **Provide and opportunity to** ***increase soil content.***
- **Research opportunities**
  - Media types for pollutant removal
  - Automated metering device integration into LID



Thank You



Questions & Comments

Please call or email:
afamia.elnakat@utsa.edu x 458-5742

References

Barrett, M.E., Kahlo, R.F., Walsh, P.M., Malina, J.F.,Jr., Charbeneau, R.J. (1997). Evaluation of the Performance of Permanent Runoff Controls: Summary and Conclusions. Center for Research in Water Resources, 97(1).

Barrett, Michael E. (2008). Effects of a Permeable Friction Course on a Highway Runoff. Journal of Irrigation and Drainage Engineering (September/October 2008), 460-465.

Barrett, Michael E., Zuber Robert D., Collins, E.R.Jr., Malina, Joseph Ward, George R., Charbeneau, Randall J. (1995). A Review and Evaluation of Literature Pertaining to the Quantity and Control of Pollution from Highway Runoff and Construction. Center for Research in Water Resources, 95(3), 130-142.

Barrett, Michael, Lantin, Anna, Austrheim-Smith, Glenn. (2004). Stormwater Pollutant Removal in Roadside Vegetated Buffer Strips. Journal of the Transportation Board (Online). 329-340.

Kearfott, Natalie L., Barrett, Michael E., Malina, Joseph F. (2005). Stormwater Quality Characterization of Roadside Shoulders Narrow Vegetated Strips. Center for Research in Water Resources, 05(10), 1-142.

Middleton, John R., Barrett, Michael E. (2007). Water Quality Performance of a Batch-Type Stormwater Detention Basin. Water Environment Research, 80(2), 172-178.

National Pollutant Removal Database. (2007). Center for Watershed Protection.

Record, Christina D., Barrett, Michael E., Charbeneau, Randall J. (2008). Stormwater Quality Benefits of a Permeable Friction Course. Center for Research in Water Resources, 08(03).

SECTION 3

CONTAMINATED SEDIMENTS

Considerations for Grain Size Analysis of Sediment

Christina Mott Frans
EcoChem, Inc.

Abstract

When requesting grain size analysis, several factors are very important to address with the analyzing laboratory prior to submitting samples. This presentation is aimed at addressing the factors that need to be decided prior to submitting the samples to the lab for analysis in order to have data that is comparable to other data sets and fills the needs of the researcher.

Considerations for Grain Size Analysis of Sediment

GETTING TO THE NITTY GRITTY OF GRAIN SIZE REPORTING

CHRISTINA MOTT FRANS - ECOCHEM, INC.

EcoChem

Grain size data are used by:

- Geologists to study trends in surface processes related to the dynamic conditions of transportation and deposition
- Engineers to study sample permeability and stability under load

And are also used by

- Geochemists use grain size to study kinetic reactions and the affinities of fine-grained particles and contaminants.
- Hydrologists use it when studying the movement of subsurface fluids and in interpreting fluid dynamics in the natural environment.

So, what do you need to think about in regard to grain size reporting to get the information you need?

First, determine which you need:

- *True* Grain Size: The sample is treated with hydrogen peroxide to remove organic material.
- *Apparent* Grain Size: The sample is processed as received with no pretreatment.

Would you rather have results reported as

Percent retained

or

Percent passing?



Then Select the Method

Methods commonly used for sediment analysis include:

- ASTM D422
- Puget Sound Estuary Protocol (PSEP)
- Plumb 1981

What are the major differences between methods?

Sieves Sizes

Defined

Or

Variable?

Defined Sieve Sizes

The Dredged Material Management Plan (DMMP) and the Sediment Evaluation Framework (SEF) allow use of both the PSEP and ASTM D422 methods.

- The PSEP method gives a choice between two sieve series. All sieves in a series must be used and the series end with the #230 (62.5 μm) sieve.
- The ASTM D422 method also gives a choice between two sieve series. Again, all sieves in a series must be used, but the series end with the #200 (75 μm) sieve.

Variable Sieve Sized

The PSEP method is used for Pacific Northwest projects and the Plumb method has been used extensively for NOAA's Status and Trends Program.

- The PSEP and Plumb methods only require use of the #230 sieve, the rest are not specified.

Hydrometer or Pipette for Fines?

ASTM D422 specifies hydrometer analysis

PSEP and Plumb specify pipette analysis

Size Classification System Differences

Some major classification scales in use are:

- Udden-Wentworth
- Unified Soil Classification System
- US Department of Agriculture

So, why does all this matter?

According to NIST:

Reporting particle size and particle size distribution information is as critical a component as designing and conducting the experiments that generate this information.

The main consideration while reporting size and size distribution data is to ensure that all pertinent information is presented, such that the experiments conducted to generate this information can be reproduced when necessary.

This feature is of particular interest for comparing and communicating the particle size and size distribution data between different laboratories.

Asbestos in Soil - Assessing Risk

Ed Cahill
EMSL Analytical, Inc.

Abstract

Soil is a difficult sample matrix for laboratory analysis.
Non homogeneity in particle size and composition is the main issue.
Numerous sampling, preparation, and analysis approaches exist, each with their own advantages and disadvantages.

Some of these methods provide an estimate of asbestos percentage while others attempt to assess risk. These approaches will be discussed and contrasted:

- Bulk Asbestos Analysis by PLM (EPA 600 method)
- Brand New ASTM Sieve Method
- California Air Resources Board (CARB) Method 435
- EPA's prototype RAFS (Releasable Asbestos FiberSampler)
- EPA's prototype Fluidized Bed Asbestos Segregator (FBAS)
- Activity Based Air Sampling

Asbestos in Soil

Ed Cahill
Vice President Asbestos Division
EMSL Analytical, Inc.
ecahill@emsl.com
856-303-2565

Soil Samples



EMSL Analytical Inc.
Cinnaminson, NJ 08077


Copyright 2013 EMSL Analytical, Inc.
3


Copyright 2013 EMSL Analytical, Inc.
4

Why Analyze for Asbestos in Soil/Rock?

Naturally Occurring Asbestos (NOA)



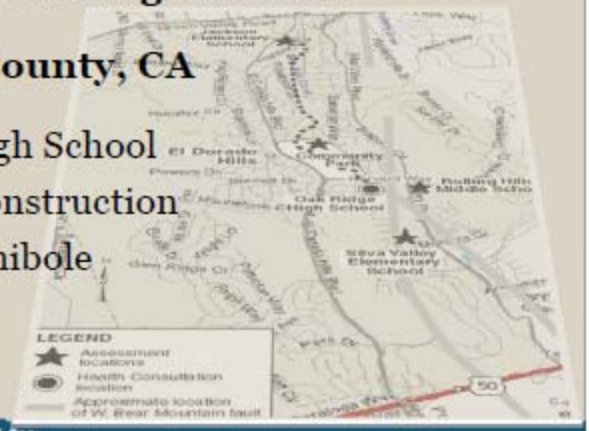
Copyright 2013 EMSL Analytical, Inc.

Why Analyze for Asbestos in Soil/Rock?

Naturally Occurring Asbestos

El Dorado County, CA

Oak Ridge High School soccer field construction disturbs amphibole asbestos.



Copyright 2013 EMSL Analytical, Inc.

Why Analyze for Asbestos in Soil/Rock?



Naturally Occurring Asbestos

Serpentine (including Chrysotile asbestos) is the state rock of California.

The aggregate used for roadbeds, rail beds, and on construction sites of all types is always a question mark.

Copyright 2013 EMSL Analytical, Inc.

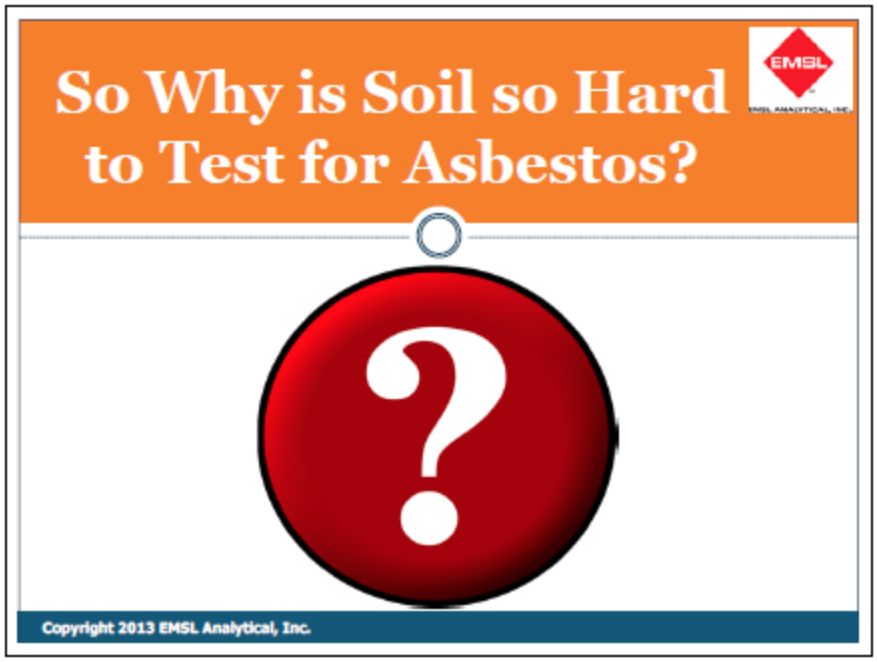
Staten Island Serpentinite

I 278 road cut. Up to 50% Chrysotile



Copyright 2013 EMSL Analytical, Inc.

Picture and info: Brooklyn CUNY.edu


So Why is Soil so Hard to Test for Asbestos?
EMSL
?
Copyright 2013 EMSL Analytical, Inc.


Soil is a Great Hiding Place
EMSL
1% Unconsolidated Chrysotile
1% Consolidated Chrysotile
Copyright 2013 EMSL Analytical, Inc.

Soil is a Great Hiding Place



Copyright 2013 EMSL Analytical, Inc.

Why is Soil so Hard to Analyze?

- Non-Homogeneity
- Grain size



Copyright 2013 EMSL Analytical, Inc.

Scales of Non-Homogeneity



The Big Picture

- Obtaining representative samples in the field can be difficult.
- Samples tend to be very non-homogeneous especially over the large areas that are typical on outdoor sites.
- How many samples for a baseball field or 100 miles of road or rail bed?

Copyright 2013 EMSL Analytical, Inc.

Scales on Non-Homogeneity

The Medium Picture

- How deep to go?
- What layers to include?



Copyright 2013 EMSL Analytical, Inc.

Scales on Non-Homogeneity

The Fine Picture

Obtaining a representative **sub**-sample in the lab is important.



Copyright 2013 EMSL Analytical, Inc.

Scales on Non-Homogeneity

The Very Fine Picture



Low mag stereoscopic view of play sand

"Large" particle size makes it difficult to get good slide mounts for light microscopy or grid preps for TEM.

The presence of even sand sized quartz crystals are a problem.

Copyright 2013 EMSL Analytical, Inc.

One way to help homogenize the samples either in the field or after submittal to the lab



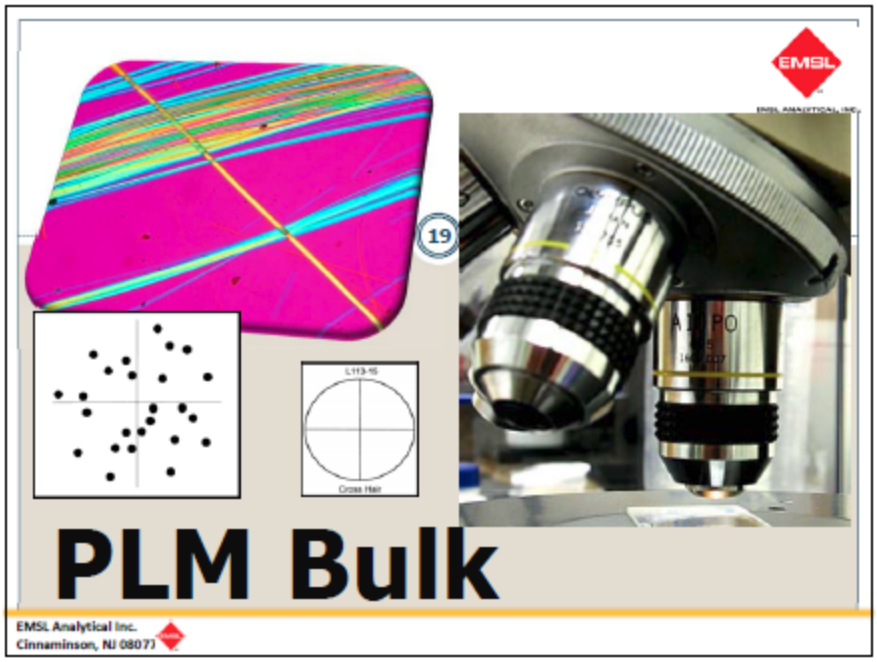
Riffle Splitting

Copyright 2013 EMSL Analytical, Inc.

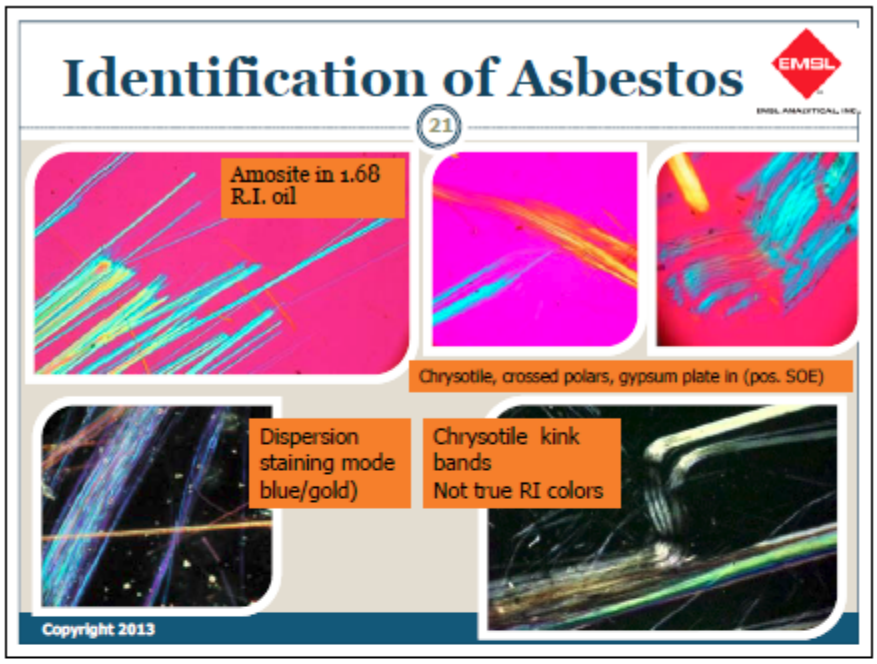
Analytical Choices
What Method to Choose?

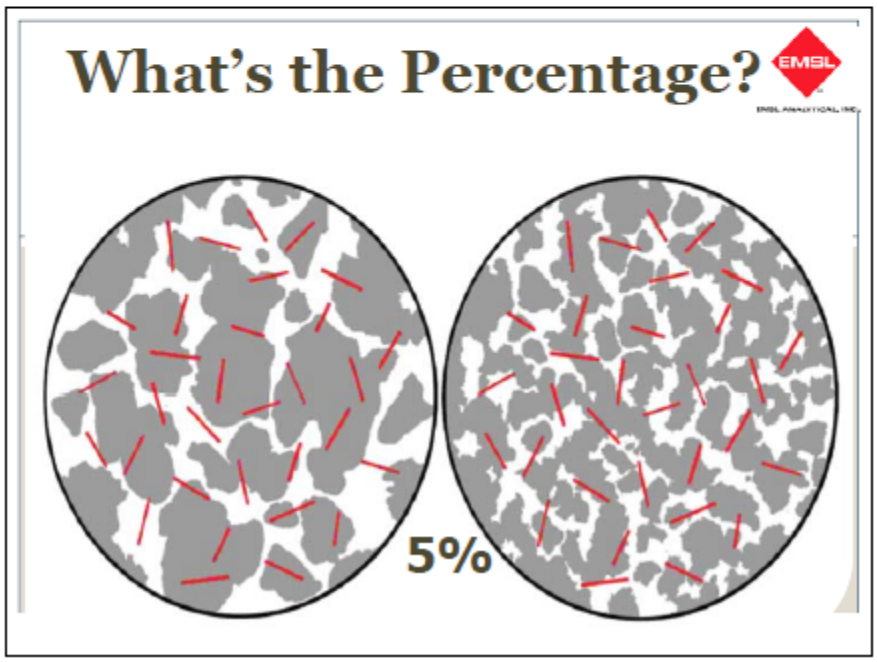


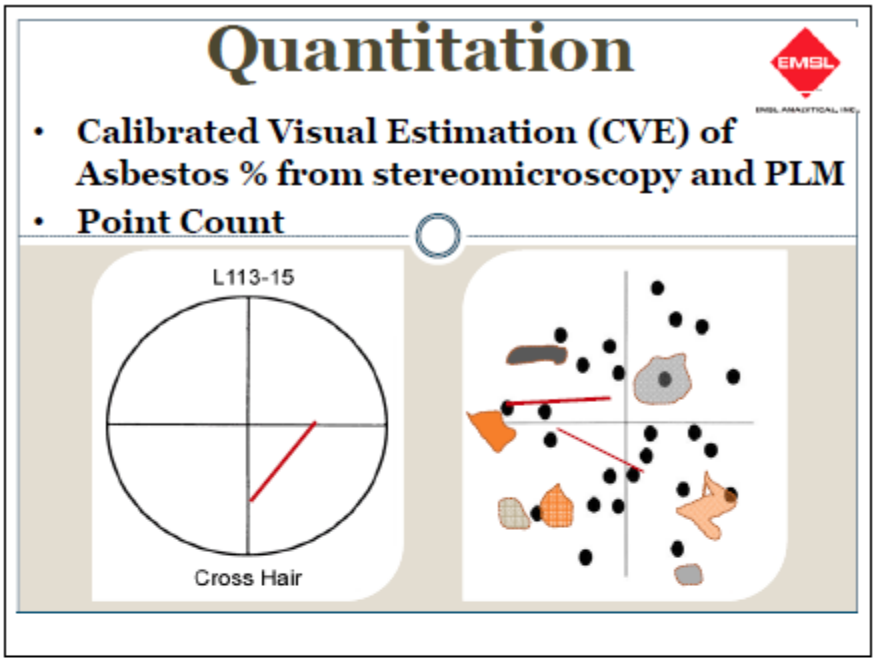
Copyright 2013 EMSL Analytical, Inc.

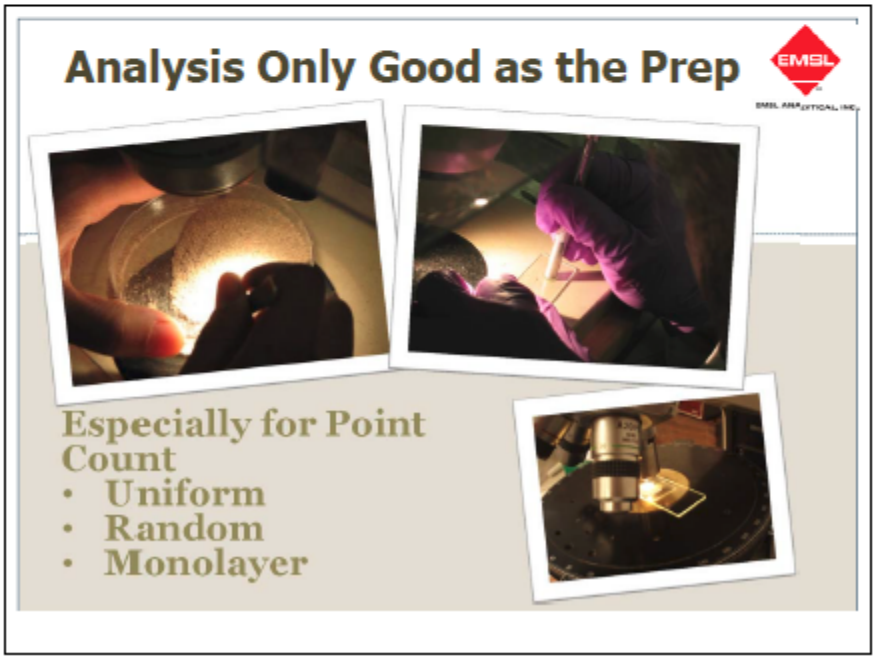

19
PLM Bulk
EMSL Analytical Inc.
Cinnaminson, NJ 08077


From Stereomicroscope to PLM
20
Recombined Light Rays After Interference
Digital Camera System
Polarized Microscope Configuration
Eyepieces
Bertrand Lens Intermediate Tube
Analyzer
Frame
Ordinary Ray
Extra-Ordinary Ray
Objectives
Birefringent Specimen
Circular Rotating Stage
Plane Polarized Light
Polarizer
Light From Source
Figure 1
Base
Focus
Copyright 2013


Identification of Asbestos
EMSL
21
Amosite in 1.68 R.I. oil
Chrysotile, crossed polars, gypsum plate in (pos. SOE)
Dispersion staining mode blue/gold)
Chrysotile kink bands
Not true RI colors
Copyright 2013


What's the Percentage?
EMSL
5%


Quantitation
EMSL
• Calibrated Visual Estimation (CVE) of Asbestos % from stereomicroscopy and PLM
• Point Count
L113-15
Cross Hair


Analysis Only Good as the Prep
EMSL
Especially for Point Count
• Uniform
• Random
• Monolayer

The 1% Rule

Risk

- 1% asbestos bound up in a floor tile is different than
- 1% asbestos bound up in a friable material is different than
- 1% asbestos not bound up in soil or
  - Settled Dust
  - Vermiculite

Copyright 2013

Limitations of "Standard" PLM

EPA PLM Method (EPA/600/R-93/116)

Method for the Determination of Asbestos in Bulk *Building Materials*

- As the title suggests and the method explains, this is a method for relatively homogenous bulk building materials, not soil.
- The final version of this method is flexible though and matrix modification prior to analysis is described



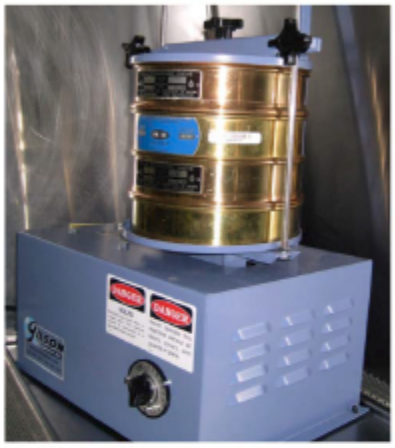
Copyright 2013 EMSL Analytical, Inc.


Two Approaches to Soil
EMSL
EMSL ANALYTICAL, INC.
Sieving
Milling
Copyright 2013 EMSL Analytical, Inc.


Alternative Approaches
EMSL
Sieving
Designation: D7521 – 13
Standard Test Method for
Determination of Asbestos in Soil
EMSL Analytical Inc.
Cinnaminson, NJ 08077

ASTM Sieve Method

1) Sample is dried
2) Weighed
3) Dry Sieved (wet option) on sieve shaker for 5 minutes
   - 19 mm sieve
   - 2 mm sieve
   - 106 micron sieve



Copyright 2013 EMSL Analytical, Inc.

ASTM Sieve Method

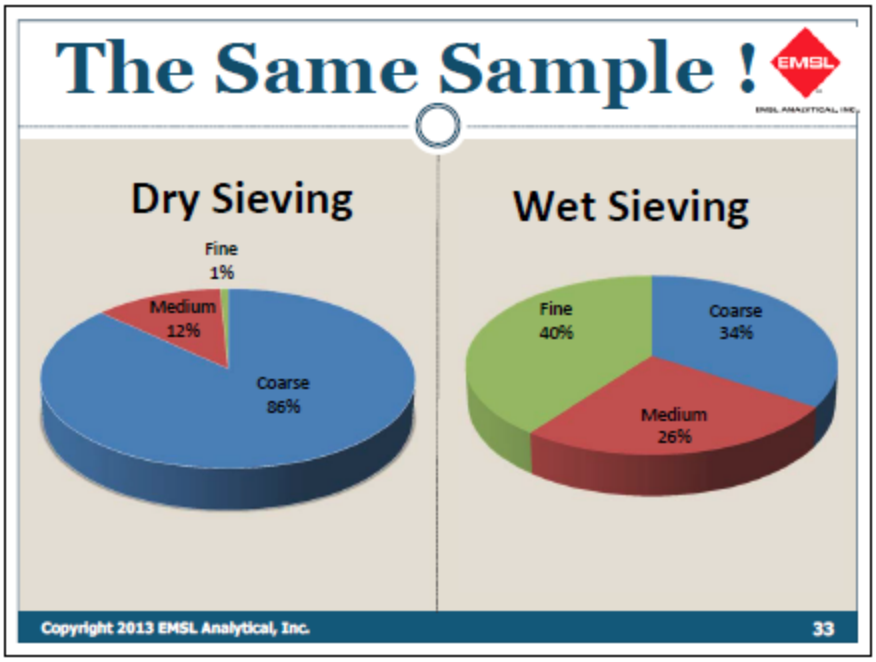
4) Weigh each fraction
5) Analyze each fraction

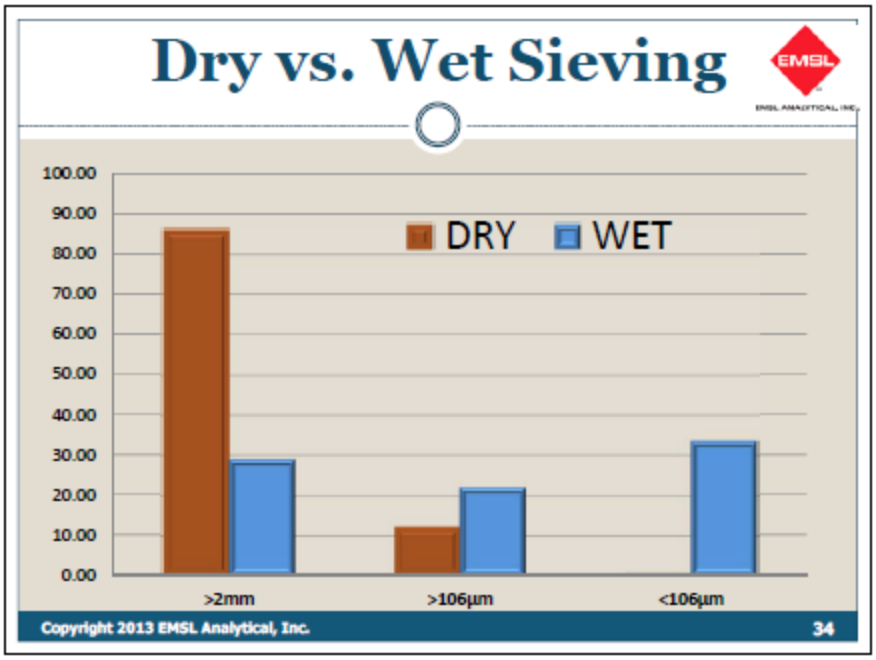


Copyright 2013 EMSL Analytical, Inc.


ASTM Sieve Method
The fine fraction is fine enough and homogenous enough for a PLM slide prep and analysis
Copyright 2013 EMSL Analytical, Inc.


Wet Sieving
EMSL
Sieve Stack
Coarse, Medium
Copyright 2013 EMSL Analytical, Inc.
32


The Same Sample !
Dry Sieving
Fine 1%
Medium 12%
Coarse 86%
Wet Sieving
Fine 40%
Coarse 34%
Medium 26%
Copyright 2013 EMSL Analytical, Inc.
33


Dry vs. Wet Sieving
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
DRY
WET
>2mm
>106µm
<106µm
Copyright 2013 EMSL Analytical, Inc.
34

ASTM Sieve Method

- If all three fractions are non detect by PLM then a TEM Analysis is performed.
- This TEM analysis is Qualitative only (detect/non detect). This enable us to find asbestos that is not visible by light microscopy (thinner than 0.25 microns)
- Finally, there is an optional Quantitative TEM analysis



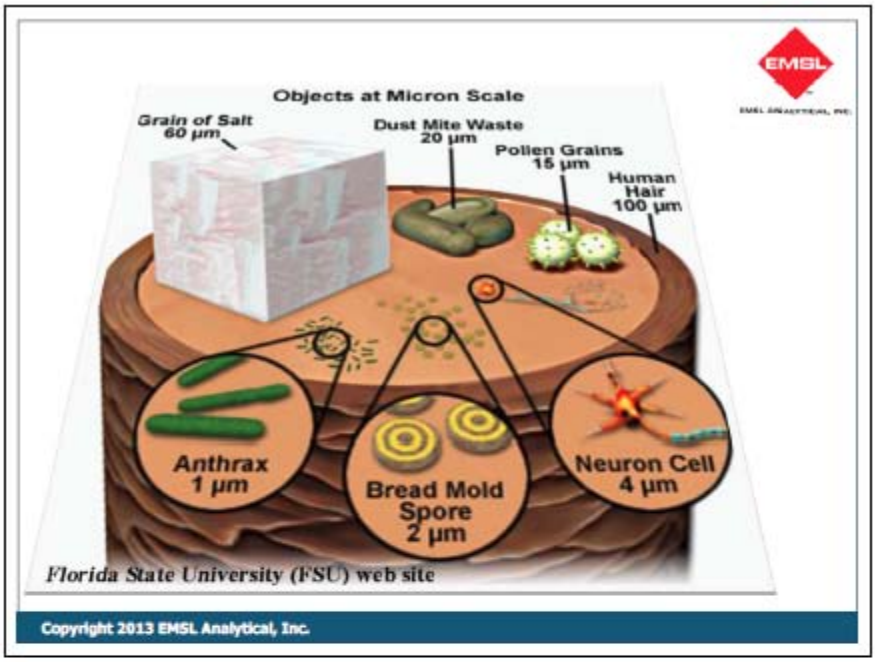
Copyright 2013 EMSL Analytical, Inc.

TEM is Typically Not Required But ...





EMSL Analytical Inc.
Cinnaminson, NJ 08077


Objects at Micron Scale
Grain of Salt
60 µm
Dust Mite Waste
20 µm
Pollen Grains
15 µm
Human
Hair
100 µm
Anthrax
1 µm
Bread Mold
Spore
2 µm
Neuron Cell
4 µm
Florida State University (FSU) web site
Copyright 2013 EMSL Analytical, Inc.


TEM Prep
Copyright 2013 EMSL Analytical, Inc.

The TEM Grid

39

Entire grid is only 3 mm diameter

Each grid square (opening) is approximately 0.01 sq. mm



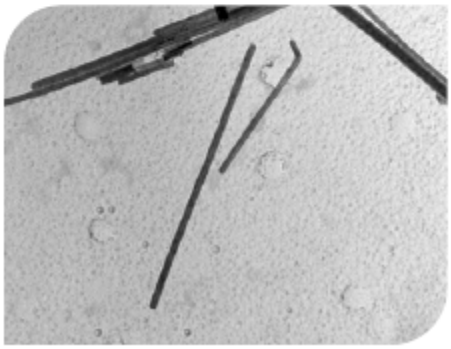
Copyright 2013 EMSL Analytical, Inc.

TEM Analysis

Analysis at 20,000X magnification vs. 400X for light microscopy

40

ASBESTOS FIBERS TOO SMALL TO SEE BY LIGHT MICROSCOPY (PCM / PLM) ARE NOW EASILY DETECTED.



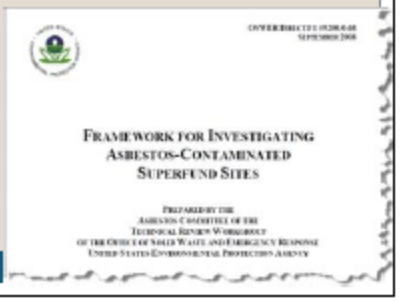
Copyright 2013

Milling (the other approach)

California Air Resource Board (CARB) Method 435

Determination of Asbestos Content of Serpentine Aggregate

- This is the current de facto standard for milling methods.
- It was developed to test for asbestos in stone not soil
- EPA framework document for guidance on Superfund sites recommends CARB 435 for soil.



FRAMEWORK FOR INVESTIGATING ASBESTOS-CONTAMINATED SUPERFUND SITES

Copyright 2013 EMSL Analytical, Inc.

CARB 435 Method

The sample is dried in a drying oven and material >3/8" is removed by sieving



Milled at minus 200 degrees C for 4-8 minutes to reduce the nominal particle size to 75 microns



Copyright 2013 EMSL Analytical, Inc.

CARB 435

After milling, the sample is analyzed by a PLM 400 or 1000 point count (0.25% or 0.1%)



Copyright 2013 EMSL Analytical, Inc.

CARB 435 Method

- One of the main advantages of the CARB Method over the sieving methods is that it enables detection of unconsolidated (loose and unbound from matrix) asbestos fibers.
- Unfortunately the resolution of the light microscope is only about 0.25 microns.
- Asbestos fibers/bundles with widths less than this are still not detected.

Copyright 2013 EMSL Analytical, Inc.

CARB 435 PLUS

TEM CARB Method for Soil

CARB Milling followed by TEM Mass Analysis by EPA 600 Section 2.5

- Milled sample is put into suspension, filtered and analyzed.
- Analysis is performed at up to 20,000X
- Identification of asbestos using X-Ray Analysis and SAED (selected area electron diffraction)
- Results are given in percent asbestos by mass
- Varying levels of analytical sensitivities are offered.

Copyright 2013 EMSL Analytical, Inc.

TEM CARB Method

Following the standard milling, a known mass is put into solution



Copyright 2013 EMSL Analytical, Inc.

TEM CARB Method





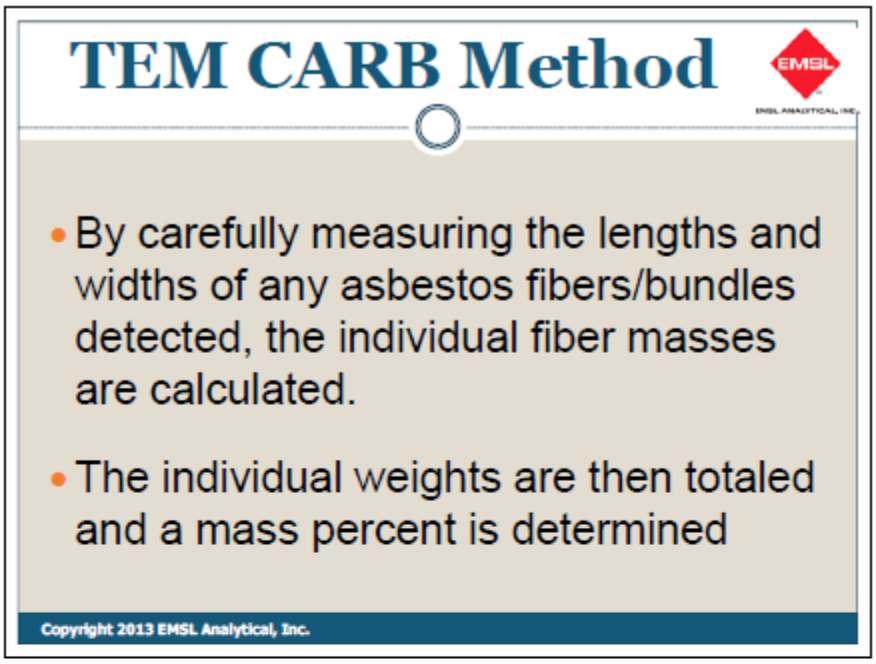
After sonication, the sample is filtered through a 0.4 micron filter

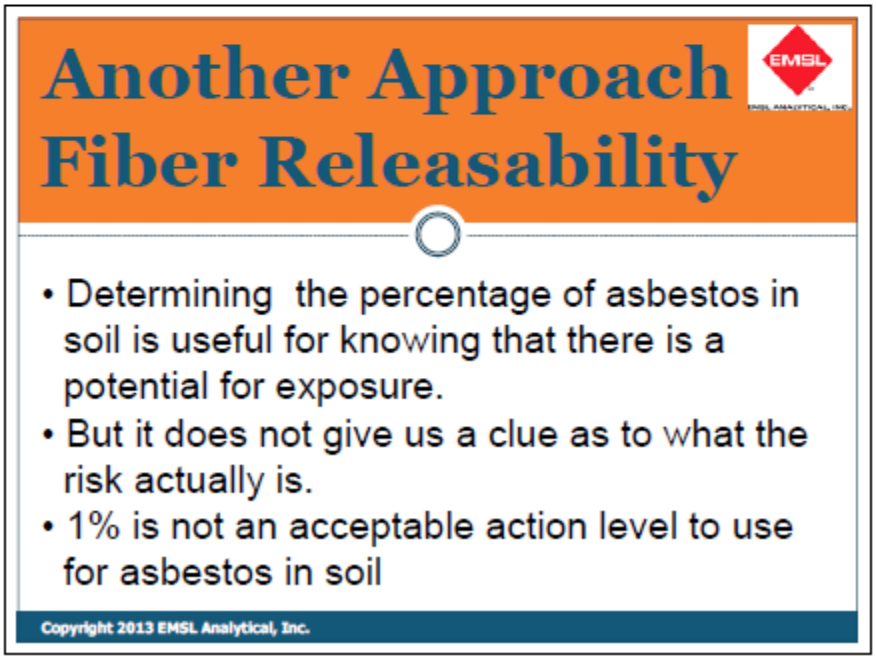
Copyright 2013 EMSL Analytical, Inc.

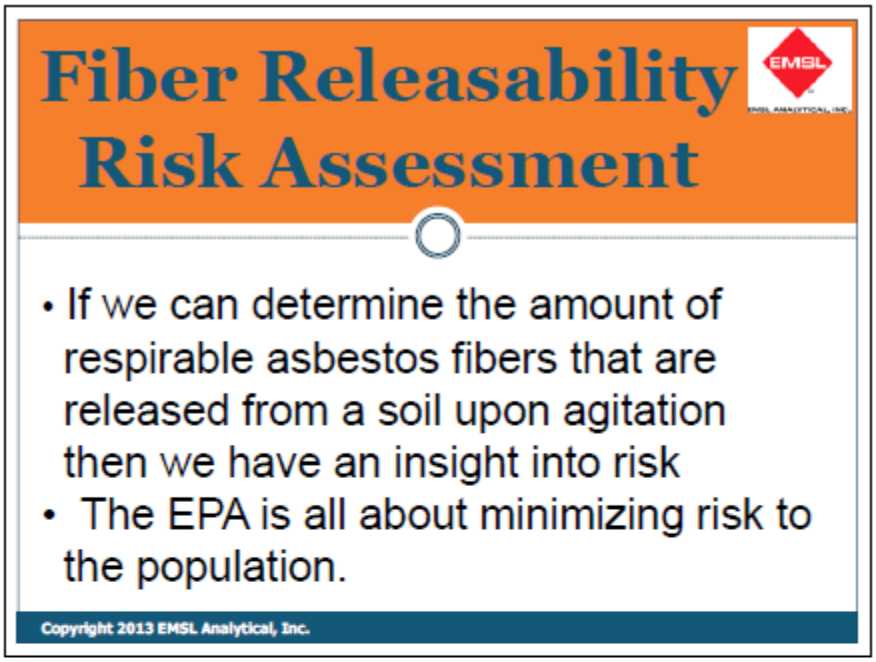
TEM CARB Method

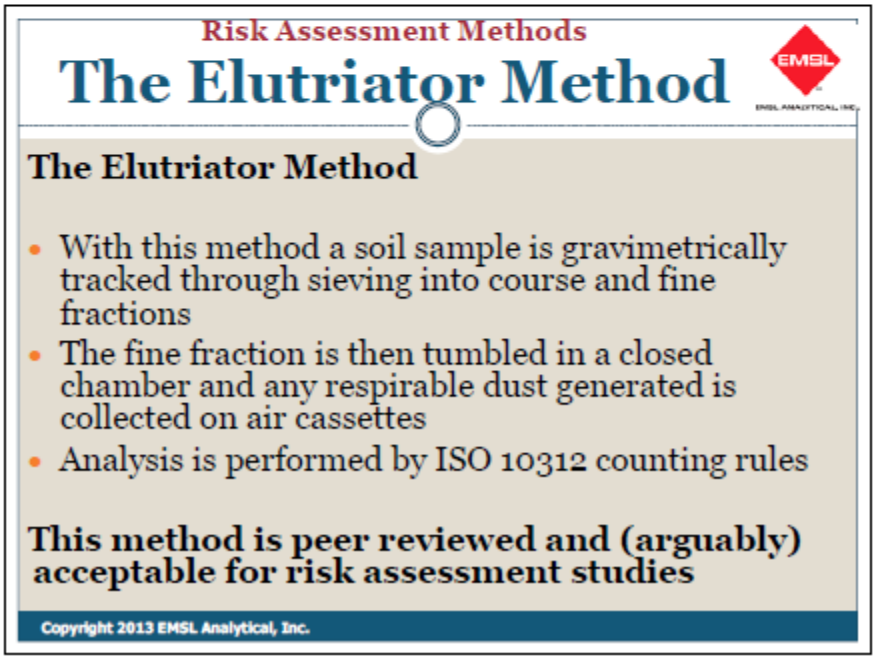


Copyright 2013 EMSL Analytical, Inc.


TEM CARB Method
EMSL
By carefully measuring the lengths and widths of any asbestos fibers/bundles detected, the individual fiber masses are calculated.
The individual weights are then totaled and a mass percent is determined
Copyright 2013 EMSL Analytical, Inc.


Another Approach
Fiber Releasability
EMSL
Determining the percentage of asbestos in soil is useful for knowing that there is a potential for exposure.
But it does not give us a clue as to what the risk actually is.
1% is not an acceptable action level to use for asbestos in soil
Copyright 2013 EMSL Analytical, Inc.


Fiber Releasability Risk Assessment
EMSL
• If we can determine the amount of respirable asbestos fibers that are released from a soil upon agitation then we have an insight into risk
• The EPA is all about minimizing risk to the population.
Copyright 2013 EMSL Analytical, Inc.


Risk Assessment Methods
The Elutriator Method
EMSL
The Elutriator Method
• With this method a soil sample is gravimetrically tracked through sieving into course and fine fractions
• The fine fraction is then tumbled in a closed chamber and any respirable dust generated is collected on air cassettes
• Analysis is performed by ISO 10312 counting rules
This method is peer reviewed and (arguably) acceptable for risk assessment studies
Copyright 2013 EMSL Analytical, Inc.

Risk Assessment Methods

The Elutriator Method

Tumbler apparatus filled with soil

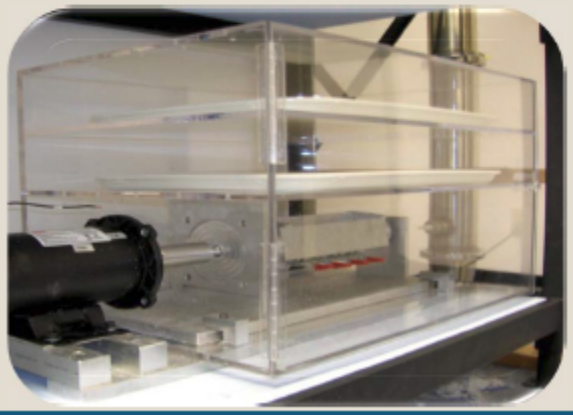


Copyright 2013 EMSL Analytical, Inc.

Risk Assessment Methods

The Elutriator Method

Tumbler inside enclosed humidity chamber



Copyright 2013 EMSL Analytical, Inc.

Risk Assessment Methods

The Elutriator Method



Air Cassettes on top of the elutriator stack.

Isokinetic sampling to catch only the respirable fraction of fibers released from the soil.

Copyright 2013 EMSL Analytical, Inc.

Field Alternatives to the Elutriator

The EPA uses other techniques in the field that also collect and measure releasable fibers from soil.

- Activity Based air Sampling
- Releasable Asbestos Field (RAF) Unit
- Fluidized Bed

Copyright 2013 EMSL Analytical, Inc.

Activity Based Air Sampling

Activity Based Air Sampling

Personnel (and sometimes area) monitoring is performed while samplers mimic likely activity for that location.





Copyright 2013 EMSL Analytical, Inc. Photos courtesy of EPA

RAF Unit



Copyright 2013 EMSL Analytical, Inc. Photos courtesy of EPA

RAF Unit



Copyright 2013 EMSL Analytical, Inc.

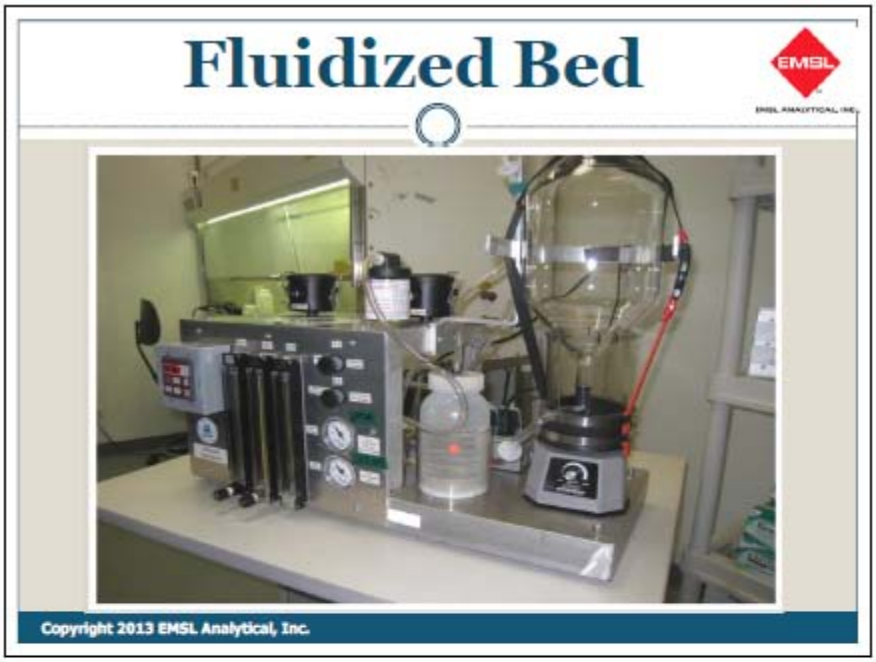
Photos courtesy of EPA

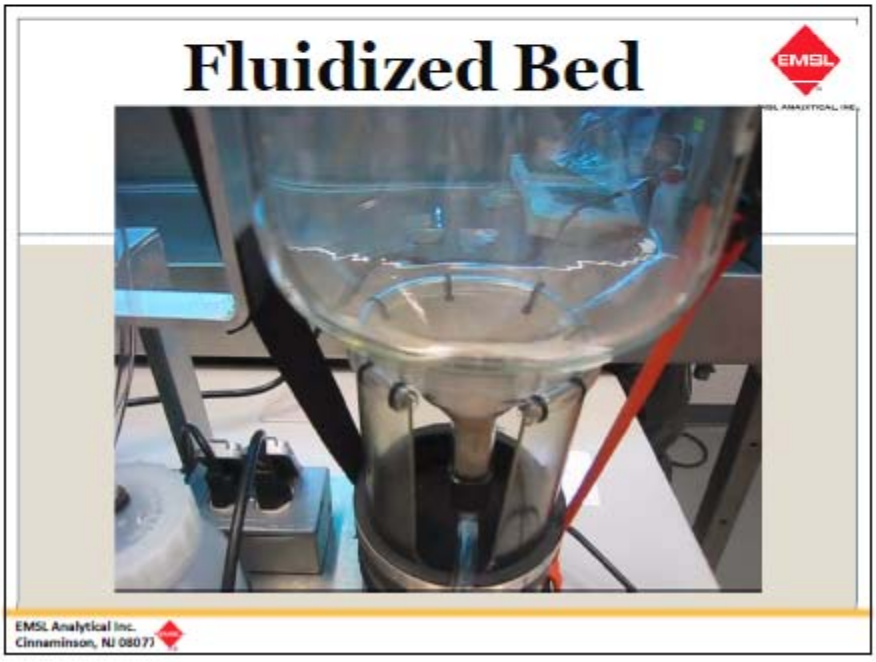
Fluidized Bed

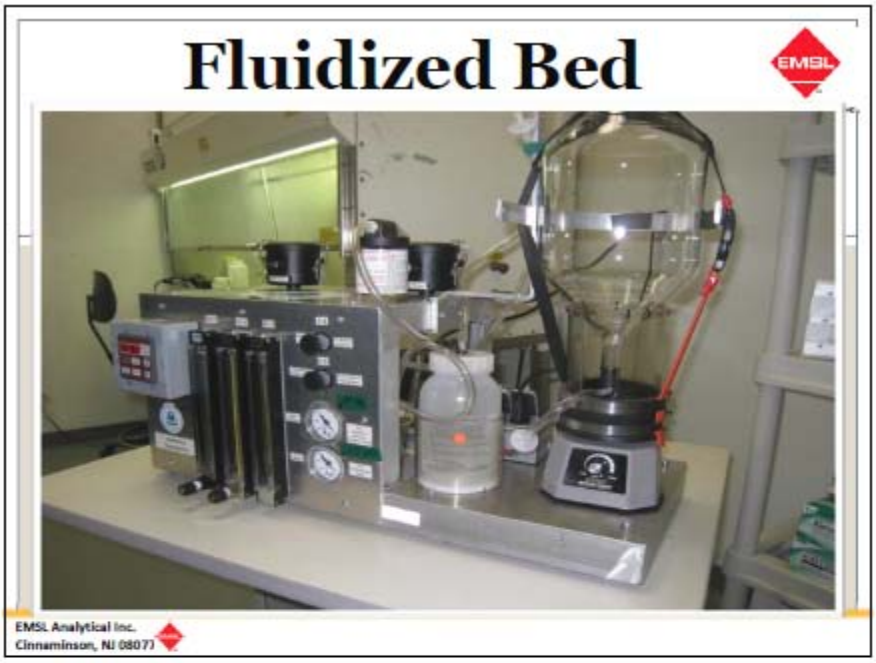
- Air is injected at a precise flow rate to get the soil sample behaving like a fluid.
- Then air samples are collected from above.



Copyright 2013 EMSL Analytical, Inc.


Fluidized Bed
EMSL
Copyright 2013 EMSL Analytical, Inc.


Fluidized Bed
EMSL
EMSL Analytical Inc.
Cinnaminson, NJ 08077


Fluidized Bed
EMSL
EMSL Analytical Inc.
Cinnaminson, NJ 08077


Fluidized Bed
EMSL
Copyright 2013 EMSL Analytical, Inc.

Summing Up

The right answer depends on the right question…

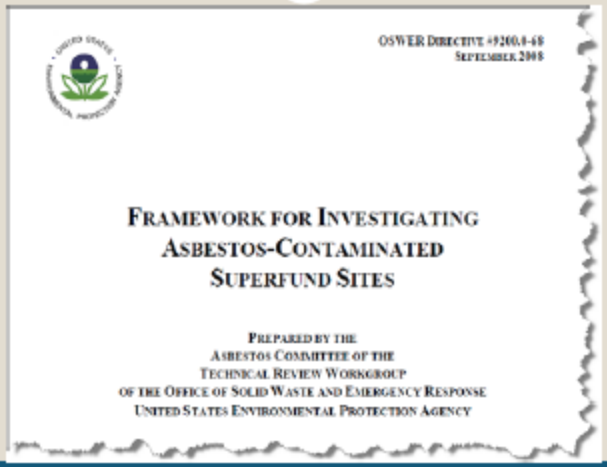
"I see building material debris in the soil. Does it have asbestos and if so how much? Do I need to dispose of it as hazardous waste?"
- ASTM Sieving Method to give % ACM in soil

"I don't necessarily see suspect asbestos but I think it might be there either from contamination (ex brake shops) or from NOA."
- PLM CARB 435 (down to 0.25% or 0.1%)
- TEM CARB 435 (EPA 600 Mass Analysis)
- ASTM Sieving Method

Does the Soil Contain Respirable Fibers?
- EPA 540-R-97-028 Superfund Method (Elutriator)
- Activity based air sampling

Copyright 2013 EMSL Analytical, Inc.

- CARB 435 mentioned
- 1% is not an appropriate action level



OSWER DIRECTIVE #9200.0-68
SEPTEMBER 2008

FRAMEWORK FOR INVESTIGATING ASBESTOS-CONTAMINATED SUPERFUND SITES

PREPARED BY THE
ASBESTOS COMMITTEE OF THE
TECHNICAL REVIEW WORKGROUP
OF THE OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Copyright 2013 EMSL Analytical, Inc.


EMSL
EMSL ANALYTICAL, INC.
EMSL ANALYTICAL, INC.
200 Route 130 North
Cinnaminson, NJ 08077
Phone (856) 303-2565
Cell (845) 238-4559
ecahill@emsl.com
www.emsl.com
Ed Cahill
Vice President, Asbestos Division
Quality Laboratory Testing Since 1981

Passive Sampling for Sediment Pore-Water

James Whetzel
Amplified Geochemical Imaging, LLC

Abstract

Sediment sampling has been an increasing field of interest to the environmental community, especially the measurement of pore-water for bio-availability studies. Various techniques are available for sampling sediment. Typically these methods involve removal and transfer of sediment and/or pore-water to containers for shipment to an outside laboratory for analysis. Passive sampling, however, can be performed to allow for in-situ sample collection without the need to for physical removal or transfer of the sediment or pore-water. In-situ passive sampling minimizes sample handling and potential for loss of volatile compounds of concern. The process is simple, cost effective, and provides semi-quantitative and/or quantitative measurement of compounds of concern. This paper describes the use of a membrane based passive sampler to quantify VOCs and SVOCs in pore-water.

Passive, Adsorbent-Based Sediment Pore Water Sampling

2013 NEMC

August 5, 2013

Jim Whetzel
Amplified Geochemical Imaging, LLC. (AGI)

Special thanks to
Kathy West, URS Corporation
Ken Alepidis and Sean Caroll, Haley & Aldrich, Inc.

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 1

Overview

- Common applications of passive sampling
- Sampler description and analysis
- Calculating concentrations
- Installation guidelines
- Case studies
  - Canal sediment – direct insertion
  - River sediment - test cell
- Conclusions

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 2

Common Applications

- Site assessment
  - Rapid, high-resolution
  - Shifts sampling from exploration to confirmation
  - Focuses more intrusive expensive sampling
- Brownfields – property transfers
- Vapor intrusion
- Monitoring
  - Groundwater long-term
  - Site remediation
- Water sampling
  - Ground & surface water, **sediment pore water**





www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 3

AGI Universal Sampler
(formerly GORE® Module and GORE-SORBER)

- GORE-TEX® Membrane
  - Inert, waterproof, vapor permeable
  - Designed for vapor diffusion
- Hydrophobic, engineered sorbents
  - VOCs, SVOCs, PAHs
- Sample integrity protected
- 4,000 surveys worldwide
  - Federal, state, international regulatory acceptance



GORE-TEX® Membrane





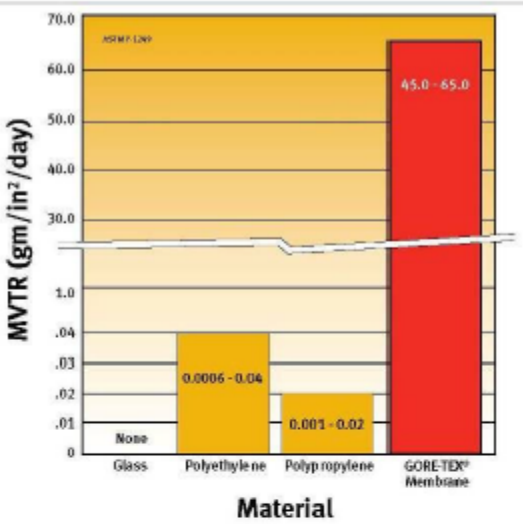
AGI Environmental Survey Kit

Triad

ETV

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 4

Vapor Transfer Rates



www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 5

Analysis

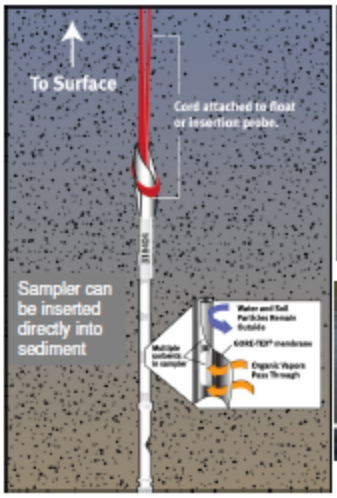
- TD\GC\MS (Modified EPA 8260C)
  - Duplicate samples
  - Screening level and accredited methods available
- Results available in mass and concentration



ACCREDITED
Testing CERT #3062.01

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 6

Installation in Sediment







Courtesy of Peregrine Ventures



Courtesy URS Corporation



Courtesy Marion Environmental

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 7

Sampler Exposure Times

Expected Concentration of Primary Contaminant (ppb)	Residence Time in Sediment (Hr)
20 to 5000	0.5
10 to 3500	1
5 to 2000	2
3 to 1000	4

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 8

Mass (ug) to Pore Water Conc. (ppb)

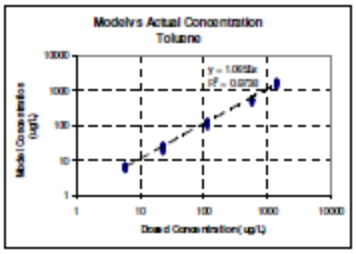
Simplified equation for water

- Single conc., time, temp

Conc (ug/L) = mass(ug)/time(Hr)/SR(L/Hr)

Multiple times, temps, and sorbed mass

Conc = (mass)^{b} /(time)$^{-d}$ /[-SRo x exp(-Ea/R(1/Tr - 1/T))]

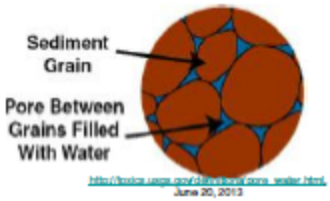


Regression output from
ln(conc) versus ln(mass), ln(time), 1/temp
b & d = exponents accounting for non-linear response
-Ea/R = correction for deviation from ref. temp
SRo = Sampling rate

Other inputs
T = water temp (K),
Tr = reference water temp (K)

www.agisurveys.net © Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 9

Mass (ug) to Pore Water Conc. (ppb)



http://toxics.usgs.gov/definitions/pore_water.html
June 20, 2013

Equation for Sediment

$Conc_{pw} = Conc_{w} / f_{pw}$

$Conc_{pw}$ = pore water concentration
$Conc_{w}$ = water concentration
f_{pw} = fraction pore water

www.agisurveys.net © Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 10

Sediment Sampling Studies

- Direct insertion of sampler
  - Canal Sediment
  - Aromatic chlorinated benzenes



Courtesy of URS Corp

- Test cell to separate solid material from pore water
  - River sediment
  - BTEX & PAHs



Courtesy of Haley & Aldrich

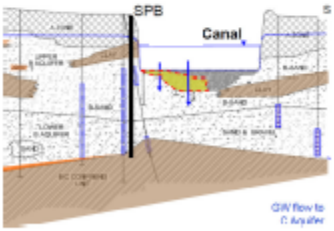
www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC Slide 11

Direct Insertion into Sediment



Background

- Former dye manufacturer
- Contaminated GW discharging into canal water and sediment



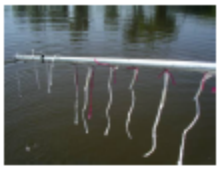
- Sheet pile barrier (SPB) installed to eliminate source
- GW below and down stream treated by interceptor well
- Selected MNA for remediation of sediment

Goal: Find a rapid deployment assessment tool for monitoring natural attenuation

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC Slide 12

Canal Sediment Sampling









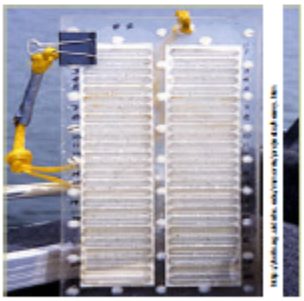
- Focus on 2 sampling locations: B, C
  - Field Duplicates BB, CC
- PPWS placed above sediment and every 3 to 4 inches
  - Quick & Simple installation
  - 5 to 60min exposure
- Comparison with Peepers
  - Exposure over several days to weeks
  - Sampling not done concurrently

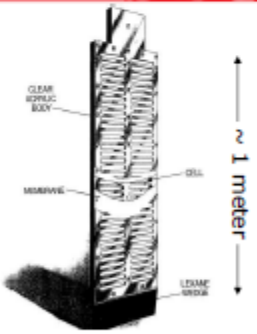
PPWS = passive pore water sampler (AGI Sampler)

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 13

Peepers (permeable sampler)





http://www.epa.gov/greatlakes/sediment/tacmain/five.html

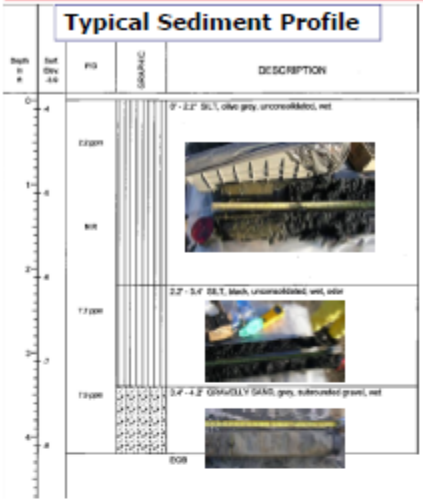
- Semi-permeable membrane covered cells filled with organic solvent or water
- Hydrophobic compounds diffuse from pore water across the membrane into the solvent

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

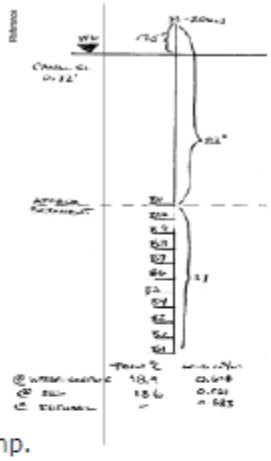
Slide 14

Canal Sediment Sampling

Typical Sediment Profile



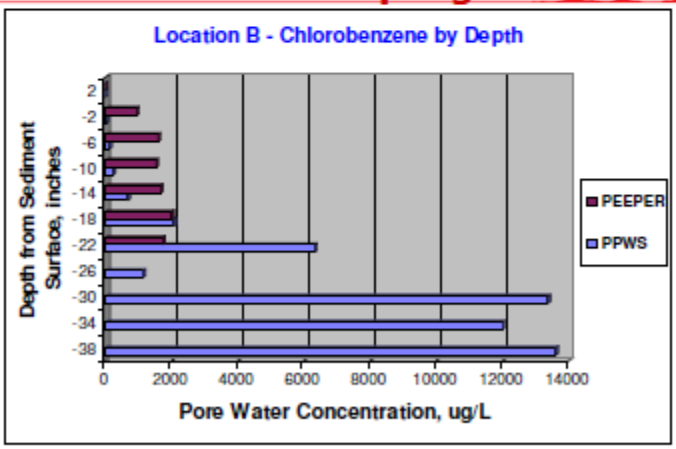
Unconsolidated silt "fluffy" to gravelly sand



- Temperature probe for sediment temp.
- Decagon EC5 moisture meter for vol. water content

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 15

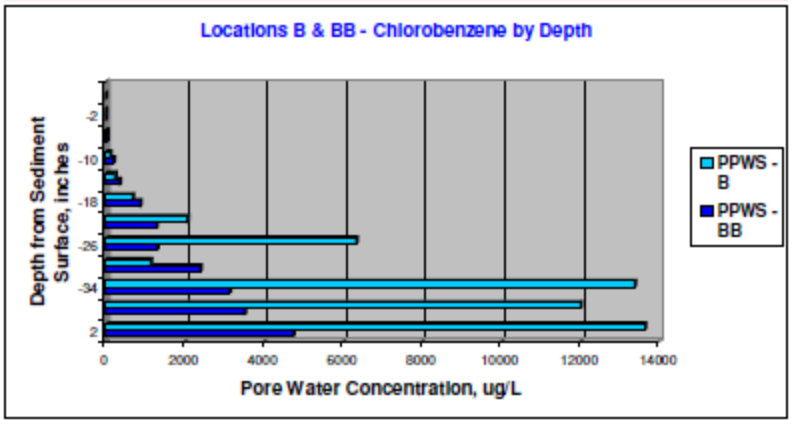
Canal Sediment Sampling



- Peeper indicates concentration relatively stable -2" to -18"
- PPWS indicates concentration increases significantly with depth

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 16

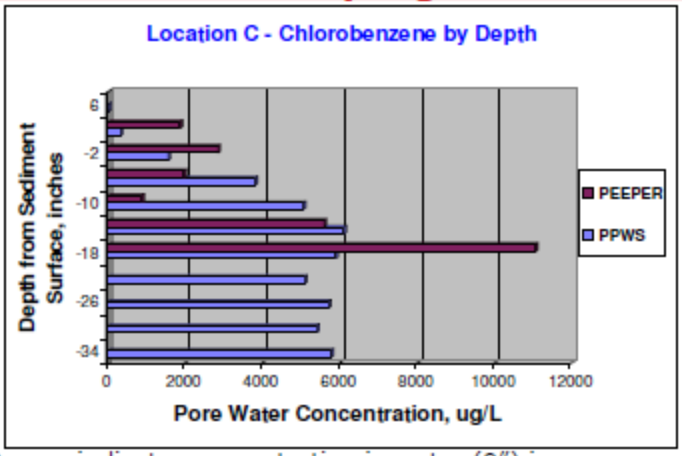
Canal Sediment Sampling



- PPWS field duplicate shows somewhat similar increasing concentration pattern with sediment depth

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 17

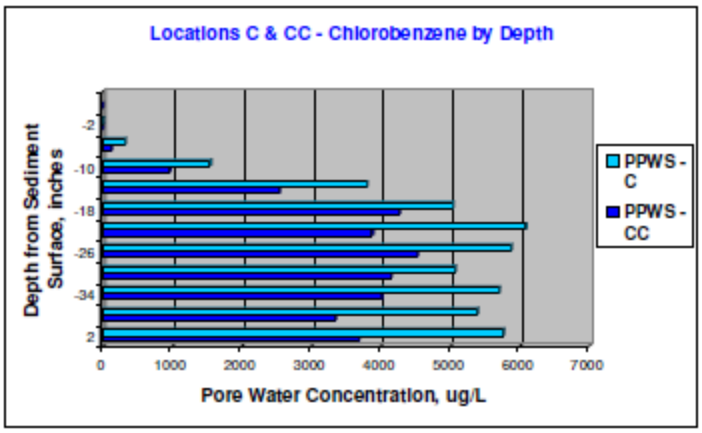
Canal Sediment Sampling



- Peeper indicates concentration in water (2") is similar to concentration in shallow sediment
- PPWS indicates concentration increases from water to sediment and levels out after ~6" depth

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 18

Canal Sediment Sampling



- PPWS field duplicate shows similar concentration pattern

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 19

Canal Sediment Sampling

Study Observations

- **Quick and simple sampling**
- **Comparison to Peepers**
  - Lower overall cost
  - Somewhat similar values at higher concentrations
  - PPWS shows greater variation in pore water concentrations
- **Sediment profile consistent between PPWS field dups**

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 20

Test Cell Sampling

Background

- Former MGP site
- COCs detected in river sediments – VOCs and PAHs
- GW and soil remediation addressing source completed
- Sediment remediation planned
  - Excavation and permeable cap placement
- Pilot scale reactive cap test cell constructed
- Problem: Micro-wells tend to clog due to matrix

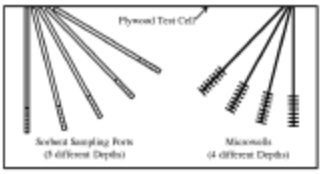
Goals:
1. **Design sampling system that won't clog during testing/ monitoring**
2. **Sampling must be able to demonstrate efficacy of capping**
   - **results must be similar to Micro-well at target concentrations**

© Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 21

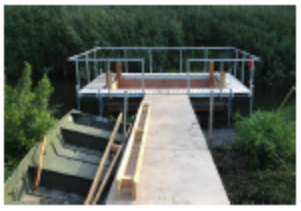
Test Cell Sampling

Evaluation of Test Cell Sampling Design

- Sampling ports for Passive Pore Water Sampling (PPWS – AGI Sampler)
- Micro-wells for low flow water sampling





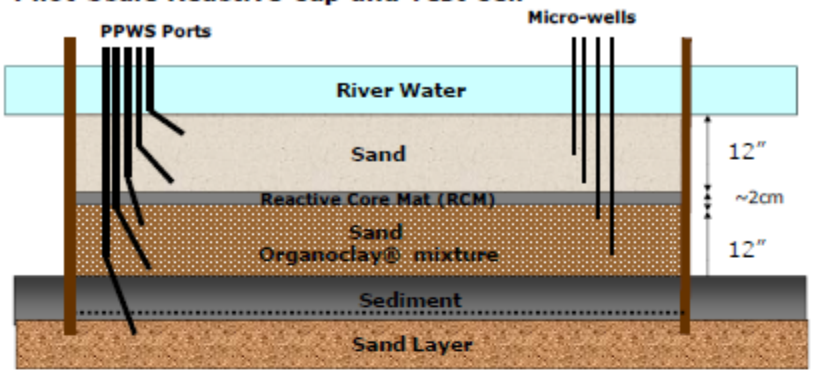




© Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 22

Test Cell Sampling

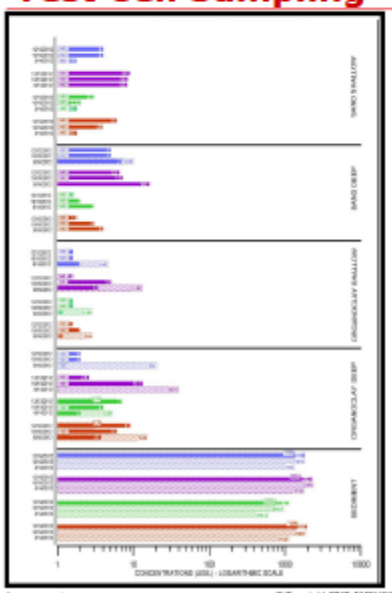
Pilot-Scale Reactive Cap and Test Cell



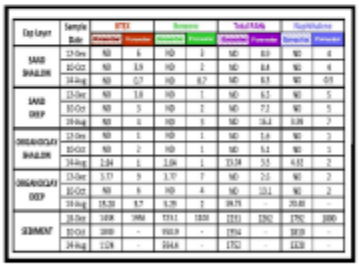
- Approximate Placement of Sampling Ports
- PPWS inserted into tubing down to end sampling port

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 23

Test Cell Sampling



PPWS v. Low Flow



- PPWS MDL > Low Flow MDL
- Excellent agreement at higher concentrations
- Met study goals

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 24

Test Cell Sampling

Test Conclusion:

- **Passive Pore Water Sampling Design capable of being used to sample pore water in test cell**
- **PPWS able to show differences in test cell zones**
- **Analytical results compare well at target concentrations**
  - -Comparison suitable for project DQOs
  - -Lower concentrations differ due to differences in MDLs
    - -PPWS Analysis MDL> Water method MDL

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 25

Conclusions

- Flexible applications
- Acceptable agreement with Peepers and Micro-well data
- Quick, simple, accurate, and cost effective solution
- Passive Pore Water Sampling attractive alternative to other sediment pore-water techniques

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 26

Extraction of Total and Methyl Mercury from a DGT

Ray Shock
TestAmerica

Abstract

Background/Objectives. Diffusive Gradients in Thin films (DGT) can be used to examine the bioavailability of mercury and methyl mercury in a variety of matrices. A 0.45mm filter allows labile mercury species to enter the sampling device to be captured on the resin gel. The DGT provides in-situ measurement of mean analyte concentrations. The goal of this study was to design an efficient sample extraction procedure to be used in a production laboratory that provides a reporting limit of 1ng methyl mercury and 10ng total mercury per DGT. Approach/Activities. The DGT was disassembled and only the resin gel was used to evaluate extraction efficiency. DGT resins were spiked with commercially available methyl mercury chloride and divalent mercury. The first extraction solution used was 0.65 mM thiourea (TU) in 0.1 M HCl, which didn't meet extraction efficiency requirements. A more aggressive solution (1.3 mM TU in 0.6M HCl) was prepared which yielded better recovery of methyl mercury. All mercury species were not effectively leached from the resin with the TU/HCl solution, so an aqua regia extraction was performed for measurement of total mercury. A four hour soak in aqua regia (8 mL HCl / 2 mL HNO3) proved to be more effective in leaching mercury from the DGT resin for total mercury analysis.

Results/Lessons Learned. This extraction process has been developed to support a pilot study and field study of a tidal estuary involved several hundred DGT sampling devices beginning summer 2012. Limited performance details were available in the literature. Current efforts have yielded 80-110% recovery for methyl mercury and 60-65% recovery for total mercury at their respective reporting limits. Completion of the tidal estuary studies will also yield statistical performance data for this process.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Extraction of Total and Methyl Mercury from a DGT

Ray Shock

©2013, TestAmerica Laboratories, Inc. All rights reserved.
TestAmerica & Design ™ are trademarks of TestAmerica Laboratories, Inc.

August 5, 2013

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Why Measure Mercury?

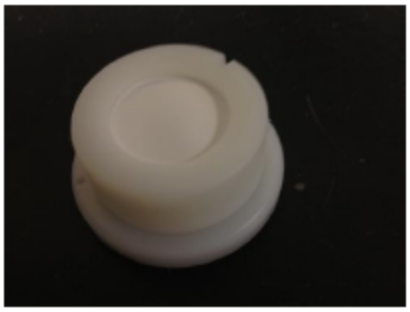


- Toxic effects in humans and wildlife
- Methyl mercury is highly bioaccumulative

2

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What is DGT?



Diffusive

Gradients in

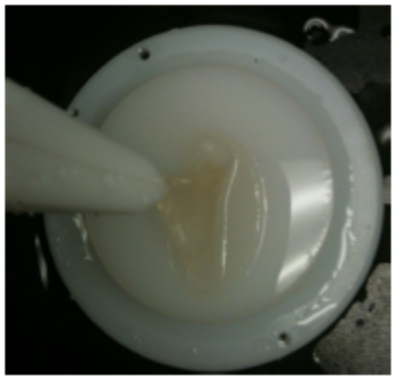
Thin films

Developed by Bill Davison and Hao Zhang at The University of Lancaster and patented in 1993.

3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Why DGT?



- In-situ
- Extended deployment time option
- Simple to deploy in the field
- Monitor water, sediments and soils
- Bioavailability surrogate

4

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What's inside the DGT assembly?



- 0.45 µm Membrane Filter
- Diffusive Gel
- Resin Gel

Chelex

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

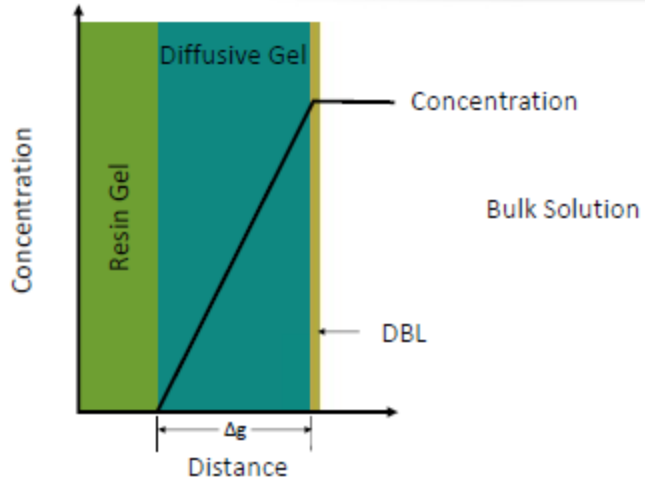
Resins



- Chelex used for most metals
- Chelex doesn't work for mercury
- 3-MFSG works for mercury species
- Polyacrylamide gel binds Hg, so agarose is preferred diffusive gel.

6

2D Representation



7

Fick's First Law of Diffusion

$$J = D\frac{\delta C}{\delta x}$$

J = flux (mol cm^{-2} s^{-1})

D = diffusion coefficient (cm^2 s^{-1})

$\delta C / \delta x$ = concentration gradient (mol cm^{-4})

When applied to DGT $\delta C / \delta x \approx C / \Delta g$

8

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Flux

$$J = D\frac{C}{\Delta g}$$

Flux is basically Mass moving through an Area over time:

$$J = \frac{M}{A\,t}$$

Combining these equations we reach the DGT equation.

9

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

DGT Equation

$$C = \frac{M\,\Delta g}{D\,t\,A}$$

C = Concentration in bulk solution

M = Mass measured from resin gel

Δg = thickness of diffusive layer

D = diffusion coefficient

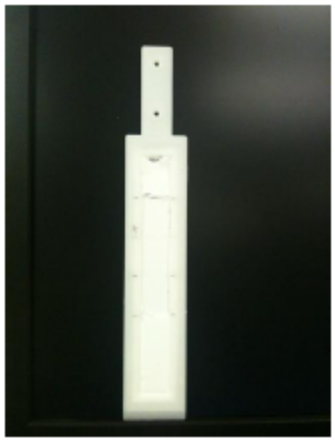
t = time of exposure to bulk solution

A = area exposed to bulk solution

10

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Determine Diffusion Coefficient

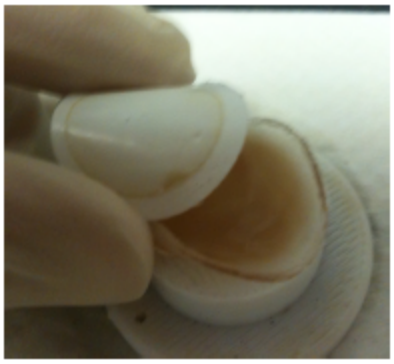


- Solution of constant concentration (C)
- Analyze resin gels over time (t)
- Measure result (M)
- Δg and A are constant
- Only unknown is D
- Literature value is 5×10^{-6} cm^2 s^{-1}

11

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Extracting Analytes



- Co-elution doesn't work
- 1.3 mM Thiourea in 0.5M HCl
  - ~ Methyl Mercury
- Aqua Regia (8 mL HCl, 2 mL HNO_3)
  - ~ Total Mercury

12

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Measuring Mass



- Methyl Mercury (1630)
  - ~ Direct Ethylation
  - ~ Automated P & T
- Total Mercury (1631E)
  - ~ BrCl Oxidation
  - ~ CVAFS Detection

13

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Laboratory Control

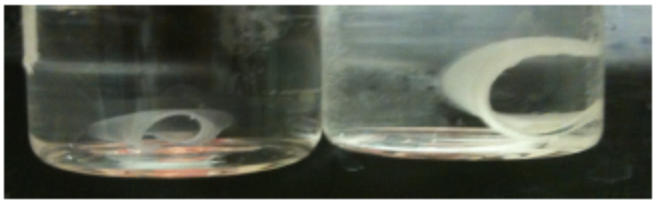


- On-going extraction efficiency monitoring
- Diffusion coefficient variability
  - ~ Matrix interference
  - ~ Bad reagents
  - ~ Resin gel variability
  - ~ Other unknowns

14

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Manufacturing Differences



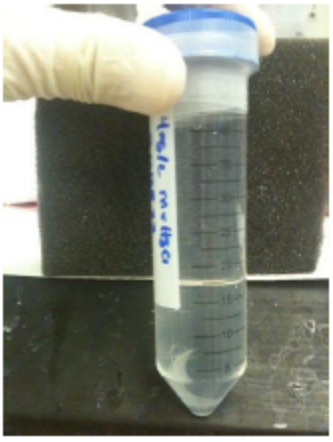
Resin Gels from two manufacturers.

- Left is a thin layer with resin sprinkled on top
- Right is thick gel with resin mixed in, then pressed flat
- Extraction efficiency is very different between the two

15

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Tumbling Resins



- Spike a fixed amount into solution
- Tumble resin gel overnight
- 97% or more adsorbed to resin gel
- Known theoretical amount on resin

16

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Particle Size Reduction

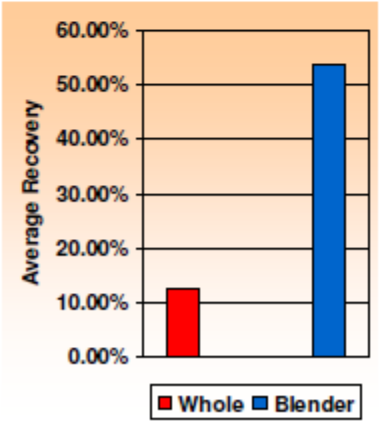


Thick Resin Gel in a Blender

17

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Extraction Efficiency



- Extraction efficiency must be consistent
- Increased extraction efficiency by about 4x
- Increased extraction efficiency leads to greater sensitivity

18

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Conclusions



- DGT has many uses and benefits
- Extraction efficiency is highly variable
- Still challenges facing commercial mercury DGT analysis

Questions?

19

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Acknowledgements

Kerry Tate

Florida Department of Environmental Protection

Hao Zhang

Bill Davison

http://www.dgtresearch.com

DGT for measurements in waters, soils and sediments

TestAmerica
Mark Bruce
Chuck Jacobs
Pat McIsaac

Thank you to those I couldn't or shouldn't mention; and those I forgot.

20

Analysis of Semi-Volatile Compounds in Marine Sediment by GC/MS-MS

Gregory Perez
City of Tacoma Environmental Services Laboratory

Abstract

Marine sediments can be among the most challenging matrices for semi-volatile analysis. Matrix effects can obscure low level analytes, while suppressing internal standard and surrogate recoveries. Reducing the sample size or diluting the extracts can reduce matrix effects. However, this often comes at the expense of meeting reporting limit requirements. Using large volume injection in conjunction with GC/MS-MS allows for smaller extraction amounts and/or higher dilutions without the loss of sensitivity or elevation of reporting limits. Tandem GC/MS-MS provides added sensitivity while filtering out background and increasing signal to noise ratios. GC/MS-MS also adds confidence to the identification of target analytes through compound specific precursor to product ion transitions.

This method is based on EPA SW-846 method 8270 and its goal is to meet challenging reporting limits as low as 5ug/Kg. This method will reduce sample amounts from 10g to 2g while meeting the project objectives.

Analysis of Semi-Volatile Compounds in Marine Sediment By GC/MS-MS

Greg Perez
Senior Environmental Analyst
City of Tacoma Environmental Services Laboratory

CENTER FOR URBAN WATERS



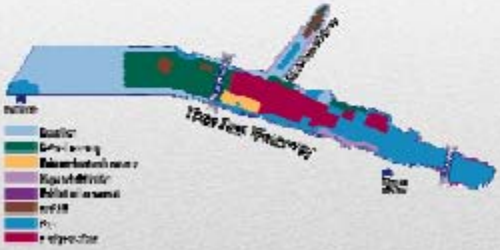
City of Tacoma Environmental Services Laboratory
Tacoma Washington

Center For Urban Waters



Thea Foss Waterway

- Thea Foss and Wheeler Osgood Waterways Remediation Project



The Project

- 1983 - EPA identified Thea Foss and Wheeler-Osgood waterways as part of the 12-acre Commencement Bay Superfund site.
- 2002 – 2006 426,000 cubic yards were dredged from the waterway, at a cost of $105 million.

History

- 2007 - Ongoing monitoring begins
- The City monitors storm drains by testing the water and sediments regularly for possible contaminants.
- This "nonpoint" source pollution comes mostly from stormwater runoff, soapy water, oil and fertilizers which travel from residential areas through the City's 18,000 storm drains and 500 miles of pipes.

History

- Sediment Quality Objectives (SQOs) were developed as part of the Commencement Bay Nearshore / Tideflats Remedial Investigation / Feasibility Study.
- The SQOs were used to identify problem chemicals, identify sources of problem chemicals, and define problem areas during the remedial design.

Sediment Quality Objectives

The City and the EPA found the following chemicals polluting the sediment in the waterways:

- **Phthalates**
- **Polyaromatic Hydrocarbons**
- **Phenolics**
- Pesticides
- Arochlors
- Metals

Sediment Quality Objectives

- Phenol
- 2-Methylphenol
- 4-Methylphenol
- 2,4-Dimethylphenol
- Pentachlorophenol

Analytes - Phenolics

- Naphthalene
- 2-Methylnaphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene

Analytes – LPAH's

- Fluoranthene
- Pyrene
- Benzo(a)Anthracene
- Chrysene
- Benzo(a)Pyrene
- Benzo(b&k)fluoranthenes
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene

Analytes – HPAHs

- Dimethyl Phthalate
- Diethyl phthalate
- Di-n-Butyl phthlalate
- Butylbenzylphthalate
- Bis(2-ethylhexyl)phthalate
- Di-n-octylphthalate

Analytes – Phthalates

- 1,3-Dichlorobenzene
- 1,2-Dichlorobenzene
- 1,4-Dichlorobenzene
- 1,2,4-Trichlorobenzene
- Hexachlorobenzene

Analytes – Chlorinated Aromatics

- Hexachlorobutadiene
- Benzyl Alcohol
- Benzoic Acid
- Dibenzofuran
- N-nitrosodiphenylamine

Analytes – Miscellaneous

- Reporting Limits

Analyte	SQO ug/Kg	Reporting Limit ug/Kg
Hexachlorobenzene	22	11
Hexachlorobutadiene	11	5.5
N-Nitrosodiphenylamine	28	14

Challenges



Challenges

- 10g sample extracted by Accelerated Solvent Extraction (ASE)



Traditional Process

- Extensive Cleanup
  - Gel Permeation Chromatography
  - Copper cleaning
  - Alumina
  - Dilution



Traditional Process

- Analysis by GC/MS



- Multiple injections
- Most samples analyzed at least twice per analyte group.

Traditional Process

- Time Intensive
- Labor intensive
- QC Issues caused by matrix interference
  - Internal Standard Failures
  - Surrogate Failures
  - Matrix Spike Failures

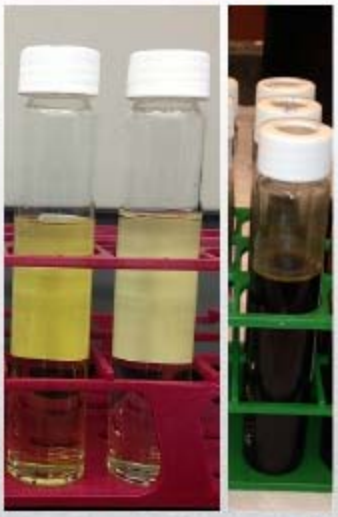
Traditional Process

- Instrument sensitivity allows
  - Smaller sample size
  - Less matrix effects
  - More specificity



A New Approach using GC/MS-MS

- Accelerated Solvent Extraction
  - 2g sample
  - Dichloromethane
  - Concentrated to 1ml



Extraction

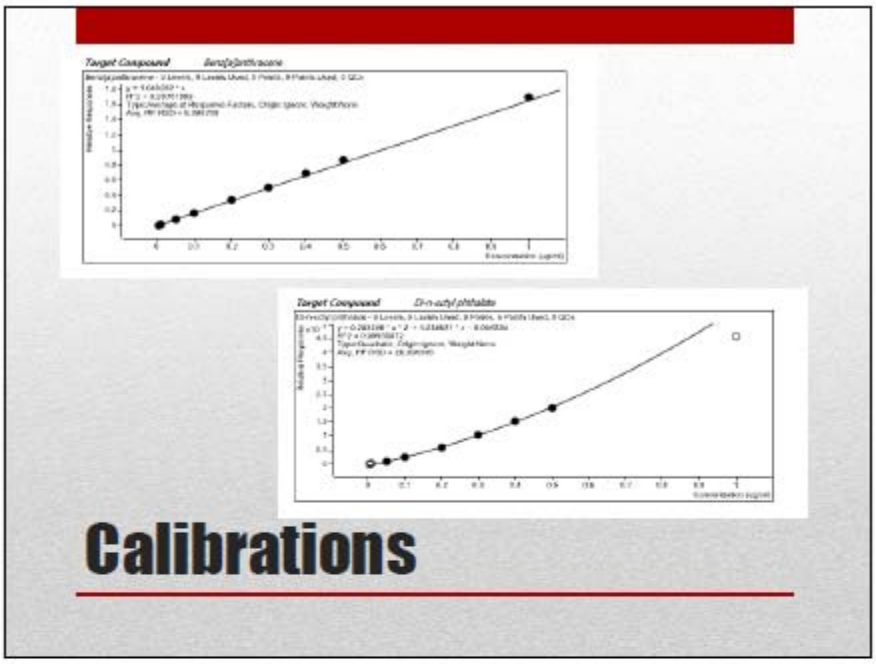
- J&W DB-5 20m X 0.18 µm X 0.18 µm
- 40° for 1 min/ 23°C/min to 260° for 0 min
- Then 10°C/min to 290°C for 4 min

- Flow 1.3ml/min
- Acquisition time 17.6 minutes

Method

- Multi Mode Injector (MMI)
- 10 µl injection (5µl X 2)

Method



Analyte	2g Result	10g data
Hexachlorobutadiene	0.6	0.5
N-Nitrosodiphenylamine	8	11
Hexachlorobenzene	9	0.6

Data

Analyte	2g	10g
	µg/Kg dry	µg/Kg dry
Fluoranthene	940	770
Pyrene	2600	1700
Butyl benzyl phthalate	490	150
bis(2-Ethylhexyl)phthalate	1000	880
Benzo(a)anthracene	650	410

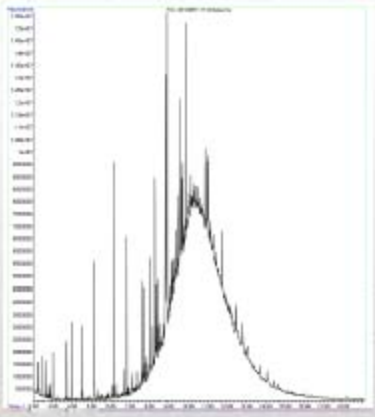
Data

2-Fluorophenol	24.0	12.4	35.3
Phenol-d5	44.0	37.5	53.5
Nitrobenzene-d5	51.0	59.1	56.9
2-Fluorobiphenyl	63.0	70.2	69.8
2,4,6-Tribromophenol	38.5	14.8	57.8
Terphenyl-d14	98.7	99.5	123
1,4-Dichlorobenzene-d4	108	109	103
Naphthalene-d8	108	109	103
Acenaphthene-d10	114	113	108
Phenanthrene-d10	113	113	106
Chrysene-d12	74.4	75.9	57.5
Perylene-d12	**28.7**	**27.8**	**17.1**

QC Recoveries – 10g

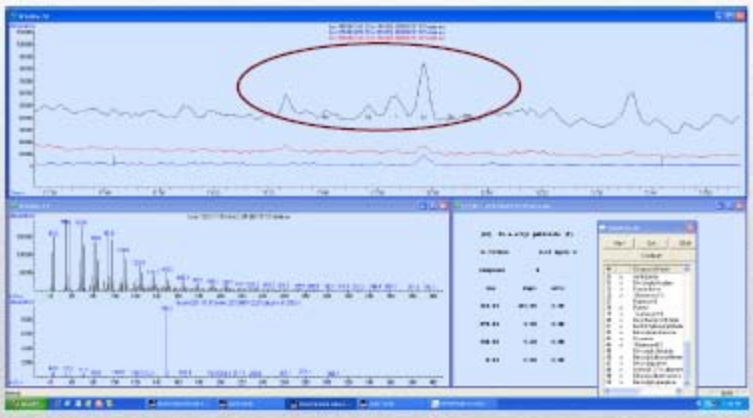
2-Fluorophenol	73.2	68	57.5	46.3
Phenol-d5	51.8	90.3	44.3	55.5
Nitrobenzene-d5	70.1	111	61.9	110
2-Fluorobiphenyl	50.2	64	43.9	54.8
2,4,6-Tribromophenol	131	149	83.4	118
Terphenyl-d14	123	128	111	97.6
1,4-Dichlorobenzene-d4	98.7	80.6	99.5	86.9
Naphthalene-d8	72.3	102	74.5	73.3
Acenaphthene-d10	**265**	**139**	**274**	**96.1**
Phenanthrene-d10	**380**	**201**	**408**	**162**
Chrysene-d12	103	102	105	117
Perylene-d12	**59.7**	**76.3**	**59.6**	**93.3**

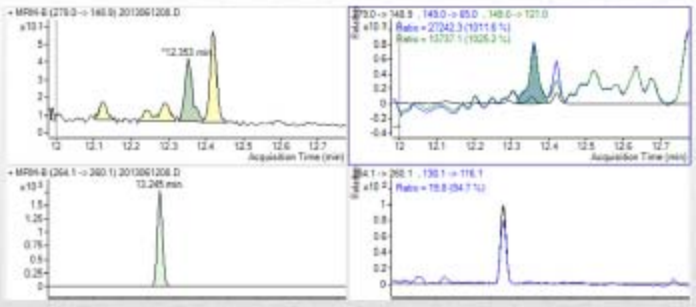
QC Recoveries – 2g



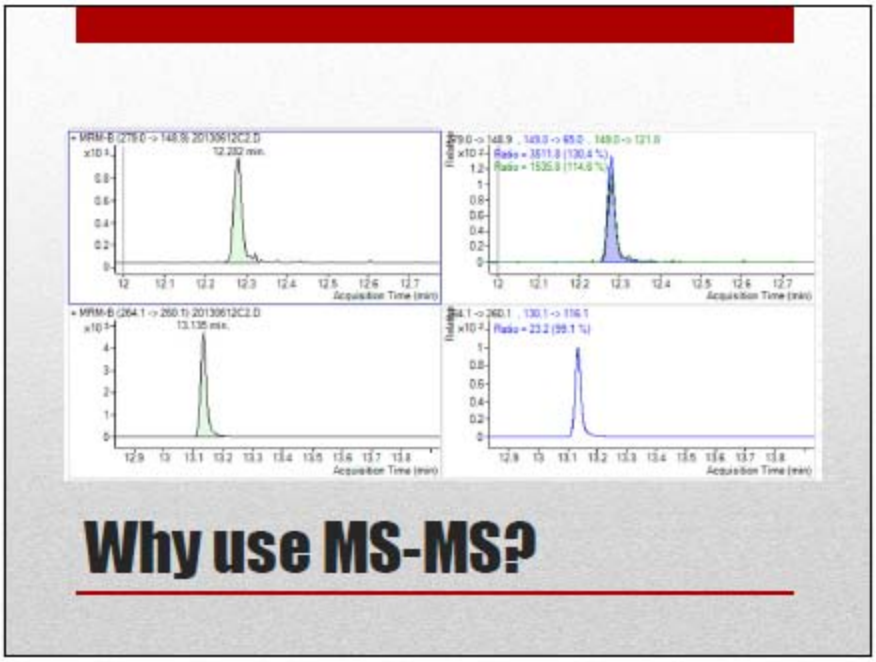
Why use MS-MS?

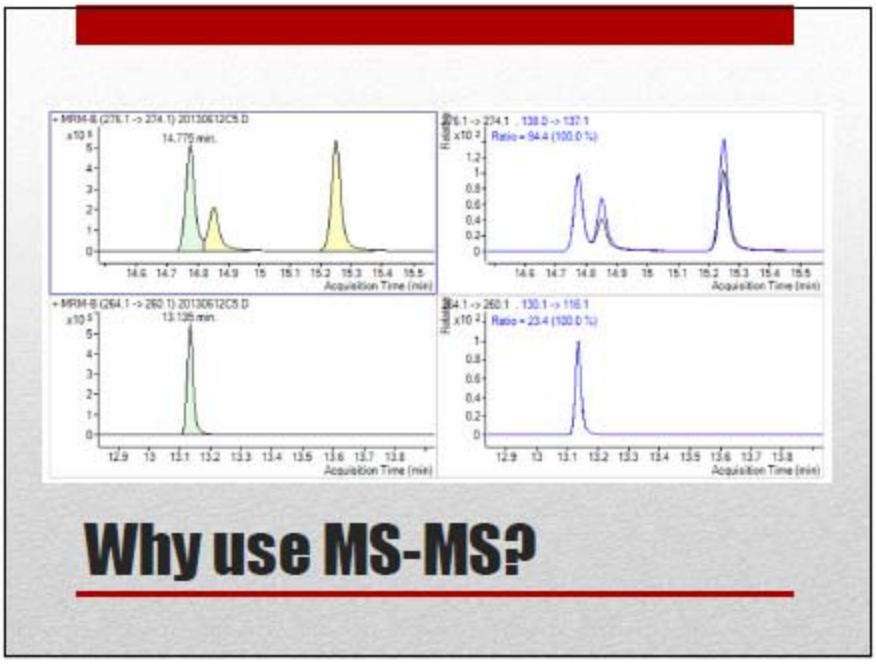
Why use MS-MS?

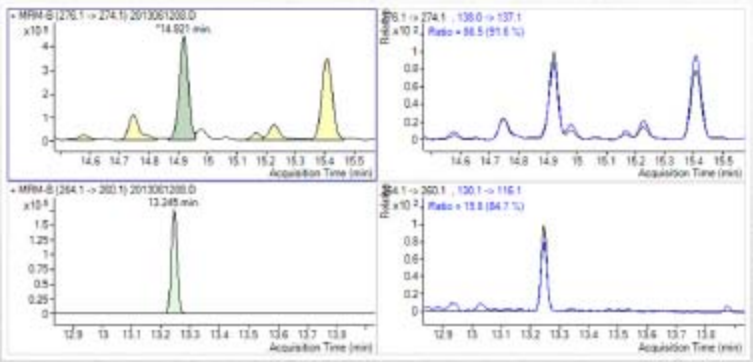




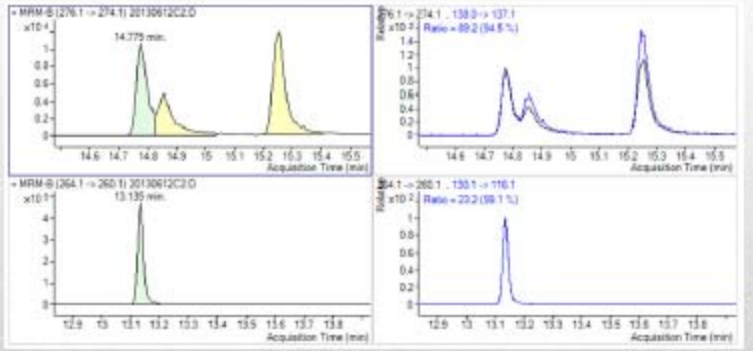
Why use MS-MS?


Why use MS-MS?

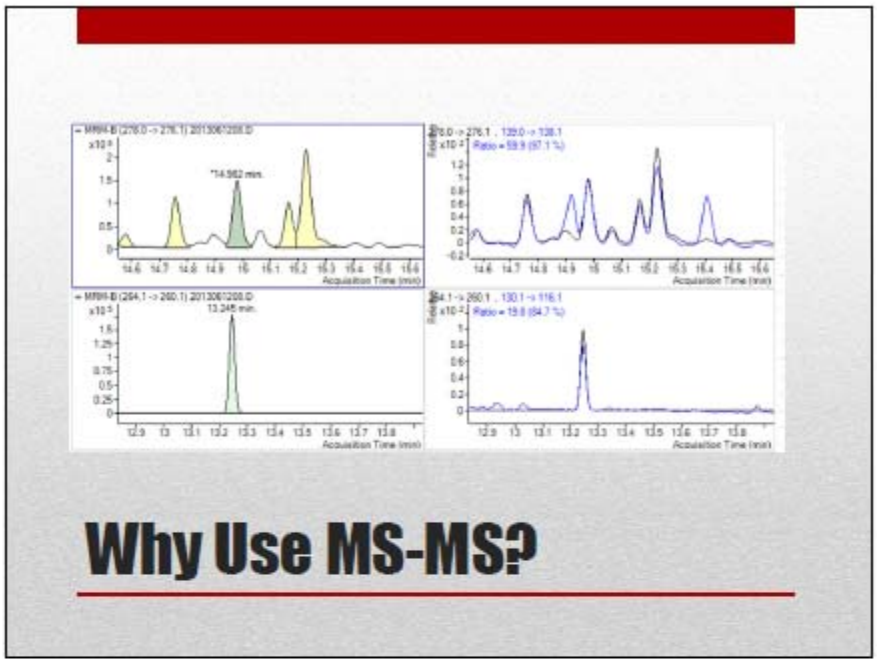

Why use MS-MS?



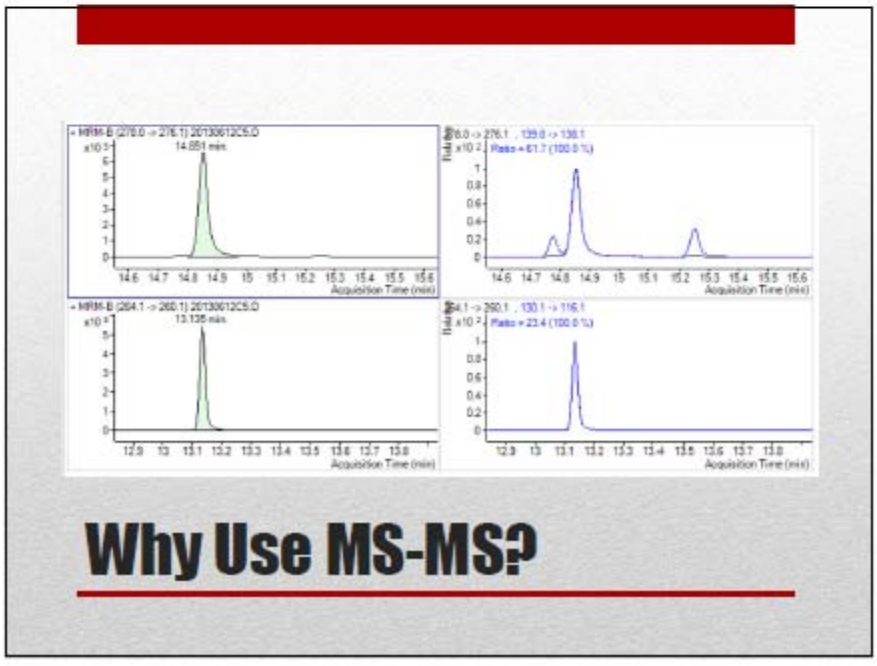
Why use MS-MS?



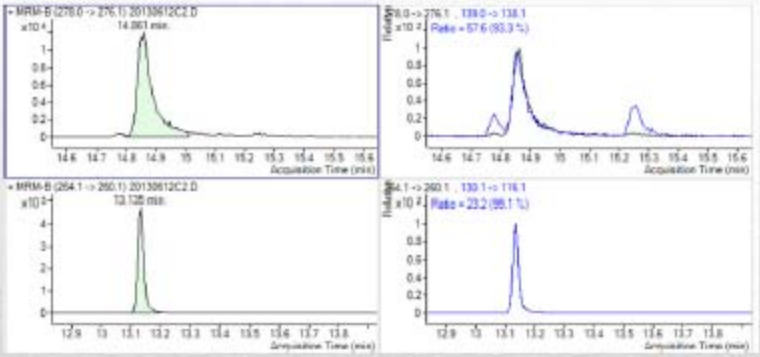
Why Use MS-MS?



Why Use MS-MS?



Why Use MS-MS?



Why use MS-MS?

- MDL for Bis(2-ethylhexyl)phthalate & Di-n-butyl phthalate did not meet the acceptance criteria. blank levels close to spike level.
- Benzoic Acid extraction recoveries were very low and erratic. MDL did not meet the acceptance criteria. MDL < mean recovery.

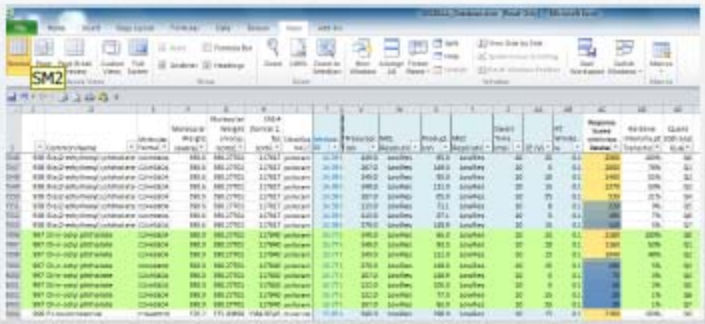
Some remaining issues

- Additional calibration points could be added to the curve to decrease the gap between MDL and MRL except for Benzyl Alcohol and Di-n-octyl phthalate.
- MMI injection could use more optimization

Some remaining issues

- Wide range of reporting limits for project makes selection of calibration points difficult.
- Have to balance sensitivity for non-detects to meet reporting limits.
- Refine method optimization by selecting less sensitive transition or collision energy for compounds requiring a higher upper range.

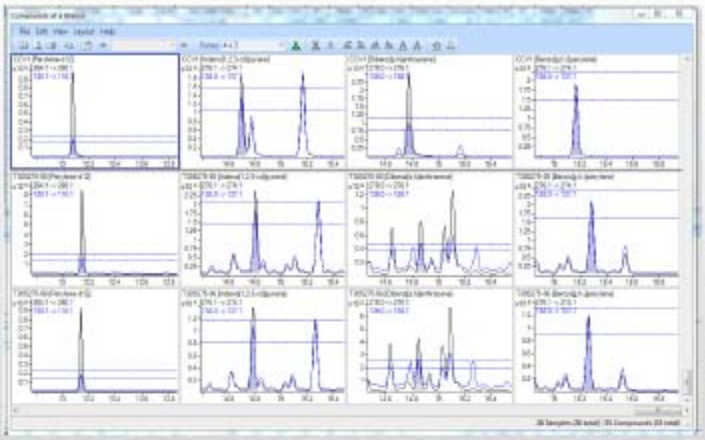
Some remaining issues



Transitions Selection

Analyte	Method RT	Precursor Ion	Product Ion	Dwell Time	Collision Energy	Relative Intensity
Indeno[1,2,3-cd]pyrene	19.23	138.1	137.1	10	10	100%
Indeno[1,2,3-cd]pyrene	19.23	137.0	136.0	10	15	89%
Indeno[1,2,3-cd]pyrene	19.23	276.0	274.1	10	40	34%
Indeno[1,2,3-cd]pyrene	19.23	138.1	125.1	10	15	20%
Indeno[1,2,3-cd]pyrene	19.23	137.0	124.0	10	15	20%
Indeno[1,2,3-cd]pyrene	17.23	274.1	272.0	10	40	8%

Transitions Selection



Compounds at a Glance

The sensitivity of the MS-MS, allows us to simplify sample prep by:

- Reducing sample size
- Minimizing the amount of extract cleanup required
- Improving extraction efficiency by increasing solvent to sample ratio

Conclusions

- MS-MS Improves analysis by:
  - Minimizing the effect of matrix in the chromatogram
  - Providing options to reduce the effect of interfering peaks.
  - Product ions add additional level of confidence in the identification of target compounds.

Conclusions

- Greg Perez
- gperez@cityoftacoma.org

- Leonora Litzi-Davis
- ldavis@cityoftacoma.org

Contact Information

SECTION 4

FIELD MEASUREMENTS, SENSORS, AND IN-SITU MONITORING

Micro-AirCore: Spatial Mapping of Atmospheric Species

Kristin Favela, Pieter Tans, Tom Jaeckle, William Williamson
Southwest Research Institute

Abstract

Micro-AirCore is a simple, effective, reusable, innovative, and low cost sampler with the ability to provide temporal and spatial resolution of a continuous air sample. When coupled with MS, the resulting time-resolved 3-D profiling can be used to rapidly create chemical maps with a limited number of samples, greatly reducing time, effort and cost. The original NOAA-developed device consists of a long stainless steel tube pre-filled with calibrated gas and allowed to ascend on a weather balloon. During ascent, the device is evacuated as it equilibrates with the decreasing atmospheric pressure. During descent, the tube is filled with atmospheric gas in an ordered manner. Diffusion inside the tube is slow enough that the collected gas remains ordered. Here is described a miniaturization of the NOAA-developed device; the large, stainless steel tube was replaced with Hydroguard fused silica tubing (0.53 mm x 30 m) and two lightweight valves having a total mass of less than 28 grams. Given the minute volumes, cavity-ring down spectroscopy was no longer feasible and a benchtop GC/MS was modified for accurate profiling. This micro-AirCore device was deployed on the SwRI-developed unmanned SkyWisp glider. As a proof-of-concept, carbon dioxide was profiled in the atmosphere up to approximately 20,000 m. A laboratory-based validation system was used for evaluating the micro-AirCore function, including accuracy and precision, for carbon dioxide. The diffusion profiles of carbon dioxide, argon, oxygen and methane were also investigated. Overall, the micro-AirCore device demonstrated an accuracy error of 2% (12CO2) and minimal diffusion over a period of 16 hours (peak width increased by a factor of 1.6). Hold-time tests were performed with lightweight gases (oxygen, carbon dioxide, methane and argon) representing the worst-case scenario for diffusion. However, even after 63 hours, mixing of the gases inside the tube was not complete. A triplet of micro-AirCore devices were deployed on the SkyWisp glider yielding a relative standard deviation of 0.08%, or 0.3 ppm, for CO2. The profile collected resulted in observation of the boundary layer with elevated CO2 levels, a region in the free troposphere with relatively constant CO2 mole fraction, and a gradual decrease in CO2 above 10,000 m. This micro-device has broad applications extending beyond vertical profiling, as fitting the device with a metering device enables horizontal collection of gases. As a proof-of-concept, the micro-AirCore was demonstrated for select EPA TO-15 compounds (1 ppm each of chloroform, benzene, hexane, and toluene). Using the laboratory-based validation system, 2 minute intervals of test gas separated by 10 minutes of nitrogen were delivered to the micro-AirCore device. After holding the gas in the tube, the contents were analyzed and the pattern of gases retained. In summary, the micro-AirCore system has enormous potential for both vertical and horizontal profiling of trace volatile chemicals, enabled by the ability of the mass spectrometer to sample minute quantities of gas in a continuous manner. This technique is applicable to many functions including chemical plume profiling for model verification and the identification of toxic chemical sources; since the system is extremely lightweight it is easily incorporated into unmanned vehicles.

AirCore Miniaturization

Kristin Favela, PhD
Tom Jaeckle
William Williamson

Pieter Tans, PhD

Southwest Research Institute

NOAA

1

Introduction

- NOAA acquires and maintains the global, regional, and local records of greenhouse gases
- NOAA's Earth Systems Research Laboratory (ESRL) invented AirCore collection device
- AirCore collects a column of atmospheric air:
  - Measure greenhouse gases as a function of altitude

2

Introduction

- U.S. Patent No. 7597014 (10/6/2009)
- Typically 100 m or longer; 1/4″ or 1/8″ diameter
- Stainless steel tubing



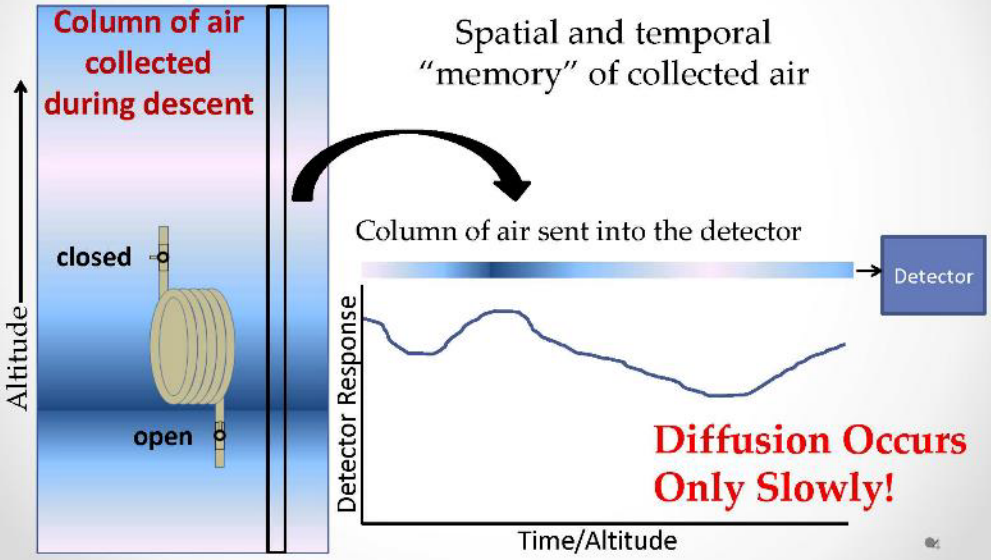
Detection via Cavity Ring Down Spectroscopy

For 1/4″, 150 m:
Total Volume = 4.7 L
Cell size = 6 mL
791 measurements

Required precision = 1 part in 4000

3

AirCore Operation



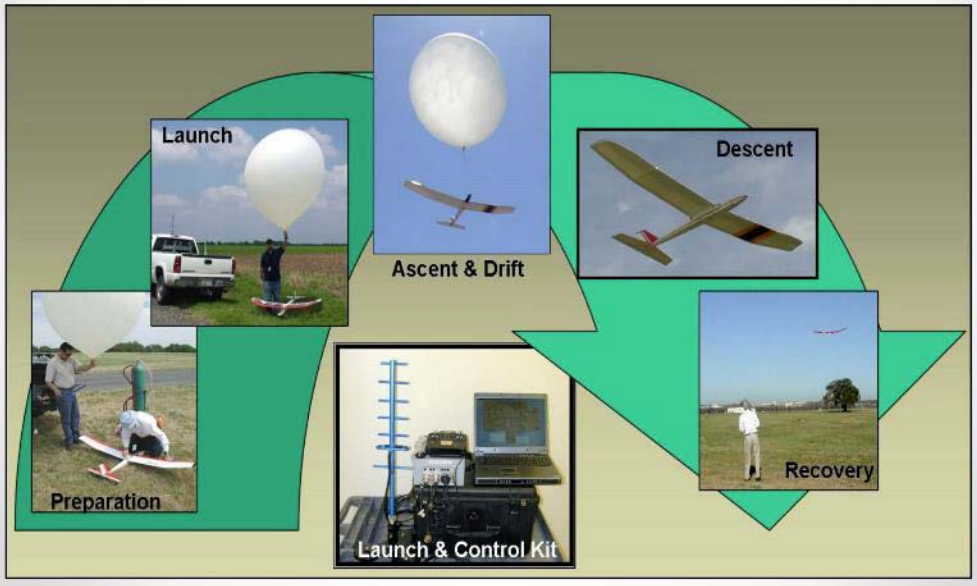
4

Introduction



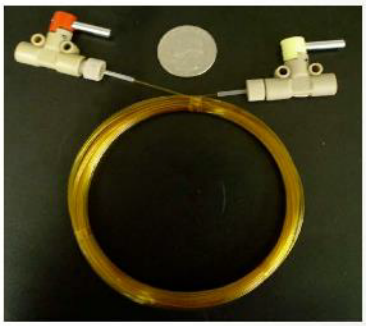
5

SwRI SkyWisp



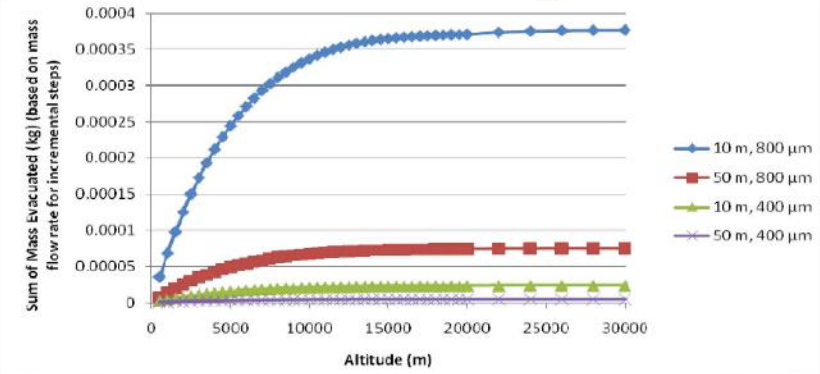
Air Core Miniaturization

- Fused Silica Tubing
  - Extremely lightweight
  - Water-resistant coatings
- Mass Spectrometric detection
- Advantages:
  - Measure many species at once
  - Extremely sensitive
  - Small sample size
- Limitations:
  - Accuracy and precision
  - Interferences (CH_4 / O)



7

Modeling



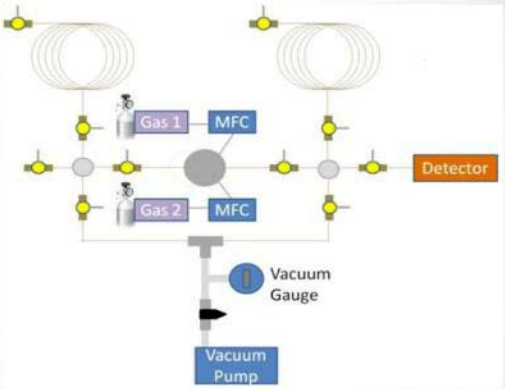
Aircore Device	Tubing Type	Length (m)	Diameter (µm)	Aspect Ratio	Total Mass Evac. (kg)[1]	Required Mass Evac. (kg)[2]
Current	Stainless Steel	150	6096	24,606	8.5×10^{-2}	5.1×10^{-3}
Miniaturized	Fused Silica	50	800	62,500	7.5×10^{-5}	3.0×10^{-5}
Miniaturized	Fused Silica	50	400	125,000	4.7×10^{-6}	7.4×10^{-6}
Miniaturized	Fused Silica	10	800	12,500	3.8×10^{-4}	5.9×10^{-5}
Miniaturized	Fused Silica	10	400	25,000	2.4×10^{-5}	1.5×10^{-6}

[1] Sum of all incremental time steps, based on mass flow rate; [2] Mass required to be evacuated to reach equilibrium by 30,000 m.

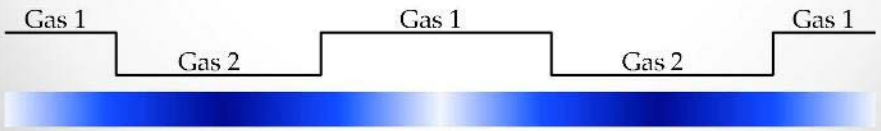
8

Laboratory Validation



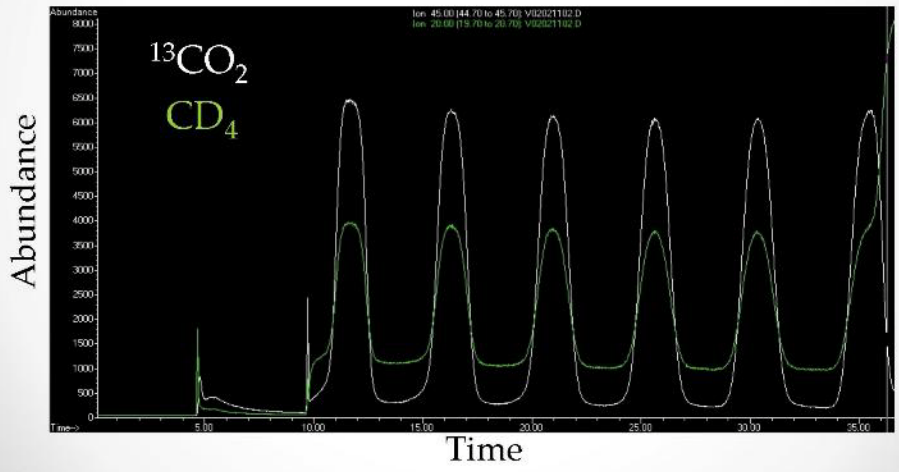


Alternating gas "slugs":

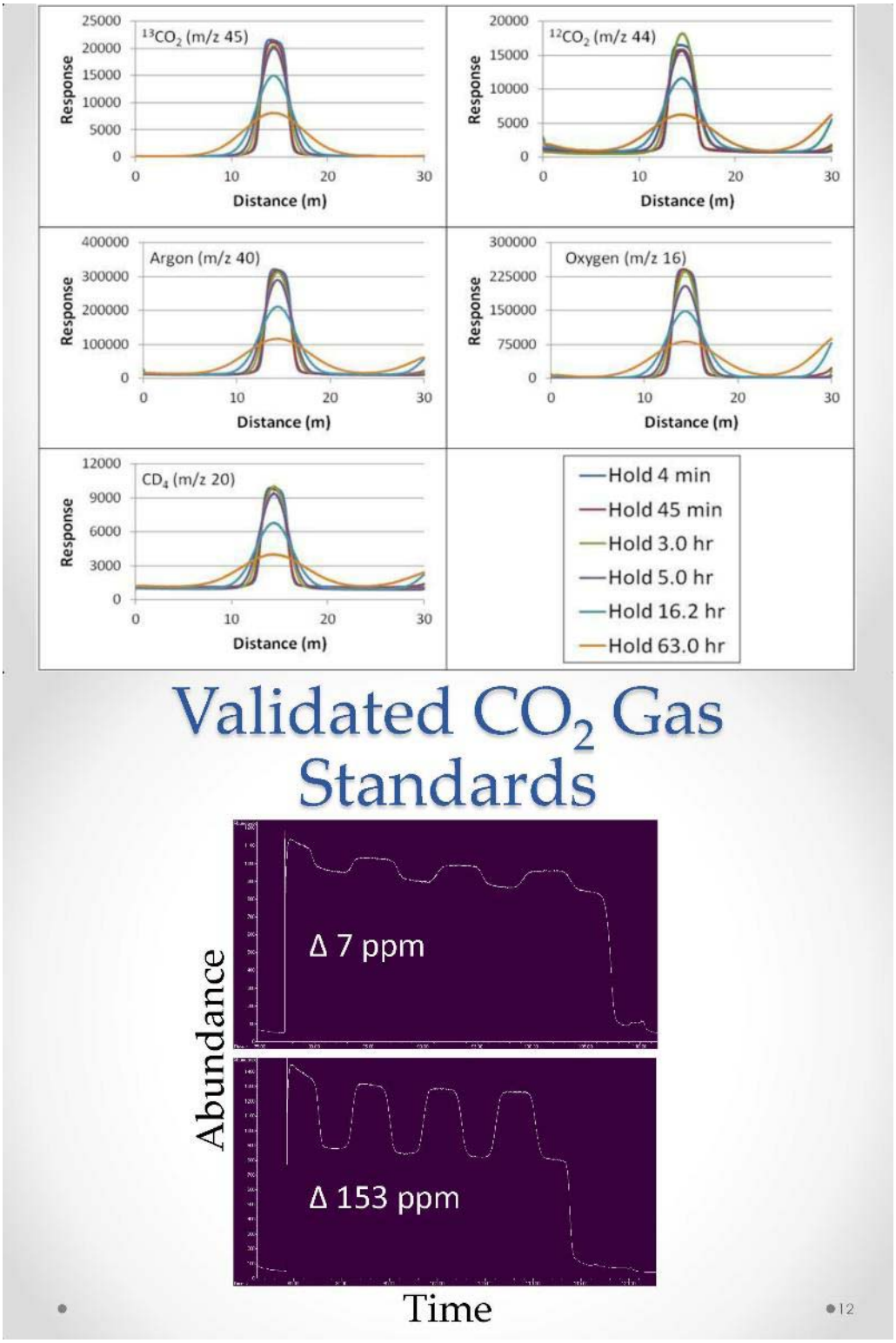


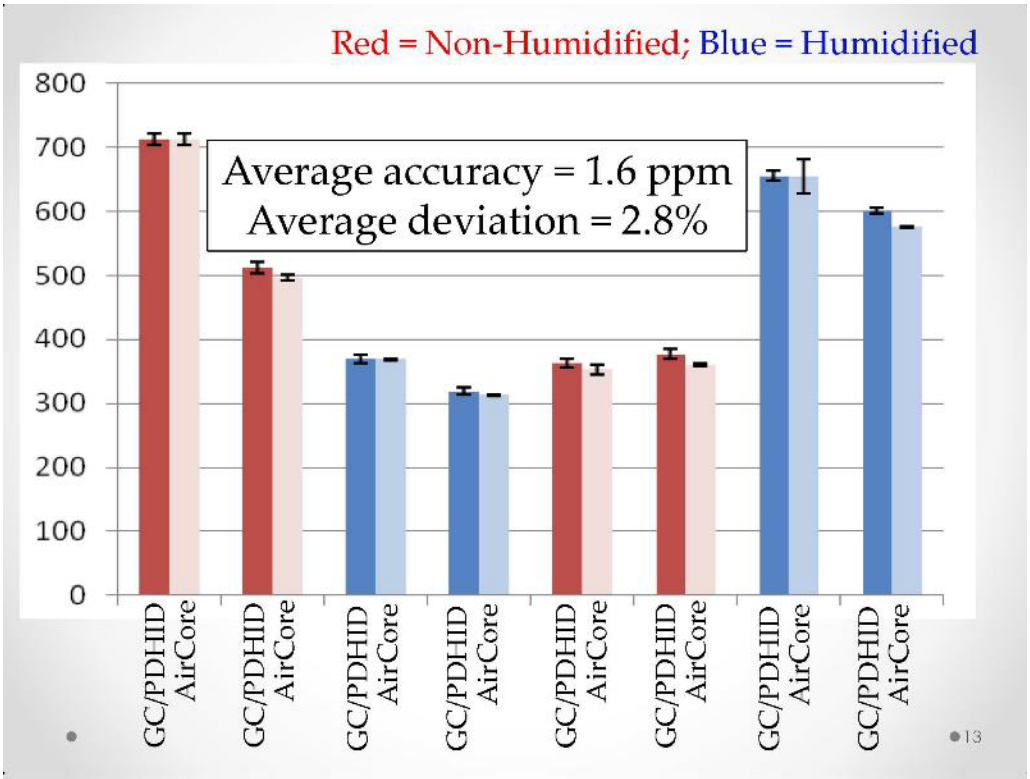
9

Laboratory Validation



10

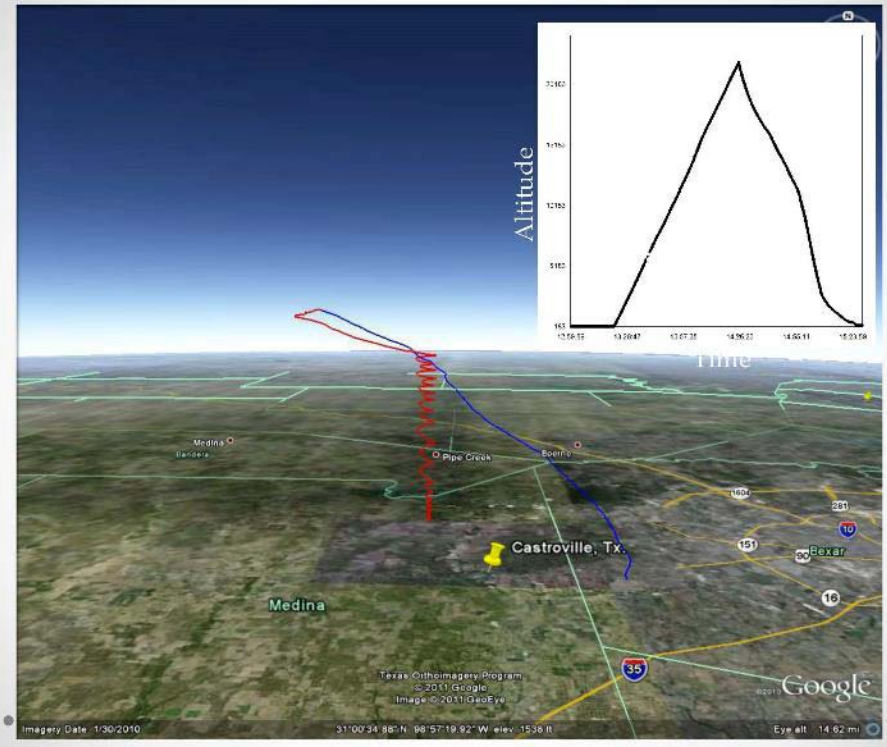

$^{13}CO_2$ (m/z 45)
$^{12}CO_2$ (m/z 44)
Argon (m/z 40)
Oxygen (m/z 16)
CD_4 (m/z 20)
Response
Distance (m)
Hold 4 min
Hold 45 min
Hold 3.0 hr
Hold 5.0 hr
Hold 16.2 hr
Hold 63.0 hr
Validated CO_2 Gas Standards
Δ 7 ppm
Δ 153 ppm
Abundance
Time
12


Red = Non-Humidified; Blue = Humidified
800
700
600
500
400
300
200
100
0
Average accuracy = 1.6 ppm
Average deviation = 2.8%
GC/PDHID
AirCore
13


Micro-AirCore Deployment
14

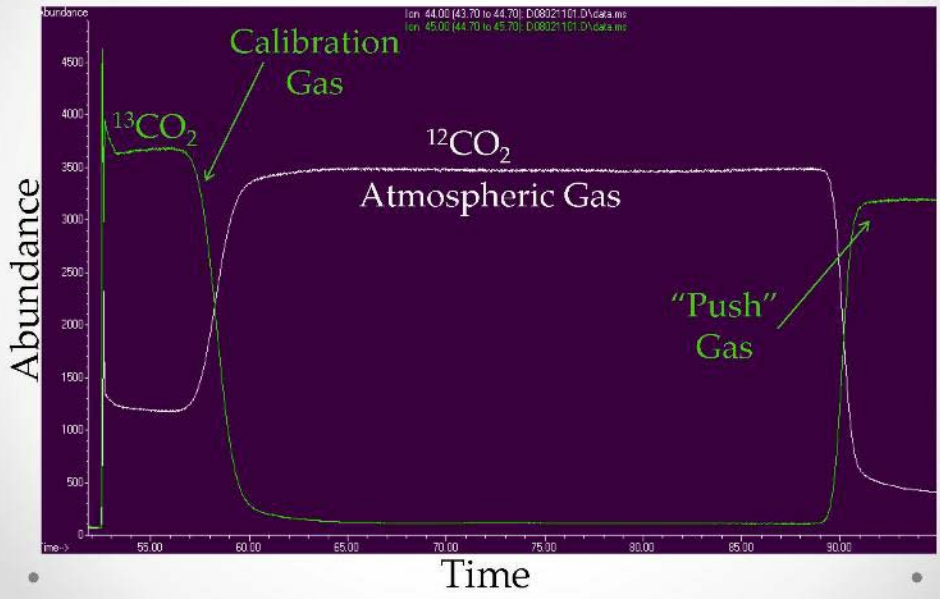


15

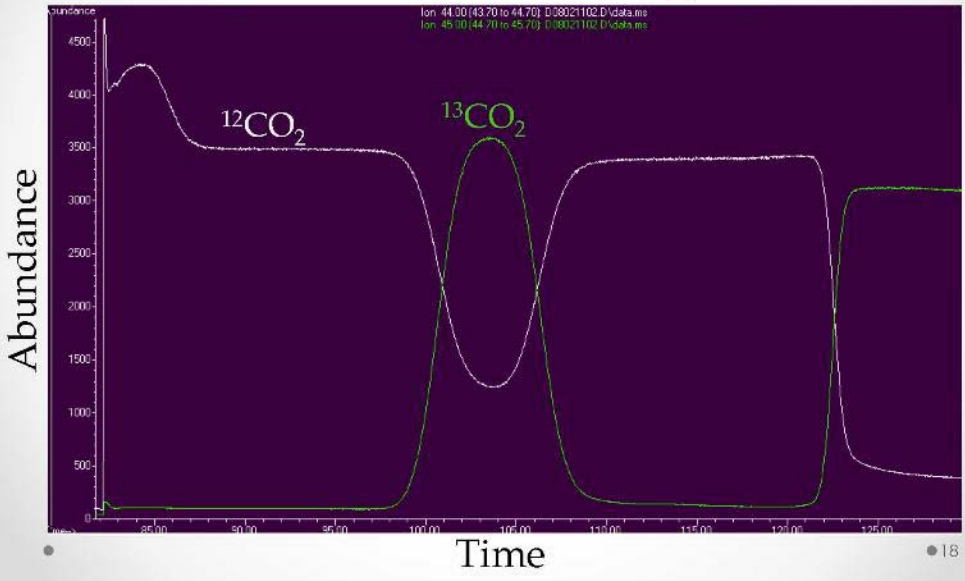

Altitude
Time
Pipe Creek
Castroville, Tx.
Medina
Bexar
Texas Orthoimagery Program
© 2011 Google
Image © 2011 GeoEye
Google
Imagery Date: 1/30/2010
29°00'34.88"N 98°57'19.92"W elev 1536 ft
Eye alt 14.62 mi

16

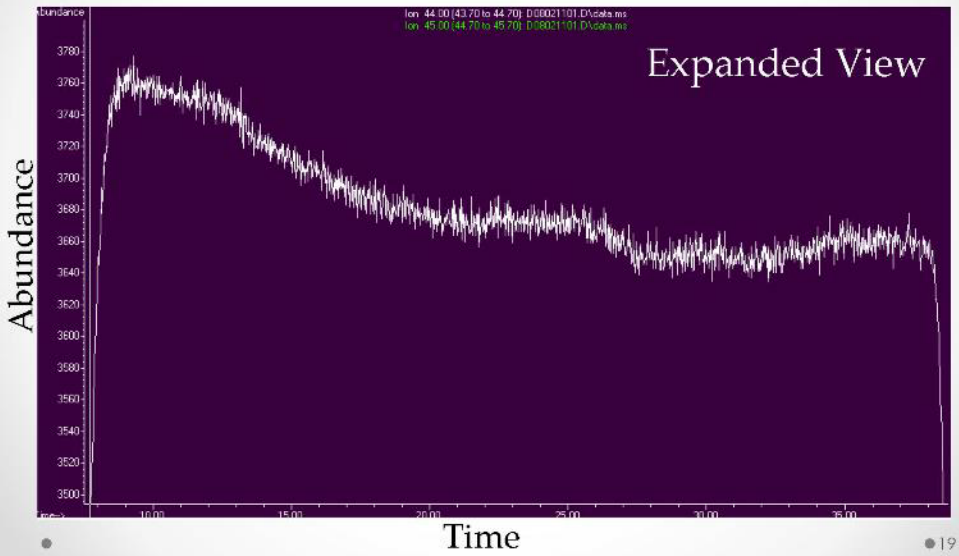
Typical Profile



Both Valves Open



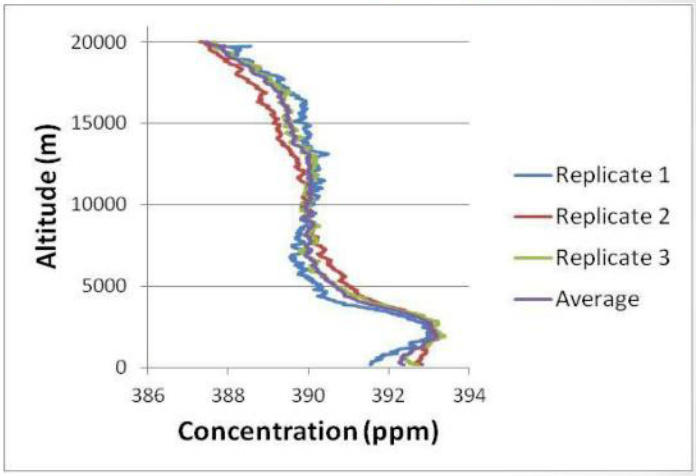
$^{12}CO_2$ Signal



19

Micro-AirCore Deployment

Overall % RSD for replicates = 0.08%



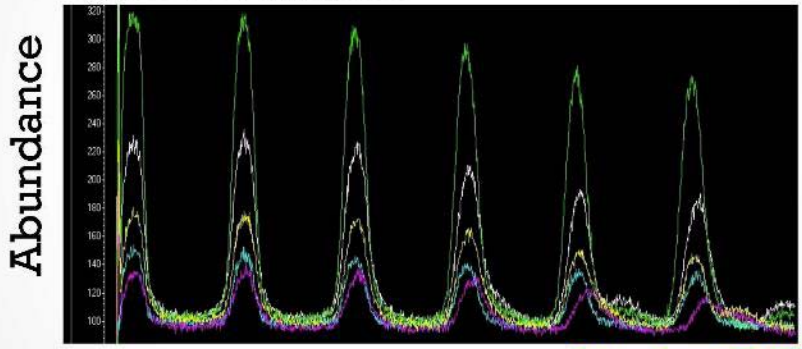
Argon is measured concurrently with CO_2 as an internal standard – is well mixed in the atmosphere

20

Beyond Greenhouse Gases

Meter flow for land-based operation

1 ppm VOC standard:

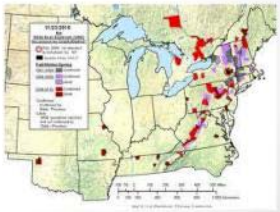


21

3-Dimensional Profiling of Caves







Metabolic profiling of White Nose Syndrome as diagnostic

22

On-Going Work / NOAA and Company

Air as Syrup: The flow and mixing of air in the AirCore

Pieter Tans[1], Colm Sweeney[2], Anna Karion[2], Tim Newberger[2], Jack Higgs[3], Sonja Wolter[2]
[1]NOAA Earth System Research Laboratory, [2]Cooperative Institute for Research in Environmental Sciences, [3]Science and Technology Corporation

23

On-Going Work / NOAA: Air as Syrup

The flow out of, and into, the AirCore during a flight can be accurately calculated with a dynamic flow model using measurements of atmospheric pressure and temperature, and of the coil temperature as a function of time.

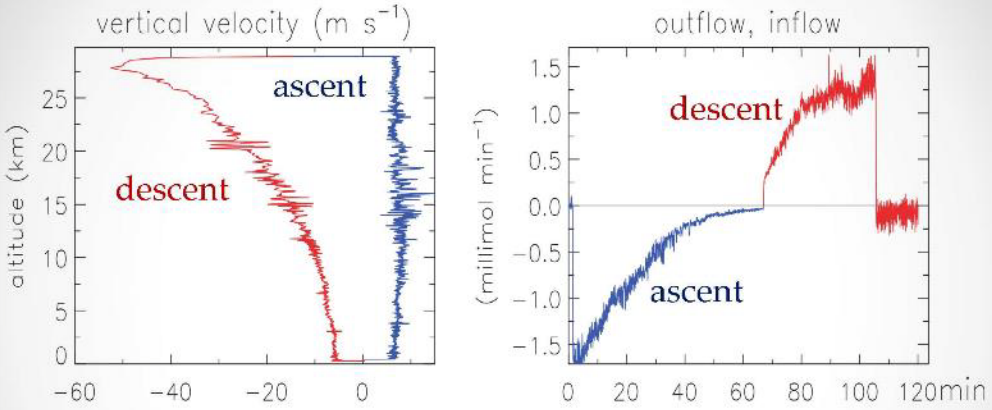
Important: viscosity is independent of pressure!



Launch from Windsor, CO by EOSS (Edge Of Space Sciences) and members of the Carbon Cycle group.

24

On-Going Work / NOAA: Air as Syrup



- 15 January 2012 flight (OK): Small (~900 cc) Aircore consisting of two sections, 26 m of 1/4" and 36 m of 1/8" diameter.
- **Right:** Valve remained open for 15 minutes after landing; it is still warming, causing sample air to be slowly expelled from the open end.

25

Considerations for the Collection of Solid Samples for Volatile Organic Analysis in an Arctic Environment: Frozen Cores and More

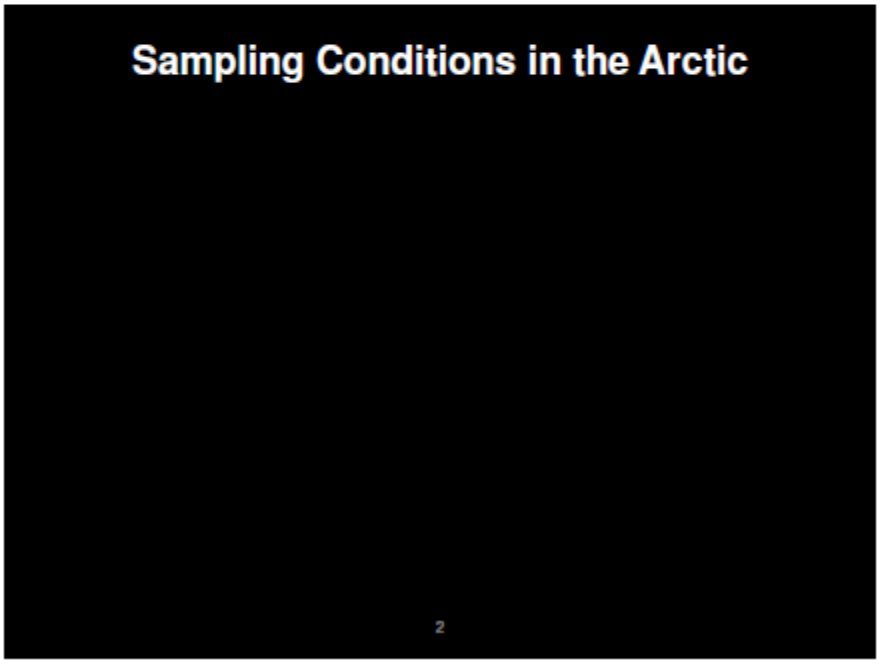
Lester J. Dupes, Rock J. Vitale, Steven J. Lennon, Joseph P. Kraycik
Environmental Standards

Abstract

The field collection of solid samples for the analysis of volatile organics by Method 5035/5035A has been inconsistently applied to environmental work since the initial release of the SW-846 Methods in 1996 and 2002, respectively. Sample collection in various types of glass jars was also removed at the same time. The sample collection methods specified in in 5035/5035A are appropriately generic and do not address soil sampling in extreme field conditions in an Arctic environment. Sample collection at subzero temperatures allow sampling equipment and personnel to move quickly over the surface, thereby reducing deleterious impact to tundra environments.

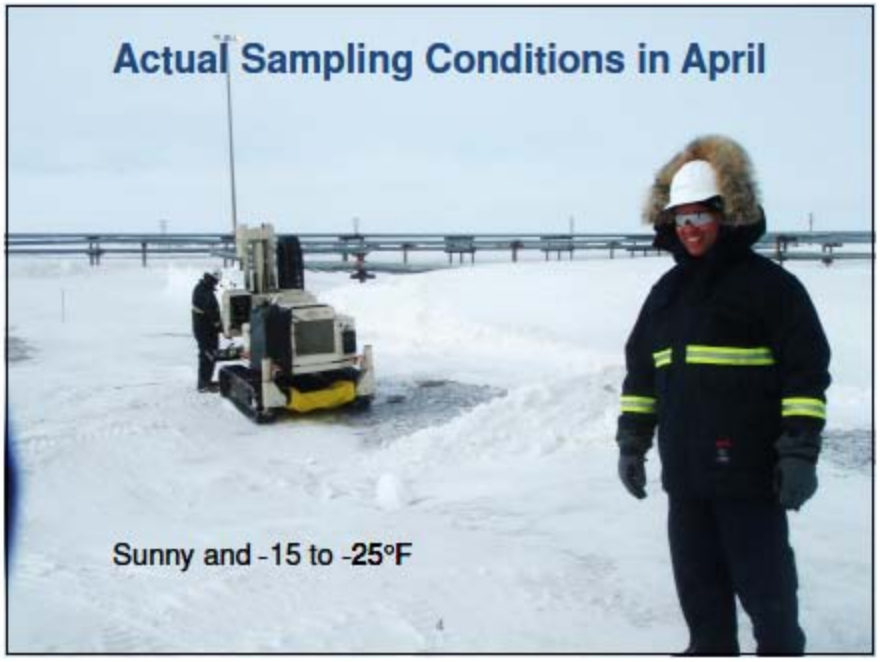
Although the data quality objective is to collect samples for volatile organics in a manner that reduces the amount of time the sample is exposed to the environment to limit the loss of volatile contaminants of potential concern (COPC), the techniques and collection of volatile organics from frozen soil cores containing tundra mat and ice lenses require special considerations which obviously are not addressed in the published method. This paper will present observations and considerations associated with winter sampling efforts conducted in subzero field conditions, deviations from methodology requirements with regard to sample collection dates and times, sample handling, subsampling, and storage and shipment requirements as well as proposed solutions and method modifications.


Considerations for the Collection of Solid Samples for Volatile Organic Analysis in an Arctic Environment: Frozen Cores and More
National Environmental Monitoring Conference
San Antonio, Texas
August 5, 2013
Lester J. Dupes, CEAC
Rock J. Vitale, CEAC
Steven J. Lennon
Joseph P. Kraycik, P.G., LEED AP
ENVIRONMENTAL STANDARDS


Sampling Conditions in the Arctic
2

Sampling Conditions in the Arctic

3



Sampling Summary

- Collection of soil samples must occur during winter to allow Geoprobe access in sensitive tundra areas.



5

ENVIRONMENTAL STANDARDS

Sampling Summary (cont.)



- Geoprobe mobilized to the surveyed sampling points
- Soil cores collected in acetate-lined sample tubes, MacroCore Sampler pushed through frozen soils.

6

ENVIRONMENTAL STANDARDS

Sampling Summary (cont.)

- Sample tubes placed in a sled and transported to the field sampling contractor's field trailer for removal of the frozen core and decontamination of the MacroCore Sampler.



7

ENVIRONMENTAL STANDARDS

Sampling Summary (cont.)



- Frozen sample cores placed in a wooden box, warmed using forced hot air, necessary to remove frozen core from MacroCore Sampler.

8

ENVIRONMENTAL STANDARDS

Sampling Summary (cont.)

- After warming for several minutes, MacroCore secured to a pipe stand and a steel rod used to force the acetate liner containing the sample out.



9

Processing the Cores

- Cores capped and transported to the consultant trailer, significant distance from the site sampling area, for further processing.
- The frozen core samples were at times maintained from 1 to 4 days in a secured large chest freezer.
- The frozen cores were typically thawed for several hours (or overnight in a locked field trailer).

10

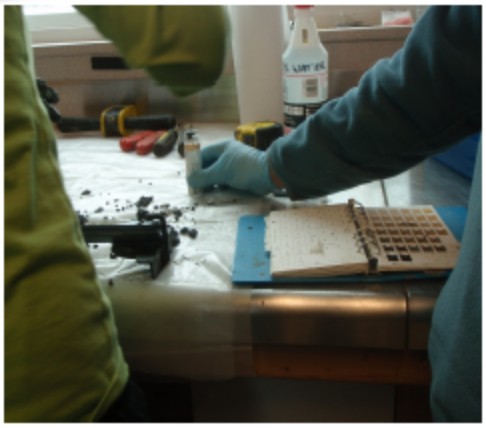
Processing the Cores (Cont.)

- The acetate liner was split, core material characterized and collecting subsamples for volatile organic analysis by Method 5035A.
- Soil samples were collected using TerraCore kits containing two vials of deionized water and one vial of methanol using standard sampling techniques detailed in Method 5035A.

11

ENVIRONMENTAL STANDARDS

TerraCore Sampling





12

ENVIRONMENTAL STANDARDS

Method 5035A Guidance

- Sections 8.2.1 and Appendix A4.0 appear to stipulate subsampling immediately upon collection and preserved.
- Preserved by immersion in deionized water and methanol analyzed within 48 hours of sample collection or frozen to < -7 ℃ within 48 hours to extend the holding time to 14 days.
- Why not just collect a methanol preserved sample?
  - Human and ecological risk assessment values to a low MDL.

13

ENVIRONMENTAL STANDARDS

Project Issues and Solutions

- Definition of Sample Collection Date and Time
  - When frozen sample core removed from environment or when thawed, split and subsampled?
  - Cannot sample frozen core, due to inability to characterize zone for sampling, ice lenses, tundra mat, cannot push TerraCore into frozen sample.
  - Collection Date and Time not well defined in literature.
  - Consistency between summer collection methods.
  - Frozen cores held 1-4 days before sampling precluded meeting goal of "immediate collection" to prevent loss of volatiles. Does it matter in a frozen core? Thawing overnight?

14

ENVIRONMENTAL STANDARDS

Project Issues and Solutions (cont.)

- Sample Preservation and Holding Time
  - Difficulty in subsampling and preservation within 48 hours.
  - Logistically challenged: Unable to ship samples to meet 48 hour holding time.
    - Sodium bisulfate not permitted by ADEC.
    - Analysis within 48 hours.
  - Onsite freezer use to freeze soil/water mixture < -7 °C.
    - Monitor freezers with freezer blanks for contamination.
    - Maintain logs of samples present.
    - Ship samples frozen to ensure compliance with method.
    - Verify samples remain frozen upon receipt at the laboratory.

15

ENVIRONMENTAL STANDARDS

Conclusions

- Extreme and unusual site conditions preclude meeting general requirements for sample collection and preservation by Method 5035A.
- Use "best-practices" to attempt meeting method requirements and project data quality objectives.
- Seek approved modifications or understanding on Method 5035A variances from regulatory agencies.

Questions?

16

ENVIRONMENTAL STANDARDS


Contact
ENVIRONMENTAL®
STANDARDS
www.envstd.com
Environmental Standards, Inc.
"Setting the Standards for Innovative Environmental Solutions"
Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577
Virginia 1208 East Market Street | Charlottesville, VA 22902 | 434.293.4039
Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590
Texas 11200 Richmond Avenue, Suite 350 | Houston, TX 77082 | 281.752.9782
Web www.envstd.com | E-mail solutions@envstd.com
17

Maximizing the Value of Existing Monitoring Technologies: Stream Temperature and Dissolved Oxygen as Best Case Examples

Bob Rose
USEPA Office of Water

Abstract

It is proposed that maximizing the value of any given water quality monitoring technology requires uniquely addressing technology dissemination, field labor logistics, data handling, and data analysis for each unique monitoring technology. As result there is likely a significant gap between the volume, quality, cost, and use of monitoring data versus the true potential, even for current technologies. As a best case example a stream temperature monitoring pilot in 2012 demonstrated the potential for very low cost technology to create statistically robust (high certainty) baselines within three months. The pilot exemplified the value and need to correlate water quality data against climatic variables where possible. A second water quality parameter, dissolved oxygen, was explored using publicly available data. An analysis technique is proposed for dissolved oxygen in free flowing streams, which was found to provide the most statistically robust results for the data analyzed. Based on these two experiences, conceptual discussion of potential information technology solutions is provided with the goal of minimized cost and maximized value.

Maximizing the Value of Existing Monitoring Technologies:

Stream Temperature and Dissolved Oxygen as Best Case Examples

Presented to 2013 Nat. Environ. Monitoring Conference

* accompanying paper to be published in the proceedings

Prepared by Bob Rose

US EPA, Office of Water
Washington, DC

rose.bob@epa.gov; 202-564-0322

Problem Statement

"...performance of community-based environmental protection is largely unknown..." (Meyer 2005)

"...almost all of [restoration reports] are not accessible to the public..." (Palmer 2007)

"...only 10% of project records indicated any form of assessment..." (Bernhardt 2005)

"...monitoring programs are predestined to fail..." (Ralph 2003)

Solution Statement

"Funding mechanisms should be established for project outcome documentation." (Palmer 2007)

"...monitoring programs must be designed before agreeing on management benchmarks..." (Ralph 2003)

"Regime standards should describe a desirable distribution of conditions for water quality over space and time..." (Poole 2004)

"...statistical reliability, affordability, dissemination of the technology and results." (Rose 2013)

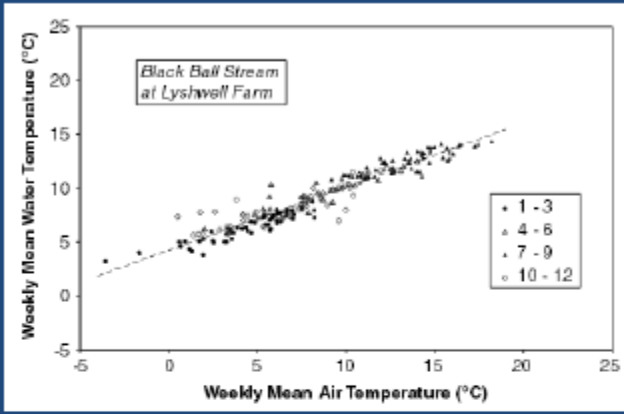
Policy Ramification (Rose 2013)



In many cases, restoration goals should be chosen based on that which we can directly monitor.

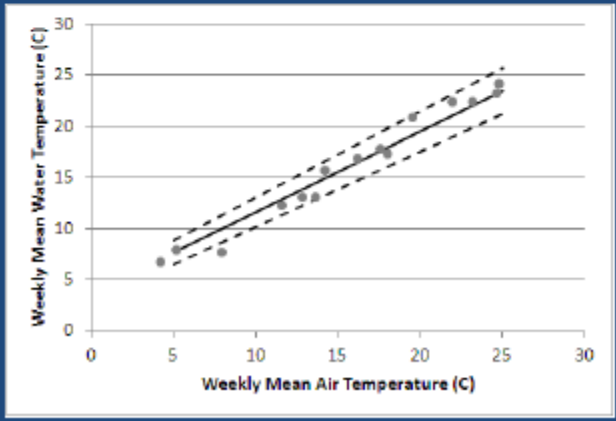
Water-Air Temperature Relationship

(Webb 2003; Pilgrim 1998; Bogan 2003)



95% certainty with just 4 months of data

(Data gathered in Fall 2012 near Washington, DC)



Advantages compared to maximum daily temperature

- Easy to quantify 95% confidence intervals
- Less sensitivity to year-to-year variability of precipitation
- Insensitive to year-to-year variability of air temperatures
- Insensitive to varied precision of sensors used
- Insensitive to random error
- Slope is insensitive to one-way bias error

Advantages (continued)

- As few as 3 months of data may be sufficient
- Depending on rainfall patterns, as many as four windows of opportunity may exist during the year
- Possible to use the same sensor at multiple sites in the same year
- The water-air temperature relationship conveys far more ecological insight (Bogan 2003; O'Driscoll 2006; Rose 2013).

Proposal: Data analysis service



- Free online service
- Purchase your own sensor or rent one
- Data is centrally stored and analyzed
- Data and results in the public domain
- Unique ID and URL for each data set
- User enters who, what, where, when…

Establishment Cost: $2M
Annual Operating: $1M

Proposal: Rental service



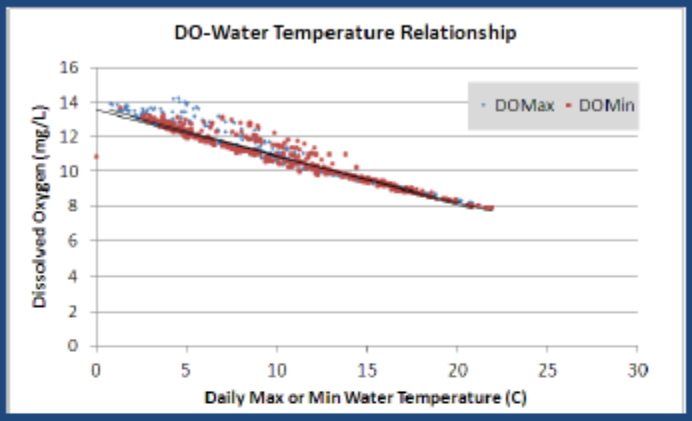
- ✓ Roughly $15.00 rental cost
- ✓ User never connects device to computer
- ✓ Device is mailed back, and data centrally downloaded.



Establishment Cost: $5M
Annual Operating: $1M
Rental Fees: At cost

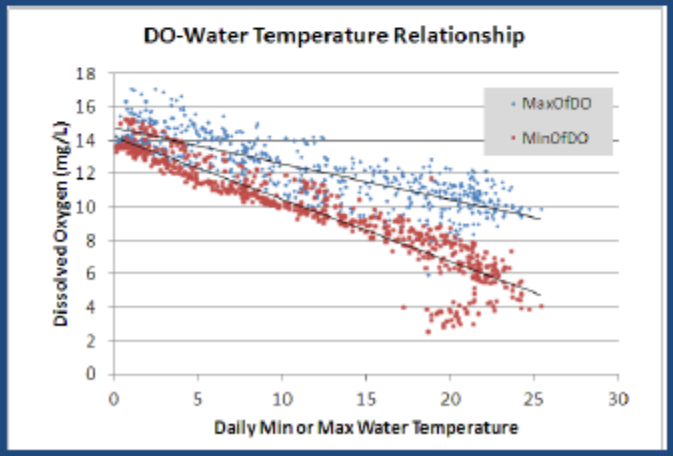
DO-Water Temperature Relationship

Moose Creek, PA (Rose 2013)



DO-Water Temperature Relationship

Crooked Creek, PA (Rose 2013)



DO-Water Temperature Relationship

- DO can have extreme variability
- No other relationships investigated had nearly the statistical reliability across a full range of 15 streams and rivers
  - 44 to 996 km2 in size
  - Very healthy to very unhealthy DO levels

DO-Water Temperature Relationship

Two components
- Daily max DO vs daily max water temperature
- Daily min DO vs daily min water temperature

Daily min and max DO are measures of photosynthesis and respiration (Wang 2003; Mulholland 2005)



The graphs constructed are are reflections of underlying causes of observed DO levels

Proposal: Rental service



✓ Roughly $400 rental cost

- Watershed associations would spend about $1,700 to purchase their own
- State agencies about $1,200
- Data regression, plotting the data, and posting in the public domain is not trivial

Data Analysis and Sensor Rental Costs

- Estimated $7M with $2M annual operating
- Or 10-year cost of $27M
  - Rental fees cover cost of sensor, mailing cost, and handling costs
- Bernhardt (2005) estimates previous 10-year restoration costs of $15B



$27M is smart investment if restoration effectiveness improves just 0.2%

Redefining Watershed Restoration and Restoration Monitoring

1. Creation of data analysis and sensor rental services,
2. Identification of other applicable water quality parameters,
3. 'Division of labor' approach to recruitment of citizens to install sensors,
4. 'Headwaters first' approach,
5. 'Restore what we can measure first' approach, and
6. Outcome-based project description.

Division of Labor Approach

- e.g., State agency and conservation groups need data the data
- National NGO promotes annual citizen monitoring campaign
- e.g., Local NGO has the skills to outreach to citizens

Example

- Local NGO outreaches to public and offers "free" sensors for select locations
- State and conservation group cover rental costs
- Outreach coincides with the national campaign

Final Conclusions

Direct monitoring of restoration progress requires uniquely addressing statistical reliability, affordability, and dissemination of the technology and results.

Each water quality parameter likely has a unique solution, if one exists.

In many cases, restoration goals should be chosen based on that which we can directly monitor.

In-Situ Simultaneous Monitoring of Water Stage and Water Quality Using Fiber Optic Sensors

Ying Huang
North Dakota State University Civil Engineering Department

Abstract

The water quality in rivers and streams is continuously altering because of unexpected changes from climate, land function, and population growths, resulting in large environmental uncertainty such as changes in soil temperature, atmospheric deposition, and even vegetation patterns. To accurately track these environmental influences and have sufficient follow-ups to prevent potential environmental hazards, an in-situ continuous water-quality monitoring system is proven to help. Traditional in-situ water-quality monitoring system collects detail water-quality related information such as temperature, specific conductance, dissolved oxygen, and pH data. These systems usually only provide periodical data collection and require complex sensor combination for overall water quality evaluation. On the other hand, advanced in-situ optical water-quality sensing systems, with unique features of compact size, high frequency, real-time and multi-parameter sensing capacity, could provide potential solutions for early warning of water-quality deterioration and science-based decision support. In this study, an optical in-situ simultaneous monitoring system for water stage, overall water quality, and the temperature is developed using long-period fiber grating (LPFG) optical fiber sensors. When part of the LPFG sensor is submerged in water, the resonant wavelength of each cladding mode of the LPFG sensor varied linearly with the submerged length (refer to water stage) and temperature, and nonlinearly with refractive index changes (referred to the water quality). Two resonant wavelengths were used to relate the water stage and overall water quality to the change in resonant wavelengths of the LPFG sensor. Sharing the same fiber line, one sequential glass packaged LPFG is used to monitor the temperature changes of the water at the same location as the other LPFG sensor. A simple algorithm for simultaneous determination of the water stage, overall water quality, and temperature was analytically formulated and experimentally validated. Benefit from the multi-parameter sensing using one single fiber line, the developed optical sensing network can potentially provide a low-cost, real-time, and high resolution solution for the in-situ water quality monitoring.

In-Situ Simultaneous Monitoring of Water Stage and Quality Using Fiber Optic Sensors

Dr. Ying Huang

Assistant Professor
Civil Engineering Dept.
North Dakota State University

NDSU NORTH DAKOTA STATE UNIVERSITY

Present at 2013 NEMC

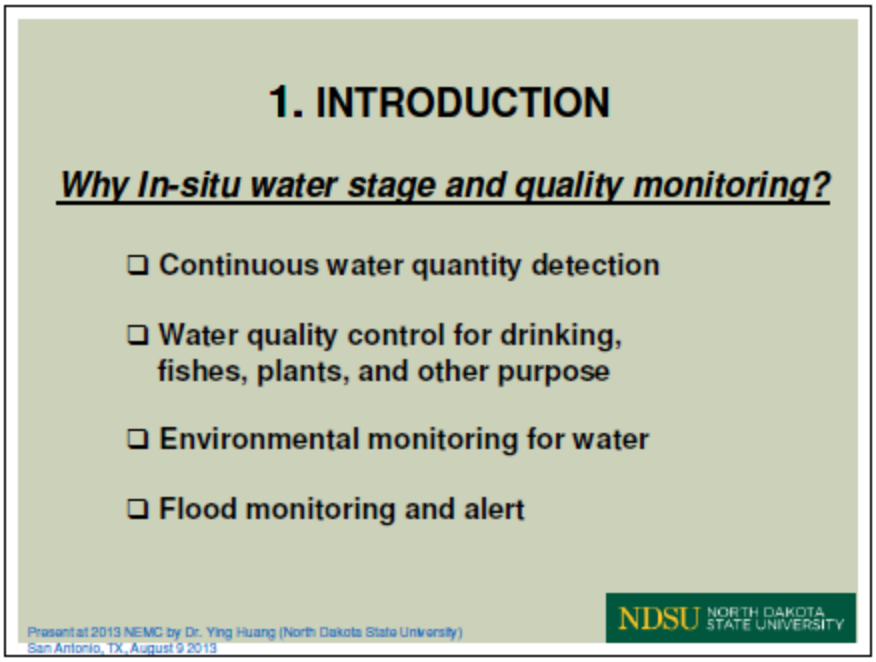
San Antonio, TX

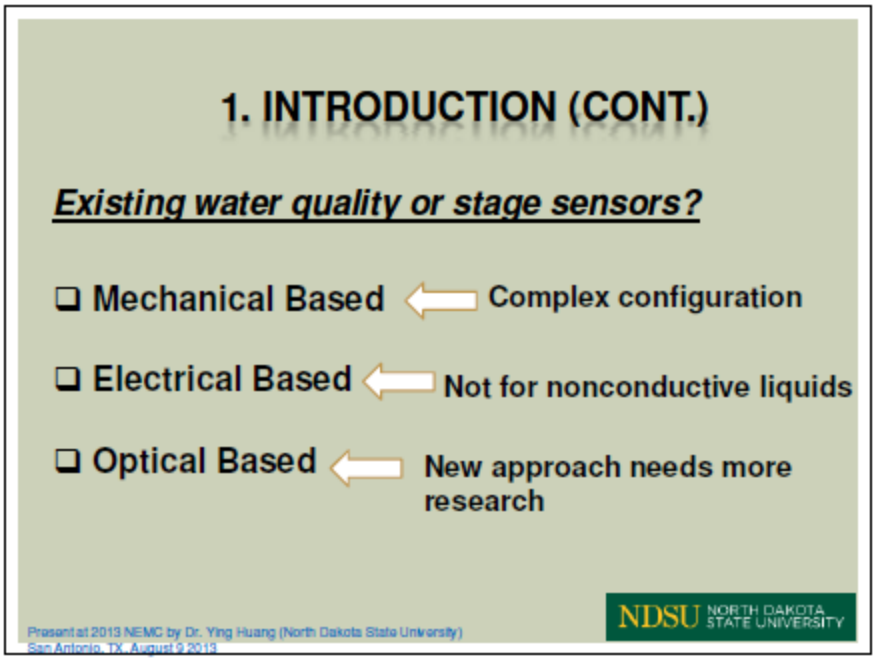
August 9 2013

Outline

1. INTRODUCTION
2. PRINCIPLES OF OPERATION
3. EXPERIMENTS AND DISCUSSION
4. IN-SUTI MEASUREMENTS
5. CONCLUSIONS AND FUTURE WORK

NDSU NORTH DAKOTA STATE UNIVERSITY


1. INTRODUCTION
Why In-situ water stage and quality monitoring?
Continuous water quantity detection
Water quality control for drinking, fishes, plants, and other purpose
Environmental monitoring for water
Flood monitoring and alert
Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013
NDSU NORTH DAKOTA STATE UNIVERSITY


1. INTRODUCTION (CONT.)
Existing water quality or stage sensors?
Mechanical Based
Complex configuration
Electrical Based
Not for nonconductive liquids
Optical Based
New approach needs more research
Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013
NDSU NORTH DAKOTA STATE UNIVERSITY

1. INTRODUCTION (CONT.)

Why optical fiber sensors?

Advantages of Optical sensors

- Compactness (small size)
- Immunity to electromagnetic interferences
- Rapid response
- Capacity for real-time monitoring

Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

NDSU NORTH DAKOTA STATE UNIVERSITY

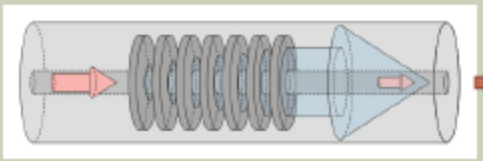
2. OPERATIONAL PRINCIPLES

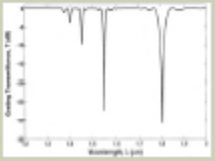
➢ **Operational principles of LPFG sensors**

- A **long-period fiber grating** couples light from a guided mode into forward propagating cladding modes where it is lost due to absorption and scattering. It is an optical fiber structure with the properties periodically varying along the fiber, such that the conditions for the interaction of several copropagating modes are satisfied. The period of such a structure is of the order of a fraction of a millimeter. The transmission spectrum has dips at the wavelengths corresponding to resonances with various cladding modes (in a single-mode fiber).

$$\lambda_{re,m} = (n_{eff,co} - n_{eff,cl,m})\Lambda$$

Eq. (1) shows that n is highly related to the environmental changes induced by surrounding refractive index





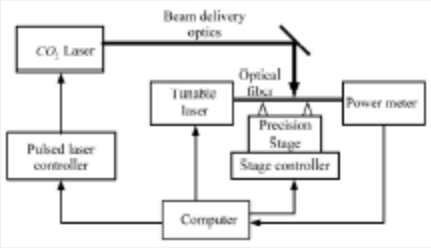
Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

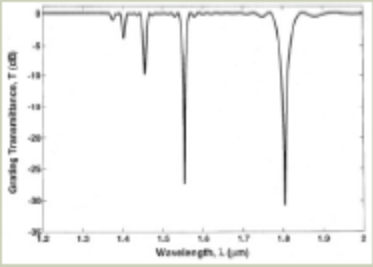
NDSU NORTH DAKOTA STATE UNIVERSITY

2. OPERATIONAL PRINCIPLES (CONT.)

➢Sensor fabrication

The first long period gratings were successfully inscribed on an optical fiber in 1996 and the modulation of a relative effective index change between the core and cladding of a LPFG sensor can be achieved by UV irradiation and CO_2 laser irradiation.





Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

NDSU NORTH DAKOTA STATE UNIVERSITY

2. OPERATIONAL PRINCIPLES (CONT.)

Long period fiber grating (LPFG), for its high sensitivity to the external RI and its durability of in-situ environment, is a good candidate for water level measurement in situ.

Khaliq et al, 2001, first apply LPFG to measure liquid Level.

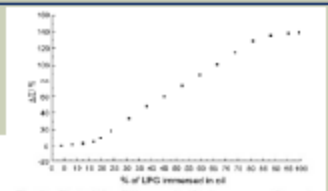


Fig. 5. Plot of the difference in the two curves shown in Fig. 4. Δλ, as a function of the percentage of the LPG im- mersed in oil.

GRICE et al, 2009, repeated the 100mm-long grating sensor for liquid level detection.

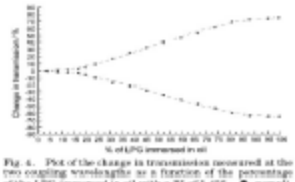


Fig. 4. Plot of the change in transmission measured at the two coupling wavelengths as a function of the percentage of the LPG immersed in oil with a RI of 1.456. ●, amplitude of the trough; ▼, amplitude of the peak. The dashed curves are theoretical plots calculated from expressions (3) and (4).

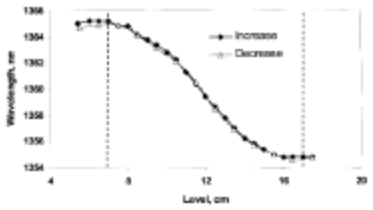


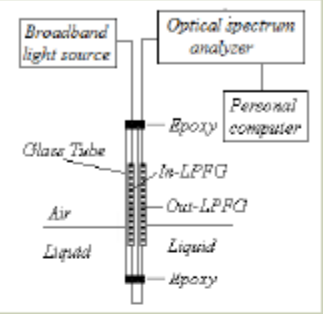
Fig. 5. Water level measurement cycle.

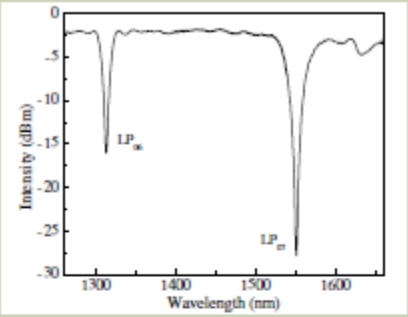
However, none multiple parameter sensing had been done yet.

Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

2. OPERATIONAL PRINCIPLES (CONT.)

- **Sensor structure**





The Out-LPFG is the major sensing component for the simultaneous measurement of liquid level and RIs. The In-LPFG is applied to compensate temperature and pressure effects on the device.

2. OPERATIONAL PRINCIPLES (CONT.)

- **Operational principles of LPFG sensors for multiple parameter sensing**

$$\lambda_{res,m} = (n_{eff,co} - n_{eff,cl,m})\Lambda \quad \text{Eq. (1)}$$

Eq. (1) can be expanded into a Taylor series at the initial surrounding refractive index (water quality: n_0) and the complete submersion of all gratings (grating length L) as follows:

$$d\lambda_{res,m} = dn_s \cdot \left.\frac{\partial \lambda_{res,m}}{\partial n_s}\right|_{n_0,L} + dL_{liquid} \cdot \left.\frac{\partial \lambda_{res,m}}{\partial L_{liquid}}\right|_{n_0,L} + dn_s dL_{liquid} \cdot \left.\frac{\partial^2 \lambda_{res,m}}{\partial n_s \partial L_{liquid}}\right|_{n_0,L}$$

$$K_{n_s,m} = -\gamma_m \cdot \frac{\mu_m^2 \lambda_{res,m}^3 n_s}{8\pi r_{cl}^3 n_{cl} \Delta n_{eff} \left(n_{cl}^2 - n_s^2\right)^{\frac{3}{2}}}$$

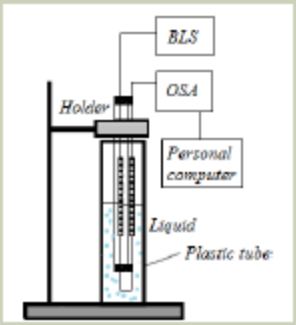
$$\frac{\partial^2 \lambda_{res,m}}{\partial n_s \partial L_{liquid}} = \frac{\partial\left(\frac{\partial \lambda_{res,m}}{\partial L_{liquid}}\right)}{\partial n_s} = \lambda_{res,m}\left(K_{n_s,m} K_{L_{liquid,m}} + \frac{\partial K_{L_{liquid,m}}}{\partial n_s}\right)$$

$$K_{L_{liquid,m}} = 0.2\frac{\lambda_{SWEEM,m}}{\lambda_{res,m}}\left(\Delta n_{eff,m,liquid} - \Delta n_{eff,m,air}\right)$$

NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION

➢Experimental setup



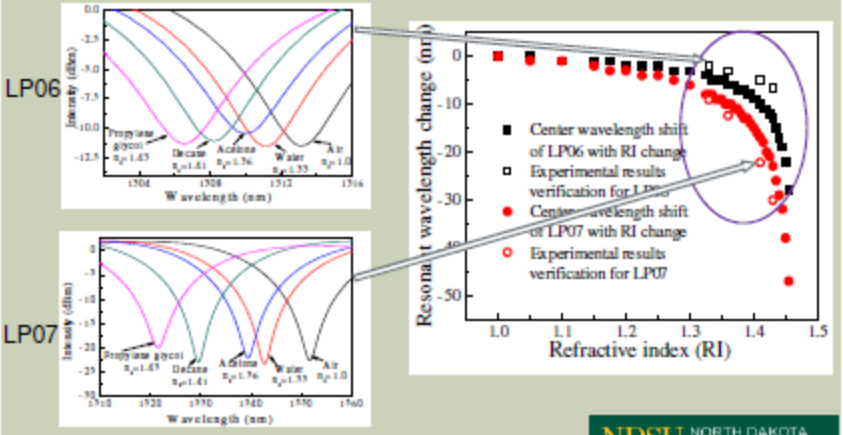


Simulated In-situ condition is used for sensor development

NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

➢Experimental results for water quality (RI) sensing

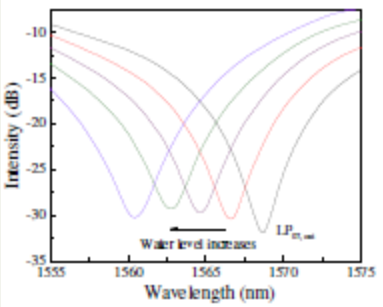


Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

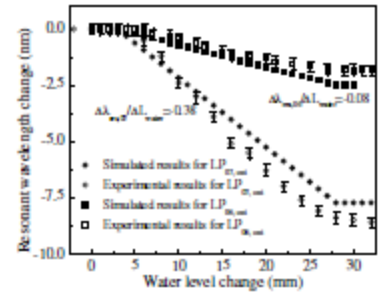
NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

➢Experimental results for water stage sensing



Transmission spectrum change with water level

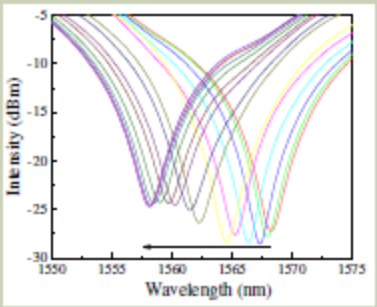


Experimental and simulated results

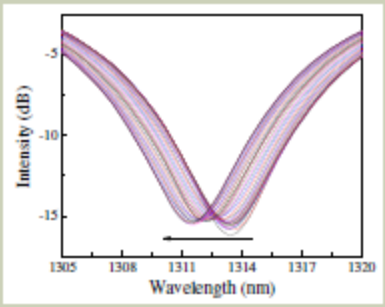
NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

➢Experimental results for cross sensitivity



LP07



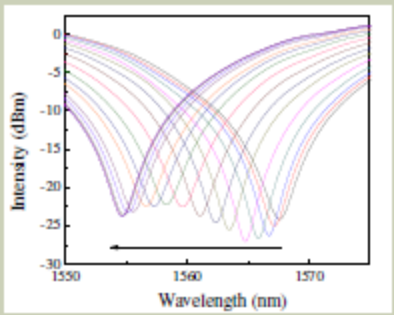
LP06

In 10% sugar solvent

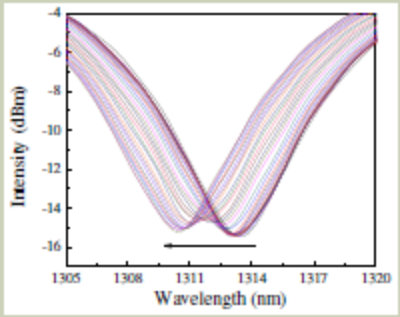
NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

➢Experimental results for cross sensitivity



LP07



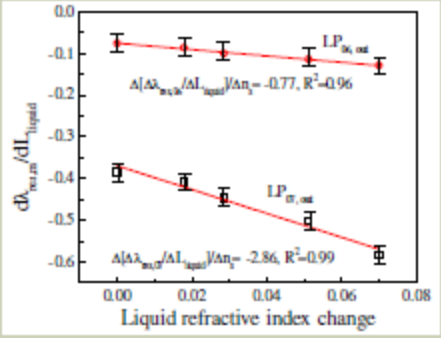
LP06

In 40% sugar solvent

NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

➢Experimental results for cross sensitivity

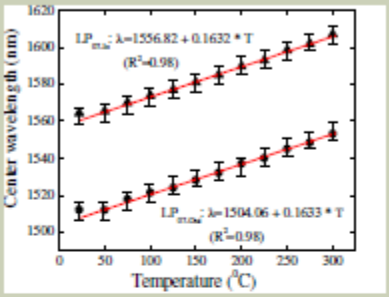


Cross sensitivity of $LP_{07, out}$ and $LP_{06, out}$ of the Out-LPFG sensor

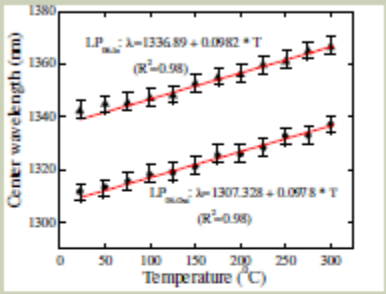
NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

- Environmental effects (temperature)



Temperature sensitivity for LP_{07}

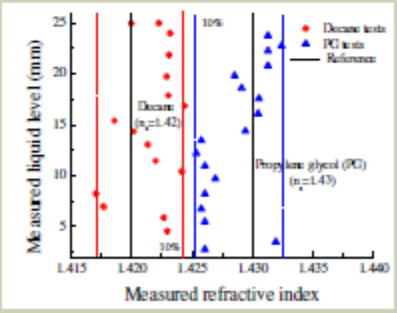


Temperature sensitivity for LP_{06}

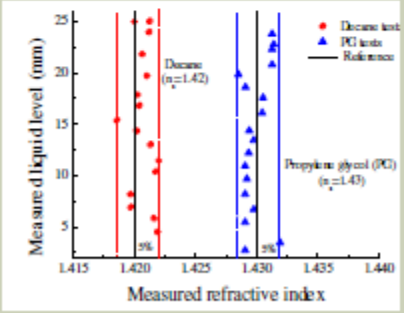
NDSU NORTH DAKOTA STATE UNIVERSITY

3. EXPERIMENTS AND DISCUSSION (CONT.)

- Experimental results for simultaneous water stage and quality sensing



Test results with Out-LPFG only



Test results with In-LPFG and Out-LPFG

Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

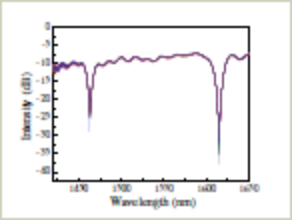
NDSU NORTH DAKOTA STATE UNIVERSITY

4. IN-SITU MEASUREMENTS



On-going: In-situ Measurement of simultaneous water quality and water level at red river, Fargo, ND





Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

NDSU NORTH DAKOTA STATE UNIVERSITY

5. CONCLUSIONS AND FUTURE WORK

- Developed an optical fiber sensor based on LPFG for simultaneous water stage (in mm) and quality (RI in 0.005) monitoring using wavelength change in real time with an accuracy higher than 5%
- Environmental effects such as temperature can be eliminated through the In-LPFG for a more accurate in-situ sensing
- Validated the sensor device through series of lab tests
- The sensor will be continuously monitor to the red river for real-time In-situ water stage and quality monitoring
- Quantify the relation between water refractive index change to its quality (PH, Conductivity, and others)

Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013

NDSU NORTH DAKOTA STATE UNIVERSITY


Thank you!
QUESTION?
?
Present at 2013 NEMC by Dr. Ying Huang (North Dakota State University)
San Antonio, TX, August 9 2013
NDSU NORTH DAKOTA STATE UNIVERSITY

Accelerated Remediation at a Region 1 Residential Clean-up Site Using PHILIS On-site Analytical Laboratories

Lawrence Kaelin, Erica Canzler, and Michael Nalipinski, USEPA Region 1 OSC
Julie Capri and Alex Bleich, CSC-Dynamac Corp

Abstract

In the spring of 2011, heavy rains flooded Stevens Brook, in St. Albans, VT. Residents at the Colony Square Apartments in St. Albans noticed coal tar waste in a sump in their basement. Residential properties north of the Colony Square Apartment were a former EPA removal site where more than 4,000 tons of PAH-contaminated soils were excavated and disposed of off-site in 2005. The City of St. Albans municipal employees noticed coal tar wastes in several area manholes, while residents in the area noted an oily odor causing the Vermont Department of Environmental Conservation (VT DEC) to temporarily stabilize the situation. After Hurricane Irene and associated heavy rains exacerbated the situation in the fall of 2011, VT DEC requested assistance from Region 1 EPA to determine whether coal tar waste contamination exists at the Colony Square apartments and on residential properties abutting Stevens Brook.

On May 7th, 2012 the Region 1 conducted surface and subsurface soil, sump water, sediment, soil gas, and indoor air sampling of select residential properties along Stevens Brook to determine the extent of coal tar waste contamination. Rapid, on site analytical results were provided by the EPA's Office of Emergency Management's CBRN Consequence Management and Advisory Team (CMAT) using their mobile laboratory assets called PHILIS. PHILIS, which stands for Portable High-throughput Integrated Laboratory Identification System, is a mobile laboratory platform accredited through the NELAC program and holds membership in EPA's Environmental Response Laboratory Network (ERLN). The contaminants of concern included benzene, naphthalene and SVOCs, particularly PAHs. In the course of approximately 4 days, over 250 samples were collected and analyzed on-site for contamination. The PHILIS provided same-day confirmatory data, allowing the OSC to make on-site decision without the need for a secondary confirmation via outside fixed lab. Region 1 OSC Mike Nalipinski was able to confer with the VT DEC representatives on a daily basis using the most recent PAH analytical data which was summarized and depicted on site maps allowing for better interpretation and clearer presentations. The OSC prepared a Time Critical Removal Action Memo (RAM) recommending soil excavation at the Colony Apartments and the installation of a system to mitigate in-door air contamination posed by the coal tar wastes. The PHILIS on-site analysis helped Region 1OSC Mike Nalipinski to:

- Direct on-going soil coring activities – maximize usage of contractor on-site assets
- Capture the boundaries of the vertical and horizontal extent of soil contamination in a single mobilization
- Determine the source and extent of the in-door air contamination in the apartment complex
- Provide rapid, on-site confirmatory data for daily decisions, briefings to local authorities (VT DEC)
- Reduce number and longevity of site visits normally required to support a Time Critical RAM
- Direct excavation activities based on data from a single site mobilization – "one and done" concept

The on-site abilities provided by PHILIS allowed the OSC to complete all the site soil assessments, excavation, removal and site restoration activities within 90 days of the initial site visit. Estimations of actual analytical cost/sample from the St. Albans site effort were determined to be below most commercial lab costs, ranging from $250-325/sample which included fuel, mob/demob costs, travel, pre deim, sample analysis, QA review and report writing. The greatest time and cost savings are to the OSC by allowing the most effective use of their site assets in an accelerated time frame. The mobilization to the Region 1's St. Albans site has provided CMAT with

useful experience and “lessons learned” which will be used to further reduce costs for future PHILIS mobilizations. This on-site analytical support via PHILIS can be provided to regional OSCs across the country.

Accelerated Remediation at a Region 1 Residential Clean-up Site Using PHILIS On-site Analytical Laboratories

U.S. Environmental Protection Agency
Lawrence Kaelin & Erica Canzler, OEM/CBRN-CMAT, Michael Nalipinski, Region 1 OSC,
and
Julia Capri & Alex Bleich, CSC-Dynamac Corp.

NEMC Conference, 2013

St. Albans Site History

Spring 2011, heavy rains flooded Stevens Brook

- Residents in nearby apartments noticed odors and coal tar wastes in basement sumps
- Workers found coal tar wastes in area manholes
- VT DEC temporarily stabilized the situation by pumping out basements and ventilating buildings



2

Site History

The property was near the former St. Albans Gas & Light Company, where 4,000 tons of PAH-contaminated soils were excavated and disposed of off-site in 2005.





Site Conditions

- After Hurricane Irene in the Fall of 2011, additional complaints of tar and oil like odors came from the apartment residents
- Contamination was suspected in soil, sump water, and brook sediment
- VT DEC requested assistance from Region 1 EPA to determine whether coal tar waste contamination exists on residential properties abutting Stevens Brook

Accelerated Remediation at a Region 1 Residential Clean-up Site Using PHILIS On-site Analytical Laboratories

U.S. Environmental Protection Agency
Lawrence Kaelin & Erica Canzler, OEM/CBRN-CMAT, Michael Nalipinski, Region 1 OSC,
and
Julia Capri & Alex Bleich, CSC-Dynamac Corp.

NEMC Conference, 2013

St. Albans Site History

Spring 2011, heavy rains flooded Stevens Brook

- Residents in nearby apartments noticed odors and coal tar wastes in basement sumps
- Workers found coal tar wastes in area manholes
- VT DEC temporarily stabilized the situation by pumping out basements and ventilating buildings



2

Region 1 Response

- Region 1 provided support to the VT DEC, responding as a Time Critical Removal under CERCLA authority
- Mike Nalipinski was assigned OSC for the St. Albans Gas & Light Site – Phase 2
- An Accelerated Remediation Clean-up Concept was proposed to minimize community impact
- Region 1 requested the use of OEM/CMAT's PHILIS mobile labs to provide on-site analysis of soil, water, soil gas and air samples

Accelerated Remediation Concept

- On-site sampling and analysis activities maximize the utilization of EPA response assets to reduce time and costs for effective site assessment and clean-up actions
- Rapid on-site laboratory results that meet all 2009 TNI requirements for accredited parameters from the PHILIS mobile labs will achieve accelerated clean-up objectives

Accelerated Remediation Goals

St. Albans Gas & Light – Phase 2

- Maximize site resources to reduce time to remediation
- Direct on-going soil coring activities using rapid analytical results to maximize usage of contractor and on-site assets
- Capture the boundaries of the vertical and horizontal extent of soil contamination in a single mobilization
- Determine the source and extent of the in-door air contamination in the apartment complex
- Provide rapid, on-site NELAC accredited, confirmatory data for daily decisions, briefings to local authorities (VT DEC)
- Reduce number and longevity of site visits normally required to support a Time Critical RAM
- Direct excavation activities based on data from a single site mobilization – "one and done" concept

Mobilization and Site Work

- On May 7th, 2012 START contractors and PHILIS mobile labs were deployed to conduct sampling and analysis to determine the extent of coal tar waste contamination
- Contaminants of concern included benzene, naphthalene and SVOCs, particularly PAHs and benzo(a)pyrene
- In the course of 4 days, over 250 samples were collected and analyzed on-site for PAH, benzene or naphthalene contamination

Region 1 START Sampling Effort



Sampling water from sump and ambient air in basements

Soil-gas samples in Tedlar bags via Geoprobe

Soil cores at surface and at depth via Geoprobe







Daily Briefing and Data Depiction

- Region 1 OSC Mike Nalipinski conferred with the VT DEC representatives on a daily basis using analytical data presented in GIS site maps
- OSC used on-site data to direct daily site work



Daily briefing with VT DEC.



Daily posting of soil data on GIS site map

OEM Support to Region 1

PHILIS Mobile Laboratory Assets

- PHILIS units are the EPA's mobile laboratory assets under the Environmental Response Laboratory Network (ERLN)
- Mission Chemical Warfare Agents (CWA) and Toxic Industrial Chemicals (TIC) in environmental samples
- They are stationed in Edison, NJ and Castle Rock, CO and can be deployed within 24 to 48 hours to support emergency response and clean-up actions



PHILIS Capabilities

- Deployable within 6 hours of notification/operational within 6 hours of being on-site
- Operate via internal generators/supplies for 4 days before restocking/refueling required
- TNI accredited for VOCs, SVOCs and PCBs in water and soil using EPA Methods 8260c/8270d/8082a. Mobile lab confirmatory analysis meets 2009 TNI requirements
- Pursuing accreditation for TO air methods and LC/MS/MS methodology for carbamates and pharmaceutical compounds
- Estimate 100-200 samples/day for CWAs and TICs (24hr operations) for all matrices
- Analysis of environmental samples for CWAs via ERLN's Ultra-dilute agent (UDA) program. Detection limits to health-based clearance via EPA's SAM methods

PHILIS Labs at St. Albans Site



APL01 – Volatiles Mobile Lab for EPA method 8260 for soil, sediment and water samples via purge & trap.

Modified TO method for benzene and naphthalene in air and soil gas via automated thermal desorption unit



Purge & Trap for soils & waters



Tedlar bag analysis – soil gas



Tenax tube analysis - air

PHILIS Labs at St. Albans Site



APL02 – semi-volatiles lab, & sample prep trailer, set up for EPA prep methods 3535A and 3545A

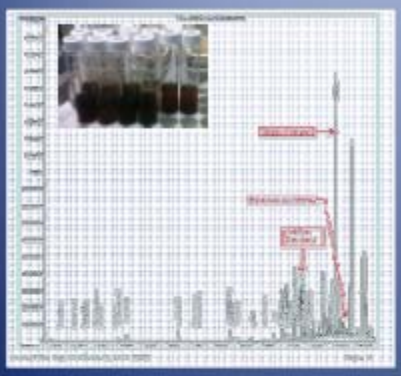
APL02 with GC/MS instruments set up for method 8270D.

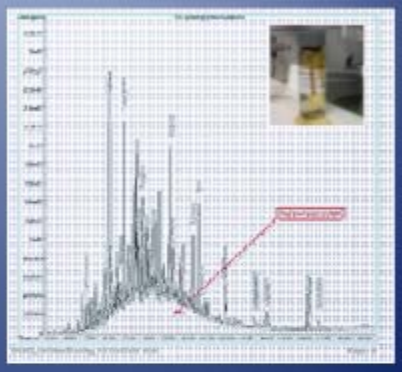


SPA01 Trailer w/automated PSE & SPE Apparatus.



Analysis of Samples





Region 1 Removal Action

- Using the rapid site sampling and analysis capability brought to bear at the St. Albans Gas & Light Site – Phase 2, the OSC was able to prepare a Time Critical Removal Action Memo (RAM) recommending soil excavation at the Colony Apartments and the installation of a system to mitigate in-door air contamination posed by the coal tar wastes

In-door air basement mitigation system



Excavations Begins

- On-site sampling and analysis defined the spatial and subsurface extent of contamination



Excavation starts at the Colony Square Apts



Common borrow Place at corner of Maple & Lasalle



Soil cores are "logged", screened and Sampled at discrete depths

Goals of Accelerated remediation Concept were Meet

- In the course of approximately 4 days, over 250 samples were collected and analyzed on-site for PAHs, benzene or naphthalene contamination in air, soil and water matrices
- Expedited RAM was issued was issued
- Accelerated remediation completed using initial data set – no new samples required
- The on-site abilities provided by PHILIS allowed the OSC to complete all the site soil assessments, excavation, removal and site restoration activities within 90 days of the initial site visit

Colony Apts Remediated

- The accelerated remediation plan for the Colony Apts accomplished on-site sampling and analysis data from a single site visit
- Top 2 feet of soil removed from specific zones identified by PHILIS on-site analysis and sent for disposal. Backfill with clean top soil
- The possibly of runoff to Steven Brooks was reduced by the rip-rap and other soil retention measures
- Official demobilization on October 2012



Colony Square Apts, September 2012 after backfill and hydro-seeding



Stevens Brook- runoff and soil retention measures, rip rap, & geo-fabric

Costs/Benefits

- Estimations of actual PHILIS analytical cost/sample from the St. Albans site effort were determined to be below most commercial lab costs, ranging from $250-325/sample which included fuel, mob/demob costs, travel, pre diem, sample analysis, QA review and report writing
- Man-hours for St Albans site were covered under the PHILIS contract. Future mobilizations may not
- Cost sharing options can be explored for future sites.
- PHILIS costs should drop ~ $50-100/sample based on "lessons learned" and optimization of assets
- The greater time and cost savings were realized for the OSC by having the most effective use of their site assets in an accelerated time frame

Future Work

- The mobilization to the Region 1's St. Albans site has provided CMAT with useful experience and "lessons learned" which will be used to further reduce costs for future Accelerated Remediation efforts and PHILIS mobilizations
- The Accelerated Remediation Concept and on-site analytical support via PHILIS or other mobile assets can be provided to EPA regional OSCs across the country
- PHILIS is an OEM national asset for the use of EPA regional and programmatic response efforts

Questions

- Mike Nalipinski, Region 1 OSC
- The CMAT POCs for the PHILIS program are: Larry Kaelin (kaelin.lawrence@epa.gov) and Terry Smith (smith.terry@epa.gov).
- OEM/CBRN-CMAT Director
  Erica Canzler(canzler.erica@epa.gov)

Comparison of Field Operations Guidelines with NEFAP

Marlene Moore
Advanced Systems, Inc.

Abstract

The U.S. EPA Field Operations Group (FOG) Guidelines provides the elements recommended for field operations in order to ensure data of known and document quality. The National Environmental Accreditation Program (NEFAP) standard for field sampling and measurements organization (FSMO) presents requirements to demonstrate the technical competence of these organizations.

The FOG guidelines and TNI FSMO standard have similar information. This presentation will compare the two documents in order for field operations to see how accreditation to the TNI standard provides data of known and document quality and meets the U.S. EPA FOG Guidelines.

COMPARISON OF FIELD OPERATIONS GUIDELINES WITH NEFAP

Presented by:
Marlene Moore
Advanced Systems, Inc.
mmoore@advancedsys.com

Objectives

- Present Elements of the U.S. EPA Guidelines for Field Operations (FOG)
- Present the National Environmental Field Activities Accreditation Program (NELAP)
- How to ensure data of known and documented quality
- How to demonstrate technical competence for field sampling and field measurements
- Demonstrate how accreditation to the The NELAC Institute's (TNI) Field Activity Standard provides data of known and documented quality from a technically competent organization that meets the U.S. EPA FOG elements.

Advanced Systems, Inc. Slide 3

FOG

- EPA RS&T Organization
  - National consistency for field activities
- Scope
  - Quality management system
  - Sampling
  - Non-sampling field activities
  - Each region defines scope of organizations
  - Voluntary

NEFAP

- TNI Standard (Volume 1)
  - Consensus
  - All stakeholders input
- Scope
  - All organizations involved in sampling and field measurements (FSMO)
  - Management system
    - Quality
    - Administrative
    - Technical operations
  - Voluntary

Advanced Systems, Inc. Slide 4

FOG

- Personnel
  - Qualifications
  - Education
  - Training
    - Up to date
    - Internal/external
  - Experience
  - Knowledge
  - Health & safety
  - Inspector training
  - Records
    - Retention schedule

NEFAP

- Personnel (5.2)
  - Management responsible for ensuring
    - Qualifications, education, training, experience, skills, knowledge
    - Demonstration of performance
  - Sufficient
  - Records
  - Job descriptions
  - Records
    - *relevant authorization(s), competence, educational and professional qualifications, training, skills and experience of all technical personnel*
    - *Contracted and employees*

Advanced Systems, Inc. Slide 5

FOG	NEFAP

• Document Control
  • Internal, generally
  • System for management
  • Procedure(s) for
  • Reviewed and approved
  • Unique identifier
  • Periodic review
  • Suitability
  • Superseded documents
  • Revision approval
  • Identify revised text
  • Training on new documents
	• Document Control (4.3)
	  • Internal and external
	  • Procedure
	  • Authorized editions available
	  • Periodically reviewed
	  • Remove obsolete documents
	  • Identify as retained for legal or knowledge
	  • Uniquely identified
	  • Changes made to documents
	  • Hand (paper copies)
	  • Electronic systems

Advanced Systems, Inc. Slide 6

FOG	NEFAP

• Records Management
  • Retention schedule
  • Evidence of actions taken and observation made
  • Procedures
	• Control of Records (4.13)
	  • *Procedures for*
	  • *identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records*
	  • *Quality records defined*
	  • *Transfer of client records and maintenance*
	  • *Held secure and in confidence*

Advanced Systems, Inc. Slide 7

FOG

- Procedure for records
  - Legible, storage, retrievable
  - Secure and confidential
  - Permanently recorded
    - Observations, calculations,
    - Measurement entries
  - Identify personnel
  - Traceable to project
  - Electronic: Backup process and security
  - Manual: pencil entries if needed due to weather
  - Error correction process

NEFAP

- Control of Records (4.13)
  - Electronic records
    - Backup, integrity, security, retrieval
  - Technical records
    - Original observations
    - Changes to records
    - Audit trail
    - Personnel identified
    - Handling errors or changes to records defined

Advanced Systems, Inc. Slide 8

FOG

- Evidence Management
  - Support federal criteria
    - Civil or criminal
  - Defines evidence
  - Procedures for
    - Identification
    - Transportation
    - Handling
    - Protection
    - Storage
    - Retention
    - Custody – defined
    - Electronic systems

NEFAP

- Not specifically stated
  - Sample handling 5.8
  - Sample collection 5.7
  - Records management 4.13
    - Legal and regulatory requirements
  - Documents stored
    - Legal or knowledge

Advanced Systems, Inc. Slide 9

FOG

- Field Documentation
  - Procedures
    - Facts and objective observations
    - Video and photographs
    - Specifics to be included with field documentation listed
      - Project/facility name, location
      - Leader, team members
      - Dates
    - Logbooks use
      - Manual
      - Electronic

NEFAP

- Field Sampling (5.7)
- Plan and procedure required
  - Available at location
  - Deviations, additions and exclusions documented
  - Sampling and test data must be recorded

Advanced Systems, Inc. Slide 10

FOG

- Date/time measurement sample collection
- Location and/or GPS coordinates
- Measurement/sample identification
- Measurement/sample collection method
- Measurement/sample collection equipment
- Calibration Initial, continuing
- Measurement values
- Sample containers
- Sample preservation
- Physical description
- Maps/sketches
- Conditions
- Photograph Log

NEFAP

- Sampler
- Environmental conditions
- Equipment
- Diagrams, map
- location
- Statistical sampling procedures
- Methods
- Date and time
- Testing (4.13)
- Sample handling 5.8

Advanced Systems, Inc. Slide 11

FOG

- Field Equipment
  - Presented for measurement – does not address other equipment
  - Procedures
    - Unique identification, labeling
    - Follow mfg operation
    - Calibrated
    - Current instructions
    - Listing of records
    - Handling out of spec equipment, maintenance
    - Reagents, materials

NEFAP

- Equipment (5.5)
  - Furnished all equipment, software
  - Procedures – handling, transport, storage, use and planning maintenance
  - Calibration, checks
  - Authorized personnel
  - Records maintained
  - Maintenance documented
  - Safeguard hardware and software from adjustments

Advanced Systems, Inc. Slide 12

FOG

- Field Inspection and Investigations
  - Procedures
    - Must be followed
    - Available
    - Accurate
    - Accessible

NEFAP

- Not specifically stated
  - Not an inspection or investigation standard

Advanced Systems, Inc. Slide 13

FOG

- Reports
  - Procedure for preparing reports
  - Included:
    - Title
    - Preparing Organization Customer name
    - Results
      - Sample
      - Measurement
      - Inspection
    - Details of conditions

NEFAP

- Report (5.10)
  - Accurate, objective, unambiguous, clear
  - Sampling conditions, procedure
  - Deviations, additions or exclusions from test method
  - Test certificate
  - Report amendments
  - Specific details listed and reported based on client request

Advanced Systems, Inc. Slide 14

FOG

- Internal Audits
  - Periodic
  - Verify operations comply with FOG
  - Independent of function
  - Qualified
  - Roles/responsibilities
    - Planning
    - Implementing
    - Reporting
  - Report
    - What was audited
    - Results of audit
    - Findings

NEFAP

- Internal audits (4.10)
  - Every year
  - Verify operations comply with TNI standard
  - All elements of management system
  - Quality manager
    - Qualified, planned, implemented, reported to personnel involved
  - Findings reported
  - Corrective actions
  - Follow-up audit
    - Verify implementation
    - Effectiveness of corrective action

Advanced Systems, Inc. Slide 15

FOG

- Corrective Action
  - From internal audit
  - Procedure
    - Investigate
    - Determine root cause
    - CA based on risk and magnitude
    - Document and implement results

NEFAP

- Corrective Action (4.11)
  - Internal audit
  - Nonconforming work
  - Complaints
  - Departures from policies and procedures
  - Additional audits if necessary
- Procedure
  - Investigate problem
  - Root cause
  - Identify corrective action
  - Implement
  - Monitor
  - Evaluate effectiveness

Advanced Systems, Inc. Slide 16

FOG

- Not Presented

NEFAP

- NEFAP
  - Organization (4.1)
  - Management system (4.2)
  - Review requests (4.4)
  - Subcontracting (4.5)
  - Purchasing (4.6)
  - Service to client (4.7)
  - Complaints (4.8)
  - Control of nonconforming work (4.9)
  - Improvement (4.10)
  - Preventive action (4.12)
  - Management reviews (4.15)

Advanced Systems, Inc. Slide 17

FOG

- Not Presented

NEFAP

- NEFAP
  - Methods and Method Validation (5.4)
  - Measurement Traceability (5.6)
  - Assuring the quality of the Results(5.9)

Advanced Systems, Inc. Slide 18

Demonstrate how accreditation to the TNI's Field Activity Standard provides data of known and documented quality from a technically competent organization that meets the U.S. EPA FOG elements.

Thank you



SECTION 5

HISTORY OF ENVIRONMENTAL MONITORING

Pre- and Early EPA Monitoring

Lawrence H. Keith
Private Consultant

Abstract

After Rachael Carson's "Silent Spring" book was published in 1962, environmental chemists began to analyze for pesticides. However, thousands of other organic chemicals from industrial sources were not able to be identified or their quantities measured. Pioneering chemists in a few labs around the world began to try to analyze for some of these unknown chemicals in rivers and industrial effluents using, for example, large columns of activated carbon extracted with chloroform and then analyzing the extracts with GC, IR, NMR, and MS. Attention on organic chemicals in drinking water first became of significant interest when chloroform was found in it everywhere in the world and the mystery of its source was finally solved. Then, when over a hundred organic chemicals were identified by GC-MS in New Orleans drinking water in 1974 and 1975, a series of national monitoring studies were initiated. These resulted in a search for a GC-MS instrument that could be used throughout the EPA. However, the defining watershed for environmental monitoring occurred in 1976 when EPA lost a suit and was required to analyze for a list of “Priority Pollutants” in industrial water sources even though there were no methods for sampling, storing, or analyzing them. The presentation concludes with a summary of how these problems (which were apparently not significant to non-chemists) were solved.

Pre- and Early EPA Monitoring

Lawrence H. Keith

National Environmental Monitoring Conference

San Antonio, TX
August 5, 2013

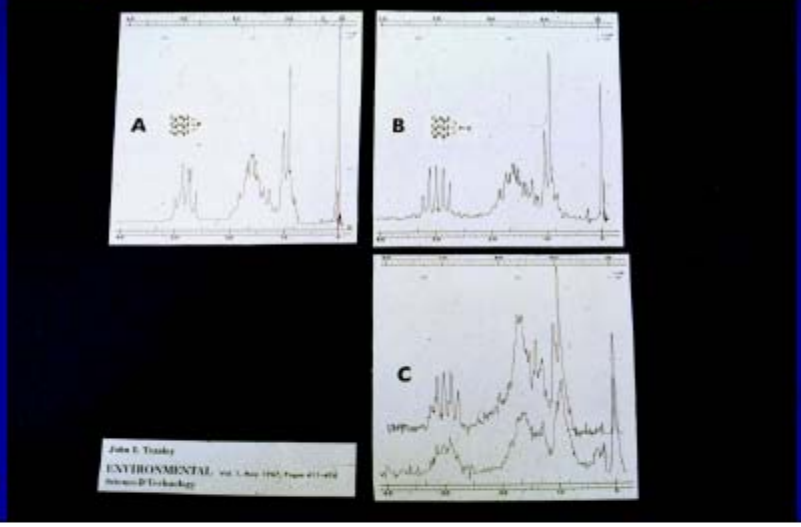
1

Pre-EPA Monitoring

- Most monitoring consisted of analyzing for inorganics (Pb, Cr, As, nitrates, nitrites, phosphates, etc) plus turbidity, pH, etc.
- Organics monitoring involved COD, BOD, etc. plus sometimes pesticides.
- Individual organic compounds monitoring evolved from solving mysteries:
  - Fish kills, taste & odor problems, etc.
  - Each mystery often took days, weeks, or months to solve. Some examples follow.

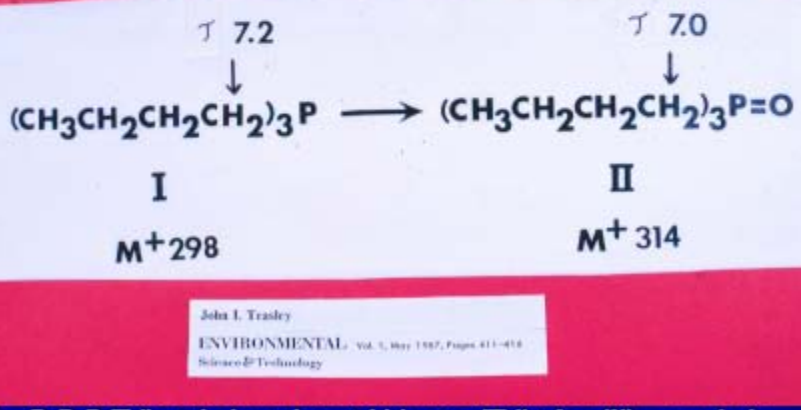
2

60 MHz NMR Spectra from Fish Kill Mystery in Charleston, SC - Teasley



3

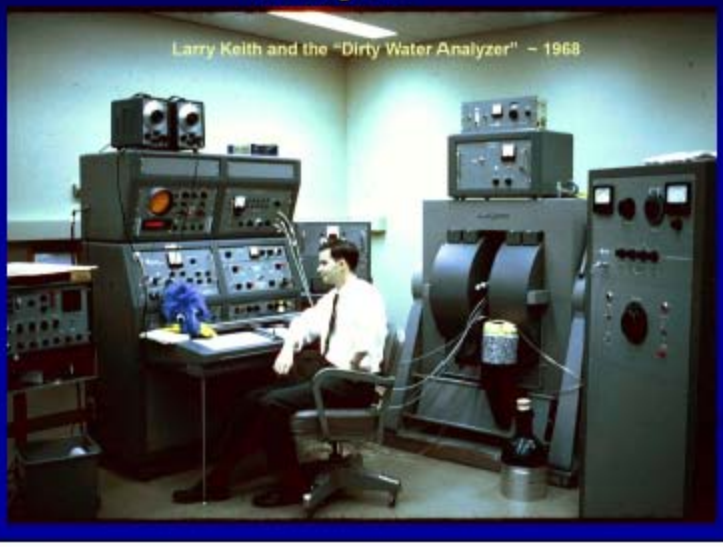
Charleston Harbor Mystery Solved



- S,S,S-Tributyl phosphorotrithioate (Tribufos (II) – made in MO) caused a big fish kill when it was oxidized in the harbor from S,S,S-Tributylphosphorotrithioite (Merphos (I))

4

100 MHz NMR Used for Pesticide Analysis



5

Mary Walker – EPA's 1st Mass Spectrometerist



- JEOL Single Focus Magnetic MS (with doorbell)

6

Downriver Paper Mill Pollution



Carbon Chloroform Extracts (CCE)

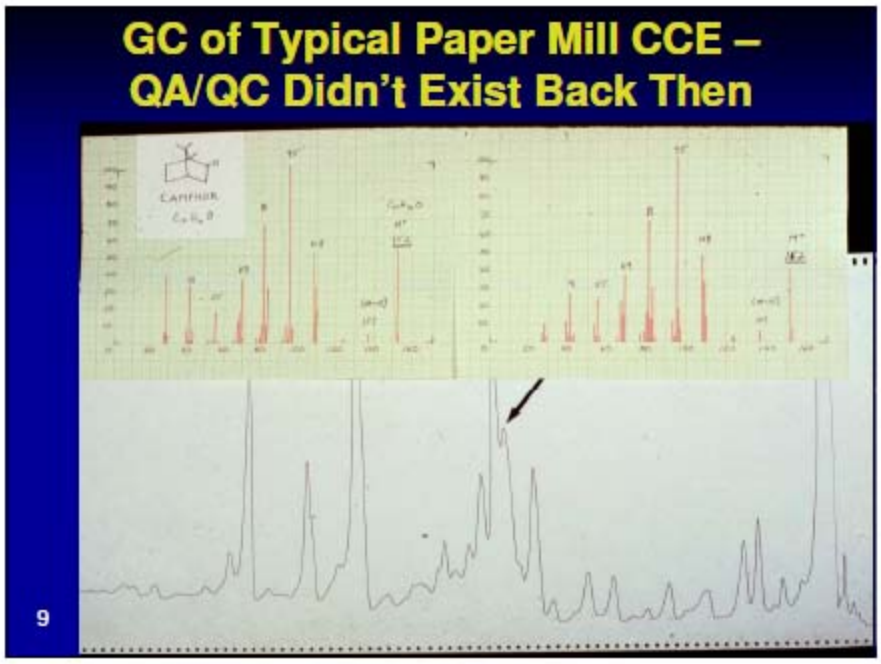


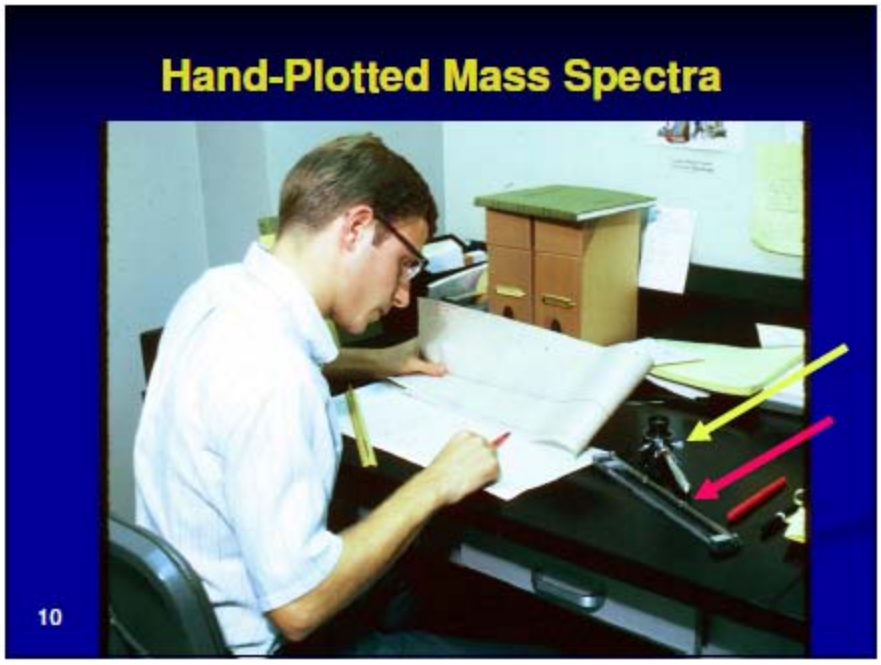




CCEs with activated carbon were used to collect water samples in the '60s

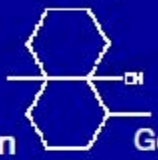
8


GC of Typical Paper Mill CCE –
QA/QC Didn't Exist Back Then
9


Hand-Plotted Mass Spectra
10

"Celinol" Structure Mystery

- Musty smelling compound in drinking water of Celina, OH
  - Separated and isolated it from a GC column
  - IR spectrum indicated "OH" (alcohol) group
  - Comparison with authentic sample of Geosmin showed very different results – NOT Geosmin

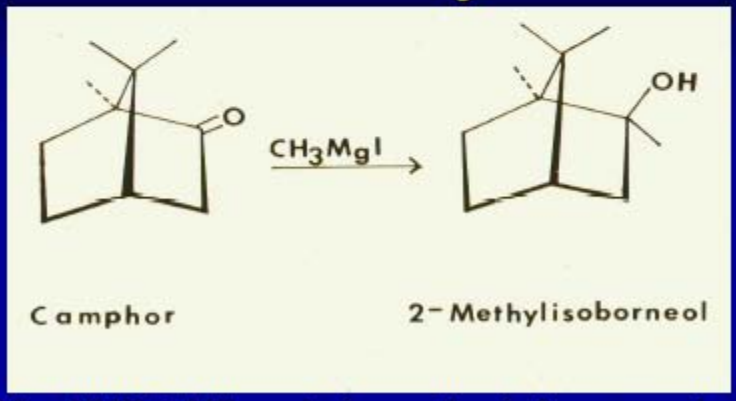


Geosmin

  - Aaron Rosen sent a sample of "Celinol" to Athens, GA lab for NMR and MS analysis

11

"Celinol" was 2-Methylisoborneol



After NMR & MS analysis, synthesis from camphor proved the structure of 2-methylisoborneol

"Classic" Chemistry

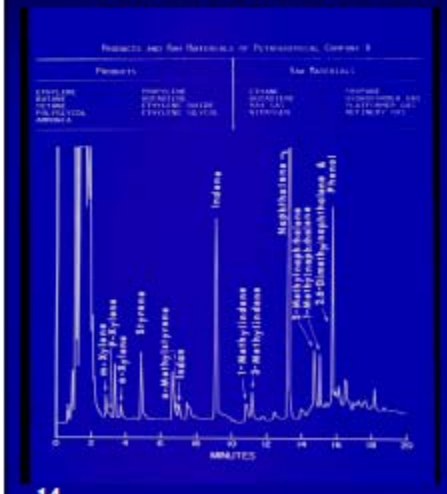
12

Early EPA

- President Nixon created EPA in Dec. 1970
- Brought together scattered environmental labs, regulatory offices, etc. in one agency
- Early focus in water centered on drinking water problems – often taste and odor
- GC-MS was recognized as a very useful combination for organic analysis
- Athens, GA lab also continued to pursue analysis of water pollutants from industrial sources – Southeast Environmental Research Lab (SERL)

13

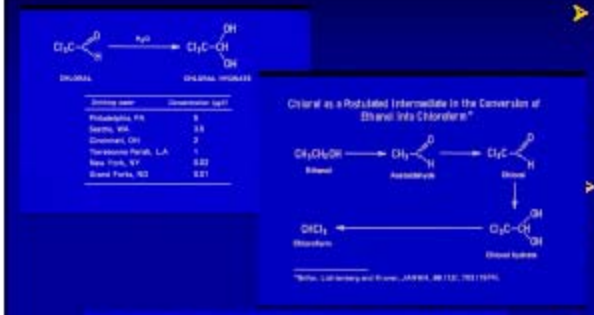
EPA Began to Collect Product & Raw Material Info From Industries



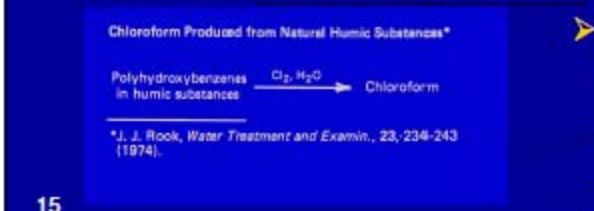
- Logical but not always useful start. 1972 Expl.
- Raw Materials:
  - Ethane, Propane, Nitrogen, Raw Gas
- Products:
  - Ethylene, Propylene, Octane, Ammonia
- Identified:
  - Xylenes, Styrenes, Naphthalenes, Indan, Indene, phenol, etc.

14

Chloroform in Drinking Water Mystery



Chloral as a Postulated Intermediate in the Conversion of Ethanol into Chloroform*



Chloroform Produced from Natural Humic Substances*

Polyhydroxybenzenes in humic substances $\xrightarrow{Cl_2,\ H_2O}$ Chloroform

*J. J. Rook, *Water Treatment and Examin.*, 23, 234-243 (1974).

- Chloroform was found everywhere in drinking water
- We thought it may come from chloral
- Actually was produced by chlorination of natural humic substances in water

15

Search for the Agency MS

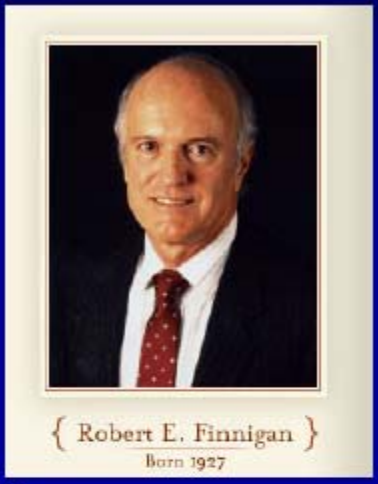


We needed an instrument that could process lots of data

- Could not continue to spend days or weeks analyzing each sample by hand
- Needed consistency in data from many EPA and state labs
- Traveled the country

16

Bob Finnigan



- Produced a "cheap" computerized MS needed to process spectra from many compounds in water
- Later provided a "clean" soil standard used as a Western soil blank for chlorinated dioxins and furans from his yard near Yosemite National Park

17

Ron Webb

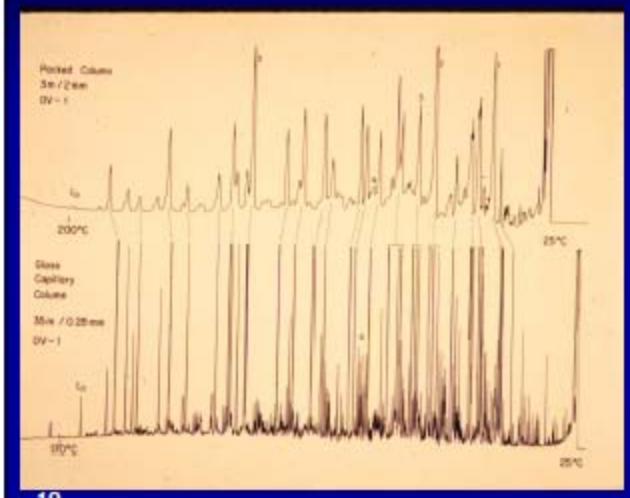




- Ron brought capillary column GC to our Athens, GA lab
- He also used a Perkin-Elmer computerized GC system to analyze water pollutants
- Separated and identified structures of many of the 209 PCB congeners in Aroclors

18

We Made All Our GC Columns



- Packed and capillary columns were all hand made.
- Ron used the J. Grob technique and a glass drawing machine

19

New Orleans Drinking Water Study

- Taste and odor problems were noticed in New Orleans drinking water (base of Miss. River)
- In July 1974 New Orleans and State of LA asked for analytical help to identify trace organics in 3 of their drinking water treatment plants.
- 70-year carbon chloroform extracts used - 1 liter water/day for 70 years
- Identified 66 organic compounds first & more work resulted in 117
- Subsequent to this report several nationwide surveys were initiated



Dec. 1975
EPA Report

20

Bill Telliard



- One summer day in 1976 a visitor from EPA in Washington, DC visited our lab in Athens, GA
- He asked for help to develop methods for sampling and analyzing a new list of pollutants – immediately!
- EPA had lost a lawsuit - June 7, 1976 Consent Decree required immediate sampling and analysis of a list of "*Priority Pollutants*" in 21 industrial categories.
- A list of "*65 pollutants*" were to be analyzed for in 15 months!

21

Some Minor Details Were Missing

- The list of "65 pollutants" could be thousands since some were classes rather than individual compounds.
- No minimum detection levels were specified.
- No standardized methods for collecting, preserving, or analyzing for thousands of chemicals at low levels in complex industrial waste waters were available.
- How could contractors submit estimated costs for sampling and analysis with these unknowns?

22

Two Meetings to Resolve Problems

- 1st Meeting - October 1976 in Kansas City, MO
  - Decided: GC-MS should be the technique of choice for analyzing specific organics
  - Decided: 10 ug/L (ppb) detection level recommended for most analytes regulation
  - Decided: All specific compounds in the list were automatically to be included (no brainer)
  - Decided: Select representative compounds for classes of compounds (hundreds/thousands)
- 2nd Meeting - November 1976 in Atlanta, GA
  - Decided: Metals and inorganics to be reported as "total" analyte concentration

23

Second Meeting in Atlanta - Cont

- Decided: Chemical standards must be commercially available for representative organic chemicals in a class or group in order to be included (I searched10 chemical catalogs)
- Recommended: Frequency of occurrence of representative compounds in water at > 5% of the total known for that class of compounds from the Shackelford/Keith list of chemicals in water (EPA-600/476-062) – (All known organics in water 1976)
- Sources: Meaningful manufacturing quantities were determined from Stanford Research Institute's 1976 "*Directory of Chemical Producers*" & from Radian Corporation's current "*Organic Chemical Producers' Data Base Program*"

24

Result: 129 Priority Pollutants



- 123 specific analytes were submitted to the plaintiffs in the Consent Decree.
- At the plaintiff's request 6 more chemicals were added to total 129 - 5 Aroclor mixtures and di-n-octyl phthalate
- Many of the original "65 pollutants" came from the New Orleans Drinking Water Study preliminary results
- 1979 ES&T pub most requested article from the journal

25

129 Priority Pollutants -> 9 Analytical Groups

1. Metals (As, Sb, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Th, Zn)
2. Asbestos
3. Total Cyanides
4. Pesticides
5. Acid-extractable Organics
6. Alkaline-extractable Organics
7. Neutral-extractable Organics
8. Total Phenols
9. Purgeable (volatile) Organics

26

First Priority Pollutant Analytical Standards

- 1978 Analytical Standards for the World – One Problem Solved!



27

Purgeable Compounds





- "Purge & Trap" method was developed by Tom Bellar and Jim Lichtenberg at EPA's Environmental Monitoring and Support Laboratory in Cincinnati, OH to analyze for volatile organic compounds
- Applied to 29 of the Priority Pollutants

28

Extractable Compounds





- Liquid-liquid extractable compounds method using methylene chloride and pH adjustment followed by concentration in a Kuderna-Danish apparatus applied Ron Webb's research.
- Used for 57 of the Priority Pollutants

29

Later Method and Analyte Improvements



L->R: Ken Lee, Larry Keith, Bill Telliard, Dale Rushneck, and Bob Beimer (on the *HMS Sinkfast*)

- Appendix C lists for petrochemicals developed over several years.
- Isotope Dilution MS methods (1624 &



Peyote cactus -- Mescal

30

1980s and 1990s

- Rapid advances in sampling and analysis of pollutants in water, air, and soil
- Analysis of chlorinated dibenzodioxins ("dioxins") and dibenzofurans important
- Regulations based on identified pollutants were promulgated
- QA and QC became important as people tried to compare and use analytical data
  - EPA's Data Quality Objective (DQO) process was introduced and widely implemented

31

Now 1,000+ Methods Available Online

National Environmental Methods Index – NEMI www.NEMI.gov



I was co-project director with Dan Sullivan at USGS

- Used by tens of thousands of scientists / year
- Took 7 years to develop – 2002 was launched
- New Version 4.0 released in July 2013

32

Thanks!

I was fortunate to be in the right place at the right time to make a difference.



33

And They Said It Couldn't Be Done: A Brief History of Environmental Water Monitoring

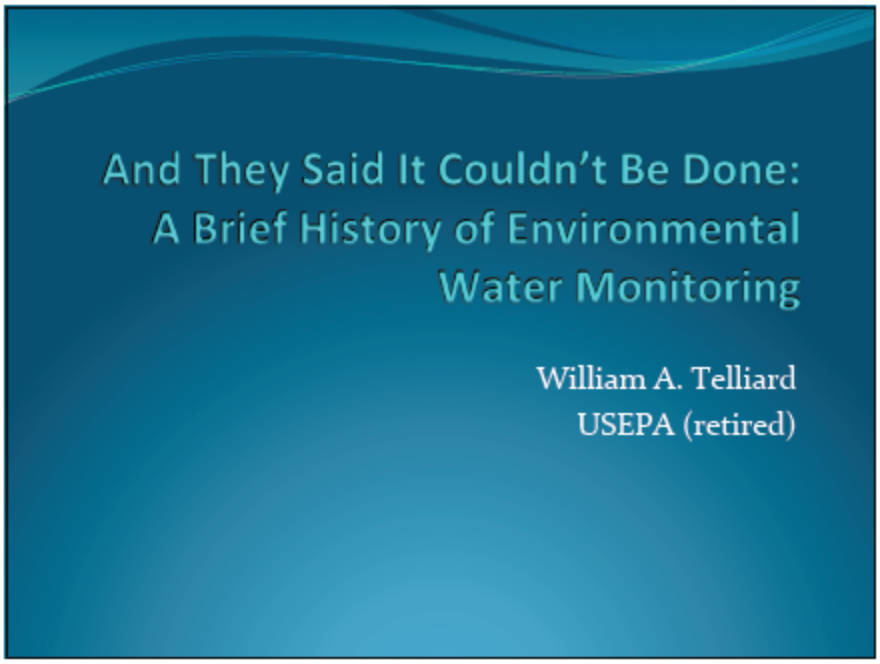
William Telliard
USEPA (retired)

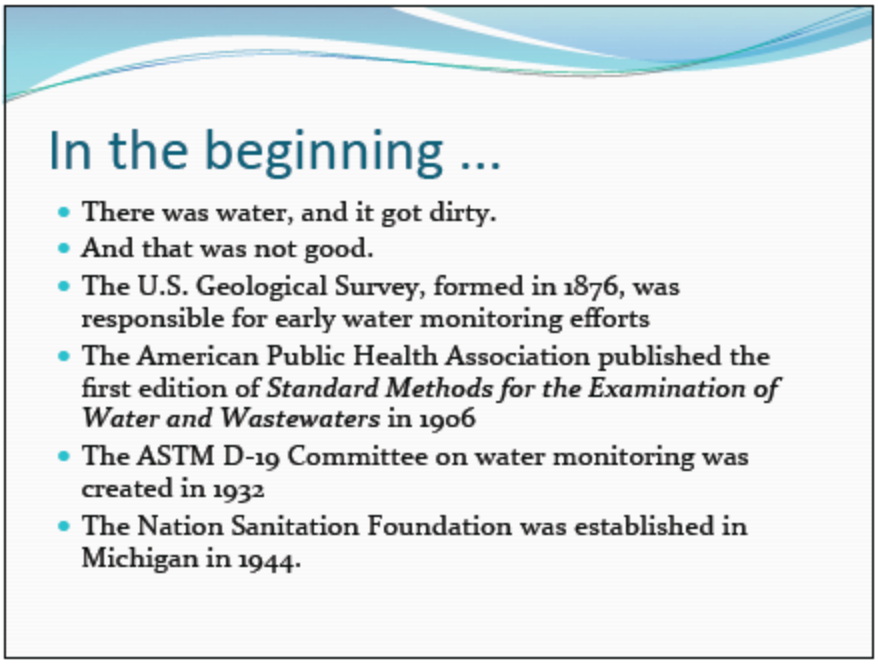
Abstract

The US Environmental Protection Agency was founded in 1970; but the Federal Water Pollution Control Act, however, had been in existence in 1965. Environmental monitoring, however, actually dates to at least the turn of the last century. The U.S. Geological Survey, formed in 1876, was responsible for early water monitoring efforts. The ASTM D-19 Committee on water monitoring was created in 1932 and the first edition of Standard Methods for the Examination of Water and Wastewaters was published in 1906. Another entity, the Nation Sanitation Foundation, was established in Michigan in 1944.

Congress enacted the Clean Water Act in 1972 and the Safe Drinking Water Act in 1974. Both require EPA to provide analytical methods for use in water monitoring and research. EPA's initial response to these monitoring needs was to draw on existing methodologies. As a result, in the 1970s the industry was measuring via milligram per liter (mg/L). As environmental science progressed and as a result of litigation, there was a need for methods to monitor compliance with national industrial wastewater limits, and new methods for this were published in 1979 (40 CFR 136). And now, many of these methods could measure to the microgram per liter level.
As environmental work progressed, EPA worked with instrument manufacturers, standards vendors, and research and commercial laboratories to refine and validate these new methods. By the early 1980s, measurements of pollutants in the low part-per-billion range was commonplace. By the end of the 1980s, concerns over the presence of dioxin in pulp and paper discharges lead EPA to develop high resolution GC/MS procedures that could measure down to part-per-quadrillion levels (the femtogram level on instrument). Instrument manufacturers responded to this need with equipment that can provide stable, reliable performance at these measurement levels. Standard vendors have developed and provided high-purity reference standards for many regulated analytes, and also provided customized mixtures of reference standards and materials such as isotopically labeled compounds--the compounds needed to support such monitoring.

We would like to discuss some of the water environmental issues of the last 43 years and the subsequent analytical techniques that have been developed to deal with the problems.


And They Said It Couldn't Be Done:
A Brief History of Environmental
Water Monitoring
William A. Telliard
USEPA (retired)


In the beginning ...
There was water, and it got dirty.
And that was not good.
The U.S. Geological Survey, formed in 1876, was responsible for early water monitoring efforts
The American Public Health Association published the first edition of Standard Methods for the Examination of Water and Wastewaters in 1906
The ASTM D-19 Committee on water monitoring was created in 1932
The Nation Sanitation Foundation was established in Michigan in 1944.

U. S. Environmental Protection Agency

- Formed in 1970
- The Clean Water Act was enacted in 1972
- The Safe Drinking Water Act was enacted in 1974
- Problem solved, right?

Not quite …

Monitoring Technologies

- In the 1970s , most monitoring of water quality was still done via simple colorimetric methods
- Industrial effluents were monitored for a few contaminants at milligram per liter levels, what we now call "chunks"
- The Cuyahoga River drew national attention when it caught fire in the summer of 1969
- By law, EPA was responsible for approving State monitoring programs, but not much else

So how did we move forward?

- Lawyers got involved
- In 1975, the Natural Resources Defense Council (NRDC) filed suit against Russell Train, the EPA Administrator, to force EPA implement the portions of the Clean Water Water that dealt with Section 307(a), for the "toxic" pollutants. (NRDC *et al. v.* Train. 8 ERC 2120)
- In 1976, EPA and the plaintiffs entered into a settlement agree via a consent decree

Consent Decree

- Required implementation on a Court-decreed schedule
- EPA had to establish "new source performance standards" for 21 industrial categories
- EPA established the "Priority Pollutant List."
  - 129 specific pollutants to be monitored
  - 14 metals
  - 113 organics
  - Asbestos
  - Cyanide

Monitoring Methods

- Given the large number of organic pollutants and the court-mandated schedule, EPA decided to use GC/MS as the basic monitoring technology whenever practical.
- EPA's laboratories in Cincinnati, OH and Athens, GA developed methods for organics, including:
  - 624 for volatiles
  - 625 for extractable organics
  - 608 for organochlorine pesticides and PCBs as Aroclors
  - 613 for 2,3,7,8- tetrachloro-*p*-dioxin
  - 200-series flame atomic absorption methods for metals

304(h) Proposal

- EPA proposed a series of methods for monitoring compliance with wastewater discharge permit limits in 1979, under the authority of Section 304(h) of the Clean Water Act
- Public comments flowed in, and in, and in …
- Virtually every aspect of every method was the subject of comment from someone
- Environmental groups generally commented that EPA was being too lax

Industry Response

- Not surprisingly, the comments from industry suggested that EPA was going way out on a limb with regard to environmental monitoring
- The use of GC/MS was criticized in general
- Claims were made that GC/MS was not, and never could be, a quantitative technique.
- "It'll never work" was a common refrain

Promulgation of Methods

- Following the 1979 proposal, EPA spent the next five years:
  - Responding to public comments
  - Refining the proposed methods
  - Developing new and improved methods or techniques to support monitoring needs
  - Incorporating newer instrumentation and other developments from instrument manufacturers into the program
- Final promulgation was on October 26, 1984

New Techniques

- In response to comments about the non-quantitative nature of GC/MS, EPA's Office of Water developed versions of the GC/MS methods that employed isotope dilution as the means of quantifying the pollutants of interest.
- Isotope dilution was not a new concept. It had been developed in the late 1930s and refined by researchers in various fields over the years.
- It did require that standards of isotopically pure materials be available.

Isotope Dilution

- The Office of Water contracted with vendors to prepare the needed isotopically pure standards
- The Office of Water developed Methods 1624 and 1625
  - Based on Methods 624 and 625
  - Added isotope dilution to reduce the variability in analyte results
  - Isotope dilution corrects analyte results for the recovery of the labeled compound added to the sample before any other processing
  - Overall improvements in both precision and accuracy

Metals Method Improvements

- Analyses of metals were confounded by the multiple forms of many of the metals of concern.
- EPA developed sample digestion techniques for "total recoverable metals" in order to capture as many forms of the priority pollutant metals as practical.
- Inductively-coupled plasma atomic absorption spectrometry (ICP) instruments became available
- EPA developed an ICP method for compliance monitoring

Methods as of 1984

- As of the 1984 promulgation of Clean Water Act compliance monitoring methods it was practical to monitor metals and organics at levels of micrograms per liter (ug/L)
- Quality control techniques had been standardized across methods
- Appropriate instrument performance checks were included in methods
- QC acceptance criteria were included in methods

And then ...

- In the late 1980s, some fool researcher discovered dioxins and furans were formed during the manufacturer of paper products via chlorine bleaching of pulp.
- The pulp and paper industry was one of the 21 industrial categories in the 1976 consent decree
- The Office of Water (and other EPA Program Offices) responded by developing new methods for dioxins and furans and using those methods to investigate discharges from the pulp and paper industry.

High Resolution GC/MS

- In order to measure dioxins and furans at very low (part per quadrillion) levels and accurately identify the analytes in the presence of various interferences, the Office of Water relied on gas chromatography and high resolution mass spectrometry (HRMS)
- Mass resolution of 10,000 allows the instrument to distinguish among analytes whose exact masses differ in the fifth decimal place
- Isotope dilution used as well

High Resolution GC/MS Methods

- EPA Method 1613 - for 17 2,3,7,8-substittued dioxins and furans
- EPA Method 1668 – for 209 polychlorinated biphenyl (PCB) congeners
- EPA Method 1614 – for 209 polybrominated diphenyl ether (PBDE) congeners (flame retardants)

Low-Level Metals Methods

- Not to be out done, metals researchers realized that some trace metals were present at much lower levels than previously thought
- USGS determined that much of their long-term monitoring data actually represented contamination of the samples during either collection or analysis, or both
- Techniques were available in the oceanographic community to overcome contamination concerns

"Clean" Metals Techniques

- In the mid-1990s, the Office of Water began developing sampling and analysis methods to overcome these contamination concerns
- A suite of "clean" techniques were drafted, tested, and released by EPA
- Method 1669 is the sampling procedure that incorporates "clean hands – dirty hands" sample collection procedures that allow measurement of metals at sub-part-per trillion levels

1600-Series Metals Methods

- **Method 1630:** Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
- **Method 1631:** Mercury in Water by Oxidation, Purge and Trap, and CVAFS
- **Method 1631 Appendix A:** Digestion Procedures for the Determination of Total Mercury in Tissues, Sludge, Sediments, and Soils
- **Method 1632:** Inorganic Arsenic in Water by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry
- **Method 1632A:** Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry

1600-Series Metals Methods (cont.)

- **Method 1637:** Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption Spectrometry
- **Method 1638:** Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry
- **Method 1639:** Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry
- **Method 1640:** Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry

Other Metals Method Materials

- Guidance on Establishing Trace Metals Clean Rooms in Existing Facilities
- Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring
- **Method 1669:** Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels
- Video: Sampling Ambient and Effluent Waters for Trace Metals

Method 1631

- Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
- Developed to determine mercury reliably at ambient water quality criteria (WQC) levels

		Lowest WQC
Method Range:	0.5 - 100 ng/L	Human health = 1.8 ng/L
MDL:	0.2 ng/L	Wildlife = 1.3 ng/L

Method 1669

- Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels
  - Incorporates clean techniques from USGS and other experts
  - Provides procedures necessary to produce reliable results at the lowest water quality criteria published by EPA
  - Designed to support collection of ambient water samples
  - Performance-based

The Cutting Edge of Science

- One of the "conventional pollutants" mentioned by name in the Clean Water Act is "oil and grease"
- Originally used as a process control parameter at wastewater treatment plants
- Methods promulgated in 1984 employed CFC-113 as the extraction solvent
- The "Montreal Protocol" required the elimination of all non-essential uses of CFCs in order to protect stratospheric ozone

Method 1664

- The Office of Water began studying replacement solvents in 1992
- Extensive testing of different solvents in effluents from a wide range of industrial categories
- Ultimately, hexane was selected as the replacement solvent of choice
- Method 1664 was proposed in January 1996 and ultimately promulgated in May 1999.
- Extensive guidance issued in conjunction with the solvent change

Cyanide

- Cyanide occurs in wastewater samples in multiple forms
- Some forms are defined by the measurement or treatment technique (e.g., cyanide amenable to destruction by chlorination)
- Currently approved methods for:
  - Total cyanide
  - Available cyanide
  - Free cyanide
- Wide variety of instrumentation applicable to these measurements

Microbiology Methods

- It's not all chemistry
- EPA has approved wastewater methods for 8 microbiological parameters:
  - 4 forms of coliform bacteria (2 fecal and 2 total)
  - *E. coli*
  - Fecal streptococci
  - Enterococci
  - *Salmonella*
- EPA also approved methods for monitoring ambient water for:
  - *Cryptosporidium*
  - *Giardia*

Microbiology Methods (cont.)

- New 1600-series microbiology methods include expanded QC requirements that are similar to those in existing chemistry methods:
  - Initial precision and recovery (IPR) study (4-sample start-up test)
  - Ongoing precision and recovery test (1 sample per batch)
  - Matrix spike samples
  - Quantitative acceptance for all QC tests

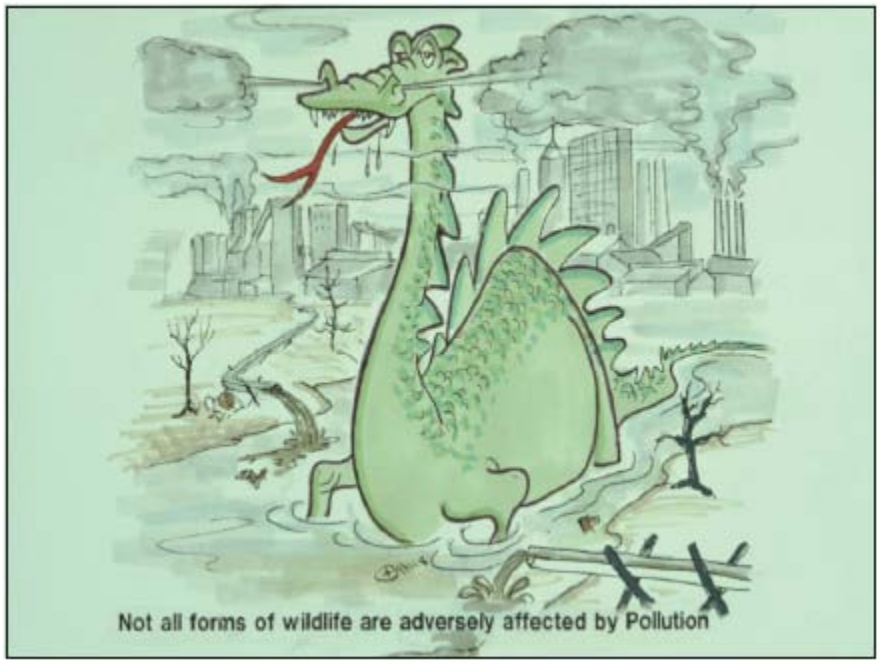
Pharmaceuticals and Personal-Care Products

- Recognizing that drugs that go down the drain may continue to affect organisms other than humans, the Office of Water developed:
  - **Method 1694:** Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS
  - **Method 1698:** Steroids and Hormones in Water, Soil, Sediment, and Biosolids by HRGC/HRMS

Where to next?

- On-line monitoring
- Continuous analysis
- Can be applied to both effluents and ambient water monitoring




Not all forms of wildlife are adversely affected by Pollution

History of the EPA Solid Waste Methods Program (SW-846)

David Friedman

Abstract

In this presentation, the author will review the history and philosophy behind the development of the Environmental Protection Agency's (EPA) Resource Conservation and Recovery Act (RCRA) methods development and promulgation program. He will discuss the development and history of "Test Methods for Evaluating Solid Waste", commonly known by its EPA document number SW-846, and how the methodology in the manual is philosophically different from those in earlier EPA methods programs such as the methods promulgated to comply with the Agency's waste water and drinking water programs. How SW-846 grew from a simple collection of recommendations to help analysts address testing of wastes to determine whether a waste exhibits one of the RCRA characteristics, into the wide ranging methods reference it is today. The author will also discuss the development of the RCRA characteristics and the methods used to determine if a waste exhibits one or more characteristics. Emphasis will be on the tests used in the Toxicity Characteristic such as the Toxicity Characteristic Leaching Procedure (TCLP) and its predecessor, the Extraction Procedure (EP).

THE HISTORY & PHILOSOPHY OF THE RCRA METHODS PROGRAM

An Old Man's **Memory** & Perspective

By
David Friedman

August 5, 2013

Overview of Presentation

- The Resource Conservation and Recovery Act (RCRA) as it impacts environmental methodology;
- History of RCRA methods program;
- History of ***Test Methods for Evaluating Solid Waste*** (SW-846);
- History of the National Environmental Monitoring Conference (NEMC);
- Viewpoint on lessons learned from 40 years in the business.

Resource Conservation & Recovery Act

- Enacted in 1976
- Initiated EPA hazardous waste program
- Defined "solid" to include liquids and gases
- In 1976, most RCRA solids were wastewaters
- First problem was what is a "hazardous waste"
- Methods Program began with defining hazardous waste characteristics

Hazardous Waste Characteristics

- Hazardous waste means a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

Hazardous Waste Characteristics

- EPA was to develop and promulgate criteria for identifying the characteristics of hazardous waste, and for listing hazardous waste, which should be subject to the provisions of this subchapter, taking into account toxicity, persistence, and degradability in nature, potential for accumulation in tissue, and other related factors such as flammability, corrosiveness, and other hazardous characteristics.

Hazardous Waste Characteristics

- In 1976, we started work to turn the statutory definition into specific sets of waste properties that one could use to determine if a particular waste was regulated.
- The four characteristics that were eventually adopted were:
- Ignitability, Corrosivity, Reactivity & Toxicity by reason of toxic chemical leachability

Test Methods for the Evaluation of Solid Waste (Sw-846)

- Characteristics are defined in terms of measurable waste properties.
- Publishing the properties and thresholds led to the request that EPA tell the regulated community how to measure the properties.
- For "method defined parameters" that was obvious.
- For non method defined parameters that was not so obvious.

Test Methods for the Evaluation of Solid Waste (SW-846)

- As a result of urgings of the regulated community, development of SW-846 began.
- Purpose was to serve as guidance for chemists on possible analytical approach to consider – not as collection of required methods.
- Required methods for use in method defined parameters were incorporated into regulations.

Test Methods for the Evaluation of Solid Waste (SW-846)

- First edition was developed by group from program, EPA Regional laboratories, and states to prevent running afoul of FACA.
- Most methods lifted from other EPA programs and adapted to RCRA program needs.
- First edition took only a few weeks to compile and issue.
- Organization of methods due to complexity of RCRA materials.

Growth of SW-846

- The technology innovation community asked that we incorporate their new technologies into SW-846.
- As long as they demonstrated that the technology worked on real world RCRA samples, we elected to do so since it meant that new technologies could obtain faster acceptance by the environmental community.

Growth of SW-846

- While initially SW-846 was published in hard copy by GPO, it soon became too costly.
- Then, we made it available thru the NTIS
- Finally, EPA had to just publish it on-line.
- Since 1985, the SW-846 program has been led first by Gail Hansen and currently Kim Kirkland.

National Environmental Monitoring Conference (NEMC)

- Started in 1984 as the ***Waste Testing and Quality Assurance*** Symposium (WTQA).
- Purpose was to serve as a forum for all sectors of our community to get together and share new of upcoming activities and actions, problems that people are encountering, and possible solutions to those problems in a non-regulatory environment.
- Idea came from Bill Telliard's Norfolk Conference.

National Environmental Monitoring Conference (NEMC)

- Held in Washington to make it easy for EPA officials to participate.
- Held in middle of summer because no one wants to come to DC in summer and hotels are much cheaper.
- About 1500 folks came to first conference.
- For many years, I relied on Gail Hansen to handle most of organizational details.

Lessons Learned

- EPA should never have issued prescriptive or required testing methods.
- EPA should establish monitoring and data quality requirements and leave it to the monitoring community to select or develop appropriate testing methodology.

Lessons Learned

- It is no secret that for many years I have felt very strongly that EPA should move away from a system of prescribing methods and move to one where EPA establishes monitoring Data Quality Objectives and leave it up to the monitoring community to do whatever is necessary to meet the DQOs.
- Measuring requirements should never be established without first determining that they can be met using current technology

Acknowledgements and Thanks

- I want to acknowledge the tremendous debt that we owe to a number of key EPA staff without whom the program would not have been successful.
- These include: Ollie Fordham ,Gail Hansen, Todd Kimmell , Kim Kirkland , Barry Lesnik ,James Poppiti, Florence Richardson, Charles Sellers, and Shen-yi Yang.
- To Lara Autry and Jerry Parr for their work in keeping the NEMC alive and for making it so successful.


Contact Information
David Friedman
David Friedman Consulting LLC
10817 Rippon Lodge Drive
Fairfax, VA 22032-2931
703-389-3821
friedmanconsulting@cox.net

The Evolution of Instrumentation for Environmental Monitoring

David C. Kennedy
Phenomenex

Abstract

2013 marks the 43rd anniversary of the founding of the US Environmental Protection Agency. From the beginning, EPA's primary weapon in the war against pollution has been environmental monitoring, i.e. the identification and measurement of the concentration of contaminants in our air, water and soil. Legal limits are set as to the type and level of contaminants allowed in the environment and environmental monitoring is then performed to determine compliance. Obviously, analytical instruments are the primary enabling tools of environmental monitoring.

Instrumentation has evolved over the years to become ever more precise and accurate, permitting the measurement of many more environmental contaminants at lower levels of detection. However, it is important to view environmental monitoring as a dynamic process, not a static one. Two factors have driven this development:

1. Concerns about new environmental dangers (dioxins, for example) highlight the need for better monitoring solutions. This drives the development of new analytical instrumentation by creating a market.
2. Correspondingly, advances in analytical technology reveal new environmental problems, such as previously unknown pollutants or known contaminants at lower levels. This, in turn, drives the need for new and/or more stringent regulations.

The essence of this process is a self-reinforcing cycle of development for both monitoring technology and regulatory requirements. Depending upon one's perspective, this process can be viewed either as a virtuous cycle or a rat race.

For example, "back in the day", organic pollutants were first monitored using vintage gas chromatographs. This required a large battery of GC methods to cover all the compounds of concern. Moreover, the packed column technology of the time gave poor resolution and detection levels were often inadequate for regulatory purpose. This unsatisfactory monitoring solution drove the development and acceptance of GCMS as the primary monitoring tool for organic pollutants. In turn, the widespread use of GCMS monitoring then identified new areas of regulatory concern, causing additional compounds to be monitored, and at lower levels of detection. As time went by, people came to understand that many organic pollutants of concern might be too hydrophilic or thermally labile to be analyzed by gas chromatography. This realization lead to the use of HPLC as a monitoring tool for certain contaminants, such as explosives and propellants. More recently, LCMSMS revealed the presence of previously unsuspected, anthropogenic pollutants of concern in water supplies and wastewater discharges. This discovery will presumably drive the use of LCMSMS as a necessary environmental monitoring tool as UCMR3 plays out its course.

So, where does this cycle end? The answer is obvious: it won't end. It can't. New environmental problems are always going to emerge that will require ever more advanced monitoring techniques. A contemporary example may be the rapid growth of hydrofracturing to enhance oil and natural gas production. There are concerns that hydrofracturing will introduce new, unknown contaminants into the water and air. Obviously, these activities must be regulated - but they can't be regulated if they can't be monitored. Are existing environmental monitoring techniques completely adequate for the job or will new ones have to be developed? Given the history of environmental monitoring, you would be a fool to bet against the latter.

In this session we will review critical developments in the history of environmental, analytical instrumentation. However, since there is such an abundance of material, only the highpoints will be covered. Rather, the primary purpose of this talk is to create a perspective on the past that will enable us to gaze - however dimly - into the future. If it is indeed true that “what is past is prologue”, then the most exciting developments in instrumentation most certainly lie ahead of us.

History of Environmental Monitoring: **Instrumentation**

August 5, 2013

David C Kennedy, PhD
Business Development Manager
Phenomenex
Torrance, CA 90501

Introduction

- Everyone knows that instrumentation has played a major role in the history of environmental monitoring
- Not a subject you can cover in just half an hour



- So, I'm going to take a more philosophical approach
  - Offer a few observations from my career
  - Try to create some helpful perspective
  - And – hopefully- make some sense past developments
    - *So that we can potentially anticipate future directions*

My Approach

- I want to focus on three things today
  - Briefly review the evolution of instrumentation
  - Try to understand how we got where we are today
  - Speculate about where might we be going in the future
- My personal perspective
  - 16 years in the analytical instrumentation business
  - 23 years in the environmental laboratory business
- Basic message
  - We've come a long way, but we aren't done yet

➢ So, let's begin at the beginning……..

Back in the Day…..

Environmental laboratories were much different than they are now……..

Well, we don't need to go that far back



A Better Example:

- The modern environmental movement began about 50 years ago (Sept. 27, 1962)
  - Mass spec and atomic emission were already well-established research tools
  - Early commercial GCs and AAs were becoming common research tools
- On the outside, these instruments look archaic and clunky to the modern eye…..
  - And, the performance of modern instruments is many orders of magnitude higher

➢But inside, the physical principles and basic functionality of scientific instruments haven't fundamentally changed in 50 years

So, what has changed?

(Hint: Note the vacuum tubes)





50 Years of Metal Analysis

Analytical Principle: Spectrophotometry
System integration: None; all functions independent
Informatics: Pen and ink, slide rule, telephone
Automation: Grad student
Price: $240.00
Productivity: 1X

Analytical principle: Mass spectrometry
System integration: Integrated analysis, data processing, communication
Informatics: Acquisition software, LIMS, LAN communication, cloud data storage
Automation: Grad student + autosampler
Price $180,000 ($23,841 in 1963 dollars)
Productivity: 10,000X (100-fold gain/$)

1963





2013

So, here we are……..

- Instrumentation has made enormous strides in productivity, sensitivity, accuracy, etc.
- Environmental measurements at the part-per-trillion level are becoming increasingly common
- In everyday life, 1 ppt has no significant meaning
  - 1 penny short out of $10,000,000,000.00
  - 2 milliseconds out of your lifetime
- But in environmental monitoring 1 ppt can be a very real number
  - ➢ A simple thought experiment shows how amazing this is

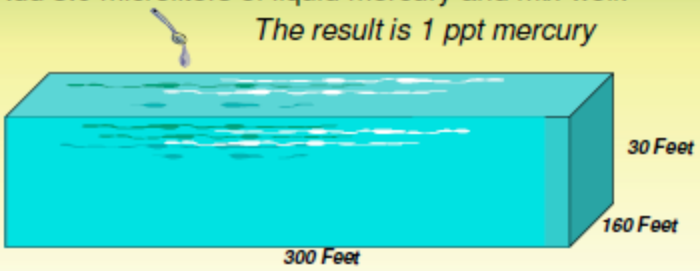
Visualize

A tank the size of a standard collegiate football field (i.e., 300 feet x160 feet)

Fill with pure water to the top of the goalposts (30 feet deep)

Add 3.0 microliters of liquid mercury and mix well:

The result is 1 ppt mercury



This level is measureable by P&T- Cold Vapor Atomic Fluorescence Spectrometry (in principle)

So, what's your point, old-timer?

- There has been an incredible revolution in instrumentation and environmental measurements
  - But most physical measurement techniques have been with us during the past 50 years
- The monitoring revolution was enabled by the advances in solid state electronics
  - For detection, data acquisition, analysis, communication and storage

➢ But, note that technology has been the enabler, not the driver.



Regulations are the Driver

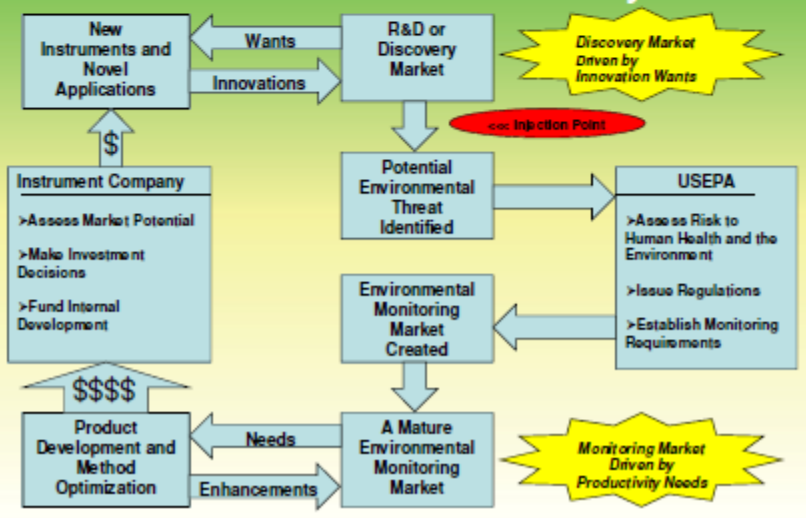
- Duh! Everyone "knows" that environmental regulations created the environmental monitoring market
- In the simple view:
  - An environmental problem is identified
  - EPA promulgates regulations and monitoring requirements
  - This creates a market for instruments and accessories (like GC and LC columns) that can meet the requirements
  - Instrument companies respond with the needed monitoring technology
  - Regulated community buys the instruments, establishing the market
- However, this simple view ignores the dynamic relationship between the development of environmental regulations and the evolution of environmental monitoring instruments

The Missing Pieces

- To be historically accurate, we need to account for:
  - Where do new environmental "problems" come from?
  - Why do new environmental regulations get created?
  - How are new monitoring instrument markets born?
- Turns out there is a synergistic relationship between:
  - *Discovery, regulation and innovation*
- This has sometimes been called:
  The Virtuous Cycle of Innovation
- However, some may see it as:
  The Everlasting Rat Race



The Innovation Cycle



Characteristics of the Innovation Cycle

- Innovative R&D instruments are the "injection point"
  - Establish the existence of new environmental threats
- Not a single market cycle
  - But a series of cycles (GC, GCMS, ICP, LCMS, etc.) in various stages of growth
- The cycles operate in parallel
  - Focused on specific threats & defined by methodology
- Markets are accumulative
  - Regulated analytes never come off the list (e.g., EPA 608)
- Markets continue for decades in their mature state
  - Purge and trap instrumentation now in 9th generation

A Current Example: PPCPs

- Oral contraceptives in use since the early1960s
  - Estrogens were certainly in wastewaters for many decades
  - But, their presence not recognized until the 1999 - 2000 USGS survey which utilized LC-MS/MS
- EPA actions:
  - Developed Method 539; SPE + LC-MS/MS for hormones in drinking water
  - Method 539 is part of current UCMR-3
  - Regulations and LC-MS/MS monitoring requirements are likely to follow (*in my opinion*)

➢ This new innovation cycle was not possible until LC-MS/MS became an established discovery tool

So, what *is* your point, old-timer?

- Understanding this 50-year-old innovation cycle can help us anticipate future developments
  - The synergistic innovation cycle will continue
  - New discovery tools will reveal previously unknown environmental threats
  - EPA will evaluate these threats and some of them will be regulated and monitored
  - New environmental instrumentation markets will be created
- So, what is the next *BIG NEW THING* likely to be?
  - Let's quickly look at some exciting new discovery tools

The Next Major Advance in Instrumental Monitoring?



Some Potential Candidates

- UHPLC-Triple TOF (and other new MS techniques)
  - 100 MS/MS spectra/sec with 1 ppm mass accuracy
- Multi-dimensional chromatography (both GC & LC)
  - GCxGC: Resolve 14,983 peaks in a single chromatogram
- LC-on-a-Chip
  - LC columns with a HETP of 0.032 micrometers
- Laboratory measurements migrating to the field
  - Explosive growth of sensor technology has enabled point-of-origin measurements
  - Much cheaper to move data rather than samples
    - ➢ Can the Star Trek Tricorder be far behind?

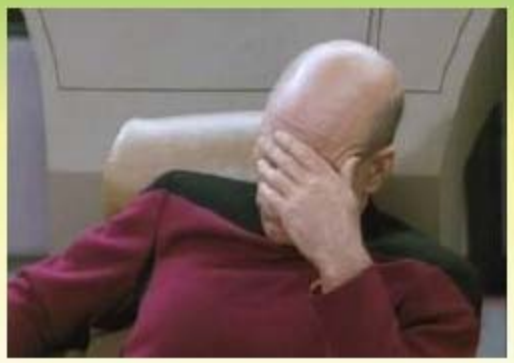
Prediction!

When these advanced instrumental techniques are applied to environmental samples, the next emerging environmental threat will be……..



Facepalm……

I forgot
to recharge
the Tricorder



But, It Doesn't Matter…..

- We don't need to try to predict the future of environmental monitoring
- Thanks to the *Cycle of Innovation*, the future will arrive soon enough
- And, as part of the environmental enterprise, we are the very people who are going to create that future!

- So, let's sit back and enjoy the ride!




phenomenex
Any Questions?
David C. Kennedy, PhD
Business Development Manager
DavidK@phenomenex.com
Phenomenex
www.phenomenex.com
411 Madrid Avenue
Torrance, CA 90501

The Evolution of Quality Assurance & Quality Control in Environmental Laboratories

David Speis
QC Laboratories

Abstract

Quality assurance and quality control (QA/QC) in environmental chemistry has progressively evolved since the passage of the Clean Water Act (CWA) in 1972 resulting in continuous improvement in environmental data quality and usability. Several pivotal events have occurred during that period, which have defined quality control and quality assurance moving the environmental laboratory community closer to the ideal of producing data of known and documented quality while improving a data user's confidence making remedial or regulatory decisions based on laboratory data.

The effects that computerization and automated data processing has had on the ability to generate QC data and the role that a national quality system standard has had on quality processes are central to this presentation. The role of these factors in the evolution of QA/QC in the environmental laboratory community will be discussed along with a brief perspective on what can be expected from QA systems in the future.

The History of Environmental Monitoring
The Evolution of Quality Assurance & Quality Control

David N. Speis
QC Laboratories
Southampton, Pennsylvania

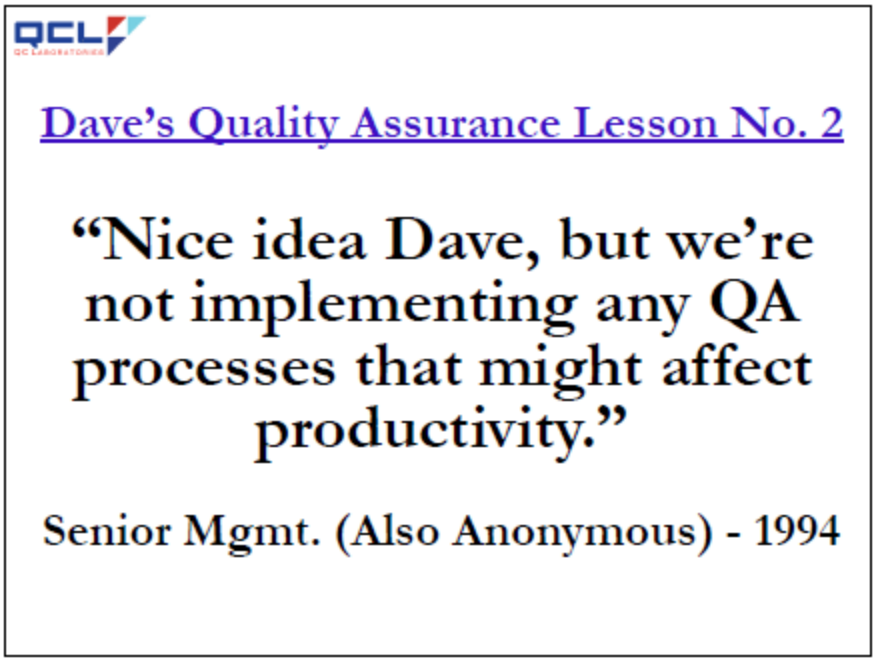
National Environmental Monitoring Conference
August 2013
San Antonio, Texas

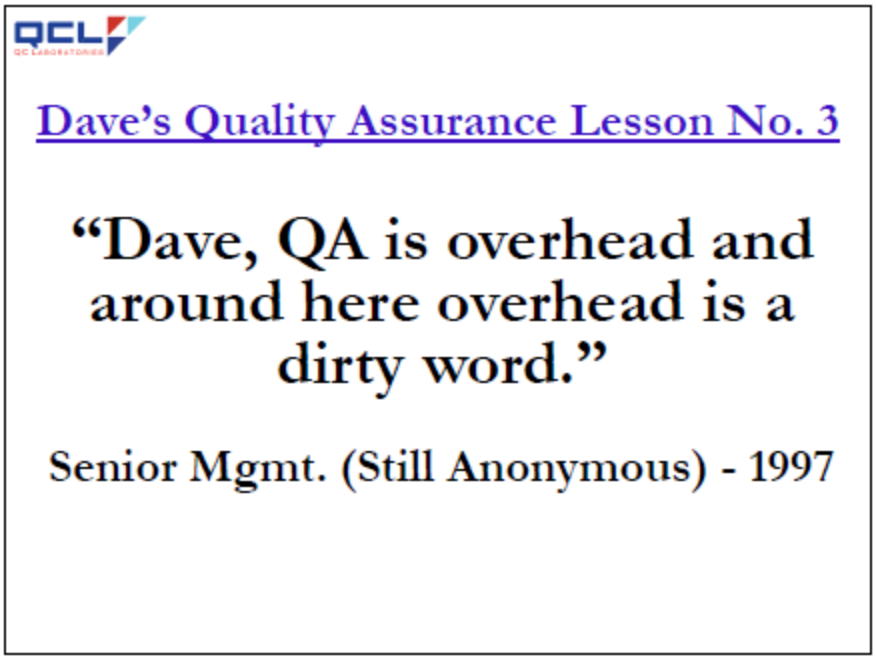
Environmental • Food • Dairy • Pharmaceutical

Dave's Quality Control Lesson No. 1

"Dave, never run a sample twice – you might get a different answer."

Dave's Mentor (Anonymous) - 1975


Dave's Quality Assurance Lesson No. 2
"Nice idea Dave, but we're not implementing any QA processes that might affect productivity."
Senior Mgmt. (Also Anonymous) - 1994


Dave's Quality Assurance Lesson No. 3
"Dave, QA is overhead and around here overhead is a dirty word."
Senior Mgmt. (Still Anonymous) - 1997

The Evolution of Quality Processes

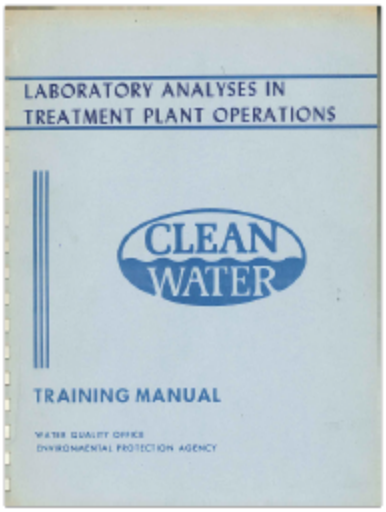
* The Dark Era: Dawn – 1979
* The Quality Control Era: 1979 – 1999
* The Quality Systems Era: 1999 – Current

Zero → Quality Control → Quality Assurance → Quality Systems

The Dark Era: Dawn – 1979

* USEPA Established by Executive Order – December 1970.
* Clean Water Act Promulgated – December 1974
  - Rule Assures Compliant Drinking Water Through Testing
  - Authority for National Primary DW Regulations; 40 CFR PT 141
* Lab Certification in its Infancy (DW Only)
  - State Environmental Agencies Not Formed,
  - Health Department Controlled – Metrics Focus
* Early Methods Manuals Do Not Contain Quality Control or Quality Assurance References
  - Standard Methods – Precision Data on Method Performance Only; Absence of QC Requirements
  - USEPA Water Analysis Training Manual – Precision Data on Method Performance Only; Absence of QC Requirements.

Early Agency Methods Manuals



- **Published: April 1971**
  - Predates CWA & SDWA
- **Discusses Accuracy, Precision, Error & Inter-laboratory QC**
- **QC Predominantly Absent**
  - Calibration Included
  - Blanks, Spikes & Other Parameters Absent
- **QA ????**

Bench Quality Assurance: EPA 1972 - 1978

"First Hand Observations"

- **Surface Water & Wastewater Program Focus**
- **High Profile Environmental Incidents Begin**
  - QC Never Expected During Sample Analysis
  - Samples Analyzed With Little Quality Control
    - Blanks - Rarely
    - Spikes – Never
    - Replicates - Never
    - Calibration – Typically Single Point
    - Inorganics Better than Organics
      - Blanks, Multi-Point Calibrations, Points Plotted for Concentration Determination

Bench Quality Assurance: EPA 1972 - 1978

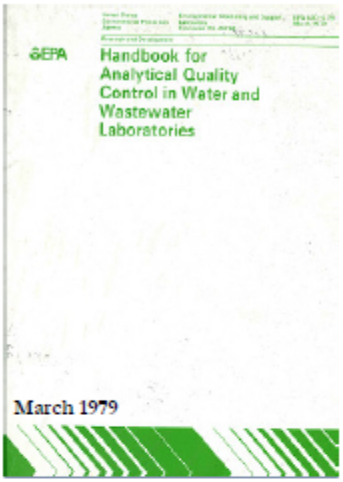
"First Hand Observations"

* **Early Pesticide Analysis**
  - Reagent Blanks - Maybe
  - Florisil Checks –Yes
  - Calibration – Single Point
    - Everything is Linear, Right?
* **Quality Assurance Never Mentioned**
  - Little Understanding of the Terms Definition
* **Producing Data of Unknown Quality and Usability**
* **Running Blanks? It Takes so Long – A War Story**

The Quality Control Era: 1979 – 1999

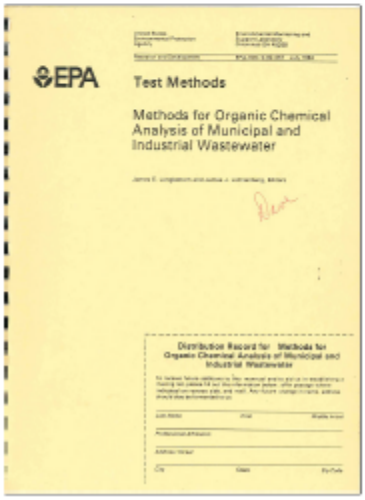
* **Methodology Supporting Monitoring Promulgated**
  - 40 CFR 136 for Organics
    - Method not Designed for High Throughput Operations
* **QC Specifications Included in Methods**
  - Emphasis on Formal Quality Control Program
    - Analyst Solely Responsible for Method QC and QC Statistics
  - Formal QC Elements Included in Methodology
    - Calibration
    - Duplicates
    - Precision & Accuracy
    - Spikes
    - Blanks
    - Surrogates
  - Quality Assurance Program Requirements Remain Absent
  - But Who is Checking?
    - Management Not Supportive of QC Efforts

The First Generation of Quality Control



- Comprehensive Approach Focusing on GLP
  - Services: Gases, Water, Ventilation
  - Instrument Selection
  - Glassware
  - Reagents & Solvents
- Quality Control for Analytical Performance
  - Control Chart Development
  - Quality Assurance in Methodological Terms
    - Calibration
    - Blanks
- Quality Assurance Programs Introduced
  - Little Specificity: Focus On Methodological Program – Analyst Focused Approach
  - Management Level Organization of QC Data
  - Comprehensive Quality System Elements Absent
- Data Handling
- Sampling

Quality Assurance in Water & Wastewater Organics Analysis



- **Methods Publish in 40 CFR 136 Appendix A in 1979**
- **Methodology Specific for NPDES Analysis**
  - Blanks
  - Field Sample Spikes
  - Duplicates
  - Surrogates for Every Sample
  - Precision & Accuracy
    - Concentration Based Range Equations
    - EPA to Publish Ranges Based on Inter-Laboratory Data
  - Demonstration of Capability

Quality Assurance in 1979

* Little Management Regard for Quality Control
* Methods Oriented for Single Technician Execution
  - Calibration Curve Plots for All Priority Pollutants Impractical
  - Computing Capability for Response Factor Calculation & Use Unavailable
* Method Precision & Accuracy Treated as Guidance
* Massive Solvent Background
  - Methylene Chloride & Acetone Un-measureable at Low Concentrations
* Field Duplicates Treated as Laboratory Precision Parameter

Game Changer #1

The Advent of Sophisticated Data Processing Software

Sophisticated Data Processing Advances Rapidly

- **Before Computers (BC) QC Data Calculated Manually**
  - Impossible for Technician to Perform Calculations Manually
    - Manual Plotting of Calibration Data
    - Manual Control Charts & Control Intervals
  - Computer Generated Response Factors Become Possibility
    - Multi-Point Calibration Becomes a Reality
- **More Computing Power Simplifies QC Data Processing**
  - Easily Verified Calibration Criteria Compliance
  - Simplified Recovery Calculations
  - Enhanced QC Decision Making
  - Data Base Storage of QC Data for Control Charting
- **Quality Control Transitions from Technician/Method to Laboratory/Method**

Quality Assurance 1980 - 1999

- **Methodological Quality Control Begins to Appear**
- **States Begin Qualifying Laboratories for Regulatory Data Production**
  - Regulatory Program Basis For Qualification
    - SDWA via Federal Statute
    - NPDES (CWA) – State Option
    - Solid/Hazardous Wastes – State Option; Later in Era
  - Focus on Method Compliance
    - Method QC
    - Operating Procedures
  - Focus on Metrics
    - Thermometer Calibration
    - Thermal Preservation Monitoring
  - Records & Documentation
- **Quality Assurance Stated in Terms of Quality Control**
- **State Certification Requirements Specify QC Manuals**
  - Analytical Procedures Focus

The Quality Systems Era: 1999 – Current

- Laboratory Quality Control Practices Mature
  - Statistical Processing of QC Data Regularly Practiced
- Management Recognizes the Business Need for Organized Quality Control Programs
- Quality Assurance Takes Center Stage
- States Begin to Focus on Quality Systems
- National Laboratory Accreditation Effort Begins
- Laboratories Transition to a Quality Systems Mentality

Game Changer #2

NELAP!!

And Then There Was Light!!

NELAC Changed the QA Dynamic

- **Established a True National QA Standard for Laboratory Operations**
  - Eliminated Arbitrary "Regulatory" Requirements
  - Eliminated CLP as the De-Facto Performance Standard
- **QA Becomes Business Necessity not Overhead**
  - QA Officers no Longer Need to Sell Quality Internally
  - Forces Involvement of Senior Management
  - Integrated QA into the Operational Effort
  - Requires Budget to Sustain QA Effort
- **Accredited Quality Systems Become The License to Conduct Business.**
- **Converted the Industry to an ISO Based System**
  - Consistent with International Practices
  - Predictable from State to State

NELAC Implementation Struggles

"Personal Observations"

- **Senior Management Slowly Recovers from Initial Shock**
  - Eliminated Arbitrary "Regulatory" Requirements
  - Eliminated CLP as the De-Facto Performance Standard
- **QA Becomes Business Necessity NOT Overhead**
  - QA Officers no Longer Need to Sell Quality Internally
  - Forces Involvement of Senior Management
  - Integrated QA into the Operational Effort
  - Requires Budget to Sustain QA Effort
- **Laboratory Leadership Continues to Expect QA Staff to "Be" the Program**
- **Converted the Industry to an ISO Based System**
  - Consistent with International Practices
  - Predictable from State to State


QCL
"From Zero to NELAP in Forty Years"
Data Transitions from Unknown Quality & Usability to Know Quality & Usability
– Forty Year Quality Objective Achieved
Detractors Claim That Data Quality Has Not Improved
– Data Quality is an Operational Execution Issue
– Generating & Presenting Data Quality Parameters Makes Information Quality Known to All
° Enhances Decision Processes Based on Data
– Evaluation of Data Quality is a Data User Decision
Laboratory Leadership Continues to Expect QA Staff to "Be" the Program
– Do Not See QA as an Inherent Operational Component
– Continue to Treat QA as Overhead – A Dirty Word

History and Future of Laboratory Accreditation

Jerry Parr
The NELAC Institute

Abstract

In 1978, the US Environmental Protection Agency (EPA) initiated a laboratory certification program for laboratories involved in analyzing drinking water and delegated the authority for operation of the program to state agencies. Over the ensuing years, many states expanded this program to include other environmental media. As a result of efforts that began in 1987, a National Environmental Laboratory Accreditation Program (NELAP) has been created and is now managed by The NELAC Institute (TNI). This presentation will summarize the activities leading up to the formation of TNI, describe in detail the core programs being performed by TNI and provide information about the future of national laboratory accreditation.

Lab Selection: 1976

- Qualifications of Staff
- Instrumentation
- Published research

Laboratory Accreditation

1980

DMRQA

SDWA

CLP

Concept that accreditation "inherently governmental" introduced

Lab Selection: 1980

- DMRQA
  - Small subset of analytes
  - No GC or GC/MS
  - Only PE samples; no inspection
- SDWA
  - Primarily state labs
- CLP ★
  - Commercial labs
  - Included GC and GC/MS
  - Site inspection
  - On-going data and performance review

Focus on method compliance

Laboratory Accreditation

State Expansion 1985



Lab Selection: 1985

- CLP loses steam
- State programs on the rise
  - Beyond DW
  - Supplemental requirements
- State certification a key factor
- Price becoming major factor

Focus shifting to state-specific conflicting requirements

A recipe for Disaster



1989 Presentation by Jack Farrell

One Large Laboratory Experience with Accreditation

THERE ARE MORE STATE CERTIFICATION PROGRAMS THAN STATES IN THE UNION - AND SOME STATES HAVE NO PROGRAMS.

- 65 + STATE PROGRAMS IN 46 STATES
- LESS THAN 10 OFFER REASONABLE RECIPROCITY REQUIREMENTS WITH OTHER PROGRAMS
- 5 STATES HAVE PROGRAMS EXCLUDING "OUT OF STATE" LABORATORIES
- $460,000 ANNUAL COSTS FOR ONE LABORATORY



Origin of National Program

- Inconsistent/nonexistent inspections;
- State programs with conflicting requirements;
- Laboratory ethical issues;
- No reciprocity among states;
- Accreditation in all areas not available;
- Customers had no access to information; and
- State programs generally viewed as inadequate by laboratory community, and some lab customers.



Impetus for Change

- 1986 - Commercial Laboratory Issues
  - De Facto CLP Accreditation
  - Inconsistency
  - Level playing field
- Meeting with Hank Habich and others at EPA
  - Need for single, comprehensive program administered by EPA



Impetus for Change

- 1986 Report to Congress
  - EPA explore the feasibility of a uniform, national environmental laboratory accreditation program.
- 1990 EMMC Report
  - A national program is a viable option,
  - EPA consult with representatives of all stakeholders, and
  - Establish a federal advisory committee.



The Beginnings of a National Program

- Committee on National Accreditation of Environmental Laboratories (CNAEL)
  - July 1991 – July 1992
- State – EPA Focus Group
  - January 1993 – September 1994
- IAETL Committee on Laboratory Accreditation



CNAEL Recommendations

- National program implemented by state agencies with federal oversight.
- Key elements of program are:
  - Performance evaluation testing,
  - On-site audits, and
  - Laboratory process and quality assurance certification.
- Program should be self-supporting.
- Should address all environmental media and all EPA programs



Options Rejected by CNAEL

- PE Samples only
- Analyst Certification
- Laboratory Manager Certification
- Laboratory Process Certification
- Resident Inspectors
- Training
- Fraud Audits



Work of the EPA/State Focus Group

- Developed a set of accreditation requirements based on ISO Guides 25, 43 and 58.
  - Proficiency testing
  - Quality system
  - On-site assessment
- Developed a proposed organizational structure.
  - Conference of state and federal officials.
  - Private sector could participate, but not vote.

Beginning of the shift from a methods focus to Quality Systems



IAETL Accreditation Committee

- A **single**, comprehensive national program for accreditation of environmental laboratories must establish:
  - Uniform, rigorous requirements for environmental testing laboratories to generate data of known and documented quality.
  - Uniform, rigorous standards under which accrediting organizations can oversee the program.
- Presented at NEMC, 1993
  - Authors included: Jack Farrell, Marlene Moore, Jerry Parr and David Speis



Formation of NELAC

- Unincorporated organization of state and federal officials who vote on requirements.
- Input from others considered.
- Implementation a voluntary decision by individual states.
- National Environmental Laboratory Accreditation Conference (NELAC) created on February 16, 1995.

> "The scope of NELAP shall encompass the necessary scientific testing to serve all EPA monitoring, compliance or other functions mandated by statutes and pursuant regulations."



Original Vision for NELAC

- States and EPA develop consensus standards that are voluntarily adopted by the states.
- EPA oversees accrediting authorities to assure uniformity.
- State grants accreditation, which is **unconditionally recognized**, by other participating authorities.
- Laboratories can voluntarily apply to any approved authority, if their home state does not participate.



NELAC Early Years

- 1995 – 1997 Development of standards
- 1997 – Approval of first standards
- 1997 – Acceptance of program by OGWDW
- 1999 – First Accrediting Authorities recognized
- January 24, 2001 – First class of laboratories accredited



Impetus for Change 1

- National Technology Transfer and Advancement Act
  - OMB A119
  - Role of consensus standards

NELAC Standard could never become a consensus standard because of lack of balance



The First Transition

- Special meeting in December 2000:
  - NELAC to become standards adoption organization only, and maintain current structure without expert committees.
- INELA created by interested group of stakeholders:
  - True consensus standards organization.
- Last NELAC Standard adopted in 2003.



Impetus for Change 2

- EPA reemphasizes their role:
  - EPA has no authority to operate a national program for all media.
  - NELAC should be a self- sustaining program, funded by its stakeholders.
- NELAC Executive Director resigned.
- EPA direct funding support ceased in 2006:
  - The Agency has continued to provide significant support both through multiple assistance agreements and direct staff support.



The Second Transition

- EPA awarded Assistance Agreement to help NELAC with self-sufficiency
  - NFSTC
- Formation of the Self-Sufficiency Task Group (SSTG)
  - Advise the NELAC Board of Directors regarding the development of a plan for NELAC self-sufficiency



Status in October 2006

- The program had achieved some success.
  - 13 Accrediting Authorities.
  - > 1000 accredited laboratories.
  - Recognized competency standard.
- Much more needed to be done.
  - The 2003 NELAC standard perceived as onerous.
  - Many states were not participating.
- Program too reliant on EPA funding.



The Future: NELAC and INELA Partnership

- Funding provided by EPA to explore options
- NELAC and INELA combined forces on November 6, 2006 to become The NELAC Institute (TNI)
- All key functions of both organizations were continued



Underlying Assumptions

- Combining operations of NELAC and INELA would result in a stronger organization.
- Combining operations would allow NELAC to achieve self-sufficiency quicker.
- Combining operations would be less disruptive to laboratories and other stakeholders.




THE NELAC INSTITUTE


WHO IS TNI?
A 501(c)3 non-profit organization.
A member organization managed by a Board of Directors.
A voluntary consensus standards development organization accredited by the American National Standards Institute (ANSI).

WHAT DO WE PROVIDE?

- Infrastructure for stakeholders
- Consensus building for establishing requirements for:
  - Organizations that accredit
  - Organizations that are accredited
  - Proficiency testing programs
- Recognition of organizations that operate accreditation programs
- Assistance to members and others



TNI Laboratory Standards

- NELAP
  - Requirements for labs
  - Requirements for ABs
  - Requirements for PT providers
  - Requirements for PT provider accreditors

Laboratory standard based on ISO 17025 but contains additional specificity to ensure applicability to environmental testing and promote consistent assessments



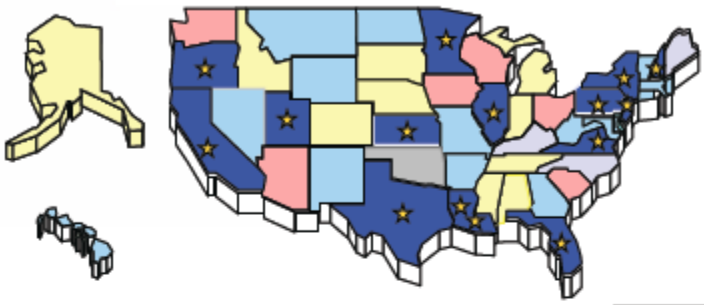
NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

- Accredits over 1600 laboratories
  - 49 states and territories
  - 9 countries
- Accreditation for all media and all environmental methods

Current Status

- 14 states recognized as NELAP ABs
  - Most offer comprehensive programs
  - OK expected to join in 2015
- 18 states Drinking Water only
- 16 states have expanded beyond drinking water
- 2 states require accreditation, but from somewhere else
- 13 states accept NELAP

The National Program Today



NELAP Accreditation Body
Working on Application
Accept NELAP
Incorporate NELAP elements
State program with significant differences
Drinking water only



Current Vision for NELAP

- ~~Stakeholders~~ develop consensus standards that are voluntarily adopted by the states.
- TNI oversees Accreditation Bodies to assure uniformity.
- State grants accreditation, which is ~~unconditionally~~ recognized, by other participating bodies.
- Laboratories can voluntarily apply to other approved bodies, if their home state does not participate.
- Non-government ABs may also grant accreditations, which may be recognized by some states



Status of NELAP

- True consensus standard widely recognized as highly effective in ensuring laboratory competence
- Program being effectively implemented across the US and internationally
- PT program used by virtually everyone
- Program will continue to evolve
  - Improvements to standards
  - Additional ABs



Summary

- A comprehensive national program for accreditation of environmental laboratories exists
- Every lab in the US may choose to participate
- 27 states accept this program
- Much more remains to be done
  - More than DW in every state
  - Apply to all laboratories
  - Remove conflicting requirements from some states
  - Allow participation of NGABs



Credits

NELAC Executive Secretaries
- Romano Trovato
- Jeanne Hankins
- Lara Phelps

NELAC Board Chairs
- Bob Stephens
- Charlie Hartwig
- Carol Batterton
- Ken Jackson
- Jim Pearson
- Chuck Brokopp
- Wayne Davis
- Silky Labie
- Aurora Shields
- Judy Duncan

Original INELA Board
- Carol Batterton
- Eddie Clemons
- David Speis
- Ken Jackson
- Tom McAninch
- Sharon Mertens
- Jackie Sample
- Alfredo Sotomayor
- Chuck Wibby
- Barbara Finazzo
- Ilona Taunton

All NELAC / INELA / TNI committee chairs and committee members



Thank You

Acknowledgements:
- Carol Batterton, TNI
- Jack Farrell, Analytical Excellence
- Joe Slayton, EPA Region 2

http://www.NELAC-Institute.org
817-598-1624

jerry.parr@nelac-institute.org



SECTION 6

MONITORING PESTICIDES IN THE ENVIRONMENT: PAST, PRESENT, AND FUTURE

A Study of Cross-Industry Pesticide Analysis in the US and Abroad

Kory Kelly
Phenomenex

Abstract

Many currently employed environmental pesticide methods were developed decades ago using then available technology. Furthermore, these methods were designed to analyze the spectrum of pesticides in then-current use, many of which are now rarely encountered in environmental samples. Consequently, a view is emerging that environmental pesticide methods are in need of updating to fully take advantage of the advances in modern instrumentation and column technology and to address the broad range of newer pesticides now in current use. In responding to this challenge, it is instructive to consider the analytical work that is being done in other areas. This session will address the progress and limitations of US pesticide analyses and look across industries and geographical boundaries for input on other pesticides identification and quantitation methodologies.

A Study of Cross-Industry Pesticide Analysis in the US and Abroad

Kory Kelly
Environmental Product Manager
Phenomenex, Inc.

US Environmental Methods

- EPA formed in 1970
- Monitoring derived from legislation that was passed in 1970's
  - Clean Water Act – 1972
  - Safe Drinking Water Act – 1974
    - Unregulated Contaminant Monitoring Program
      - No more than 30 contaminants every 5 years (not only pesticides)
  - Resource Conservation and Recovery Act (RCRA) - 1976
    - Amended Solid Waste Disposal Act of 1965

Success and Influence of US EPA

- US is a leader in environmental monitoring
  - Food and exports seem to be priorities elsewhere
- US EPA methods are known nearly worldwide
  - Many countries are using EPA methods directly or variants of the methods with local compounds added
- This trend is stronger with some methods
  - Volatiles
  - Semi-volatiles



Analysis of US EPA Pesticide Methods

Environmental methods have not kept pace with additional analytes

- Some methods are from 1995 or earlier (8151, 507, 508, 525)
- 8081B, 8151, and 8318 are from 2007 but without significantly altered compound lists
  - 8081B has 19 'possible' additional analytes, but not 'extensively validated'
  - Most labs are analyzing the original 20 chlorinated pesticides
- Of the 20 most common pesticides, some are not in regulated methods
  - USDA most detected in fruits/vegetables – 15 / 20 not regulated
  - USDA most detected in groundwater – 10 / 20 not regulated
  - USDA most detected in drinking water – 8 / 20 not regulated
  - US EPA most commonly used – 5 / 20 not regulated

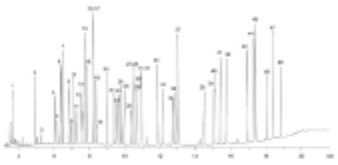
Slide 4

KT5 what's "some?" Do we know the number (even approximate)... of 20 most commonly regulated X are not in regulated methods. "Some" makes me doubt.
Kali Tudela, 7/26/2013

Limitations of Methods (cont.)

Methods have not kept up with advances in instrumentation

- Still using ECD and NPD
  - Very sensitive, very selective, and inexpensive (sort of…)
  - Not qualitative for additional compounds
  - Limited number of compounds due to chromatographic co-elutions



Is it Time to Update the Environmental Science?

- Current US Methods have approximately ~170 total pesticide analytes
  - 500 + 600 + 8000 series
- However, with exception of 525.2, all methods use ECD and NPD for sensitivity but cannot identify unknown analytes





This Isn't New

- Labs and the EPA have known this
- Work is currently under way to update some methods
  - EPA 608 is currently being expanded
    - Relying on input from the EPA, labs, and vendors

Can we stay ahead of the curve for 10 years from now?

How?

Many Diverse Sources

- Japan – Has a 'Positives List' that includes over 700 compounds, of which many are pesticides
- Europe – Already running Environmental Pesticide Screens, but also running Multi-Residue Screens on food.
  - 60% of methods by GC/MS; 40% by LC/MS/MS
- Asia – Both Environmental and Food methods used for pesticides
- Brazil and Latin America – Currently developing extensive programs to support food exports

- US EPA + USFDA – Both screening and quantifying pesticides …from food!
  - Domestic samples from across state lines as well as international

Europe

- Regulations are structured quite differently
  - Compliance monitoring is ISO-based
  - Have specific compound lists
  - Have mandated detection limits
  - Some even specify individual matrices
- No other conditions are specified!
  - Don't specify detectors
  - Don't even specify a technique
- Allows labs the freedom to change and improve approaches and then validate via proficiency test



The USEPA Legacy

- USEPA Methods have lead the world for many years and have been very successful, particularly for pesticides KT7
- The chlorinated list in particular has been monitored throughout the world for decades and the detection of these compounds is now very rare
- However, this success has created some ironies
  - Some EU labs are using USEPA target compounds as Surrogates and Internal Standards
  - Most US Labs have not had a positive hit for DDT or other chlorinated pesticides in decades
  - Unfortunately, other significant peaks are present in chromatograms, but remain unidentified



Slide 10

KT7 I think this is a great statement to have in here. We may want to place it (or something similar) towards the beginning to boost the confidence before starting to show all the shortcomings.
Kali Tudela, 7/26/2013

European Pesticide Trends

- Followed USEPA methods as written until 10-15 years ago
- New regulations continued to add more and more analytes
- Gradual migration from individual detectors (ECD & NPD) to GC/MS Screening
  - Original methods used ECD and NPD for detection with MS verification
  - More methods are now only GC/MS using Internal Standards for quantitation
  - Many labs even using LC/MS/MS



Pesticide Compounds

- List is constantly increasing
  - Most farmers are following regulations and using approved pesticides
  - Some farmers are using new pesticides that may be common outside of the EU, but not regulated by the EU
  - Labs are forced to evolve with the evolving list of analytes







Learning from the Food Industry

Similarities

- Testing for multiple classes of pesticides to ensure public health
- Similar analytes at similar concentration levels

Differences

- More complicated matrix issues
- List of analytes is expanded to account for pesticides used abroad that may be on imported food products.
- Higher exposure to fungicides
- Lower exposure to herbicides

FDA Pesticide Methods

- Enforces EPA's Pesticide Tolerances in Food
  - Food Quality Protection Act of 1996
- Originally followed US EPA Environmental Methods
- Switched to GC/MS methods and increased the list to 360 pesticides
  - Most samples are negative
  - Scan for qualitative identification
  - Use a 'Targeted' method to quantify
- **Still** working with EPA personnel to update methods

Further Evolution of FDA Methods

- This approach worked well, but FDA wanted lower detection
- Therefore, methods are migrating from MS to QQQ
  - Provides better quantitation than ECD and NPD, but also provides verification
- LC/MS/MS is playing a much larger role in pesticide analysis
  - Hundreds of compounds accessible by LC/MS/MS

Some FDA Observations

- FDA expects very low levels because of application cycles
  - Possibly have already overcome sensitivity problems
- Organophosphorus pesticides are not common any more
- Fewer Carbamate pesticides are seen
- Still seeing positives for Chlorinated pesticides
- Constantly identifying new pesticides
- Current list of analytes is over 650!
- Fungicides are common (although mostly post-harvest)
  - Boscalid is the most commonly detected compound
  - Still seeing carbendazim often
  - Seeing Pyrimethanil, fludioxonil, cyprodinil, thiabendazole

Some FDA Observations (cont.)

- QQQ offers unforeseen advantages and savings
  - Decreased sample preparation cost (first quad acts as filter)
  - Easier sample preparation (no fractionation)
  - Lower detection levels than GC/MS, NPD and ECD
  - Provides conclusive answers, particularly with complicated samples / chromatograms

The USEPA Pesticide Challenge

- USEPA has already developed Multi-Pesticide Methods
- The Agency is currently working on improvements
- People are already be reaching outside of the EPA
- However, a widespread, systematic collaboration with other disciplines and world areas would be highly beneficial

Conclusion

- I am not proposing that anyone discard what has taken so long to build
- Not proposing we adopt GC/MS/MS (at least, not yet)

- However, a healthy environment consists of pure food as well as clean air and clean water
- The food industry has developed many advanced methods for monitoring pesticides and other environmental pollutants
- Many food methods are versatile and still provide detection limits required for environmental requirements

Questions?

Collaborative Opportunities for Analytical Method Development

Lara Phelps
U.S. EPA Office of the Science Advisor

Abstract

The US Environmental Protection Agency's (i.e., EPA's or the Agency's) Forum on Environmental Measurements' (FEM) conducted an assessment of all Agency monitoring programs and observed some prevalent recurring themes. We need to:

- Support method development, so we can readily implement state-of-the-art monitoring technology into monitoring studies and programs to solve environmental problems;
- Establish a consistent and framework with a requirement to register all Agency data in an Agency catalogue; and
- Consistently enforce data quality to create greater confidence in the reliability of data and greater insurance of its appropriate use.

We have the specific measurement and monitoring opportunities to foster internal and external leveraging for meeting the Agency's mission of protecting human health and the environment.

The Agency's Science Policy Council (now the Science and Technology Policy Council [STPC]) established the FEM to promote internal consistency and consensus on measurement methodology, monitoring, technology, and laboratory science issues with multi-program impact. Collaborations are and need to continue forming to meet highest-priority, feasible project areas, and a long-term process has recently been deployed internally to continually identify and resolve method needs.

COLLABORATIVE OPPORTUNITIES FOR ANALYTICAL METHOD DEVELOPMENT

Lara P. Phelps, Senior Advisor, Office of the Science Advisor
US Environmental Protection Agency

National Environmental Monitoring Conference 2013
Monday, August 5, 2013

Overview

- Background
  - Office of the Science Advisor
  - Forum on Environmental Measurements
- Method Tools
- Environmental Monitoring Assessment
- Collaborative Engagement
- Contact Us

Office of the Science Advisor (OSA)

- **OSA Purpose** – To support the Science Advisor's key responsibilities:
  - Advise EPA Administrator on science and technology (S&T) issues;
  - Hold a corporate view and coordinate cross-agency S&T policy issues;
  - Resolve conflicts on science and science policy;
  - Provide a vision on S&T and advance emerging issues; and
  - Serve as face and spokesperson for agency science overall.
- **OSA Initiatives** – Science and Technology, Measurement, Monitoring, Modeling, Risk, Human Health, Information Management

Forum on Environmental Measurements (FEM)

- **FEM Purpose** – To promote consistency and consensus on measurement methodology, monitoring, technology, and laboratory science issues with multi-program impact.
- **FEM Initiatives**:
  - Validate and disseminate methods for sample collection and analysis.
  - Ensure monitoring studies are scientifically rigorous and statistically sound to yield representative measurements.
  - Employ a quality systems approach to ensure data gathered and used by the Agency is of known and documented quality.

FEM Areas of Focus

- Improving the Quality of Agency Methods
- Implementation of the Performance Approach
- Communication/Outreach
- Method Detection/Quantitation and Calibration
- General Laboratory Competency
- National Environmental Accreditation
- National Environmental Monitoring Conference
- Monitoring, Information, Technology, and Opportunities Resources (MonITOR)
- Data Management

Method Collections



Flexible Measurements

- Increased emphasis on flexibility in choosing sampling and analytical approaches to meet regulatory requirements for measurements;
- Development of processes for validation that confirm that measurements meet quality requirements;
- Increased collaboration with stakeholders to develop validation processes for new measurement technology; and
- Rapid assessment of new or modified technologies, methods and procedures.



Validation and Peer Review

- Chemical Methods
- Radiochemical Methods
- Sampling for Chemical and Radiochemical Methods
- Microbiological Methods
- Emergency Response Methods
- Environmental Sampling Techniques that Support the Detection and Recovery of Microorganisms from the Environment



  - *Laboratory Toxicity Testing Methods of Analysis – Coming Soon*

Method Detection

- Environmental Measurement Glossary
- Detection Limit/Quantitation Limit Summary Table
- Method Detection/Quantitation: Program Use/Needs
- Calibration Curves: Program Use/Needs



Method Formatting

- A standardized method format, developed in the 1990s, has been used by EPA Program Offices as the template for revising old and writing new methods. This format establishes a consistent framework for all Agency Methods.
  - Office of Air Quality Planning and Standards, Emissions Measurement Center
  - Office of Ground Water and Drinking Water
  - Office of Resource Conservation and Recovery



Monitoring Assessment

- **Purpose** – The Agency needed to synthesize monitoring programs to expand our scientific capabilities, information, and knowledge to meet the Agency's mission of protecting human health and the environment.



- **Charge** – Conducted a stepwise process to produced:
  - an inventory of routine monitoring programs;
  - a list of needs and data gaps; and
  - a list of collaborative and/or leveraging opportunities.

Definition of Monitoring

Monitoring is the measurement or assessment of environmental stressors and related parameters in various media, humans, plants, or animals to:

- Determine **status and trends** of core physical, chemical, and biological indicators of ambient conditions in the nations air, land, and water resources;
- Inform rule-making and to **measure compliance** with statutory and regulatory requirements;
- Inform **risk and exposure** assessments;
- Develop **public and ecosystem** health advisories; or
- Support **research** investigations including new method development or evaluation.

Assessment Results

- **Produced Databases:**
  - an inventory of routine monitoring programs;
  - a list of needs and data gaps; and
  - a list of collaborative and/or leveraging opportunities.
- **Indentified Common Themes:**
  - Measurement and Method Development
  - Data Management
  - Data Analysis or Assessment
  - Emergency Response

Common Themes

- Measurement and Method Development
  - Lack of environmental measurement techniques and analytical methods for routine monitoring.
  - State of the art monitoring technology needs to be developed and utilized.
- Emergency Response
  - Preparedness for responding to emergency situations.
  - More flexible array of methods and monitoring technology to potentially identify unknown compounds at low concentrations in a time-sensitive manner.

Measurement Challenges

- Methods development research needs exceed available resources.
- New monitoring requirements and emergency situations continually strain existing resources.
- Ability to investigate new complex environmental issues are constrained by resources.

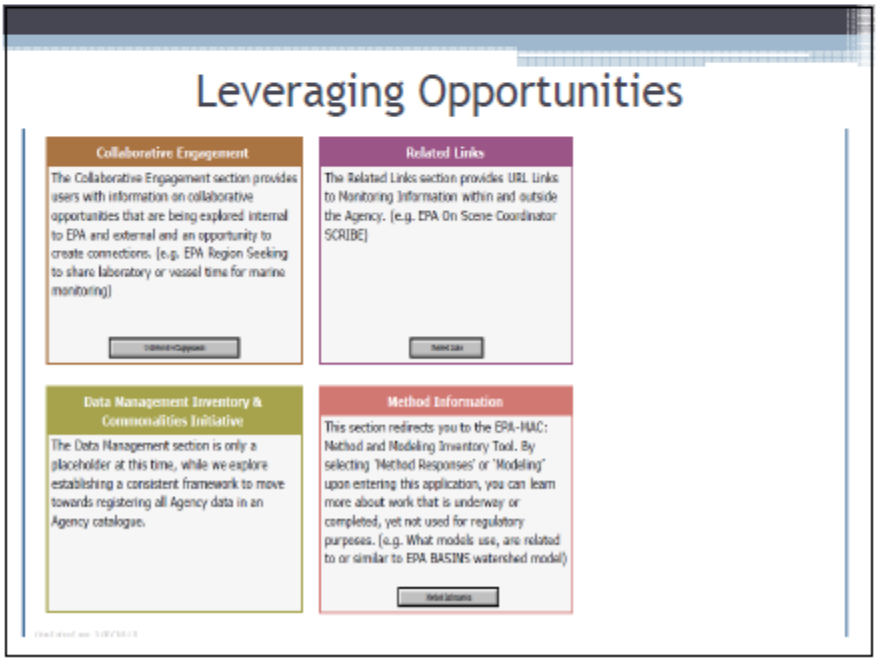
RESOURCES!!!



MonITOR - Agency System

- Access to an inventory of routine monitoring programs where you can both search for information and enter additional information.
- Access to a list of needs and data gaps across Agency programs for discovering potential project opportunities and sharing them.
- A collaborative toolbox of programs and 'want ads listing' for seeking engagement/ expertise to leverage opportunities.
- Method development activities and solutions.


Data Gaps & Needs Inventory
EPA United States Environmental Protection Agency
LEARN THE ISSUES
SCIENCE & TECHNOLOGY
LAWS & REGULATIONS
ABOUT EPA
Advanced Search
A-Z Index
EPA Home > MonITOR Home
Contact Us
Share
Monitoring Information, Technology & Opportunities Resources
MonITOR
At the direction of the Science and Technology Policy Council (STPC), the Forum on Environmental Measurements (FEM), with participation from all Agency program and regional offices and the Office of Research and Development (ORD), evaluated the Agency's monitoring programs. This assessment resulted in the creation of MonITOR to establish a sustainable mechanism for our programs to share:
an inventory of routine monitoring programs across the Agency;
a list of needs and data gaps; and
a list of collaborative opportunities.
This website acts as a conduit to link EPA's information for monitoring programs with EPA monitoring data gaps and needs. This website additionally provides information to link users to various monitoring methodologies and programs throughout EPA. A key feature of the MonITOR site is the ability for users to examine potential collaborative leveraging opportunities and links between current monitoring programs and the identified monitoring needs and gaps.
Login
User Name:
Password:
Create a Login | Reset Password
Quick Links
Background/History
Monitoring Program Inventory
Data Gaps & Needs Inventory
Collaborative Engagement
Related Links
Data Management Inventory & Commonalities Initiative (Coming soon)
Method Information
Monitoring Program Inventory
The Program Monitoring Inventory provides searchable information on current monitoring programs and databases funded and/or used by EPA. (e.g. EPA Lead Monitoring Program and FDA Pesticide Residue Program)
Data Gaps & Needs Inventory
The Monitoring Gaps & Needs enables the searchable viewing of data gaps and needs that were identified by Agency program and Regional offices and ORD. (e.g. EPA ORD request for Monitoring Air Contaminants from CAFOs)


Leveraging Opportunities
Collaborative Engagement
The Collaborative Engagement section provides users with information on collaborative opportunities that are being explored internal to EPA and external and an opportunity to create connections. (e.g. EPA Region Seeking to share laboratory or vessel time for marine monitoring)
Related Links
The Related Links section provides URL Links to Monitoring Information within and outside the Agency. (e.g. EPA On Scene Coordinator SCRIBE)
Data Management Inventory & Commonalities Initiative
The Data Management section is only a placeholder at this time, while we explore establishing a consistent framework to move towards registering all Agency data in an Agency catalogue.
Method Information
This section redirects you to the EPA-MAC: Method and Modeling Inventory Tool. By selecting 'Method Responses' or 'Modeling' upon entering this application, you can learn more about work that is underway or completed, yet not used for regulatory purposes. (e.g. What models use, are related to or similar to EPA BASINS watershed model)

The Agency is working to . . .

. . . support more method development.
. . . establish a framework to register all data.
. . . enforce data quality.



Through . . .

. . . funding opportunities.
. . . exploring projects of mutual interest with collaborators.
. . . outreaching to partners with mutual interest.
. . . examining exiting systems and programs.

Collaborative Engagement



- Small Business Opportunities
  - http://www.epa.gov/osbp/
- Grants and Fellowship Information
  - http://www.epa.gov/epahome/grants.htm
- Partnership Programs
  - http://www.epa.gov/partners/index.htm
- Cooperative Research and Development Agreements

What is next . . .

- Continuously Identify Project Needs
- Explore the Use of Existing Tools and Systems
- Establish More Internal and External Collaborative Relationships
- Find New (and Existing) Funding Opportunities
- Continue Outreach to Stakeholders



Summary

- The issues we face are more complex and subtle than in the past; so, the need for the best science is greater than ever now.
- There is a need for more flexible, innovative methods and monitoring technology to identify potentially unknown compounds at low concentrations in a time-sensitive manner.
- Much has been accomplished, but there are always new challenges and, unfortunately, emergency response situations to be faced.
- Collaboration with partners within and outside of the Agency provides leveraging opportunities for greater success in cleaning-up our world's environment.



Contact Us

Lara P. Phelps
Phone: 919-541-5544
E-mail: phelps.lara@epa.gov

- Office of the Science Advisor
  - http://www.epa.gov/osa
- Forum on Environmental Measurements:
  - http://www.epa.gov/fem

SDWA Perspective on Pesticide Monitoring

Andrew Eaton
Eurofins Eaton Analytical Inc.

Abstract

USEPA has been developing pesticide methods for drinking water analysis since the early 1990s. Most of the methods promulgated before the advent of the Unregulated Contaminant Monitoring Rules (UCMR1, UCMR2, UCMR3) were either GC or GCMS methods and were very prescriptive in nature. This was largely because the SDWA REQUIRES EPA to specify methods for compliance monitoring.

Beginning with the Contaminant Candidate List (CCL), and the start of monitoring programs under the UCMRs, EPA's approach to pesticide monitoring under the SDWA evolved in multiple ways.

1) The drinking water program began utilizing LC-MS-MS methods to a much greater extent
2) There are more options built into the methods
3) Preservation & holding time studies are much more rigorous than in earlier methods
4) MRL determinations are much more rigorous, using the LCMRL concept
5) Reporting limits are being pushed down into the ppt range.
6) The drinking water program is revisiting some of the older methods and letting vendors assist with improvements, as long as there are multi-lab validations and LCMRL determinations.

Under the UCMR3 program, less than a dozen laboratories were able to gain approval for the more sophisticated methods, which did not even include pesticides. Multi lab validation studies for newer EPA drinking water pesticide methods have shown that some analytes are much more rugged than others, and because EPA is committed to ensuring that new drinking water methods can be used by a reasonably large number of labs, some of the newer methods are ending up with shorter analyte lists than EPA would probably like. As interest continues to evolve in lower and lower levels, the EPA drinking water program will also likely continue to evolve and use more advanced analytical techniques, such as direct injection LC-MS-MS and online pre-concentration, while still trying to ensure that these analytical methods are available to a sufficient number of laboratories.



Andrew Eaton, Ph.D., BCES
Lab Technical Director

Eurofins Eaton Analytical Inc.
Monrovia, CA 91016

The SDWA Perspective on Pesticide Analysis

Presentation Outline



A brief history of drinking water standards and methods

General trends in methods

Impact of new technologies

UCMR3 – Harbinger for the future for SDWA?

The future?

A Global Perspective on Standards



- US drinking water standards (and hence methods) have historically focused on health limits (also a regulatory requirement)
- EU standards have focused on the "precautionary principle" and used "group" concepts
- WHO standards have focused on health, but not with the same constraints, but also considered emerging contaminants

So typically regulatory limits are WHO > EPA >> EU

# of analytes with regulatory limits EPA > WHO >> EU

eurofins | Eaton Analytical

3

US Drinking Water Methods Did Not Start Out Focused on Ultra-Low Levels



- Current regulations for drinking water quality essentially became important with the Public Health Service and **were predominantly inorganics.**



7. RECOMMENDED ANALYTICAL METHODS

7.1 Analytical methods to determine compliance with the requirements of these Standards shall be those specified in *Standard Methods for the Examination of Water and Wastewater*, Am. Pub. Health Assoc., current edition and those specified as follows.

- Methods came from Standard Methods
- The Safe Drinking Water Act, first promulgated in 1974, authorized EPA to set standards AND specify methods.



eurofins | Eaton Analytical

4

Safe Drinking Water Act (1974)



The first 18 interim standards were set in 1975 for:

- six synthetic organic chemicals (man-made chemicals which contain carbon, such as pesticides)
- ten inorganic chemicals (substances of mineral origin that do not contain carbon)
- turbidity (the cloudiness of water)
- total coliform bacteria (bacteria that are used as indicators of fecal contamination in water) [9]

eurofins | Eaton Analytical

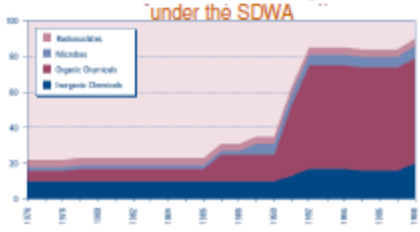
5

Drinking Water Standards- 1975-2000



- 1976 – Radionuclide regulations
- 1979 – THM regulation
- 1986 – the 83 contaminants…. (also mandated EPA to regulate 25 new contaminants every 5 years)
- 1996 – Set the framework for the concept of the UCMR (requiring utilities to monitor and report unregulated contaminants of public health concern)

Number of contaminants regulated under the SDWA



eurofins | Eaton Analytical

6

SDWA Regulatory Process



Current Approach

- 1996 SDWA Amendments
- Plan-Do-Check-Act

Contaminant Candidate List (CCL)

- CCL1 – March 1998 (60 contaminants)

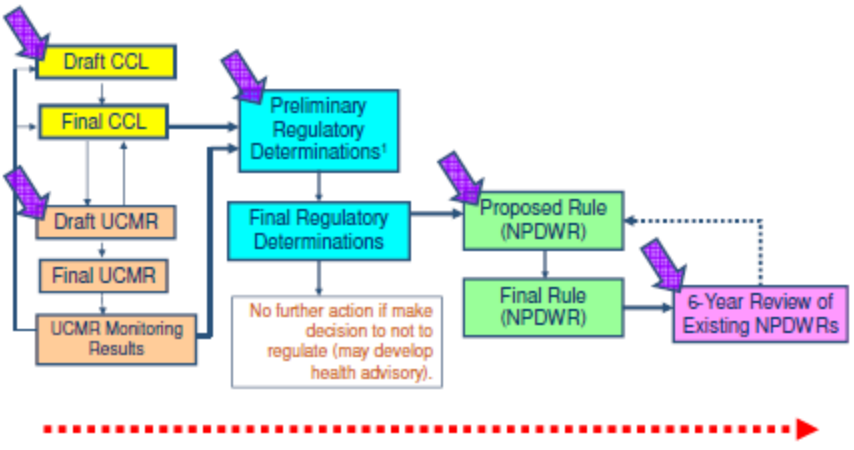
Unregulated Contaminant Monitoring Rule (UCMR)

- UCMR1 – Sept. 1999 (26 contaminants)

eurofins | Eaton Analytical 7

SDWA Regulatory Process -Opportunities for Impacting It





eurofins | Eaton Analytical

Three Criteria Used to Determine Whether or Not to Regulate



EPA is required to develop an MCLG and MCL for a contaminant if the Administrator determines that:

1. The contaminant may have an adverse human health effect [CCL]
2. The contaminant occurs or is likely to occur in drinking water at a level of public health concern [UCMR]
3. Regulation of the contaminant presents a meaningful opportunity for health risk reduction [Regulatory Determination]

USEPA Analytical Methods 1975- 2000



- 1970s – Main source of methods was Standard Methods
- 1979-1983 - Manual for Chemical Analysis of Water and Wastes
  - Essentially an inorganic methods manual
- 1987 – First EPA methods for DW organics (VOCs)
- 1992-95 – First EPA DW methods for SemiVoa/Pesticides
- 1994-2000 – Updates to Inorganic Methods and elimination of many old methods

2000 to the Present – Game Changing ERA



Drinking Water Standards	Analytical Methods
• Information Collection Rule →	ppb levels of DBPs
• UCMR1 (2001-2005) →	Perchlorate at 4 ppb MRL. MRLs for Compounds HRL driven (example: nitrobenzene)
• UCMR2 (2008-2010) →	LC-MS-MS and GC-MS-CI methods introduced, but only nitrosamines at sub ppb levels
• UCMR3 (2013-2015) →	Almost entirely sub 0.1 ppb MRLs Method sensitivity driven

eurofins | Eaton Analytical

11

UCMR1 – Limited Pesticides and "High" MRLs



- USEPA 525.2, USEPA 515.4,
  - All routine in drinking water labs
  - MRLs in the 0.5 ppb and up range
- USEPA 526,
  - New method, but still reasonable (ppb) MRLs
- Note: Lots of "non pesticides" in UCMR1

eurofins | Eaton Analytical

12

UCMR1 - Results



- We saw DCPA (Dacthal) commonly (~5% of systems), but at levels well below WELL ESTABLISHED health reference levels
  - Nobody really cared….
  - EPA made a conscious decision to NOT regulate DCPA
- All the other pesticides
  - Essentially no detects

eurofins | Eaton Analytical 13

UCMR2 Pesticide Methods, MRLs, Results

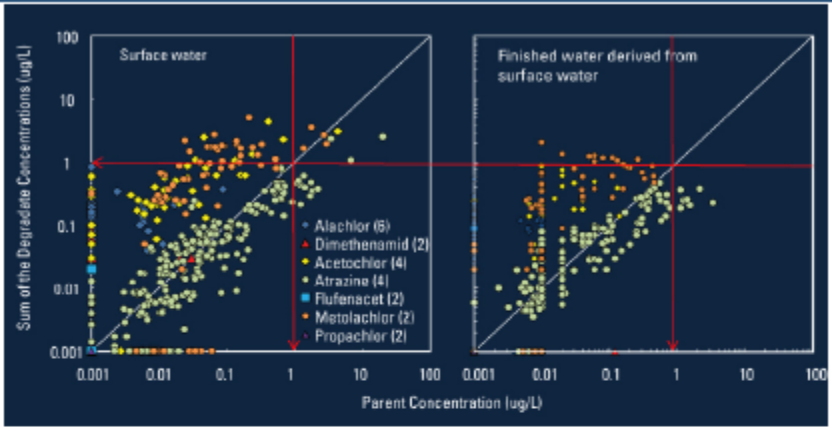


- Almost all brand new methods
  - 525 (again), 535 (first LC-MS-MS method),
  - but still ppb range reporting limits
- 525/535 paired to look for degradates
  - EXPECTED to see acetanilides and degradates frequently
  - MRLs set at 1 to 2 ppb, based on HRLs
- But the ONLY thing EPA really saw were nitrosamines
  - mainly NDMA in >25% of systems

eurofins | Eaton Analytical 14

Acetanilides: the Impact of MRL AND Sampling Period Selection





In contrast, UCMR2, with MRLs of 1-2 ppb, had <0.1% detects of these compounds, but the degradates did represent 90% of the hits

eurofins | Eaton Analytical

Data from Delzer (ASDWA, 2012) 15

Changes in Perspective for UCMR3



- Low frequency of detects for UCMR1 and UCMR2
  - Why are we monitoring non-detects?
- Results for acetanilide herbicides were counterintuitive
- Wrong compounds? Or wrong levels? Or wrong frequency?
  - EPA opted to focus on the "wrong levels" issue
- Hence UCMR3 changed from being HRL driven to being MRL driven (mostly…)

eurofins | Eaton Analytical 16

Another Factor Influencing Where EPA is Going



- Development of the LCMRL concept to establish reporting levels
- Minimizing the DL/MDL for SDWA compliance
- But making MRLs much more rigorous in determination
  - PIR concept
  - Validation daily

eurofins | Eaton Analytical 17

UCMR3 Analytes – Generally Method Driven Limits



- Metals by 200.8 - 0.2 to 1 ppb MRLs (prior 1 – 10 ppb)
- Hexavalent chromium – 0.03 ppb MRL
- 1,4-Dioxane – 0.07 ppb MRL
- VOCs – 0.03 to 0.2 ppb MRL (current 0.5 ppb)
- PFCs – 0.01 to 0.09 ppb MRL (methods can go lower…)
- Hormones – 0.0001 to 0.0008 ppb MRL
- Chlorate – 20 ppb MRL

NOTE THAT ARE ACTUALLY NO PESTICIDES IN UCMR3

eurofins | Eaton Analytical 15

UCMR3 MRL Comparison with UCMR1/UCMR2 MRLs



- For organics the UCMR3 MRLs are
  - 100-1000x LOWER than UCMR1&2 (except nitrosamines)
- For metals the UCMR3 MRLs are
  - 10-100X lower than perchlorate in UCMR1
- Only chlorate has a "high" MRL
  - i.e. > 1 ppb

eurofins | Eaton Analytical 19

So What Do the Low MRLs Mean?



- As chemists we know there is no such number as "0", so there is an inherently greater likelihood of detection as we look lower.
  - How much greater is the critical question
- Do the health effects numbers justify looking this low?
  - Will this provide communications challenges?
- Are the lessons we learned in geochemistry and oceanography relevant for new methods?
  - As we go lower, can we truly trust the results?

eurofins | Eaton Analytical 20

New SDWA Methods – Continuing the Trend of Trace Contaminants…



- Most of EPA's methods development work in the last 5 years has been focused on:
  - Pushing MRLs much lower (e.g. 522, 524.3, 539)
  - Using LC-MS-MS direct injection or SPE techniques to identify less volatile compounds
    - 536 (triazines and degradates) 50 ppt….
    - 537 (PFCs) 10-100 ppt…
    - 538 (organophosphates) 50-500 ppt…
    - 539 (hormones) 0.1-1 ppt…
    - 540 (CCL3 organics) 10-100 ppt…

eurofins | Eaton Analytical 21

Other Things in the Works at EPA for Drinking Water



- It generally takes EPA 2-3 years to develop and finalize a method, particularly when they are trying to respond to requests for increased flexibility.
- Recent UCMR4 stakeholders webinar demonstrated some of this development
  - Reaching out for comments to chemists
  - But not always receptive to comments…

eurofins | Eaton Analytical 22

Challenges as We Go Lower

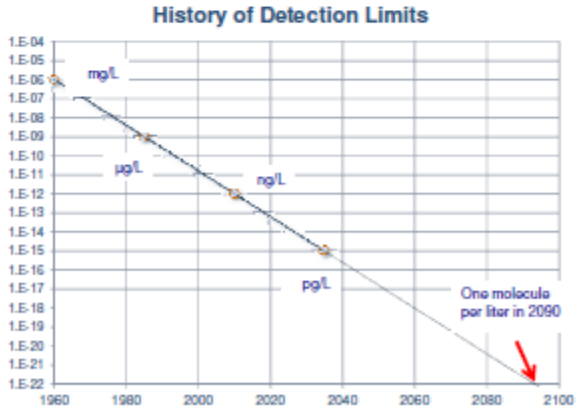


- Instrument sensitivity is not a real issue
  - The LCMRL is a good concept in PRINCIPLE
  - But defining "MRLs" is…and EPA still doesn't have that as rigorous as it might be…
- Samplers are not trained on proper precautions
  - Lessons from oceanography…
- Many drinking water labs are not used to these levels
  - Potential for blank contamination
- UCMR3 will give EPA a feel for how labs do at these levels

eurofins | Eaton Analytical 23

Analytical Technology is Truly Driving Drinking Water Evaluation





But, surely there is a point where it means nothing

It also means we can't afford to keep up by buying more and more treatment – or more and more expensive instruments…

courtesy of Dr. Rhodes Trussell

eurofins | Eaton Analytical

Conclusions



- As analytical methods have improved, our "goals" as far as identifying contaminants have improved.
  - And the public becomes more "aware"
- EPA SDWA perspective has also "changed the rules" in that analytical methods (and "groups") seem to now be driving regulations rather than health effects.
- With the reduction in minimum reporting levels, the frequency of detection will increase (UCMR3 already demonstrates that) and labs will have to be sure results are dependable and defensible.

eurofins | Eaton Analytical

25

Any Questions?



Dr. Andy Eaton
Technical Director
andyeaton@eurofinsus.com

Eurofins Eaton Analytical, Inc.
www.eatonanalytical.com
750 Royal Oaks Drive
Monrovia, CA 91016 USA

Monitoring Pesticides in the Environment: Past, Present and Future

Shen-yi Yang
U.S. EPA Office of Resource Conservation and Recovery

Abstract

The SW-846 methods are being used by various programs, including RCRA, Superfund, TSCA, and Homeland Security. ORCR deals with complex wastes and materials that are being managed or used in many different ways (e.g., landfilling, land application, incineration, recycling, etc.). The thresholds for analytes in a waste (or a material) are calculated from risk models, vary pending on the volume and form of the waste (or material), and how it is managed (or used), therefore, the thresholds are not set values as MCLs for drinking water or NPDES permit levels for monitoring point-source discharges.

ORCR strongly supports the performance approach and follows this approach in the RCRA testing program to the extent feasible. See http://www.epa.gov/fem/approach.htm for more information about the Performance Approach. To better analyze various wastes and materials, ORCR develops sample preparation and determinative procedures for extraction, clean-up, concentration and analysis that are specific for various sample matrices. For the analysis of total and/or leachable concentrations of pesticides in a solid or a waste, as described in Chapter Two of the SW-846 Methods Compendium, analysts can select methods for extraction (3500 series), and/or leaching (1300 series). The resulted extract and/or leachate can then be cleaned (3600 series), concentrated, and analyzed (8000 series). Analysts should select and combine appropriate methods for the desired target analytes in the matrix of concern, at the level of concern, to meet project-specific data quality objectives.

ORCR has developed determinative procedures for various organic chlorine pesticides, organophosphorus-, organonitrogen-, organosulfur- pesticides, herbicides, carbamates, and its related compounds in extracts from solid and liquid matrices using GC/ECD (Method 8081, 8151), GC/AED (Method 8085), GC/FPD or NPD (Method 8141), HPLC (Method 8318) and GC/MS (Method 8270). In these GC- and HPLC- methods, the presence of compounds may be confirmed by a second column or advanced technique (e.g., GC/MS). In 2012, ORCR made available a new determinative procedure that uses GC/NICIMS (Method 8276) for the analysis of technical toxaphene and 8 environmentally significant congeners in various environmental matrices, including groundwater, soil, sediment and fish.

When having a new analytical method is necessary and resources are available, ORCR will form a focus group for the development and validation of the new method. ORCR will collaborate with scientists from inside and outside of EPA who have interest, extensive knowledge and experience in working with the study compound(s) and/or analytical technology. The validated method will then be reviewed and approved for publication for inclusion in SW-846, by the RCRA Organic Work Group.

Monitoring Pesticides in the Environment: Past, Present and Future

The RCRA Perspective



Shen-yi Yang

Office of Resource Conservation and Recovery

Environmental Measurement Symposium

August 5, 2013

SW-846 Methods

- Developed and being used for characterization, monitoring, remediation and re-use of wastes and materials;
- Being used to support various EPA programs, including RCRA, CERCLA, TSCA, and Homeland Security;
- Deal with a wide variety of matrices, including waste and materials, environmental media, and biota;
- To better deal with complex matrices and to generate useful and defensible data for risk decisions, ORCR has separate methods for sample preparation and determinative analysis:
  - Inorganic analytes – digestion (3000 series) or leaching (1000 series), and determinative analysis (6000 and 7000 series)
  - Organic analytes – extraction (3500 series) or leaching (1000 series), and cleanup/concentration (4000 series) and determinative analysis (8000 series)
- Therefore, the project team needs to design appropriate analytical strategy to prepare and analyze samples for the analytes and matrices of interest at the levels of their concern.

2

Past

Prior to 2007 –

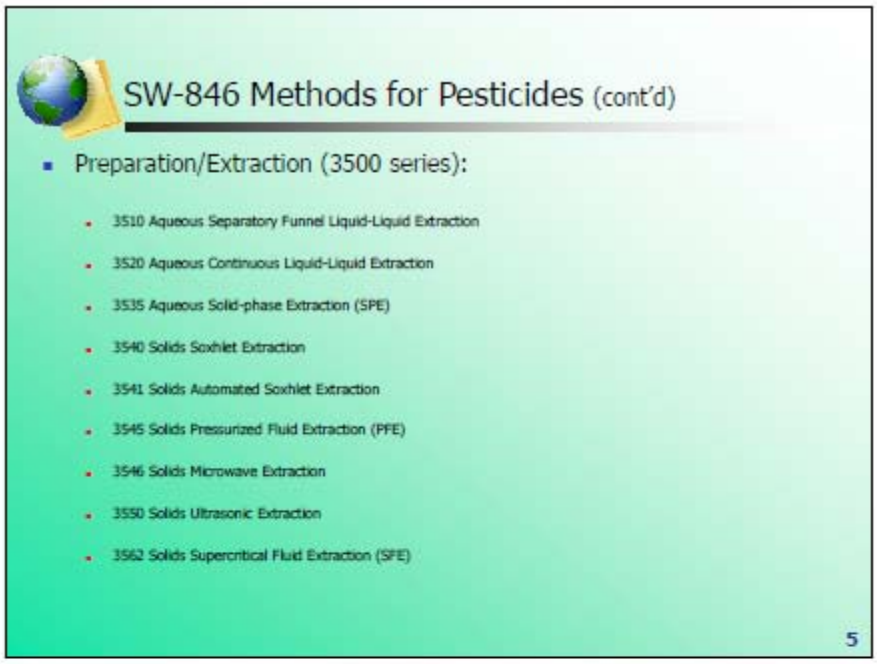
- SW-846 methods were developed for the analysis of pesticides that are listed in Toxicity Characteristic (TC), Appendix VIII (hazardous constituents) and Appendix IX (groundwater monitoring for hazardous waste treatment, storage and disposal (TSD) facilities):
  - Using GC with ECD, ELCD, FPD, or NPD detector(s) with second column or MS confirmation (Methods 8081, 8085, 8141 and 8151);
  - Using GC with MS (Method 8270);
  - Using HPLC with fluorescence (Method 8318);
  - Using HPLC, reverse phase, with MS or UV detection and internal/external standards quantitation, with an option of using MS/MS with collision activated dissociation (CAD) or wire-repeller CAD (Method 8321).
- EPA Office of Pesticide Programs (OPP) Analytical and Environmental Chemistry Laboratories also have methods available.

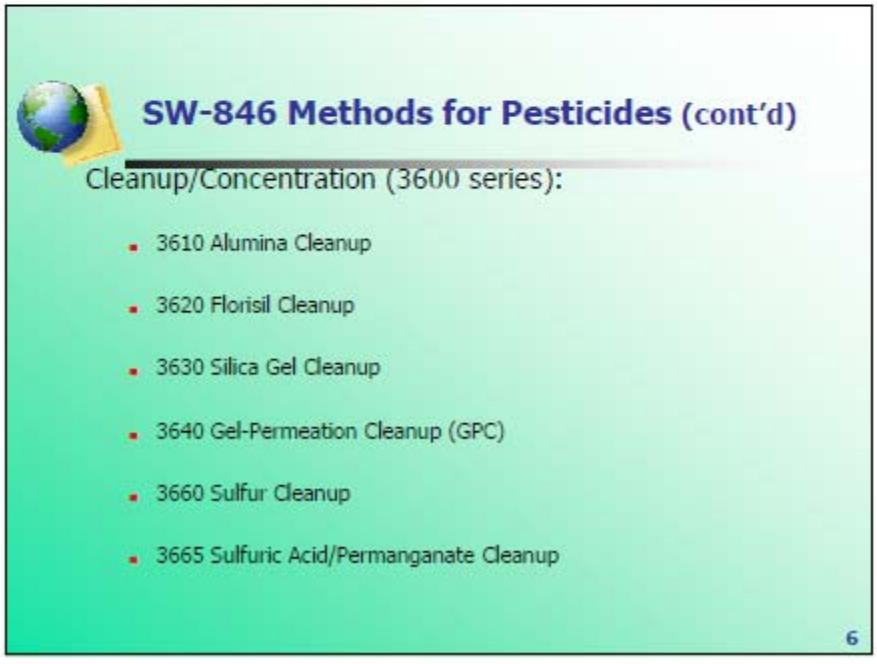
3

SW-846 Methods for Pesticides

- Screening using immunoassay (4000 series):
  - 4040 Soil Screening for Toxaphene by Immunoassay
  - 4041 Soil Screening for Chlordane by Immunoassay
  - 4042 Soil Screening for DDT by Immunoassay
  - 4051 Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Immunoassay
  - 4670 Triazine Herbicides as Atrazine in Water by Quantitative Immunoassay

4


SW-846 Methods for Pesticides (cont'd)
Preparation/Extraction (3500 series):
3510 Aqueous Separatory Funnel Liquid-Liquid Extraction
3520 Aqueous Continuous Liquid-Liquid Extraction
3535 Aqueous Solid-phase Extraction (SPE)
3540 Solids Soxhlet Extraction
3541 Solids Automated Soxhlet Extraction
3545 Solids Pressurized Fluid Extraction (PFE)
3546 Solids Microwave Extraction
3550 Solids Ultrasonic Extraction
3562 Solids Supercritical Fluid Extraction (SFE)
5


SW-846 Methods for Pesticides (cont'd)
Cleanup/Concentration (3600 series):
3610 Alumina Cleanup
3620 Florisil Cleanup
3630 Silica Gel Cleanup
3640 Gel-Permeation Cleanup (GPC)
3660 Sulfur Cleanup
3665 Sulfuric Acid/Permanganate Cleanup
6

SW-846 Methods for Pesticides (cont'd)

Determinative Analysis:

- 8081 organochlorine pesticides using GC/ECD or ELCD;
- 8085 semivolatile organohalide, organophosphorus, organonitrogen and organosulfur pesticides using GC/AED;
- 8141 organophosphorus pesticides, triazine herbicides, and carbamates and related compounds using GC/FPD or NPD or ELCD;
- 8151 certain chlorinated acid herbicides and related compounds using GC/ECD;
- 8270 using GC/MS;
- 8276 technical toxaphene and congeners using GC-CINI/MS;
- 8318 N-methylcarbamates using HPLC;
- 8321 organophosphorus compounds, phenoxyacid herbicides, and carbamates by HPLC/TS/MS (or UV detection) with the selected reaction monitoring (SRM) mode to provide greater sensitivity. An optional confirmation procedure is also provided to employ MS/MS with collision activated dissociation (CAD) or wire-repeller CAD.

7

Current

Recent 5 years (2008 to 2013)-

- ORCR has looked into degraded compounds from pesticides that are persistent in the environment and ecosystems using GC/MS and internal standards quantitation;

  Example -
  - Method 8276 – Determine toxaphene and toxaphene congeners by GC-NICI/MS;
  - As recommended by OIG, OSWER was directed by the EPA Deputy AA to develop a new analytical protocol for toxaphene degradation products;
  - ORCR worked with ORD and Region 4 to develop a new method (8276);
  - Method 8276 was validated by 8 labs for groundwater, soil, and sediment and posted on RCRA Methods website for public comment and use in March 2010.
  - Method 8276 was expanded to include fish and was posted on RCRA Methods website in Sept. 2012.
- Degraded compounds in the environment and ecosystems may or may not be the same as pesticide residues in foods;
- Methods with advanced technology are (being) developed by universities, private industry and EPA chemists for the analysis of new pesticides and degraded pesticide products in air, water and foods;

8

Future

- When needed and resources are available, ORCR will collaborate with method developers and stakeholders to validate new methods for inclusion in SW-846;
- ORCR has been in the past and will continue to collaborate with method developers and stakeholders for methods development/revision, evaluation, and approval
  - Validation studies (single and multi-labs)
  - ORCR Methods Focus Groups and Workgroups
- Suggestions??

9

Relevant Contact Information THANKS!!!

- Methods Team Home Page: www.epa.gov/SW-846
- MICE
  - Phone: (703) 818-3238
  - E-mail: mice@techlawinc.com



- Shen-yi Yang
  - Phone: (703) 308-0437
  - E-mail: yang.shen-yi@epa.gov

10

Pesticide Analysis: Now and in the Future?

Robert Wyeth

Abstract

Laboratories across the country have been utilizing US EPA methods to analyze select organochlorine, organophosporus and other pesticides for years. With the persistence and potential impacts of these organic constituents in the environment, these analyses using existing methodology will continue to be required. However many of these chemicals are no longer in use and attention also needs to be directed at other pesticide materials currently in use. This presentation will review current pesticides being utilized, their persistence, potential health effects and what, if any, methods are available to assess their potential impacts on human health and the environment.

Pesticide Analysis Now and in the Future

Robert Wyeth
Independent Consultant
West Seneca, NY

What is a Pesticide

A pesticide is any substance or mixture of substances intended for:

- Preventing
- Destroying
- Repelling, or
- Mitigating any pest

Refers to insecticides, herbicides, fungicides and various other substances used to control pests (insects, animals, unwanted plants, fungi and microorganisms).

Types of Pesticides

Chemical pesticides

- Carbamate pesticides
- Organochlorine insecticides
- Pyrethroid pesticides

Biopesticides

- Microbial pesticides
- Plant incorporated protectants (PIP)
- Biochemical pesticides

More

- Algicides
- Antifouling agents
- Antimicrobials
- Attractants
- Disinfectants
- Biocides
- Disinfectants
- fumigants
- Herbicides
- Insecticides
- Miticides
- Mollusicides
- Nematicides
- Pheromones
- Repellents
- Rodenticides
- Defoliants
- Dessicants
- Insect growth regulators
- Plant growth regulators

World and U.S. Amount of Pesticide Active Ingredient Used

By Pesticide Type, 2006 and 2007 Estimates

Year	Type	World Market		U.S. Market		U.S. % of World Market
		Mil lbs	%	Mil lbs	%	
2006						
	Herbicides (1)	2,018	39%	498	44%	25%
	Insecticides	955	18%	99	9%	10%
	Fungicides	519	10%	73	6%	14%
	Other (2)	1,705	33%	457	41%	27%
	Total	5,197	100%	1,127	100%	22%
2007						
	Herbicides (1)	2,096	40%	531	47%	25%
	Insecticides	892	17%	93	8%	10%
	Fungicides	518	10%	70	6%	14%
	Other (2)	1,705	33%	439	39%	26%
	Total	5,211	100%	1,133	100%	22%

Note: Totals may not add due to rounding. Does not include wood preservatives, specialty biocides, and chlorine/hypochlorites.

(1) "Herbicides" include herbicides and plant growth regulators.

(2) "Other" includes nematicides, fumigants, and other miscellaneous conventional pesticides, and other chemicals used as pesticides such as sulfur, petroleum oil, and sulfuric acid.

Source: EPA estimates based on Croplife America annual surveys, USDA/NASS, and EPA proprietary data.

Most Commonly Used Conventional Pesticide Active Ingredients, Agricultural Market Sector, 2007, 2005, and 2003Estimates (Ranked by Range in Millions of Pounds of Active Ingredient)

Active Ingredient	Type	2007		2005		2003	
		Rank	MM of lbs	Rank	MM of lbs	Rank	MM of lbs
Glyphosate	Herbicide	1	180-185	1	155-160	1	128-133
Atrazine	Herbicide	2	73-78	2	70-75	2	75-80
Metham Sodium	Fumigant	3	50-55	3	39-44	3	45-50
Metolachlor	Herbicide	4	30-35	5	27-32	6	28-33
Acetochlor	Herbicide	5	28-33	6	26-31	5	30-35
Dichloropropene	Fumigant	6	27-32	4	30-35	7	20-24
2,4-D	Herbicide	7	25-29	7	24-28	4	30-35
Methyl Bromide	Fumigant	8	11-15	8	12-16	8	13-17
Chloropicrin	Fumigant	9	9-11	10	9-12	9	9-12
Pendimethalin	Herbicide	10	7-9	9	9-12	10	9-12
Ethephon	Plant Growth Regulator	11	7-9	11	8-10	15	6-7
Chlorothalonil	Fungicide	12	7-9	13	7-9	14	7-9
Metam Potassium	Fumigant	13	7-9	20	4-6	20	4-6
Chlorpyrifos	Insecticide	14	7-9	15	6-8	13	7-9
Copper Hydroxide	Fungicide	15	6-8	12	8-10	12	7-9
Simazine	Herbicide	16	5-7	17	5-7	17	6-7
Trifluralin	Herbicide	17	5-7	14	7-9	11	8-10
Propanil	Herbicide	18	4-6	18	4-6	18	5-7
Mancozeb	Fungicide	19	4-6	16	6-8	16	6-7
Aldicarb	Insecticide	20	3-4	21	3-5	25	4-6

Regulatory Perspective

EPA regulates the use of pesticides under the authority of two federal statutes: the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and the Federal Food, Drug and Cosmetic Act (FFDCA).

Analysis for pesticides is performed consistent EPA methods for air water and soil, the FDA Pesticide Analysis Manual (PAM) and AOAC methods. NIOSH and OSHA have methods for pesticides.

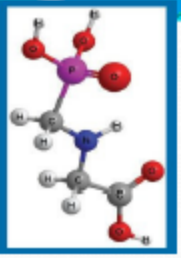
Manufacturers are also required to submit analytical test methods as a part of their required registration.

Methods are available from EPA's Office of Pesticide Programs (OPP) Analytical and Environmental Chemistry Laboratories

Focus on Top 10

1. Glyphosate
2. Atrazine
3. Metham Sodium
4. Metolachlor
5. Acetochlor
6. Dichloropropene
7. 2,4-D
8. Methyl Bromide
9. Chloropicrin
10. Pendimethalin

GLYPHOSATE



Glyphosate [N-(phosphonomethyl)-glycine]is a non-selective herbicide that works by stopping the plant from producing an enzyme it needs to make protein for proper growth. Glyphosate is widely used in agriculture, industrial weed control, forestry, and in outdoor residential applications. It comes in a number of chemical forms but most of the formulated products contain the isopropylamine salt. The toxicity of glyphosate is influenced by the surfactant in the product.

Round-up by Monsanto is an example glyphosate.

Glyphosate Analysis

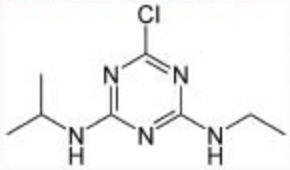
Glyphosate is a post emergent herbicide which rapidly degrades in the environment. Due to its heat sensitivity and polar nature, amongst other chemical properties, analysis methods utilize ion/liquid chromatography.

Methods also include aminomethylphosphonic acid (a primarily degradation product) and glufosinate (a compound simliar to glyphosate in chemical structure and use).

Glyphosate Methods

- EPA Method 547 LC/Fluorescene with post column derivitatization (water)
- USGS 01-454 LC/MS with SPE (water)
- OSHA PV2067 LC/UV after deriviatization (air)
- Numerous literature articles virtually all liquid chromatography

ATRAZINE



Atrazine [2-chloro-4-(ethylamino)-6-isopropylamino) s-triazine] is widely used herbicide for control of broadleaf and grassy weeds. Effective in 1993, its uses were greatly restricted.

Analysis for Atrazine, with some exceptions, is multi-component analysis.

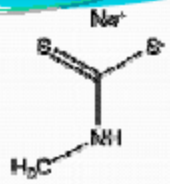
Due to ecological concerns over Atrazines and other Trazines, numerous methodologies are available for use in numerous matricies.

Atrazine Methods

Analyses are approved for use with GC (ECD or NPD detectors), GC/MS, Immunoassay and High Resolution GC/MS:

- EPA Methods 505, 507, 508.1, 525.2, 527 (with SPE), 1699 and 8141B with derivitization
- EPA Method 4670 (quantitative immunoassay)
- USGS Methods O-1121-9, O-2060-01, O-3106-93, and O-1126-95
- ASTM Method D5475

Metham Sodium (or Potassium) (methyldithiocarbamate salts)



Metham (or Metam) sodium is a soil fumigant used as a pesticide, herbicide, and fungicide. It is one of the most widely used pesticides in the United States, with approximately 50 million pounds used in 2007. Metham sodium is the sodium salt of methyldithiocarbamate. Other names include Carbathion, Carbathione, carbothion and metham sodium (or the potassium salt).

Upon exposure to the environment, metam sodium decomposes to form methyl isocyanate.

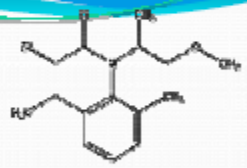
Metham Sodium Methods

No specific methods are currently referenced/available for analysis of Metham Sodium in environmental or related matrices.

Methods suggested based upon ability to analyze other dithiocarbamate type constituents include:

- EPA 630 and 630.1 (no compound specific), 8270D, 531.1, 531.2, and 8321 (LC/UV or LC/MS)
- USGS O-1126-95, O-1131-95 and O-1433-01

Metolachlor



Metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-2 methoxy-1-methyl) acetamide]is widely used as an herbicide. It is a derivative of aniline and is a member of the chloroacetanilide herbicides. It is highly effective toward grasses but its application is also controversial.

Metolachlor has been detected in ground and surface waters throughout the U.S. It is classified as a Category C pesticide by the US EPA which indicates limited evidence of carcinogenicity. Evidence of the bioaccumulation of metolachlor in edible species of fish as well as its adverse effect on the growth and development raise concerns on its effects on human health.

Metolachlor Methods

Numerous EPA are available fro Metolachlor including:

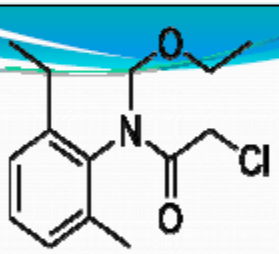
- Method 507 GC/NPD
- Method 508.1GC/ECD with LSE (C-18)
- Method 525.2 GC/MS with LSE
- Method 551.1 GC/ECD micro L/L
- Method 535 LC/MS-MS SPE (particularly applicable for degrades)

Other available methods include:

- ASTM D-5475
- USGC O-3106-93 GC/NPD SPE
- USGS O-1126-95 GC/MS SPE
- USGS O-1433-01 GC/MS SPE
- USGS O-1121-91 GC/MS SPE

A number of immunoassay techniques also available.

ACETOCHLOR



In the US, Acetochlor was registered by the EPA as a direct substitute for many herbicides of known concern. The EPA imposed several restrictions and conditions on the use of acetochlor. It is utilized as a pre-emergence application or for pre-planting application with soil incorporation particularly for corn. It's the main active ingredient in Acenit, Keystone, Guardian, Harness, Relay, Sacemid, Surpass, Top-Hand, Trophy and Winner. It is used to control weeds in corn, and is particularly useful as a replacement for Atrazine for many weeds.

Acetochlor Methods

Numerous EPA methods are available for analysis of Acetochlor including:

- Method 535 LC/MS-MS with SPE
- Method 526 GC/MS with SPE
- Method 525.2 C/MS with LSE

USGS also lists Acetochlor in methods:

- O-1126-95, -01 GC/MS with SPE
- O-1433-01 GC/MS with SPE
- O-2002-01 GC/MS with SPE

A number of immunoassay techniques are also available

Rounding out the Top 10

#6 Dichloropropene

- Soil fumigant (toline) amongst other uses, Method 1624 most prominent method of analysis. Numerous other methods also available.

#7 2,4-D (2,4-dichlorophenoxyacetic acid)

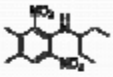
- common systemic pesticide/herbicide used in the control of broadleaf weeds. It is one of the most widely used herbicides in the world, and is the third most commonly used herbicide in North America.[lit] is a synthetic auxin (plant hormone). It was a major ingredient in Agent Orange alongside its chemically similar relative, 2,4,5-T ,4-D.
- Most prominent methods of analysis EPA 515.1 and 8151A, numerous methods including immunoassay also available

#8 Methyl Bromide (bromomethane)

- Until its production and use was curtailed by the Montreal Protocol, bromomethane was widely applied as a soil sterilant mainly for production of seed but also for some crops such as strawberries and almonds . In commercial large-scale monoculture seed production unlike crop production, it was of vital importance to avoid contaminating the crop other herbicides.
- Most prominent methods of analysis EPA 524.2, 8021, 624, 1624, and 8260B, numerous methods including immunoassay also available

#9 Chloropicrin [trichloro(nitro)propane]

- Chloropicrin is used as a fumigant to control pests found in the soil. Although less common, it can be used as a poison for vertebrates, such as rabbits. Chloropicrin is commonly used in combination with other fumigants, such as methyl bromide, for increased potency and as a warning agent. Chloropicrin has been used in chemical warfare.
- The only analytical method including chloropicrin is EPA Method 551.1 (GC/ECD with L/L)

#10 Pendimethalin 

- Herbicide used in pre-emergence and post-emergence applications to control annual grasses and certain broadleaf weeds which interfere with growth, development, yield and quality of agricultural and horticultural crops . It protects crops like wheat, corn, soybeans potatoes, cabbage, peas, carrots and asparagus.
- No methods are cited for pendimethalin but should be amenable to GC/NP or LC/MS technologies upon extraction. Manufacture method should be available from registration.

Environmental Fate and Ecotoxicology

Equally as important from a fate and toxicology perspective is the fate of these pesticides in the environment and what are their degradation products.

The advantage of many of these pesticides relative to historically used materials is their short half-life in the environment.

Studies, primarily by the manufacturer, provided upon registration, pr esent data on fate and ecotoxicology. A compilation of information (the Ecotoxicity Database and the Pesticide Fate Database) is managed by the EPA Office of Pesticide Programs and can be assessed through their offices.

Commercial Testing Industry Preparedness

While most of the currently used pesticides have references to applicable methodologies that should be directly useable or readily adaptable for use, few commercial laboratories are conducting these analysis today.

One significant reason to the commercial labs is lack of demand. But this is likely to change!

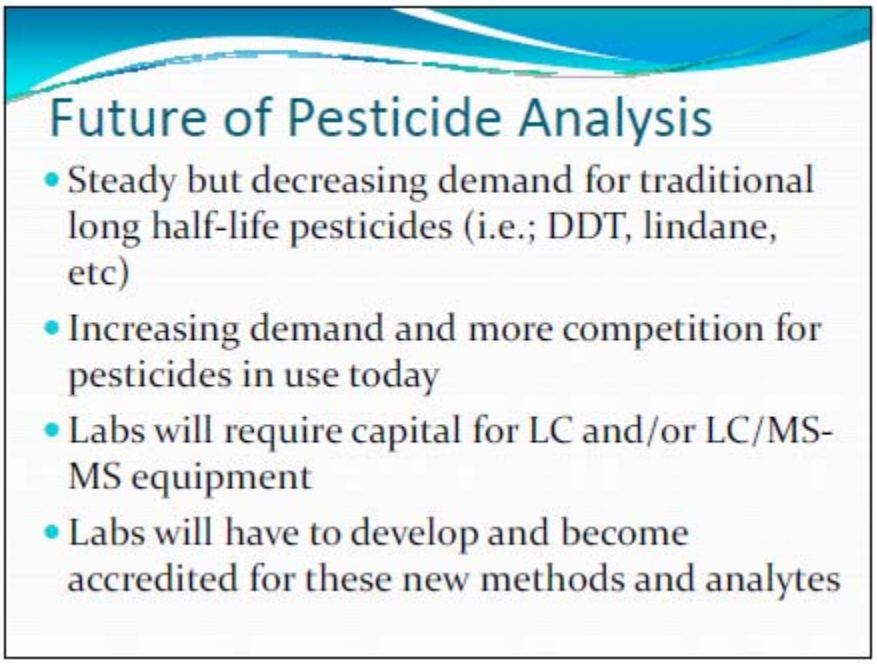
Pesticides in the Commercial Lab

Generally prepared to respond to requests for:

- Organochlorine pesticides
- Organophoshorus pesticides
- Herbicides

Almost always by GC (with selective detectors) or GC/MS.

Many labs still do not utilize or even have LC on-line let alone LC/MS-MS.


Future of Pesticide Analysis
• Steady but decreasing demand for traditional long half-life pesticides (i.e.; DDT, lindane, etc)
• Increasing demand and more competition for pesticides in use today
• Labs will require capital for LC and/or LC/MS-MS equipment
• Labs will have to develop and become accredited for these new methods and analytes

Changes in Technical Innovation and Customer Expectations Associated with the Use of LC-MS to Solve Challenges Encountered whilst Ensuring Food and Environmental Safety

Simon Hird

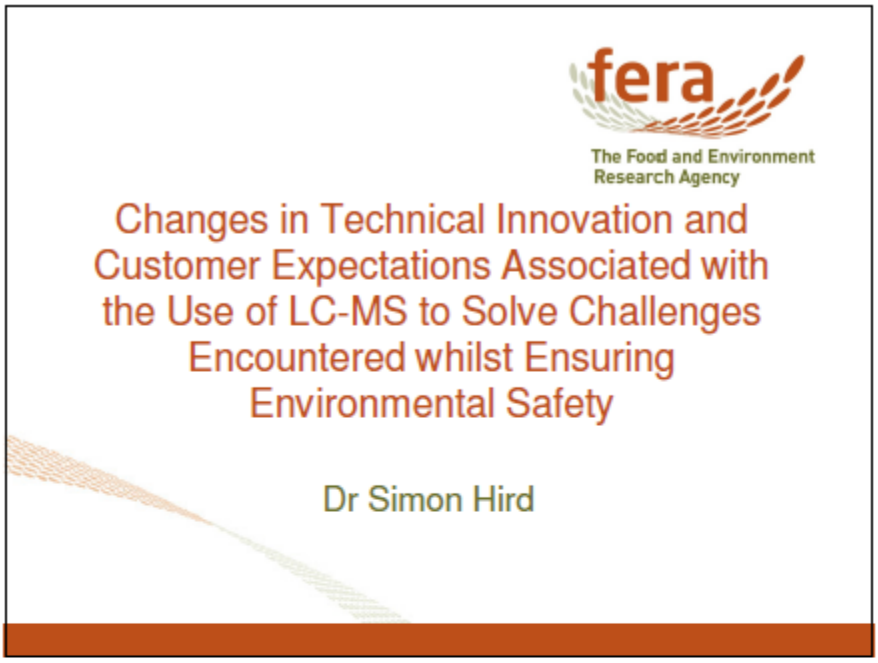
The Food and Environment Research Agency

Abstract

Pesticides and veterinary medicines are widely used to combat diseases and pests that adversely affect the production of vegetable and animal foodstuffs. Residues of those compounds can sometimes find their way to the human consumers via food, drinking water or contamination of the environment. The European Union (EU has defined statutory limits for such residues in an attempt to regulate the presence of such contaminants in the environment and food chain.

Residue testing supports the enforcement of legislation, to ensure trading compliance and to conduct surveillance in environmental samples and dietary components for assessment of consumer risk and compliance with good agricultural practice. In the UK pesticide residues are monitored by a variety of competent authorities. The Chemical Residues Directorate are responsible for managing the surveillance of a range of foodstuffs each year to check compliance with approvals and that the concentrations of residues do not exceed MRLs. Pesticide residues in drinking water are monitored by Water Supply Companies who report findings to the Drinking Water Inspectorate. The law essentially requires supplies to be free of residues. Pesticide residues in rivers, lakes and groundwater are monitored by the Environment Agency (or equivalent). MRLs, known as Environmental Quality Standards, have been set for a number of pesticides.

Residue testing historically relied on analytical strategies based on the combination of a variety of specific screening and confirmatory methods typically based on the use of GC-MS. With the exception of niche areas such as testing for antimicrobial activity in animal tissues, current approaches are dominated by multi-residue methods with generic extraction, probably no or very limited cleanup, followed by determination using GC-MS and LC-MS techniques. Such methods are fast, sensitive, informative and greatly reduce costs especially in terms of $/analyte. Today we are confident that we can successfully detect, quantify and identity almost any type of regulated residue at the level of interest in a wide range of foodstuffs, animal tissues or environmental samples using high throughput laboratory-based systems. However, the use of “cocktails” of drugs to promote growth in animals re-enforces the need for even greater sensitivity for targeted analyses. In addition, developments in both food and environmental testing have switched to searching for the unlikely and the unexpected including residues of pharmaceuticals. Non-targeted approaches are employed to capture more information on the composition of the sample (extract) or to compare samples and the identification of any unknown compounds that are detected constitutes a considerable challenge. In addition, attempts have been made to utilise rapid, direct analyses that either avoid the need for any chromatography or exclude the need for any extraction. This presentation explores the analytical transformations that have taken place during the previous decade, the drivers for change (and for maintaining the status quo) and the resulting shift in customer expectations.


fera
The Food and Environment Research Agency
Changes in Technical Innovation and Customer Expectations Associated with the Use of LC-MS to Solve Challenges Encountered whilst Ensuring Environmental Safety
Dr Simon Hird


fera
The Food and Environment Research Agency
Overview
• Introduction
• Implementing the EU Water Framework Directive
• Analytical approaches
• Targeted analysis
• Non-targeted screening
• Identification of unknowns
• Metabolite workflows
• Summary

Solving the problems of air, water and soil pollution within UK government

- Department of Environment, Food and Rural Affairs (Defra)
  - **Food and Environment Research Agency**
  - Environment Agency
  - Centre for Environment, Fisheries and Aquaculture Science
- Health and Safety Executive
  - Health and Safety Laboratory
- Independent bodies
  - Drinking Water Inspectorate

The Food and Environment Research Agency

- Executive agency of The Department for Food, Environment and Rural Affairs (Defra)
  - Turnover 2011/12 ca. £70 million
  - 950 staff
  - Main laboratories located near York
    - £135 M laboratory of 300,000 ft2 within a secure site of 80 acres
  - Customers are UK Government Departments, EU but **also many commercial organisations**

Laboratory facilities near York

fera
The Food and Environment Research Agency





Plant and crop protection
Food chain safety
Environmental risk assessment
Crisis response

Diverse interests…

fera
The Food and Environment Research Agency



Analysis for chemical safety and quality of our food

fera
The Food and Environment Research Agency



- Environmental contaminants
  - Dioxins, PCBs, PFCs, BFRs, metals …
- Natural toxicants
  - Mycotoxins, phycotoxins
- Residues
  - Pesticides
  - Veterinary medicines
- Processing contaminants
  - Acrylamide, furan, 3-MCPD…







Analysis for chemical safety and quality of our food

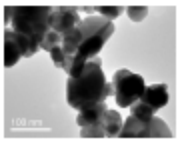
fera
The Food and Environment Research Agency

- Additives
  - Colours, sweeteners…
- Authenticity
  - Origin of food
- Deliberate adulteration
  - Melamine, "Sudan" dyes…
- Packaging migration
  - Bisphenol-A…
- Nanotechnology



"You may not feel any healthier right away, but you'll definitely feel more smug."



Environmental applications

fera
The Food and Environment Research Agency



- Monitoring
- Ecotoxicology studies
- Fate and behaviour of chemicals
  - Field studies
    - Pesticides in crops, soils etc.
    - Transport of chemicals
  - Degradation studies
    - Veterinary medicines in manure
  - Linked to QSAR modelling
  - Nanoparticles



Legislation within the EU

fera
The Food and Environment Research Agency

- EU has adopted a substantial and diverse range of environmental measures aimed at improving the quality of the environment
  - Member States have to implement the legislation
- One recent challenge has been the implementation of the EU Water Framework Directive (WFD)
  - Resulted in the updating of national water quality monitoring programmes across Europe

Water Framework Directive (Directive 2000/60/EC)

fera
The Food and Environment Research Agency

- EU water policy aims for good quality water for all
- Water Framework Directive (WFD) established a legal basis to protect and restore clean water across Europe
- Places special emphasis on the ecological quality of waters.
- Objective of the WFD is to get all water into a healthy state by 2015

Analysis required to support the Water Framework Directive

fera
The Food and Environment Research Agency

- Monitoring of priority substances and other pollutants, including new emerging substances, in surface waters
- It requires the implementation of temporal and spatial trend monitoring programs
- The use of integrative matrices (biota and sediments) is strongly recommended to achieve such objectives for hydrophobic substances
  - Not just about water analysis

Analysis required to support the Water Framework Directive

- The WFD lists Priority Substances as chemical pollutants that pose a significant risk to (or via) the aquatic environment at EU level
  - The most dangerous are listed as Priority Hazardous Substances
- Member States have to monitor their concentrations in target matrices and meet the Environmental Quality Standards (EQS)
  - Equivalent to the maximum allowable concentration but determined by ecological impact

Water Framework Directive

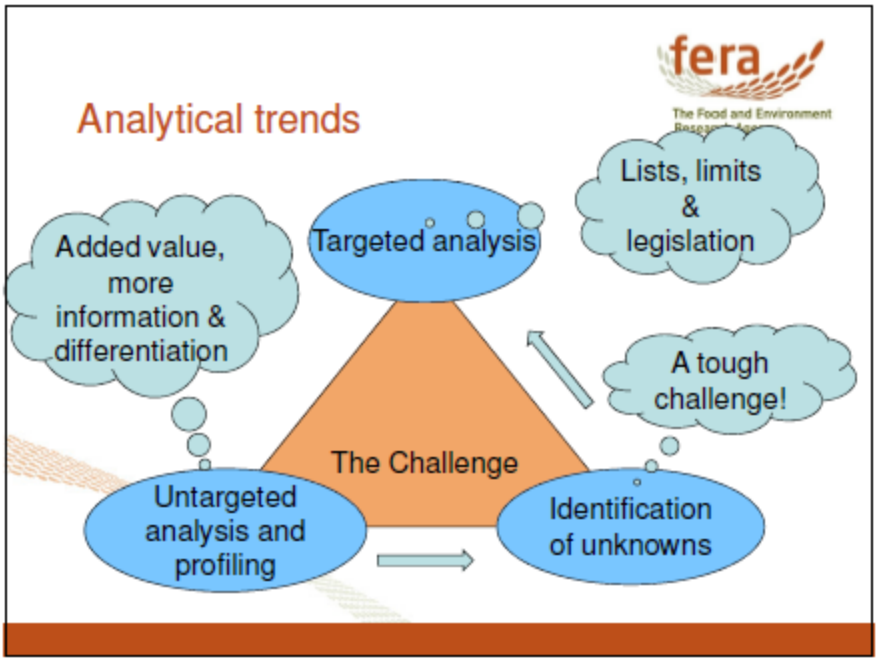
- Establishes minimum performance criteria for methods of analysis to be applied across the EU when monitoring water status, sediment and biota
- Demonstrating the quality of analytical results
  - Validated, implemented and documented in accordance with the ISO/IEC-17025 standard
  - LOQ must be ≤30% of the EQS with a maximum uncertainty of ± 50
  - Often challenging analytically!
    - *e.g.* EQS for cypermethrin in surface water is 80 pg/l

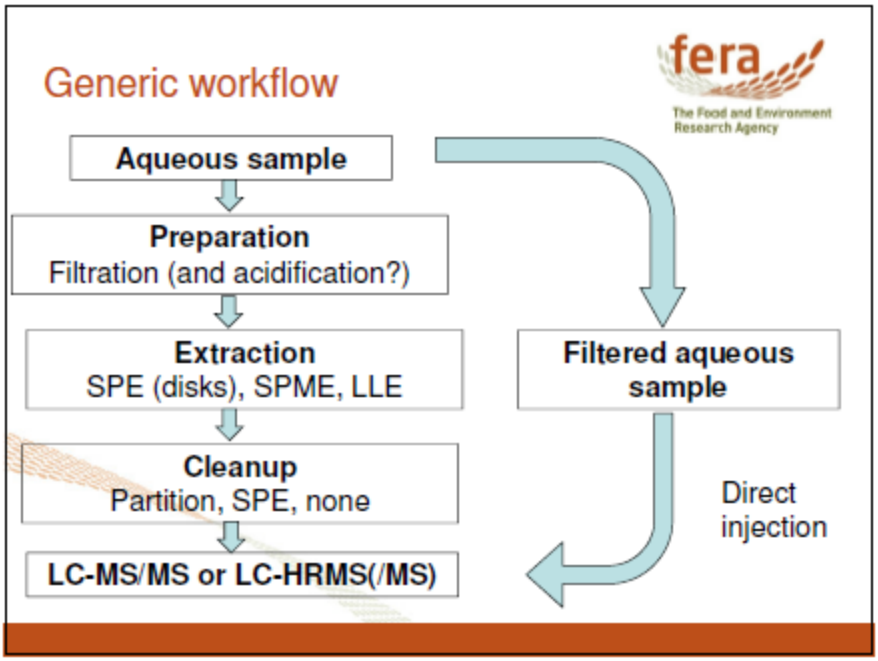
New substances recently added to WFD priority list

- Plant protection product substances:
  - Aclonifen, Bifenox, Cypermethrin, Dicofol, Heptachlor/Heptachlorepoxide, Quinoxyfen
- Substances used in biocidal products:
  - Cybutryne, Dichlorvos, Terbutryn Industrial chemicals: Perfluorooctane sulfonic acid (PFOS), Hexabromocyclo-dodecane (HBCDD)
- Combustion by-products:
  - Dioxins and dioxin-like PCBs
- Pharmaceutical substances:
  - 17-α-ethinylestradiol, 17-β-estradiol, Diclofenac

Analytical requirements

- Concern that not all analytical methods in current use are fit for the purpose of monitoring priority substances for compliance with EQS
- Need for innovative technologies with which to develop methodologies to facilitate rapid testing for organic contaminants to low levels of detection
- Various analytical approaches possible

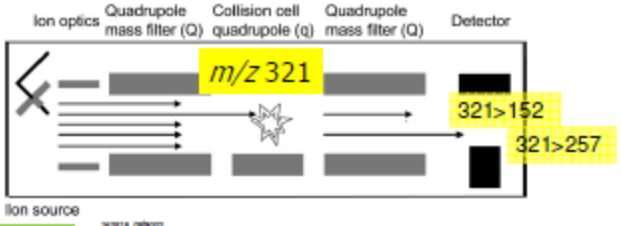

fera
The Food and Environment
Analytical trends
Lists, limits & legislation
Targeted analysis
Added value, more information & differentiation
A tough challenge!
The Challenge
Untargeted analysis and profiling
Identification of unknowns


fera
The Food and Environment Research Agency
Generic workflow
Aqueous sample
Preparation
Filtration (and acidification?)
Extraction
SPE (disks), SPME, LLE
Cleanup
Partition, SPE, none
LC-MS/MS or LC-HRMS(/MS)
Filtered aqueous sample
Direct injection

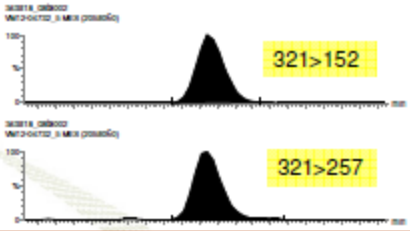
Targeted analysis using LC-MS/MS

- Having two analysers increases the selectivity that ensures interfering peaks from other analytes or matrix are rarely observed
- Less isobaric interferences
- Lower limits of detection become achievable
  - Direct injection of aqueous samples
- Provides a greater degree of confidence for identification
- Most common variant is the triple quadrupole

MS/MS selected reaction monitoring (SRM)



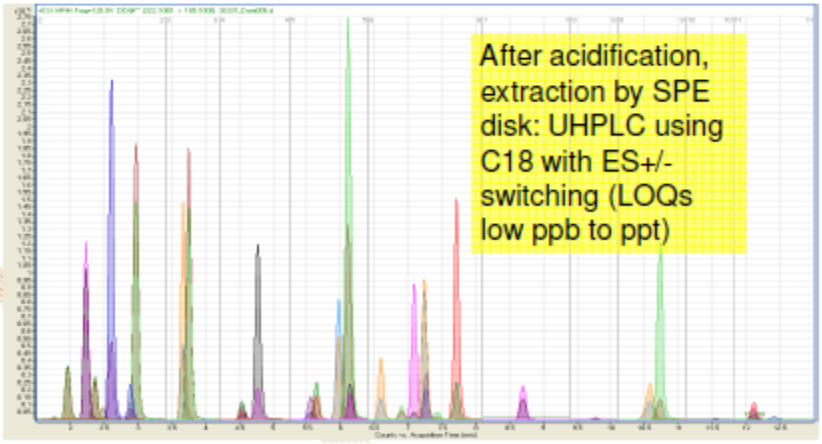
Identification through comparing ion ratios with those from standards



LC-MS/MS analysis of emerging contaminants

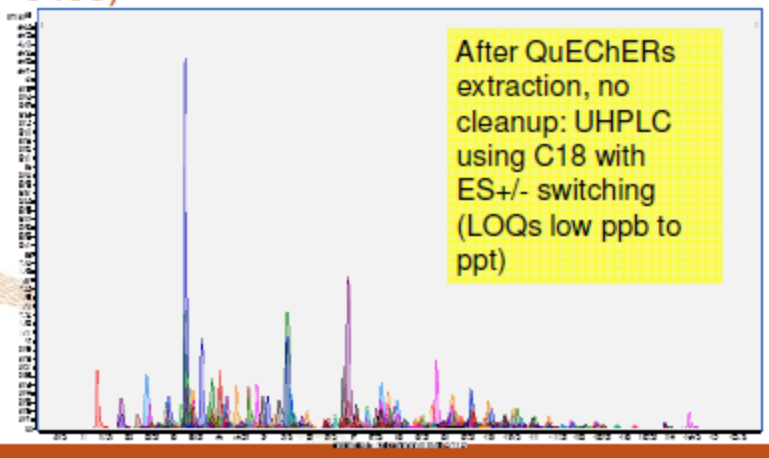
- Not all new substances!
  - Previously undetected or not considered a risk
- Pharmaceuticals
- Personal care products
- Pesticides
- Endocrine disruptors including
  - Perfluorinated compounds (PFCs)
- Fire retardants
- Transformation products of all of the above

32 pesticides from water using Agilent 1290-6460)



240 pesticides by UHPLC-MS/MS (SRM): Agilent 1290-6490)

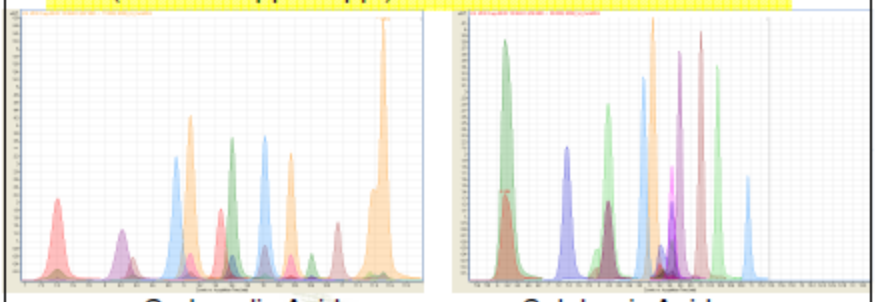
fera
The Food and Environment Research Agency



Perfluorinated compounds from mink using Agilent 1290-6490

fera
The Food and Environment Research Agency

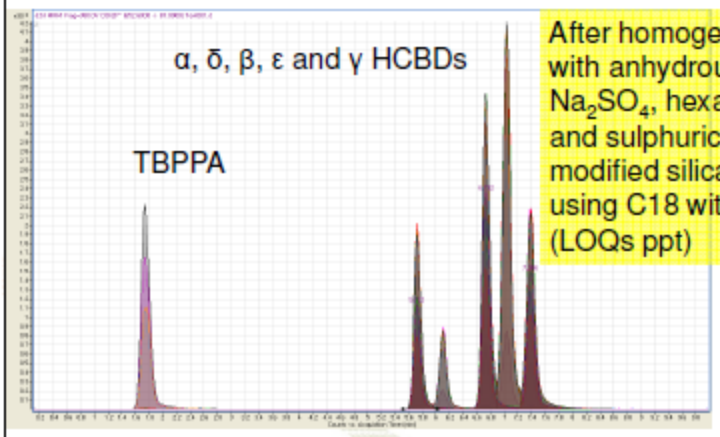
After homogenisation with methanol, partition with KOH and WAX SPE: UHPLC using a fluorinated column with ES- (LOQs low ppb to ppt)



Carboxylic Acids | Sulphonic Acids

Brominated fire retardants from fish using Agilent 1290-6460

fera
The Food and Environment Research Agency

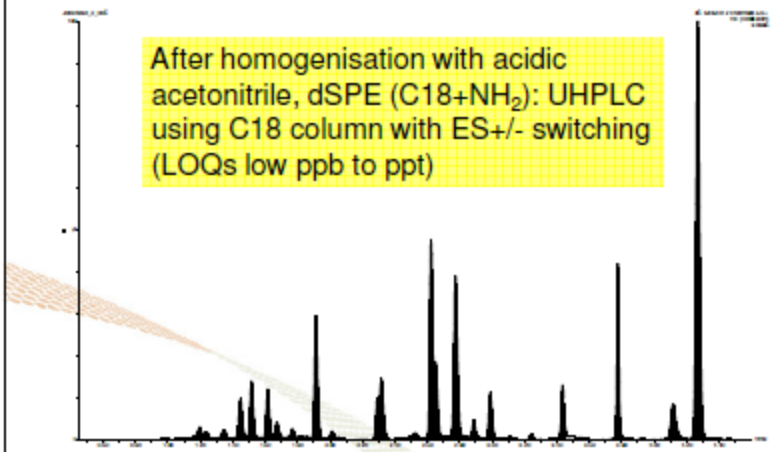


After homogenisation, with anhydrous Na_2SO_4, hexane/DCM and sulphuric acid modified silica: UHPLC using C18 with ES- (LOQs ppt)

Pharmaceuticals and veterinary medicines in farmed fish using Waters Acquity and Xevo TQ-S

fera
The Food and Environment Research Agency

After homogenisation with acidic acetonitrile, dSPE (C18+NH_2): UHPLC using C18 column with ES+/- switching (LOQs low ppb to ppt)

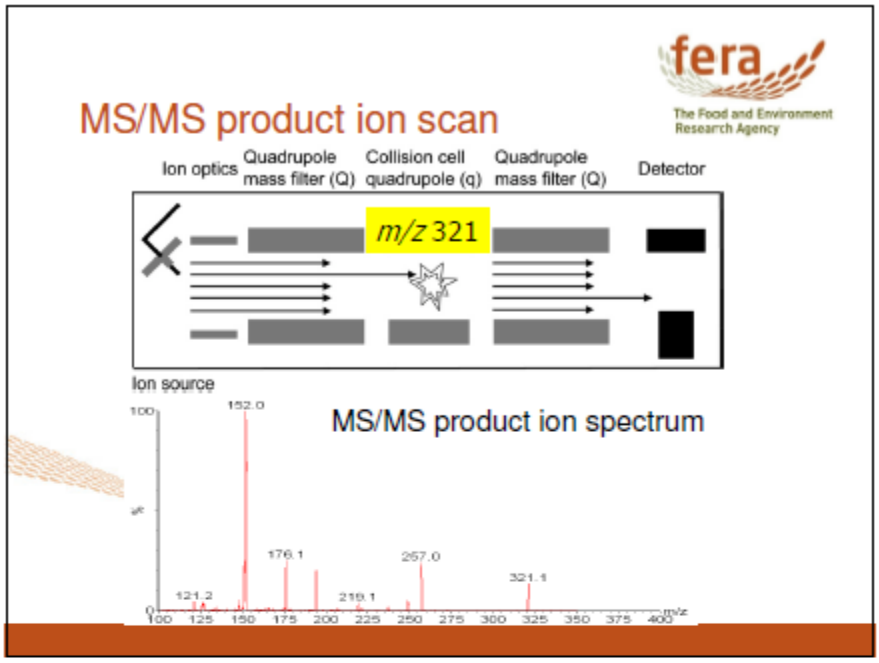


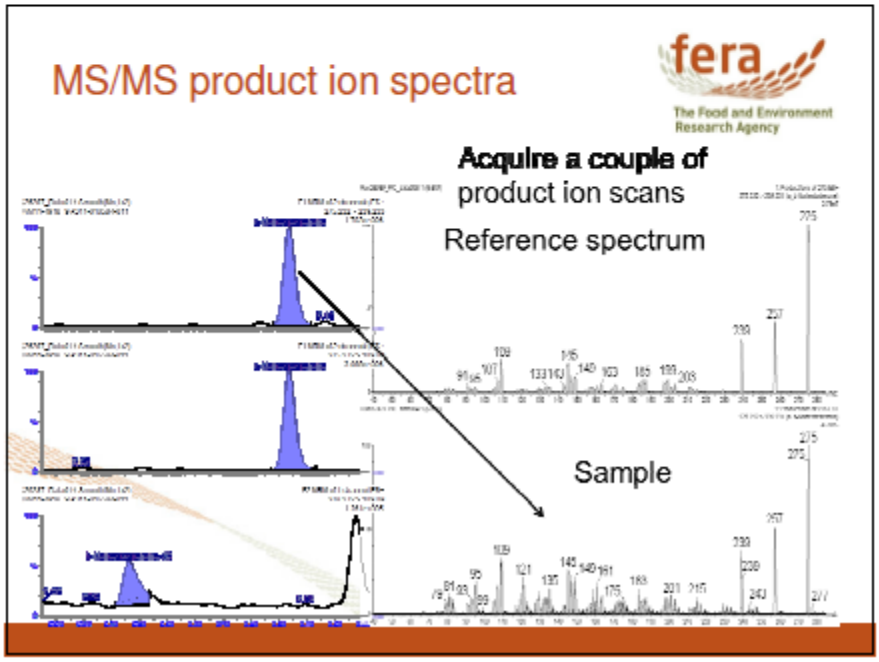
Trends in targeted analysis

- Transfer of methods from conventional to highly selective mass spectrometers
  - HPLC with UV and FD to LC-MS/MS
- Achieve required LODs/LOQs even in complex matrices
  - Simplifies sample extraction and clean-up
  - Opens up scope for multi component analysis
  - Reduce analysis times
- Must also provide unambiguous identification
  - Move away from ion ratios to MS/MS and mass spectral compound libraries?

Limitations with QqQ devices

- Scope of analysis limited to pre-programmed transitions selected
- Product ion scans (MS/MS)
  - An precursor ion of a particular *m/z* is selected in Q1, fragmented in the collision cell (q) and products scanned out from Q2
  - Slow scan speed limits the sensitivity of QqQ
  - Searching spectral libraries so no longer have to acquire data from a standard
- Quadrupole-linear ion trap hybrid (QqLIT)


MS/MS product ion scan
fera
The Food and Environment Research Agency
Ion optics
Quadrupole mass filter (Q)
Collision cell quadrupole (q)
Quadrupole mass filter (Q)
Detector
m/z 321
Ion source
MS/MS product ion spectrum
152.0
176.1
257.0
321.1
121.2
219.1


MS/MS product ion spectra
fera
The Food and Environment Research Agency
Acquire a couple of product ion scans
Reference spectrum
Sample

Limitation of targeted approach

- Need reference standards
- Need to program methods with RTs of analytes and specific transitions to monitor
- The targeted approach will fail to detect other contaminants present in the sample
  - Unable to go back and "mine" the data later

Trends in non-targeted analysis

- Transfer of methods from specific methodologies to those providing data for comparison with databases
- An alternative so-called "non-targeted" approach
  - LC-HRMS
    - Database searching via mass measurements
  - LC-HRMS/MS
    - Also provides spectral library searching
  - Non-targeted acquisition but initial data processing tends to be still targeted…

Non-targeted acquisition

- Use of "high resolution" instruments
  - Time of flight (ToF) or orbitrap mass analysers
  - Full spectral information
  - High mass resolving powers and mass resolution
    - Specifications vary significantly
  - Good mass accuracy
  - Good sensitivity through improved ion optics
  - Variable acquisition speeds

Holcapek *et al*. (2012). *J. Chromatogr. A* 1259: 3

Comparison of ToF with orbitrap

Mass analyser	Resolving power ($x10^3$)	Mass accuracy (ppm)	Acquisition speed (Hz)
Q	3-5	Low	2-10
IT	4-20	Low	2-10
Tof	10-60	1-5	10-100
Orbitrap	100-240	1-3	1-5

Q, ToF and orbitrap also include common hybrid configurations with Q or LIT as the first mass analyser providing MS/MS or MS^n capabilities

Data processing for screening

- Peak detection by extracting those ions matched with entries in a database
  - Can be psuedo molecular ions and fragments
- Recognition is based upon measurement of:
  - Accurate mass
  - Isotope pattern
  - Retention time (if available)
  - A response threshold
- Results are reported as a "hit list" with or without creating chromatographic peaks

Non-targeted screening

- In food safety data are rarely interrogated for analytes other than those in the database
- Emphasis has been on screening
  - The aim of validation for pesticides in food is to have no more than a 5% false-negative rate
- Methods and software parameters tend to be optimised to find a practical balance between reported false positives and false negatives

Non-targeted screening

- To be effective data processing must be automated and quick
- Minimise false negatives whilst generating a manageable number of false detects
  - Apply tolerances on response threshold, retention time and isotopic fit and the presence of a second diagnostic ion
- It requires more computing power and data management/storage than that traditionally associated with LC-MS analyses using QqQ instruments

Validation using samples that previously tested positive using LC-MS/MS

Agilent 1290-6230 ToF

Commodity (sample numbers)	Incurred samples	
	Automated - no intervention (± 5 mDa)	Data processing + Analyst intervention
Lettuce (10)	93%	97%
Grape (20)	93%	99%
Pear (20)	93%	94%

35 different pesticides, 169 residues, between 0.01 – 0.78 mg/kg

Non-targeted screening

- The scope of this approach is limited by the content and size of the database
- Screening for other compounds not listed the database is by deconvolution for detection and then assignment of a scored list of possible elemental formulae based upon measured mass and isotopic fit
- The most likely candidates are further scrutinised by employing additional data or by extra analyses

Trying to identify unknowns…

- Assignment of a structure for a peak detected by accurate mass alone is unlikely unless:
  - Compound detected has a significant mass defect between the monoisotopic mass of an element and the mass of its isotopic cluster
  - Is known in the chemical literature, a reference database or an internet resource
- The first crucial step is to obtain correct elemental compositions

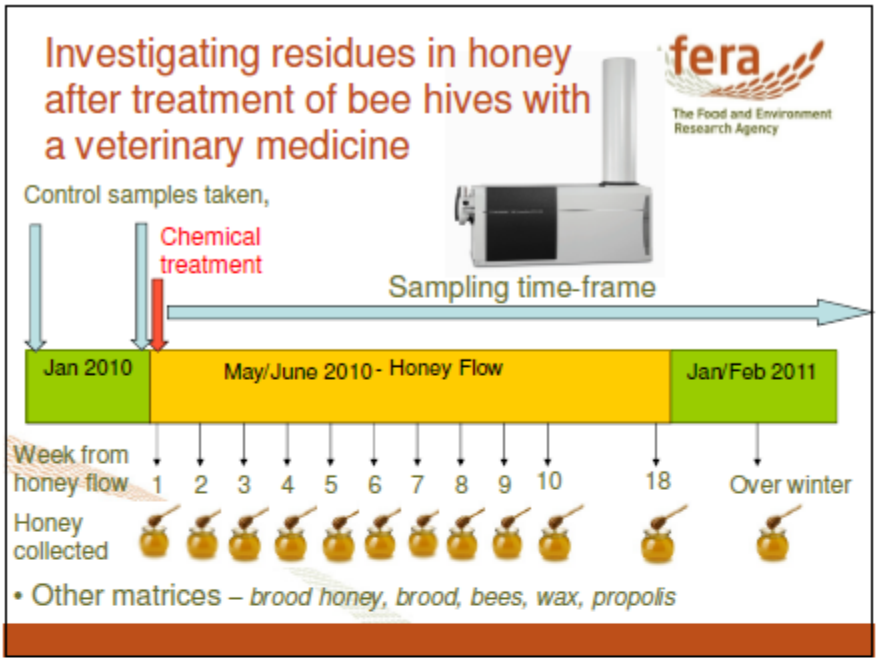
Trying to identify unknowns…

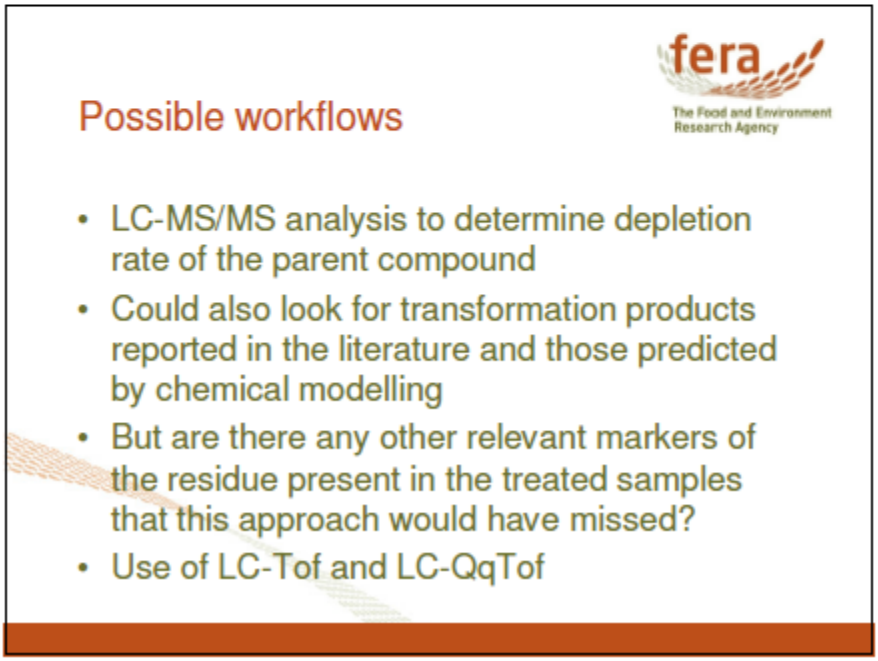
- Accurate mass measurement < 1 ppm
- Information about isotope pattern
- Fragmentation data from MS/MS or MS^n experiment
  - Accurate mass measurement of precursor and/or product
- *In silico* fragmentation or fragmentation trees to aid *de novo* characterisation

Work flows for investigating transformation products

- Use of work flows more associated with analysis of metabolites
  - Looking for differences between treated and control samples
    - Profiling as used for metabolomics
  - Looking for specific transformations
    - As used for metabolite identification




Investigating residues in honey after treatment of bee hives with a veterinary medicine
fera
The Food and Environment Research Agency
Control samples taken,
Chemical treatment
Sampling time-frame
Jan 2010
May/June 2010 - Honey Flow
Jan/Feb 2011
Week from honey flow
1 2 3 4 5 6 7 8 9 10 18
Over winter
Honey collected
• Other matrices – brood honey, brood, bees, wax, propolis


Possible workflows
fera
The Food and Environment Research Agency
• LC-MS/MS analysis to determine depletion rate of the parent compound
• Could also look for transformation products reported in the literature and those predicted by chemical modelling
• But are there any other relevant markers of the residue present in the treated samples that this approach would have missed?
• Use of LC-Tof and LC-QqTof

Looking for differences between treated and control samples

The Food and Environment Research Agency

Also called Tylosin B

Compound	Responses Control	Dosed	Mass	Retention Time /min
C10H14O9S	1	29501	310.0364	7.78
C29H39N15	1	48106	597.3501	9.36
C36H63N3O16	1	156943	793.4211	9.36
Desmycosin	1	920521	771.4407	9.36
C44H78N4O19	1	63375	964.5091	9.79
C47H78N2O17	1	78075	942.5303	9.79
1099.5529@9.8047	1	87355	1099.5529	9.80
C52H87NO22	1	56072	1077.5734	9.80
C38H63NO13	1	73486	741.4294	9.99
Tylosin A	1	2690789	915.5209	9.99
C38H63NO12	1	222141	725.4347	9.99
C44H71N7O15	1	330487	937.5005	10.00

- From 1288 entities detected, only 4 components were associated with hive treatment
- Proposed a number of possible empirical formulae
- 2 tentatively identified by comparison of RT with standards

Looking for specific transformations

The Food and Environment Research Agency

- Tentative identification of:
  - Parent (tylosin A)
  - Demethylation (tylosin C)
  - Glycosylation (glycosylated tylosin A)
- Missed
  - Tylosin B
    - Loss of mycarose not included as a transformation
- Need to have a good understanding of likely transformations in various environments

Summary of the two metabolite approaches

- Profiling the whole "fringerprint" *vs.* looking for specific transformations
- Assign molecular formula to accurate mass
- Assign likely structure to formula
  - Complimentary use of MS/MS
  - Need standards to generate a library
- Expert knowledge of the application optimises use of the software and need decent computing power
- Can be applied to environmental analyses

LC-MS does have an Achilles heel…

- Electrospray suffers from ion suppression from co-elution of co-extractive component
- Impacts upon:
  - "Detectability" and hence true reporting limit
  - Possible reporting of false negative results
  - Accuracy of quantification
- Applies to targeted, non-targeted and profiling
- Matrix-matching of calibrants and/or use of stable isotope analogues for correction

Future challenges

- Targeted analysis
  - More analytes in more samples, quicker, for less and with lower reporting limits…
- Untargeted analysis
  - Try to identify as much of the analytical data as possible from which the relevance and significance is determined by informatics
- Directed analysis?
  - Only identity the significant (*e.g.* "active", "toxic" or estrogenic) peaks/components…

Directed analysis

Genotoxic





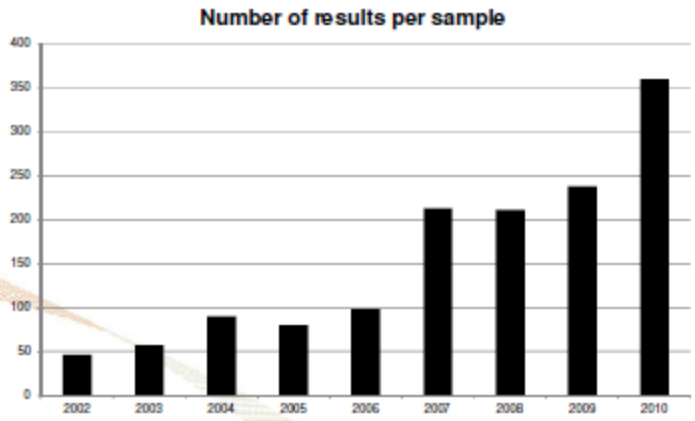




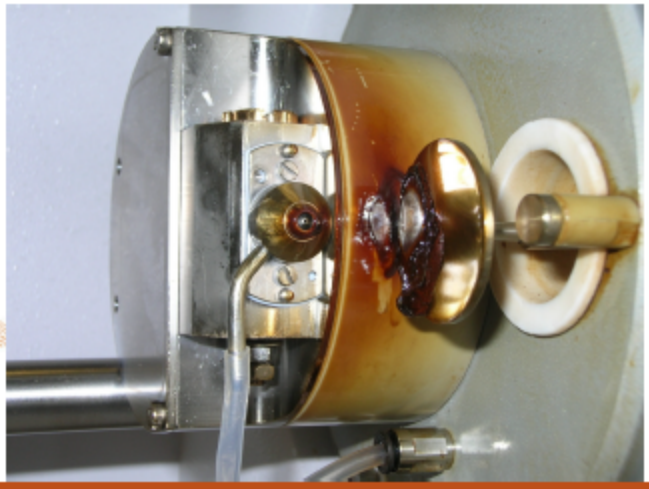
Summary

- Development of target compound analysis
  - Focus on multi residue approaches
  - Continued use of LC-MS/MS
  - Increased use of GC-MS/MS for non-polars
- Implementation of non-targeted approaches
  - Increased use of LC-HRMS
  - Database searching
  - Complimentary use of MS/MS libraries
  - Profiling and metabolite identification
- Customer expectations?

More for less…



Training is essential!



Acknowledgements

- Targeted analysis: LC-MS/MS team at Fera
- Non-targeted analysis: Richard Fussell and Tony Lloyd
- Transformation work: Richard Fussell, Danny Chan and Jonathan Tarbin
- CRD, VMD, FSA and various commercial organisations for funding
- Agilent Technologies, Waters and Thermo Scientific for support

The Analysis of Environmental Pesticides in Asia

Kory Kelly
Phenomenex

Abstract

In recent years there has been increased interest and concern regarding the monitoring of pesticides in Asian countries. This has been driven by two factors: 1) rapid industrialization of the region and the corresponding environmental impacts, and 2) globalization of the world food supply, with Asia fast becoming the primary origin of many agricultural commodities. In this dynamic, there is an increased risk for contamination of air, water, soil and food and effective environmental monitoring is critically important.

The quality and effectiveness of pesticide monitoring and analytical practice vary widely in Asia. It can range from primitive to highly advanced depending upon the level of sophistication of local analytical technology and the effectiveness of local regulatory and enforcement practices. The analytical methodology employed varies widely depending upon the extent to which US and European practices have been adopted and upon the level of local improvisation. In this presentation we will survey the analytical practices for pesticide analysis in several Asian countries and compare and contrast these with the more familiar US practices.

Analysis of Environmental Pesticides in Asia

Kory Kelly
Phenomenex

Introduction

- Pesticide pollution follows use and production
- Largest agricultural areas
  - China
  - India
  - South-East Asia
  - Korea
  - Pakistan
- Largest Pesticide Producers
  - India
  - China



Harmonization?

- Unlike the EU, no consistent regulation for all of Asia
- Southeast Asia →Food and Agricultural Organization of the United Nations (FAO)
- China and India running their own methods
- Different areas are analyzing their local pesticides
  - Exception : export crops may follow importer' s regulations

MINISTRY OF ENVIRONMENT AND FORESTS
Government of India

Analysis of Pesticides - China

- Largest consumer and second largest producer of pesticides in the world
  - Produces 850,000 tons/year
  - 2,600 manufacturing facilities
  - $190 Billion in agricultural business
- Immediate focus is on manufacturing safety
  - Largest exposures are reported to blowing dust, poor storage at manufacturing and local use levels
- Little use of protective equipment while applying pesticides
  - Does result in contamination and spills



Analysis of Pesticides – China (cont.)

- Environmental contamination is monitored by State Environmental Protection Administration (SEPA)
  - Established in 1988
- Specifics are left to each state
- Regulations are still evolving
  - Fipronil used on rice killed nearby shrimp farms
  - Carbofuran used has proven detrimental to red-crowned cranes
  - Aldicarb has resulted in large scale contamination of ground waters
- Environmental samples are analyzed like food samples, often in the same facilities



Analysis of Pesticides – China (cont.)

- Ministry of Agriculture regulates nearly 400 residue limits (crop based)
- Each province responsible for testing residues within the province (54 units doing testing)
  - Some state labs, some working with universities
  - Most using GC or LC (non-MS)
  - Oversight and enforcement not consistent
- Main focus is food for export, not environment
- Trailing production of new pesticides
  - >2500 new pesticide products since 2005.



China Summary

- Environmental analysis is required at the federal level, but specifics are left to the state levels.
- As of 2011, LC and GC were most common, but not for long
- Analysis is continually evolving, but mainly internally
  - Based upon exposure and experience
  - Methods and state regulations were reactionary
- Implementing strict regulations for food exports
  - When will environmental regulations catch up?



Analysis of Pesticides - India

- Sixth largest producer of pesticides
  - 85 Million metric tons (2011), $3.8 Billion
  - 55% are for export
  - Insecticides account for most production
- ~25 % of arable land registered as using pesticides



Analysis of Pesticides - India

- Insecticide Act, 1968 and the Insecticides Rules, 1971
  - Prevention of risk to human beings and animals
- Environment Protection Act, 1986
- Though rules exist, education and enforcement is very limited
  - Use of illegal pesticides
  - Spills, storage leaks, and illegal disposal
  - Farmers looking for immediate results
  - Labeling and usage not monitored
    - Monocrotophos kills 23 school children in June, 2013



Analysis of Pesticides – India (cont.)

- "According to the Alliance for Sustainable and Holistic Agriculture (ASHA), out of the top 15 most-consumed pesticides in India, 11 figure in the list of 67 globally-banned pesticides."
- Testing does occur
  - GCMS screening methods for 240+ pesticides that vary depending on the crop
  - Soil and water samples are also run, though rare
  - Insufficient infrastructure to adequately monitor
    - Most crops are locally grown by family farms



India Summary

- Testing procedures do exist and are relatively advanced.
  - GCMS is used, as well as ECD and NPD
- The frequency of food and environmental testing is sorely lacking
- Regulation focuses more on quality of pesticides than detection of residues or environmental contamination



South East Asia

- Recent collaboration under FAO from 2000
- Cambodia, Indonesia, Malaysia, Philippines, Thailand, Vietnam, Singapore, Lao Peoples Democratic Republic, Myanmar
- All countries were not consistent
  - Lists of pesticides
  - Procedures
  - Quality Control
  - Resources
- Pesticides were illegally being imported from other countries
- Harmonization based upon input from other organizations and documents (US FDA, EU, OECD, NAFTA, etc…)
- Programs approve, register, and monitor pesticides
- Continual work in progress (2000-2011+)



Trends by Country

- Malaysia – nine labs (1,000 samples / year; 2-3% > MRL)
  - Following Environmental Quality Act 1974 (air and waste)
  - Environmental Quality Act 1985 (waste from factories)
  - Food Act 1983
  - Department of Environment monitors the effects of pesticides in the environment
  - chlorpyrifos, profenophos, fenvalerate, cypermethrin, cyfluthrin, ethion, prothiophos, phosalone, dichlorvos and dithiocarbamate



Trends by Country

- Thailand – nine labs (60,000 samples / 8 years; 2-5% > MRL)
  - GC, LC, GCMS, LCMS
  - cypermethrin, chlorpyrifos, profenophos, triazophos and dimethoate
- Phillipines – six labs (4,300 samples / year; 2-4% > MRDL)
  - GC, GCMS, LC
  - cypermethrin, chlorpyrifos, profenophos and permethrin
- Vietnam – five labs (5,000 samples / year; 9.5% > MRL)



Summary Southeast Asia

- Some countries have previously developed methods
- Not everyone is at the same point
- Not all countries have the infrastructure to monitor domestically
  - Myanmar, Lao PDR, Cambodia
- Pesticides methods are still being harmonized
  - Resources and information are being shared

Korea

- Not officially participating in FAO program
- Have a developed pesticide program for foods and feeds
- Rather low rate of foods above MRL (<1%)
  - Farmers are notified of positive tests, resulting in probation
  - Testing at field, transportation, and retail sites
  - Testing for 252 compounds over 41 crops



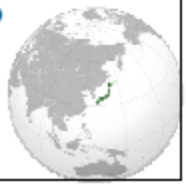
Japan

- A significant user of pesticides (~150,000 tons/year)
- Are a significant producer of pesticides (sixth in world)
- Import 34 million tons of agricultural products annually
- Developed program for testing toxic compounds for imported products
  - 2006 introduced a positive list of 758 compounds
    - Most are pesticides (~600)
    - Provided MRL based upon Codex toxicity data
    - Some compounds cannot be found at any levels
    - Each year approx 150 chemicals are re-examined



Testing???

- A Japanese import company is typically primarily responsible for import quality.
  - Exporter can test and certify through approved labs
- There is no one method to test for all of these compounds
- Some compounds are not amenable to GC
- Some compounds are not amenable to LC
- Both approaches are being used in parallel to achieve the greatest coverage



Positive List Testing

- Utilize both GC/MS and LC/MS/MS methods
- Japanese Ministry of Health, Labour, and Welfare (MHLW) provides methods for detection
  - >260 pesticides by GC/MS with SIM conditions, retention indices, ions, and detection limits.
  - 42 pesticides by LC/MS/MS with conditions, retention times, ions, and detection limits
  - 25 additional pesticides by LC/MS/MS
  - Provide extraction methods from vegetables, animals, fats, honey, milk, etc…



Further Information

- GC/MS methods have been published that analyze and quantitate >400 pesticides
- LC/MS/MS methods published identify and quantitate >160 pesticides
- There are analytical labs in the US that test for the positive list compounds
  - 3 Official labs
  - 23 Registered labs

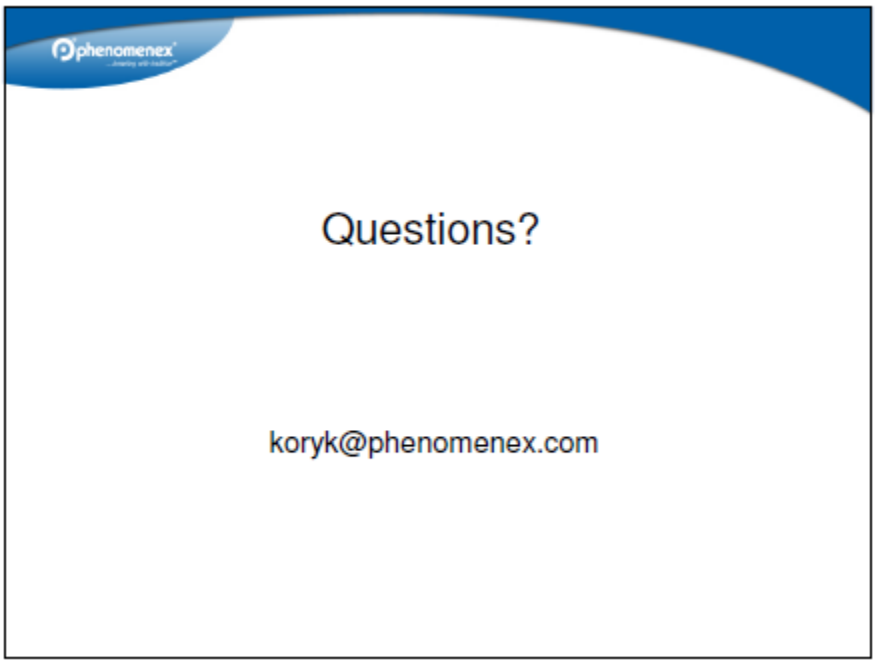


Scope of Pesticides Analysis

- Though environment is a priority, environmental analyses are not always separate
- Many regulations cover Water, Food, and Feed
  - Little mention of soils
- Most requirements are performance based and DON' T provide analysis guidelines
  - No column
  - No extraction technique
  - No analysis technique
  - Only safety levels

Trends of Pesticide Analysis

- This lack of prescriptive methodology has allowed methods to evolve
- Instrumentation is shifting from GC/ECD and GC/NPD to GC/MS and LC/MS/MS
- Analyte lists are growing
- Nobody has currently the full answer
  - If they did, it would already be out of date

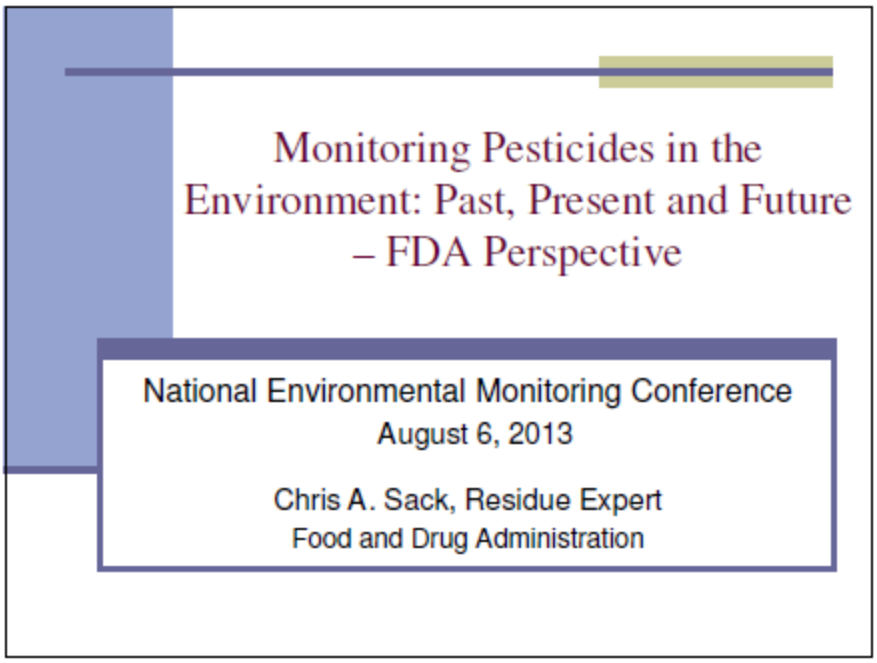

Questions?
koryk@phenomenex.com

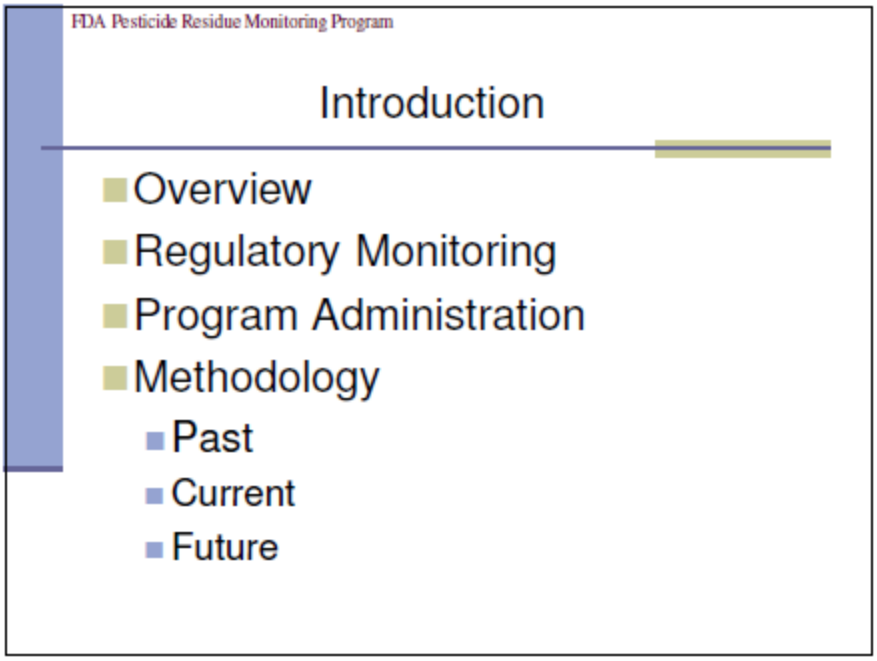
The FDA Perspective

Chris A. Sack
Food and Drug Administration

Abstract

The FDA pesticide program must meet the challenge of analyzing thousands of pesticides and industrial chemicals at extreme (ppb ? ppm) levels in essentially infinite matrices with complexities ranging from water to feeds/foods/herbals; and, in most cases, the analysis must be completed within day for as many as 50 samples per day. To meet this challenge the FDA pesticide program incoporates both targeted and screening analytical approaches. Using the targeted approach, pesticides are analyzed and quantitated against standards for over 240 compounds by LC-MS/MS in 15 minutes, and more than 200 pesticides by GC-MS/MS in 20 minutes. Each sample is additionally screened to detect over 650 pesticides using full scan GC-MS coupled with spectral deconvolution against standardized MS spectra and retention indices. Looking to the future, FDA is working to expand pesticide and toxin coverage by additionally screening with LC coupled with high resolution mass spectroscopy. Also, under evaluation is a procedure to streamline import sample processing by prescreening pesticides and toxins on the surface of raw agricultural commodities using ambient pressure desorption with high resolution mass spectrometry at the port of entry.


Monitoring Pesticides in the Environment: Past, Present and Future – FDA Perspective
National Environmental Monitoring Conference
August 6, 2013
Chris A. Sack, Residue Expert
Food and Drug Administration


FDA Pesticide Residue Monitoring Program
Introduction
Overview
Regulatory Monitoring
Program Administration
Methodology
Past
Current
Future

FDA Pesticide Residue Monitoring Program

Overview - Challenges

- Food and feed matrices
  - Imports: > 11 million per year
  - Domestic: ???
- Pesticides and other contaminants
  - 1000s that are known
  - Range: 10 ppb - ???
- Analyses
  - Up to 50 samples per day per lab
  - Timeframe: 1 day for imports

FDA Pesticide Residue Monitoring Program

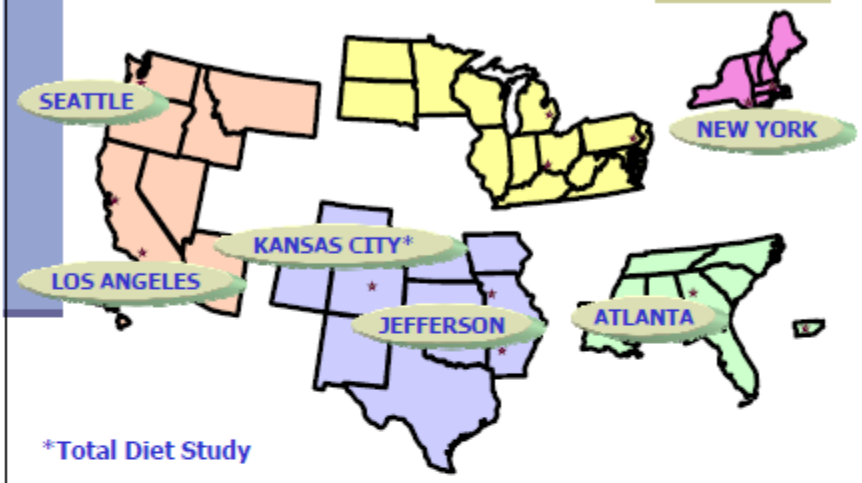
Overview - Programs

- Regulatory Monitoring
- Total Diet Study
- Special Assignments

FDA Pesticide Residue Monitoring Program

Overview

6 PESTICIDE LABORATORIES

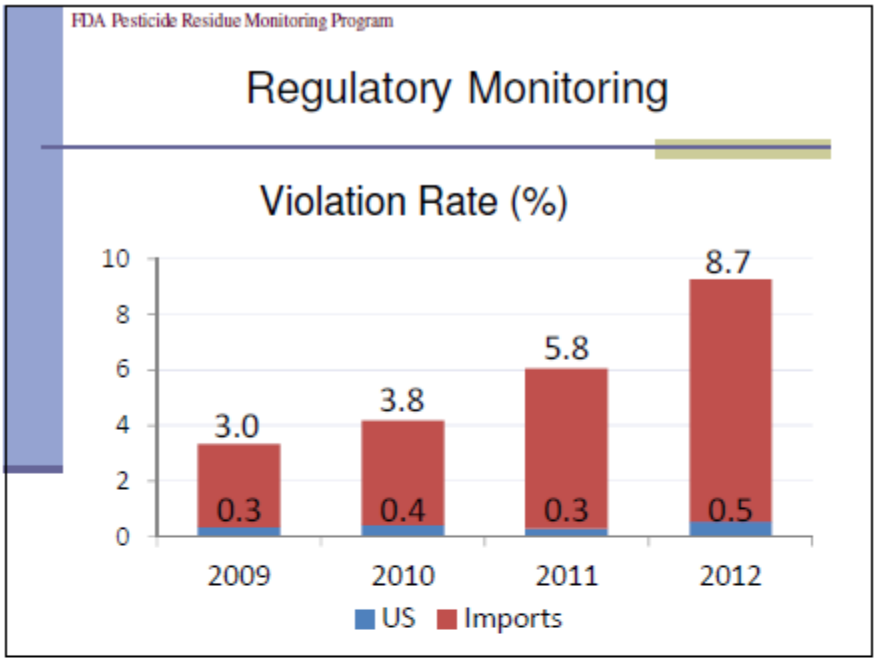


*Total Diet Study

FDA Pesticide Residue Monitoring Program

Overview – Regulatory Analysis

- Sample types:
  - Raw agricultural products
  - Processed foods (limited)
  - Spices/botanicals
  - Miscellaneous
- Samples: 5000 - 7000 per year
- Target: ~ 400 pesticides per sample
- Detect: ~ 220 different residues per year



FDA Pesticide Residue Monitoring Program

Regulatory Monitoring

Year	Violative Residues	Violation Type (%)	
		No MRL	Exceeds MRL
2009	603	96.8	3.2
2010	686	94.5	5.5
2011	996	96.0	4.0
2012	1189	96.8	3.2

FDA Pesticide Residue Monitoring Program

Regulatory Monitoring

Most commonly found violative residues (2010–12)

Carbendazim	313	Profenofos	61	DDT	48
Permethrin	179	DCPA	59	Thiophanate-methyl	47
Tricyclazole	104	Endosulfan	57	Pirimiphos methyl	46
Quintozene	100	Pyrimethanil	54	Prochloraz	45
Ethion	70	Procymidone	53	Cypermethrin	41
Chlorpyrifos	70	Lambda-cyhalothrin	51	Tebuconazole	40
Triazophos	69	Buprofezin	51	Carbofuran	40

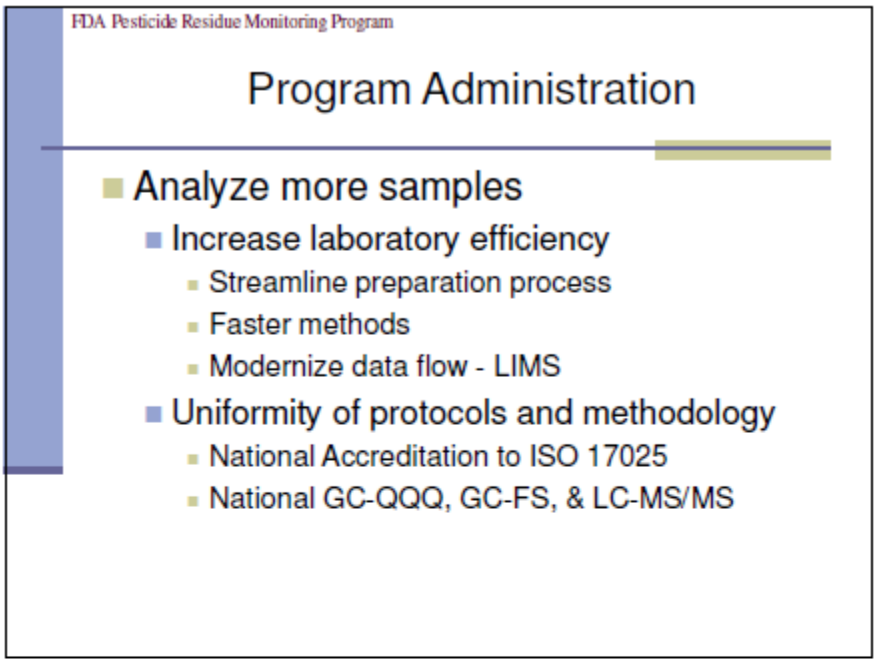
FDA Pesticide Residue Monitoring Program

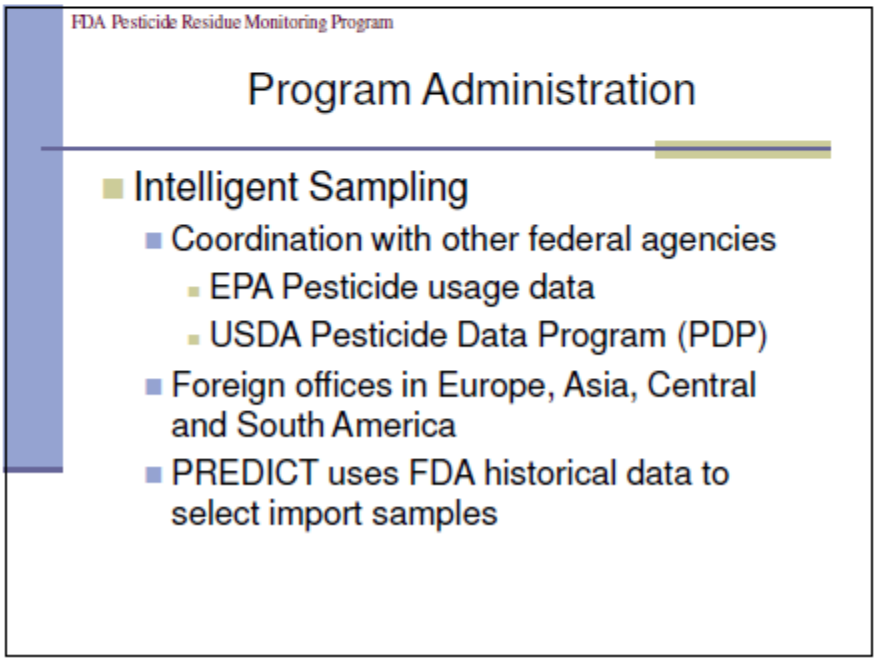
Regulatory Monitoring

Top violative products (2010–12) *

Product	Vio %	Product	Vio %
Capsicums	41	Spinach	15
Basil	35	Sweet potatoes	15
Cilantro	30	Citrus juice	14
Tea	26	Grapes, raisins	12
Rice products	25	Blackberries	12
Papaya	25	Peppers, hot	11
Taro/dasheen	20	Red beets	11
Prickle pear	20	Leeks	10

* > 50 samples analyzed


FDA Pesticide Residue Monitoring Program
Program Administration
Analyze more samples
Increase laboratory efficiency
Streamline preparation process
Faster methods
Modernize data flow - LIMS
Uniformity of protocols and methodology
National Accreditation to ISO 17025
National GC-QQQ, GC-FS, & LC-MS/MS


FDA Pesticide Residue Monitoring Program
Program Administration
Intelligent Sampling
Coordination with other federal agencies
EPA Pesticide usage data
USDA Pesticide Data Program (PDP)
Foreign offices in Europe, Asia, Central and South America
PREDICT uses FDA historical data to select import samples

FDA Pesticide Residue Monitoring Program

Program Administration

- Coordination with states
  - FERN
  - MOUs
- International coordination/outreach
  - Attendance international workshops
  - International Food Safety Training Lab
  - International Capacity Building and Development

FDA Pesticide Residue Monitoring Program

Program Administration



FDA Pesticide Residue Monitoring Program

Methodology – Past

Pesticide Analytical Manual

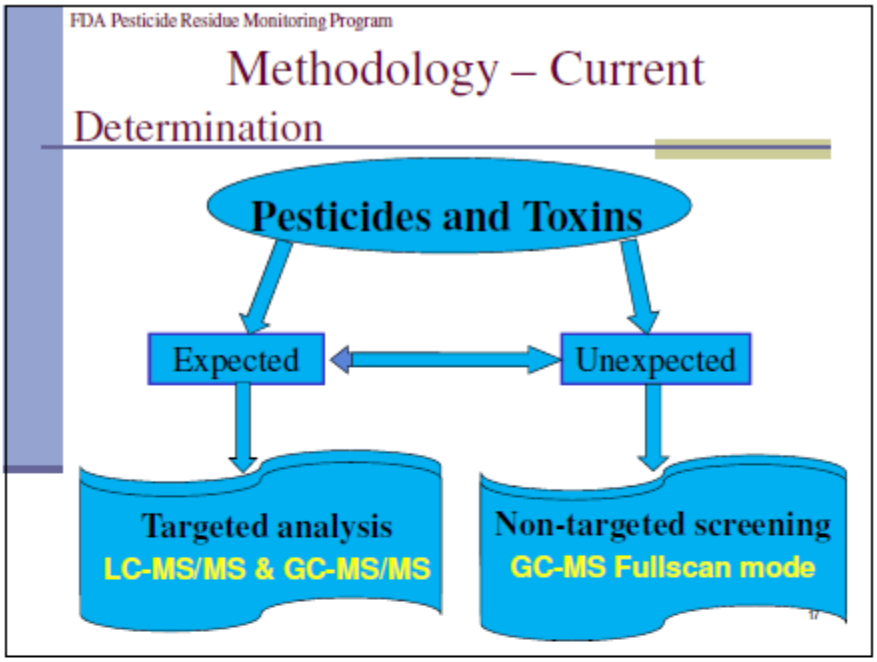
- Technology of 70s – 80s
- Extraction: Large
- Cleanup: Complex and tedious
- Determination: GC with selective detection
  - Orgranophosphates: FPD
  - Organohalogens: ECD, XSD, ELCD
  - Organonitrogens: NP
- Identification by retention indices

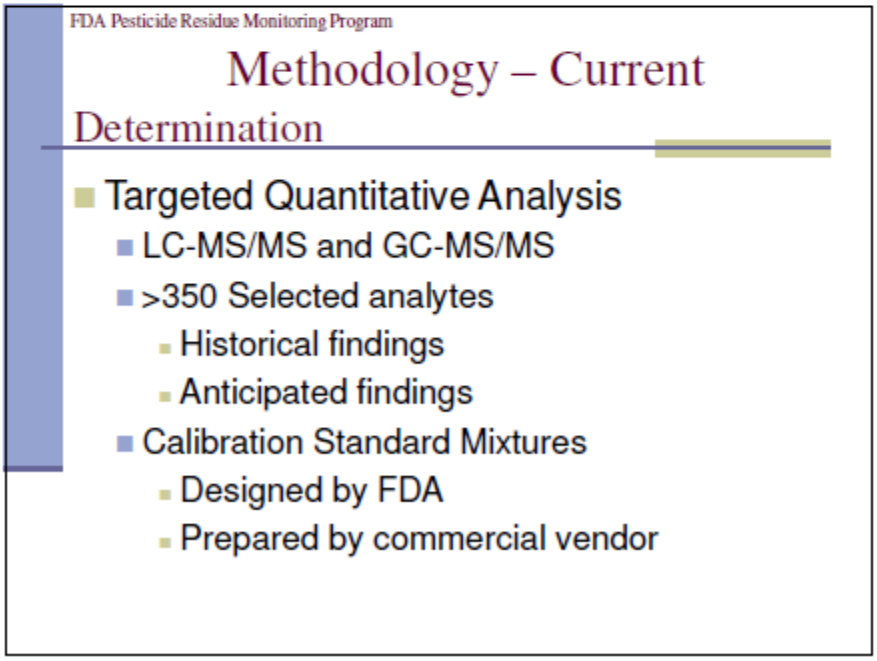
FDA Pesticide Residue Monitoring Program

Methodology – Current

Extraction/Cleanup

- Acetone extraction (two labs)
  - Sample plus acetone
  - Saltout
  - SPE cleanup
- QuEChERS modified (four labs)
  - Sample plus acetonitrile
  - Saltout
  - SPE cleanup
    - LCMS: PSA only or dilute extract
    - GCMS: PSA + C18 and/or GCB, or equivalent


FDA Pesticide Residue Monitoring Program
Methodology – Current
Determination
Pesticides and Toxins
Expected
Unexpected
Targeted analysis
LC-MS/MS & GC-MS/MS
Non-targeted screening
GC-MS Fullscan mode


FDA Pesticide Residue Monitoring Program
Methodology – Current
Determination
Targeted Quantitative Analysis
LC-MS/MS and GC-MS/MS
>350 Selected analytes
Historical findings
Anticipated findings
Calibration Standard Mixtures
Designed by FDA
Prepared by commercial vendor

FDA Pesticide Residue Monitoring Program

Methodology – Current Determination

- Qualitative Screening Analysis
  - GC-MS in fullscan mode (GC-FS)
  - No standards required
  - Spectral Library Technique

FDA Pesticide Residue Monitoring Program

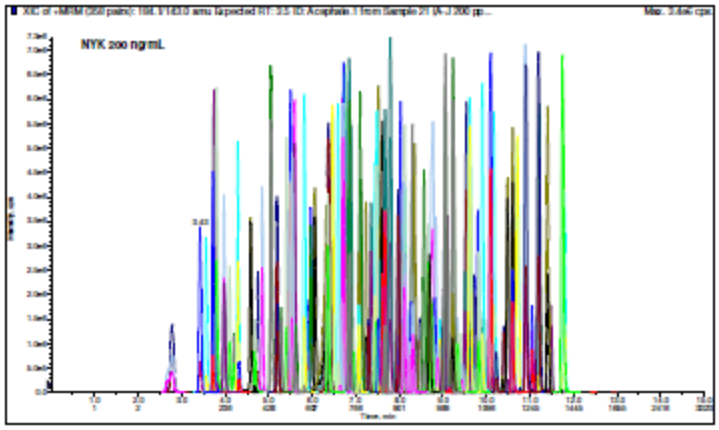
Methodology – Current Determination: LC-MS/MS

- Scope: >240 pesticides in 15 minutes
- Chromatography: reverse phase
- Columns: C_{18}
  - 100 x 2.1 mm, ~3 µm
  - 50 cm x 4.6 mm, 1.9 µm
- Mass Spectrometer parameters
  - Ionization: Positive electrospray
  - Detection: scheduled MRM (two transitions)
- Detection Limit: < 10 ppb for most compounds
- JAFC 2011, Vol 59, pp 6383ff

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: LC-MS/MS



Standard containing 190 pesticides

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: LC-MS/MS

Pesticide	PPB	Pesticide	PPB
Boscalid	128	Novaluron	9
Pyraclostrobin	54	Hexythiazox	5
Cyprodinil	47	Spiromesifen	2
Azoxystrobin	45	Propiconazole	1
Pyrimethanil	41	Acetamiprid	1
Chlorantranilaprole	23	Carbendazim	1
Fludioxinil	22	Methomyl	0.7
Fenhexamid	20	Thiophanate methyl	0.5
Bifenazate	9	Methoxyfenozide	0.3
Myclobutanil	9	Fenpyroximate	0.2

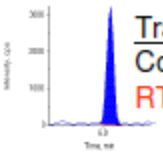
Residues found in composite of 3 strawberry samples

FDA Pesticide Residue Monitoring Program

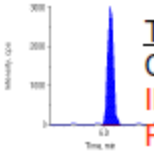
Methodology – Current

Determination: LC-MS/MS

Sample

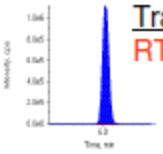


Trasistion-1
Conc: 0.3 ng/g
RT: 6.07

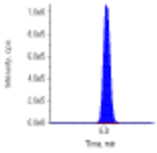


Transition-2
Conc: 0.3 ng/g
IRATIO 85*
RT 6.06

Standard 50 ng/mL



Transition-1
RT 6.02



Transition-2
IRATIO 99*
RT 6.02

Methoxyfenozide in strawberry @ 0.3 ppb

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: GC-MS/MS

- Scope: > 200 pesticides in 20 minutes
- Agilent 6890GC
  - Retention time locking
  - Backflushing mid column
- Agilent 7000 MS/MS
  - MRM (2-4 transitions/compound)
- Detection Limit: 1 - 10 ppb for most analytes
- USFDA Lab Information Bulletin 4521

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: GC-MS/MS

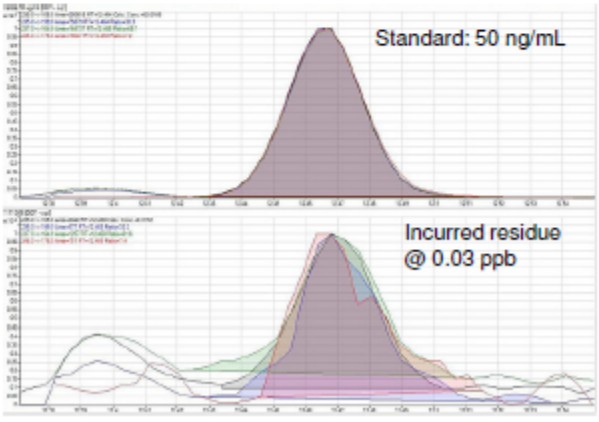
Pesticide	PPB	Pesticide	PPB
THPI	237	Bifenthrin	7
Boscalid	128	Quinoxyfen	3
Pyraclostrobin	54	Spiromesifen	2
Cyprodinil	47	Propiconazole	1
Pyrimethanil	41	Fenpropathrin	0.7
Azoxystrobin	37	Biphenyl	0.3
Captan	27	Chlorpyrifos	0.1
Fludioxinil	22	Folpet	0.1
Fenhexamid	20	p,p'-DDE	0.1
Bifenazate	9	p,p'-DDT	0.04
Myclobutanil	9	o,p'-DDT	0.03
Malathion	8		

Residues found in composite of 3 strawberry samples

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: GC-MS/MS



o,p'-DDT in strawberry

FDA Pesticide Residue Monitoring Program

Methodology – Current

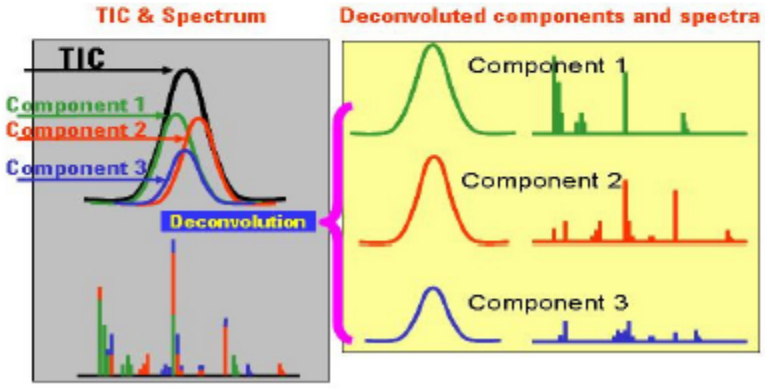
Determination: GC-FS

- Scope: > 900 compounds in 20 minutes
- Screen for library matches - no standards
- Agilent GC-MSD pesticide library
- Identification:
  - Spectral matching of AMDIS deconvoluted spectra
  - Retention time

FDA Pesticide Residue Monitoring Program

Methodology – Current

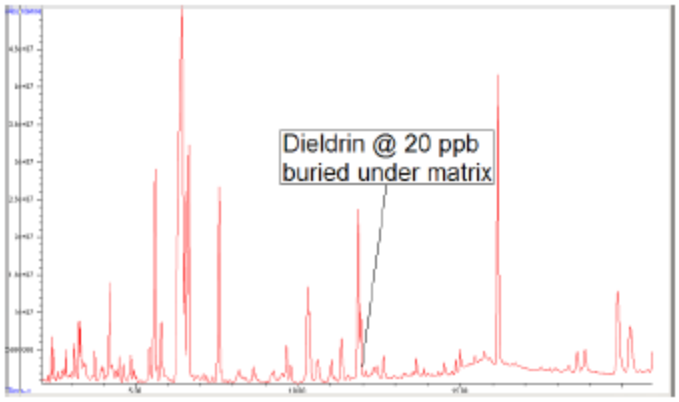
Determination: GC-FS



AMDIS Deconvolution

FDA Pesticide Residue Monitoring Program

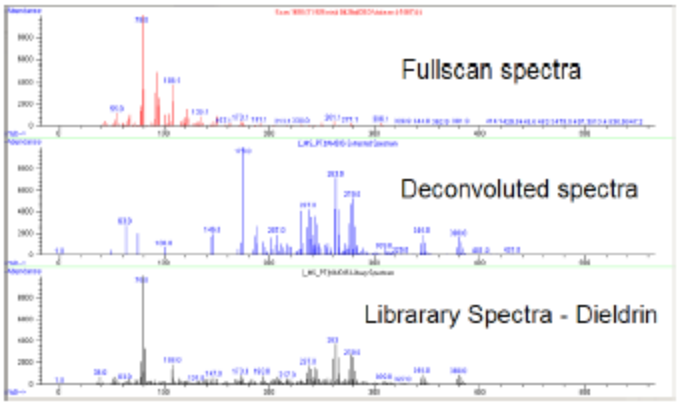
Methodology – Current Determination: GC-FS



Celery fullscan TIC

FDA Pesticide Residue Monitoring Program

Methodology – Current Determination: GC-FS



Dieldrin spectra

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: GC-FS

		AMDIS		NIST	
R.T.	Compound Name	Match	R.T. Diff	Reverse Match	Hit Num.
2.5858	Naphthalene-d8	99	-0.0	91	1
2.942	Carvone	75	-0.3	91	2
3.341	EPTC	94	-7.2	89	2
6.977	Anthracene	80	-5.4	88	5
7.9576	Diisobutyl phthalate	75	1.2	94	11
9.214	Di-n-butylphthalate	65	0.0	90	18
9.658	Parathion	82	2.5	76	2
11.925	**Dieldrin**	**79**	**1.5**	**61**	**2**
14.3189	Chrysene-d12	79	-12.1	91	1
14.8515	Bis(2-ethylhexyl)phthalate	96	3.3	85	7
15.7388	Permethrin I	60	6.5	63	2
15.833	Permethrin II	63	7.0	79	
16.516	Cypermethrin II	40	11.7	57	1

Celery deconvolution report

FDA Pesticide Residue Monitoring Program

Methodology – Current

Determination: GC-FS

Residues discovered and transferred to the LC-MS/MS and GC-MS/MS targeted analyses:

- Fluopicolide
- Spiromesifen
- Spirodiclofen
- Flonicamide
- Chlorfenapyr
- Etoxazole
- Bifenazate
- Etoxazole
- Fenamidone
- Famoxadone
- Quinoxyfen
- Sudan I*

**Food color prohibited in US - not added to target analysis*

FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening

- Screening Approach
  - "Semi"- targeted
    - Collect full spectral/RT data
    - Knowns: Libraries
    - Unknowns: Investigate
  - Reduce real-time processing/maintenance
- Technology - HRMS
  - DART
  - LCMS

FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening: DART

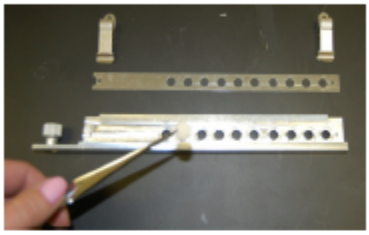
- Method
  - Swab sample
  - Analyze swab by DART-HRMS
- Scope: > 500 pesticides and toxins
- Analysis time: 7.5 minutes/sample
- Implementation:
  - Fast screen of imports at port of entry
  - Forward suspect violations for quantitative analysis

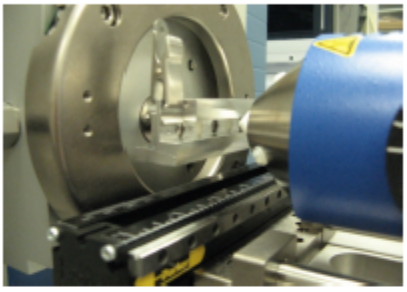
FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening: DART

Custom foam rail autosampler





FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening: DART

Ionization



$$He(2^3S) + nH_2O \rightarrow [(H_2O)_{n-1} + H]^+ + OH^- He(1^1S)$$
$$[(H_2O)_n + H]^+ + M \rightarrow [M + H]^+ + nH_2O$$

FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening: DART

Thermo Exactive Orbitrap

- Resolution
  - 100,000 @ 1 scan per second
  - 10,000 at 10 scans per second
- Mass accuracy: <1 ppm
- Scan speed: → 10 per second
- Scan range: 50 – 4000 m/z
- Detection Limit: < 10 ng/ml (100 ppb) most compounds



FDA Pesticide Residue Monitoring Program

Methodology – Future

Residue Screening: LCMS

- Thermo Exactive Q-Orbitrap
  - LC: Reverse Phase uHPLC
  - Ionization ESI^+
  - MS Library: HR molecular ion & fragments
  - Screen > 600 pesticides @ ≤ 10 ppb
  - Expand to other chemical contaminants: mycotoxins, plant toxins, veterinary drugs, dyes, emerging organic pollutants, and unknown contaminants
- LC-QTOF: under investigation

FDA Pesticide Residue Monitoring Program

Conclude

- Continuous Improvement
  - Domestic & international cooperation
  - Smarter sampling
  - Faster sample preparation
  - Screening technologies

FDA Pesticide Residue Monitoring Program

Acknowledgements

- David Eide & Michael Smoker (FDA-Kansas City)
- Jon Wong (FDA-CFSAN)
- Greg Mercer & Barb Neuhaus (FDA-Seattle)
- Lorrie Lin & Sara Edison (FDA Forensic Chemistry Center)

Environmental Monitoring: Where Will Technology Be in 10 Years?

Paul Winkler
AB Sciex

Abstract

In the last 20 years environmental analyses have undergone radical changes in techniques and capability. This presentation will briefly discuss the progression of analytical techniques from the beginning of environmental monitoring up to the techniques currently available today. The discussion will then move beyond where the technology is currently and speculate about where monitoring may be in the next ten years. How to apply these new technologies to environmental analysis will also be discussed.


PUSHING THE LIMITS IN MASS SPECTROMETRY
Environmental Monitoring: Where will technology be in 10 years?
Paul Winkler
AB SCIEX
AB SCIEX


AB SCIEX
Things you should know
THE DISCLAIMER
• The discussion will be about LC/MS for environmental applications (no omics)
• These are my musings, not official AB Sciex statements
• This is intended to be a technology talk, not a vendor talk
• The historical discussion is a broad swipe and any omission is not intentional
2

Outline

- Historical Evolution of LC/MS
- Current technology and areas for improvement
- Where will be in the future?

©2013 AB SCIEX

Historical evolution of LC/MS

- 1968 – Direct Liquid Injection (Tal'roze)
  - Not suitable to reverse phase
  - Low sensitivity and reliability
- 1975 – Atmospheric Pressure Chemical Ionization (Horning)
- 1976 – Moving Belt (McFadden)
  - First interface to provide EI spectra
  - Mechanically complex, memory effects and poor reverse phase performance

©2013 AB SCIEX

Historical evolution of LC/MS

- 1978 – Thermospray (Vestal)
  - Operated with reverse phase chromatography
  - Poor stability but adequate sensitivity
- 1982 – Atmopspheric Pressure Chemical Ionization (Henion)
  - Good perfomrance with reverse phase separations
  - Good sensitivity
- 1984 – Electrospray (Fenn)
  - Superior sensitivity and stability
  - Good performance with reverse phase solvents
  - Wide compound application

©2013 AB SCIEX

Historical evolution of mass spectrometry

- 1934 – Double focusing magnetic sector
- 1953 – Quadrupole (Paul)
- 1956 – GC/MS (McLafferty)
- 1978 – Triple quadrupole MS (Yost)
- 1984 – QTOF (Glish)
- 2000 – Orbitrap
- 2003 – Qtrap (Hager)
- 2004 – Differential mobility spectrometry

©2013 AB SCIEX

The last 20 years

- 1993
  - Ion Spray
  - Thermospray
  - Particle Beam
  - Single quadrupole and triple quadrupole instruments
  - Sensitivity in the low PPM range
  - Poor operational stability
  - Environmental applications just beginning to be developed
  - Selectivity limitations require significant cleanup

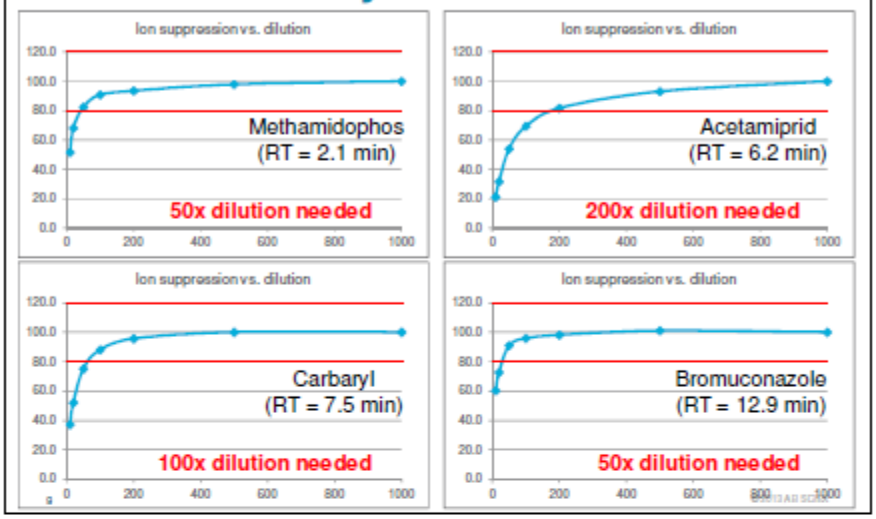
© 2013 AB SCIEX

The last 20 years

- 2013
  - Electrospray
  - APCI
  - Triple quadrupoles, Qtraps, Orbitraps and QTOFs
  - Improved selectivity with MRM^n, differential mobility
  - Sensitivity in the low PPT range
  - Very stable operational stability
  - Better instrumentation for compound identification and confirmation
  - Several environmental applications – flame retardants, pesticides, PPCP, explosives, perchorate, UMCR….

© 2013 AB SCIEX

The Next Ten years?



The next 10 years?

- Matrix Interference with Electrospray
  - Expect to see electrospray sources that exhibit significantly less ionization suppression
  - Especially important for environmental applications as this will allow direct injection analyses and easier soil extractions

The next 10 years?

- Improvements to APCI sources

Relative Sensitivities of ESI and APCI to 31 Pharmaceutical Compound Test Suite		
ESI ≤ APCI	8 Compounds	25%
APCI 5 to 20x lower than ESI	10 Compounds	32%
APCI 20 to 100x lower than ESI	2 Compounds	6%
APCI > 100x lower than ESI	11 Compounds	35%

11

©2013 AB SCIEX

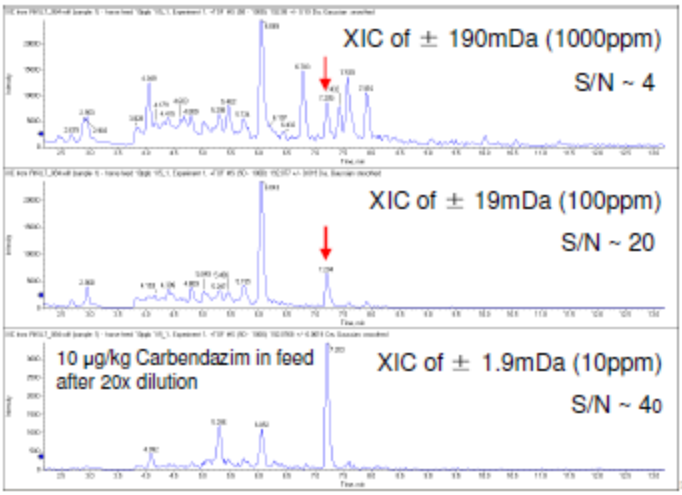
The next 10 years?

- APCI source improvements
  - Better source design to improve transmission of ions from the source region to the mass spec
  - Inherent freedom from APCI will drive an increase in these methods in environmental analyses

12

©2013 AB SCIEX

The next 10 years?



12

© 2013 AB SCIEX

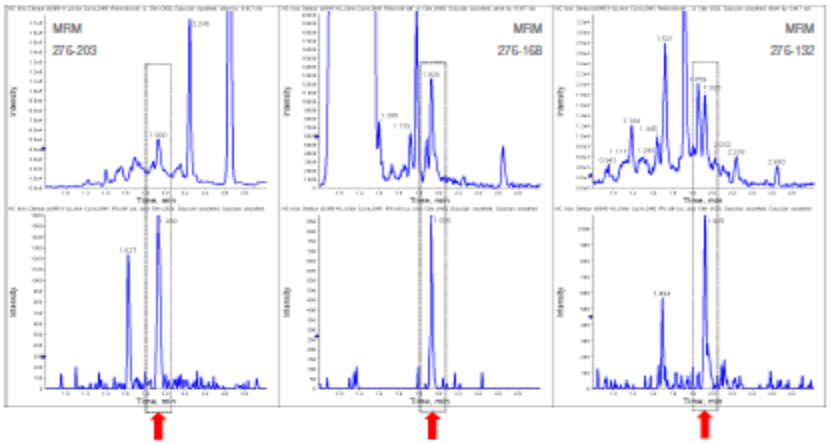
The next 10 years?

- Selectivity
  - Improvements in resolution for QTOF type instruments with less loss of sensitivity
  - Operational resolution of QTOFs in the range of 100,000

14

© 2013 AB SCIEX

The next 10 years?



Detection on QTRAP® 5500 with SelexION™ (top: no DMS, bottom: DMS with IPA)

©2013 AB SCIEX

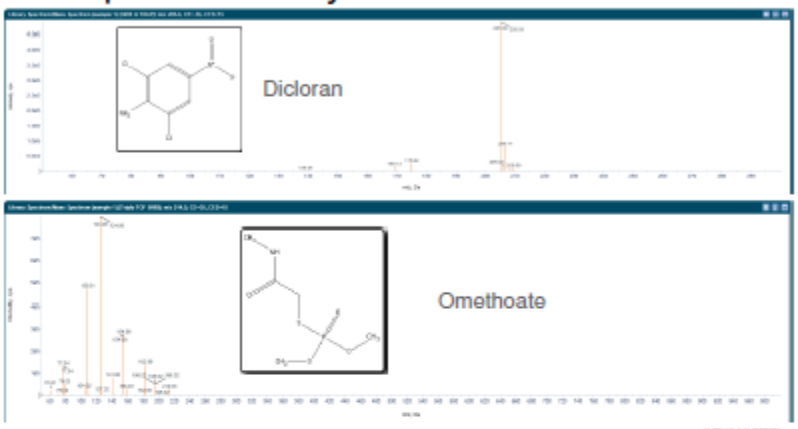
The next 10 years?

- Selectivity
  - Improved transmission for differential mobility devices
  - Differential mobility will be especially important for environmental applications as this will radically reduce the demands of sample preparation

©2013 AB SCIEX

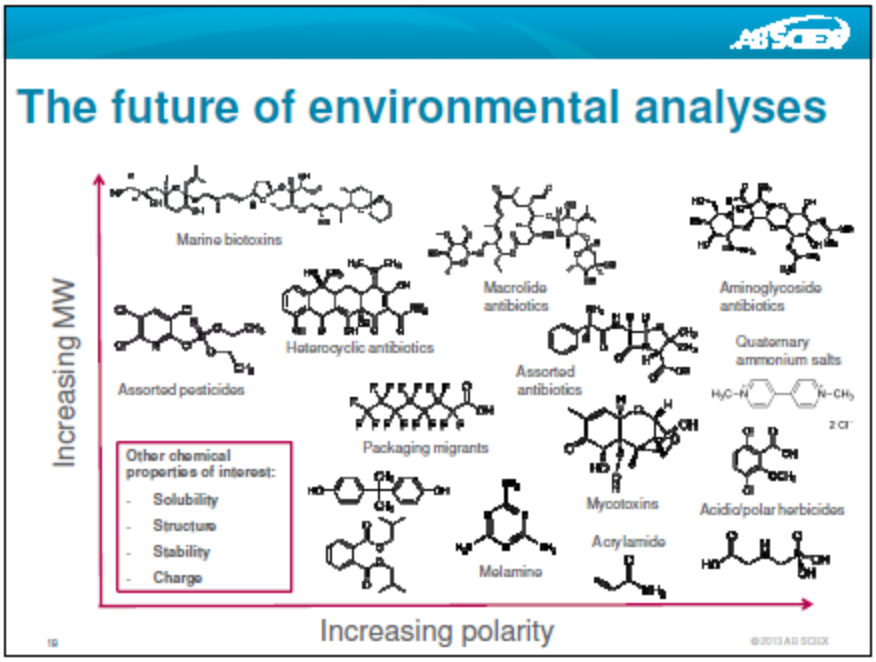
The next 10 years?

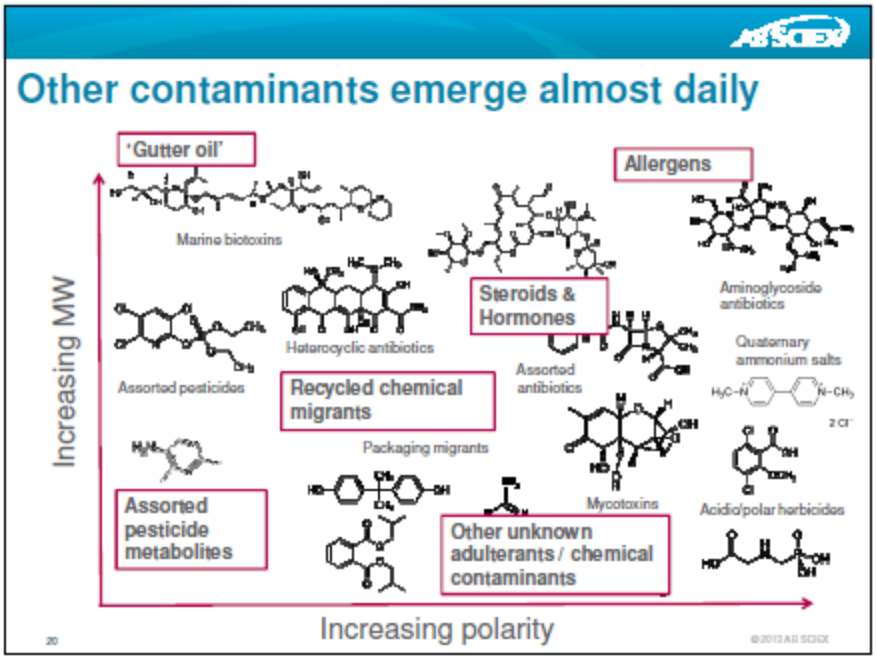
- Compound Identity/Confirmation



The next 10 years?

- Improvements to collision processes to increase the information content in MS/MS spectra
- Need to identify detections with more certainty as environmental LC/MS applications increase
- Reliance on MRM ratios will not be sufficient information for compound confirmation. Will require full scan MS/MS
- Will need accompanying increase in scan speed to obtain data for 3-6 second wide peaks


The future of environmental analyses
Marine biotoxins
Macrolide antibiotics
Aminoglycoside antibiotics
Heterocyclic antibiotics
Assorted pesticides
Assorted antibiotics
Quaternary ammonium salts
Packaging migrants
Other chemical properties of interest:
- Solubility
- Structure
- Stability
- Charge
Mycotoxins
Acidic/polar herbicides
Melamine
Acrylamide
Increasing MW
Increasing polarity


Other contaminants emerge almost daily
'Gutter oil'
Allergens
Marine biotoxins
Steroids & Hormones
Aminoglycoside antibiotics
Heterocyclic antibiotics
Assorted pesticides
Recycled chemical migrants
Assorted antibiotics
Quaternary ammonium salts
Packaging migrants
Assorted pesticide metabolites
Mycotoxins
Acidic/polar herbicides
Other unknown adulterants / chemical contaminants
Increasing MW
Increasing polarity

Ten years from now:

- Decrease in matrix interference will make LC/MS the method of choice for a large section of environmental analyses
- Applications will include possibly an equal mix of APCI or ESI methods
- Compound confirmation in LC/MS analyses will be similar to TIC's from GC/MS today but with a much wider compound range
- Data that is obtained will have comprehensive catalogue of all chemicals present allowing retrospective review

21

©2013 AB SCIEX

Thank you for listening !



22

©2013 AB SCIEX

SECTION 7

TOPICS IN SHALE GAS EXPLORATION

Challenges of Managing Water in the Marcellus Play

Nick Inkenhaus
Range Resources

Abstract

The management of water resources poses considerable challenges to natural gas operators seeking to develop the Marcellus shale in Pennsylvania. Although the play overlies a seemingly water-rich region the sourcing, storage, transfer, reuse, and disposal of water for drilling and completions operations are far from straight forward. Range Resources' approach uses the fundamental characteristics of the Marcellus shale to challenge the conventional rules of thumb for water quality requirements in completions operations. This unconventional approach to water management has led to innovative solutions which serve to both protect the water resources of the Commonwealth and to provide maximum flexibility to operations.

RANGE RESOURCES®

NEMC – Challenges of Managing Water in the Marcellus Play

August 5, 2013

Nick Inkenhaus
Water Resources Engineer

Water Requirements for Marcellus Shale

- Completion typically requires 3-5 million gallons of water
- Pump rates range from 70 – 100 bpm
- Is that a lot of water?
  - 5 million gallons is 1.8 inches of water over an area of 100 acres, the approximate drainage area of a well
  - PA receives about 40 inches of rainfall per year
  - If the productive area of the Marcellus takes 50 years to drill, annual water use over the productive area would be 0.04 inches of water per year or 1/10th of 1% of annual rainfall

Water Requirements for Marcellus Shale

Water use per million btu of energy:

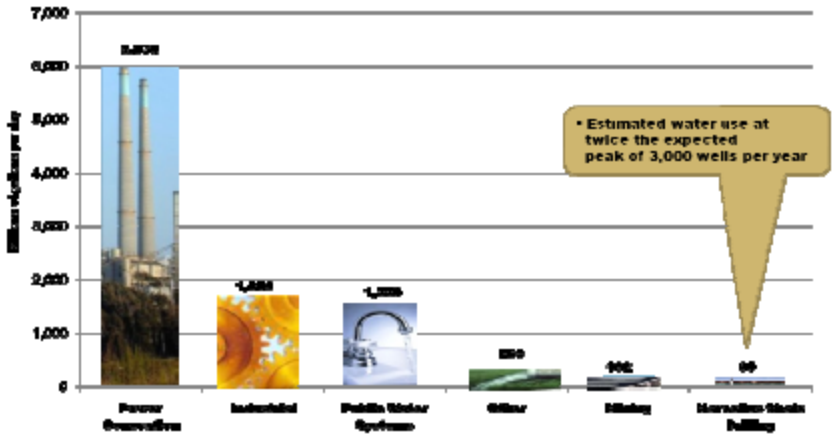
•Deep shale natural gas	0.60-5.80 gallons
•Marcellus Shale gas – avg	1 gallon
•Nuclear (uranium ready to use in a power plant)	8-14 gallons
•Conventional oil	8-20 gallons
•Synfuel-coal gasification	11-26 gallons
•Coal (delivered power plant)	13-32 gallons
•Oil shale	22-56 gallons
•Tar sands/oil sands	27-68 gallons
•Fuel ethanol from corn	2,510-29,100 gallons (irrigation)
•Biodiesel from soy	14,000-75,000 gallons (irrigation)

Shale gas production uses less water than any other significant energy source

Source: U.S. Dept. of Energy

RANGE RESOURCES® | 3

Water Usage Comparison



Source: USGS, Pennsylvania Water Consumption

RANGE RESOURCES® | 4

Source Requirements

- Reliability/Seasonality
- Quality/Compatibility
- Location/Proximity



RANGE RESOURCES® | 5

Sources - Municipal



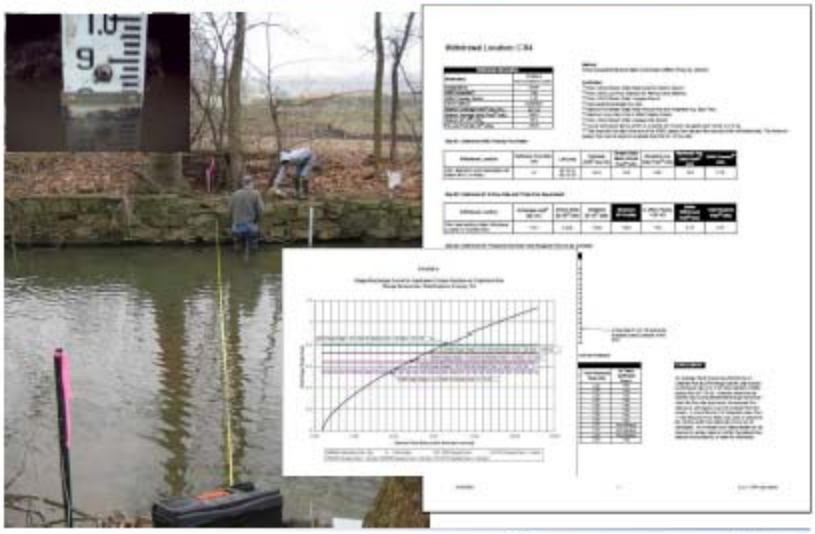
RANGE RESOURCES® | 6

Sources – Surface Water



RANGE RESOURCES | 7

Sources – Surface Water



RANGE RESOURCES | 8

Water supply sources

- **Larger streams, rivers, and reservoirs**
  - PA DEP has adopted SRBC method for analyzing water withdrawal and must approve all water management plans
  - Water can be safely withdrawn at reasonable rates all year with exceptions for very dry periods
  - Protection of downstream uses
  - Cumulative impact considerations
- **Reuse is now a significant water source**
  - 29.5% of Range's total PA water usage in 2011 was from reuse
  - 29% of Range's total PA water usage in 2012 was from reuse

Sources – Alternative



TABLE 1 – WATER QUALITY AND QUANTITY

Parameter	Value
Mine Pool #1	1.9 billion gallons
Mine Pool #2	1.8 billion gallons
Average Discharge Flow	695 gpm
Average pH	6.8
Average Alkalinity	112 mg/l
Average Acidity	82 mg/l
Average Total Iron	109.5 mg/l
Average Total Manganese	1.1 mg/l
Average Total Aluminum	0.6 mg/l
Average Sulfates	761 mg/l

Parameter	Min	Max	Average	Units
Flow	80	45,553	1,638	gpm
pH	2.8	8.6	5	
TSS	2	656	29	ppm
TDS	144	3,486	1,120	ppm
Chlorides	1	348	31	ppm
Sulfate	5	2,800	416	ppm
Hardness	74	1,559	435	ppm
Iron (total)	0	238	19	ppm
Magnesium (total)	2	525	47	ppm

PA DEP – Orphaned Mine Discharge Project

Sources – Alternative





Parameter	Value	Units
pH	5.0-9.0	
TSS	30	ppm
5-Day BOD	30	mg/l

EPA Secondary Treatment Standard

RANGE RESOURCES | 11

Water Transfer



RANGE RESOURCES | 12

Water Transfer

- **Minimize Trucking**
  - Source water, 800 - 900 trucks per well
  - Flowback, ~180 trucks per well
  - Proximity is key
- **Pumping and Pipelines**
  - Temporary
    - Integrity
    - Distance
  - **Permanent network**
    - Link large sources to storage locations
  - **Noise Mitigation**





Water Transfer

- **3rd Party Engineer Develops Test**
  - Pipe rating
  - Component ratings
  - Layout
  - Weather conditions
- Separate Testing Firm Executes
- Approximately 8 hours
- Any failure results in re-test
- Scheduled 3-7 days prior to frac
- Procedure/test for each job



Treatment, Reuse, and Disposal

- 10-30% of water flows back to surface near-term after completions activities; balance is bound in micro fractures in shale
- Water flowed back after frac contains salts and other naturally occurring dissolved minerals present in ancient sea water
- Water is gathered and removed from site by either truck or pipeline
- Management methods during 2011/2012:
  - Recycle
  - Injection wells
  - Advanced treatment facilities



RANGE RESOURCES® | 15

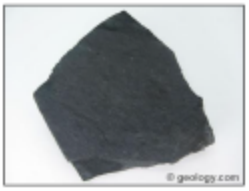
Recycling - Challenging Convention

Simplified Fluid Design

- Slickwater with scale inhibitor and biocide

Water Quality

- Shale permeability
  - Production mechanism
  - Water mobility



nanodarcy, nD, 1 x 10^{-9} D



millidarcy, mD, 1 x 10^{-3} D

Challenge conventional rules of thumb

Parameter	Conventional Limits	Considerations
pH	6.0 to 8.0	Fluid Stability, Scaling
Chlorides	<20,000 mg/L	Fluid Stability
Iron	<20 mg/L	Fluid Stability
Ca, Mg, Ba, SO_4, CO_3, ...	f(P,T,pH) (+/- 350 mg/L)	Scaling
Bacteria Count	<100/100 mg/L	Bacteria Growth
Suspended Solids	<50 mg/L	Skin
Oil & Soluble Organics	<25 mg/L	Fluid Stability

RANGE RESOURCES® | 16

Recycling - Challenging Convention

Timeline

- Fall 2008
  - Range formed Water Resources Group
- April 2009
  - Started accumulating recycle water
- August 2009
  - Competed first recycled water frac



RANGE RESOURCES® | 17

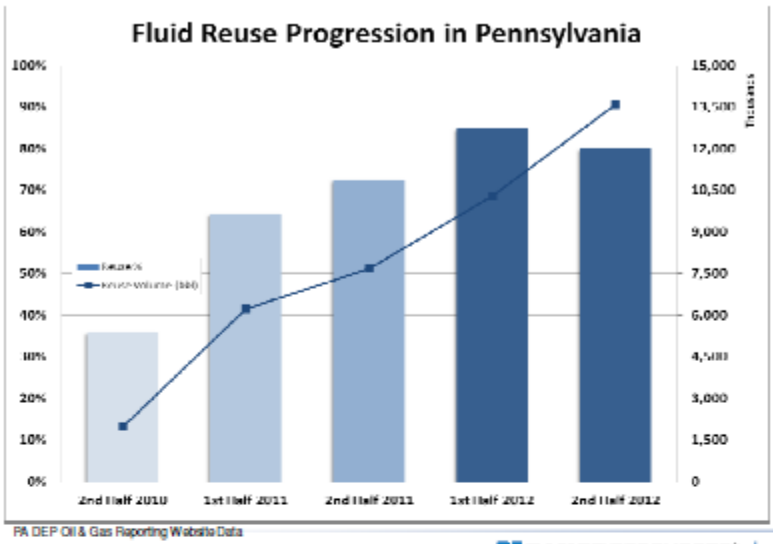
Range's Water Recycling Program

Rapidly Evolving Technology

- Recycling technology did not develop in other shale gas plays due to abundant opportunities for disposal by injection into deep rock formations
- Recycling in the Marcellus play has been driven by lack of other disposal options and regulatory framework
- Technology will continue to improve rapidly
  - Completions designs
  - Chloride tolerant friction reducers

RANGE RESOURCES® | 18

Industry Recycling Progression in PA



PA DEP Oil & Gas Reporting Website Data

RANGE RESOURCES® | 19

Range's Water Recycling Program

Throughout the first half of 2013:

- Southern Marcellus Operations
  - Flowback
    - Recycle – **100%**
  - Production Brine
    - Recycle – **100%**
  - Drilling Fluids
    - Recycle – **88.3%**

- **Overall Recycle Rate – 98.1%**

RANGE RESOURCES® | 20

Thank You



Nick Inkenhaus
Water Resources Engineer
Range Resources – Appalachia, LLC
Southern Marcellus Shale Division
724-743-6700

Additional Information:

www.rangeresources.com

www.marcelluscoallition.org

Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania

Shahla Farhat
GSI Environmental Inc.

Abstract

Testing of 1701 water wells in northeastern Pennsylvania shows that methane is ubiquitous in groundwater, with higher concentrations observed in valleys vs. upland areas and in association with calcium-sodium-bicarbonate, sodium-bicarbonate, and sodium-chloride rich waters – indicating that, on a regional scale, methane concentrations are best correlated to topographic and hydrogeologic features, rather than shale gas extraction. In addition, our assessment of isotopic and molecular analyses of hydrocarbon gases in the Dimock Township suggest that gases present in local water wells are most consistent with Middle and Upper Devonian gases above the Marcellus sampled in the annular spaces of local gas wells. Combined, these findings suggest that the methane concentrations in Susquehanna County water wells can be explained without the migration of Marcellus shale gas through fractures, an observation that has important implications for understanding the nature of risks associated with shale-gas extraction.

Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania

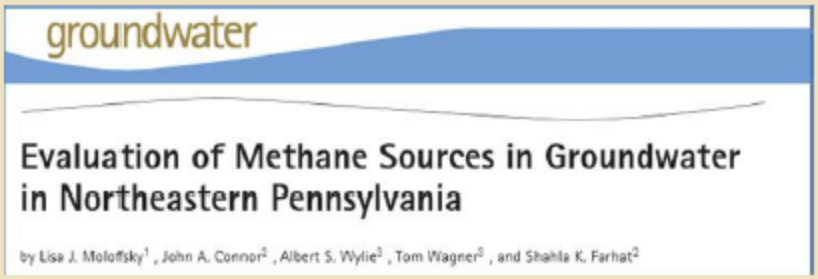
GSI ENVIRONMENTAL





Shahla K. Farhat
GSI Environmental Inc., Houston, Texas
(713) 522-6300 skfarhat@gsi-net.com

Source of Today's Discussion


groundwater

Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania

by Lisa J. Molofsky[1], John A. Connor[2], Albert S. Wylie[3], Tom Wagner[3], and Shahla K. Farhat[2]

L.J. Molofsky, J.A. Connor, A.S. Wylie, T. Wagner, and S.K. Farhat Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania, *Groundwater* Vol. 51, No. 3 – May-June 2013 (pages 333-349).

Stray Gas Impacts: *Why do we care?*

Hydrocarbon Gas Composition:

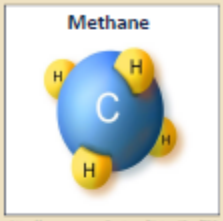
- > 95%: Methane
- < 5%: Ethane, propane, butane, etc.

Does methane pose a health hazard?

- Methane is not toxic below the lower explosive limit of 5% (50,000 ppm)
- No long-term health effects

Key Problem:

- Methane is **EXPLOSIVE** in concentrations above the lower explosive limit
- Methane can act as an ***asphyxiant*** at high concentrations



http://www.energy.alberta.ca/NaturalGas/723.asp



House Explosion, Bradford County, PA

Methane in Groundwater: *Anthropogenic or Natural Sources?*

Natural Sources

- Swamps, lakes, and glacial sediments
- Shallow gas-bearing deposits
- Coal seams



Source: http://en.wikipedia.org/

Anthropogenic Sources

- Gas pipelines
- Subsurface storage reservoirs
- Coalbed methane recovery
- Municipal waste landfills
- Oil and gas wells



Source: http://www.pnl.gov/science

Methane in Groundwater: *Natural Sources*

Swamps, Lakes, Sediment



- Swamps, lakes, and glacial sediments
- Shallow gas-bearing deposits
- Coal seams

Natural Gas Seeps





Bubbling Springs/ Ponds







Methane in Groundwater: *Anthropogenic Sources*

Landfill Gas



- Gas pipelines
- Coalbed methane recovery
- Municipal waste landfills
- Subsurface storage reservoirs
- Oil and gas wells

Oil and Gas Extraction



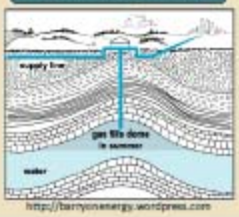
Coalbed Gas



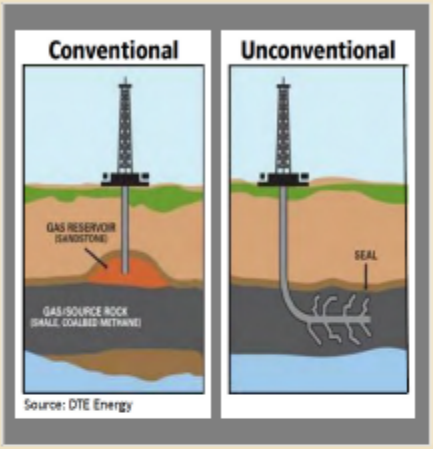
Natural Gas Pipeline



Gas Storage Field



Methane in Groundwater: *Sources Associated with Oil and Gas Extraction*



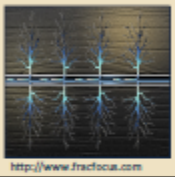
Similarities:
Well Construction

Same casing & cementing design/ practices

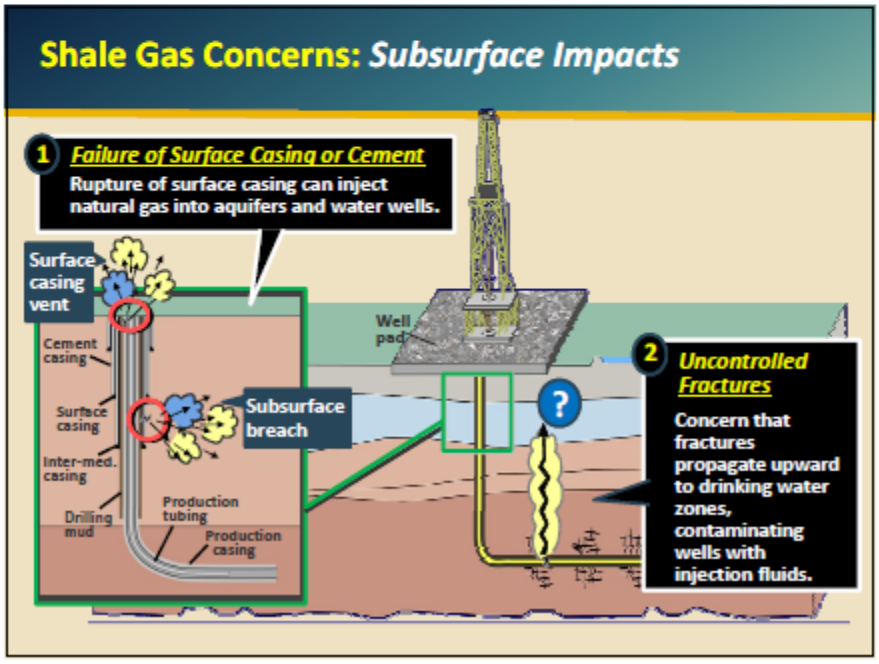
Differences:
Extraction Technique

Hydraulic fracturing is used to extract shale gas



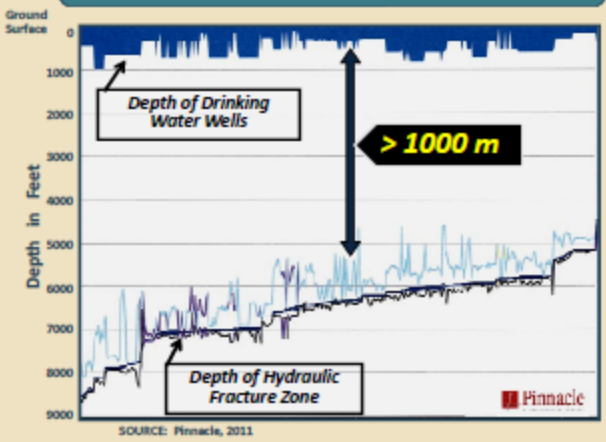


Shale Gas Concerns: *Subsurface Impacts*



Uncontrolled Fractures: *Impact on Drinking Water?*

Mapped Fractures in Marcellus Shale

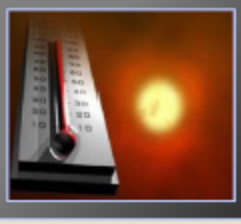


- Microseismic mapping of hydraulic fractures shows no impact on DW aquifers.
- Fracture migration limited by "bleed out," stratigraphy, laws of physics, etc.

How do You Characterize Gas Sources? *Microbial vs. Thermogenic Gas*

Thermogenic

Formed via breakdown of organic material under high temps. and pressures at depth



Microbial

Formed via biodegradation of organic material in shallow subsurface



KEY POINT: ***Presence of thermogenic gases is often considered automatically related to oil and gas operations.***

Thermogenic and Microbial Gas: *Can Migrate Through Both Anthropogenic and Nat. Pathways*

	Anthropogenic	Natural
Microbial 	▪ Municipal Waste Landfills	▪ Wetlands (swamps and lakes) ▪ Glacial Till and Alluvium
Thermogenic 	▪ Deep Oil and Gas Deposits ▪ Coalbed Extraction ▪ Natural Gas Systems ▪ Pipelines ▪ Subsurface Storage Reservoirs	▪ Shallow Gas Bearing Units ▪ Coal Seams

Methane in Groundwater: *Anthropogenic or Natural?*

Gas Well Migration



House Explosion, Western PA

Natural Gas Seep



Eternal Flame Falls, NY

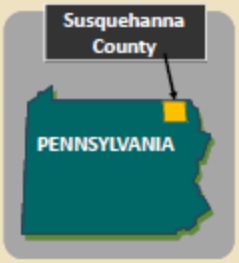
KEY POINT: ***Multiple sources of methane in shallow groundwater. Source identification challenging.***

Practical Guidelines for Evaluation of Methane Impacts on Groundwater

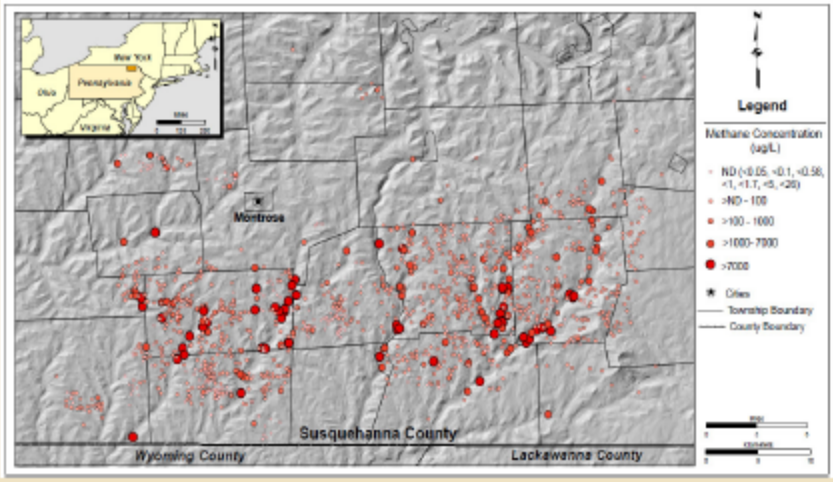
Case Study:
- Marcellus, NE PA

Lessons Learned:
- Lines of Evidence for Stray Gas Studies

Shale Gas Development:
- Implications for Baseline Monitoring

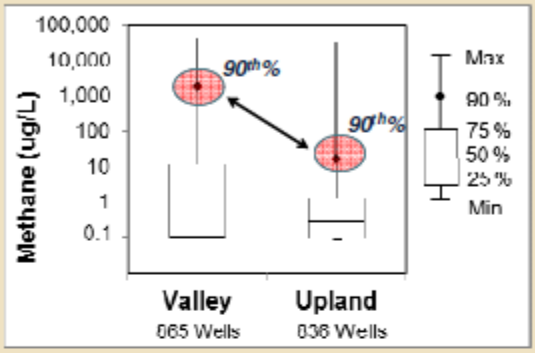


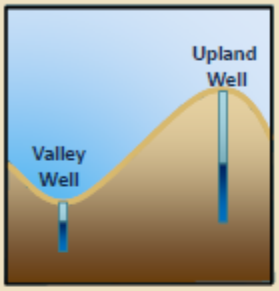
Methane Concentrations in GW: *Susquehanna County, NE Pennsylvania*



KEY POINT: *CH_4 concentrations appear correlated with topography.*

Distribution of Valley Vs. Upland Methane Concentrations

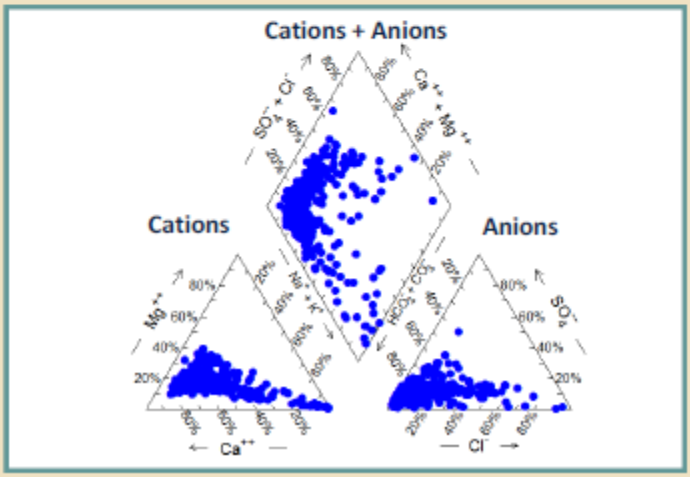




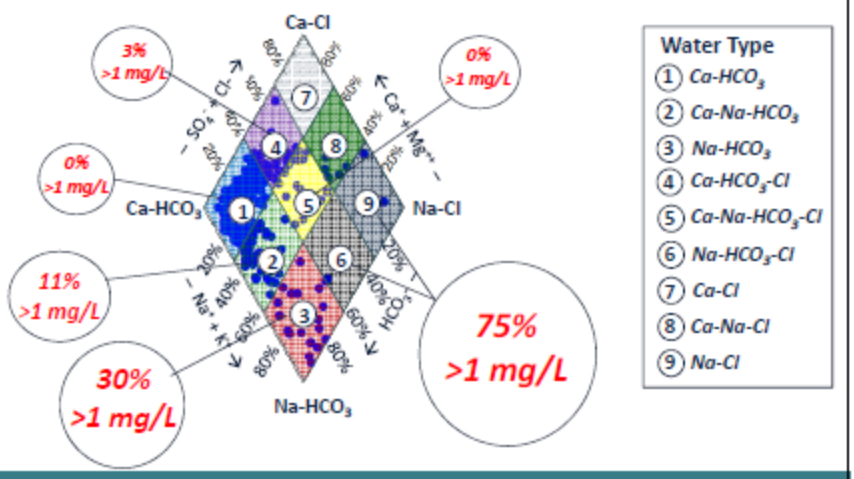
KEY POINT: *Upper-Range (90th %) concentrations are significantly higher in valleys vs. uplands.*

Classification of Water by Major Ions

>400 Pre-Drill Water Well Samples, NE Pennsylvania

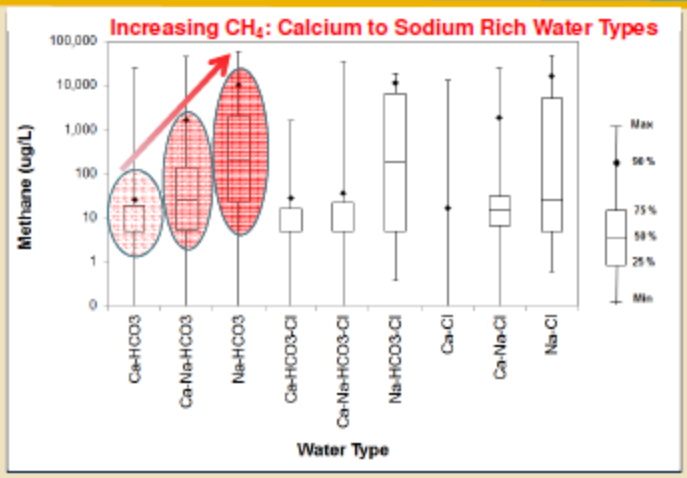


Relation of Methane to Water Type



KEY POINT: *Water type indicates expected range of methane concentrations.*

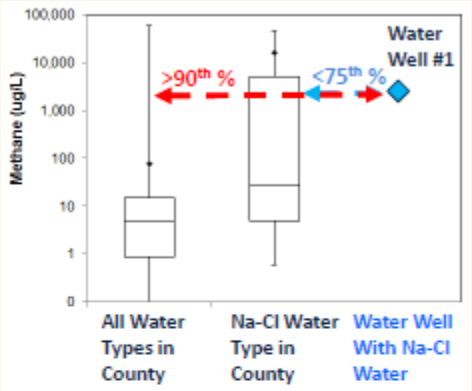
Methane Distribution per Water Type



KEY POINT: *Different water types have predictable methane distributions.*

Using Water Type to Assess Probability of an Impact

Water type is predictive of natural methane ranges.



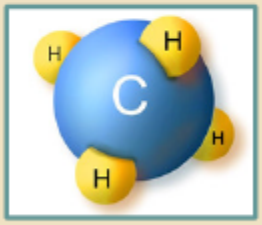
Methane in the water well is within common range of the natural CH_4 conc.'s observed in Na-Cl water.

KEY POINT: *Understanding water geochemistry can assist in proper identification of impacts.*

Methods for Improved Baseline Characterization: *Key Ion Ratios*

Key Indicators for Fresh Water Impact by Methane

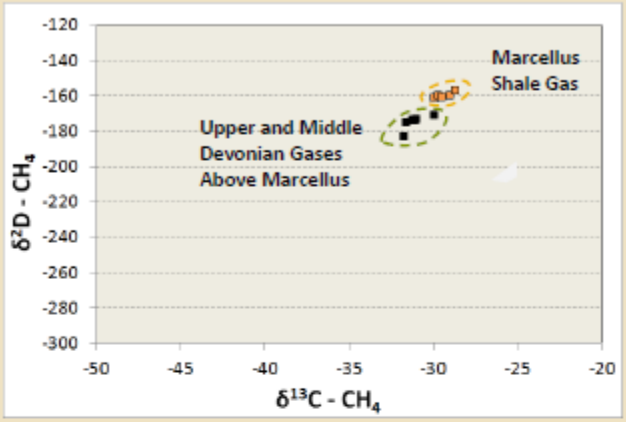
Type of Reaction	Electron Acceptor	Expected Indicator Compound Response
Microbial Oxidation of Methane $CH_4 + O_2 \rightarrow CO_2$	Oxygen	O_2 ↓
	Nitrate	NO_3 ↓
	Sulfate	SO_4^{-2} ↓
	Manganese	Mn^{+2} ↑
	Ferric Iron	Fe^{+2} ↑
Associated Changes:		HCO_3 ↑ Ca^{+2} ↓ pH ↑



↑ = *Increase*
↓ = *Decrease*

KEY POINT: *Indicator compound concentrations in GW can be used to track stray gas impact.*

Isotope Analyses: *Source Gases Identified by Pennsylvania DEP and Cabot*

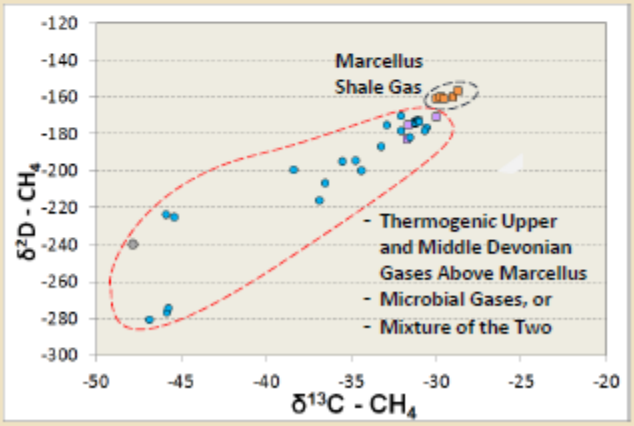


Source Gases

- Marcellus Production Gas (PA DEP & Cabot)
- Annular Spaces of Casing Strings and Well Cellar (PA DEP)

KEY POINT: *Local Marcellus shale gas may be distinguished from shallower overlying Upper and Middle Devonian gases.*

Isotope Analyses: *Water Well Gases Sampled by PA DEP and Cabot Oil*



Source Gases

- Marcellus Production Gas (PA DEP & Cabot)
- Annular Spaces of Casing Strings and Well Cellar (PA DEP)
- Water Wells (PA DEP & Cabot)
- Salt Springs State Park (Cabot)

KEY POINT: *Dissolved gases from local water wells are consistent with microbial or shallow thermogenic sources.*

RPSEA Project: *Reducing the Environmental Impact of Shale Gas Development*

Project Team

GSI ENVIRONMENTAL

A&M

Scope

- Baseline Sampling/ Stray Gas Guidelines
- Air Emissions Assessment
- Produced Water Analyses

Support

- Regulatory (PA, NY, OH, TX, OK)
- Industry (15)
- NGO's: GWPC, HARC, others
- Academic / Consulting (9)

Objective

Achieve World Peace *(and improved envir. monitoring) through better management of baseline and stray gas data.*



Credit: Bennett V/Flickr

Quality and Legal Issues Associated with Unconventional Drilling

David A. Gratson, Rock J. Vitale; Environmental Standards
Brian J. Clark; Buchanan Ingersoll & Rooney PC

Abstract

Unconventional gas energy and production activity have greatly increased the demand for high quality, defensible analytical measurements of domestic wells and drinking water sources. The presumptive liability, which may be associated with changes in water chemistry after drilling, is of particular concern to both water users and energy companies. A number of states and organizations have developed guidance documents that include required analytes and analytical methods that are to be used prior to and after drilling has been performed. Measurement of these analytes has inherent uncertainty from both laboratory and site-specific sources. It can be quite a challenge to evaluate whether an impact has occurred when only a single data point is typically available prior to drilling, yet many samples may be collected post drilling if an impact from the drilling is suspected. Specifically, what are the legal implications if a few analytes show increase concentration post drilling?

This presentation will explore the laboratory and site-specific data quality challenges and describes how these can impact the legal questions. Additionally, the presentation will discuss how multiple lines of evidence, including the laboratory measurements, site specific geochemistry, and published literature can be effectively used in data evaluation. The presentation will also highlight how the overall documented quality aspects incorporated into the project's sampling, laboratory analysis, and data analysis plan should be guided by the very real litigation potential associated with these gas energy and production activities.

Quality and Legal Issues Associated with Unconventional Drilling

National Environmental Monitoring Conference
San Antonio, Texas
August 5, 2013



David A. Gratson, CEAC - Environmental Standards, Inc.
Brian J. Clark - Buchanan Ingersoll & Rooney PC
Rock J. Vitale, CEAC - Environmental Standards, Inc.

ENVIRONMENTAL STANDARDS

Agenda

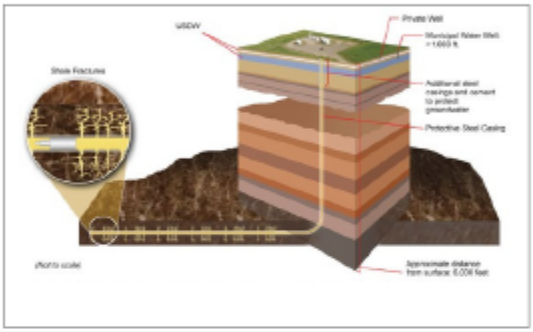
- Potential Risks with Unconventional Drilling
- Baseline and Post-Drilling Analyses
- Overview of Pre- and Post-Drilling Data Analysis: Usability Hinges on Quality and Applicability
- Development of Accurate Conceptual Site Models
- Legal Questions

2

ENVIRONMENTAL STANDARDS

Unconventional Concerns

- Can subsurface fluids migrate to drinking water resources. What local geologic or man-made features might allow this?



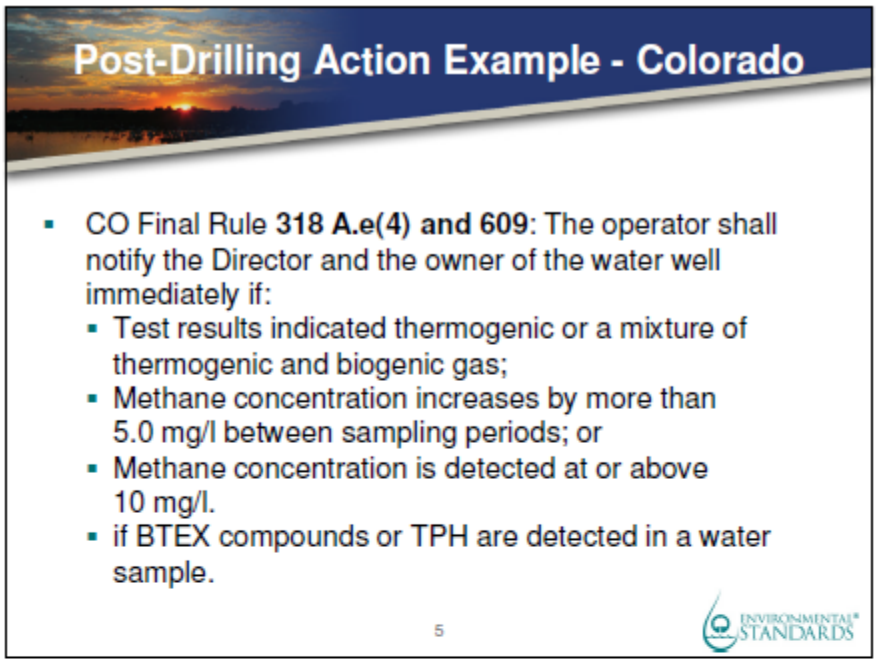
Risks

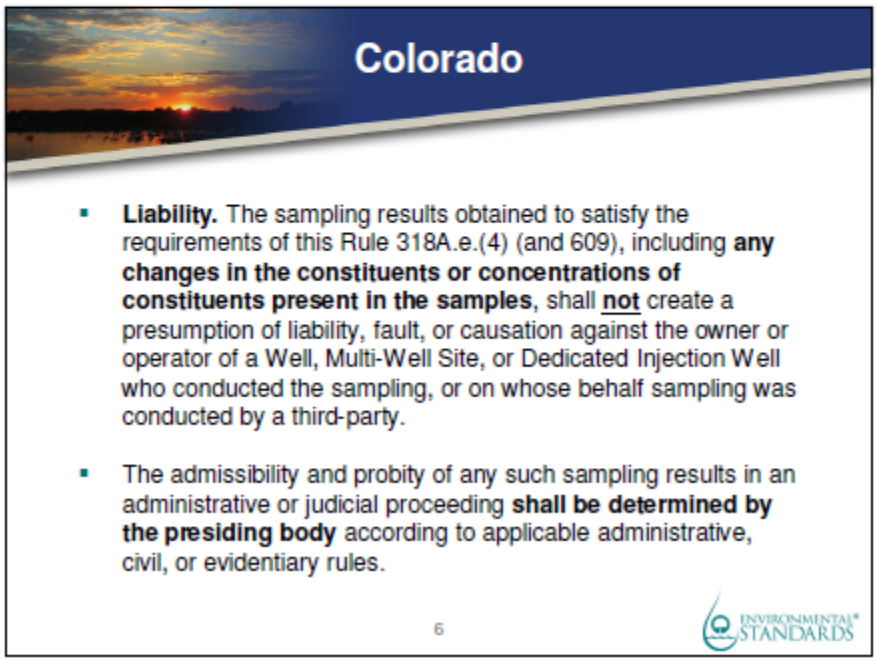


- Historic sites with prior issues
  - *e.g.*, same well, prior contamination
- Local geology, differentiate activity from background
- Presumption of contamination
  - Different state approaches

4

ENVIRONMENTAL STANDARDS


Post-Drilling Action Example - Colorado
CO Final Rule 318 A.e(4) and 609: The operator shall notify the Director and the owner of the water well immediately if:
Test results indicated thermogenic or a mixture of thermogenic and biogenic gas;
Methane concentration increases by more than 5.0 mg/l between sampling periods; or
Methane concentration is detected at or above 10 mg/l.
if BTEX compounds or TPH are detected in a water sample.
5
ENVIRONMENTAL STANDARDS


Colorado
Liability. The sampling results obtained to satisfy the requirements of this Rule 318A.e.(4) (and 609), including any changes in the constituents or concentrations of constituents present in the samples, shall not create a presumption of liability, fault, or causation against the owner or operator of a Well, Multi-Well Site, or Dedicated Injection Well who conducted the sampling, or on whose behalf sampling was conducted by a third-party.
The admissibility and probity of any such sampling results in an administrative or judicial proceeding shall be determined by the presiding body according to applicable administrative, civil, or evidentiary rules.
6
ENVIRONMENTAL STANDARDS

Pennsylvania



- Act 13 (2012): increased the presumption of liability for water supply contamination for unconventional wells. Unless rebutted, the **Act presumes that an operator is responsible for pollution of a water supply if the affected water supply is 2,500 feet from an unconventional well and that pollution occurred within 12 months of the later of completion**, drilling, stimulation, or alteration of the unconventional well.

  Operators found to have impacted water supplies within the time and distance provisions of the presumption of liability must provide temporary potable water until the supplies are restored or replaced.

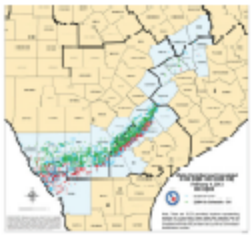
- A person liable for a well control emergency is **responsible for all response costs incurred by the department** (Please see §3219.1 and §3254.1 of the Act).

7

ENVIRONMENTAL STANDARDS

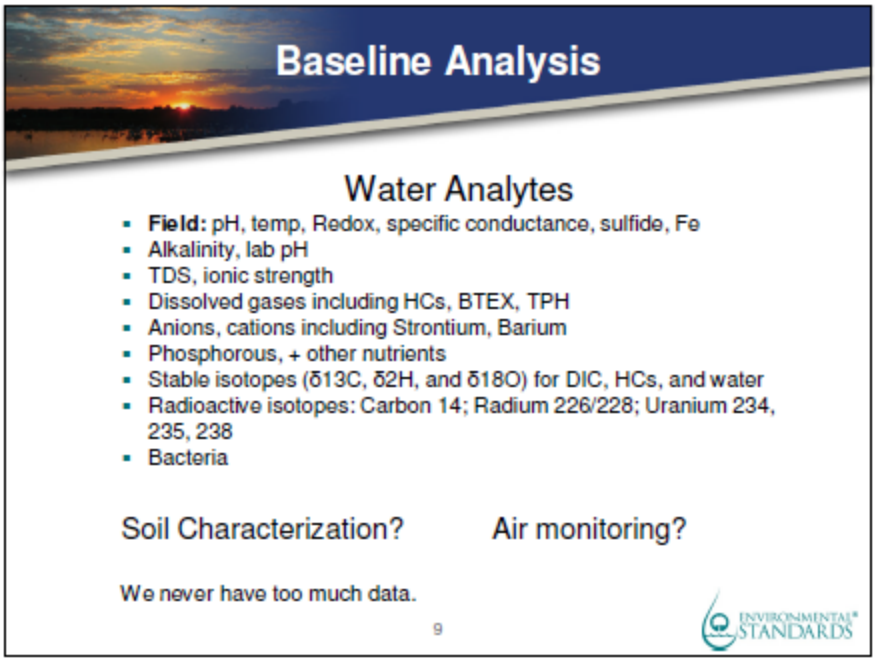
Texas - Legal Background

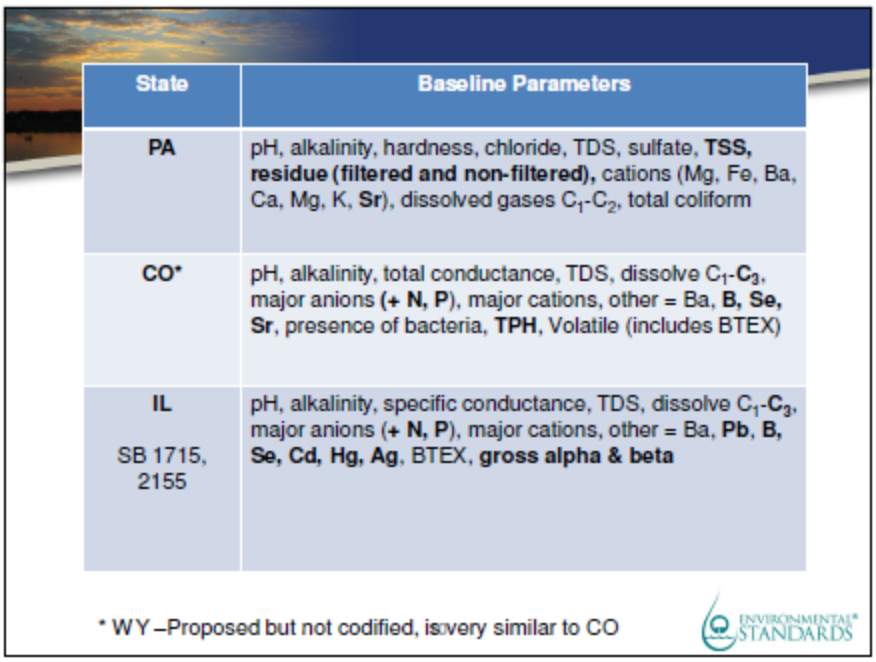
- The Texas Commission on Environmental Quality (TCEQ) serves as the state's primary environmental regulatory agency.
- The Railroad Commission protects surface and subsurface water from contamination by oil field operations.
- Groundwater Conservation Districts (GCDs) are local units of government that are created to manage groundwater resources within their boundaries, with rules providing for conservation, preservation, and protection of groundwater.



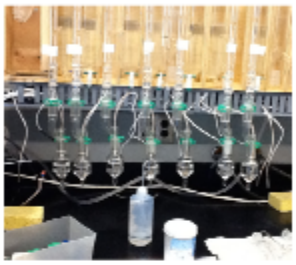
8

ENVIRONMENTAL STANDARDS


Baseline Analysis
Water Analytes
Field: pH, temp, Redox, specific conductance, sulfide, Fe
Alkalinity, lab pH
TDS, ionic strength
Dissolved gases including HCs, BTEX, TPH
Anions, cations including Strontium, Barium
Phosphorous, + other nutrients
Stable isotopes (δ13C, δ2H, and δ18O) for DIC, HCs, and water
Radioactive isotopes: Carbon 14; Radium 226/228; Uranium 234, 235, 238
Bacteria
Soil Characterization?
Air monitoring?
We never have too much data.
9
ENVIRONMENTAL STANDARDS


State
Baseline Parameters
PA
pH, alkalinity, hardness, chloride, TDS, sulfate, TSS, residue (filtered and non-filtered), cations (Mg, Fe, Ba, Ca, Mg, K, Sr), dissolved gases C1-C2, total coliform
CO*
pH, alkalinity, total conductance, TDS, dissolve C1-C3, major anions (+ N, P), major cations, other = Ba, B, Se, Sr, presence of bacteria, TPH, Volatile (includes BTEX)
IL
SB 1715, 2155
pH, alkalinity, specific conductance, TDS, dissolve C1-C3, major anions (+ N, P), major cations, other = Ba, Pb, B, Se, Cd, Hg, Ag, BTEX, gross alpha & beta
* WY –Proposed but not codified, is very similar to CO
ENVIRONMENTAL STANDARDS

Additional Reference for Analytes



- **US EPA** Congressionally Mandated Study (additional analytes include SVOCs, TPH, range of VOCs, low MW acids, surfactants)
- **USGS**
  - **Pavillion, WY**: analytes included "environmental tracers" 14C, fluorinated compounds, tritium, stable gases, helium isotopes.
  - **Texas**: San Antonio River Authority to initiate and refine an appropriate suite of water-quality measurements for detecting and monitoring hydraulic fracturing-derived contaminants in surface water and **sediments** of the lower San Antonio River watershed, Texas. Data in review - to be completed this year.

11

ENVIRONMENTAL STANDARDS

Data Analysis

- Concentration with time pre/post, all parameters
- Diagrams of relationships
  - Piper, Stiff, Durov diagrams
  - Carbon, hydrogen, oxygen isotope ratios
  - C1/C2+ vs δ13C of methane (Bernard plot) and variations of "wet" constituents
  - Specific conductance versus anions
  - Strontium or other isotope ratios
  - Dissolved Inorganic Carbon isotopes
  - 14C
- Historic Data Options
  - USGS studies
  - http://pubs.usgs.gov/sir/2013/5015/ (Surface water)
  - http://pubs.usgs.gov/sir/2012/5198/ (Groundwater)

12

ENVIRONMENTAL STANDARDS

Issues with Data Analysis

Challenge is to use a single baseline sample to make an argument and a conceptual site model that is consistent.

- Variability of analytes - temporal complicates
- "Uniqueness" of parameter(s) (e.g. GCxGC TOFMS)
- Multivariate (*e.g.*, Durov diagram)

Quality of each parameter and measurement is critical to data analysis.

- **Example of Importance**: Penn State, Center for Rural Pennsylvania: Bromide Lab error – see later slide.

13

ENVIRONMENTAL STANDARDS

Comparison of Dissolved, Cold Tap Headspace and Wellhead Methane for Well #2

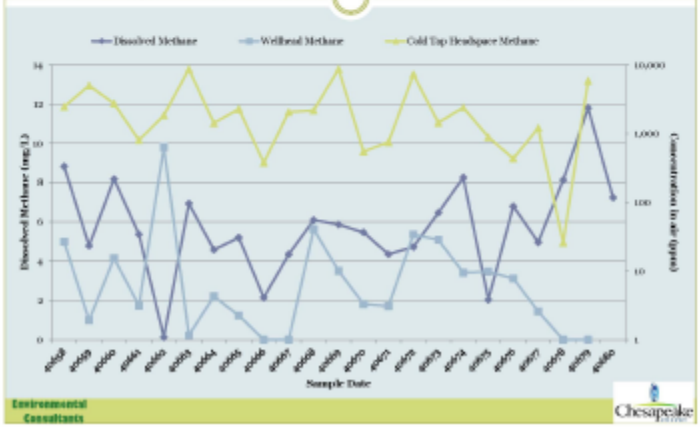
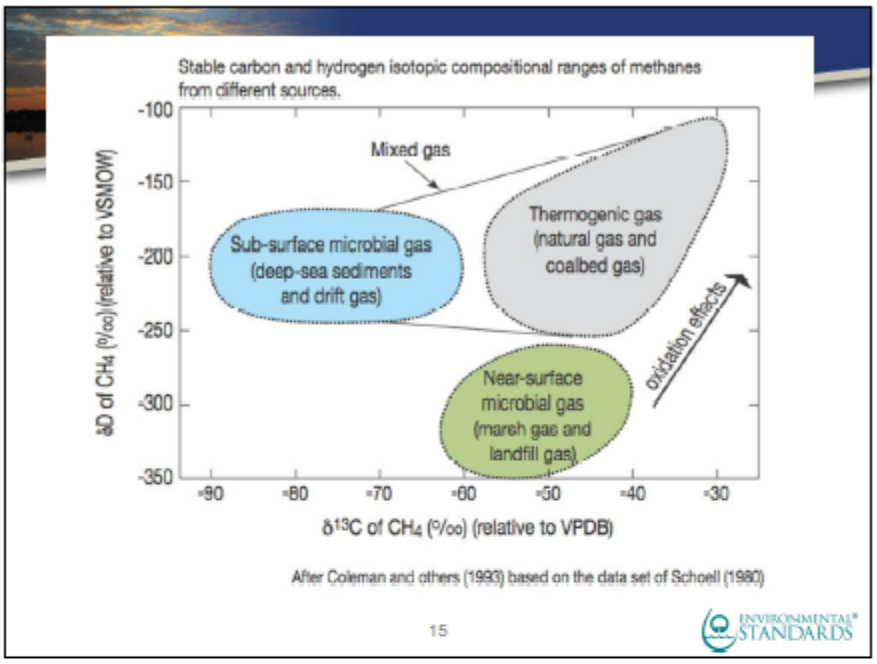
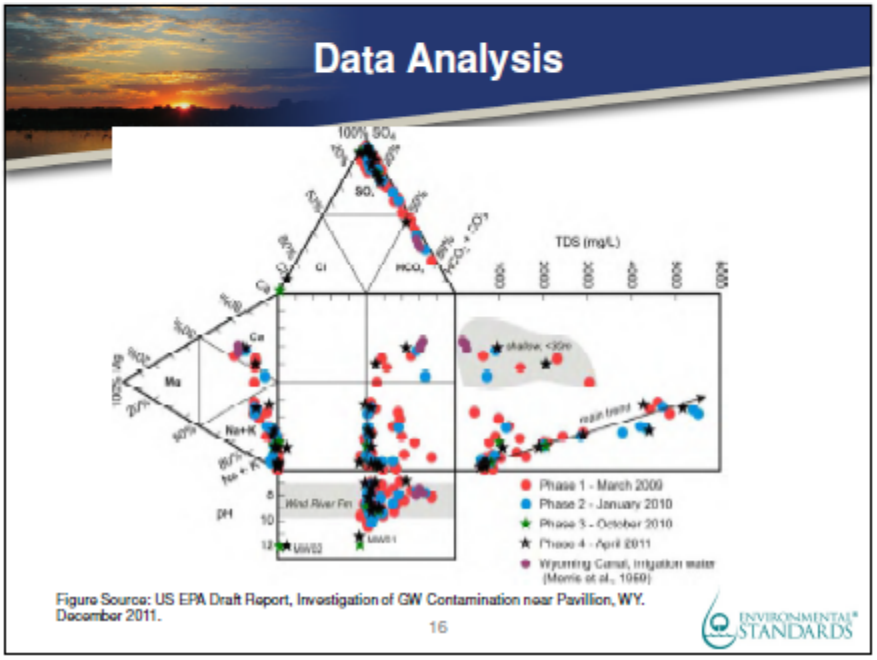


Figure Source: Coleman and McElreath, GWPC Presentation, 2012.

14

ENVIRONMENTAL STANDARDS


Stable carbon and hydrogen isotopic compositional ranges of methanes from different sources.
Mixed gas
Sub-surface microbial gas (deep-sea sediments and drift gas)
Thermogenic gas (natural gas and coalbed gas)
Near-surface microbial gas (marsh gas and landfill gas)
oxidation effects
δD of CH4 (‰) (relative to VSMOW)
δ13C of CH4 (‰) (relative to VPDB)
-100
-150
-200
-250
-300
-350
-90
-80
-70
-60
-50
-40
-30
After Coleman and others (1993) based on the data set of Schoell (1980)
15
ENVIRONMENTAL STANDARDS


Data Analysis
TDS (mg/L)
Phase 1 - March 2009
Phase 2 - January 2010
Phase 3 - October 2010
Phase 4 - April 2011
Wyoming Canal, irrigation water (Morris et al., 1969)
Figure Source: US EPA Draft Report, Investigation of GW Contamination near Pavillion, WY. December 2011.
16
ENVIRONMENTAL STANDARDS

Data Analysis

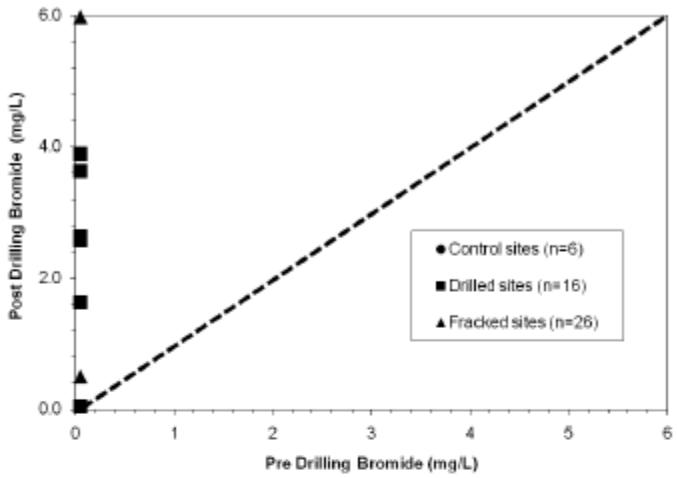


Figure Source: The Center for Rural Pennsylvania, Penn State University, Oct. 2011.

17

Complications of Data Analysis

Contamination

- Water Sources (*e.g.*, DI water): characterize first – same methods, same exact steps as samples
- Non-disposable contact. Cleaning agents (characterized?)

- Usability may require data validation of analytical QA/QC

18

Colorado - Quality Guidelines

- All data must undergo data quality review (App. B) and you must **sign** (to acknowledge):

  Are the data suitable for release for incorporation into the Colorado Oil and Gas Conservation Commission environmental database?

- Complaint Procedures
- Within 48 hours of receipt of complaint

COGA Voluntary Baseline Groundwater Quality Sampling Program, November 15, 2011.

19

ENVIRONMENTAL STANDARDS

Colorado Data Review

Review includes:

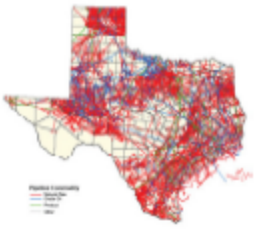
- Well and Field Sampling (not reproduced here).
- **Laboratory**
  - Proper custody was maintained from the time of sampling until receipt by the laboratory.
  - All samples were analyzed for the requested analyses.
  - Proper laboratory methods were used.
  - All sample holding times were met.
  - Laboratory quality assurance samples such as matrix spikes and matrix spike duplicates were collected and analyzed according to the laboratory method, and all laboratory quality control sample results were within method acceptance limits.
  - All field quality control samples meet the data quality objectives listed above.
- Specify corrective actions needed and dates by when those corrective actions should be completed.

20

ENVIRONMENTAL STANDARDS

Why Perform Pre-Project Audits and Data Validation

- Example of steps for analysis of δ13C in Methane:



Methane mole % analysis:
- Calibration, daily QC checks of GC
- Report C1-C3+ as Mole %

Stable Isotopes of carbon analysis:
- Conversion of each hydrocarbons to CO_2, and capture of each for analysis.
- Analysis (each CO_2) by IMS: m/z 44,45,46, dual inlet or continuous flow, calibration, daily checks, reference checks, ^{17}O correction.

21

ENVIRONMENTAL STANDARDS

NELAC Accreditation and Labs

- Range of accreditors.
- Our experience has shown some data can still be method non-compliant, or it does not meet project requirements, yet is from a NELAC accredited laboratory.
- Some baseline analytes not from NELAC accredited laboratories or fully published methods: *e.g.*, stable isotopes, 14C, surfactants.

THE NELAC INSTITUTE

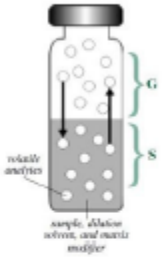
22

ENVIRONMENTAL STANDARDS

Analytical Method Complications

EPA Methods and Standard Industry Practice

- RSK-175: no Federal codified method
- Variables left to labs:
  - Sample handling (bottle opened?)
  - Calibration samples versus standards.
  - Interference from high salinity, surfactant with headspace versus calibration.
  - Sample collection and preservation.



23

ENVIRONMENTAL STANDARDS

Data Analysis



- Develop a Conceptual Site Model
  - Cross-checked using standard water quality checks and relationships correlate with information on regional and site-specific geology and hydrology.
- Look for multiple lines of evidence.
- Include variability/uncertainty in the analysis.

24

ENVIRONMENTAL STANDARDS

Hypothetical Situations

Baseline	Post-Drilling
Methane 20 ug/L in GW	Methane 28 ug/L (saturated)
No isotopic data	No isotopic data, but can be taken
Major cations and anions similar to post-drilling	

Baseline	Post-Drilling
Methane 20 ug/L in GW	Methane similar to baseline
No isotopic data	No isotopic data, but can be taken
Barium is 10X higher in post-drilling	

25

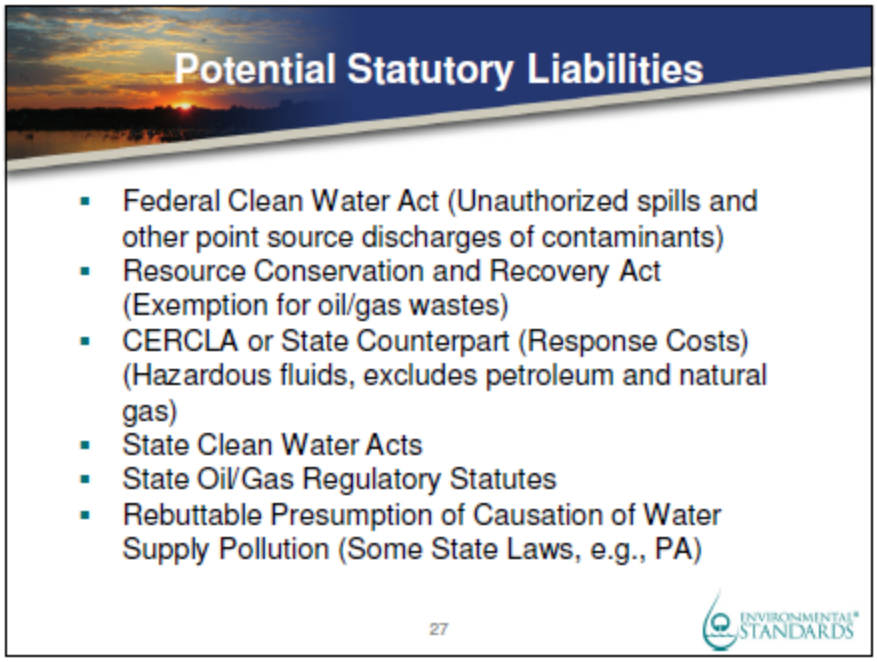
ENVIRONMENTAL STANDARDS

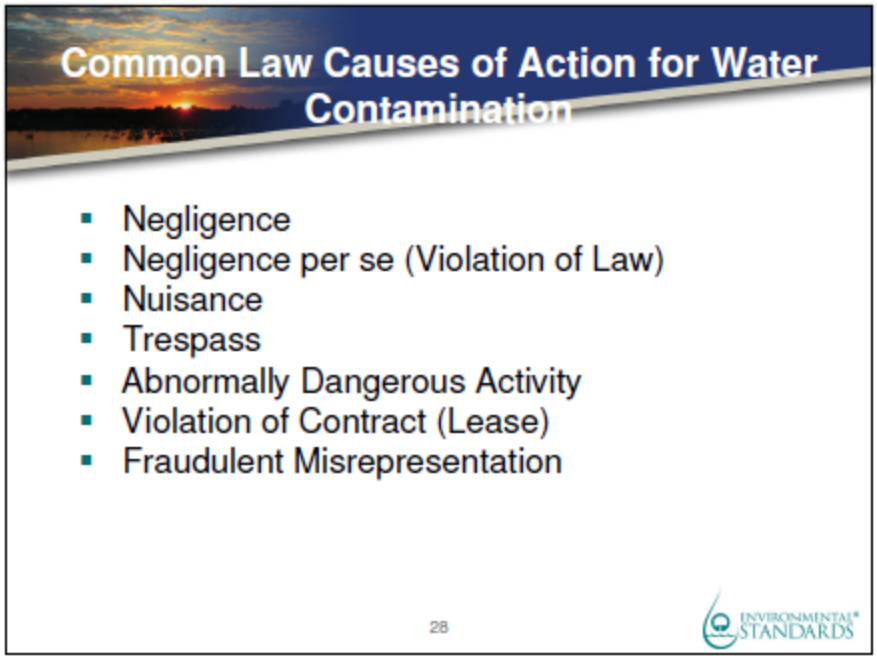
Regulatory Basis of Unconventional

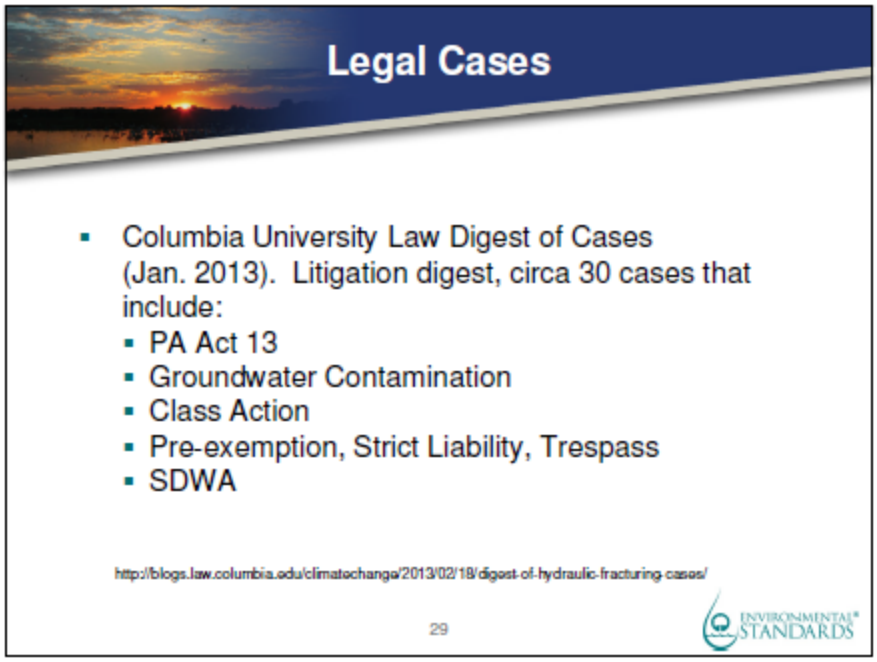
- SDWA, but 2005 amendments exclude fracking.
- CAA: upstream gas production, transportation, and storage (measurement).
- Federal Underground Injection:
- States/Native American Land.
  - BLM extends the comment period deadline to August 23, 2013 on public and native land.
  - Surface and mineral ownership cloudy.
  - CERCLA (federal superfund) hazardous substances in fracking fluids.

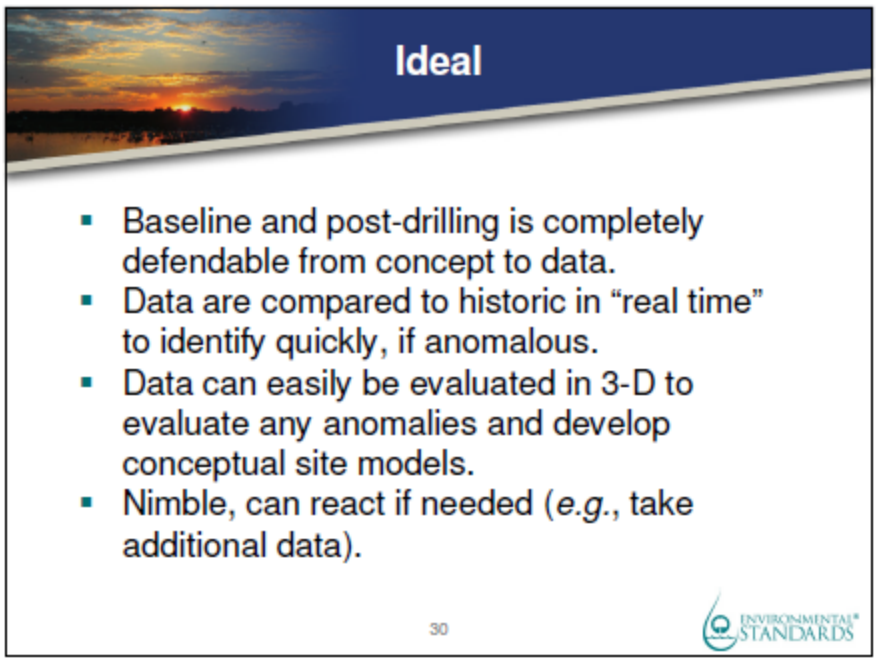
26

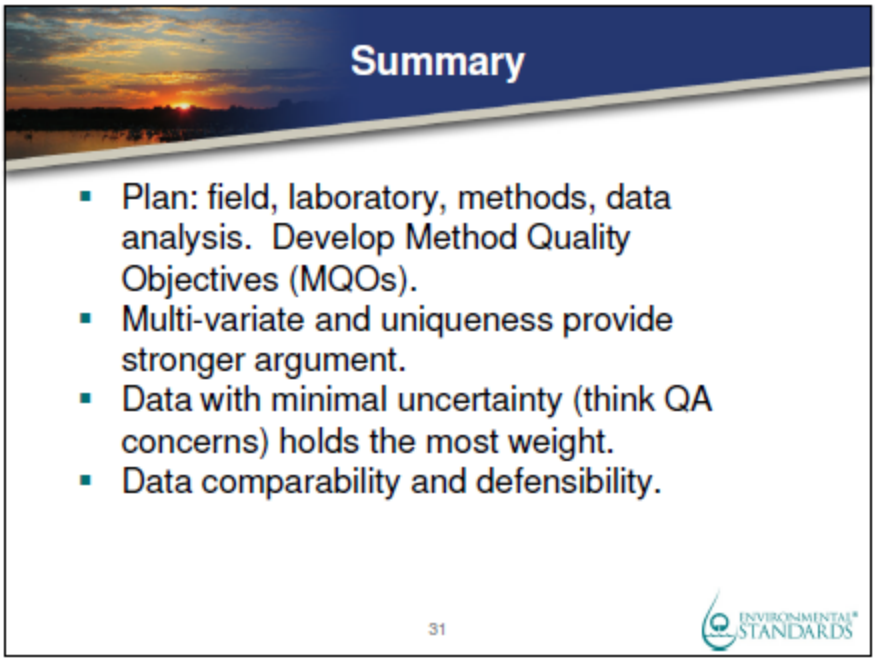
ENVIRONMENTAL STANDARDS


Potential Statutory Liabilities
Federal Clean Water Act (Unauthorized spills and other point source discharges of contaminants)
Resource Conservation and Recovery Act (Exemption for oil/gas wastes)
CERCLA or State Counterpart (Response Costs) (Hazardous fluids, excludes petroleum and natural gas)
State Clean Water Acts
State Oil/Gas Regulatory Statutes
Rebuttable Presumption of Causation of Water Supply Pollution (Some State Laws, e.g., PA)
27
ENVIRONMENTAL STANDARDS


Common Law Causes of Action for Water Contamination
Negligence
Negligence per se (Violation of Law)
Nuisance
Trespass
Abnormally Dangerous Activity
Violation of Contract (Lease)
Fraudulent Misrepresentation
28
ENVIRONMENTAL STANDARDS


Legal Cases
Columbia University Law Digest of Cases (Jan. 2013). Litigation digest, circa 30 cases that include:
PA Act 13
Groundwater Contamination
Class Action
Pre-exemption, Strict Liability, Trespass
SDWA
http://blogs.law.columbia.edu/climatechange/2013/02/18/digest-of-hydraulic-fracturing-cases/
29
ENVIRONMENTAL STANDARDS


Ideal
Baseline and post-drilling is completely defendable from concept to data.
Data are compared to historic in "real time" to identify quickly, if anomalous.
Data can easily be evaluated in 3-D to evaluate any anomalies and develop conceptual site models.
Nimble, can react if needed (e.g., take additional data).
30
ENVIRONMENTAL STANDARDS


Summary
Plan: field, laboratory, methods, data analysis. Develop Method Quality Objectives (MQOs).
Multi-variate and uniqueness provide stronger argument.
Data with minimal uncertainty (think QA concerns) holds the most weight.
Data comparability and defensibility.
31
ENVIRONMENTAL STANDARDS


Contacts
ENVIRONMENTAL STANDARDS
www.envstd.com
Buchanan Ingersoll & Rooney PC
David Gratson 505-660-8521/281-752-9782
Rock Vitale 610-935-5577
Brian J. Clark, Attorney at Law
717-237-4823
Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577
Virginia 1208 East Market Street | Charlottesville, VA 22902 | 434.293.4039
Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590
Texas 11200 Richmond Avenue, Suite 350 | Houston, TX 77082 | 281.752.9782
Web www.envstd.com | E-mail solutions@envstd.com
32

Environmental Forensic Investigation of Hydraulic Fracturing Fluids Used in Shale Gas Wells in the Eastern United States

Frank L. Dorman, Jessica Westland, Nathaniel Girer
Penn State University

Abstract

Recently there has been considerable interest in gas well drilling into the Marcellus shale in the Eastern United States. In states such as Pennsylvania, Ohio and New York, there has been a dramatic increase in the development of such wells, but this has not been without controversy. While the gas-drilling industry claims that their processes are completely safe and undamaging to the environment, several environmental groups strongly claim otherwise. Adding to the controversy, the process of hydraulic fracturing of these wells may use various chemicals that are not without concern. The industrial companies claim to self-disclose their formulations, but this is an overstatement, as the exact compositions are not revealed. If a hydraulic fracturing caused some environmental contamination, it would not be easy to determine the source of the contamination due to the lack of disclosure and oversight of the operators. This results in potentially complex environmental forensics analytical method development and sample analysis to determine if a contamination event has occurred, and who the principle polluter may be.

This presentation will address the sampling, sample preparation and analysis of these materials. Various sample preparation strategies will be discussed. GCxGC-TOFMS will be used as the determinative technique due to its inherent advantages over other possible techniques. Finally data will be presented that may allow for the development of protocols to determine both composition of these fluids, and possible point source of pollution should an event occur.

GCxGC-TOFMS Analysis of Drilling and Hydraulic Fracturing Fluids used in Gas Wells in the Eastern US

Frank L. Dorman, Jessica Westland and Nathaniel Girer

Penn State University

Shale Gas Wells in Eastern US:

- Marcellus Shale:
  - Gas producing formation between 4000 to 8500 feet from surface
  - "Reachable" in PA, NY, OH, WV, and part of Ontario
  - Rapid increase in drilling in last five years
  - Property owners are leasing land to drilling companies
    - Receive money based on amount of extracted gas
  - Drilling companies have received tax benefits
  - This is an extremely polarizing issue – very few people do not have a strong opinion either pro or con.

Chemicals Used by Hydraulic Fracturing Companies in Pennsylvania For Surface and Hydraulic Fracturing Activities (PA DEP website)

1,2,4-Trimethylbenzene	Glycol Ethers (includes 2BE)
1,3,5 Trimethylbenzene	Guar gum
2,2-Dibromo-3-Nitrilopropionamide	Hemicellulase Enzyme
2.2-Dibromo-3-Nitrilopropionamide	Hydrochloric Acid
2-butoxyethanol	Hydrotreated light distillate
2-Ethylhexanol	Hydrotreated Light Distilled
2-methyl-4-isothiazolin-3-one	Iron Oxide
5-chloro-2-methyl-4-isothiazotin-3-one	Isopropanol
Acetic Acid	Isopropyl Alcohol
Acetic Anhydride	Kerosine
Acie Pensurf	Magnesium Nitrate
Alchohol	Ethoxylated Mesh Sand (Crystalline Silica)
Alphatic Acid	Methanol
Alphatic Alcohol	Polyglycol Ether Mineral Spirits
Aluminum Oxide	Monoethanolamine

Hydrofrac Chemicals Continued

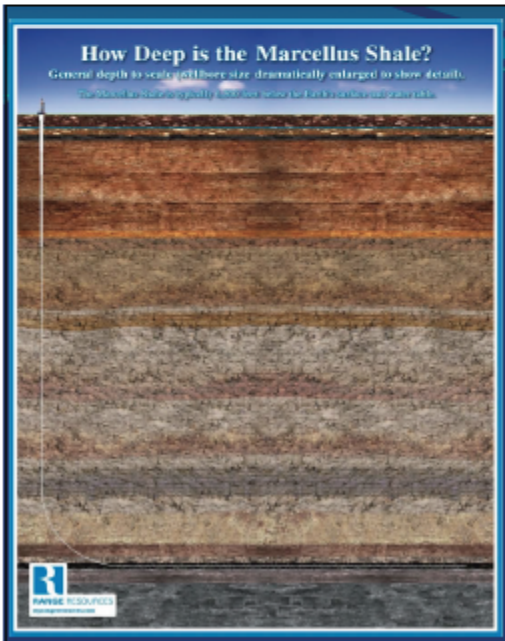
Ammonia Bifluoride	Naphthalene
Ammonia Bisulfite	Nitrilotriacetamide
Ammonium chloride	Oil Mist
Ammonium Salt	Petroleum Distallate Blend
Ammonia Persulfate	Petroleum Distillates
Aromatic Hydrocarbon	Petroleum Naphtha
Aromatic Ketones	Polyethoxylated Alkanol (1)
Boric Acid	Polyethoxylated Alkanol (2)
Boric Oxide	Polyethylene Glycol Mixture
Butan-1-01	Polysaccharide
Citric Acid	Potassium Carbonate
Crystalline Silica: Cristobalite	Potassium Chloride
Crystalline Silica: Quartz	Potassium Hydroxide
Dazomet	Prop-2-yn-1-01
Diatomaceus Earth	Propan-2-01
Diesel (use discontinued)	Propargyl Alcohol
Diethylbenzene	Propylene

Hydrofrac Chemicals Continued

Doclecylbenzene	Sulfonic Acid Sodium Ash
E B Butyl Cellosolve	Sodium Bicarbonate
Ethane-1,2-diol	Sodium Chloride
Ethoxlated Alcohol	Sodium Hydroxide
Ethoxylated Alcohol	Sucrose
Ethoxylated Octylphenol	Tetramethylammonium Chloride
Ethylbenzene	Titaniaum Oxide
Ethylene Glycol	Toluene
Ethylhexanol	Xylene
Ferrous Sulfate Heptahydrate	
Formaldehyde	
Glutaraldehyde	



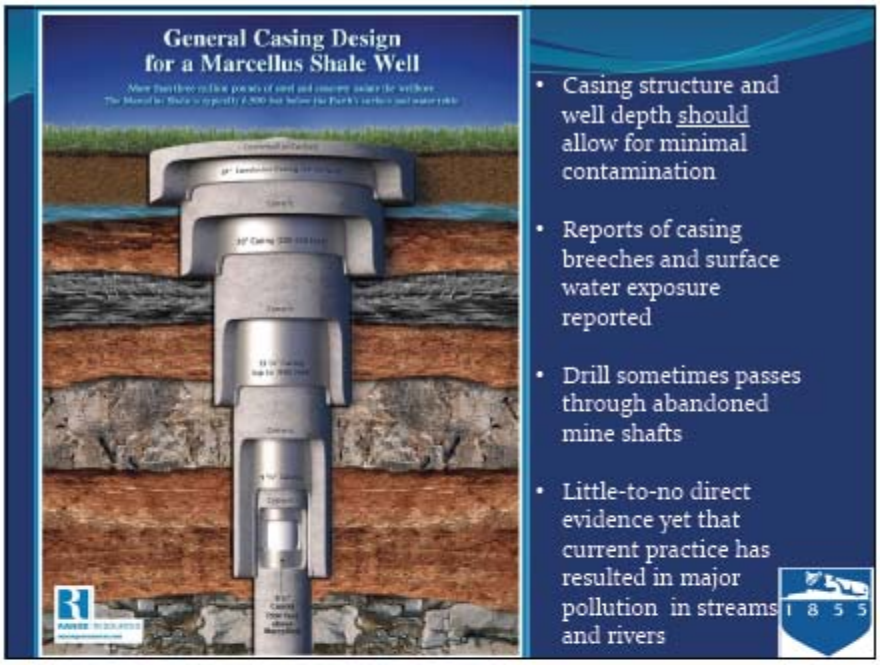


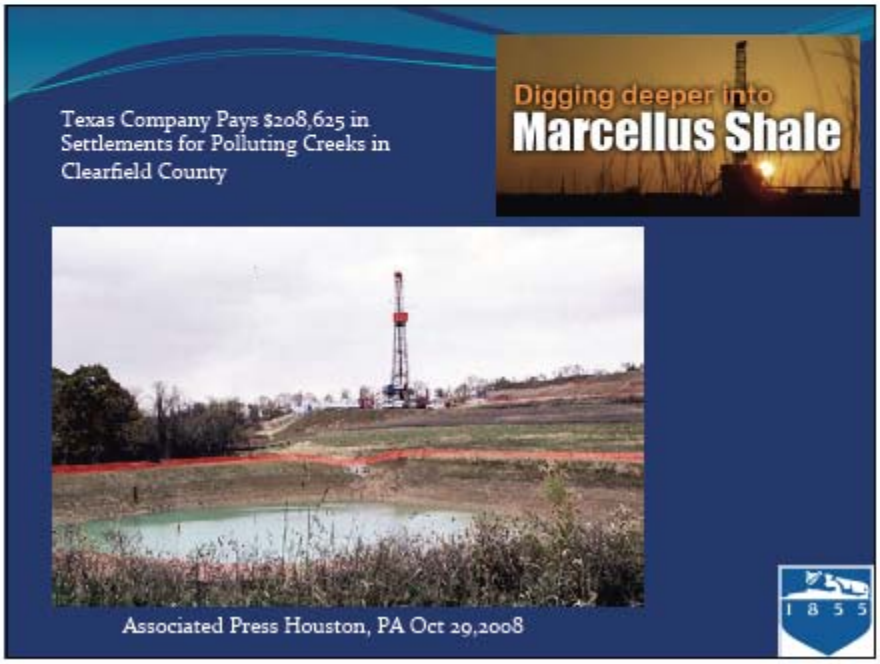


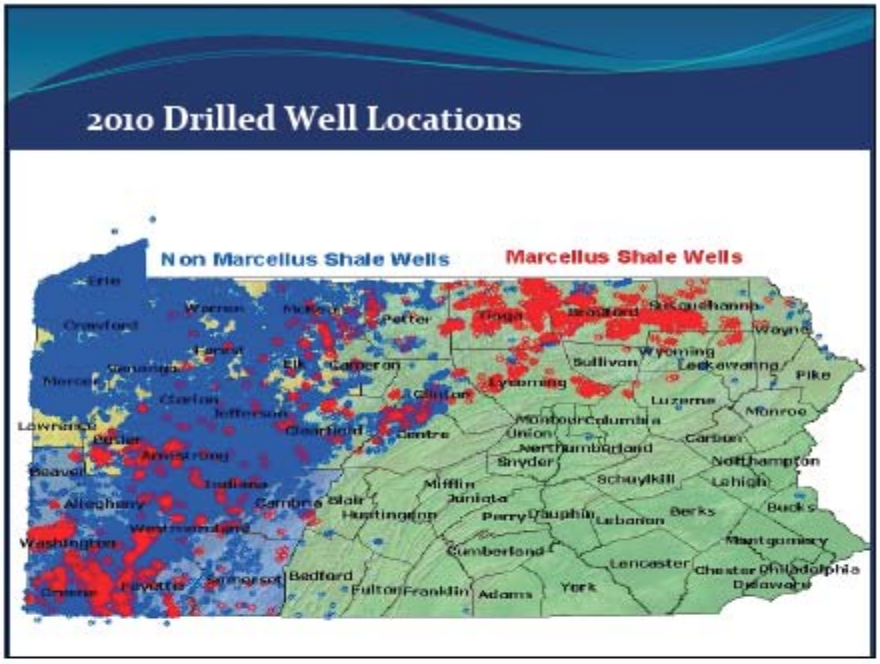
Gas well steps:

- Well is drilled
  - Horizontal boring in vein
- Casings are installed
- Hydraulic fracturing
- Pressure release
- Collection of Flowback water
- Disposal of collected material
  - Recent procedure
  - Not all material is collected
  - Recycling practice?




General Casing Design
for a Marcellus Shale Well
• Casing structure and well depth should allow for minimal contamination
• Reports of casing breeches and surface water exposure reported
• Drill sometimes passes through abandoned mine shafts
• Little-to-no direct evidence yet that current practice has resulted in major pollution in streams and rivers
1855


Texas Company Pays $208,625 in Settlements for Polluting Creeks in Clearfield County
Digging deeper into
Marcellus Shale
Associated Press Houston, PA Oct 29,2008
1855


2010 Drilled Well Locations
Non Marcellus Shale Wells
Marcellus Shale Wells
Erie
Crawford
Warren
McKean
Potter
Tioga
Bradford
Susquehanna
Wayne
Forest
Elk
Cameron
Sullivan
Wyoming
Lackawanna
Pike
Mercer
Venango
Clarion
Clinton
Luzerne
Monroe
Lawrence
Jefferson
Clearfield
Centre
Montour
Columbia
Union
Carbon
Butler
Armstrong
Northumberland
Snyder
Northampton
Beaver
Indiana
Schuylkill
Lehigh
Mifflin
Juniata
Allegheny
Cambria
Blair
Huntingdon
Perry
Dauphin
Lebanon
Berks
Bucks
Westmoreland
Washington
Montgomery
Cumberland
Lancaster
Chester
Philadelphia
Delaware
Fayette
Somerset
Bedford
Fulton
Franklin
Adams
York


Wells in PA mapped by type – Search by Spud Date 2012
http://www.philly.com/philly/news/special_packages/inquirer/169172846.html

Companies are "Self Reporting"

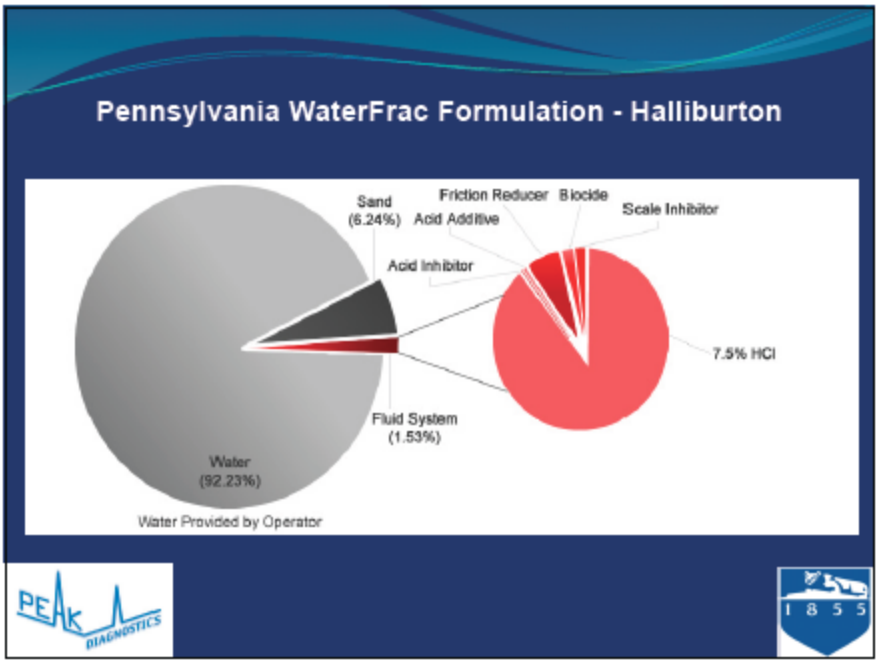
- Range Resources
- Halliburton
- Others?

- What is actually reported is not specific, so far…

- Fracfocus.org also lists information

Pennsylvania WaterFrac Formulation - Halliburton

Product Name	Additive	Purpose	Concentration	U.S. MSDS
BE-9™	Biocide	Prevents or limits growth of bacteria that can cause formation of hydrogen sulfide and can physically plug flow of oil and gas into the well	0.3 gal/1000 gal	
FE-1A™	Acid Additive	Prevents precipitation of iron oxides during acid treatment	5 gal/ 1000 gal of HCl acid volume	
FR-66™	Friction Reducer	Allows fracture fluid to move down the wellbore with the least amount of resistance	0.5 - 1 gal/1000 gal	
HAI-OS™	Corrosion Inhibitor / Acid Inhibitor	Prevents acid from causing damage to the wellbore and pumping equipment	0.1-2.0 gal/1000 gal of HCl acid volume	
7.5% Hydrochloric Acid (HCl)	Acid / Solvent	Removes scale and cleans wellbore prior to fracturing treatment	1000-4000 gal run ahead of frac	
LP-65™	Scale Inhibitor	Prevents build up of certain materials (i.e. scale) on sides of the well casing and the surface equipment	0.25 - 0.5 gal/1000 gal	
Sand – Common White 100 Mesh	Proppant	Holds open fracture to allow oil and gas to flow to well	0.5 - 1.0 lbs	
Sand – Premium White 40/70 Mesh	Proppant	Holds open fracture to allow oil and gas to flow to well	0.75 - 3.0 lbs	
Sand – Premium White 30/50 Mesh	Proppant	Holds open fracture to allow oil and gas to flow to well	2.0 - 3.0 lbs	
Water	Base Fluid	Base fluid creates fractures and carries proppant, also can be present in some additives	N/A	Supplied by Customer



Composition of Components in Marcellus Shale Hydraulic Fracturing Fluid

RANGE RESOURCES

Common Name & Supplier	Supplier Chemical Name	Common Description	Hazardous Component listed on MSDS	Purpose	MSDS Component Weight % of Chemical	Gallons MSDS Component in Well	Maximum Concentration of MSDS Component of Total Stage Fluid	
							% Vol	% Weight
7.5% HCl Mixture (ProcTech)	37% HCL	concentrated HCl Acid	HCL	Cleans perforation	37.0%	443.09	0.0084%	0.0034%
	CI-100	Corrosion Inhibitor	Methanol	Protects casing	95.0%	5.19	0.0001%	0.0001%
			Propargyl Alcohol	Protects casing	5.0%	0.22	0.0000%	0.0000%
	NE100	Non- Emulsifier	No hazardous ingredients	Prevents emulsions	0.0%	N/A	N/A	N/A
	FE100L	Iron Chelator	No hazardous ingredients	Prevents precipitation	0.0%	N/A	N/A	N/A
						TOTAL	0.0085%	0.0035%
Friction Reducer (ProcTech)	FRW-200 or FRW-3	Friction Reducer	No hazardous ingredients	Reduce friction down casing	0.0%	N/A	N/A	N/A
Scale Inhibitor (Multichem)	MX 588-2	Scale Inhibitor	No hazardous ingredients	prevents scale deposits	0.0%	N/A	N/A	N/A
Antibacterial Agent (Multichem)	Biotox	Antibacterial Agent	4,4-Dimethyloxazolidine	eliminates bacteria in water	75.0%	781.18	0.0150%	0.0140%
			3,4,4-Trimethyloxazolidine		5.0%	51.79	0.0010%	0.0009%
			2-Amino-2-methyl-1-propanol		1.0%	10.85	0.0002%	0.0002%
			Formaldehyde Amine		0.5%	4.72	0.0001%	0.0001%
	BMC B-8650	Antibacterial Agent	Glutaraldehyde	eliminates bacteria in water	50.0%	148.56	0.0029%	0.0026%
			Methanol		0.0%	1.49	0.0000%	0.0000%
						TOTAL	0.0191%	0.0192%
						SUMMARY	by vol % 0.028%	by weight % 0.023%

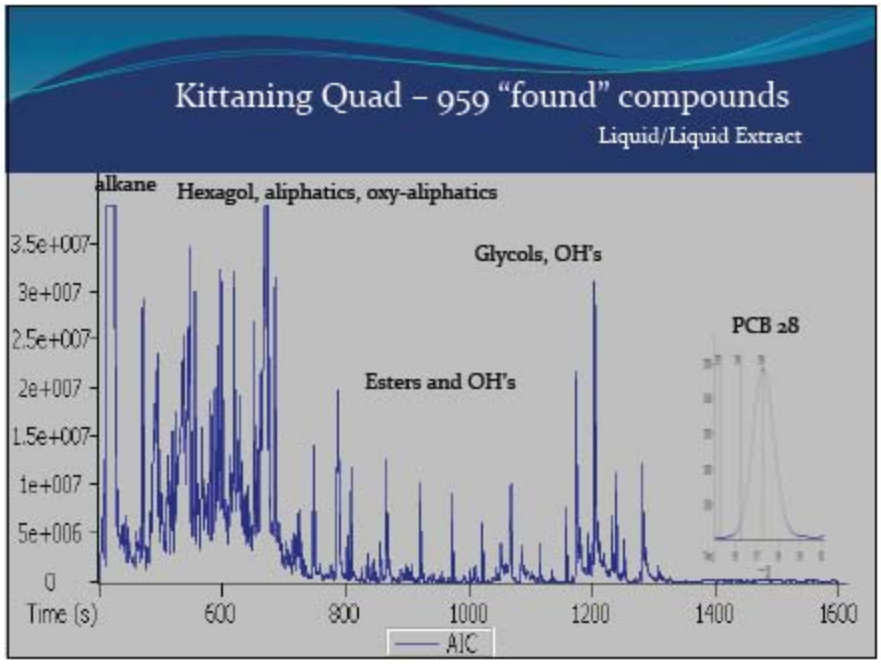
What is this information useful for?

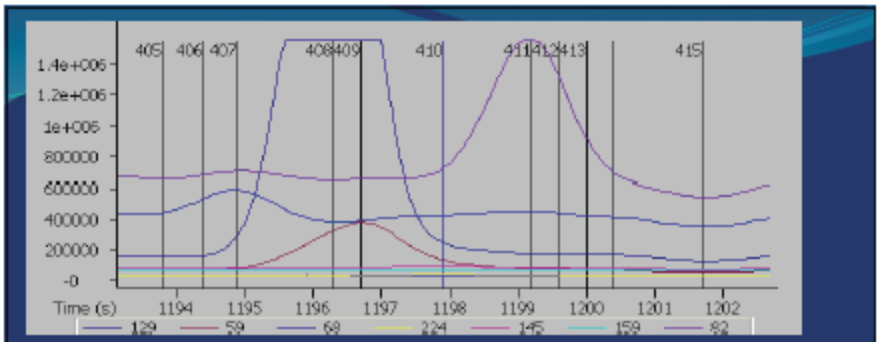
- Not much, really
  - Listed compounds are not a complete tabulation
  - No actual formulations are given
  - Samples are not easy to obtain
  - Many people are concerned at mere mention of "chemicals"
- Can we investigate this as scientists?

Analytical Method?

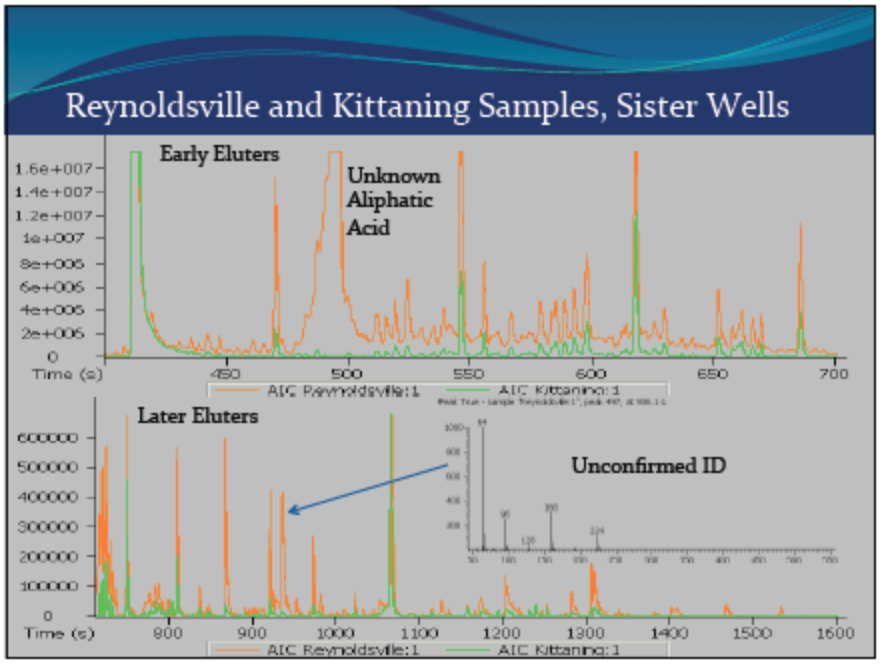
- GC-MS or GCxGC-MS rather obvious
  - We use both…
- Time-of-Flight would be preferred mass spectrometer
  - Samples may be quite complex
  - Much easier deconvolution
  - Discovery applications


GCxGC-TOFMS


Kittaning Quad – 959 "found" compounds
Liquid/Liquid Extract
alkane
Hexagol, aliphatics, oxy-aliphatics
Glycols, OH's
PCB 28
Esters and OH's
3.5e+007
3e+007
2.5e+007
2e+007
1.5e+007
1e+007
5e+006
0
Time (s)
600
800
1000
1200
1400
1600
AIC



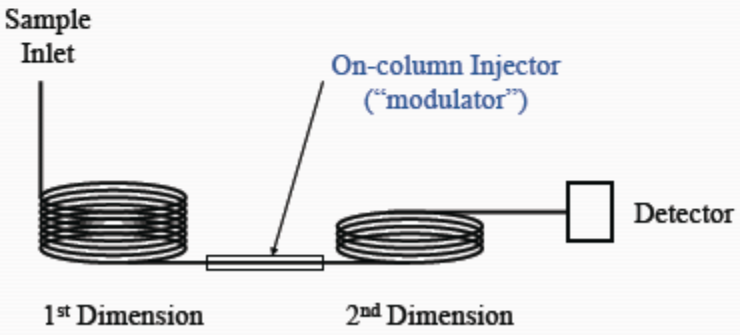
Peak #	Name	R.T. (s)	Similarity
405	Cyclohexane, 1,2,3-trimethyl-, (1à,2à,3à)-	1193.8	787
406	Undecane, 2,6-dimethyl-	1194.4	805
407	Fumaric acid, decyl pent-4-enyl ester		1194.9
	783		
408	Adipic acid, 2-ethylcyclohexyl isohexyl ester	1196.3	881
409	Octadecanamide	1196.7	919
410	Sulfurous acid, butyl 2-ethylhexyl ester	1197.9	737
411	Fumaric acid, eicosyl trans-hex-3-enyl ester	1199.2	939
412	Dichloroacetic acid, 1-cyclopentylethyl ester	1199.6	785
413	1,5,9,13-Tetradecatetraene	1200	728
414	7,9-Dimethyl-8-nitrobicyclo[4.3.1]decan-10-one	1200.4	822

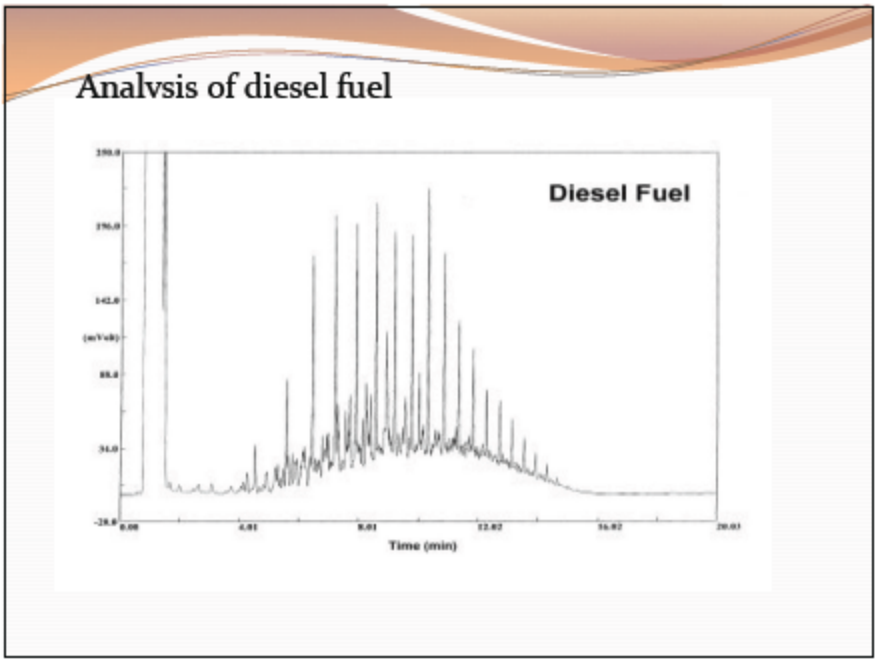


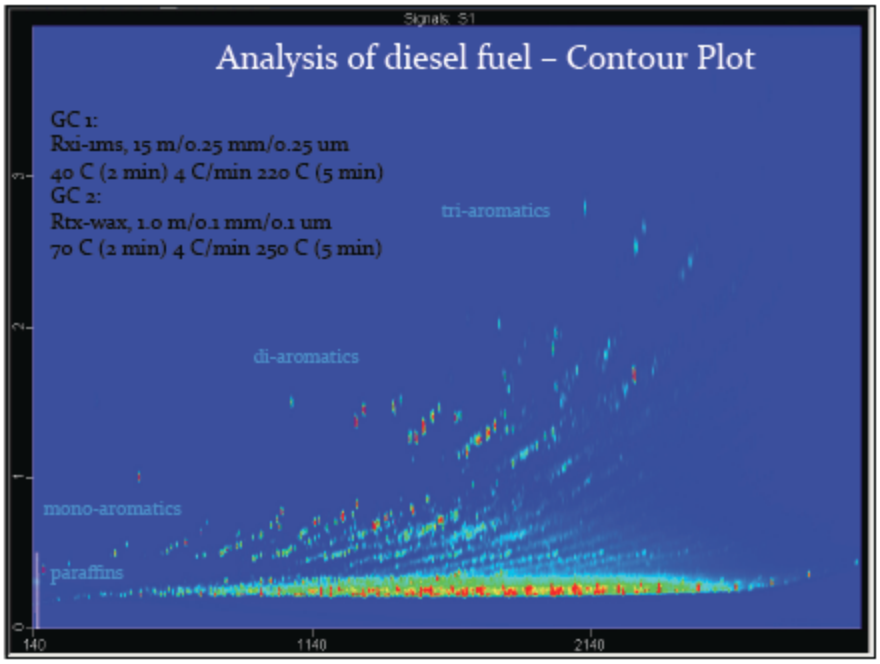
Early Conclusions

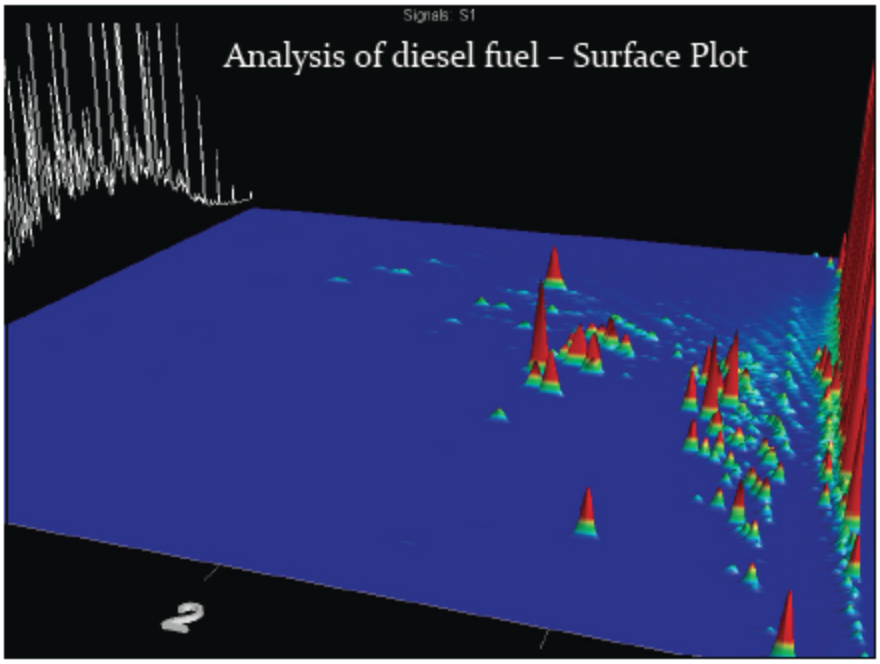
- Each Well has a different chemical signature
- Samples are very complex
  - UCM's in almost all 1D chromatograms
- Explanation to "peer" audience is nearly impossible using " GC and GC-MS techniques"
- Chemical complexity can be quite high in these samples

Comprehensive 2D GC Instrumentation (Phillips and Liu, 1989)




Analysis of diesel fuel
Diesel Fuel
Time (min)


Signals: S1
Analysis of diesel fuel – Contour Plot
GC 1:
Rxi-1ms, 15 m/0.25 mm/0.25 um
40 C (2 min) 4 C/min 220 C (5 min)
GC 2:
Rtx-wax, 1.0 m/0.1 mm/0.1 um
70 C (2 min) 4 C/min 250 C (5 min)
tri-aromatics
di-aromatics
mono-aromatics
paraffins
140
1140
2140



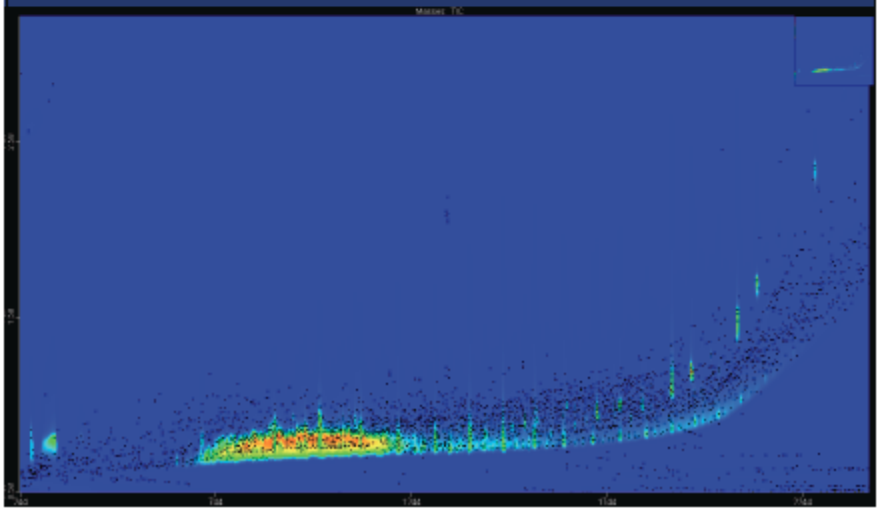
Gas Chromatograph Conditions

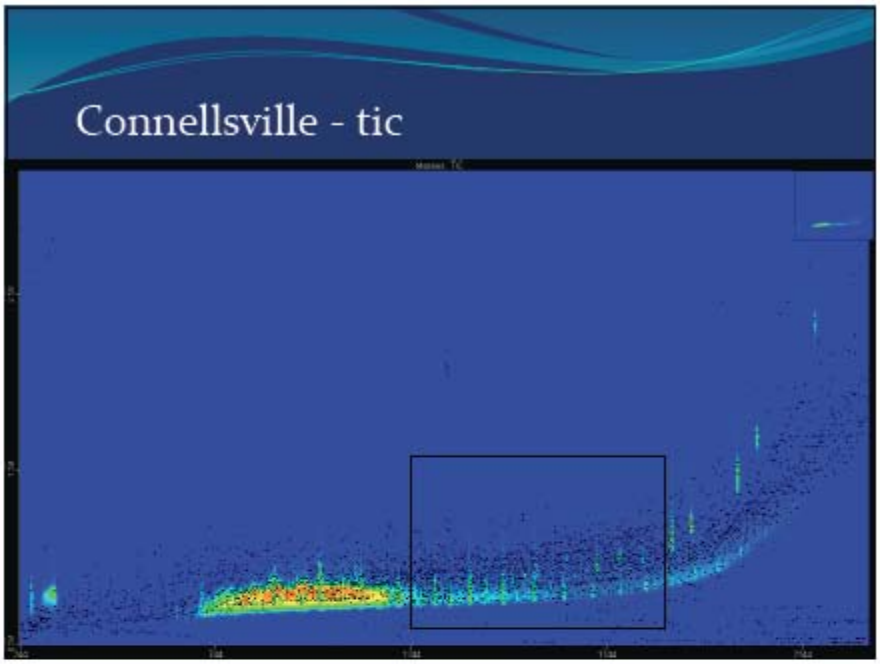
- Agilent 7890
- Column:
  - 1st Dimension Restek Rtx-Dioxin2
    - 40M X 0.18mm i.d. X 0.18 mm df
  - 2nd Dimension Restek Rxi-17Sil MS
    - 1M X 0.15mm i.d. X 0.15 mm df
- Injector:
  - Split, 10:1 ratio, Restek Precision liner
  - 250 C
  - 1.0 mL/min, He, constant flow
- Oven Programs:
  - 40 C (1), 8 C/min 305 C (7)
  - 15 C offset for second dimension
  - 30 C modulator offset

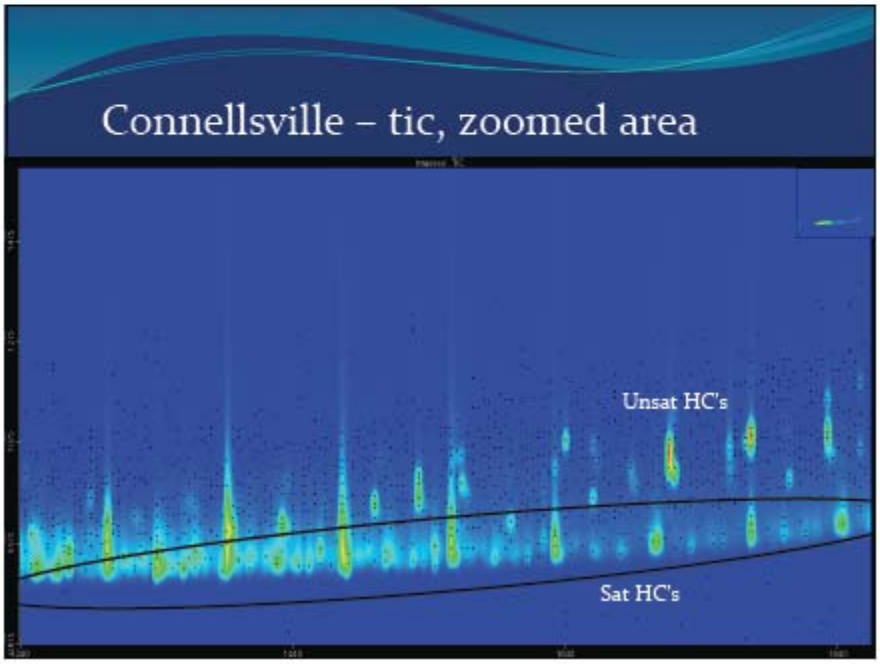
TOF Mass Spec Conditions

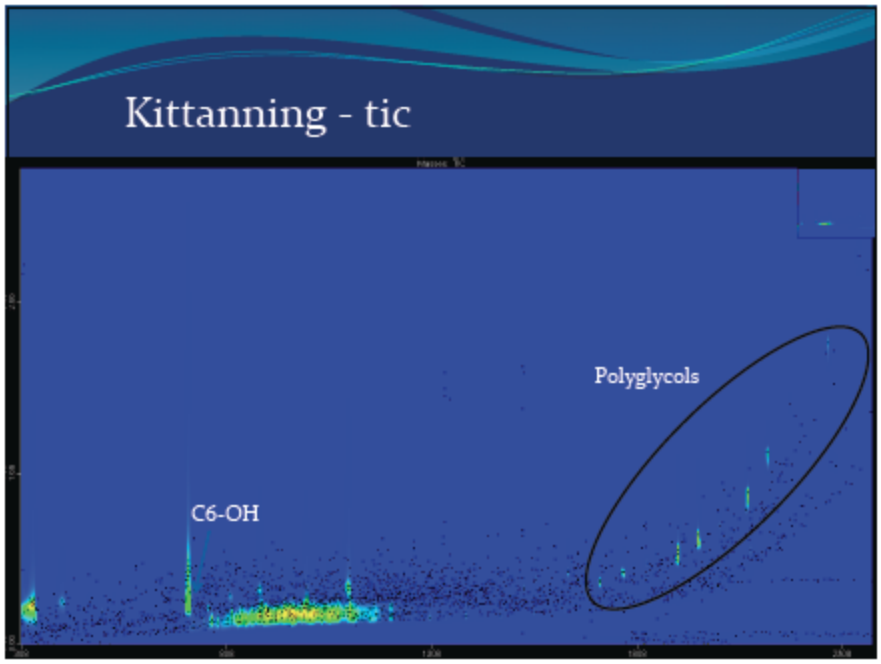
- Nominal Mass:
  - Transfer line 240 C
  - Source Temperature 200 C
  - 200 sec filament delay
  - 45 – 550 amu
  - 200 spectra/sec
- Accurate Mass:
  - 2 kHz extraction frequency
  - HR mode (25,000 resolution) < 1 ppm accuracy
    - Can achieve 50,000 resolution
  - 200 spec/sec
  - 45 – 530 amu
- NIST 2008 Library for spectral searching

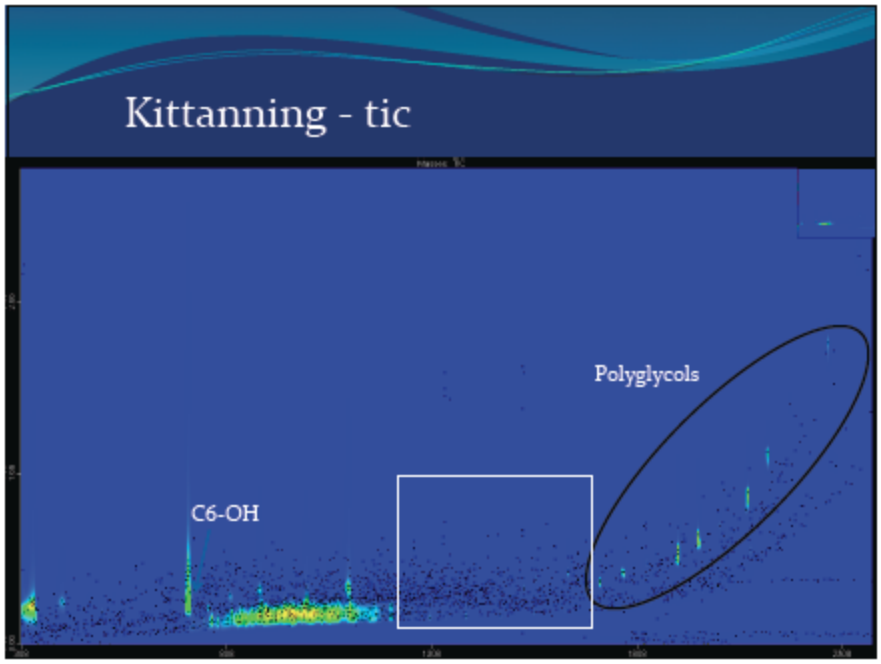
Connellsville - tic

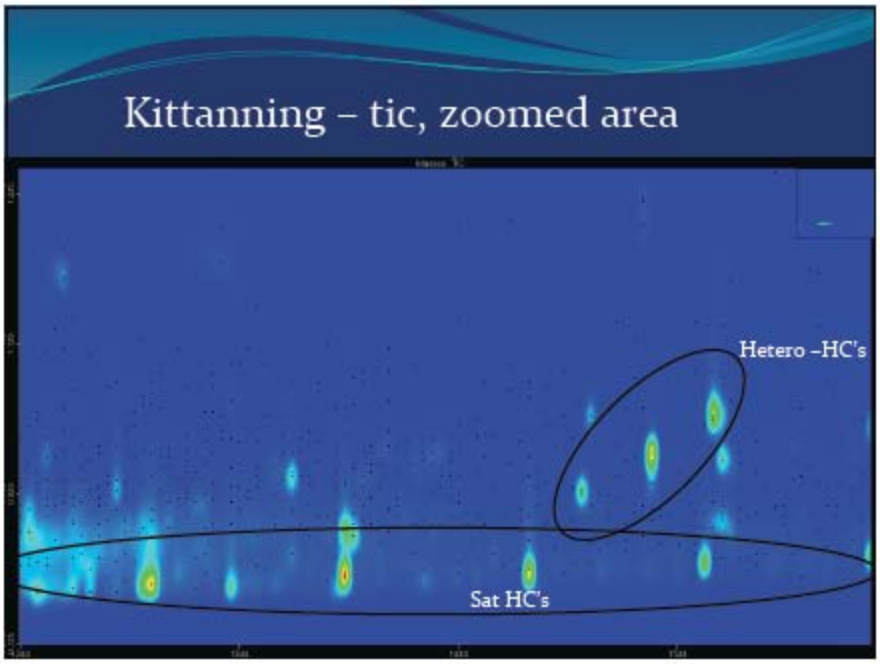


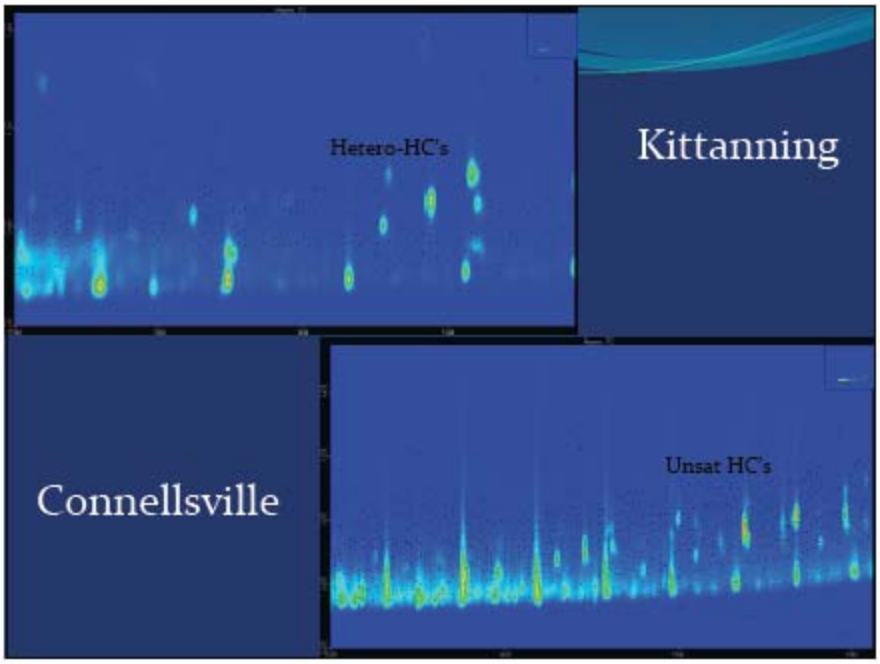

Connellsville - tic


Connellsville – tic, zoomed area
Unsat HC's
Sat HC's


Kittanning - tic
Polyglycols
C6-OH


Kittanning - tic
Polyglycols
C6-OH


Kittanning – tic, zoomed area
Hetero –HC's
Sat HC's


Hetero-HC's
Kittanning
Connellsville
Unsat HC's

Preliminary Conclusions:

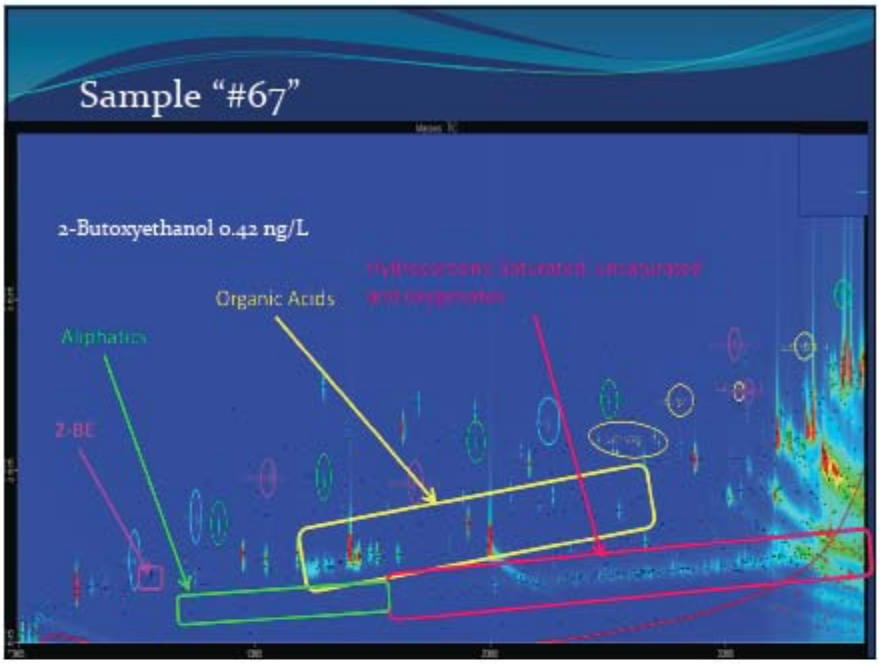
- GCxGC-TOFMS creates a "picture" that is likely MUCH more understandable to forensic data users
- Wastewater treatment does not reduce/eliminate many compounds
- Well dynamics and treatment dynamics are more easily determined using these techniques
- Possibility of high-resolution, full mass range mass spectrometry coupled to GCxGC provides tremendous analytical ability for characterization of frac fluids

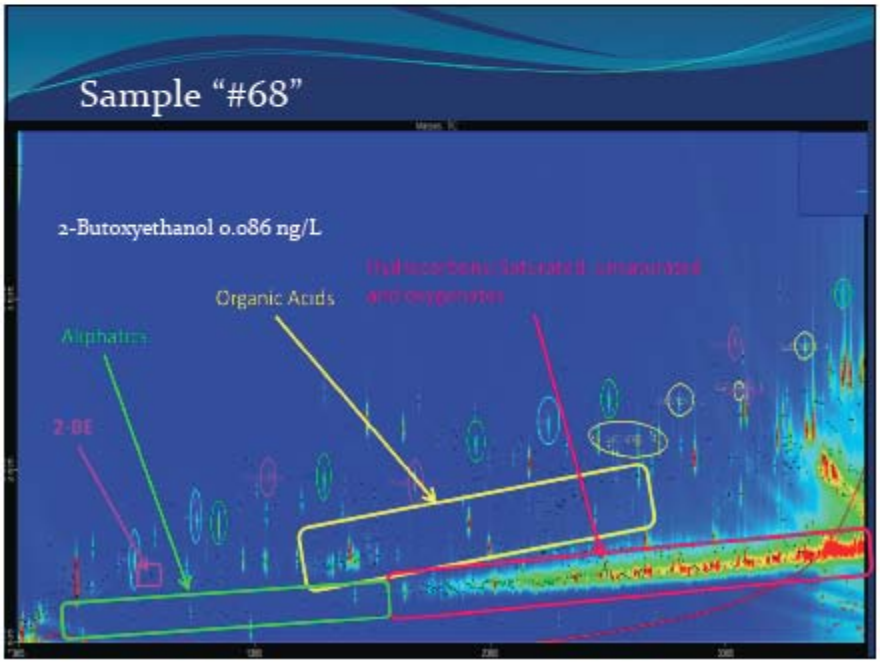


Recent Pennsylvania Well Water Sample:

Sampled collected following nearby drilling and hydrofracing

1.) What is causing the "discoloration"?
2.) Is it related to the gas well?
3.) If there is a relationship, can it be proven?


Sample "#67"
2-Butoxyethanol 0.42 ng/L
Organic Acids
Aliphatics
2-BE

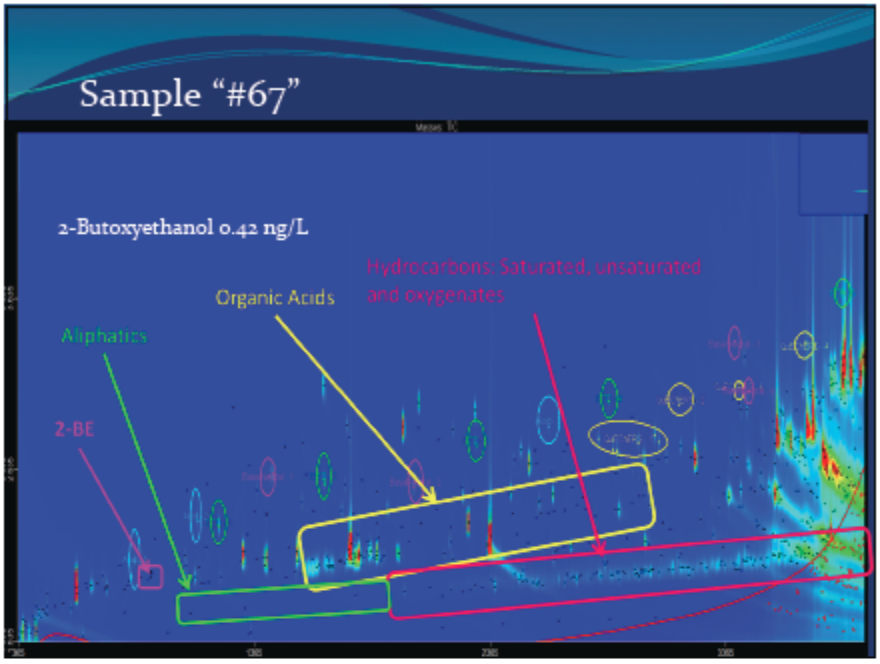

Sample "#68"
2-Butoxyethanol 0.086 ng/L
Organic Acids
Aliphatics
2-BE

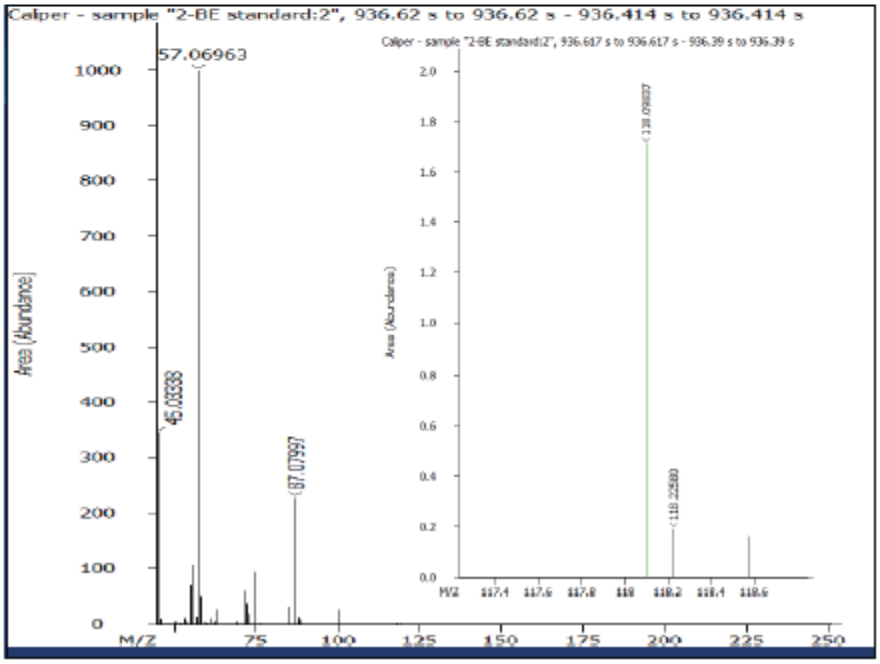
Limited Reference Materials: Other Analytical Options?

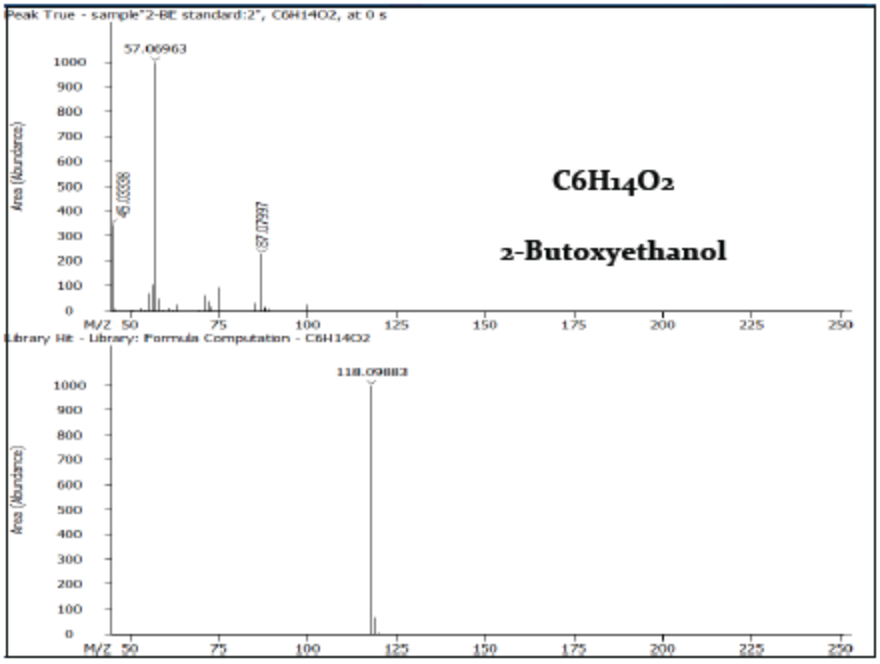
- Discovery Work May Benefit From Accurate Mass
  - Especially with lack of reference materials
  - Determination of molecular formula?
  - Confirmation of molecular formula
- GCxGC-High-Resolution TOFMS

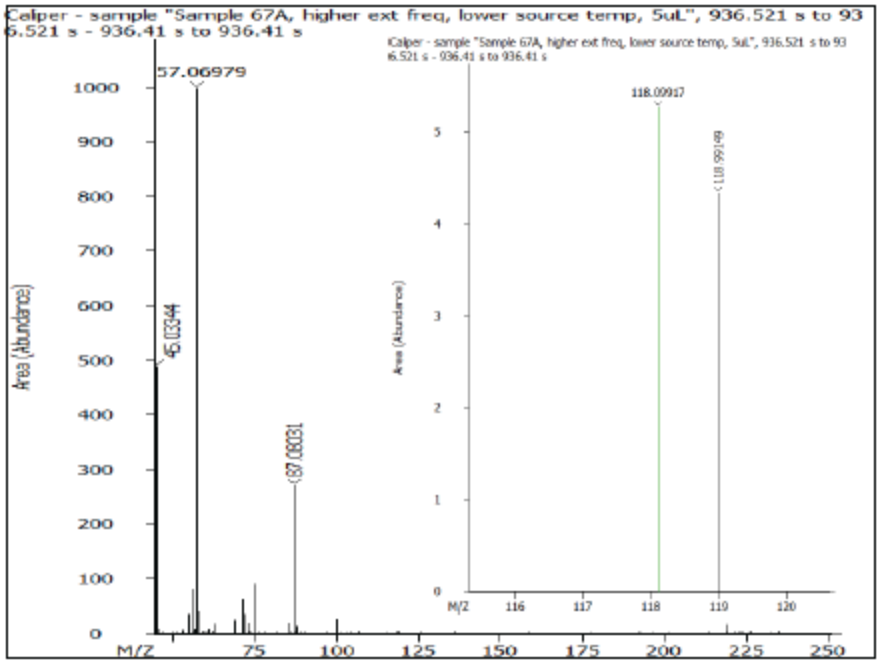
Preliminary Data, Prototype Instrument:

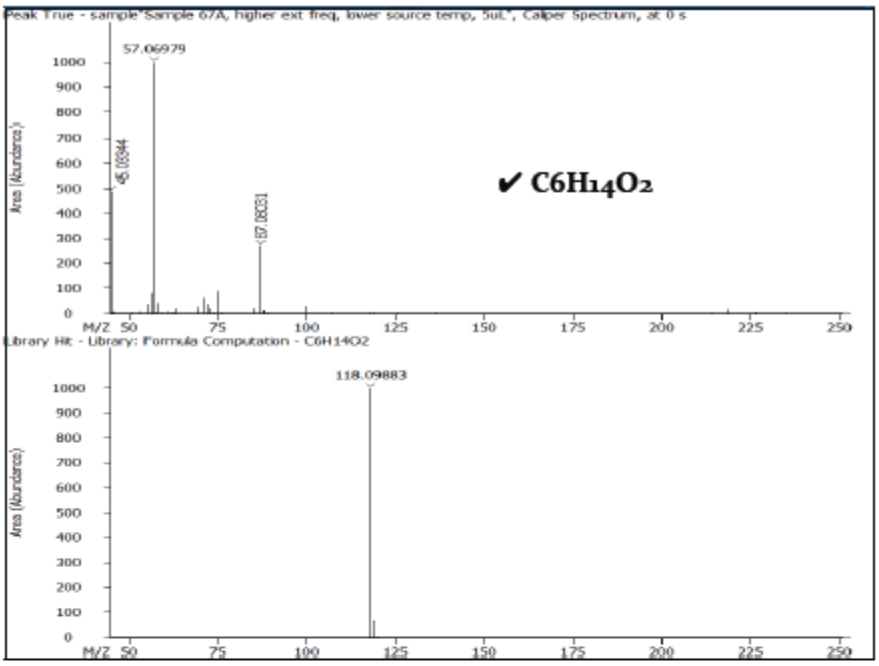
- 1st Dimension:
  - 40 m x 0.18 mm x 0.18 um Rtx-Dioxin-2
- 2nd Dimension:
  - 1.7 m x 0.18 mm x 0.18 Rxi-17Sil MS
- 1 ml/min column flow, 10:1 split
- 40 (1) 2.5 deg/min to 320 deg (10)
- 10 C Secondary oven offset
- 200 spec/sec
- 45 – 530 u
- 2 kHz extraction frequency
- HR mode (25,000 resolution) < 1 ppm accuracy
  - Can achieve 50,000 resolution


Sample "#67"
2-Butoxyethanol 0.42 ng/L
Hydrocarbons: Saturated, unsaturated and oxygenates
Organic Acids
Aliphatics
2-BE


Caliper - sample "2-BE standard:2", 936.62 s to 936.62 s - 936.414 s to 936.414 s
57.06963
45.03338
87.07997
Area (Abundance)
M/Z
Caliper - sample "2-BE standard:2", 936.617 s to 936.617 s - 936.39 s to 936.39 s


Peak True - sample"2-BE standard:2", C6H14O2, at 0 s
57.06963
45.03338
87.07997
Area (Abundance)
M/Z
C6H14O2
2-Butoxyethanol
Library Hit - Library: Formula Computation - C6H14O2
118.09883


Caliper - sample "Sample 67A, higher ext freq, lower source temp, 5uL", 936.521 s to 93
6.521 s - 936.41 s to 936.41 s
57.06979
45.03344
87.08031
118.09917
118.09149
Area (Abundance)
M/Z



Final Conclusions:

- Analytical Approach Has been successful in the determination of drilling fluid/frac fluid infiltration into a drinking water system
- Finding has been corroborated by methane isotope data showing Marcellus infiltration
- Gas companies have secured area and have moved residents
- Details to come in planned publication

Thanks to My Research Group Members:





Thank You for your attention

fld3@psu.edu

A Survey of Telemetry-Enabled Sensors for Onsite Characterization of Flowback Water from Hydraulic Fracturing

Sayan Chakraborti, MRI Global, et al

Abstract

An integrated suite of sensor technologies to monitor flowback water and environmental parameters related to shale gas development efforts would have widespread benefits to both industry and regulators. It is anticipated that the ability to provide real-time monitoring data at wellheads or post-well treatment tanks would help the shale gas industry to address several environmental concerns that are currently being raised by regulators and environmental groups regarding flowback water. This paper will describe the ongoing results from a survey of currently available telemetry-enabled sensors that could be integrated into a network and installed for real-time monitoring and characterization of flowback water. The paper will present commercially available sensor technologies that have the potential for real-time application at shale gas sites and discuss their capabilities and limitations for field implementation. Characteristics of these candidate sensors, including their ability to monitor constituents of concern, cost, durability and ruggedness, software integration platform, and other relevant factors will be compiled based on industry and vendor data. In addition, the paper will present plans for future proof-of-concept field testing of the most promising candidate sensor technologies at a shale gas production site.

MRIGlobal

National Solutions Worldwide Impact

A Survey of Telemetry-Enabled Sensors for Onsite Characterization of Air and Flowback Water from Hydraulic Fracturing

Sayan Chakraborti, A. Miller, and S. Shore (*MRIGlobal*)
M. Boerste and J. Myers. (*URS Professional Solutions LLC*)
Wyatt, D (*URS Corporation, RES/NETL*)

Presented at NEMC 2013
August 5, 2013

MRIGlobal

Presentation Outline

- Overview of MRIGlobal
- Rationale for sensors and project goals
- Water sensors review
- Air sensors review
- Identified gaps
- What's next?

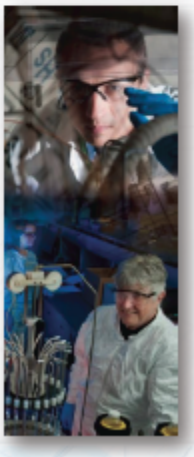


Overview of MRIGlobal

Midwe MRIGlobal MRI

National Solutions Worldwide Impact

Overview of MRIGlobal



- Founded and headquartered in 1944 in Kansas City, Missouri
- Independent, not-for-profit
- Areas of business:
  - Energy and Environment
  - Engineering and Infrastructure
  - Global Health and Security
  - National Security and Defense

MRIGlobal Energy Solutions

- Management & Research Operations for DOE
  - National Renewable Energy Technology Laboratory (NREL)
  - National Energy Technology Laboratory (NETL)
- Shale Gas Support Services
  - Analytical data collection
  - Methods development
  - Community outreach
- Testing and Evaluation
  - Technology verification
  - Technology scale-up and commercialization





Rationale for Sensors

- Flowback water needs treatment prior to discharge, and therefore constituents need to be monitored
- The EPA is studying the potential impacts of hydraulic fracturing on drinking water
- In addition to concerns over water pollution, there is increasing concern over air emissions

MRI Global

Project Goals

- Create a list of both water and air potential parameters of interest in shale gas
- Survey commercially available real-time sensors and instruments for monitoring the parameters identified in part 1
- Compile information on sensor capabilities with respect to various analytes and identify gaps in sensor technologies

MRI Global

Environmental Monitoring Opportunities

Sensor Opportunities for Fossil Fuel Extraction

Medium/Raw Material		Transport Pathway		Affected Environmental Media	
Physical State	Material or waste name	Air	Natural Water	Ambient Air	Waterbody or Aquifer
Gas	natural gas, EOR gas (CO_2,N_2)	leak, exhaust, soil vapor	fracture contact zone	air plume, low air	area wells, deep water
Liquid	oil, natural gas liquids, waters (raw, prepped, flowback, produced, treated)	mist, vapor	source level, stormwater (StW) runoff/outfall or seepage, industrial outfall mixing zone, groundwater (GW) plume core	air plume	resource level trend, outfall mixing zone fringe, GW plume fringe
Semi-Solid	coal, drill mud, injection water additives	dust, fumes	StW runoff/outfall or seepage	air plume	StW outfall mixing zone, GW plume

Project scope limited to areas highlighted in yellow

Water Parameters of Interest

- Physical: Temperature, pressure, turbidity, conductance, pH, ORP
- Organic: THC, CH_4, BTEX
- Inorganic: Dissolved oxygen (DO), Cl-, As, Other Metals
- Others: Na, K, B, Ba, Sr, Br-, SO_4-, C_2H_6, C_3H_8, Naphthalene, CH_3OH

Water – Physical Parameters

(a sample of compiled data)

Vendor	Product ID	Water Physical						
		Temp	Press	Depth	Turb	Cond*	pH	ORP	Other
Global Water	various	x	x	x		x	x	x	
HACH	Hydrolab DS5X (or MS5)	x	x	x		x	x	x	chlorophyll, blue green algae, Rhodamine WT, PAR, Tot Diss Gas
Xylem/YSI	EXO2 (or EXO1)	x	x	x		x	x	x	total algae (chlorphyll , blue-green)
INW	Multi-Parameter Sensor	x	x	x		x	x	x	
In-Situ	Aqua Troll 400	x	x			x	x	x	
S::Scan		x	x						

Water – Organic Analytes

(a sample of compiled data)

Vendor	Product ID	Water Organic							
				Individual					
		TOC	PAH	CH_4	Benzene	Toluene	Ethyl benzene	Xylene	Other
Xylem/YSI	EXO2 (or EXO1)								fDOM
YSI/Turner	Turner Sensor Adapter, Cyclops-7				x	x	x	x	Offers oil (crude/ fine), PTSA, Napthalene, etc.
Petrosense	CMS-1500 Envirologger w/ DHP-485				x	x	x	x	
S::Scan		x							
Franatech	Various, specs listed are for methane			x					
Contros	HydroC CH4 sensor, various others		x	x					
Pro-Oceanus	PSI Mini-Pro CH4			x					

TOC = Total Organic Carbon
PAH = Poly-Aromatic Hydrocarbons

Water – Inorganic Analytes

(as sample of compiled data)

Vendor	Product ID	Water Inorganic					
		Nonmetals				Metals	
		TIC	DO	Cl-	Other	As	Other
Global Water	various		x	x			
HACH	Hydrolab DSSX (or MS5)			x			
Xylem/YSI	EXO2 (or EXO1)		x	x	NH_4^+, NO_3^-		
INW	Multi-Parameter Sensor		x				
In-Situ	Aqua Troll 400		x				
Trace Detect	Arsenic Guard				F-	x	Se, Cu, Fe
Mercury Instruments	Mercury Process Analyzer PA-2						Hg
Franatech	Various, specs listed are for methane	x	x		H_2, H_2S, CO_2		
Contros	HydroC CH4 sensor, various others	x			CO_2		
Pro-Oceanus	PSI Mini-Pro H2S				S^{2-}		
Chemtrac	HydroACT 300/600/1200			x	Free Cl, Total Cl, Cl Dioxide,		

TIC = Toxic Industrial Chemical
DO = Dissolve Oxygen

Water Sensors – Summary Findings

- 5 companies were identified which could monitor all of the physical parameters
- Multiple companies offered products for CH_4 detection
- Multiple companies offered DO and Cl- products
- Products were also found to monitor for NH_4^+, NO_3^-, H_2S

Air Parameters of Interest

- Gas (organic): Methane, ethane, butane, propane, BTEX
- Gas (inorganic): CO_2, Oxygen, H_2S, N_2
- Metals

Sensors for Gas (Organic)

A sample of compiled data)

Vendor	Instrument	Gas Organic							Stbl Iso	
			Individual						CH_4	
		THC	CH4	C2H6	C3H8	n-butane	iso-butane	Other	C	H
RAE Systems	ppbRAE 3000 (PID)							VOCs		
Syft	Voice 200 (SIFT-MS)							VOCs (BP<200 C and Molar Mass < 300 Da)		
Enmet	EX-5120		x	x	x	x	x	Propylene, Pentane, Ethylene, Isopropanol, Hexane, Methanol, Ethanol, ETO, Acetic Acid, Toluene		
Enmet	GSM60		x	x	x	x	x			
Aeroqual	series 500		x					VOC and Nonmethane Hydrocarbon		
Aeroqual	series 930		x					VOC, Formaldehyde,		
Aeroqual	AQM60							Non-methane Hydrocarbons, VOCs,		

Sensors for Gas (Organic)

(continued)

Vendor	Instrument	Gas Organic							Stbl Iso	
			Individual						CH_4	
		THC	CH4	C2H8	C3H8	n-butane	iso-butane	Other	C	H
Owlstone	Lonestar Portable Analyzer							Benzene, Xylene, Toluene, Acetone, Formaldehyde		
California Analytical Instruments	Cal Analytical 600 series FTIR			x	x			Acetylene, Chloroform, Dichloroethylene, Ethanol, Ethyl Benzene, Formaldehyde, Methane Toluene, MEK,		
California Analytical Instruments	Innova 3433							Methanol, Ethanol, Toluene,		
Dynament	IR Gas Sensors	x	x	x	x	x	x	Ethanol, Ethylene, Ehtylene Oxide, Hexane, Methyl Bromide, Propene, Propylene,		
Figaro	Provides Individual Sensors to Monitor Gases		x					Alcohol, Solvent Vapors,		

Sensors for Gas (Inorganic)

(A sample of compiled data)

Vendor	Instrument	Gas Inorganic					
		Nonmetals				Metals	
		CO_2	O_2	H_2S	Other	Hg	Other
Tekran	2537B + 1135 cal. (AuCVAFS)					x	
Technical Associates	PTG-7L, incl. ion filter				Tritium		
Tech. Ass. (Overhoff reseller)	Model 357				Tritium		
Enmet	SDS-97D		x	x			
Enmet	GSM60	x	x	x			
Brooks Rand Labs	Total Hg Systems					x	
Ion Science	GasClam	x	x	x	CO		
Ion Science	MVI Portable Mercury Detector					x	
Tiger Optics	Prismatic	x			CO, H_2		
Picarro	G2401	x			CO		
Aeroqual	series 500	x		x	Ammonia, CO, Hydrogen, Nitrogen Dioxide, Ozone, Sulphur Dioxide,		

Air Sensors – Summary Findings

- Many options are available for monitoring emissions of organic gases emissions
- In addition to the analytes of interest: sensors for ammonia and nitrogen dioxide are widely available

Gaps Identified

- Limited number of sensors was found for the analytes in the table
- Need for increased wireless communication
- Need for integration of all the sensors

Medium	Analyte
Water	Na, K, B, Ba, Sr, Br-, SO_4^-, C_2H_6, C_3H_8, Naphthalene, CH_3OH
Gas	As, Isotopes, Total Hydrocarbons (THC)

What's Next?

- Select sensors identified in the survey
- Integrate the selected sensors into a real-time monitoring package
- Work with industry partners to determine an appropriate testing site
- Deploy the system for real world testing

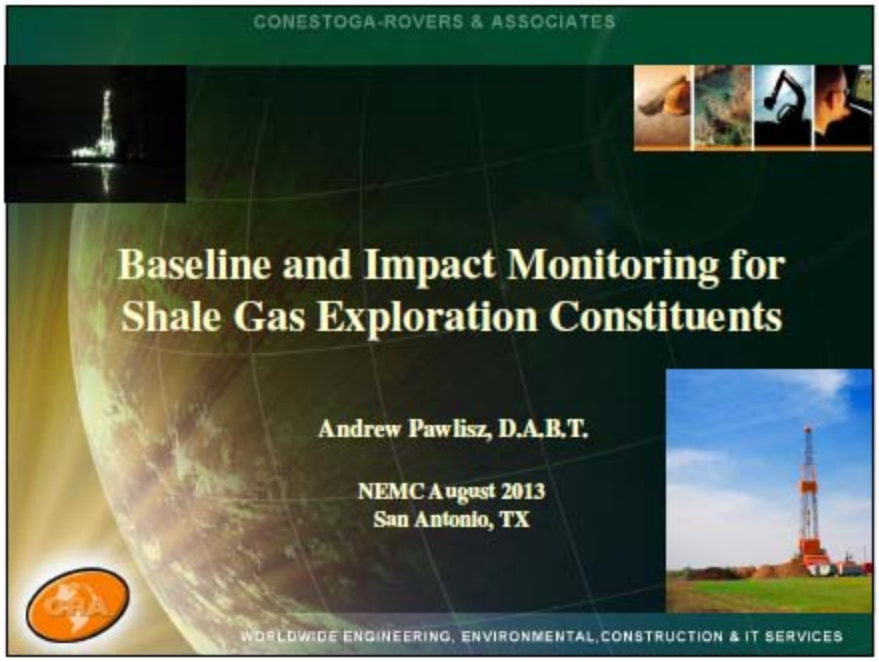

MRIGlobal
National Solutions Worldwide Impact
Thank You
Contact Information
Sayan Chakraborti
MRIGlobal, Kansas City
(816) 753 7600 x1505
schakraborti@mriglobal.org

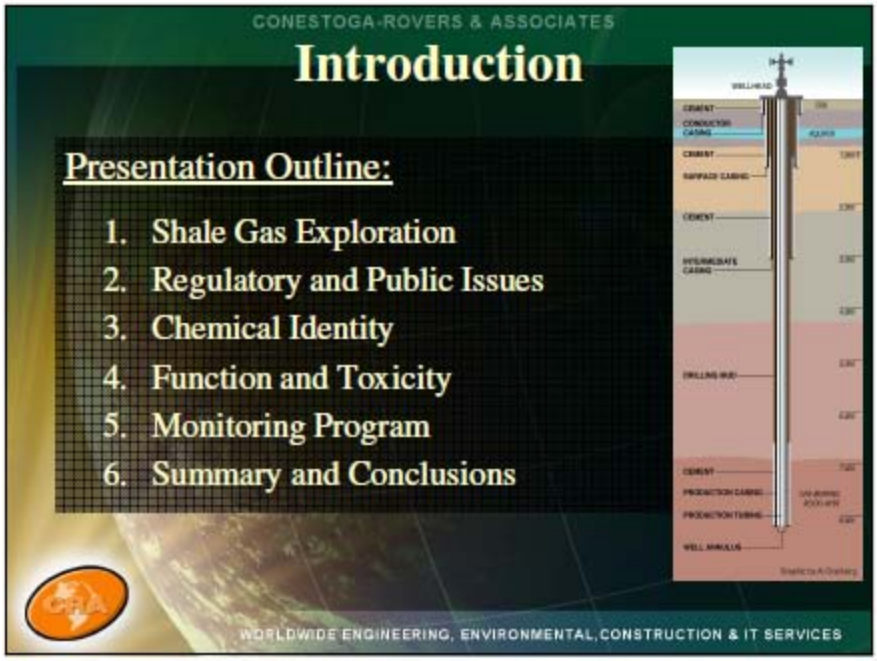
Baseline and Impact Monitoring for Shale Gas Exploration Constituents

Andrew Pawlisz
Conestoga-Rovers & Associates

Abstract

Increased application of hydraulic fracturing (i.e., fracking) technology, where water, friction reducers, proppants, disinfectants, surfactants, thickeners, scale inhibitors, corrosion inhibitors, and acids are injected into deep shale formations to extract natural gas, has increased calls from the regulatory community and the public for a closer scrutiny of this activity to ensure that fracking is environmentally safe. The growth in fracking has been unprecedented as vast new shale gas plays are discovered and explored across the world. The tremendous expansion in fracking exploration, and the commensurate increase in groundwater extraction/deep chemical injection, have raised concerns over effects on groundwater supplies and land surrounding the drilling sites. Through due-diligence, liability protection, and/or regulation, baseline sampling is increasingly a standard procedure associated with advancing shale gas exploration wells. A unique challenge in fracking sites baseline sampling is the design of sampling locations and the requisite analyte list, not to mention the interpretation of potential impacts results. This presentation is devoted to discussing the critical aspects of a sampling program, what to test for, and how to provide a risk-based interpretation of analytical results.


CONESTOGA-ROVERS & ASSOCIATES
Baseline and Impact Monitoring for Shale Gas Exploration Constituents
Andrew Pawlisz, D.A.B.T.
NEMC August 2013
San Antonio, TX
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Introduction
Presentation Outline:
1. Shale Gas Exploration
2. Regulatory and Public Issues
3. Chemical Identity
4. Function and Toxicity
5. Monitoring Program
6. Summary and Conclusions
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Shale Gas Exploration

- Increased application of hydraulic fracturing (frac) technology in US and worldwide
- First fracturing experiment in 1947
- Over 40 North American shale plays in exploration and development
- Over 1 million frac operations completed in US
- Further expansion projected

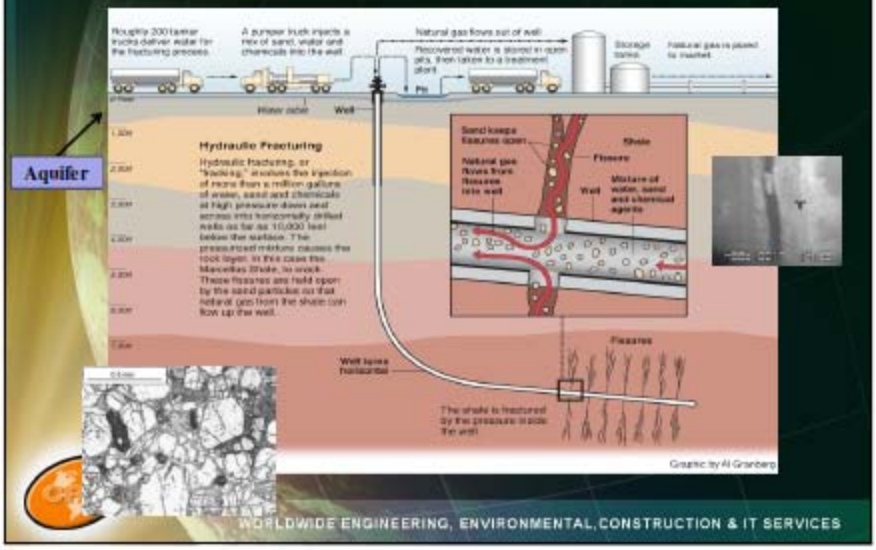
Source: King (2011)



WORLDWIDE ENGINEERING, ENV

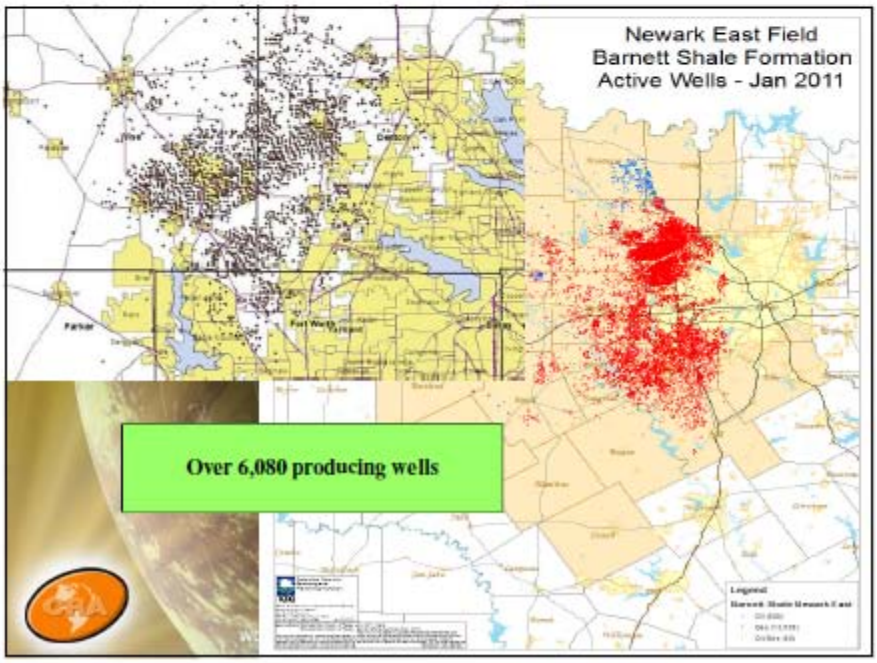
CONESTOGA-ROVERS & ASSOCIATES

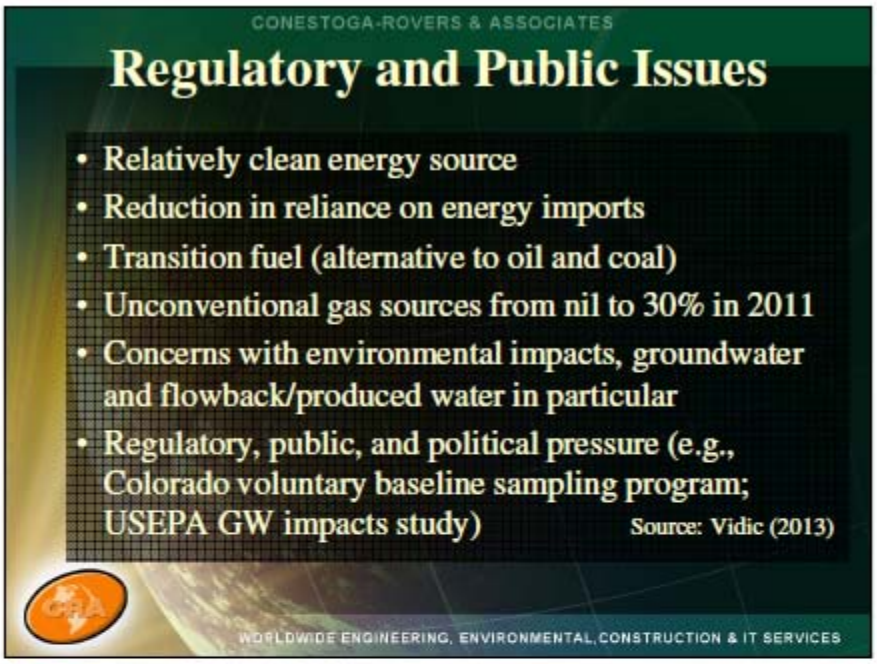
Shale Gas Exploration

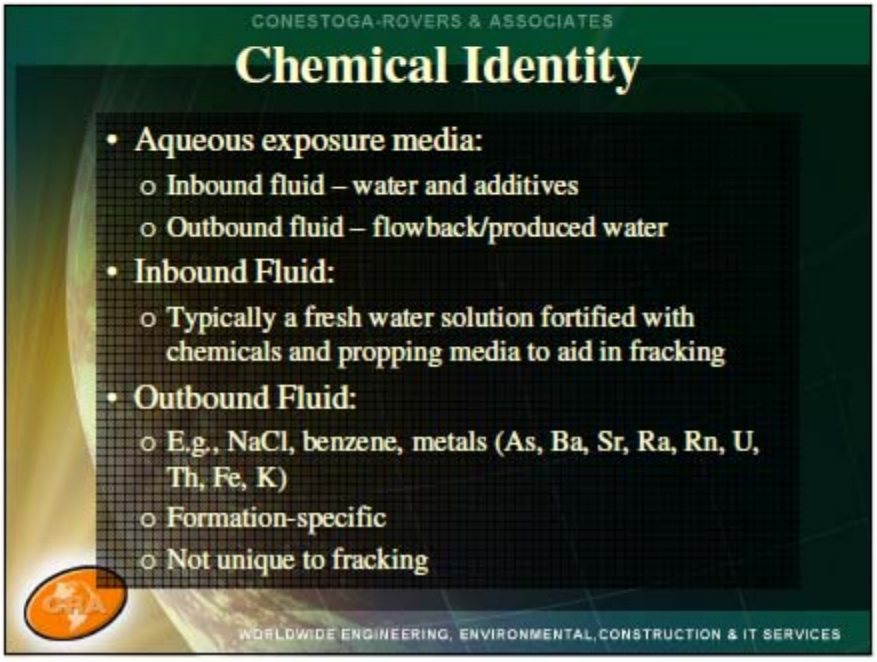


WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Lower 48 states shale plays
Bakken
Marcellus
Woodford
Fayetteville
Barnett
Eagle Ford
Haynesville-Bossier
eia
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


Newark East Field
Barnett Shale Formation
Active Wells - Jan 2011
Over 6,080 producing wells


CONESTOGA-ROVERS & ASSOCIATES
Regulatory and Public Issues
• Relatively clean energy source
• Reduction in reliance on energy imports
• Transition fuel (alternative to oil and coal)
• Unconventional gas sources from nil to 30% in 2011
• Concerns with environmental impacts, groundwater and flowback/produced water in particular
• Regulatory, public, and political pressure (e.g., Colorado voluntary baseline sampling program; USEPA GW impacts study)
Source: Vidic (2013)
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Chemical Identity
• Aqueous exposure media:
o Inbound fluid – water and additives
o Outbound fluid – flowback/produced water
• Inbound Fluid:
o Typically a fresh water solution fortified with chemicals and propping media to aid in fracking
• Outbound Fluid:
o E.g., NaCl, benzene, metals (As, Ba, Sr, Ra, Rn, U, Th, Fe, K)
o Formation-specific
o Not unique to fracking
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Chemical Identity

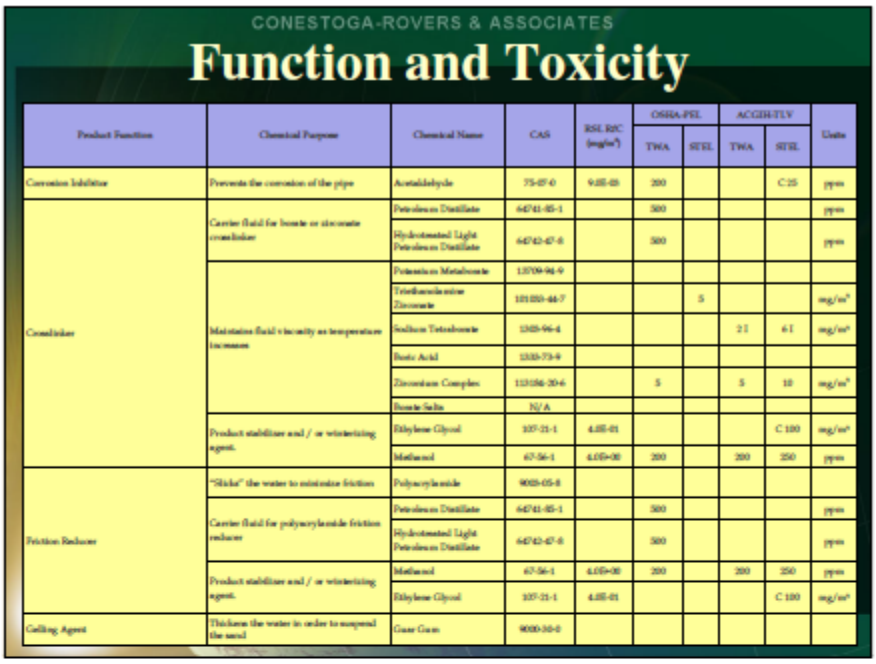
- As many as 750 chemicals used (US Energy and Commerce 2012)
- Multiple formulations (mixtures)
- USEPA identified over 1,000 chemicals for further assessment (USEPA 2012; draft report to be issued in 2014)
- 347 unique CAS entries by FracFocus registry (8 states require listing on fracfocus.org)
- Trade Secret constituents exempt
- Many not monitored under the DWA and 27 may be hazardous (USEPA 2012)
- Fracking fluid composition (Fontaine 2008):
  - Water (up to 99%; 2 to 7 MG per well; 10% recovered as flowback and up to 90% recycled)
  - Proppants (up to 1.9%)
  - Friction reducers (0.025%)
  - Disinfectants (up to 0.05%)
  - Surfactants (up to 0.002%)
  - Thickeners (not common)
  - Scale inhibitors
  - Corrosion inhibitors (up to 0.5%)
  - Acids



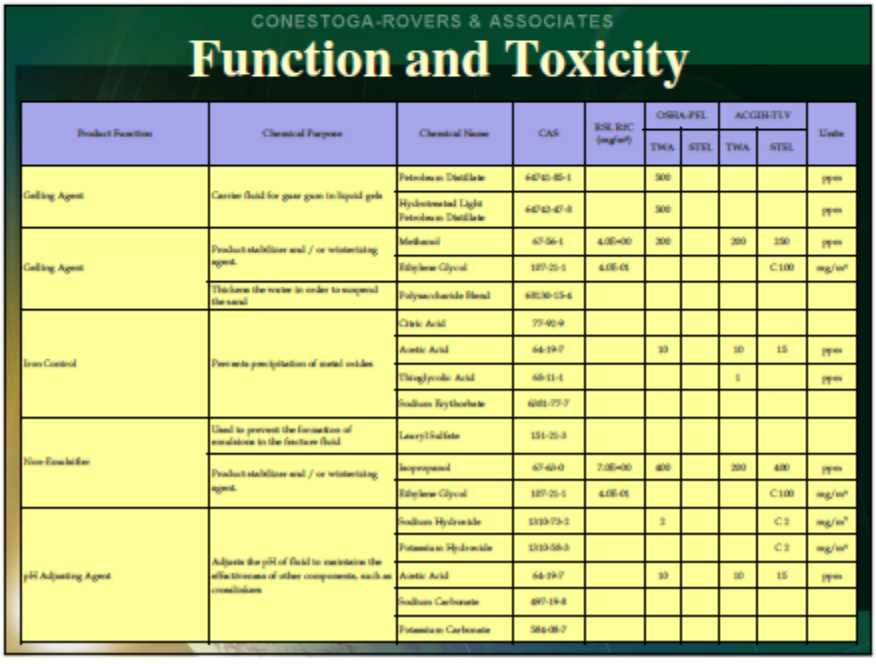
CONESTOGA-ROVERS & ASSOCIATES

Function and Toxicity

Product Function	Chemical Purpose	Chemical Name	CAS	RSL RfC (mg/m³)	OSHA-PEL		ACGIH-TLV		Units
					TWA	STEL	TWA	STEL	
Acid	Helps dissolve minerals and initiate cracks in the rock	Hydrochloric Acid	7647-01-0	2.0E-02	5			C 2	ppm
Biocide	Eliminates bacteria in the water that produces corrosive by-products	Glutaraldehyde	111-30-8	8.0E-05				C 0.05	ppm
		Quaternary Ammonium Chloride	12125-02-9				10	20	mg/m³
		Tetrakis Hydroxymethyl-Phosphonium Sulfate	55566-30-8						
Breaker	Allows a delayed break down of the gel	Ammonium Persulfate	7727-54-0						
	Product Stabilizer	Sodium Chloride	7647-14-5						
	Allows a delayed break down the gel	Magnesium Peroxide	14452-57-4						
		Magnesium Oxide	1309-48-4		15		10 I		mg/m³
	Product Stabilizer	Calcium Chloride	10043-52-4						
Clay Stabilizer	Prevents clays from swelling or shifting	Choline Chloride	67-48-1						
		Tetramethyl Ammonium Chloride	75-57-0						
		Sodium Chloride	7647-14-5						
Corrosion Inhibitor	Product stabilizer and / or winterizing agent	Isopropanol	67-63-0	7.0E+00	400		200	400	ppm
		Methanol	67-56-1	4.0E+00	200		200	250	ppm
	Prevents the corrosion of the pipe	Formic Acid	64-18-6	3.0E-04	5		5	10	ppm



Product Function	Chemical Purpose	Chemical Name	CAS	RSL RfC (mg/m³)	OSHA-PEL		ACGIH-TLV		Units
					TWA	STEL	TWA	STEL	
Corrosion Inhibitor	Prevents the corrosion of the pipe	Acetaldehyde	75-07-0	9.0E-03	200			C 25	ppm
Crosslinker	Carrier fluid for borate or zirconate crosslinker	Petroleum Distillate	64741-85-1		500				ppm
		Hydrotreated Light Petroleum Distillate	64742-47-8		500				ppm
	Maintains fluid viscosity as temperature increases	Potassium Metaborate	13709-94-9						
		Triethanolamine Zirconate	101033-44-7			5			mg/m³
		Sodium Tetraborate	1303-96-4				2 I	6 I	mg/m³
		Boric Acid	1330-73-9						
		Zirconium Complex	113184-20-6		5		5	10	mg/m³
		Borate Salts	N/A						
	Product stabilizer and / or winterizing agent.	Ethylene Glycol	107-21-1	4.0E-01				C 100	mg/m³
		Methanol	67-56-1	4.0E+00	200		200	250	ppm
Friction Reducer	"Sticks" the water to minimize friction	Polyacrylamide	9003-05-8						
	Carrier fluid for polyacrylamide friction reducer	Petroleum Distillate	64741-85-1		500				ppm
		Hydrotreated Light Petroleum Distillate	64742-47-8		500				ppm
	Product stabilizer and / or winterizing agent.	Methanol	67-56-1	4.0E+00	200		200	250	ppm
		Ethylene Glycol	107-21-1	4.0E-01				C 100	mg/m³
Gelling Agent	Thickens the water in order to suspend the sand	Guar Gum	9000-30-0						



Product Function	Chemical Purpose	Chemical Name	CAS	RSL RfC (mg/m³)	OSHA-PEL		ACGIH-TLV		Units
					TWA	STEL	TWA	STEL	
Gelling Agent	Carrier fluid for guar gum in liquid gels	Petroleum Distillate	64741-85-1		500				ppm
		Hydrotreated Light Petroleum Distillate	64742-47-8		500				ppm
Gelling Agent	Product stabilizer and / or winterizing agent.	Methanol	67-56-1	4.0E+00	200		200	250	ppm
		Ethylene Glycol	107-21-1	4.0E-01				C 100	mg/m³
	Thickens the water in order to suspend the sand	Polysaccharide Blend	68130-15-4						
Iron Control	Prevents precipitation of metal oxides	Citric Acid	77-92-9						
		Acetic Acid	64-19-7		10		10	15	ppm
		Thioglycolic Acid	68-11-1				1		ppm
		Sodium Erythorbate	6381-77-7						
Non-Emulsifier	Used to prevent the formation of emulsions in the fracture fluid	Lauryl Sulfate	151-21-3						
	Product stabilizer and / or winterizing agent.	Isopropanol	67-63-0	7.0E+00	400		200	400	ppm
		Ethylene Glycol	107-21-1	4.0E-01				C 100	mg/m³
pH Adjusting Agent	Adjusts the pH of fluid to maximize the effectiveness of other components, such as crosslinkers	Sodium Hydroxide	1310-73-2		2			C 2	mg/m³
		Potassium Hydroxide	1310-58-3					C 2	mg/m³
		Acetic Acid	64-19-7		10		10	15	ppm
		Sodium Carbonate	497-19-8						
		Potassium Carbonate	584-08-7						

CONESTOGA-ROVERS & ASSOCIATES

Function and Toxicity

Product Function	Chemical Purpose	Chemical Name	CAS	RSL RfC (mg/m³)	OSHA-PEL		ACGIH-TLV		Units
					TWA	STEL	TWA	STEL	
Scale Inhibitor	Prevents scale deposits in the pipe	Copolymer of Acrylamide and Sodium Acrylate	25987-30-8	6.0E-01					
		Sodium Polyacrylate	N/A						
		Phosphonic Acid Salt	N/A	1.0E-02					
Surfactant	Used to increase the viscosity of the fracture fluid	Lauryl Sulfate	151-21-3						
	Product stabilizer and / or winterizing agent.	Ethanol	64-17-5		1000			1000	ppm
		Methanol	67-56-1	4.0E+00	200		200	250	ppm
		Isopropanol	67-63-0	7.0E+00	400		200	400	ppm
	Carrier fluid for the active surfactant ingredients	Naphthalene	91-20-3	3.0E-03	10		10	15	ppm
	Product stabilizer	2-Butoxyethanol	111-76-2	1.6E+00	50		20		ppm



WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Monitoring Program



- Sentinel Constituents:
  - Representative
  - Not easily biodegradable
  - Easy to test for
  - Have solid standards
  - Detection limits to meet toxicity thresholds
  - Results can be used for many purposes (i.e., 29 potential carcinogenic risk drivers; USEPA 2012)



WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Monitoring Program

- Colorado Baseline Sampling:
  - Major cations and anions (e.g., Ca, Na, Cl)
  - TDS
  - Metals (Fe, Mn, Se)
  - Nutrients (N and P)
  - Methane
  - pH
  - Conductivity
  - BTEX
- Need to capture operation constituents
  - Inbound and outbound
- Support data for a risk/impact assessment



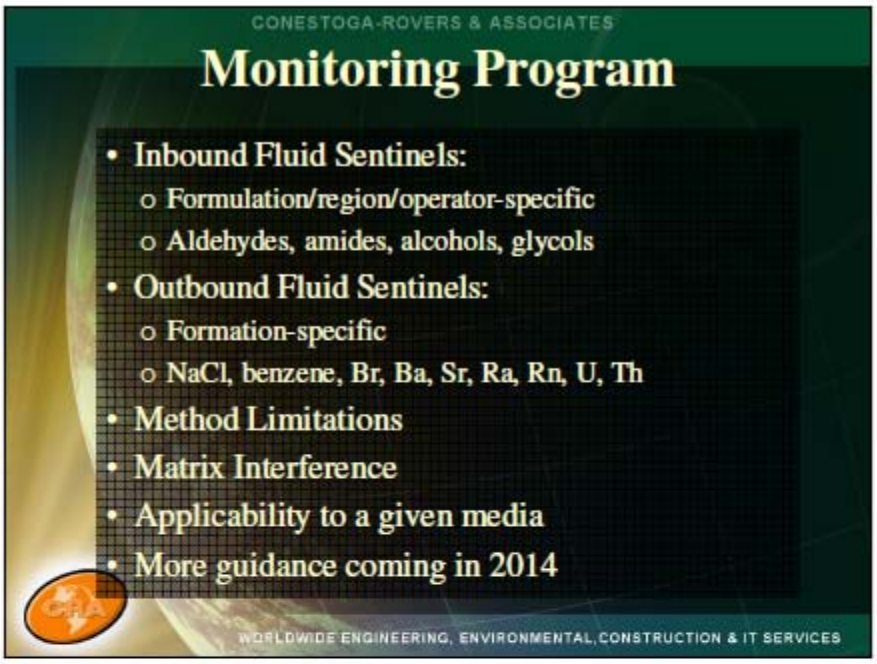
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

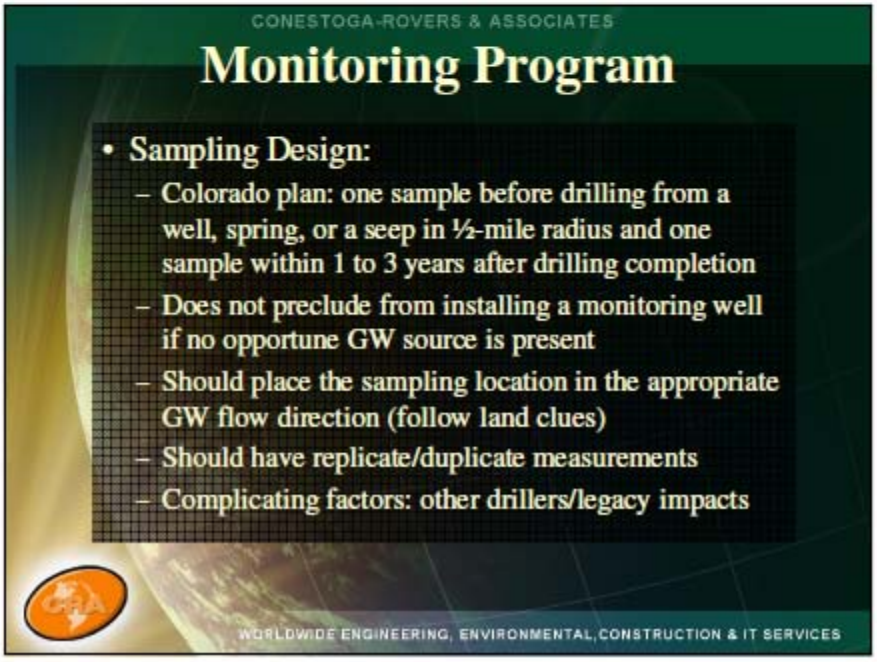
CONESTOGA-ROVERS & ASSOCIATES

Monitoring Program

- Proposed Analytical Methods (USEPA 2012):
  - Alcohols: SW-846 Methods 5030 and 8260C
  - Aldehydes: SW-846 Method 8315
  - Alkylphenols: No standard method
  - Alkylphenol ethoxylates: No standard method
  - Amides: SW-846 Methods 8032A (and 8316)
  - Amines (alcohols): No standard method
  - Hydrocarbons: SW- 846 Methods 5030 and 8260C
  - Carbohydrates: No standard method
  - Ethoxylated alcohols: ASTM D7485-09
  - Glycols: Region 3 Draft SOP
  - Halogens: SW-846 Method 9056A
  - Inorganics: SW-846 Methods 3015A and 6020A
  - Radionuclides: SW-846 Method 9310

WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Monitoring Program
• Inbound Fluid Sentinels:
o Formulation/region/operator-specific
o Aldehydes, amides, alcohols, glycols
• Outbound Fluid Sentinels:
o Formation-specific
o NaCl, benzene, Br, Ba, Sr, Ra, Rn, U, Th
• Method Limitations
• Matrix Interference
• Applicability to a given media
• More guidance coming in 2014
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Monitoring Program
• Sampling Design:
– Colorado plan: one sample before drilling from a well, spring, or a seep in ½-mile radius and one sample within 1 to 3 years after drilling completion
– Does not preclude from installing a monitoring well if no opportune GW source is present
– Should place the sampling location in the appropriate GW flow direction (follow land clues)
– Should have replicate/duplicate measurements
– Complicating factors: other drillers/legacy impacts
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Monitoring Program

- Monitoring strategy applicable to:
  - Surface releases/spills
  - Groundwater impacts
  - Blow-outs (air and other exposure media)
  - Storage pond testing
  - Soil and sediment testing
  - Waste characterization
  - Forensic/culpability investigations
  - Wastewater treatment systems



WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

CONESTOGA-ROVERS & ASSOCIATES

Summary and Conclusions

- Tremendous growth to explore unconventional gas plays
- Regulations and monitoring requirements lagging, but increasingly catching up
- Stakeholder pressure to ensure no impacts on environment
- Enough information available to design and implement a baseline monitoring program for various media
- Resulting data can be multipurposed (from voluntary due diligence to risk assessment)
- Some challenges associated with finding sentinel chemicals and appropriate analytical methods
- Design program with a goal in mind (i.e., produced water vs. frac fluid risk drivers)
- Multidisciplinary team approach can help

WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES


CONESTOGA-ROVERS & ASSOCIATES
Thank You
Krum, TX – July 2013
WORLDWIDE ENGINEERING, ENVIRONMENTAL, CONSTRUCTION & IT SERVICES

Challenges in Microbial Assays of Produced Waters

Keith McLeroy
Schlumberger

Abstract

Most often oil and gas produced waters are allowed to either accumulate in storage tanks or ponds until further disposed of or treated for reuse. During this detention time, bacterial growth can occur and proliferate. These bacteria in turn can cause negative effects on treatment and reuse applications. An inherent issue with culturing and monitoring for these bacteria is the complexity of the water chemistry matrices and the overall biomass of the system. These matrices can interfere with traditional bacteria growth media and colony color indicator broths. This presentation examines the various methodological approaches that are utilized in both field and laboratory analyses for bacteria in oil/gas produced waters and to facilitate discussions among industry leaders. Additional considerations will focus on what problems can occur with those methods and what future microbiological protocols will the industry need in the future.

Challenges in Microbial Assays of Produced Waters

L. Keith McLeroy

Technical Advisor, M-I SWACO/Schlumberger

Schlumberger

Introduction

Abstract

Most often oil and gas produced waters are allowed to either accumulate in storage tanks or ponds until further disposed of or treated for reuse.

During this detention time, bacterial growth can occur and proliferate. These bacteria in turn can cause negative effects on treatment and reuse applications.

- This presentation examines the various methodological approaches that are utilized in both field and laboratory analyses for bacteria in oil/gas produced waters and to facilitate discussions among industry leaders.

Schlumberger

Bacteria Concerns in Produced Waters

Causes	and	Affects
• Are ubiquitous in the environment		• Difficult to keep them under control
• Will be encountered in all aspects of water related processes in oil/gas exploration and production		• Water sources can be at times, loaded with high concentrations of bacterial growth. i.e.: the source, stagnation and organic concentrations
• Bacteria are present in sands, muds, tankers and piping		• Meaning that nothing is ever "disinfected" nor "sterile"
• Pre and post production aspects of oil/gas drilling add to the proliferation of bacteria growth		• Activities can add to enhancement of bacterial growth and contamination
• Bacteria growth alters chemistry		• Producers of H2S, biofilm, acids and other negative effective copmpounds

Schlumberger

Bacteria Related Topics

Complexity of Water Matrix

These Matrix Problems Cause Difficulties in Culturing

Commonly Utilized Assay Methods don't Necessarily Work in Produced Waters

There is No Consistency of Bacteria in All the Various Produced Waters We See

Schlumberger

"What is the Best Method to Use for Bacterial Monitoring in the Oil & Gas Industry"? Ask First:

What Aspect(s) of the Microbial Community is (are) of Concern?

Potential Transport of Opportunistic Bacteria into the Operator's Water Supply? How?

Formation Souring? And MIC? Disinfection Loading?

Others?

Once you know what you need/want to control, then selection of the appropriate method becomes more selective.

Schlumberger

Considerations

Sampling (Poor Sampling Will Contribute to Poor Results)

Uneven Bacterial Distribution Throughout a System

Lack of a Background Bacterial Baseline

Organic Loading (FOOD)

Aerobic, Anaerobic or Facultative (as a Biomass)

Schlumberger

Other Considerations

An Absolute Understanding of the Microbiological Protocol That You are Employing (What interferences exist for that specific protocol?)

Lack of Using Known Bacteria Cultures (As a Positive Growth Reference)

Thought: Are the results of bacterial testing an absolute or an approximation? And what do you plan to do with the data?

Schlumberger

Produced Water Bacteria 101

Planktonic- are any organisms that live in the water column and are incapable of swimming against a current

Sessile- are organisms associated with biofilm development and corrosion related issues. They are protected in antagonistic environments such as produced waters, by growing as colonies encased in an extracellular matrix of carbohydrates (exopolysaccharide)

Schlumberger

FACTS!

According to the NACE International, "attached microbes (sessile bacteria) are normally the most important biological component of the bacterial ecology of an oilfield system".

Methods utilized for planktonic bacteria are of limited use for assaying sessile species. One must then consider that both of these bacteria will exist in all aspects of water related applications of the oilfield and that they should have protocols listed for assessing both.

Schlumberger

Assaying in Produced Water

Sulfate-Reducing Bacteria (SRB)

Iron-Oxidizing Bacteria (IOB)

Heterotrophic Biofilm-Forming Bacteria (HBB)

Acid-Producers (APB)

Others?

Schlumberger

Noted Methods Review

American Petroleum Institute Method API RP 38, similar in part to NACE Standard TMO194-94: Field Monitoring of Bacterial Growth in Oilfield Systems. (Commonly called "The Bug-Bottle Method")

API RP38- MPN Plate Count

HACH® BART-Bottles

Various Present/Absent Bottle Protocols

Others?

Schlumberger

Emerging Technology

ELSIA-PCR (polymerase chain reaction) DNA sequencing technique

Enzyme substrate fluorescence technique

Epifluorescence microscopy (acridine orange stain method)

On-line monitoring

Others?

Schlumberger

Starting Techniques and Protocols

- Sampling
- Complete Understanding of Method
- Matrix Interferences
- Establishing a Biomass Baseline
- Selecting the Proper Protocol and Media
- The More Advanced Assays Require Additional Steps and Considerations

Schlumberger

Review of Concerns Common in PW Bacterial Assay

- Chemistry of the PW
- Sampling Locations
- Modifying the Protocol
- False Positives
- Color Changes
- Turbidity/Solids
- Others?

Schlumberger

Complex Issues Related to Advanced Assays

- Matrix Interferences
- Enzymes and Oil Don't Mix
- Troubleshooting and Method Modifications
- Need a Good Grasp of the Reactions
- Use Known Bacteria Strains

Schlumberger

Future Concepts

- Microbiology Will Need to Be a Focal Point in All Oil/Gas Production Activities
- Current Protocols and Revisions
- On-Going R&D, Industry & Academia
- Instrumentation, Real-Time Monitoring
- What Else?

Schlumberger


Thank You!
?
Keith McLeroy
Technical Advisor
lmcleroy@slb.com
281-561-1465
Schlumberger

Applied Ion Analysis of Various Water Matrices in Hydraulic Fracturing Process

Jay Gandhi
Metrohm USA

Abstract

Hydraulic fracturing is the use of fluid and material to create or restore small fractures in a formation in order to stimulate production from new and existing oil and gas wells. This creates paths that increase the rate at which fluids can be produced from the reservoir formations.

The process includes steps to protect water supplies. To ensure that neither the fluid that will eventually be pumped through the well, nor the oil (or gas) that will eventually be collected enters the water supply, steel surface or intermediate casings are inserted into the well to depths of between 1,000 and 4,000 feet. Once the cement has set, then the drilling continues from the bottom of the surface or intermediate cemented steel casing to the next depth. This process is repeated, using smaller steel casings each time, until the oil and gas-bearing reservoir is reached (generally 6,000 to 10,000 ft).

Water and sand make up 98 - 99.5% of the fluid used in hydraulic fracturing. In addition, chemical additives such as acid solutions, scale inhibitors, stabilizing agents, corrosion inhibitors, friction reducing agents, gelling agents, etc. are used - exact formulation will vary depending on the well.

In this presentation, collaborative approach with USEPA to perform chemical analysis methodologies using ion analytical instruments will be discussed.

Metrohm USA Inc.

Ion Analysis of Hydraulic Fluids in Fracking Process

Presented by
Jay Gandhi*, PhD
Metrohm USA

Metrohm USA Inc.



Metrohm USA Inc.

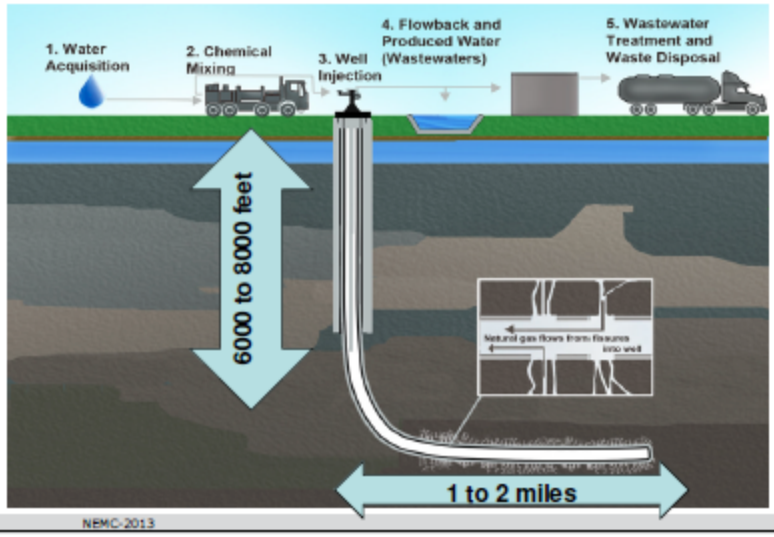
What we will cover today

- Background – Hydraulic Fracking
- Ion Analysis Applications
  - Wet Chemistry methods
  - Anions
  - Cations
  - Organic Acids
- Summary

NEMC-2013 3

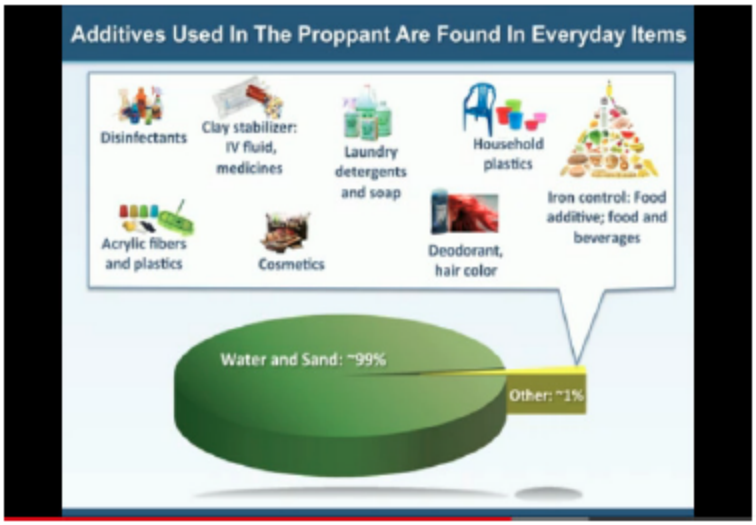
Metrohm USA Inc.

Hydraulic Fracking Water Cycle



NEMC-2013 4

Metrohm USA Inc.



NEMC-2013 5

Metrohm USA Inc.

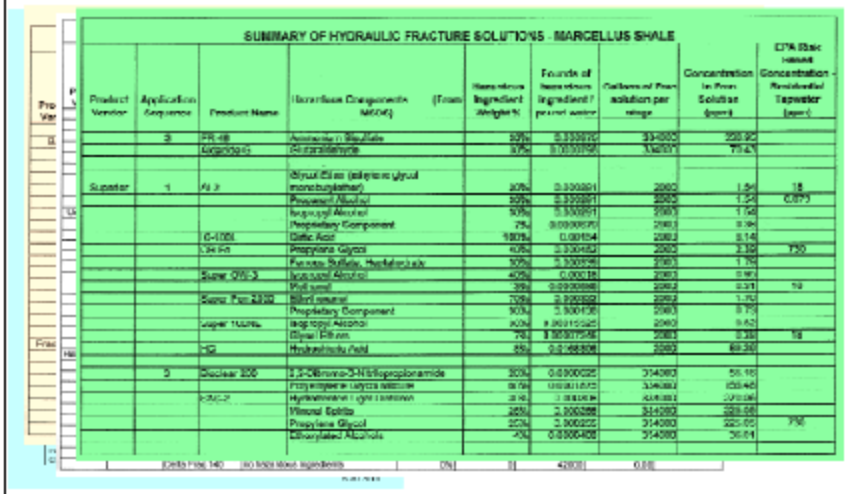
Types of Water Matrices

- **Fresh Feed water**
- **Flowback water (Produced Water)**
  - ✓ High Ionic Water (up to 30% Salt Concentration)
- **Characterization of "Retention Pond"**
- **Recycling water**
- **Discharge water (for WTP)**

NEMC-2013 6

Metrohm USA Inc.

List of Chemicals from various sources



SUMMARY OF HYDRAULIC FRACTURE SOLUTIONS - MARCELLUS SHALE

Product Vendor	Application Sequence	Product Name	Description Components (From MSDS)	Maximum Ingredient Weight %	Pounds of maximum ingredient / pound water	Gallons of Pure solution per range	Concentration in Pure Solution (ppm)	CTA Estimated Concentration - Recirculated Tapwater (ppm)
	3	FR-48	Ammonium Sulfate	30%	0.333333	33-005	999.99	
		Acrylamide	Acrylamide	0%	0.000999	10.001	19.41	
Superior	1	AI-2	Glycol Ether (ethylene glycol monobutylether)	30%	0.333333	2003	1.54	15
			Propanol Alcohol	30%	0.333333	2003	1.54	0.075
			Isopropyl Alcohol	10%	0.333333	2003	1.745	
			Proprietary Component	7%	0.000000	2003	0.94	
		C-100X	Citric Acid	100%	0.00154	2003	0.14	
		LSI-54	Propylene Glycol	40%	0.000462	2003	2.39	730
			Peroxide Sulfate, Hydrolyzate	30%	0.300000	2003	1.75	
		Super OB-2	Isopropyl Alcohol	40%	0.000308	2003	0.951	
			Walnut	3%	0.030000	2003	0.31	10
		Super Flo 2202	Ethoxylated	70%	0.000462	2003	1.75	
			Proprietary Component	30%	0.300000	2003	0.75	
		Super 100XL	Isopropyl Alcohol	30%	0.000231	2003	0.63	
		Super Flo	Ethoxylated	7%	0.000308	2003	0.38	10
		HCl	Hydrochloric Acid	5%	0.016808	2003	89.36	
	3	Sucker 205	2,2-Dibromo-3-Nitrilopropionamide	20%	0.000022	314283	56.16	
			Polyethylene Glycol Monostearate	5%	0.000154	314283	69.46	
		X-Cide	Hydrotreated Light Distillate	30%	0.000231	314283	207.09	
			Mineral Spirits	25%	0.000288	314283	229.05	
			Propylene Glycol	20%	0.000222	314283	222.00	730
			Ethoxylated Alcohols	10%	0.000408	314283	28.64	

Metrohm USA Inc.

Water Matrix needs to be considered

- In any industry, there is no such thing as "accident or incident" free!!!!
- Hence in an accident of well casing break, damage or leak……there will be a possibility of contaminating
  - Source of Ground water
  - Ground water tables depending of chemical mobility
  - Surface water (rivers and lakes)
- **So for next 1.5 years USEPA is very active to establish baseline of water sources in every state where fracking is involved or potential of fracking is possible**

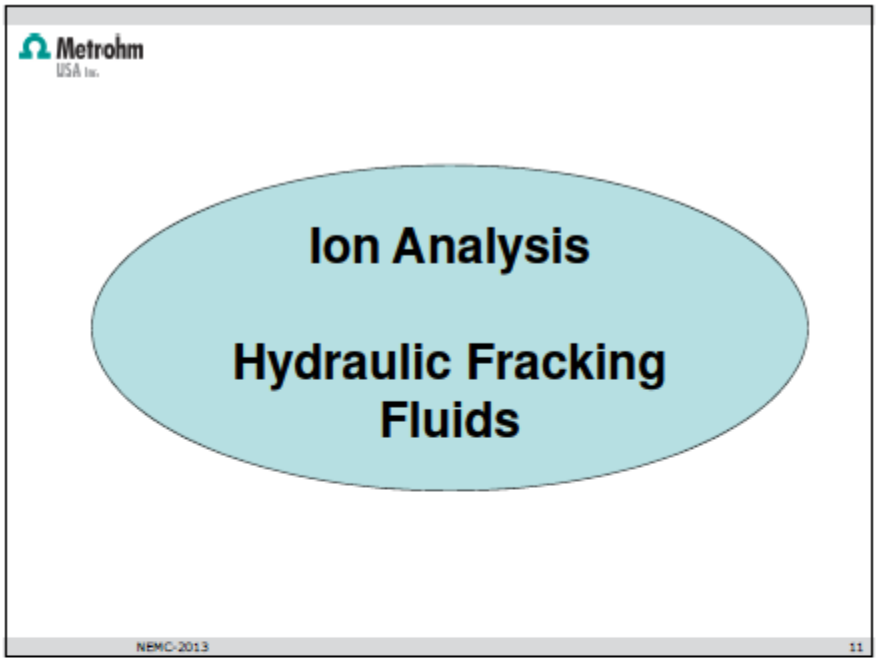
NEMC-2013 9

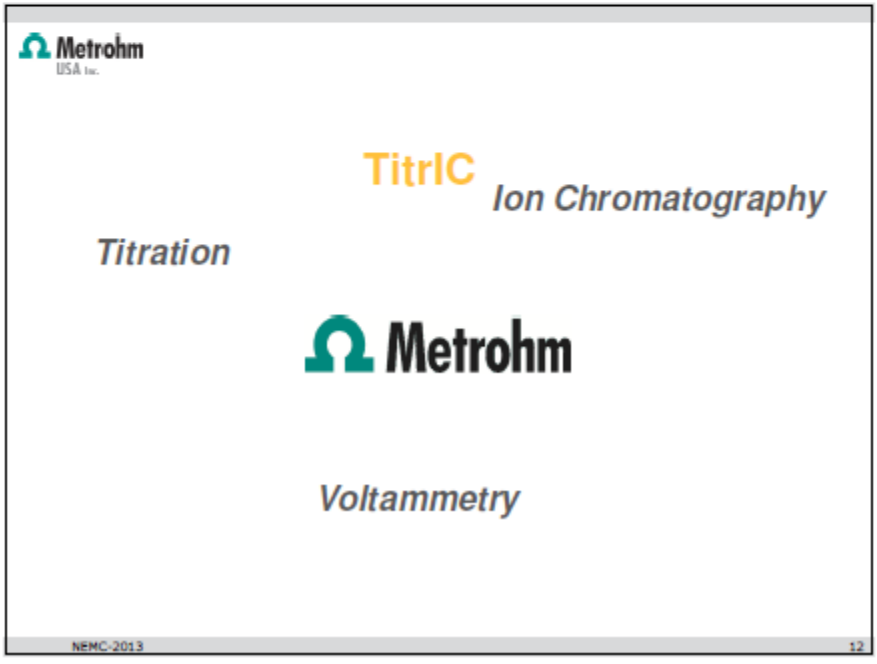
Metrohm USA Inc.

So at every Fracking sites there will be following regulatory methods apply

- ***Under safe Drinking Water Act***
  - USEPA method 300
  - USEPA method 552
  - USEPA method 557
  - ASTM method 6919 (MUR)
  - All applicable methods for organics and wet chemistry
- ***Under OSW***
  - Modified USEPA method 300
  - Modified ASTM method 6919
  - Method for Low molecular OA
  - Method for Glycols
  - Methods for gas detection
  - Other Methods under development

NEMC-2013 10


Metrohm
USA Inc.
Ion Analysis
Hydraulic Fracking Fluids
NEMC-2013
11

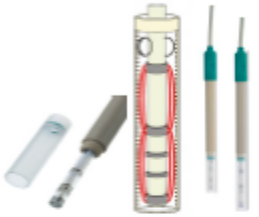

Metrohm
USA Inc.
TitrIC
Ion Chromatography
Titration
Metrohm
Voltammetry
NEMC-2013
12

Metrohm USA Inc.

Wet Chemistry Methods

- pH
- Conductivity
- Alkalinity





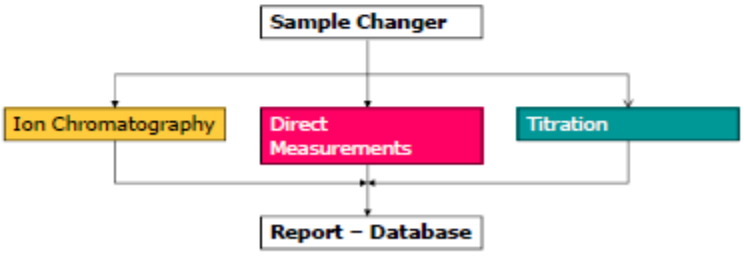


NEMC-2013 13

Metrohm USA Inc.

TitrIC - the principle

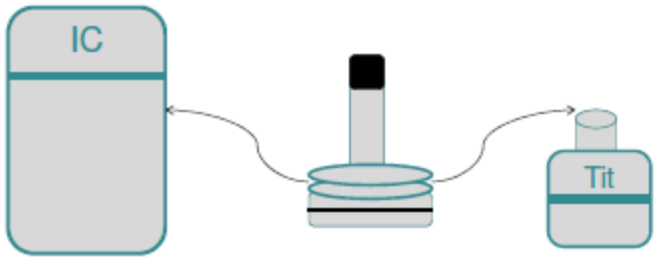
One Sample Changer – One Datbase for all systems



NEMC-2013 14

Metrohm USA Inc.

TitrIC pro – the basic setup



NEMC-2013 15

Metrohm USA Inc.

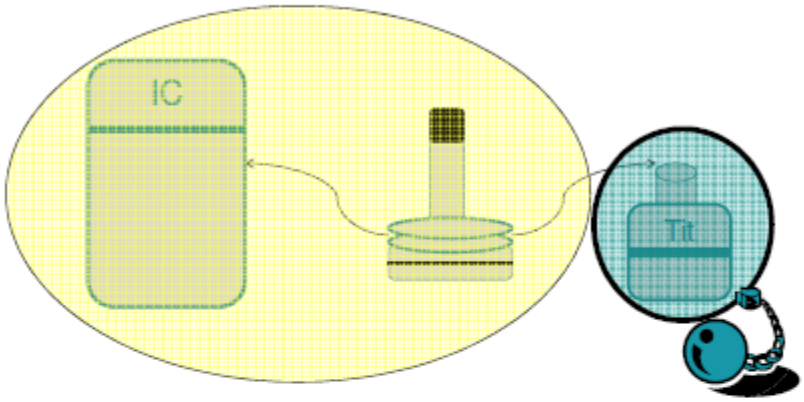
TitrIC pro – a step forward

- ***tiamo™*** & **MagIC Net**
- MagIC Net is the Master – *tiamo™* is Slave
  - *tiamo™* does conductivity, pH, m, p, Ca, Mg upon request
  - Titration data is transfered to MagIC Net database

NEMC-2013 16

Metrohm USA Inc.

TitrIC pro – the basic setup



NEMC-2013 17

Metrohm USA Inc.

TitrIC pro - titration equipment

- 905 Titrando
- iAquatrode plus
- 856 Conductivity module
- Conductivity flow trough cell
- External vessel

Additionally for TitrIC pro I:

- Combined polymembrane electrode Ca



NEMC-2013 18

Metrohm USA Inc.

TitrIC pro

How are Combo Kits added?



- All TitrIC pro systems come with a T connector
- Separate liquid handling for Titration and Ion Chromatography (except for the needle part)



NEMC-2013 19

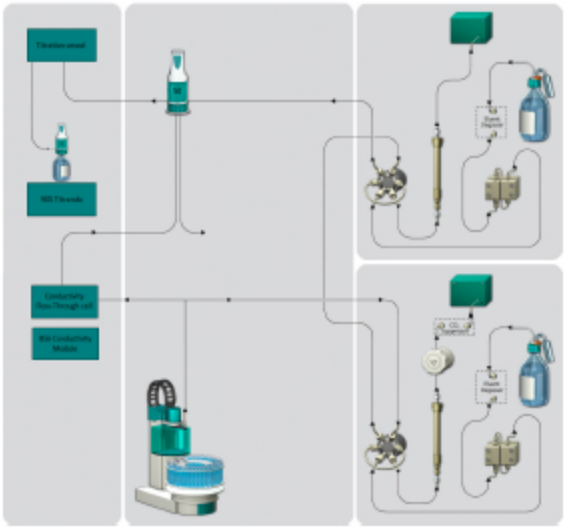
Metrohm USA Inc.

TitrIC pro

TitrIC pro II

Analysis of:

- conductivity,
- temperature,
- pH
- m
- p
- AnCat



NEMC-2013 20

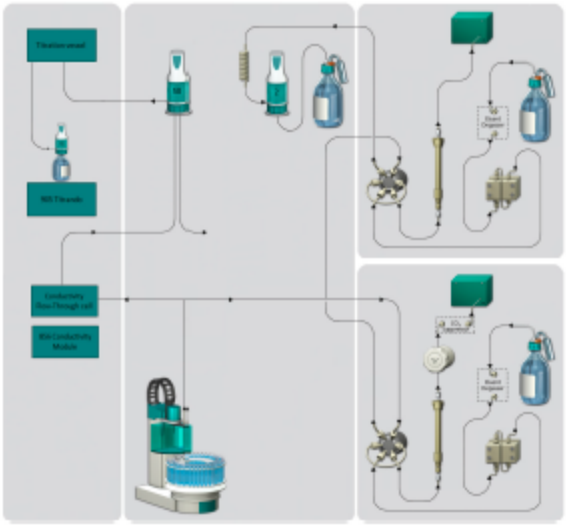
Metrohm USA Inc.

TitrIC pro

TitrIC pro II

Analysis of:

- conductivity,
- temperature,
- pH
- m
- p
- AnCat + MiPT



NEMC-2013 21

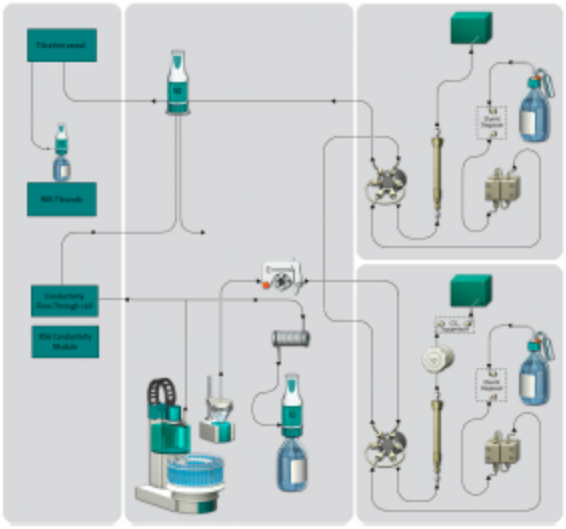
Metrohm USA Inc.

TitrIC pro

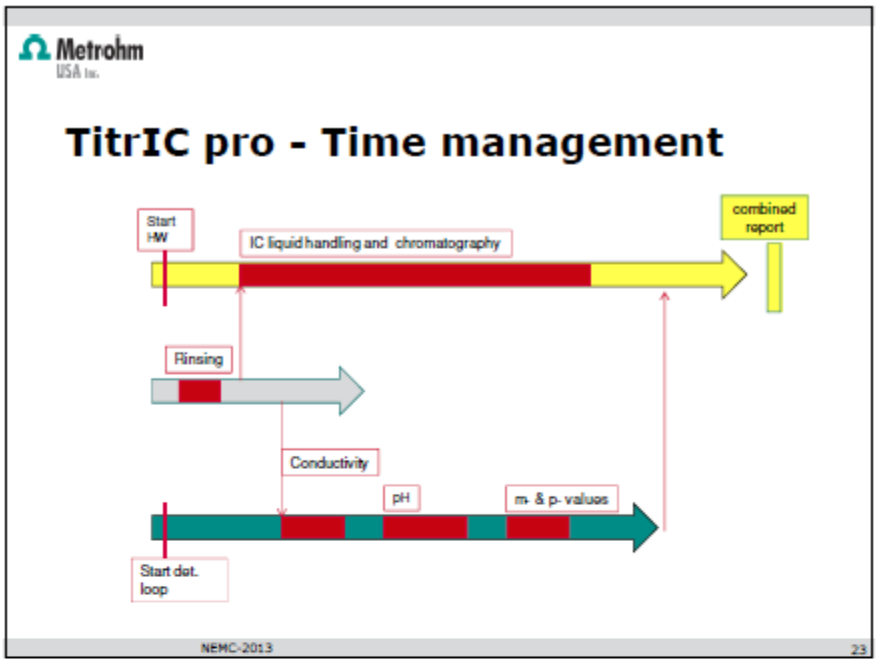
TitrIC pro II

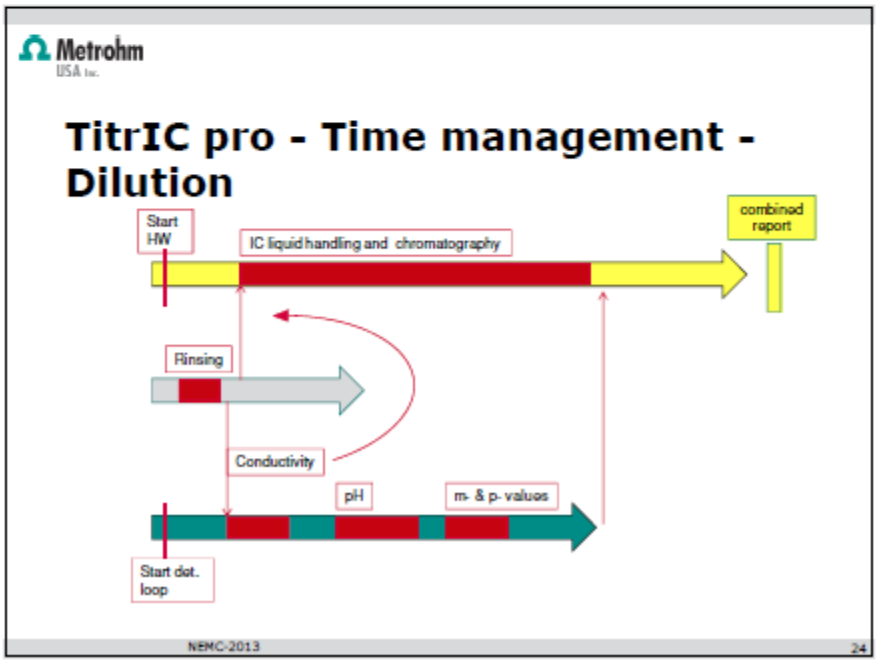
Analysis of:

- conductivity,
- temperature,
- pH
- m
- p
- AnCat + Dilution



NEMC-2013 22


Metrohm
USA Inc.
TitrIC pro - Time management
Start HW
IC liquid handling and chromatography
combined report
Rinsing
Conductivity
pH
m- & p- values
Start dat. loop
NEMC-2013
23


Metrohm
USA Inc.
TitrIC pro - Time management - Dilution
Start HW
IC liquid handling and chromatography
combined report
Rinsing
Conductivity
pH
m- & p- values
Start dat. loop
NEMC-2013
24

Metrohm USA Inc.

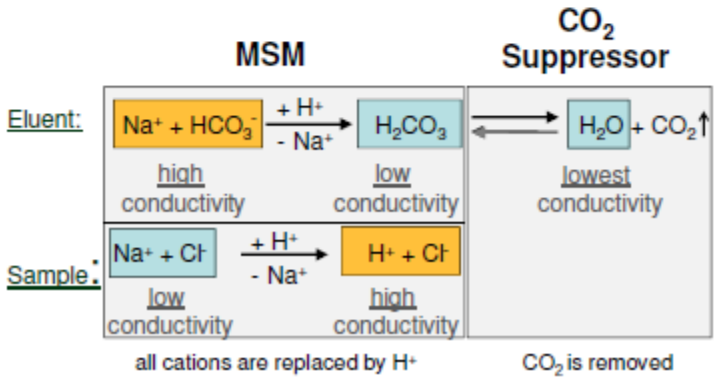
- Ion Chromatography
  - Anions
  - Cations
  - Organic Acids

NEMC-2013 25

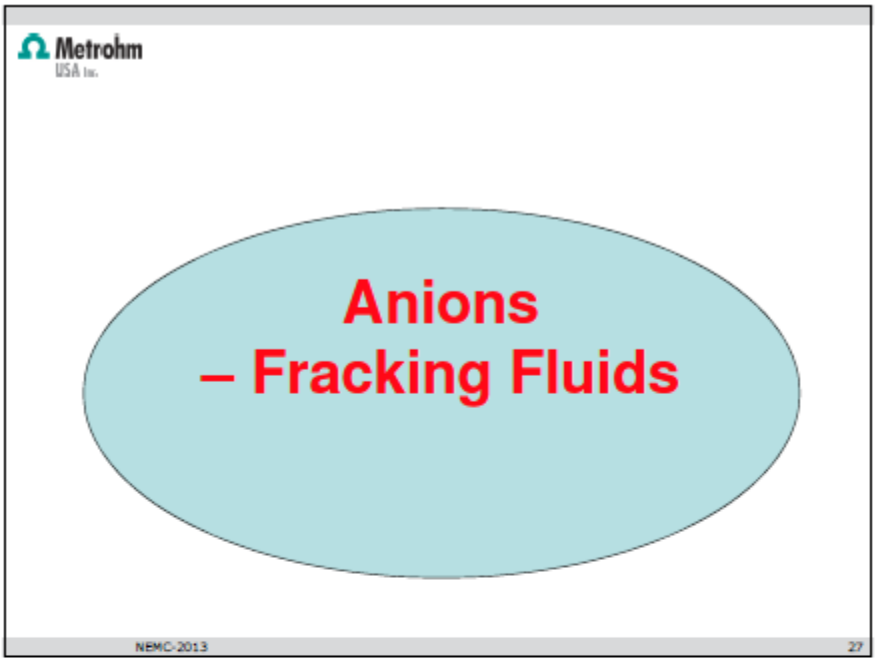
Metrohm USA Inc.

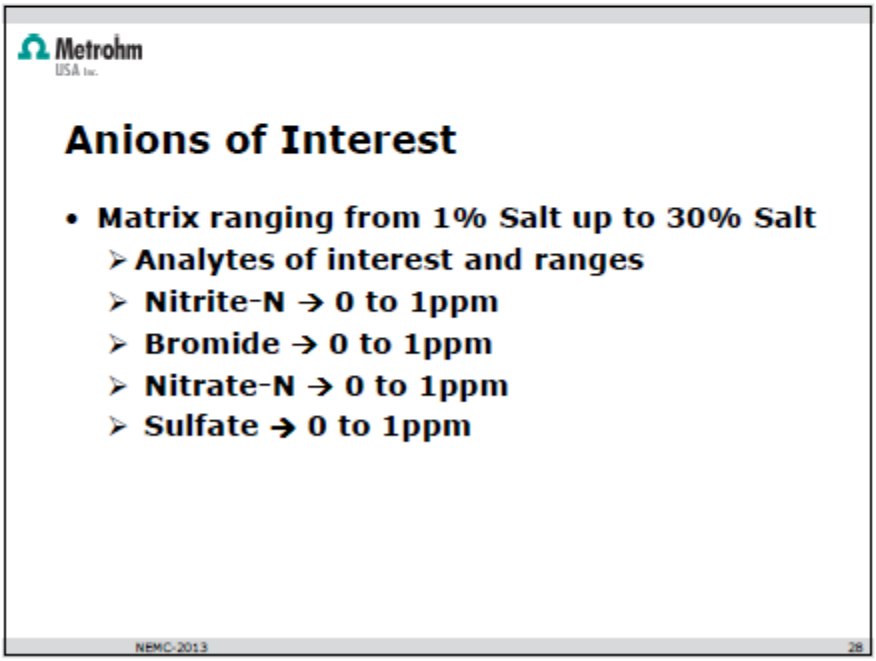
Suppression

Reduction of the background conductivity and increase of analyte conductivity.



NEMC-2013 26


Metrohm
USA Inc.
Anions
– Fracking Fluids
NEMC-2013
27


Metrohm
USA Inc.
Anions of Interest
• Matrix ranging from 1% Salt up to 30% Salt
➢ Analytes of interest and ranges
➢ Nitrite-N → 0 to 1ppm
➢ Bromide → 0 to 1ppm
➢ Nitrate-N → 0 to 1ppm
➢ Sulfate → 0 to 1ppm
NEMC-2013
28

Metrohm USA Inc.

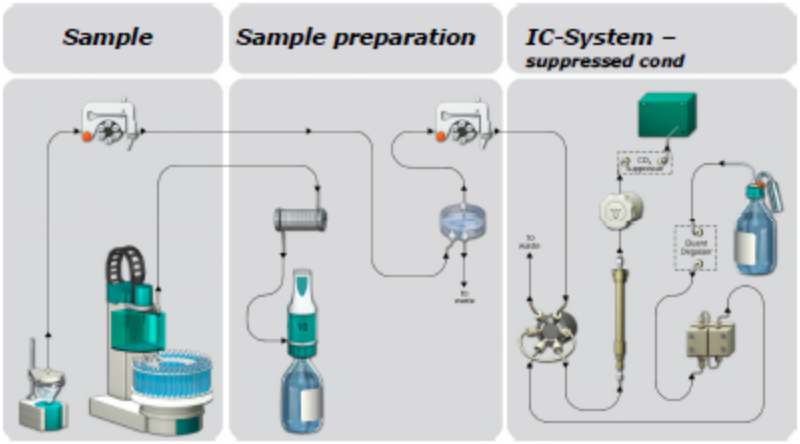
Instrument set-up



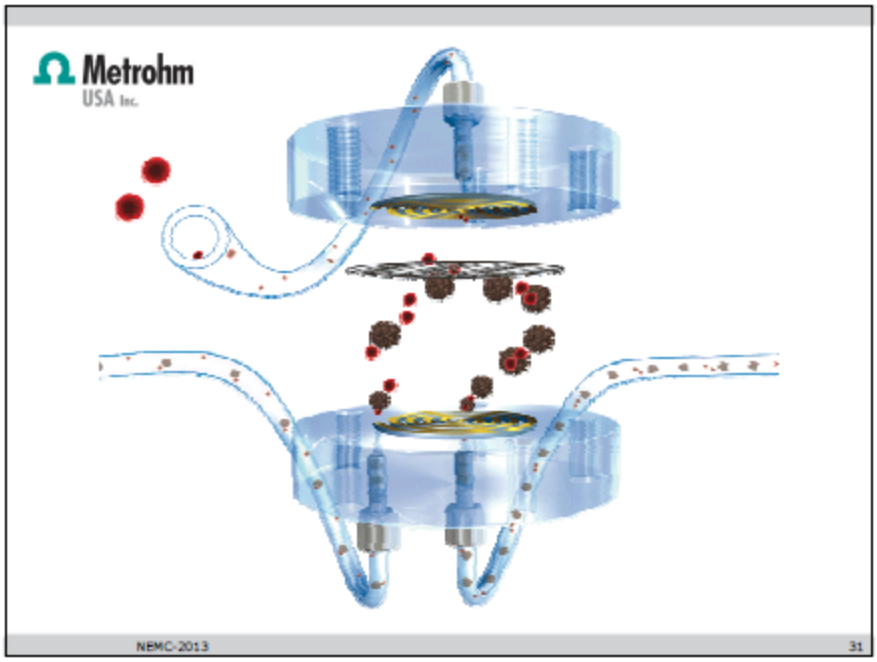
NEMC-2013 29

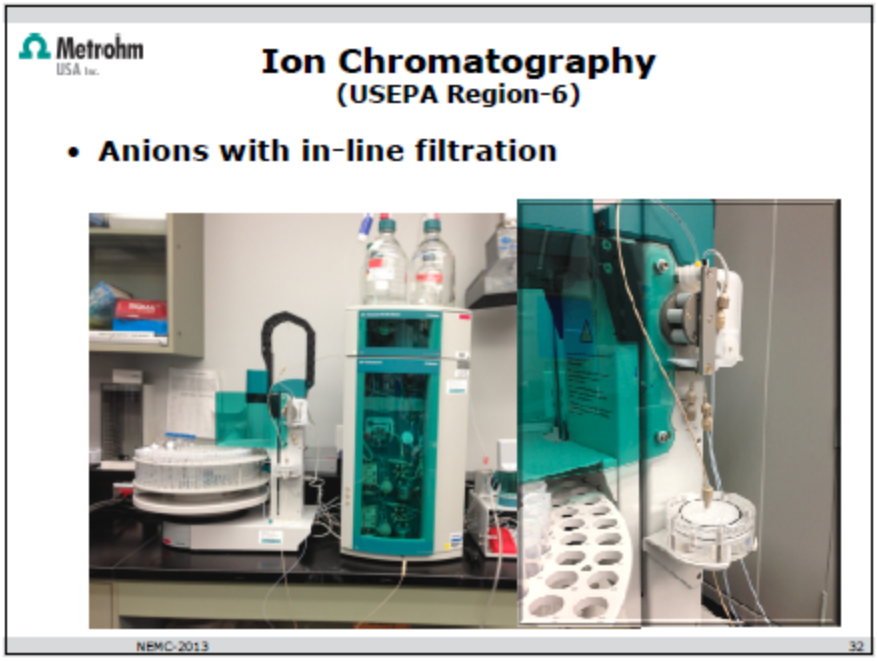
Metrohm USA Inc.

Metrohm Inline Dilution with filtration



NEMC-2013 30


Metrohm
USA Inc.
NEMC-2013
31


Metrohm
USA Inc.
Ion Chromatography
(USEPA Region-6)
• Anions with in-line filtration
NEMC-2013
32

Metrohm USA Inc.

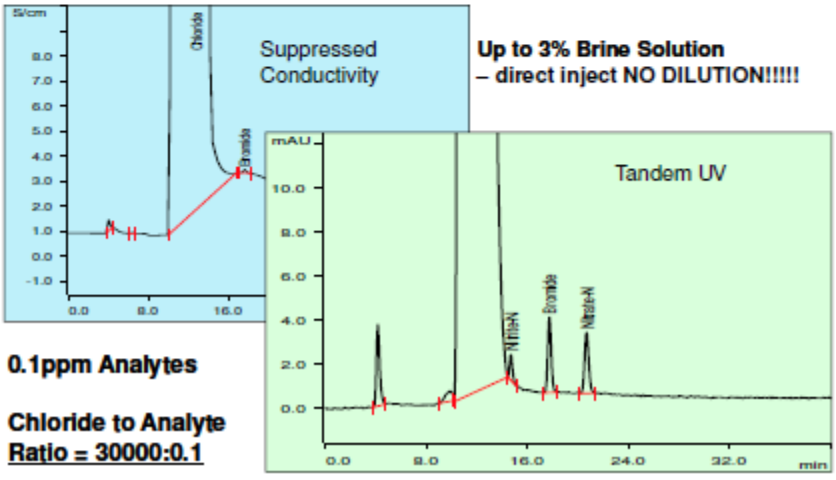
Anions IC Conditions

- ***Column:*** Metrosep ASUPP7-250 (4mm x 250mm)
- ***Sample Loop:*** 10uL
- ***Eluent:*** 3.2mM Na_2CO_3 + 1.0mM $NaHCO_3$ + 2% Acetonitrile
- ***Eluent Flow:*** 0.7mls per minute
- ***Suppressor Solutions***
  - Regen: 100mM Sulfuric Acid + 10% Acetonitrile
  - Rinse: UHP DI water + 10% Acetonitrile
- ***Detection:*** Suppressed Conductivity with Tandem UV

NEMC-2013 33

Metrohm USA Inc.

Anions – Fracking Solutions



Up to 3% Brine Solution – direct inject NO DILUTION!!!!!

0.1ppm Analytes

Chloride to Analyte Ratio = 30000:0.1

NEMC-2013 34

Metrohm
International

IC-MS

Applications





NEMC-2013 35

Metrohm
International

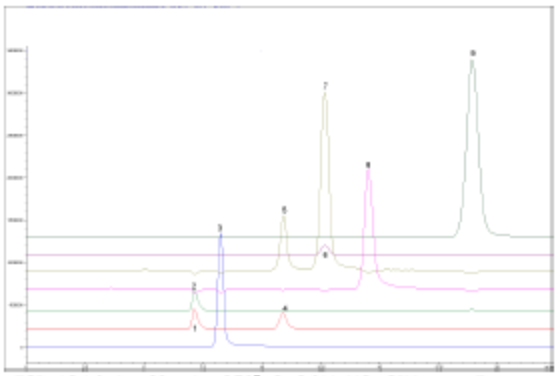
IC-MS

Anions



Metrosep A Supp 5 – 150		
1; 2	Bromide	79; 81
3	Nitrate	62
4; 5	Phosphate	79; 97
6; 7	Sulfate	97;99
8	Oxalate	89
9	Thiosulfate	113
		m/z

3.2/1.0 mmol/L Na_2CO_3/ $NaHCO_3$; 0.7 mL/min; 10 ppm Standard



ESI: 13 L/min; 60 psig; 350° C; 3 kV MS: SIM neg.; Frag. 70V

NEMC-2013 36

Metrohm
International headquarters

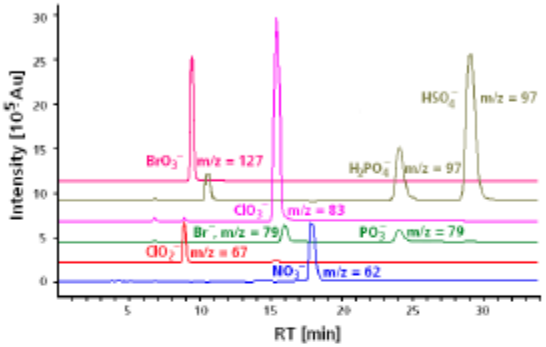
IC-MS

Anions – Oxyhalides



Metrosep A Supp 5 – 250		
1	Chlorite	67
2	Bromate	127
4	Chlorate	83
5	Bromide	79
6	Nitrate	62
7	Phosphate	79
8	Phosphate	97
9	Sulfate	97
		m/z

3.2/1.0 mmol/L Na_2CO_3/ $NaHCO_3$; 0.7 mL/min;
10 ppm Standard



ESI: 13 L/min; 60 psig; 350° C; 3 kV MS: SIM neg.; Frag. 70V

NEMC-2013 37

Metrohm
International headquarters

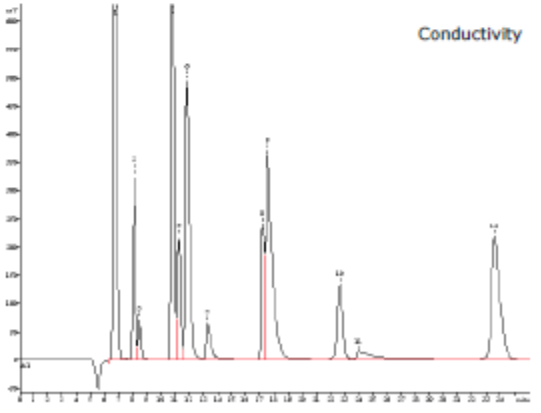
IC-MS

Anions – Halo Acetic Acids: Standard



A Supp 5 – 100 + A Supp 1			
1	Fluoride	7	DBAA
2	MCAA	8	Nitrate
3	MBAA	9	Bromide
4	Chloride	10	Phosphate
5	DCAA	11	TCAA
6	Nitrite + BCAA	12	Sulfate

3.2/1.0 mmol/L Na_2CO_3/ $NaHCO_3$; 0.7 mL/min;
10 ppm Standard



NEMC-2013 38

Metrohm
International

IC-MS

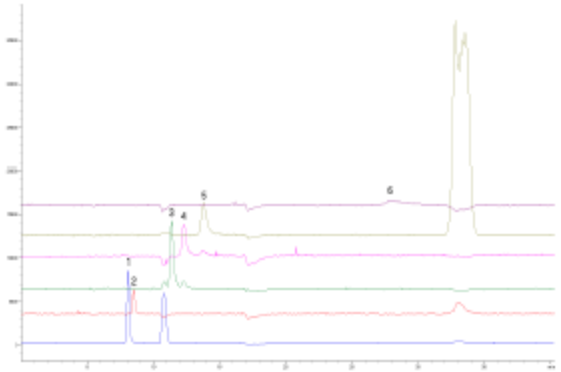
Anions – Halo Acetic Acids: Standard

MS

A Supp 5 – 100 + A Supp 1		
1	MCAA	93
2	MBAA	137
3	DCAA	127
4	BCAA	171
5	DBAA	217
6	TCAA – CO_2	117
		m/z

10 ppm Cl^-, NO_3^-, SO_4^{2-}

3.2/1.0 mmol/L Na_2CO_3/ $NaHCO_3$; 0.7 mL/min; Standard 10 ppb HAAs



ESI: 13 L/min; 60 psig; 350° C; 5 kV MS: SIM neg.; Frag. 70 V

NEMC-2013 39

Metrohm
USA Inc.

Cation Analysis

Suppressed or Non-Suppressed?

NEMC-2013 40

Metrohm USA Inc.

AWIC US6-0177-052013

List of target Cations by Ion Chromatography (ASTM D6919)

- Modification to this ASTM method is required
- Matrix 30% NaCl solution – ***Flowback Water***
- Target analytes at 1ppm Detection level
  - Potassium
  - Calcium
  - Magnesium
  - Strontium
  - Barium
  - ❖ Manganese
  - ❖ Copper
  - ❖ Nickel
  - ❖ Zinc
  - ❖ Cobalt

Also Low Molecular weight Amines

NEMC-2013 41

Metrohm USA Inc.

AWIC US6-0177-2013

Cation IC Conditions

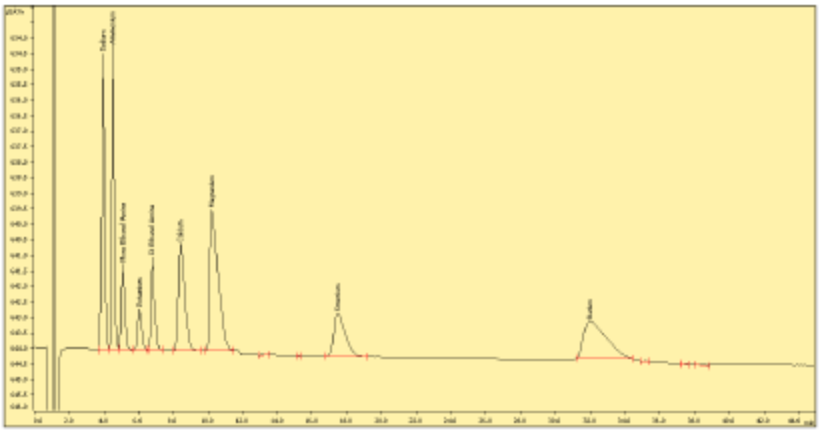
- ***Column:*** Metrosep C6 (4mm x 100mm)
- ***Sample Loop:*** 15uL
- ***Eluent:*** **2mM Oxalic Acid + 2mM PDCA + 2% Acetonitrile**
- ***Eluent Flow:*** 0.9mls per minute
- ***Detection:*** Non Suppressed Conductivity

NEMC-2013 42

Metrohm USA Inc.

AW IC US6-0177-2013

Cations and Amines – Fracking Solutions



NEMC-2013 43

Metrohm USA Inc.

Low Level Ammonium Ion in presence of High Sodium Ion

NEMC-2013 44

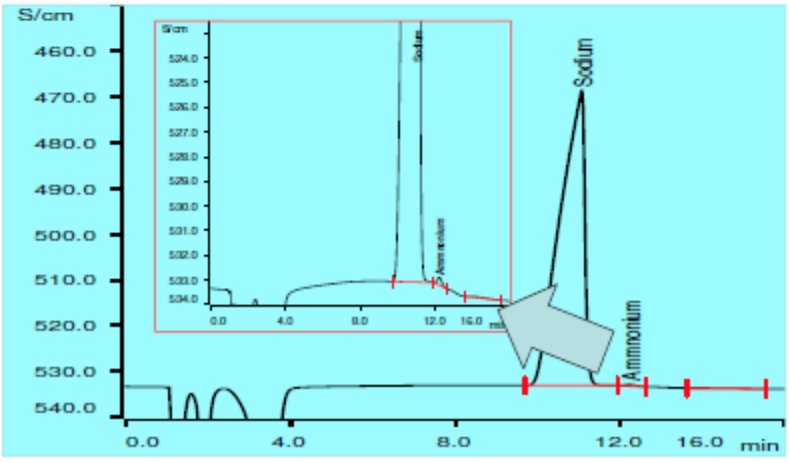
Metrohm USA Inc.

Cation IC Conditions

- ***Column:*** Metrosep C6 (4mm x 150mm)
- ***Sample Loop:*** 10uL
- ***Eluent:*** **1.75mM Oxalic Acid**
- ***Eluent Flow:*** 0.9mls per minute
- ***Detection:*** Non Suppressed Conductivity

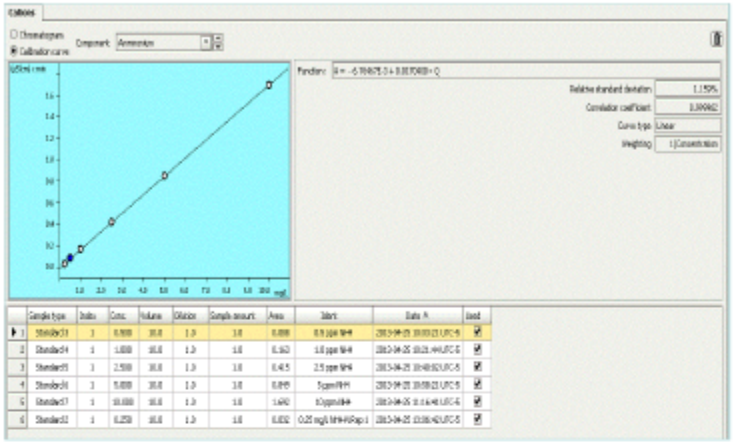
NEMC-2013 45

Metrohm USA Inc.



NEMC-2013 46

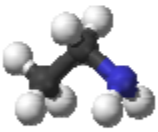
Metrohm
USA Inc.



Calibration from 0.1 ppm to 10.0 ppm

NEMC-2013 47

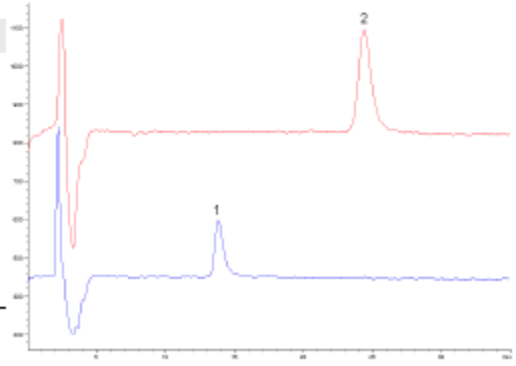
Metrohm
International Headquarters



IC-MS

Cations – Ultra Trace Analysis of Amines

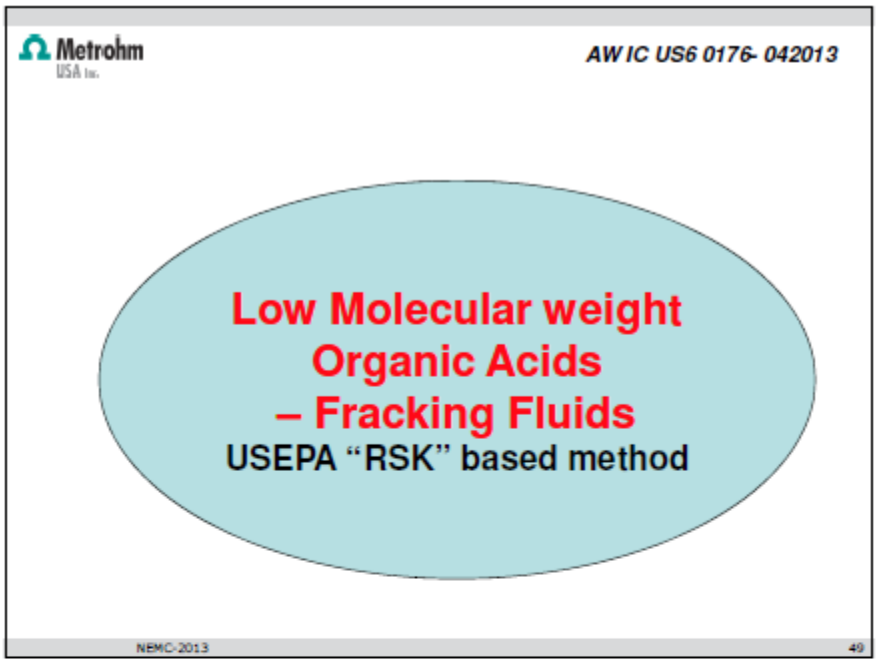
Metrosep C 4 - 100		
1	Diethylamine	0.2
2	Triethylamine	0.2
		ppb

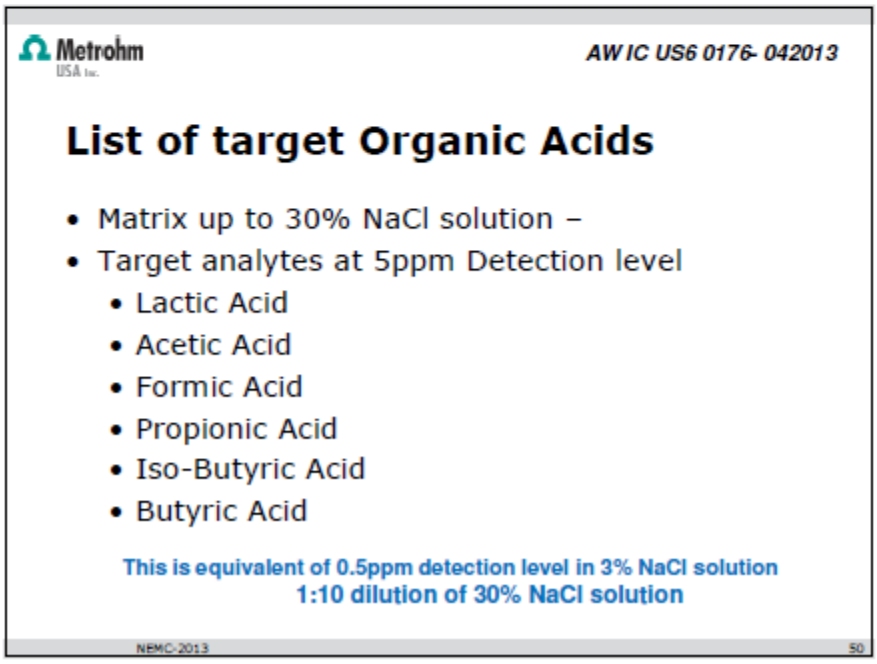


4.0 mmol/L tartaric acid/
10 % ACN; 0.5 mL/min;
350 µL; m/z 74 & 102

ESI: 13 L/min; 60 psig; 350° C; 3.0 kV MS: SIM pos.; Frag. 70 V

NEMC-2013 48


Metrohm
USA Inc.
AW IC US6 0176- 042013
Low Molecular weight
Organic Acids
– Fracking Fluids
USEPA "RSK" based method
NEMC-2013
49


Metrohm
USA Inc.
AW IC US6 0176- 042013
List of target Organic Acids
Matrix up to 30% NaCl solution –
Target analytes at 5ppm Detection level
Lactic Acid
Acetic Acid
Formic Acid
Propionic Acid
Iso-Butyric Acid
Butyric Acid
This is equivalent of 0.5ppm detection level in 3% NaCl solution
1:10 dilution of 30% NaCl solution
NEMC-2013
50

Metrohm USA Inc.

AW IC US6 0176- 042013

Organic Acid IC Conditions

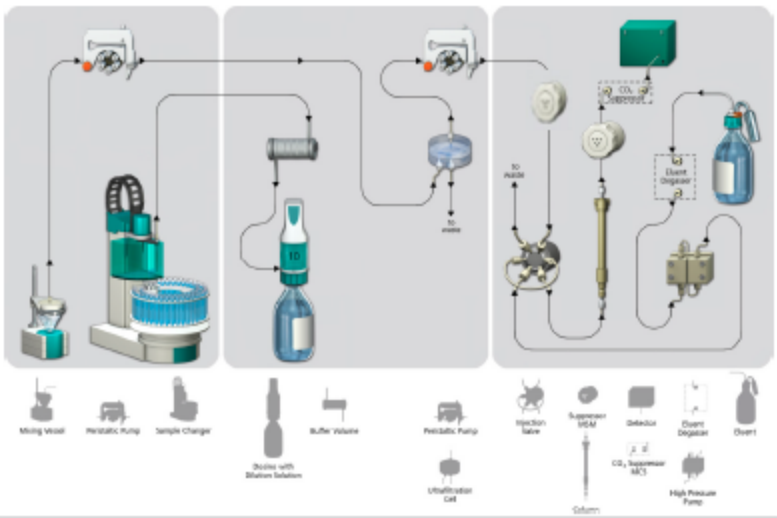
- ***Column:*** Metrosep OA-250 (4mm x 250mm) (Ion Exclusion Column)
- ***Sample Loop:*** 50uL *(In-line Cation removal – MISP)*
- ***Eluent:*** 0.5mM H_2SO_4
- ***Eluent Flow:*** 0.5mls per minute
- ***Metrohm Suppressor Solutions***
  - **Regenerant:** 50mM LiCl
  - **Rinse:** UHP DI water
- ***Detection:*** Inversed Suppressed Conductivity

NEMC-2013 51

Metrohm USA Inc.

AW IC US6 0176- 042013

Inline Automatic Dilution, filtration and cation removal setup

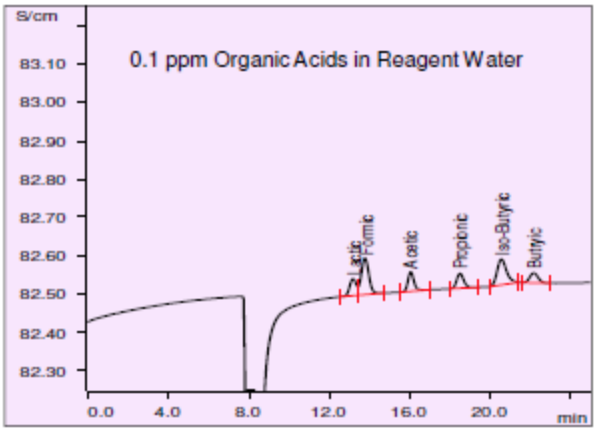


NEMC-2013 52

Metrohm USA Inc.

AWIC US6 0176- 042013

Organic Acids – Fracking Solutions



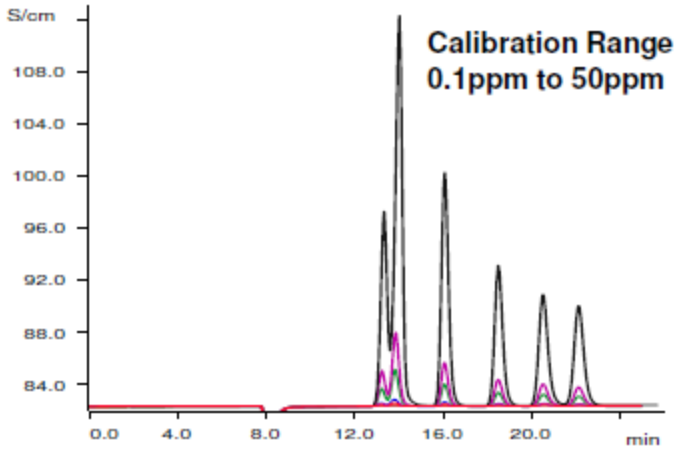
- Lactic
- Formic
- Acetic
- Propionic
- Iso-Butyric
- Butyric

NEMC-2013 53

Metrohm USA Inc.

AWIC US6 0176- 042013

Calibration Curves

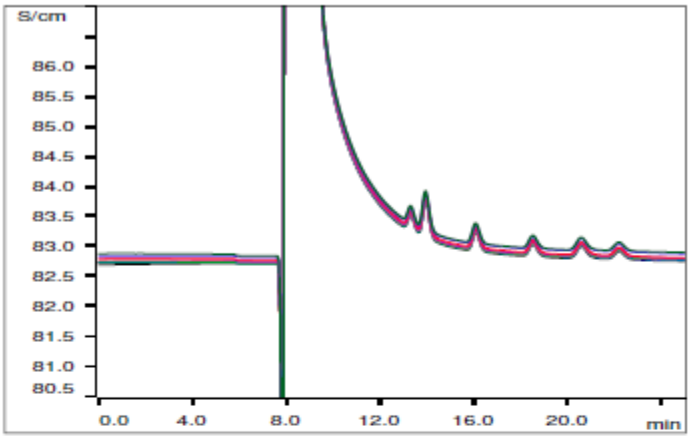


NEMC-2013 54

Metrohm USA Inc.

AW IC US6 0176- 042013

0.5 ppm OA in 3% NaCl matrix



NEMC-2013 55

Metrohm USA Inc.

Summary

- ✓ History of Hydraulic Fracking
- ✓ Ion Analysis (Combined automated systems) for
  - ✓ Wet Chemistry
  - ✓ Ion Chromatography

NEMC-2013 56

Metrohm USA Inc.

What has not been presented yet

- Electrochemistry measurement (VA) hyphenated with Ion Chromatography for Metals analysis and Ion Chromatography for Total Ion Balance
- Ethylene and Propylene glycol analysis at single digit ppb level detection using ONLY Ion Chromatography…….

NEMC-2013 57

Metrohm USA Inc.

Acknowledgements

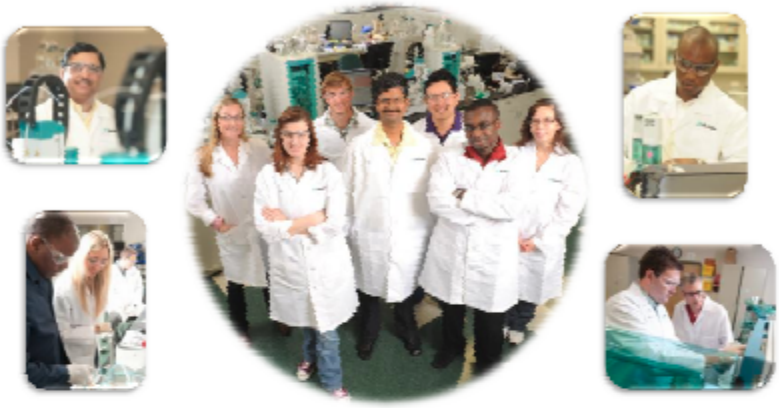
- **Mr. David Neliegh** – USEPA Region – 6
- **Dr. Melvin Ritter** – USEPA Region – 6
- **Mr. Johnson Mathew**– USEPA Region – 6
- **Mr. William Telliard** – Retired USEPA - DC
- **Ms. Marvyln Humphrey** – USEPA Region – 6
- **Metrohm AG applications team**
  especially, **Dr. Katinka Ruth** and **Dr. Andrea Willie**
- **Dr. Chunlong Zhang**– University of Houston – Clearlake
  - Mr. Brian Wilson and Ms. Jahnavi – Graduate students

NEMC-2013 58

Metrohm USA Inc. Metrohm Canada

Thank you for listening

The many faces of Metrohm Applications



Let us help you become the expert in your lab!

NEMC-2013 59

Metrohm USA Inc.



60 NEMC-2013

SECTION 8

MODELING, MAPPING, AND GEOSPATIAL TOOLS

Pre-Serve Mapping Tool to Help Protect Endangered Plant Species

David J. Healy
Stone Environmental Inc.

Abstract

The Stone has developed a Web Mapping Tool to protect threatened and endangered plant species from potential impacts resulting from the agricultural use of herbicides that contain glyphosate. Through a simple four-step process, the application, Pre-serve.org, quickly helps licensed growers of crops containing the Roundup Ready trait determine which, if any, pesticide mitigations are required based upon the specific location of their fields. During this session, we will demonstrate through a series of steps to determine which, if any, mitigations are necessary for their location. This multi-step strategy is a clear and simple process, which allows many growers to exit Pre-Serve in the first few steps. In the initial steps, users are asked about their application methods and rates, as well as the state and county where their fields are located. If a user indicates that the fields planned to receive the application of a glyphosate agricultural herbicide are located in a county containing glyphosate use limitation areas (ULAs), then the user is directed to an interactive mapping application that allows the comparison of the locations of the specific fields and the ULAs. The mapping application provides a background map to help users identify their field locations using “Google Maps-like” navigation. Once a user has zoomed in on the field locations, a report are available that provides detailed use limitations, including a description of the species habitats to be aware of within the ULAs.



Pre-Serve Mapping Tool to Help Protect Endangered Plant Species

Presented by:
David J. Healy
National Environmental Monitoring Conference
San Antonio, Texas
August 6, 2013

STONE ENVIRONMENTAL INC

Background

- The Endangered Species Act (ESA) requires EPA to ensure that pesticides registered under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) will not "adversely impact" U.S. federally-listed threatened and endangered species (TES) or "destroy or adversely modify" any critical habitat for that species.
- EPA determines whether pesticide use in a certain area may adversely impact a listed TES.
- EPA will require geographically-specific pesticide use limitations in the pesticide registration terms if limitations on pesticide use are necessary to protect listed species in that area,
- EPA disseminates this information via Endangered Species Protection Bulletins through an online system called "Bulletins Live".

Motivation for Pre-serve

- EPA's Bulletins Live site does not yet include many pesticides that could potentially impact listed species.
- Bulletins Live is not a Web Mapping Site.
- Very difficult to comply without a tool.
- As part of its stewardship program, Monsanto Company decided to proactively address communication to licensed-growers of crops containing the Roundup Ready® trait by providing appropriate glyphosate use limitations.
- Support the protection of listed plant species from potential impacts resulting from the agricultural use of herbicides containing glyphosate.

Objectives for Pre-Serve Tool

- To provide licensed growers of Roundup Ready crops with a simple tool to quickly determine if their fields are within glyphosate Use Limitation Areas that might impact TES.
- Growers licensed to grow crops containing Roundup Ready technology are required (under the terms of the license agreement) to observe all mitigation instructions on the Pre-Serve website.

Application Development Steps

- Pre-Serve was developed as an ArcGIS Server application.
- Software development environment:
  - Microsoft Visual Studio 2005 using the following technologies: Visual Basic .NET, ASP.NET, Esri's Web ADF API, and Java Script.
- To enable faster, higher performance mapping, cached map services were used throughout Pre-Serve.
- As many as five separate map services were created per map in order to achieve the desired look of the mapping in both the interactive map viewer and the report.

Application Data Sources

- Endangered Species Sites from NatureServe
- Critical Habitat Areas from USFWS
- These areas were buffered to account for spray drift
- Basemaps from Esri

Application Demonstration

- http://pre-serve.stone-env.net

Thank you and Questions!

- For Additional Information:

dhealy@stone-env.com

David J. Healy | Vice President | Applied Information Management | Stone Environmental Inc.
535 Stone Cutters Way, Montpelier, Vermont 05602
802.229.1879 office 978.761.8409 mobile
www.stone-env.com/aim

Detection of Melt Pond from Aerial Photos through Object-Based Image Classification Scheme

Xin Miao

Missouri State University Department of Geography, Geology and Planning, et al

Abstract

Melt ponds are pools of open fresh water on surface of Arctic sea ice in the warmer months and have a significant influence on Earth's radiation balance since they strongly absorb solar radiation rather than reflecting it as snow and ice do. However, manually delineating of melt pond from remotely sensed images is time-consuming and labor-intensive. In this study, we use the object-based remote sensing classification scheme to extract melt ponds efficiently from 1,727 aerial photos taken during the Chinese Arctic Exploration in 2010. Our results illustrate the spatial distribution and morphological characters of melt ponds in different latitudes of the Arctic Pacific sector. This method can be applied to massive photos and images taken in past years and future years, in deriving the melt pond distribution and changes through years. The results can be used to fine-tune climate models.

NEMC 2013 August 5-9, San Antonio, TX

Detection of Sea Ice/ Melt Pond from Aerial Photos through Object-based Image Classification Scheme

Xin Miao[12], Hongjie Xie[2], Zhijun Li[3], Ruibo Lei[4]

[1]Department of Geography, Geology and Planning, Missouri State University

[2]Department of Geology, University of Texas at San Antonio

[3]Dalian University of Technology

[4]Polar Research Institute of China

Introduction 1

Sea Ice and Climate Change



- The lowest Arctic summer sea ice extents with a new record summer minimum (3.4 million km2) set on 13 September 2012.
- The shrinking summer sea ice extent could be the first of the tipping points of the climate dominos.
- Consequences: higher water temperature due to the positive feedback of albedo (melt ponds), more powerful and frequent storms, rising sea levels, diminished habitats for polar animals, and more pollution due to fossil fuel exploitation and/ or increased traffic.

(Yohe *et al.*, 2007; Marshall, 2013; Parkinson and Comiso, 2013)

Introduction2

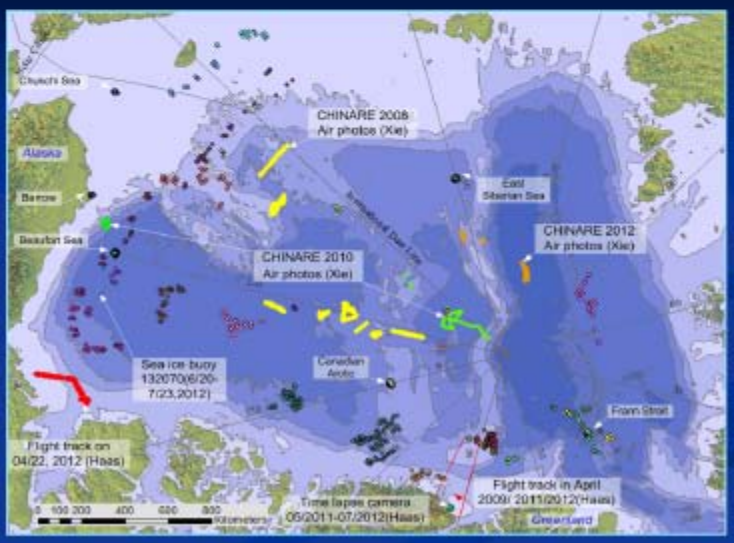
High Spatial Resolution Image Processing

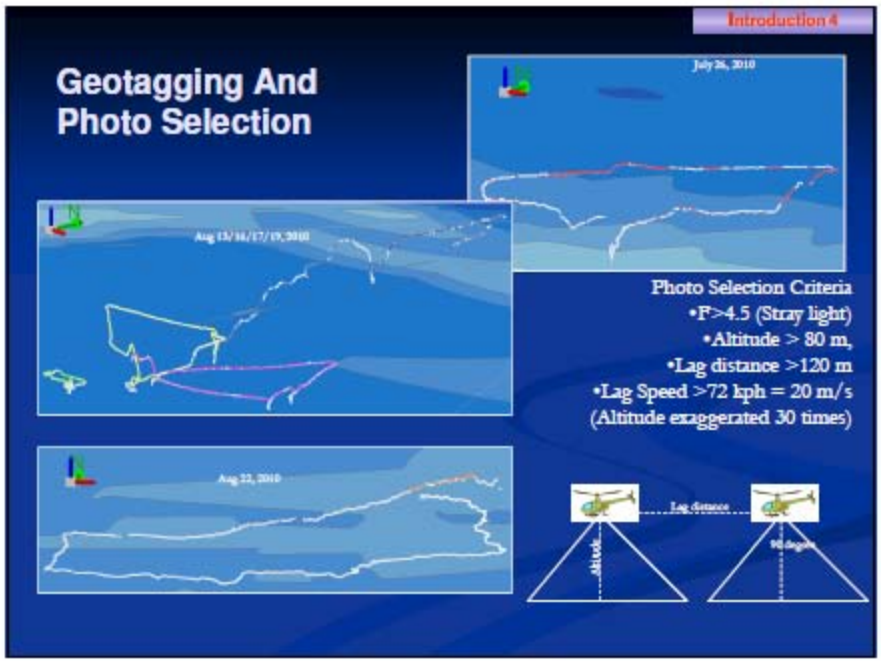
- Arctic sea ice models: e.g. Los Alamos Sea Ice (CICE) model coupled with POP (Parallel Ocean Program) in the NCAR CESM.
- Require high spatial resolution image data in the Arctic area to calibrate and verify the model, e.g. USGS Global Fiducials Library (GFL), and Survey aerial photos such as CHINARE 2010 *et al.*
- Manually delineating of sea ice/ melt pond is time-consuming and labor-intensive, need a reliable and efficient image batch processing scheme.

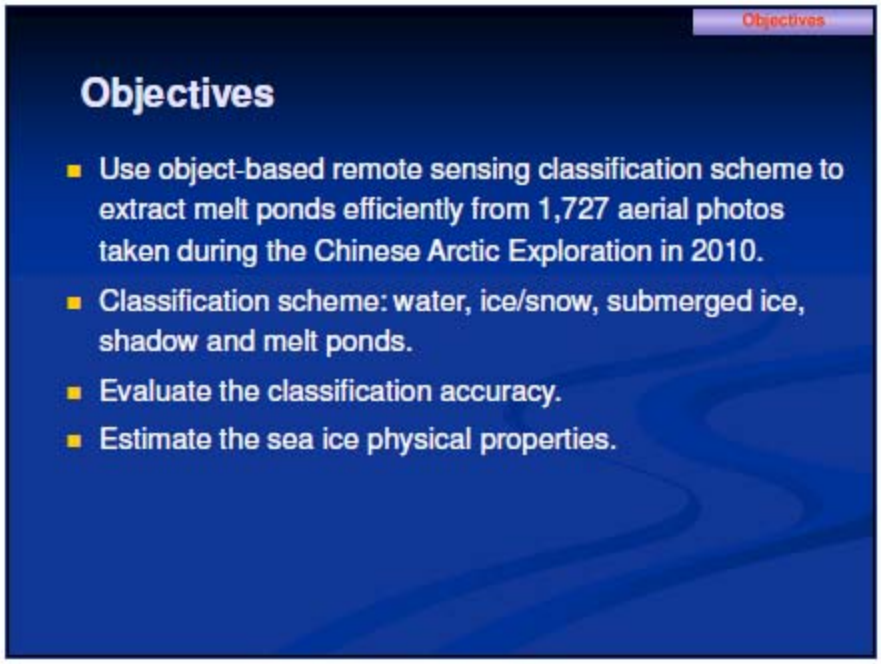
(Kim *et al.*, 2006; Hunke, 2010; Hunke and Lipscomb, 2010)

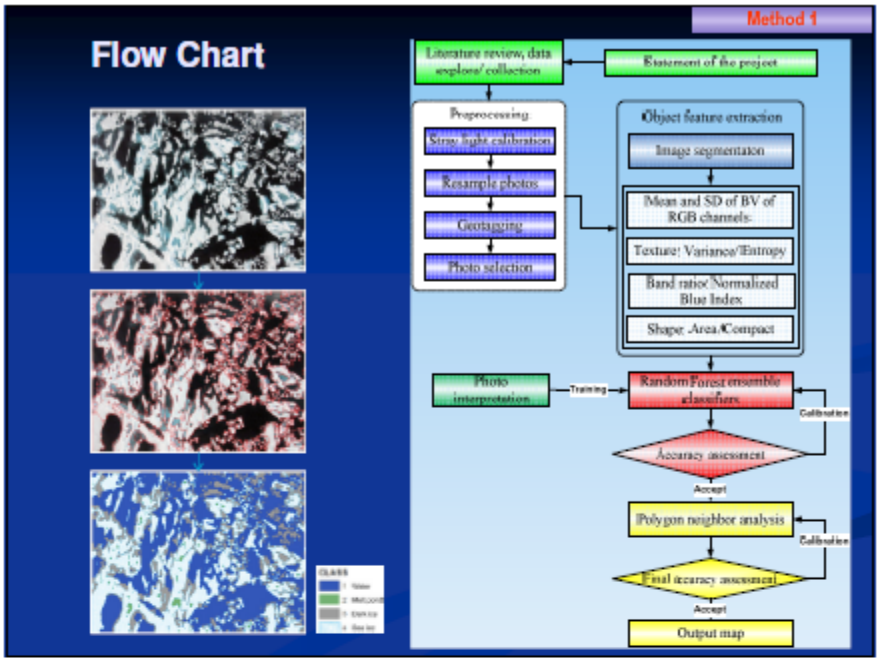
Introduction3

Study Area

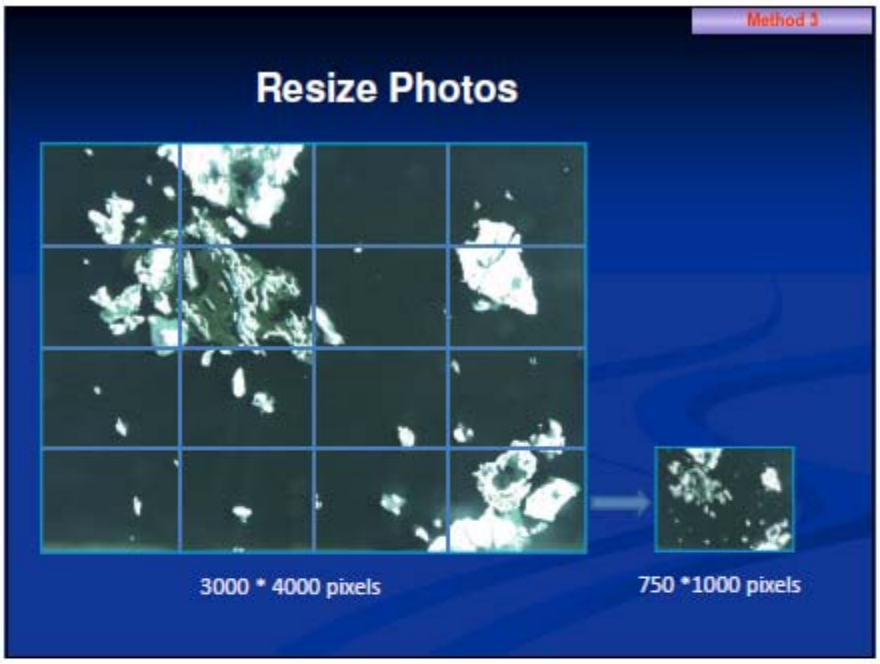


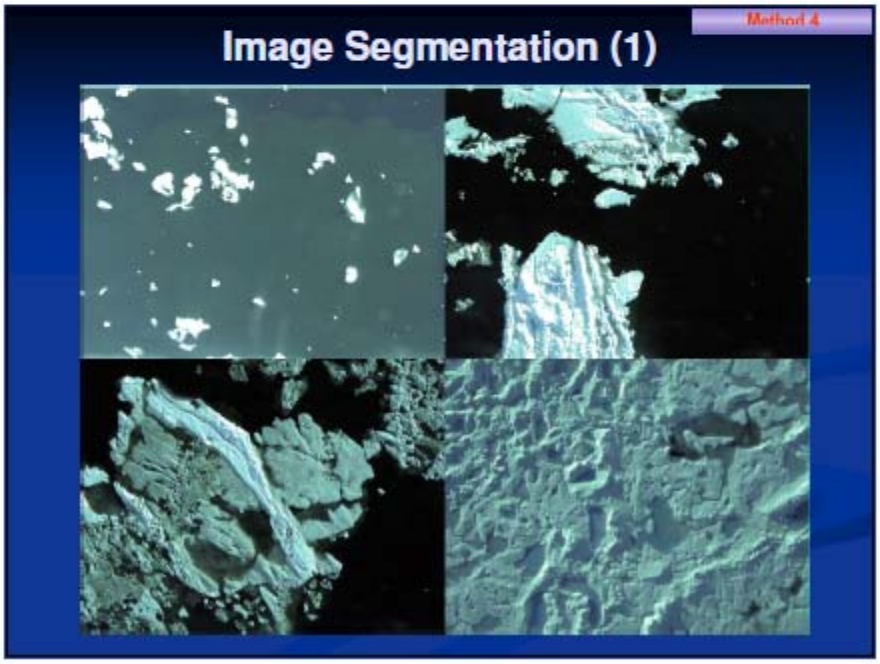

Introduction 4
Geotagging And Photo Selection
July 26, 2010
Photo Selection Criteria
•F>4.5 (Stray light)
•Altitude > 80 m,
•Lag distance >120 m
•Lag Speed >72 kph = 20 m/s
(Altitude exaggerated 30 times)
Lag distance
Altitude

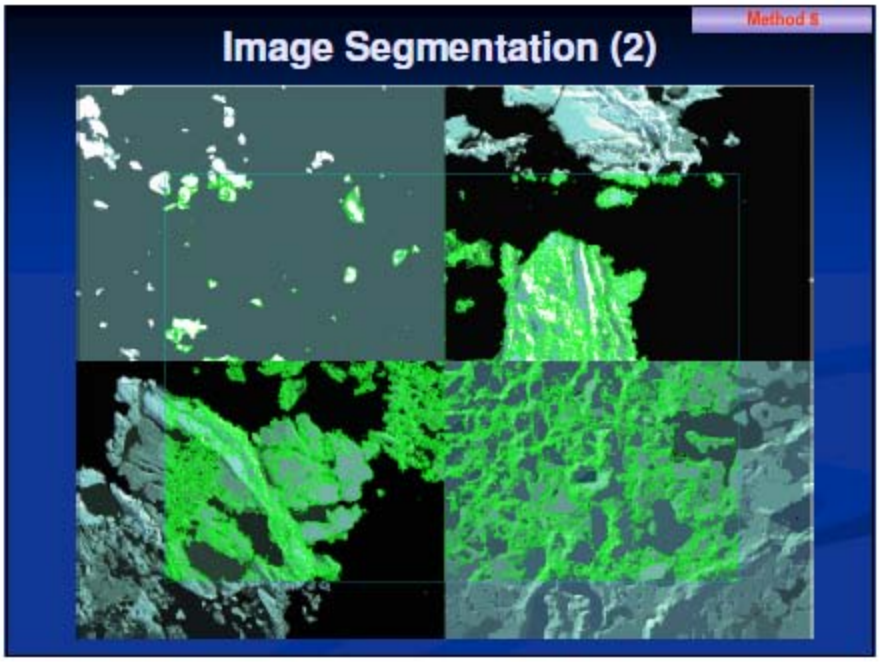

Objectives
Objectives
Use object-based remote sensing classification scheme to extract melt ponds efficiently from 1,727 aerial photos taken during the Chinese Arctic Exploration in 2010.
Classification scheme: water, ice/snow, submerged ice, shadow and melt ponds.
Evaluate the classification accuracy.
Estimate the sea ice physical properties.

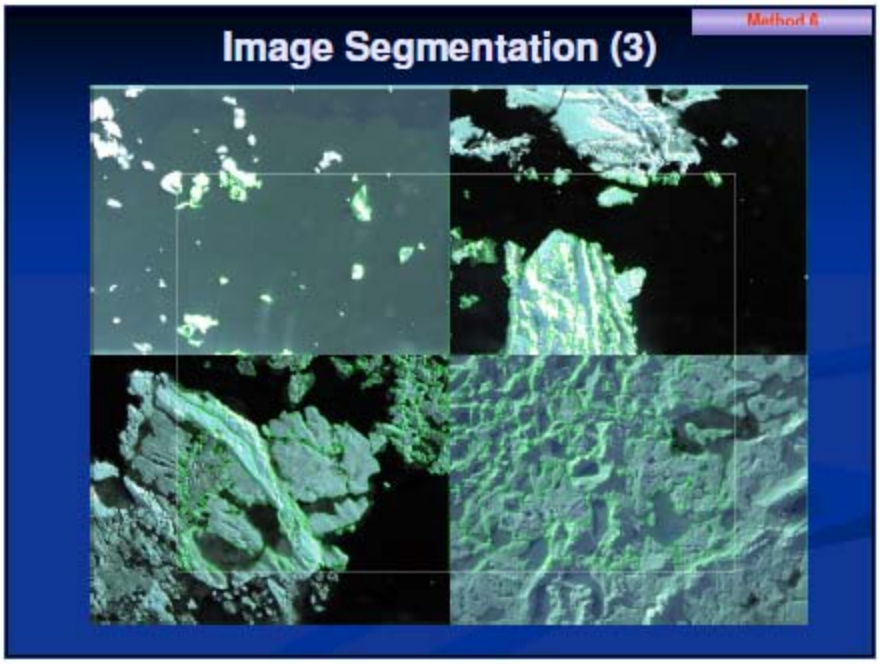

Method 1
Flow Chart
Literature review, data explore/ collection
Statement of the project
Preprocessing
Stray light calibration
Resample photos
Geotagging
Photo selection
Object feature extraction
Image segmentation
Mean and SD of BV of RGB channels
Texture: Variance/Entropy
Band ratio/ Normalized Blue Index
Shape: Area/Compact
Photo interpretation
Training
Random Forest ensemble classifiers
Calibration
Accuracy assessment
Accept
Polygon neighbor analysis
Calibration
Final accuracy assessment
Accept
Output map


Method 2
Red Stray Light Removal
test_00012
072610_012
test_00092
072610_092
Resolution: 12.1 megapixels
CCD Size: 1/1.7"
Zoom lens: 7.4 mm - 44.4 mm - F/2.8-4.8
Focal Length Equivalent to 35mm Camera: 35 - 210 mm Max
Shutter Speed: 1/2500 sec


Method 3
Resize Photos
3000 * 4000 pixels
750 *1000 pixels

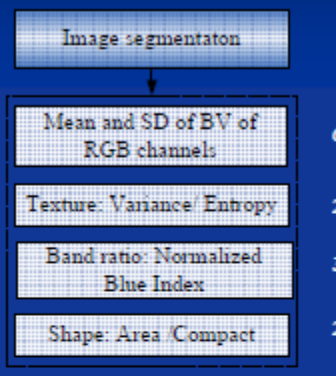

Method 4
Image Segmentation (1)


Method 5
Image Segmentation (2)

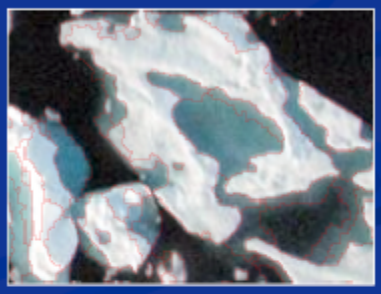

Method 6
Image Segmentation (3)

Method 7

Feature Extraction



- Extract 13 Spectral, Texture, Band Ratio and Shape Features
- BR1= (B-R)/(B+R)
- BR2= (B-G)/(B+G)
- BR3=(G-R)/(2B-R-G)
- 'True Area/ Compact' used in morphological analysis



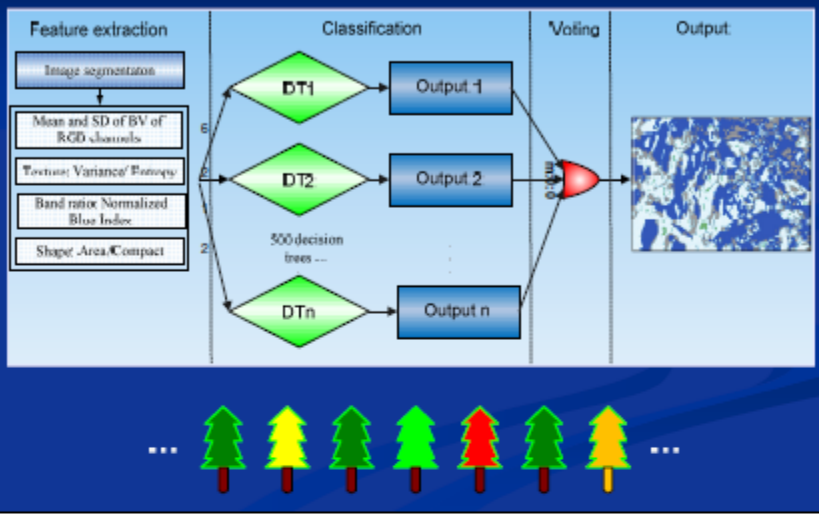
Method 8

Classification scheme

#	Class Name	Class Description
1	Water	Arctic ocean, objects are rather dark and smooth.
2	Submerged ice	Ice submerged under water along the edge, usually shown as color cyan or blue due to mixed reflection from ice surface and water.
3	Shadow	Darker objects on the ice/snow caused by ridges and low solar elevation angle. Shadow will be combined into Ice/snow for calculation of ice concentration. Shadow will also be used for calculation of ridge height.
4	Ice/snow	Bright white objects due to high reflectance of ice/snow.
5	Melt pond	Pools of open water formed on sea ice. Melt pond will be used for calculation of fresh water volume.

Method 9

Random Forest: A Ensemble Method



Method 10

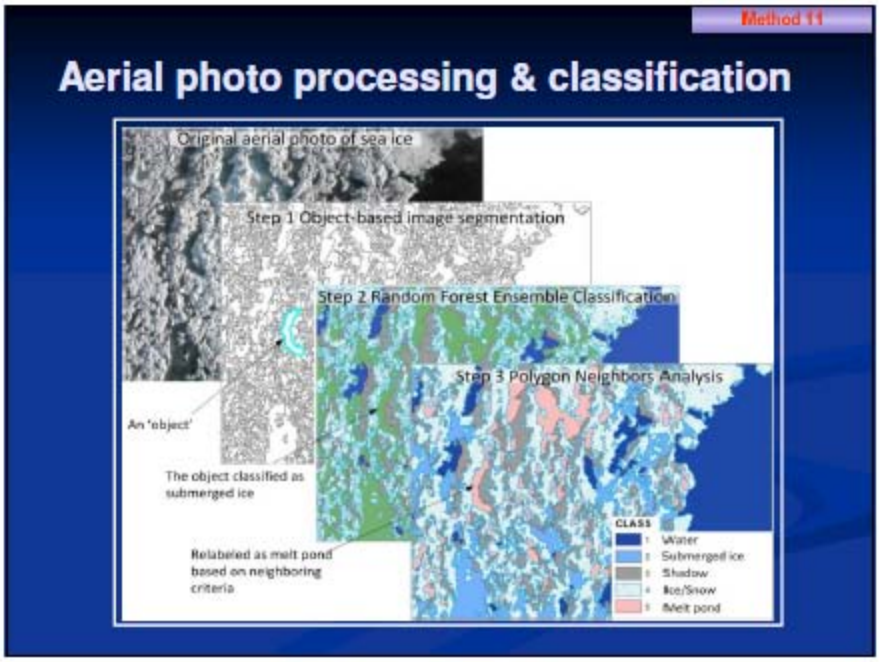
Polygon Neighbors Analysis (PNA)

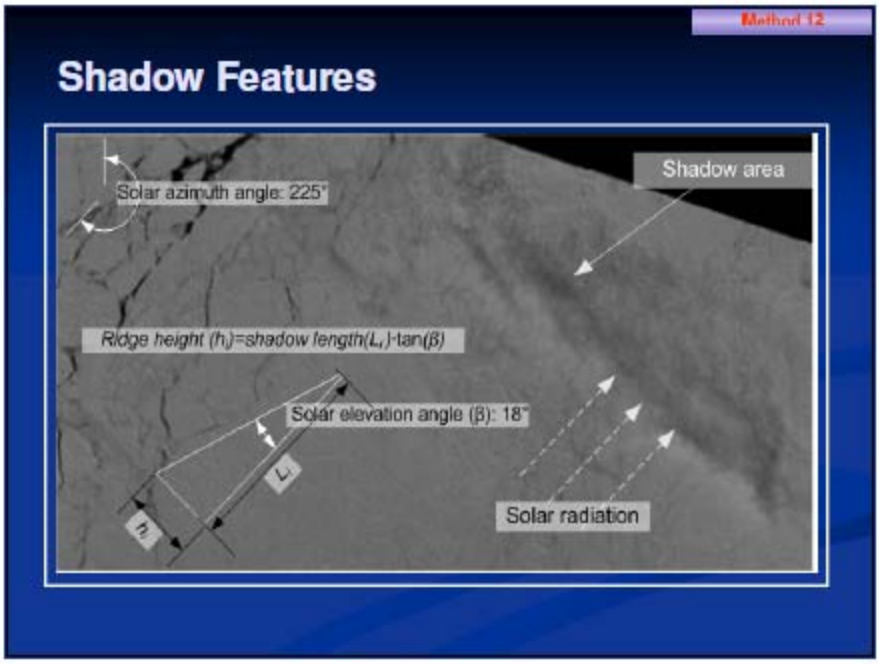


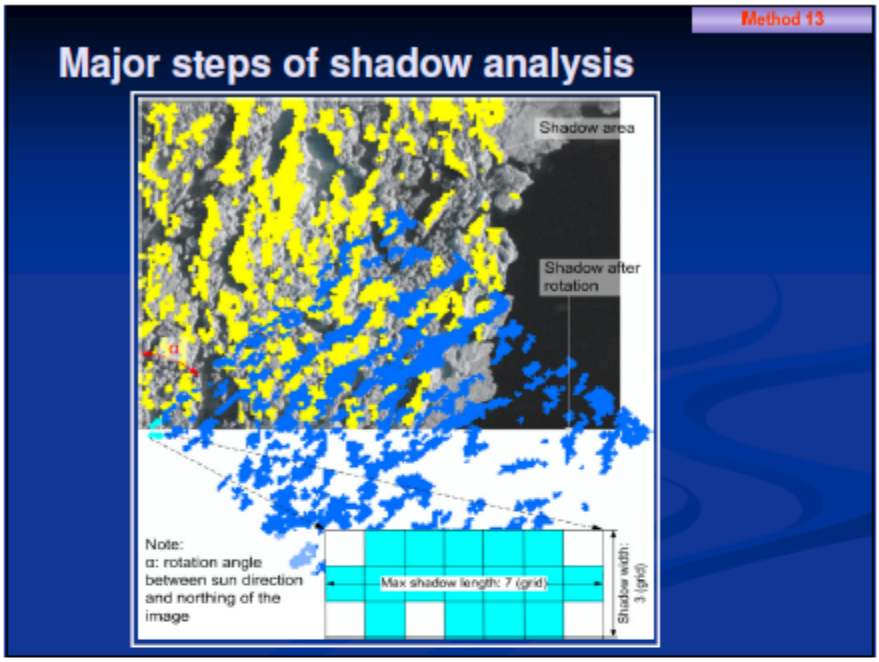
- Difficult to separate 'melt ponds' from 'dark ice';
- Melt pond should not be adjacent to water or submerged ice;
- Vector operation, good match for image segmentation;
- Still time consuming (14 h).

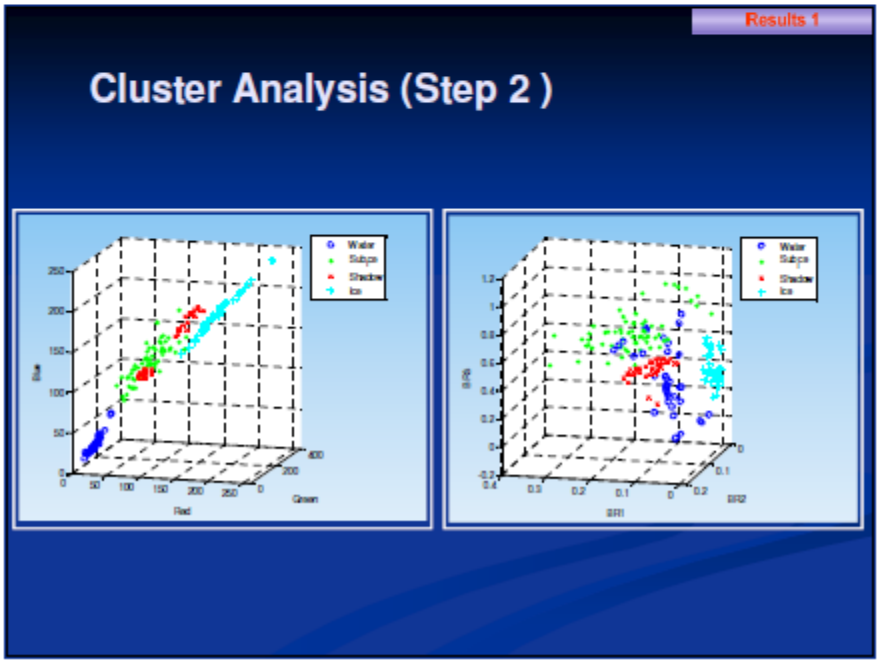
```
# Create a search cursor using an SQL expression
sel_src_ID=[] # Create an empty list to take all detected OBJECTID in f2

expression = "(src_CLASS=2 AND nbr_CLASS=1 AND Ratio > 0.00) OR (src_CLASS=2 AND nbr_CLASS=3 AND Ratio > 0.05)"
    # Melt pond should not be adjacent to water or submerged ice
with arcpy.da.SearchCursor(f5, ("src_OBJECTID","src_CLASS", "nbr_CLASS", "Ratio"), where_clause=expression) as cursor:
    for row in cursor:
        sel_src_ID.append(row[0])
```


Method 11
Aerial photo processing & classification
Original aerial photo of sea ice
Step 1 Object-based image segmentation
Step 2 Random Forest Ensemble Classification
Step 3 Polygon Neighbors Analysis
An 'object'
The object classified as submerged ice
Relabeled as melt pond based on neighboring criteria
CLASS
1 Water
2 Submerged ice
3 Shadow
4 Ice/Snow
5 Melt pond

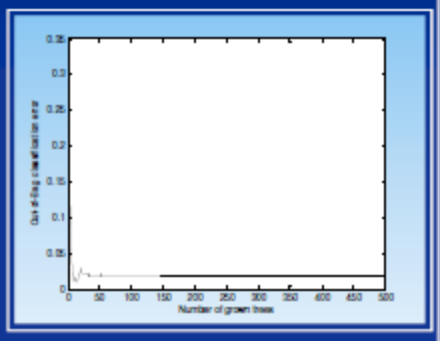

Method 12
Shadow Features
Solar azimuth angle: 225°
Shadow area
Ridge height (h)=shadow length(L)·tan(β)
Solar elevation angle (β): 18°
L
h
Solar radiation

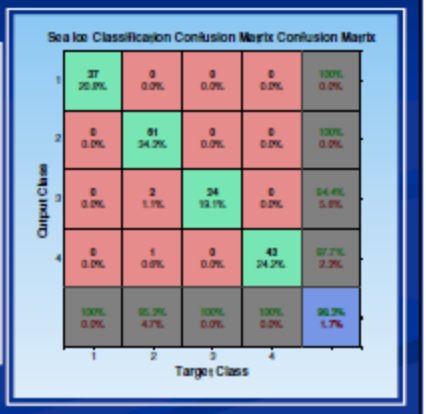

Method 13
Major steps of shadow analysis
Shadow area
Shadow after rotation
α
Note:
α: rotation angle between sun direction and northing of the image
Max shadow length: 7 (grid)
Shadow width: 3 (grid)


Results 1
Cluster Analysis (Step 2)
Water
Subpix
Shadow
Ice
Red
Green
Blue
BR1
BR2

Results 2

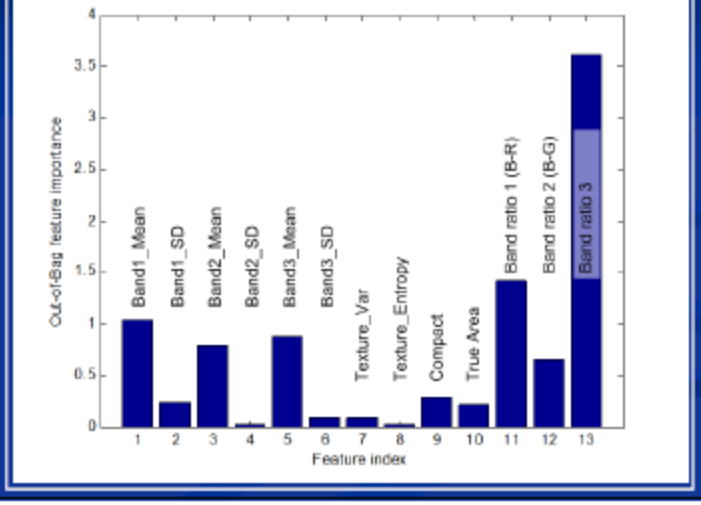
Classification (Step 2) Accuracy

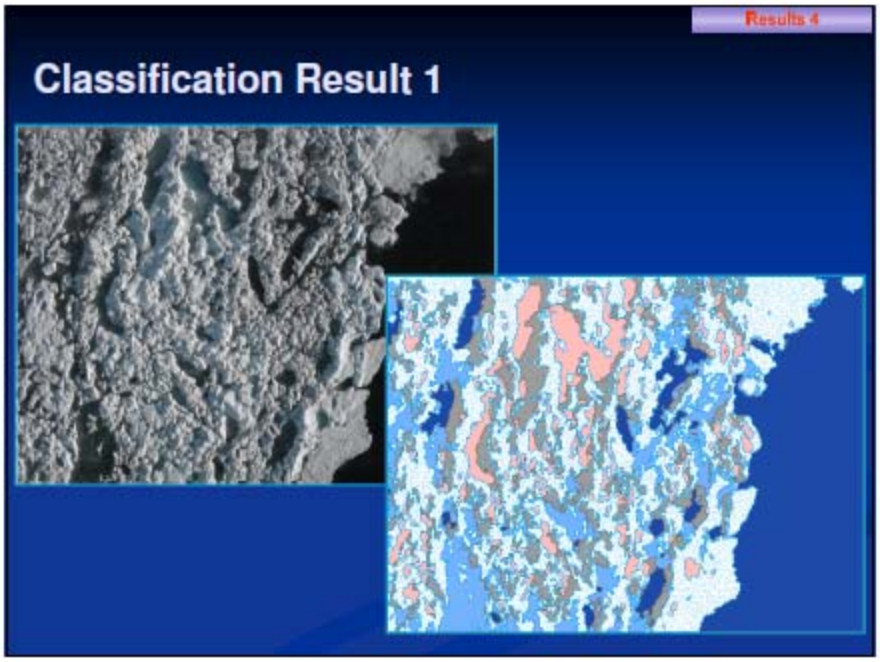


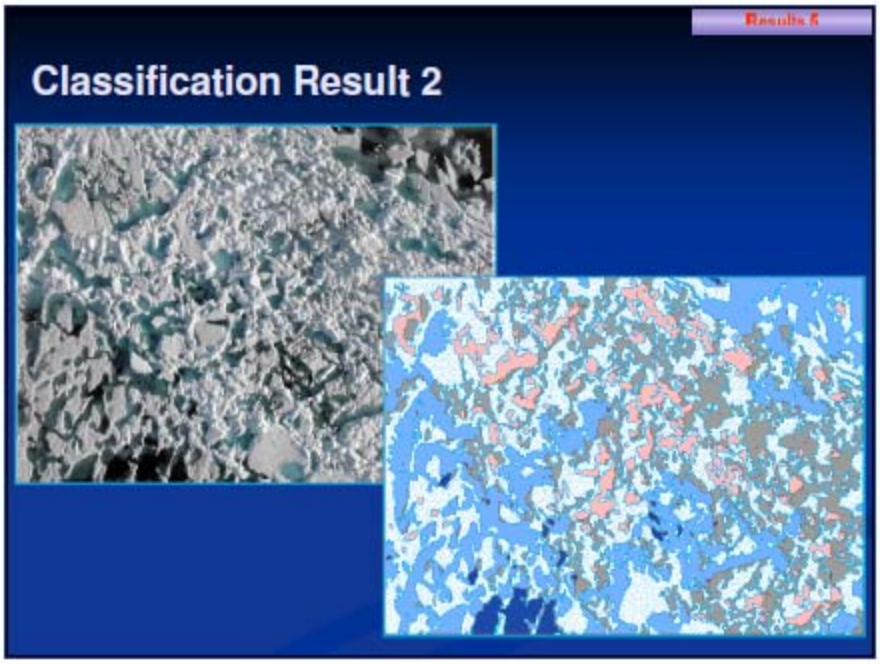


Results 3

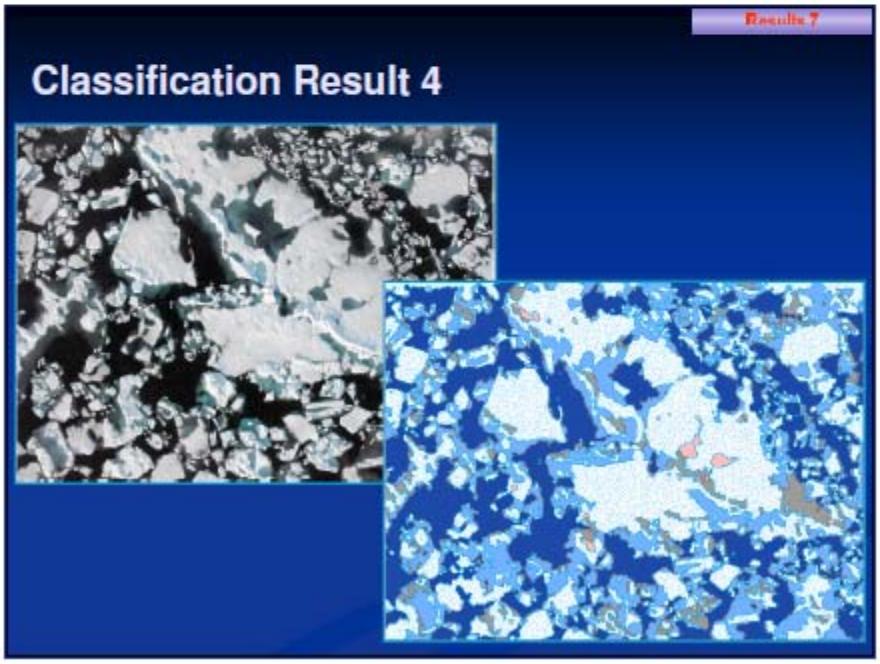
Feature Importance




Results 4
Classification Result 1


Results 5
Classification Result 2


Results 6
Classification Result 3


Results 7
Classification Result 4

Results 9

Derivable Sea Ice Physical Properties

#	Name	Description
1	Ice concentration	Fraction of ice-cover in a given area
2	Ice edge	Boundary between an area of ice and open ocean
3	Floe size distribution	Probability Density Function of ice floe diameters (or areas)
4	Melt pond distribution	Probability Density Function of melt pool diameters(or areas)
5	Fresh water of melt ponds	Product of the areas and depths of melt ponds
5	Lateral melting	Melt rate of ice at the edges of ice floes
6	Surface roughness	Probability Density Function of the elevation of ice above level ice
7	Ridge height	Height of the (usually) linear features above the surrounding level or undeformed ice
8	Fractional heat transferring into the ocean	Cumulative fraction of solar heat incident on ice/snow, submerged ice, melt ponds, and open water, weighted by the area and transmittance of each component

Conclusion 1

Conclusions

- Object-based classification is an efficient and accurate strategy to classify sea ice.
- Random forest can largely increase classification accuracy.
- Polygon neighbor analysis can extract spatial relationship between objects, providing further information to separate submerged ice and melt ponds.
- Sea ice roughness can be derived automatically from shadow.
- Errors often happen when a mixture of shadow, submerged ice and melt ponds.

California Pesticide Use Reporting and Mapping Tool

David Healy
Stone Environmental Inc.

Abstract

The Stone has developed a Web Mapping Tool that uses California Pesticide Use Reporting database data maintained by the California Department of Pesticide regulation. This rich database application contains 11 years of pesticide use (2000-2010) data on 1,278 chemicals on 280 crop uses for every section (640 acres) where a chemical is used. The data is collected by counties and then aggregated by the state. To help automate and facilitate its use, Stone created a FLEX-based ArcGIS Server application to present and visualize the data. We will demonstrate the application's functionality during this session. Key elements of the application visual animation of pesticide use over time using year slider; using the dynamic legend, click on section for bar chart of 11 year history; optimized responsiveness; options for filter (chemical, units, sites, and year). The tool allows the user to get a good understanding of the historic use and amount and their locations. This tool allows easy understanding of where there may be environmental issues related to chemical use.



California Pesticide Use Reporting and Mapping Tool

Presented by:
David J. Healy
National Environmental Monitoring Conference
San Antonio, Texas
August 6, 2013

Stone Environmental Inc

Background

- EPA Pesticide Registration Requires Pesticide Risk Assessment Studies:
  - Need to know where chemicals are used to conduct study.
- California Pesticide Use Reporting Database (CA PUR)
  - Historic Use for over 1,200 chemicals on 280 different applications.by section geography.
- Very Difficult to Use
  - The CA PUR "csv" file for 11 years of data exceeded 5 GB of reported usage.
- Historically we had developed a number of data extraction tools to accomplish this task.

Motivation for CA PUR Mapping Tool

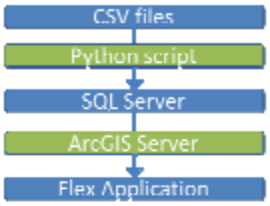
- Need for quick visual understanding of enormous quantity and unusable reporting data
- Need for a simple data extraction tool by sub-geography
- Need to easily target a usage and chemical risk study

Objectives for CA PUR Web Mapping Tool

- Make it easy to use
- Ability to visualize usage by chemical by use
- Summarize by variety of geography
  - Watershed, county, or sections
  - Define use types of interest
- Simplify effort to conduct risk analyses

Development Steps

- Transform the data from the CSV files to a SQL Server database by developing a Python script.
- SQL Server was chosen for its large data storage and indexing capabilities
- After a several weeks of processing, the data took up almost 20 million rows.
- Ready to be used by our skilled team of modelers to make ad hoc queries without having to process multiple years of text files.

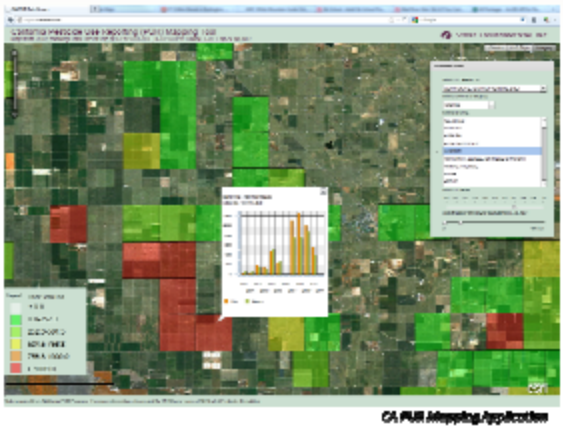


Application Development

- Each record is now tied to a specific geography (Township, Range, and Section)
- ArcGIS Server FLEX application was developed.
- After running SQL commands to summarize the data by geography, it was published to the internet via an ArcGIS Server map service.

Demonstration

- http://capur.stone-env.net/extract/CAPUR_Viewer.html



CA PUR Mapping Application

Thank You!

- Data Viewer is Free
- Data Extraction Feature Requires a Subscription
- Questions and Comments

- For Additional Information:

dhealy@stone-env.com
David J. Healy | Vice President | Applied Information Management | Stone Environmental Inc.
535 Stone Cutters Way, Montpelier, Vermont 05602
802.229.1879 office 978.761.8409 mobile
www.stone-env.com/aim

SECTION 9

SPOTLIGHT ON METHOD 8270 INSTRUMENTATION

Agilent GC/MS Hardware, Software, and Consumables Optimized for the Analysis of US EPA Method 8270

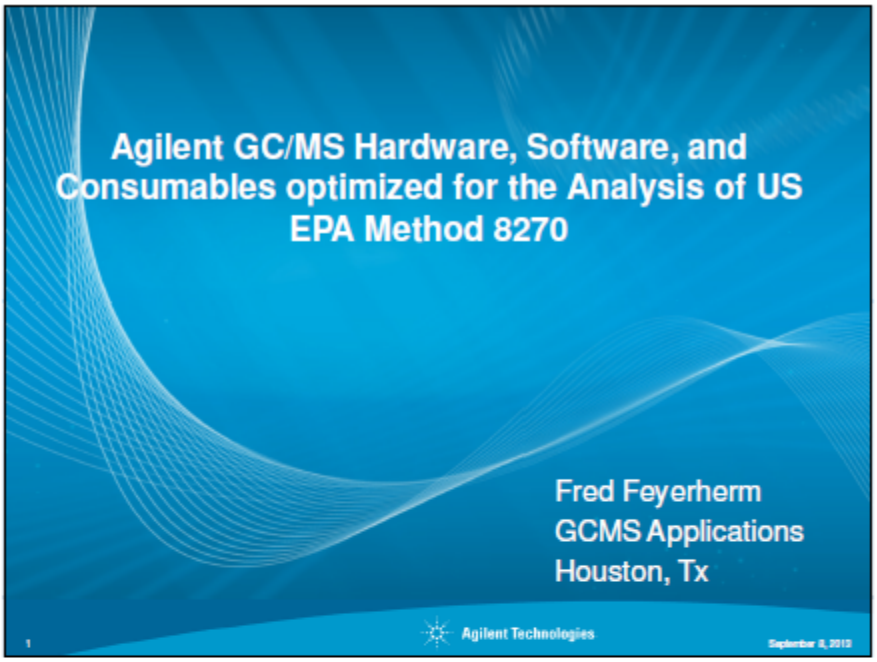
Fred Feyerherm
GCMS Applications

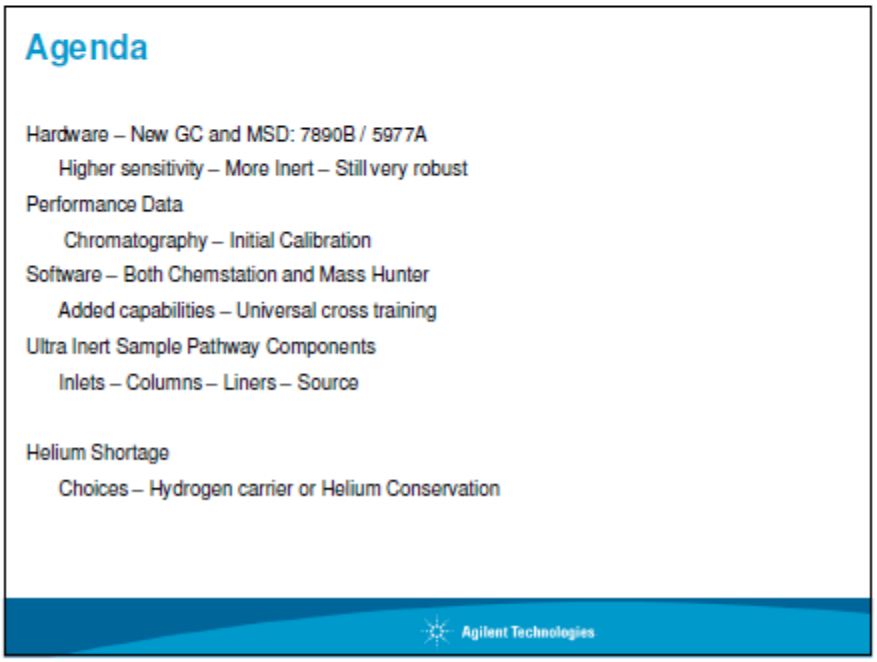
Abstract

This presentation will focus on the Agilent GC/MS system for the analysis of US EPA Method 8270. US EPA Method 8270 is used to determine the concentration of semi volatile organic compounds in extracts prepared from a variety of matrices that include: solids, soil, air, and wastewaters. This presentation will provide details on performance metrics such as detection limits, sample to sample cycle time, and calibration range. Discussion will include DFTPP tuning and tune stability.

Tips and tricks will be offered for analysis of “very dirty” extracts. A software demonstration will be shown on data analysis and reporting.

The topic of helium conservation and the use of alternative carrier gases such as hydrogen will also be covered.


Agilent GC/MS Hardware, Software, and Consumables optimized for the Analysis of US EPA Method 8270
Fred Feyerherm
GCMS Applications
Houston, Tx
Agilent Technologies
1
September 8, 2013


Agenda
Hardware – New GC and MSD: 7890B / 5977A
Higher sensitivity – More Inert – Still very robust
Performance Data
Chromatography – Initial Calibration
Software – Both Chemstation and Mass Hunter
Added capabilities – Universal cross training
Ultra Inert Sample Pathway Components
Inlets – Columns – Liners – Source
Helium Shortage
Choices – Hydrogen carrier or Helium Conservation
Agilent Technologies

7890B / 5977A GCMS

Ultimetal Inert Inlets
Helium Conservation Mode
Easy Switch to H2 Carrier



New Pumps
Extractor Source
Low Energy Sleep Mode
Low Femtogram Detection Limits

Agilent Technologies

3

New Extractor Ion Source for 5977



Increase in ion count
- ✓ True increase in sensitivity

Better trace level precision
- ✓ Lower IDL and MDL

Agilent Technologies

Page 4

Performance Data: Many Different 8270 Methods

Different compound lists

Different calibration ranges

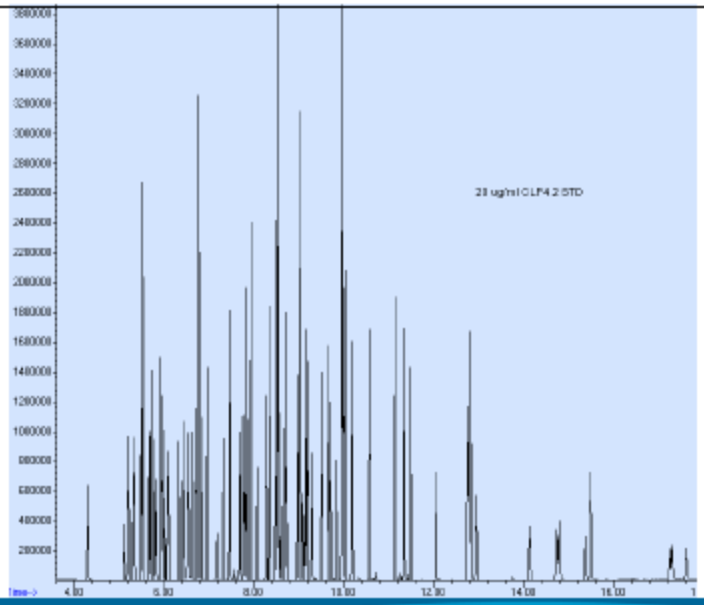
For example: High 2 – 100 ug/ml

Low 0.1 – 10 ug/ml

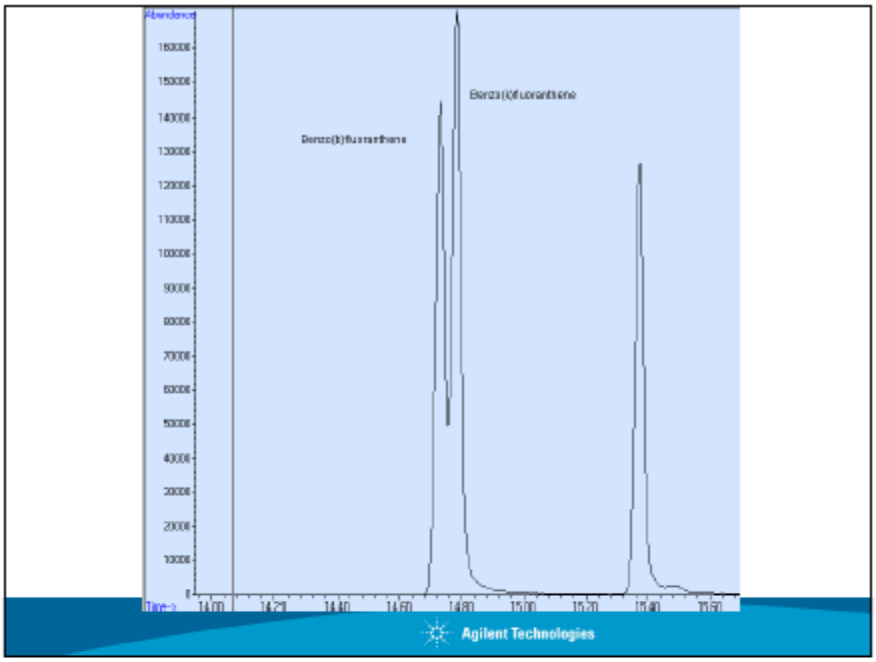
Different reporting limits

Data shown is from EPA Region 6 Lab in Houston

Agilent Technologies



Agilent Technologies



Performance Data – most critical: ical & Perf Eval

Compound	100	80	50	20	10	5	2	Avg	%RSD
1) I 1,4-Dichlorobenzen...	ISTD								
2) SEP 2-Fluorophenol...	1.013	1.001	0.994	0.990	1.000	1.013	0.983	1.000	1.04
3) SEP Phenol-d5 (Surr2)	1.237	1.221	1.231	1.247	1.225	1.235	1.233	1.233	0.68
4) MCP Phenol	1.275	1.288	1.289	1.301	1.304	1.310	1.315	1.297	1.09
5) SEP 2-Chlorophenol...	1.170	1.161	1.168	1.177	1.177	1.172	1.169	1.172	0.53
6) TCP bis(2-Chloroet...	1.071	1.081	1.077	1.088	1.089	1.084	1.111	1.086	1.16
7) MCP 2-Chlorophenol	1.208	1.219	1.213	1.216	1.209	1.222	1.223	1.215	0.65
8) TCP 1,3-Dichlorobe...	1.399	1.417	1.412	1.419	1.407	1.439	1.447	1.420	1.22
9) MCP 1,4-Dichlorobe...	1.406	1.427	1.429	1.448	1.453	1.462	1.472	1.440	1.42
10) TCP Benzyl Alcohol	0.900	0.905	0.908	0.873	0.852	0.838	0.834	0.872	3.40
11) SEP 1,2-Dichlorobe...	0.832	0.844	0.842	0.861	0.861	0.875	0.893	0.858	2.45
12) TCP 1,2-Dichlorobe...	1.326	1.353	1.366	1.369	1.376	1.385	1.398	1.368	1.70
13) TCP 2-Methylphenol	0.959	0.972	0.975	1.000	0.988	0.972	1.000	0.981	1.60
14) TCP bis(2-Chlorois...	1.110	1.153	1.174	1.209	1.203	1.219	1.266	1.191	4.23
15) TCP Acetophenone	1.539	1.535	1.561	1.577	1.556	1.569	1.618	1.562	1.89
16) TCP 3-&/or 4-Methy...	1.284	1.293	1.287	1.310	1.287	1.301	1.299	1.294	0.73
17) MCP N-Nitroso-di-p...	0.748	0.759	0.758	0.769	0.754	0.754	0.781	0.761	1.46
18) TCP Hexachloroethane	0.487	0.505	0.505	0.502	0.501	0.512	0.518	0.504	1.91
19) I Naphthalene-d8 (IS...	ISTD								
20) SEP Nitrobenzene-d5...	0.294	0.297	0.297	0.298	0.305	0.303	0.307	0.300	1.60
21) TCP Nitrobenzene	0.299	0.304	0.308	0.307	0.317	0.317	0.319	0.310	2.48
22) TCP Isophorone	0.548	0.547	0.543	0.541	0.549	0.547	0.556	0.547	0.93
23) TCP 2-Nitrophenol	0.177	0.182	0.180	0.174	0.171	0.165	0.154	0.172	5.78
24) TCP 2,4-Dimethylph...	0.265	0.268	0.266	0.255	0.260	0.264	0.264	0.263	1.58
25) TCP bis(2-Chloroet...	0.354	0.357	0.358	0.359	0.361	0.365	0.368	0.360	1.34
26) TCP Benzoic Acid	0.165	0.193	0.178	0.144	0.097	0.060	0.082	0.124	50.018
27) TCP 2,4-Dichloroph...	0.292	0.293	0.290	0.284	0.282	0.276	0.268	0.283	3.20
28) MCP 1,2,4-Trichlor...	0.333	0.336	0.337	0.333	0.341	0.348	0.342	0.337	1.13
29) TCP Naphthalene	0.908	0.919	0.928	0.938	0.954	0.972	0.987	0.943	3.23
30) TCP 4-Chloroaniline	0.374	0.376	0.374	0.369	0.359	0.347	0.334	0.357	7.23
31) TCP Hexachlorobuta0...	0.210	0.211	0.210	0.207	0.210	0.212	0.213	0.211	0.89
32) TCP Caprolactam	0.068	0.068	0.079	0.076	0.073	0.069	0.065	0.071	7.15
33) MCP 4-Chloro-3-met...	0.260	0.258	0.254	0.248	0.241	0.235	0.235	0.247	4.26
34) TCP 2-Methylnaphth...	0.556	0.562	0.564	0.560	0.565	0.565	0.585	0.565	1.68

Agilent Technologies

Software – Both Chemstation and Mass Hunter

Chemstation - Enviroquant

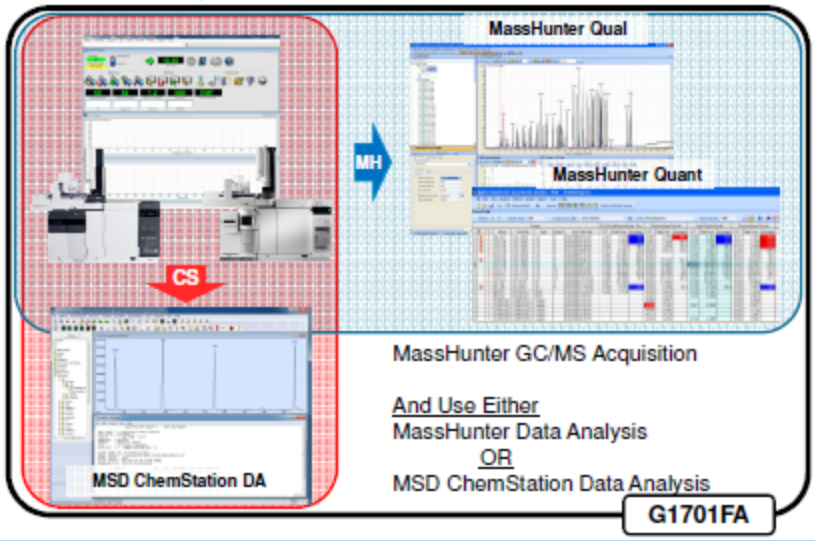
- Classical tools for analysis and reporting

Mass Hunter

- New platform with new capabilities
- Batch mode calibration tools
- All Agilent MS platforms (GCMS, GC-QQQ, LCMS, ICP-MS)

Agilent Technologies

GC/MSD Software



MassHunter GC/MS Acquisition

And Use Either
MassHunter Data Analysis
OR
MSD ChemStation Data Analysis

G1701FA

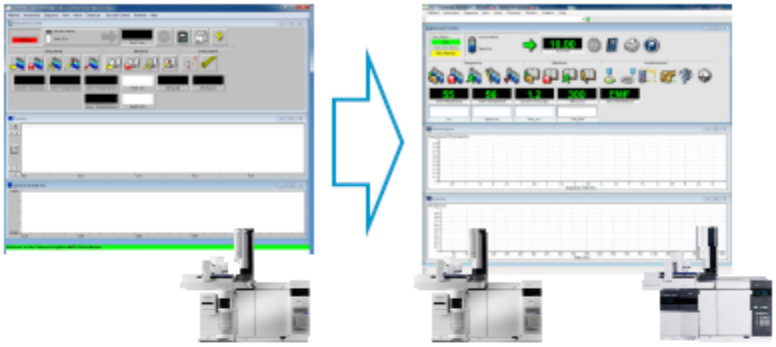
10

Agilent Technologies

GC/MSD Acquisition Methods

MSD Productivity ChemStation

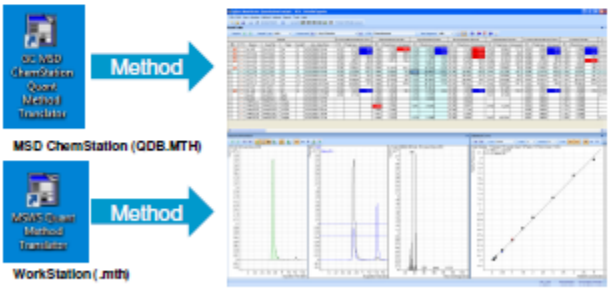
MassHunter GC/MS Acquisition



GC/MS Acquisition Methods are Transparent
from MSD ChemStation to MassHunter GC/MS (Except PAL Autosampler)

Migrate Quantitative Methods to MassHunter Format

MassHunter Quant



Agilent Inert Flow Path Solution



Inert Flow Path Split/Splitless Inlet

UltiMetal Plus treatment creates inert surface 7890 inlet weldment & shell

- Limit adsorption / degradation active analytes in contact with hot metal
- Target trace GC/MS active compound analysis
- Combine with Agilent's UI Liners, UI gold seals, UI GC columns



UltiMetal Plus surface treatment

Helium Shortage Issue

What can we do?

- There are only two realistic choices:
  - Switch to a different carrier gas such as Hydrogen
  - Implement Helium conservation measures

Agilent Technologies

Hydrogen Carrier – brief summary

Agilent has advised H2 carrier for 8270 for over 15 years

Mainly for faster runs and better GC resolution

Easy to convert with a little guidance

Use a 20m x 0.18 column with 0.5 ml/min flow

Set inlet temp to 230C (avoids HCl formation with MeCl2)

EPA Region 8 in Golden, Co has been using H2 for over a year

Both for VOA's and 8270

But methods have to be re-validated – new RT's

Agilent Technologies

New Approach: Helium Conservation

While the GC is just sitting there, it is blowing gas out the vents 24/7

- Minimum flow is about 25 ml/min per S/SL inlet
- 1440 min/day x 25ml = 36,000 ml/day = 36 liters/day per inlet

If the GC is idle, you can switch to a cheaper standby gas such as nitrogen

- Helium cost is 17 cents per cubic foot, N2 is 0.03 cents per cubic foot (prices vary by area)
- Cheapest source of N2 is liquid LN2 dewars

Nitrogen Switching

- Manual valve (any GC)
- Electronic valve (5890, 6890, 7890)
- Fully Automatic EPC (7890B option) (7890A in July)

Agilent Technologies

Helium Conservation Tools

Helium Conservation

- Smarter helium use with new hardware/software tools
- No need to revalidate existing GCMS methods
  - RT's are the same
  - Performance is the same

Agilent Technologies

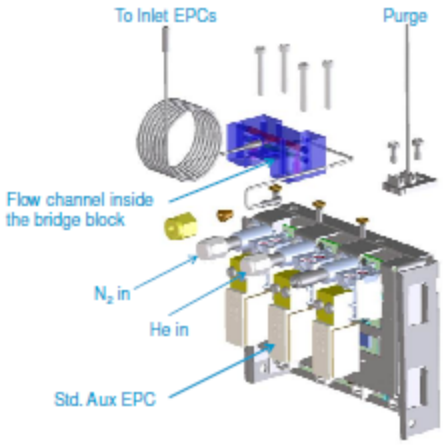
Reducing Helium Use With Conservation

New 7890B Helium Conservation Module

- Automatically switches carrier gas supply to N_2 Standby during idle time
- Integrates into the new 7890B Sleep and Wake function
- Combined with Helium Gas Saver to ***GREATLY*** reduce helium consumption

Helium Conservation Module

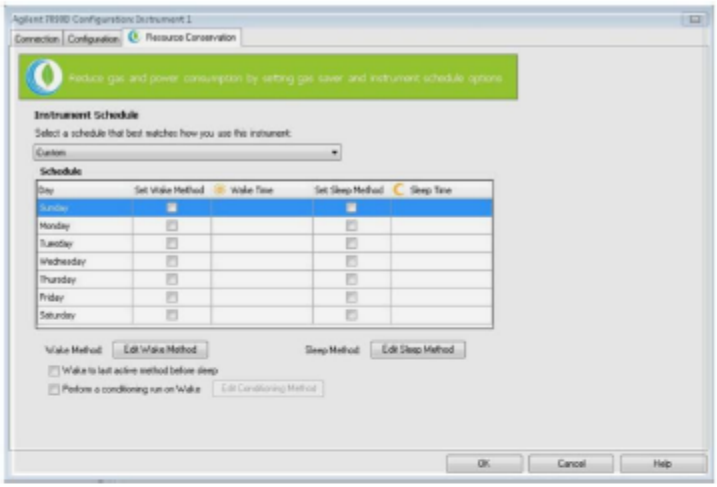
Seamlessly integrated onto 7890 GC hardware and software



- Based on EPC module
- Fully controlled by Agilent data systems
- Precise pressure control between tank and GC
- Switch between gases within 2-5 min depending on flow setting

How It Works: Configuring Sleep/Wake Operation

Simple, Straight Forward Setup



Future Developments

Self-cleaning ion source

Improved PAH peak shape at 1.0 picogram levels

Micro-extraction with LVI

Acknowledgements

David Spencer, Diane Gregg	EPA Region 6 Houston, Tx
Vince Marti	EPA Region 8 Golden, Co

Call or email me for specific guidelines:

Fred Feyerherm

- fred_feyerherm@agilent.com
- 713-392-8493 cell

Agilent Technologies

Meeting Requirements for USEPA Method 8270 Using a Highly Sensitive, Robust, and Easy-to-Use GC/MS

Ed George
Bruker

Abstract

USEPA Method 8270 has been used to analyze a variety of complex sample matrices using full scan GC/MS. The method also allows selected ion monitoring (SIM), for significantly lower detection limits. Mixed mode scan methods, such as SIM/Scan, have the benefits of lowering detection limits and simultaneously providing full scan data for library search confirmation.

Lower detection limits require a very inert pathway from the injection point to the ion source. In addition, the ability to easily manage large numbers of SIMs with full scan in mixed mode for acquisition and data handling is critical for efficient method set up and workflow in the laboratory.

The Bruker SCION SQ GC/MS has an inert ion source with revolutionary ion optics for robust operation and can obtain part-per-billion sensitivity even in full scan analysis. In addition, software known as Compound Based Scanning (CBS) makes it easier than ever before to set up, optimize, and maintain complex mixed mode methods. Additional tools such as tune-to-target and custom EPA reporting templates round out a complete solution for USEPA Method 8270.

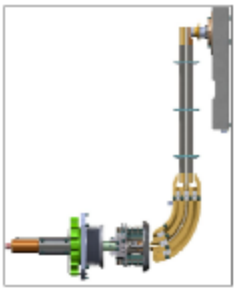

BRUKER
SCION™ GC-MS
A Highly Sensitive, Robust, and Easy-to-Use GC/MS
Spotlight on Method 8270 Instrumentation
NEMC 2013, San Antonio, Texas
Chemical and Applied Markets
Copyright 2012 Bruker Corporation. All Rights Reserved.


Method 8270- The Lab Pain Points
BRUKER
holding times
reporting
Start up costs
productivity
dynamic range
Tune stability
new methods
automation
throughput
sustained sensitivity
Ease of use
downtime
turnover
connectivity
flexibility
sample matrix
Cost of ownership
data review
support
bench space
run time
competition
data integrity
Chemical and Applied Markets
Copyright 2012 Bruker Corporation. All Rights Reserved.

SCION™ SQ Innovations

- Hardware
  - Robust Axial Ion Source- High Productivity, Maximize Uptime
  - Curved Optics with lens-free design- Noise Elimination = High Sensitivity
  - EDR-Extended Dynamic Range- Increased Working Range
  - Large capacity turbo pump – Get up and running fast



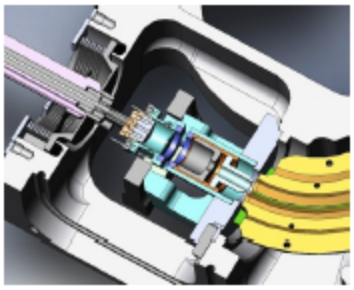


Chemical and Applied Markets

Copyright 2013 Bruker Corporation. All Rights Reserved.

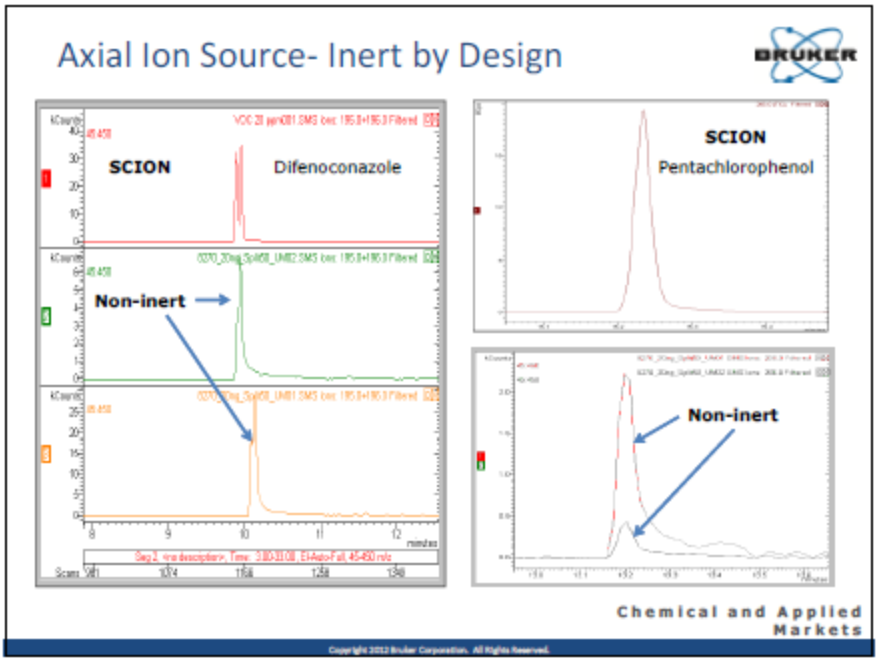
Axial Ion Source- Inert by Design

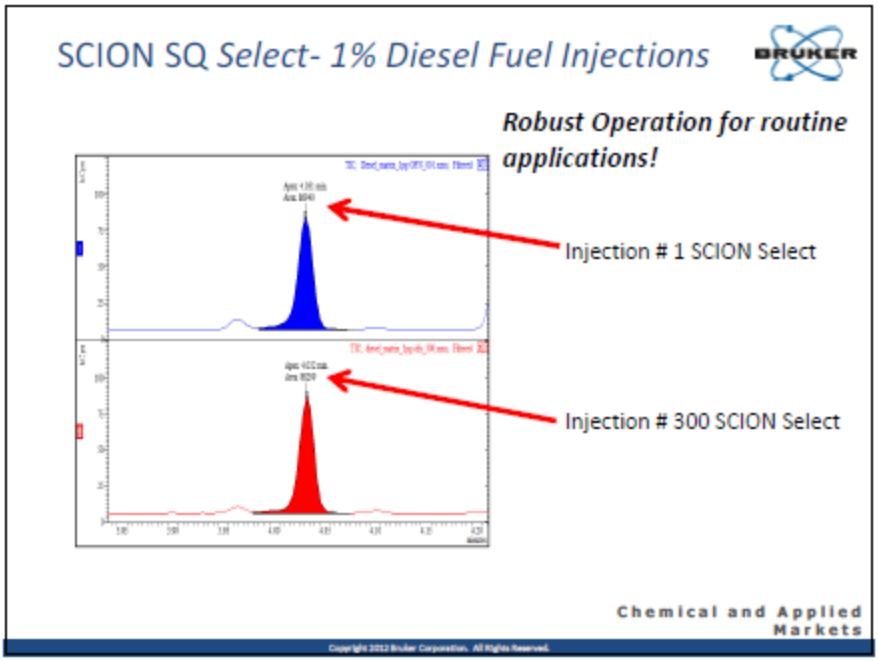
- Laminar flow-through source
- Reduces contact of ions with hot surfaces
- Uniquely designed to *avoid matrix build-up* on ion source parts
- *Dual filaments* for high productivity
- 300L/s pumping capacity



Chemical and Applied Markets

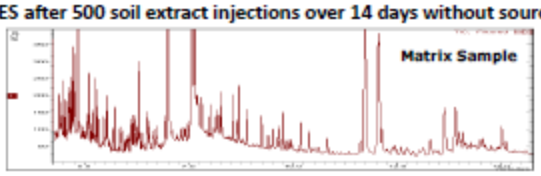
Copyright 2013 Bruker Corporation. All Rights Reserved.

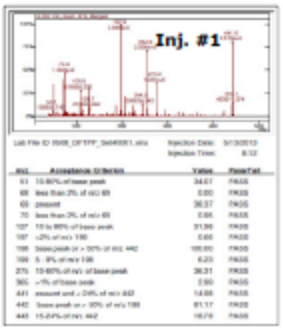

Axial Ion Source- Inert by Design
SCION
Difenoconazole
Non-inert
SCION
Pentachlorophenol
Non-inert
Chemical and Applied Markets

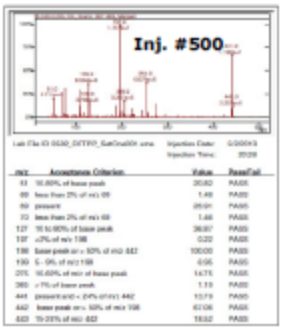

SCION SQ Select- 1% Diesel Fuel Injections
Robust Operation for routine applications!
Injection # 1 SCION Select
Injection # 300 SCION Select
Chemical and Applied Markets

Axial Ion Source- Tune Stability

- **DFTPP PASSES after 500 soil extract injections over 14 days without source cleaning**





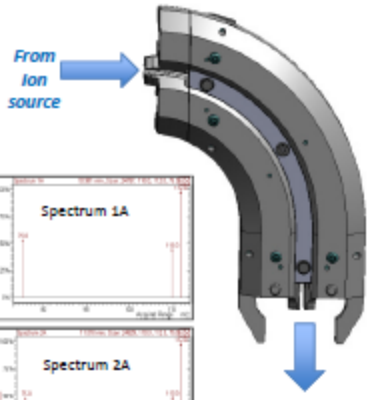


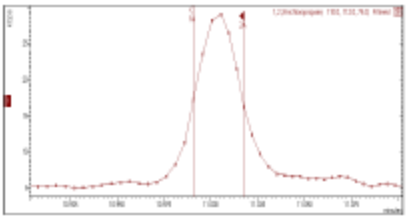
Chemical and Applied Markets

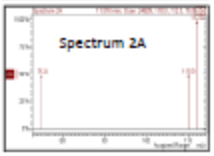
Copyright 2012 Bruker Corporation. All Rights Reserved.

Curved Ion Optics: Extreme FS Sensitivity

- 90 Degree Curved q0
  - Reduces neutral noise for trace level GC/MS analysis
  - Results are– ***higher S/N, excellent library match, and stable ion ratios !***





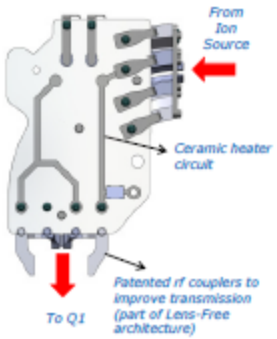


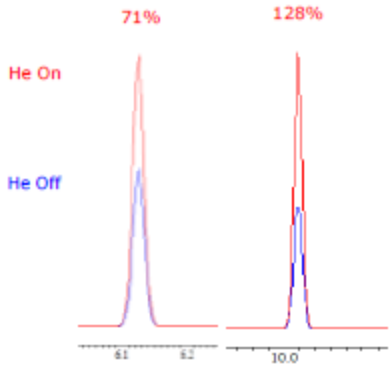
SCION SQ response for 1,2,3-Trichloropropane at 0.03 ppb by Purge and Trap -Ion ratios consistent across the peak.

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Added sensitivity- Active focusing q0 option





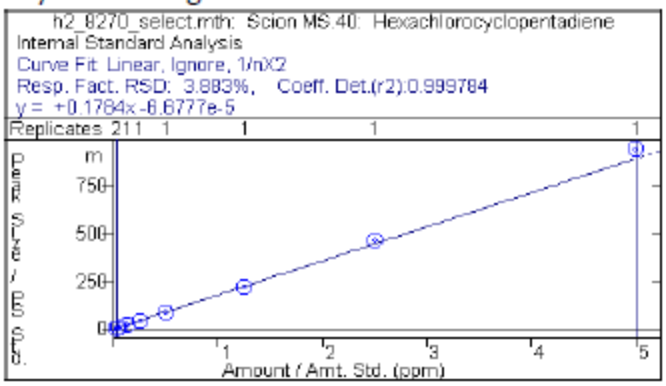
Small amount of He added to sealed q0 slows down ions for better focusing and transmission to the mass filter

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EDR Detection System- Linear Range

- Excellent sensitivity without sacrificing linear dynamic range



Calibration curve 1 to 200 ppm for Hexachlorocyclopentadiene

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EDR Detection System- Quality Spectra

- Avoid detector saturation at high concentrations, get quality spectral library matches



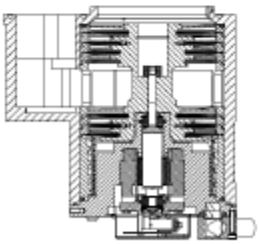
200 ppm calibration standard for 8270 spectrum taken at peak apex

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Best-in-class high-capacity turbo pump

- Enables fast pump-down for *higher productivity*
- CI ready (can handle high gas loads)
- New high-capacity **300/400** **L/s design (*Leybold-Turbovac series*)
  - MTBF is 8yrs

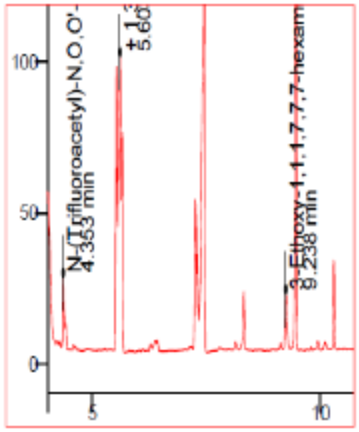


User Benefit: Higher Productivity
Fast Pump-down and CI field-upgradeable

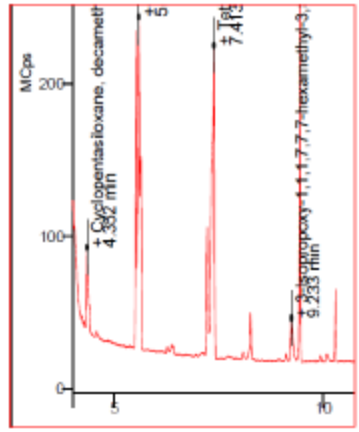
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Fast Pump-down-Ready for use



TIC Before Source Removal



TIC After 25 min Pump Down

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.



Software Innovation

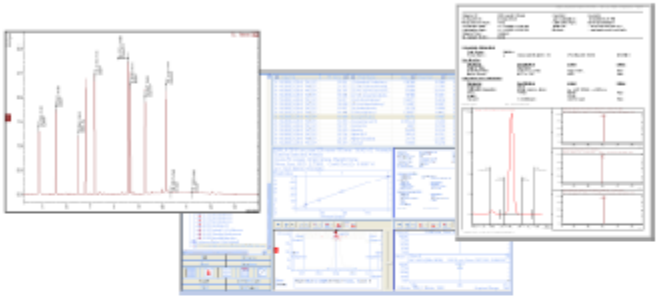
Tuned for Productivity

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

SCION SQ Software innovations

- Software
  - EasySIM™- Covert full scan to SIMs , combine with CBS
  - Compound Based Scanning (CBS)- Easy method development and maintenance
  - EnviroPro™ Reporting Software



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EasySIM™ - Adding SIM to FS Methods

Single ion monitoring SIM is an acquisition mode that greatly increases sensitivity for all or any target components. Changing full scan methods to include mixed mode FS-SIM can be very tedious and time consuming. Many systems require a complete method rebuild. EasySim make this a snap!

- Step 1- Load Existing Full Scan Method File
- Step 2- Select "Convert to SIM/Scan" with EasySIM™
- Step 3- Let CBS fill in your tables with optimized conditions

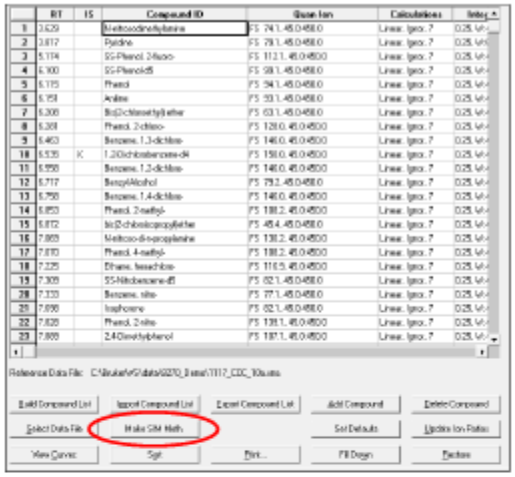
.....Acquisition table and data handling table updated simultaneously
.....SIMs automatically optimized for best sensitivity
.....Simply view the segments and run your sample!

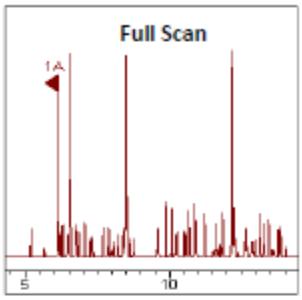
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EasySIM™ + Compound Based Scanning

- From full scan method- Click 'Make SIM Method'



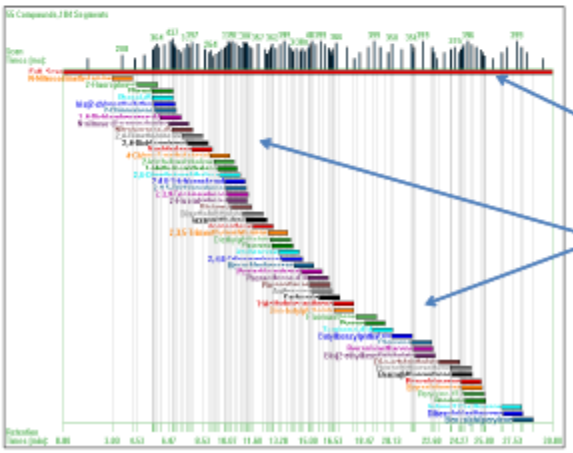


Chemical and Applied Markets

Copyright 2013 Bruker Corporation. All Rights Reserved.

EasySIM™ + Compound Based Scanning

- CBS creates complex SIM/Scan method



Original Full SCAN segment

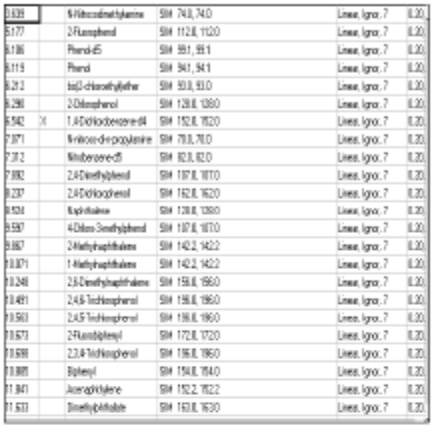
SIM segments added and optimized automatically by CBS

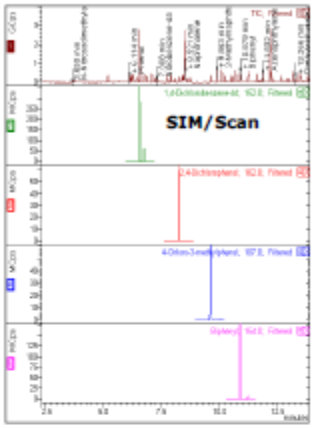
Chemical and Applied Markets

Copyright 2013 Bruker Corporation. All Rights Reserved.

EasySIM™ + Compound Based Scanning

- Data handling and acquisition tables auto-updated
- Simply acquire your SIM/Scan data files!





Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EnviroPro™ - Turning Data into Invoices

- Delivers reports that meet your customer's requirements
- EPA reporting protocols, such as tune check, CLP program, tentatively identified compound (TIC) reports etc.



Chemical and Applied Markets

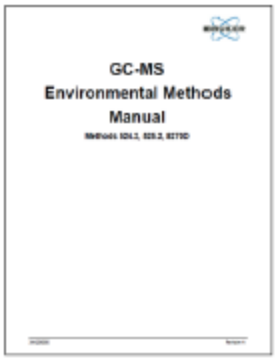
Copyright 2012 Bruker Corporation. All Rights Reserved.

Bruker – Getting you going from the Start

- SCION GC-MS Environmental Methods Manual for USEPA Methods



GC-MS Environmental Manual and Methods CD
The CD contains method and data files for EPA method **524.3**, **525.2** and **8270D**



GC-MS Environmental Manual Only (PDF)

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.



SCION™ GC-MS

Method 8270
Environmental Sample Analysis

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Method 8270 Challenges

- Wide variety of acids, bases, and neutrals
- Strict quality control guidelines
- Market desire for lower reporting limits, even in very dirty matrices
  - Addition of mixed-mode scanning
  - Need for managing large number of SIMs
  - Desire to calibrate and report lower limits in full scan of targets and TICs
  - This challenges inertness of the entire GC/MS system- how can I keep it running longer with minimal maintenance?

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

8270 GC/MS Conditions

Method for semi-volatile compounds in waste water and sludge/sediment samples

Column: BR-5ms, 30 M x 0.25mm x 0.25 um

GC Column Conditons			
Temp	Rate (C/min)	Hold(min)	Total Time(min)
45		3	3
120	30	1	6.5
310	10	5	30.5

MS Full Scan Conditions	
Mass Range:	45-450 da
Scan Time:	200 ms
Resolution:	Unit
Fil. Delay:	2.0 min
Source Temp:	300 C
Trans Line Temp:	280 C

Pulsed-split injection

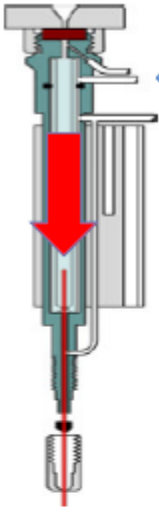
Injector Temp:	250 C
Pressure pulse:	40 psi for 0.25 min
Column flow:	1 ml/min

Desired FS CAL Range: 75 ppb to 30 ppm

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Advantage of Pulsed-Split Injection



High pressure in (40 psi) during injection

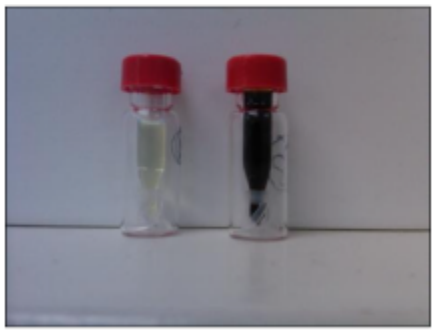
Split flow out

During the pulsed-split injection, the inlet is set to 40 psi with split vent at 70:1. Under this condition, the column flow is near 5 ml/min, allowing rapid transport of analytes to column. The actual split ratio is near 14:1.

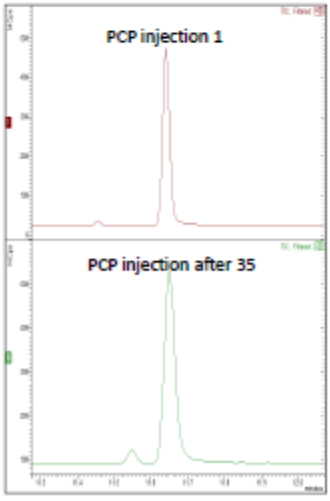
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

8270 Sludge Extract



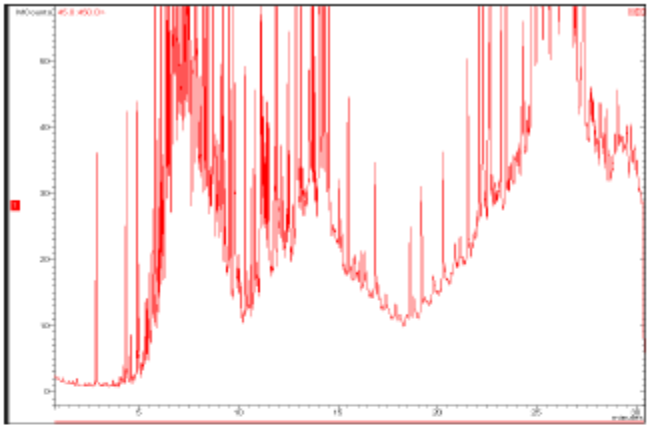
Left- Blank Extract; Right-Sludge Extract



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Heavy Matrix Injections-Soil Extract Full Scan

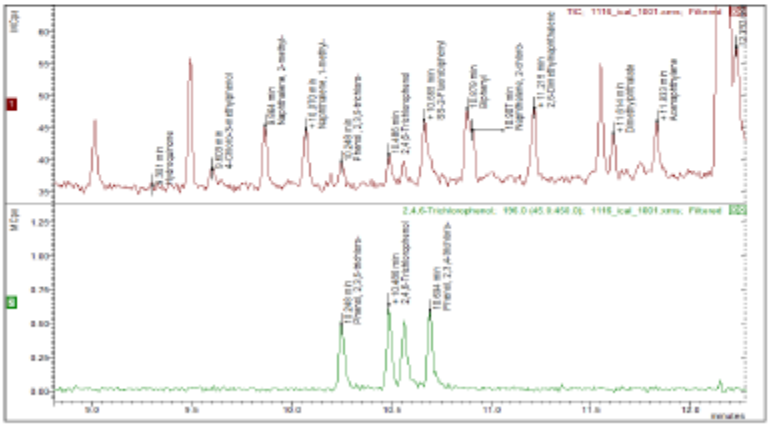


TIC of highly contaminated soil extract from EPA 8270.

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Good Full-scan sensitivity

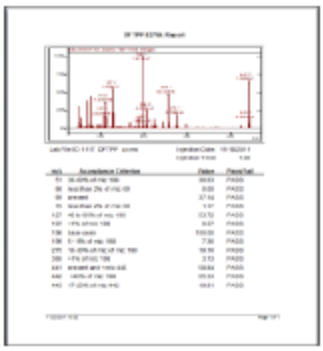


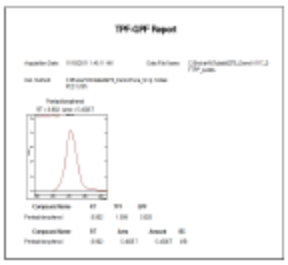
Full Scan of 75 ppb calibration standard (Top) and extracted ion chromatogram (bottom) for the trichlorophenols

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Passing method QC requirements



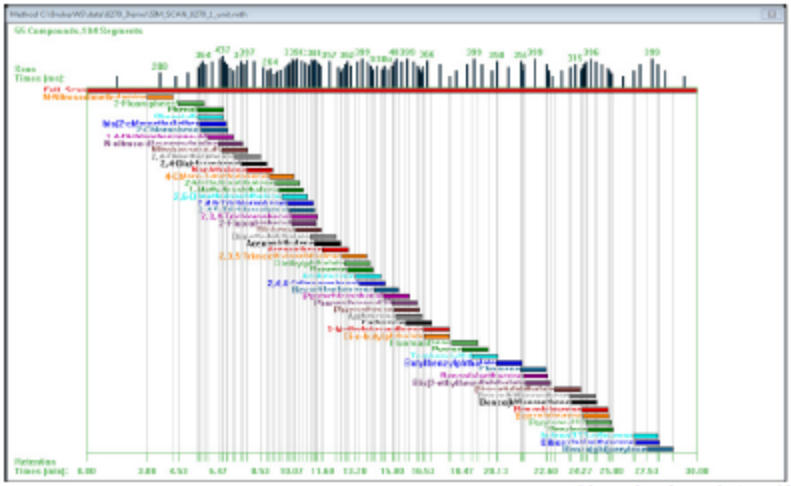


Compound	Method 8270 Criteria (Min RRF)	RRF on SCION SQ Cal Range 0.075-30ppm
N-nitroso-di-n-propylamine	0.05	0.109
Hexachlorocyclopentadiene	0.05	0.138
2,4-Dinitrophenol	0.05	0.149
4-Nitrophenol	0.05	1.03

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

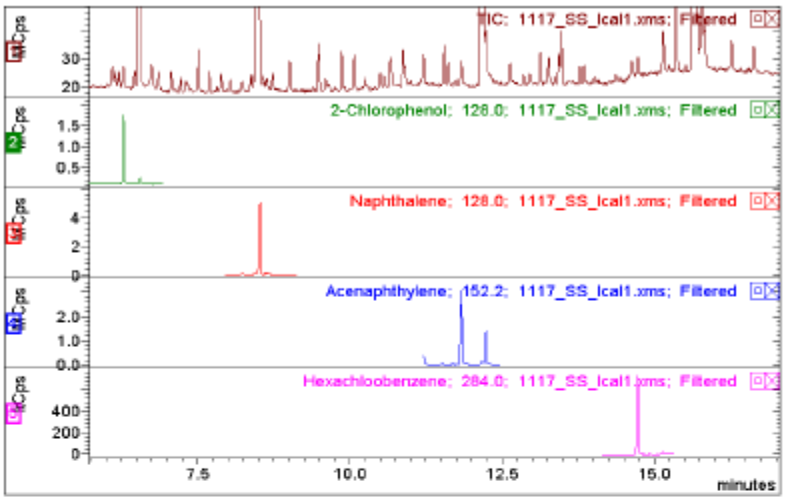
SIM/Scan segments for 55 8270 targets compounds



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

SIM/Scan 75 ppb



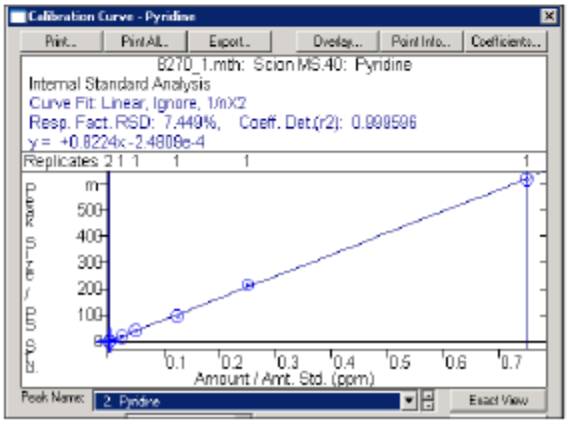
Chemical and Applied Markets

31

Copyright 2012 Bruker Corporation. All Rights Reserved.

Calibration Statistics- Full Scan

Overall Calibration Statistics-100 compounds total:
Average % RSD = 11.62 %
Average Correlation Coefficient =0.9989

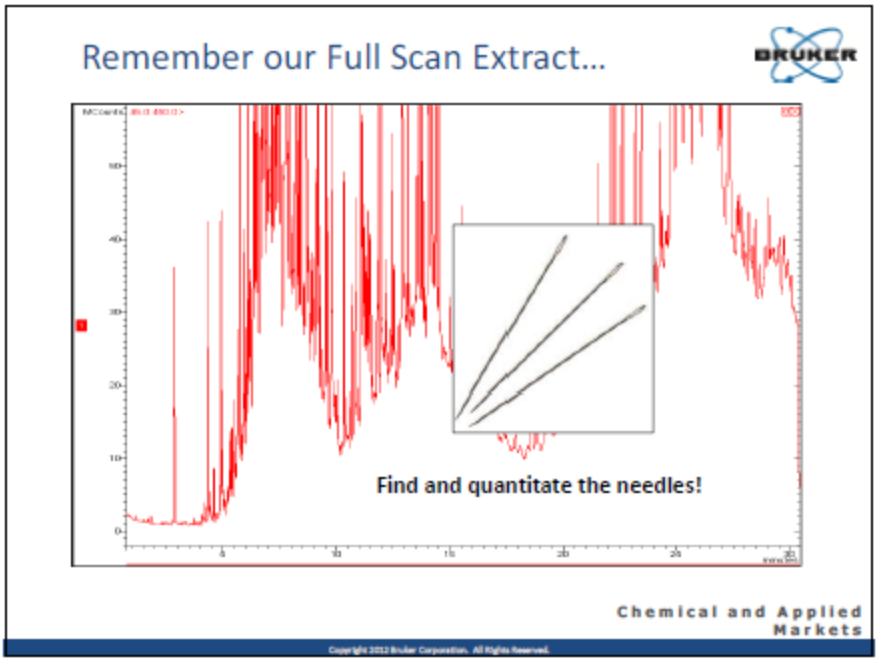


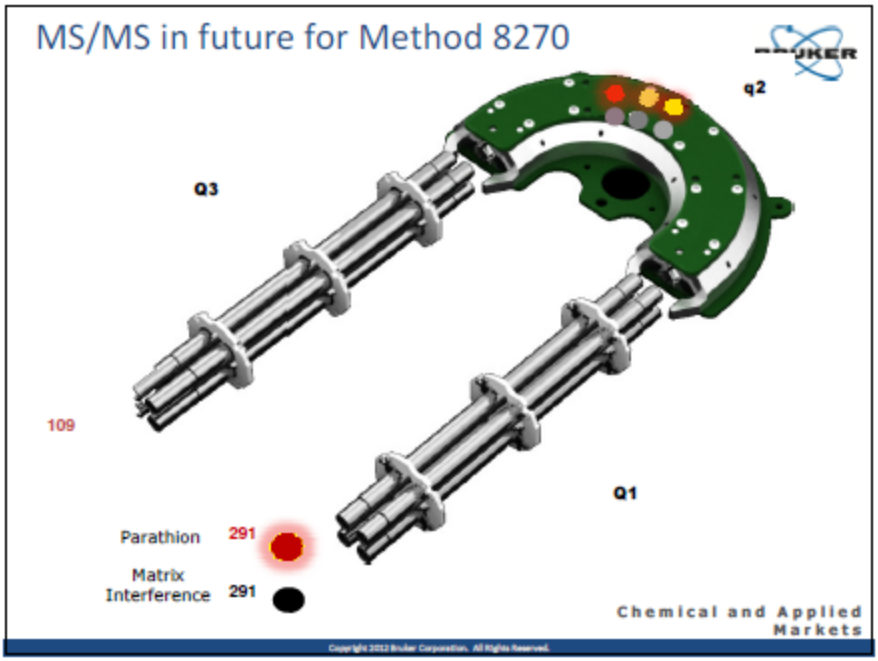
75 ppb-30 ppm Full Scan

Chemical and Applied Markets

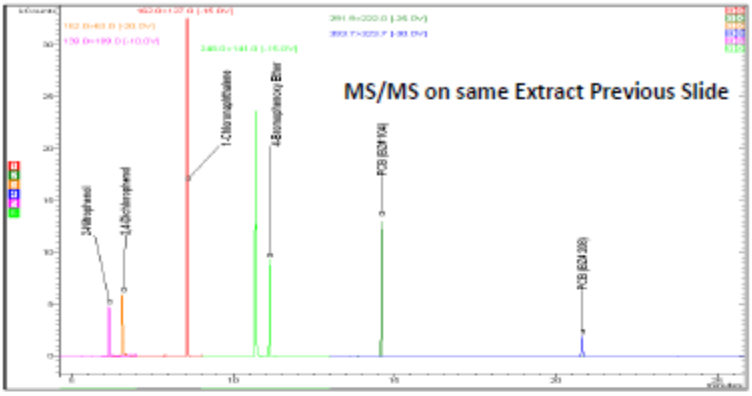
33

Copyright 2012 Bruker Corporation. All Rights Reserved.


Remember our Full Scan Extract…
Find and quantitate the needles!
Chemical and Applied Markets


MS/MS in future for Method 8270
q2
Q3
109
Q1
Parathion 291
Matrix Interference 291
Chemical and Applied Markets

MS/MS for Method 8270

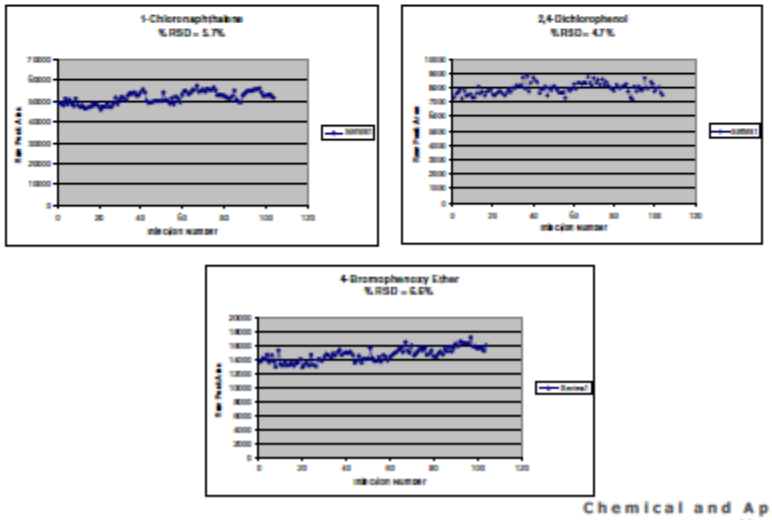


MS/MS on SCION in soil extract, 15-20 pg injected on column – pulsed-split

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

MS/MS Precision Examples: 100 Injections at 100 ppb in Sludge Extract



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

See our Poster- 8270 with Hydrogen



Application Note #1820230

Performance of Method 8270 Using Hydrogen Carrier Gas on Bruker SCION™ GC-MS

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Thank You

www.scionhasarrived.com

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Optimizing EPA Method 8270: PerkinElmer Clarus SQ8 Gas Chromatograph/Mass Spectrometer (GC/MS)… Meeting the Challenges and Optimizing Results and Profitability

Lee Marotta
PerkinElmer

Abstract

This presentation will focus on method performance and criteria of EPA method 8270 using the PerkinElmer Clarus SQ8 GC/MS.

In addition to data from the conventional method, novel approaches to this method will be discussed including reducing sample size, as low as 1mL extraction volume, and meet drinking water detection limits. There are many advantages to using smaller sample volumes, as follows:

- Improve profitability by reducing laboratory operating costs by requiring less extraction solvent (up to 300x less), minimize refrigerator space needs (smaller containers), and requiring less high cost glassware;
- Optimize productivity by reducing sample preparation time improving laboratory efficiency;
- Enhance instrument uptime by injecting smaller amounts of matrix which equates to higher profits (especially for 8270;
- Is much more environmentally friendly!

There are many disadvantages of extracting one liter of sample. Why use 1 liter when 1mL can do the job especially for 8270?

Because of the improvements in technology and improvements in ease of use, the Clarus SQ8 GC/MS can enhance profitability in addition to improving the quality of results.

The NEW

Clarus SQ 8™ GC/MS

PerkinElmer

For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH



Optimizing EPA Method 8270: PerkinElmer Clarus SQ8 Gas Chromatograph/Mass Spectrometer (GC/MS) … Meeting the Challenges and Optimizing Results and Profitability

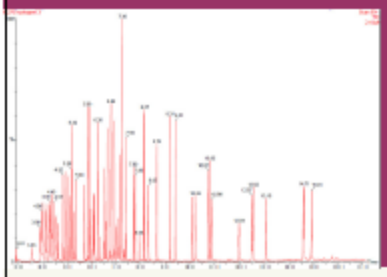
Lee Marotta, Sr Field Application Scientist

© 2013 Perkin Elmer

PerkinElmer

For the Better

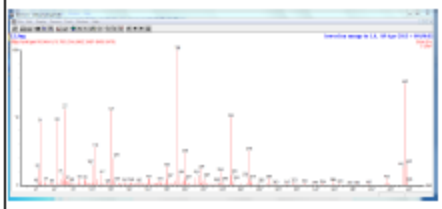
HUMAN HEALTH | ENVIRONMENTAL HEALTH



Hydrogen vs Helium

© 2013 Perkin Elmer

DFTPP in Hydrogen Passes





Passes tuning criteria!

3

Passing Criteria

- All targets quant and qualifying ions were compared in hydrogen versus helium
- All other criteria were met



4

Reducing Sample Amount

PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

Why should we reduce sample amount for analysis?

©2013 Perkin Elmer

Using 1mL instead of 1L sample delivers you more profits…



- **By enhancing productivity**
  - Elimination of concentration step increases throughput
  - Able to use faster methods, such as SPE
- **By reducing costs**
  - Save on expensive extraction solvent required for liquid/liquid extractions
  - Save on precious refrigerator space and glassware
  - Save on disposal costs of recovered solvents
  - Save on shipping costs
- **By increasing instrument uptime**
  - Injecting less sample matrix = cleaner system = more time running samples
- **By delivering better performance**
  - Meeting required detection limits
  - Enhancing recoveries
  - Optimizing dynamic range

… use less solvent … evaporate less solvent into environment … a "greener" analysis

PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

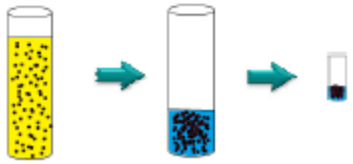
1 mL sample size (or 40mL)

7

© 2013 Perkin Elmer

1 liter liquid/liquid extraction: Disadvantages

- 1.0 liter of sample
- Extract with 300 mL dichloromethane
- Concentrate to 1mL
- Separate Phases
- Inject



- **Disadvantages**
  - High costs (solvent, glassware, shipping)
  - Requires more space
  - Large containers
  - Laborious sample prep
  - Expensive
  - Environmentally unfriendly

Enhance sample prep time and save on laboratory costs!



- 1mL sample volume (or 40mL)
  - Easily meet DL requirement
- Extract with 1mL of DCM
- Separate phases
- Inject organic phase or use SPE
- Inject!

- Advantages:
  - Reduced operating costs
    - Requires less space (smaller containers)
    - Significantly less solvent used
  - Enhanced instrument uptime!
  - Faster sample prep improves lab efficiency
  - GREENER analysis!!!

PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH



Data and Injector Functions

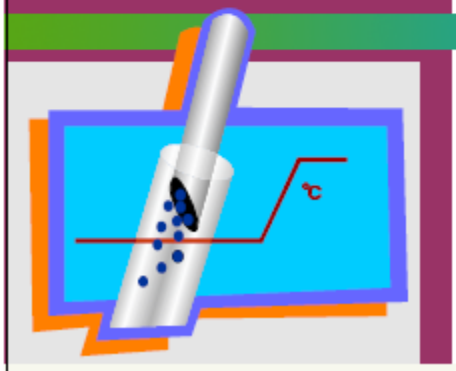
10

© 2013 Perkin Elmer

PAH detection limits using 1mL extraction volume

Injection Volume	Calibration Range	Lowest Conc Analyzed (DL)
1uL Full Scan	0.4 to 200 ppb	0.4 ppb
1uL SIM	0.2 to 200 ppb	0.2 ppb
5uL Full Scan	0.2 to 50 ppb	0.2 ppb
5uL Sim	0.06 to 50 ppb	0.06 ppb
10 uL Full Scan	0.08 to 50 ppb	0.08 ppb
50 uL Full Scan	0.02 to 50 ppb	0.02 ppb

11



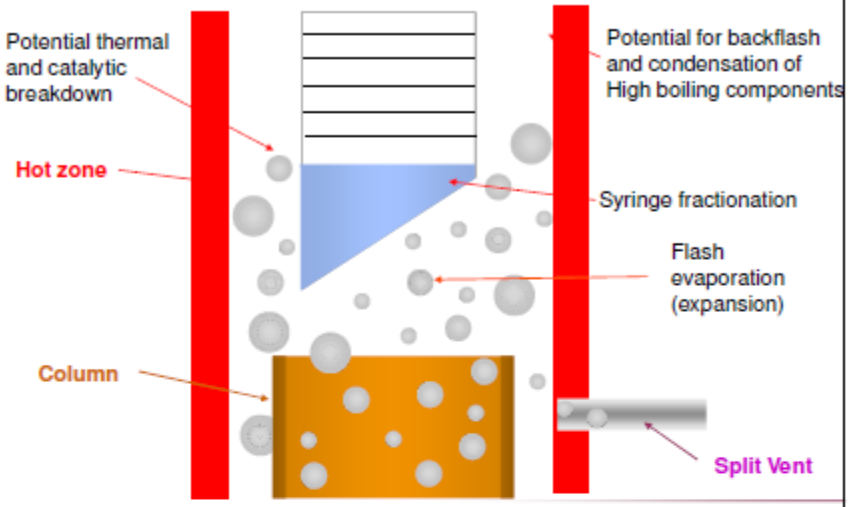
PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

Why use controlled volatilization (solvent purge) injections instead of hot splitless injections?

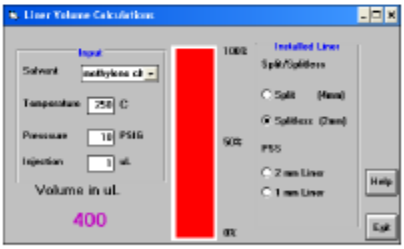
© 2013 Perkin Elmer

Disadvantages to hot (flash-vaporizing) injections



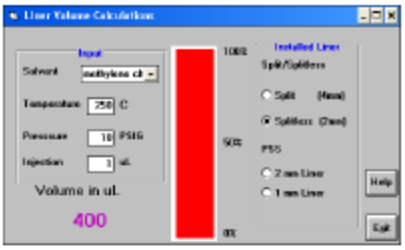
Keeping your analytes in the liner: Potential backflash

- Backflash of analytes due to vapor expansion volume of solvent in hot injector exceeding the available volume of liner … full injection will not make its way to column.
- Vapor (with sample) can enter pneumatics causing contamination requiring maintenance
- Affect
  - Poor precision and recovery
  - Condensation of high boiling components causing discrimination
  - Carryover into later injections causing "ghost peaks" and poor performance



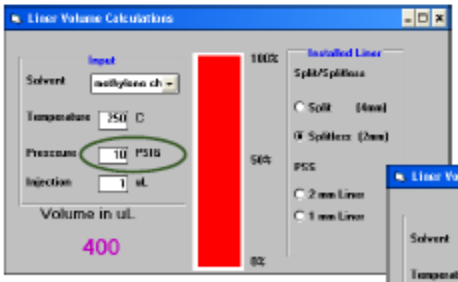
Why does this happen … *avoid* Backflash

- Liner Volume … Equation of a cylinder
  - (Liner length)(π) r^2
    - Example for a 4cm x 2mm liner:
    - (4cm)(0.2cm/2)^{2}π
- Parameters to consider (V = nRT/P)
  - Injector temperature
  - Injection volume
  - Injector pressure
  - Solvents (have different expansion volumes)
- In this example, a 1µL injection of DCM at 10 psig and 250°C expands to a 400µL vapor volume which exceeds the volume of the liner being used

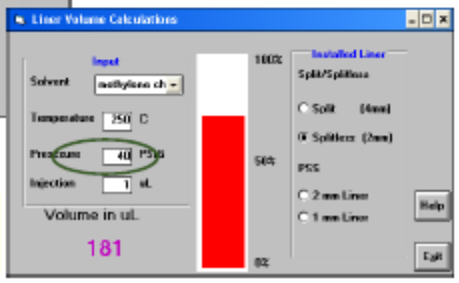


Vapor Expansion: ex. Dichloromethane – 1 uL injection volumes

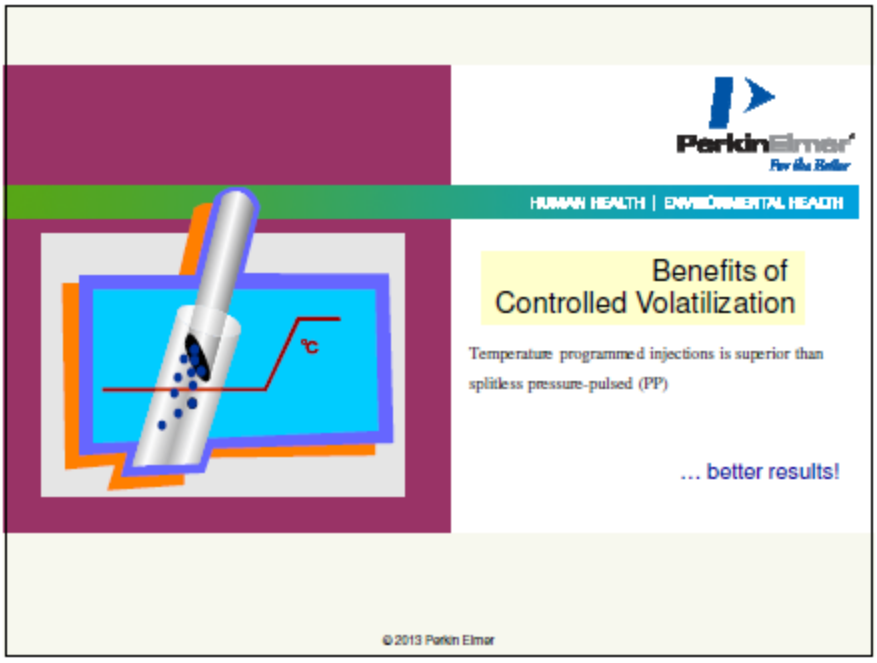
Effect of Pressure

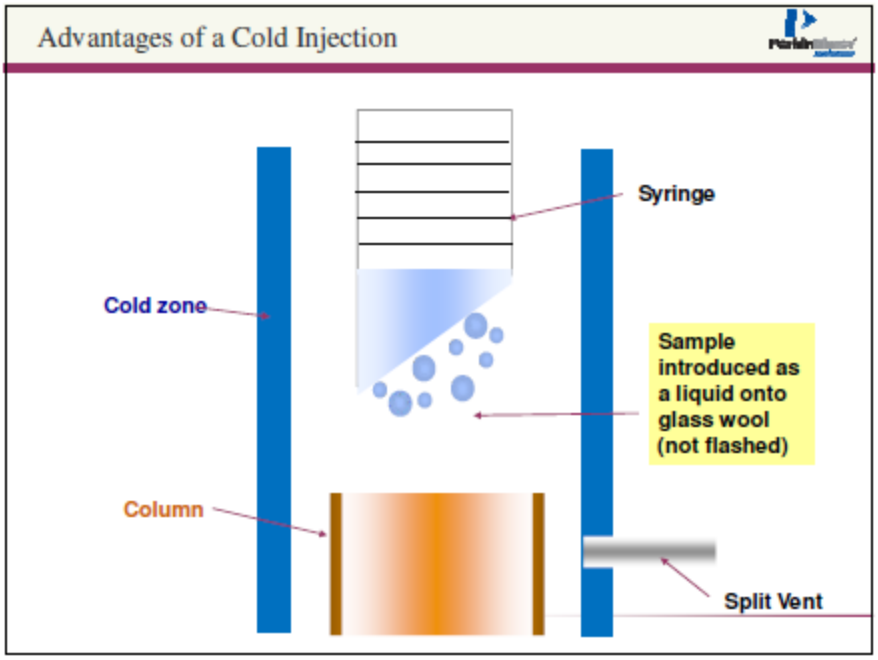


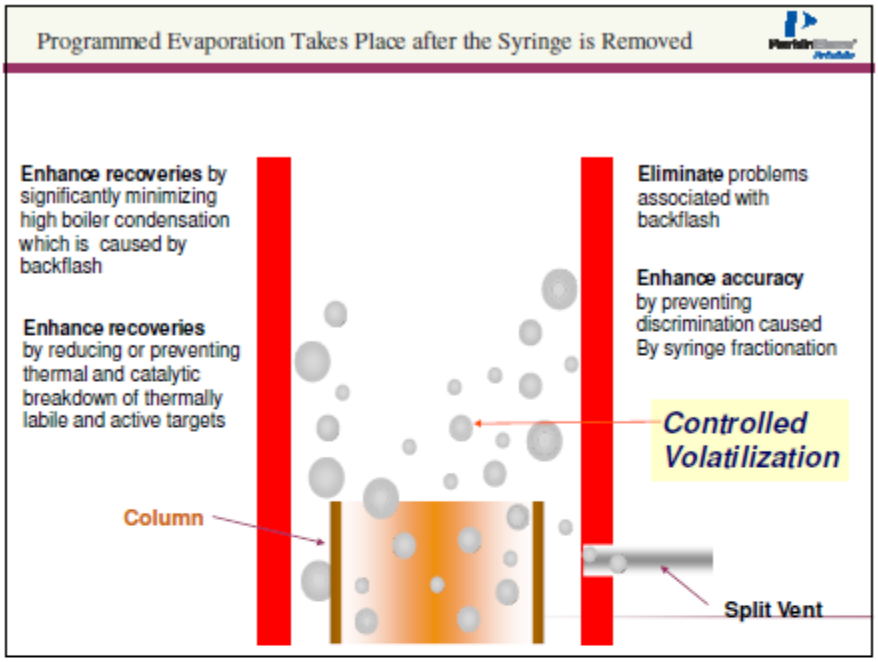
Advantages to Pressure Pulse
reduce vapor expansion

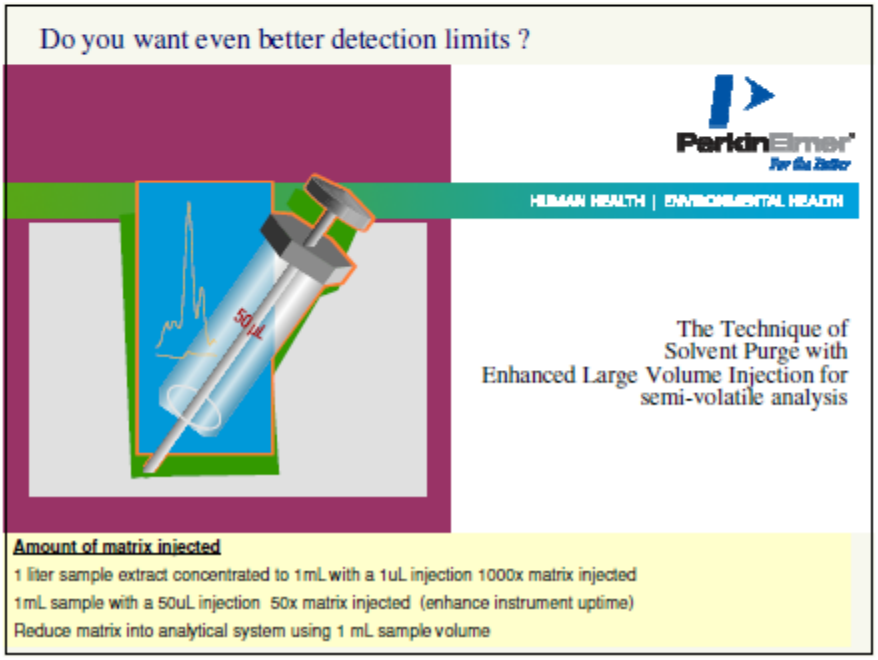


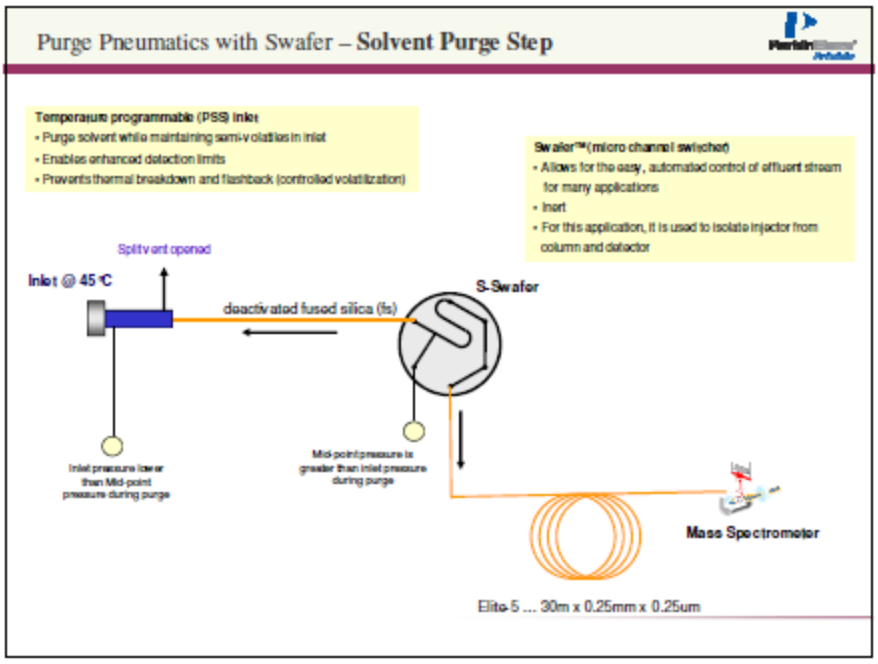
Pressure Pulse during injection
V=nRT/P.
Increase pressure reduces vapor expansion

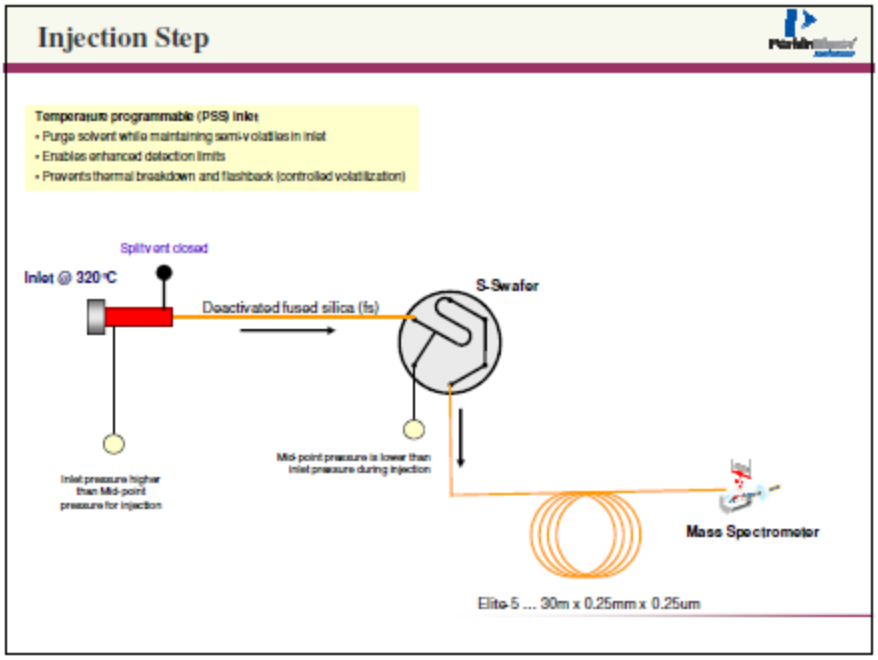

PerkinElmer
For the Better
HUMAN HEALTH | ENVIRONMENTAL HEALTH
°C
Benefits of
Controlled Volatilization
Temperature programmed injections is superior than splitless pressure-pulsed (PP)
... better results!
© 2013 Perkin Elmer


Advantages of a Cold Injection
Syringe
Cold zone
Sample introduced as a liquid onto glass wool (not flashed)
Column
Split Vent


Programmed Evaporation Takes Place after the Syringe is Removed
Enhance recoveries by significantly minimizing high boiler condensation which is caused by backflash
Enhance recoveries by reducing or preventing thermal and catalytic breakdown of thermally labile and active targets
Eliminate problems associated with backflash
Enhance accuracy by preventing discrimination caused By syringe fractionation
Controlled Volatilization
Column
Split Vent

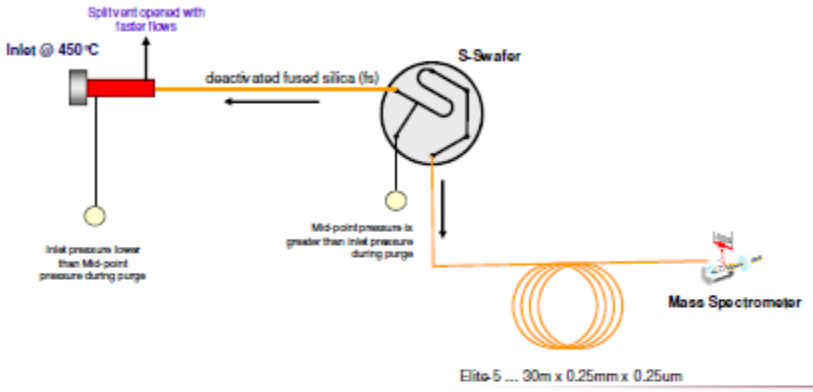

Do you want even better detection limits ?
PerkinElmer
For the Better
HUMAN HEALTH | ENVIRONMENTAL HEALTH
50 µL
The Technique of Solvent Purge with Enhanced Large Volume Injection for semi-volatile analysis
Amount of matrix injected
1 liter sample extract concentrated to 1mL with a 1uL injection 1000x matrix injected
1mL sample with a 50uL injection 50x matrix injected (enhance instrument uptime)
Reduce matrix into analytical system using 1 mL sample volume


Purge Pneumatics with Swafer – Solvent Purge Step
Temperature programmable (PSS) inlet
• Purge solvent while maintaining semi-volatiles in inlet
• Enables enhanced detection limits
• Prevents thermal breakdown and flashback (controlled volatilization)
Swafer™ (micro channel switcher)
• Allows for the easy, automated control of effluent stream for many applications
• Inert
• For this application, it is used to isolate injector from column and detector
Split vent opened
Inlet @ 45°C
deactivated fused silica (fs)
S-Swafer
Inlet pressure lower than Mid-point pressure during purge
Mid-point pressure is greater than inlet pressure during purge
Mass Spectrometer
Elite-5 ... 30m x 0.25mm x 0.25um

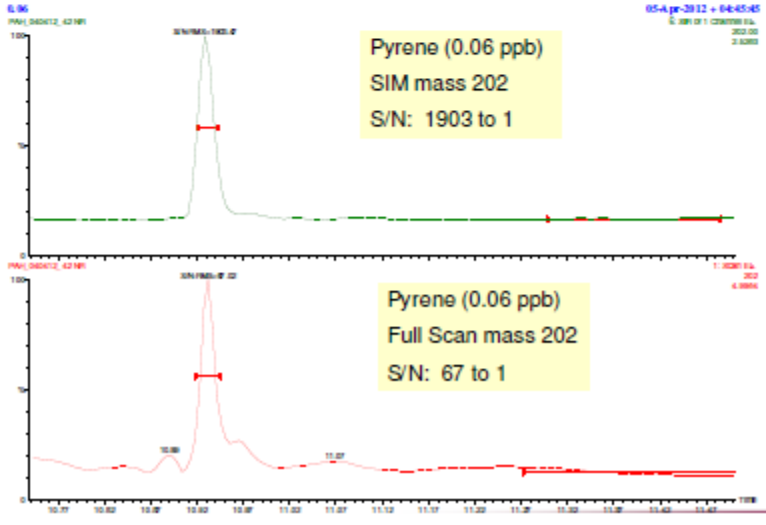

Injection Step
Temperature programmable (PSS) inlet
• Purge solvent while maintaining semi-volatiles in inlet
• Enables enhanced detection limits
• Prevents thermal breakdown and flashback (controlled volatilization)
Split vent closed
Inlet @ 320°C
Deactivated fused silica (fs)
S-Swafer
Inlet pressure higher than Mid-point pressure for injection
Mid-point pressure is lower than inlet pressure during injection
Mass Spectrometer
Elite-5 ... 30m x 0.25mm x 0.25um

Bake Step

Temperature programmable (PSS) inlet
- Purge solvent while maintaining semi-volatiles in inlet
- Enables enhanced detection limits
- Prevents thermal breakdown and flashback (controlled volatilization)



Full Scan/Single Ion Monitoring: Both Acquisitions in One Injection!



PAH detection limit results varying injection volume

	0.4 ppb		0.2 ppb		0.2 ppb		0.06 ppb		0.08 ppb		0.02 ppb	
	1uL FS		1uL SIM		5uL FS		5uL SIM		10uL FS		50 uL FS	
Name	r^2	S/N	r^2	S/N	r^2	S/N	r^2	S/N	r^2	S/N	r^2	S/N
2-fluorobiphenyl (Sur)	0.9952	51 : 1	0.9990	232 : 1	0.9958	306 : 1	0.9964	268 : 1	0.9984	111 : 1	0.9990	238 : 1
p-Terphenyl-d14 (Sur)	0.9989	355 : 1	0.9980	56 : 1	0.9959	460 : 1	0.9956	561 : 1	0.9994	313 : 1	0.9997	1118 : 1
Napthalene	0.9957	75 : 1	0.9969	103 : 1	0.9998	410 : 1	0.9985	357 : 1	0.9998	142 : 1	0.9987	446 : 1
Acenapthalene	0.9998	311 : 1	0.9962	109 : 1	0.9983	118 : 1	0.9973	330 : 1**	0.9952	30 : 1	0.9988	20 : 1
Acenapthene	0.9972	30 : 1	0.9994	81 : 1	0.9982	410 : 1	0.9965	50 : 1	0.9987	47 : 1	0.9981	557 : 1
Fluorene	0.9990	343 : 1	n/a	n/a	0.9987	386 : 1	0.9983	455 : 1	0.9997	100 : 1	0.9983	232 : 1
Phenanthrene	0.9980	375 : 1	0.9962	420 : 1	0.9983	773 : 1	0.9970	324 : 1	0.9988	327 : 1	0.9994	335 : 1
Anthracene	0.9989	130 : 1	0.9993	62 : 1	0.9981	280 : 1	0.9989	261 : 1	0.9967	70 : 1	0.9986	83 : 1
Fluoranthene	0.9997	1232 : 1	0.9998	485 : 1	0.9987	865 : 1	0.9955	407 : 1	0.9976	250 : 1	0.9950	201 : 1
Pyrene	0.9983	322 : 1	0.9989	457 : 1	0.9993	771 : 1	0.9991	671 : 1	0.9996	230 : 1	0.9992	368 : 1
Benzo (a) anthracene	0.9991	1100 : 1	0.9981	224 : 1	0.9990	550 : 1	0.9999	463 : 1	0.9996	206 : 1	0.9983	476 : 1
Chrysene	0.9991	1949 : 1	0.9994	252 : 1	0.9996	175 : 1	0.9994	405 : 1	0.9997	380 : 1	0.9999	241 : 1
Benzo (b) fluoranthene	0.9950	25 : 1	0.9992	220 : 1	0.9981	60 : 1	0.9993	28 : 1	0.9983	117 : 1	0.9979	16 : 1
Benzo (k) fluoranthene	0.9960	101 : 1	0.9945	474 : 1	0.9998	35 : 1	0.9996*	27 : 1	0.9962	155 : 1	0.9987	15 : 1
Benzo (a) pyrene	0.9985	n/a	0.9992	56 : 1	0.9994	10 : 1	0.9993	33 : 1	0.9951	10 : 1	0.9950	17 : 1
Indeno (1,2,3-cd) pyrene	0.9974	35 : 1	0.9985	247 : 1	0.9976	71 : 1	0.9959*	67 : 1	0.9971	15 : 1	0.9966	101 : 1
Dibenzo (a,h) anthracene	0.9988	258 : 1	0.9990	301 : 1	0.9990	40 : 1	0.9950*	62 : 1	0.9995	41 : 1	0.9973	90 : 1
Benzo (g,h,i) perylene	0.9968	85 : 1	0.9959	220 : 1	0.9950	150 : 1	0.9993	147 : 1	0.9974	27 : 1	0.9989	203 : 1

* removed lower level point from curve
**0.2 point not 0.06 point

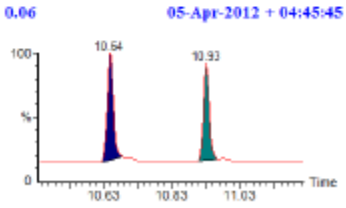
25

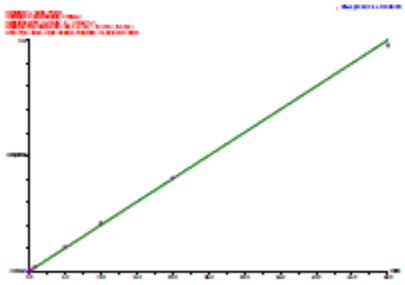
Pyrene Calibration from 0.06 to 50 ppb (10uL injection) SIM

Extraction Volume: 1mL

Concentration: 0.06 ppb
Fluoranthene and Pyrene

r^2: 0.9992





26

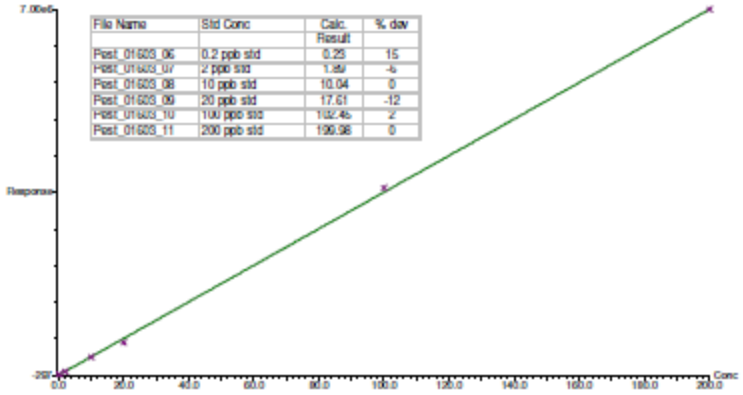
7 level Calibration – Full Scan processing from FS/SIM Acquisition

Chlordane – 0.2 ppb to 200 ppb

Extraction Volume: 1mL

Compound 8 name: Chlordane
Coefficient of Determination: 0.998640
Calibration curve: 34980.8* x + -297.362
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

File Name	Std Conc	Calc. Result	% dev
Pest_01603_06	0.2 ppb std	0.25	15
Pest_01603_07	2 ppb std	1.89	-6
Pest_01603_08	10 ppb std	10.04	0
Pest_01603_09	20 ppb std	17.61	-12
Pest_01603_10	100 ppb std	102.46	2
Pest_01603_11	200 ppb std	199.98	0



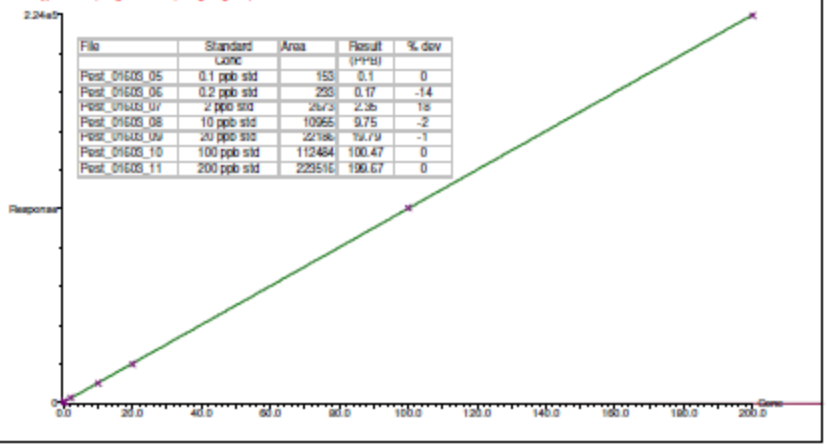
7 level Calibration – SIM processing from FS/SIM Acquistion

Aldrin – 0.1 ppb to 200 ppb

Extraction Volume: 1mL

Compound 6 name: Aldrin
Coefficient of Determination: 0.999394
Calibration curve: 1119.20* x + 41.5440
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

File	Standard Conc	Area	Result (PPB)	% dev
Pest_01603_05	0.1 ppb std	153	0.1	0
Pest_01603_06	0.2 ppb std	233	0.17	-14
Pest_01603_07	2 ppb std	2673	2.35	18
Pest_01603_08	10 ppb std	10955	9.75	-2
Pest_01603_09	20 ppb std	22186	19.79	-1
Pest_01603_10	100 ppb std	112484	100.47	0
Pest_01603_11	200 ppb std	223516	199.67	0



Increasing Productivity, Efficiency and Performance

- Meet required reporting limits while using less sample
  - New detector technology
  - SIFI
  - Larger injection volumes
- Inject less matrix – cleaner system means enhanced instrument uptime increasing productivity
- Extract less sample – reduce operating costs (less solvent, less glassware and less storage space required)
- Adds up to faster return on investment and a more productive laboratory with improved recoveries

Enhancing Instrument uptime …

PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

Injecting less matrix
Extending maintenance interval!
Experiments performed at environmental testing lab

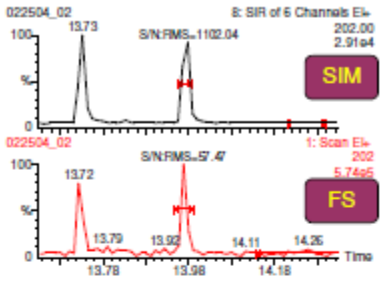
100mL injection volume

Collected at an Environmental Testing lab in Shelton, CT

© 2013 Perkin Elmer

Results Comparing 1L to 100mL

- Detection limit achieved 10x improved over regulated detection limits for all targets
- More Clocks achieved than 1L extract because less matrix being injecting
- 1.0uL splitless injection



From Matrix spike
Pyrene – 0.025 ppb
100mL extract conc to 5mL

PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH



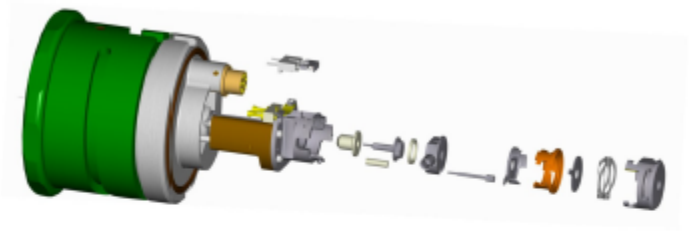
Getting more from your GC/MS!

Enable lower detection limits!

© 2013 Perkin Elmer

Easy to Use and Maintain … SMARTSource

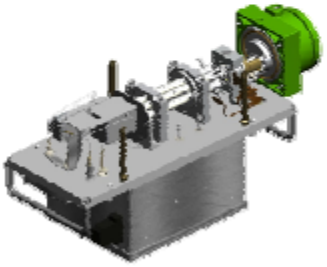
Now it is "Plug and Play" with a twist no wires to remove

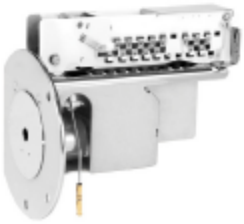


Change source components in under 5 minutes **with no tools**

Enhance Performance … Enhance Uptime!

- Clarifi Detector
  - Enhance Sensitivity
  - Increase Operating Range
  - More Flexibility
  - Longer Life – Less Downtime
  - Enhance Library Matches





… most sensitive (improve detection limits) and robust (increase throughput)!



The Clarus SQ8 GC/MS

Thank you

Contact Information
lee.marotta@perkinelmer.com

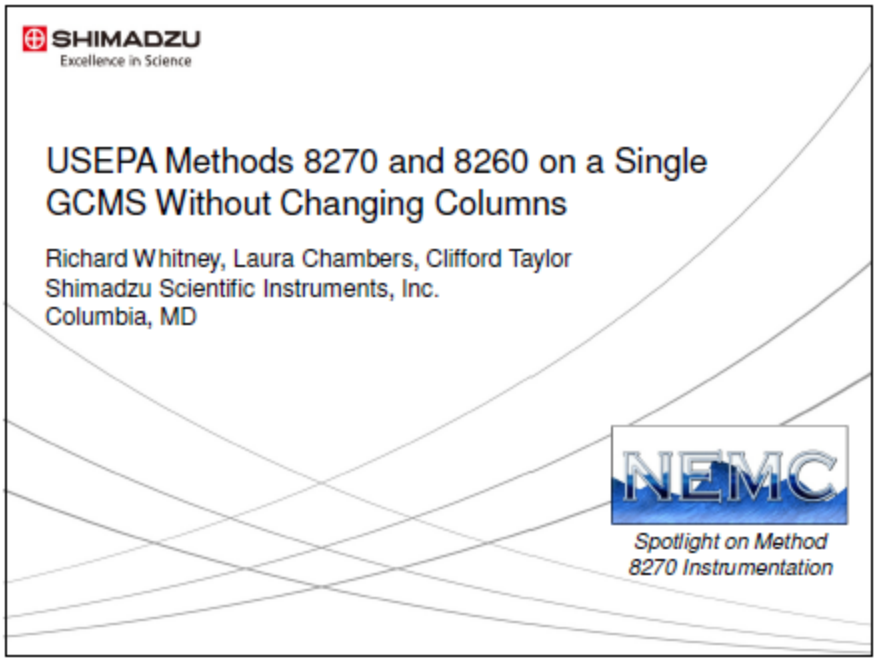
USEPA Methods 8270D and 8260C on a Single GCMS without Changing Columns

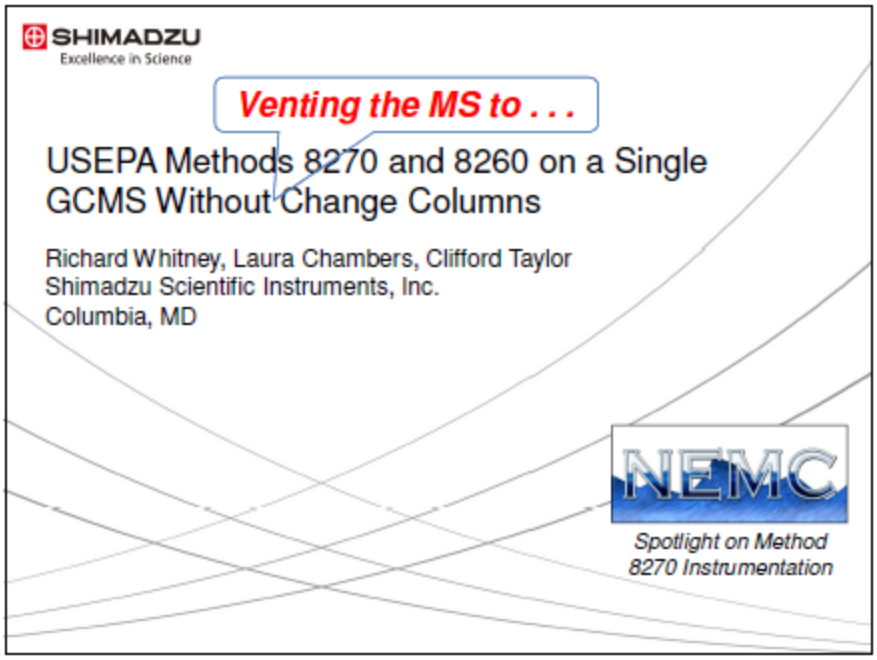
Laura Chambers, Richard Whitney, Clifford Taylor
Shimadzu Scientific Instruments, Inc.

Abstract

USEPA Methods 8270D (semi-volatiles) and 8260C (volatiles) typically require dissimilar chromatographic columns with incompatible maximum temperatures. Historically, laboratories performing these analyses have found it necessary to allocate separate GCMS instrumentation for the two analysis modes, or perform frequent reconfiguration (column changing) to run these methods on a single GCMS unit. Venting the MS system to change analytical columns can be time-consuming and inefficient, however productivity can be improved significantly using the Shimadzu Twin Line MS Kit. With this configuration, two capillary columns are simultaneously installed in the MS, and the user can easily switch between dissimilar applications without venting the mass spectrometer to change the column.

Instrument hardware configuration and operating conditions with two dissimilar capillary columns will be described. Data will be presented which illustrate instrument performance of USEPA Method 8270D when run on a single GCMS with two columns simultaneously installed in the same MS. Data will include chromatography, calibration results, accuracy and precision statistics, and method detection limits (MDLs).


SHIMADZU
Excellence in Science
USEPA Methods 8270 and 8260 on a Single GCMS Without Changing Columns
Richard Whitney, Laura Chambers, Clifford Taylor
Shimadzu Scientific Instruments, Inc.
Columbia, MD
NEMC
Spotlight on Method 8270 Instrumentation


SHIMADZU
Excellence in Science
Venting the MS to . . .
USEPA Methods 8270 and 8260 on a Single GCMS Without Change Columns
Richard Whitney, Laura Chambers, Clifford Taylor
Shimadzu Scientific Instruments, Inc.
Columbia, MD
NEMC
Spotlight on Method 8270 Instrumentation

SHIMADZU

Problem

- Small laboratory
- Limited budget
- Multiple applications
- No time



The Big Bang Theory – CBS.com

3

SHIMADZU

Solution

- 8260 and 8270
- Single GCMS
- Two inlets, two columns
- No venting



The Big Bang Theory – CBS.com

4

SHIMADZU

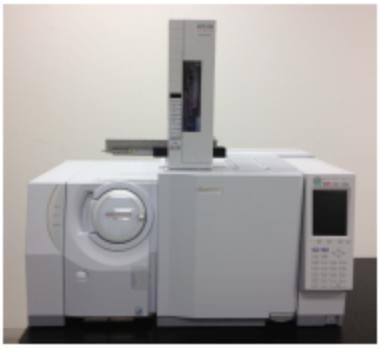
What We Did

- Instrument configuration
- Optimize method parameters
- Analytical results (aka data)

5

SHIMADZU

Instrument Configuration



GCMS-QP2010 SE
Production Workhorse

6

SHIMADZU

Instrument Configuration

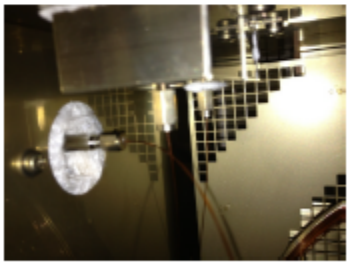


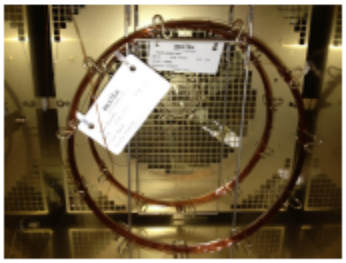
GCMS-QP2010 SE
Production Workhorse

7

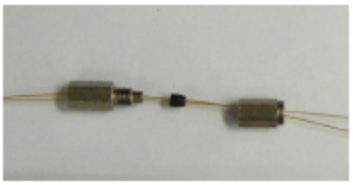
SHIMADZU

Instrument Configuration (cont.)





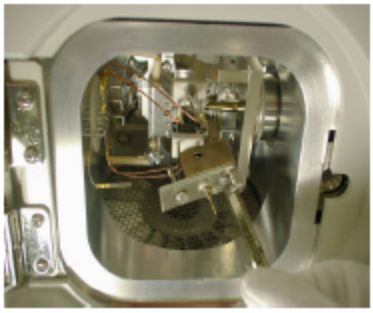
GCMS Twin Line Kit



8

SHIMADZU

Instrument Configuration (cont.)

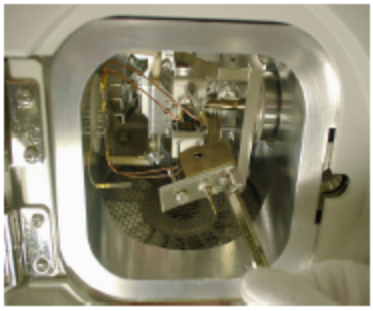


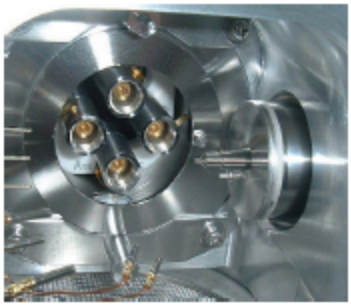


9

SHIMADZU

Instrument Configuration (cont.)

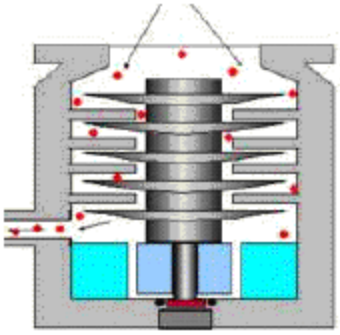




10

SHIMADZU

Instrument Configuration (cont.)





58 L/sec (He)
Pfeiffer TMP
(Rotary pump 30 L/min)

11

SHIMADZU

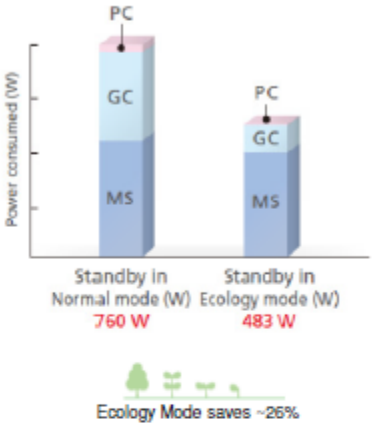
Instrument Configuration (cont.)



12

SHIMADZU

Instrument Configuration (cont.)



13

SHIMADZU

Instrument Configuration (cont.)

Parameter	EPA Method 8260	EPA Method 8270
Sample introduction	Purge-and-trap	Liquid syringe
Liner	Shimadzu multi-purpose split liner, no glass wool	Shimadzu multi-purpose split liner, no glass wool
Injection conditions	Split 75:1	Split 10:1
Column	Rxi-624Sil MS 20 m x 0.18 mm x 1.4 µm	Rxi-5Sil MS 20 m x 0.18 mm x 0.18 µm
Maximum column temperature	Program = 320 °C	Program = 350 °C
Carrier gas	Helium, constant linear velocity mode	
MS pump	Single stage TMP, max flow 4 mL/min (He)	
MS interface	225 °C	
Ion source	EI, 200 °C	

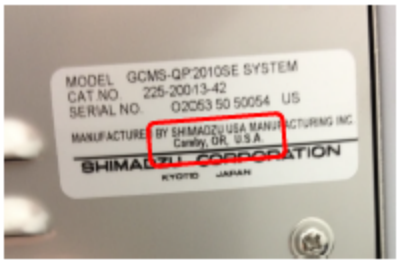
14

SHIMADZU

Instrument Configuration (cont.)

Born in Kyoto
Made in the USA







15

SHIMADZU

Method Optimization

- Primary objectives
  1. Keep total column flow rate below 4 mL/minute
  2. Keep maximum oven temperature below 320 °C
  3. Keep GC run time as short as practical



The Big Bang Theory – CBS.com

16

SHIMADZU

Method Optimization (cont.)

Parameter	Method 8260 Primary	Method 8270 Inactive
Column constant linear velocity	45 cm/second ~0.8 mL/min	30 cm/second ~0.5 mL/min
Maximum total column flow	~1.3 mL/minute	
Oven program	35 °C (5 min) 20 °C/min to 220 °C (hold 2.5 min)	NA
GC run time	12.5 minutes	NA

17



SHIMADZU

Method Optimization (cont.)

Parameter	Method 8260 Inactive	Method 8270 Primary
Column constant linear velocity	30 cm/second ~0.5 mL/min	40 cm/second ~0.7 mL/min
Maximum total column flow	~1.2 mL/minute	
Oven program	NA	45 °C (0.5 min) 25 °C/min to 315 °C (hold 4.2 min)
GC run time	NA	16 minutes

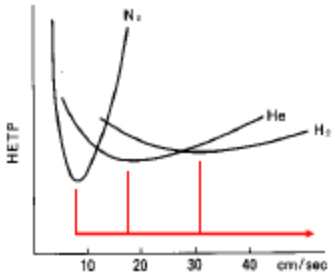
18



SHIMADZU

Why Constant Linear Velocity?

Van Deemter Plot



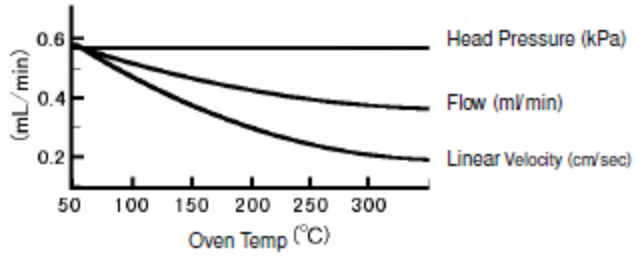
Optimal LV for each carrier Gas

Linear Velocity – Isothermal Oven

19

SHIMADZU

Why Constant Linear Velocity? (cont.)



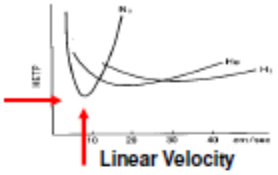
With temperature programming:
1. Viscosity of gas increases
2. Gas expands
3. Flow rate and LV drop

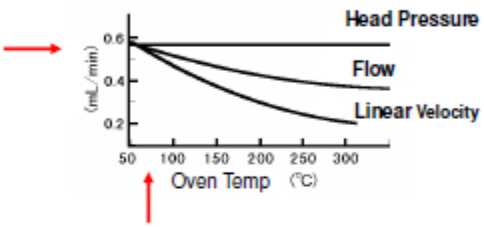
20

SHIMADZU

Why Constant Linear Velocity? (cont.)

Constant Pressure





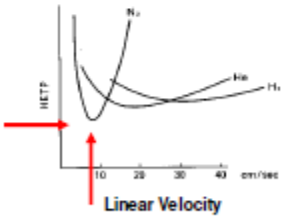
21

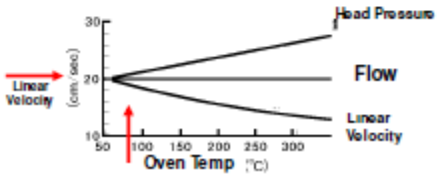


SHIMADZU

Why Constant Linear Velocity? (cont.)

Constant Flow



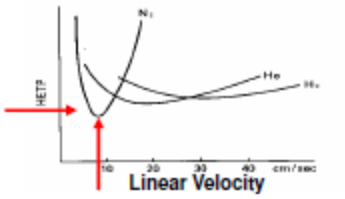


22

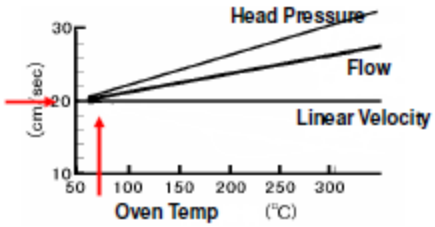


SHIMADZU

Why Constant Linear Velocity? (cont.)



Constant
Linear Velocity

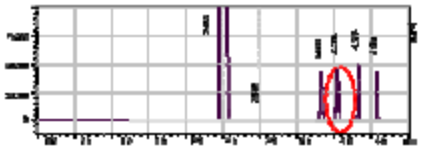




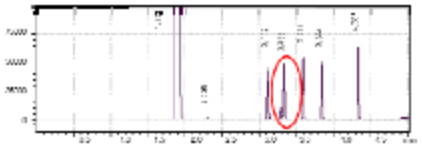
23

SHIMADZU

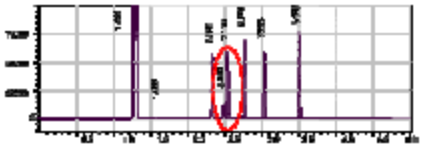
Why Constant Linear Velocity? (cont.)



Constant Pressure
Linear velocity = 15 cm/sec



Constant Flow
Linear velocity = 20 cm/sec



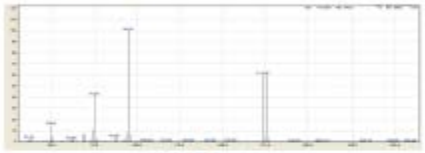
Constant Linear Velocity
Linear velocity = 30 cm/sec



24

SHIMADZU

Analytical Results



BFB Spectrum

Data	Data File Path
Data1:	C:\GCMSsolution\Data\8260 Test for Twin-Line\VOA ICA

4-Bromofluorobenzene

m/z	Spectrum Check Criteria	Result	Status
50	15 to 40% of mass 95	15.325219	Pass
75	30 to 60% of mass 95	41.968955	Pass
95	Base Peak, 100% Relative Abundance	100.000000	Pass
96	5 to 9% of mass 95	6.736341	Pass
173	< 2% of mass 174	0.694586	Pass
174	> 50% of mass 95	60.567094	Pass
175	5 to 9% of mass 174	7.049975	Pass
176	> 95% but < 101% of mass174	99.366573	Pass
177	5 to 9% of mass 176	6.571022	Pass



From Helium to Hydrogen: GC-MS Case Study on SVOCs in Water

Dwain Cardona
Thermo Fisher Scientific

Abstract

The global helium shortage and price increase cause more and more laboratories to migrate to hydrogen as a carrier gas. This transition is easy for the GC methods utilizing FID, TCD, ECD, and other non-mass-selective detectors. However, for the GC-MS methods, especially complex and regulated ones, migration to hydrogen carrier gas presents significant challenges. In addition to the changes in chromatographic conditions due to the physical property differences of hydrogen, its chemical reactivity brings about chemical reactions in the mass spectrometer's ion source that do not occur with helium.

The analysis of semi-volatile organic compounds (SVOCs) in wastewater by EPA Method 8270 involves identification and quantitation of more than 120 analytes of varying chemical structure, polarity and volatility. The diversity of the analytes in this method and the requirement to meet DFTPP tuning criteria present particular challenges when migrating from helium to hydrogen carrier.

We will present and compare data of fast GC-MS analysis of SVOCs performed on TRACE 1310 GC coupled to ISQ single quadrupole mass spectrometer utilizing helium and hydrogen carrier gases. Key modifications to both GC and MS set up in hardware and methods necessary for successful migration to hydrogen carrier gas will be discussed and effect of each parameter on the data quality will be demonstrated. The final, optimized and validated method fully migrated to hydrogen carrier gas with improved peak shape, resolution, run time, and sensitivity will be presented. Study on instrument detection limits and robustness will be presented alongside ion ratio stability and MS library search reliability.

ThermoFisher SCIENTIFIC

From Helium to Hydrogen: GC-MS Case Study on SVOC's in Water

Dwain Cardona
Senior Applications Scientist
Thermo Fisher Scientific

The world leader in serving science

Helium and Profitability of Drinking Water Testing Labs





2

ThermoFisher SCIENTIFIC

Helium to Hydrogen Migration: Practicalities

- **Hydrogen Carrier Gas:**
  - Van Deemter Curve
  - Thermo Scientific Position
  - Hydrogen Safety Points
  - Cylinders vs. Generators
- **GC-MS Tuning**
  - Baking & HC Background
  - Water Spectrum Check
  - Resolution Assurance
  - Target Tuning (DFTPP & BFBs)
- **GC Inlet and Column**
  - Maintenance
  - Mode of Injection
  - Liner Selection
  - Column Selection
- **Performance:**
  U.S. EPA Methods 524 & 525
  - Linearity (measuring accuracy)
  - Sensitivity (MDLs)
  - Spectral Integrity
  - Ion Ratio Stability

***Before* you migrate to hydrogen carrier gas on your GC-MS**

3

ThermoFisher SCIENTIFIC

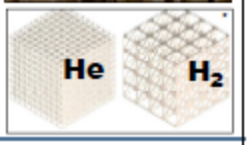
Carrier Gases: Physical Properties

Property	He	H_2	N_2	Ar
Molecular Mass, Da	4	2	28	40
Density, kg/m³	0.18	0.09	1.25	1.78
Diffusion Coefficient, cm²/s	0.55	0.60	0.15	0.20
Viscosity, Pa•s × 10^6	23.2	10.3	20.9	27.0
u_{opt}, cm/s	20	40	12	<10









Carrier Gas **Density**: Less is Better

Diffusion Coefficient: More is Better**

Dynamic **Viscosity** : Less is Better

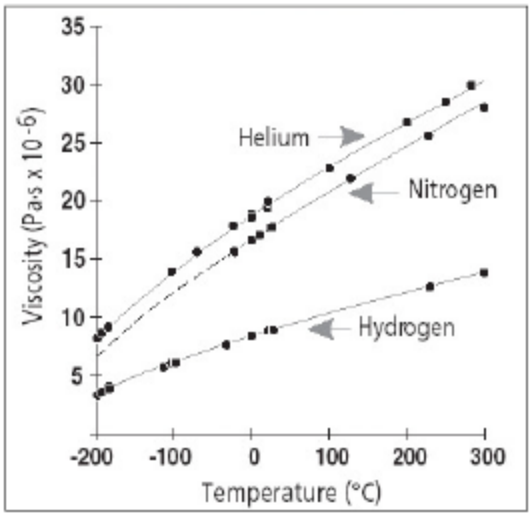
4

* Crystal Lattice Density Analogy only, O.Fryazinov ;A.Pasko; V.Adzhiev Computer-Aided Design 2011, 43(3) 265-277

** On the RHS of the van Deemter curve, that is.

ThermoFisher SCIENTIFIC

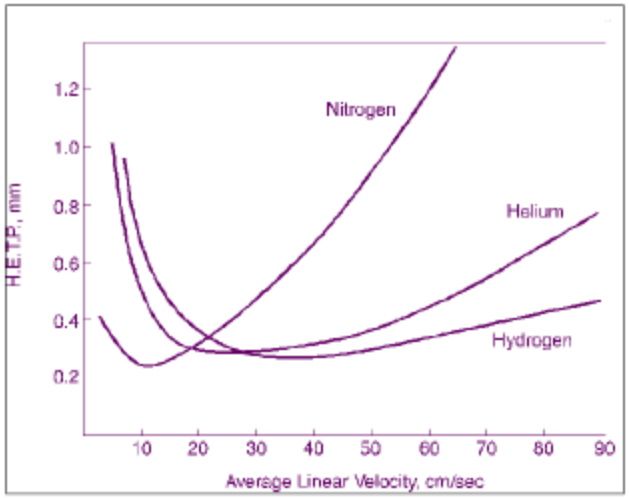
Dynamic Viscosity vs. Temperature



5

ThermoFisher SCIENTIFIC

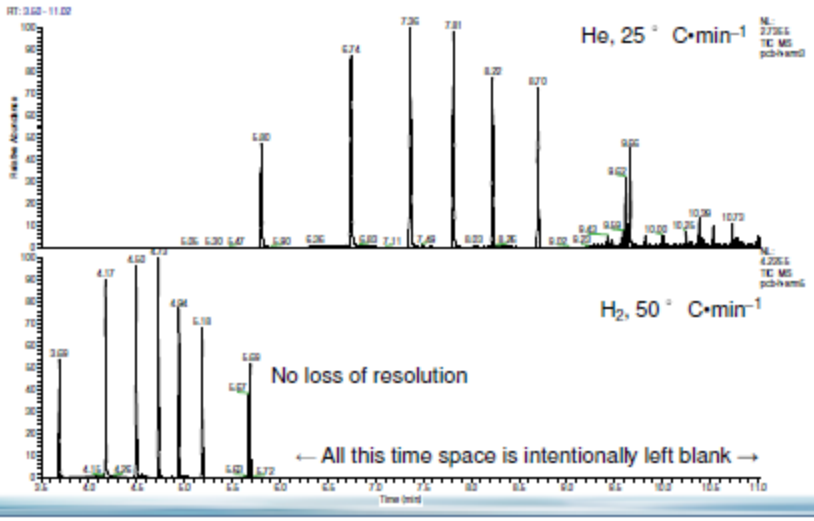
Carrier Gases Efficiencies: Van Deemter Plots



8

ThermoFisher SCIENTIFIC

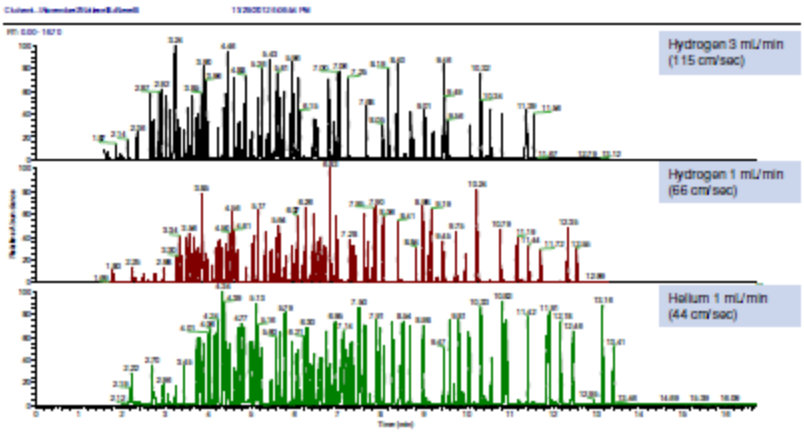
Effect of GC Oven Heating Rate: PCB Mix



7 Polychlorinated Biphenyls Mix ran by Dirk Claus, Interscience, www.is-x.be

ThermoFisher SCIENTIFIC

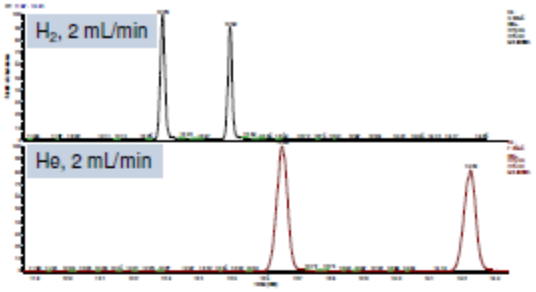
Effect of Flow Rate



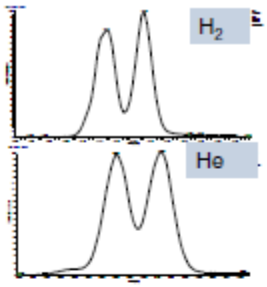
8

ThermoFisher SCIENTIFIC

Peak Shape and Critical Separations



Indeno[1,2,3-cd]pyrene & benzo[g,h,i]perylene



Benzo[b&k]fluoranthene

MINIMIZED BAND BROADENING OF PAHs

9

ThermoFisher SCIENTIFIC

Thermo Scientific Position on Hydrogen with GC-MS

- **Hydrogen Kit**
  - Required to Run with H_2
  - Required for H_2 Specifications
  - Includes Hydrogen Sensor
  - Requires 300 L/s Turbo Pump
- **Thermo Scientific™ Hydrogen Systems**
  - ISQ™ Single Quadrupole GC-MS
  - TRACE™ 1300 Series GC
  - TSQ™ 8000 GC-MS/MS
  - Explosion Tested & Safety Certified
- **Upgrades in the Field**
  - All existing ISQ GC-MS Systems are either already H_2 capable or are upgradeable with 300 L/s Turbo and H_2 Kit
  - IF you decide to use your existing Thermo Scientific™ DSQ™, DSQ II & ITQ GC-MS with H_2, you do so at your own risk (no Safety Certification)



10

ThermoFisher SCIENTIFIC

ISQ GC-MS Hydrogen Carrier Installation Specifications

- **ISQ Single Quadrupole GC-MS**
  - Guaranteed installation specifications with hydrogen carrier gas
  - Choice of either He or H_2 on installation spec sign-off
  - PCI/NCI same S/N!

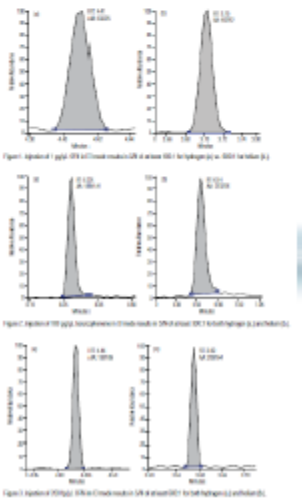
Standard Installation Specifications*

Mode / Concentration	He	H_2
In EI mode, 1 µL of 1 pg/µL octafluoronaphthalene (OFN) will produce the following minimum signal to noise for m/z 272 when scanning from 50 – 300 u:	1,500:1	100:1
In PCI mode, 1 µL of 100 pg/µL benzophenone will produce the following minimum signal to noise for m/z 183 when scanning from 80 – 230 u using methane reagent gas:	300:1	300:1
In NCI mode, 2 µL of 100 fg/µL of OFN will produce the following minimum signal to noise for m/z 272 when scanning from 50 – 300 u using methane reagent gas:	600:1	600:1

* Requires Hydrogen Kit for H_2.

ThermoFisher SCIENTIFIC

ISQ GC-MS Technical Brief - AB52360



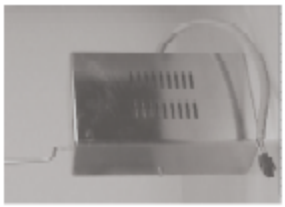


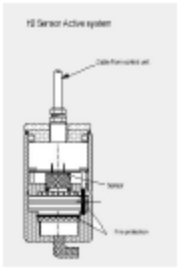
Moving from Helium to Hydrogen as a Carrier Gas for the Thermo Scientific ISQ GC-MS System

ThermoFisher SCIENTIFIC

Hydrogen Gas Safety

- Safety Precautions
  - Hydrogen sensor in GC oven
  - Venting hydrogen
  - The risk is minimal
  - Can be estimated & prevented





- Safety Facts on ISQ GC-MS and TSQ 8000 GC-MS
  - Explosion Tested & Explosion Certified
  - No detaching/flying pieces *even* IF hydrogen inside goes *boom*...
  - It is really hard in practice to reach explosive limits of hydrogen in the lab space ...
  - ... and the GC oven is monitored by the sensor

13

ThermoFisher SCIENTIFIC

Hydrogen Purity Specifications

- GC-MS Hydrogen Generator
- O_2 < 0.01 ppm
- H_2O < 1 ppm
- THC N/A

- Hydrogen Grade 5.0 UHP
- O_2 < 1 ppm
- H_2O < 3 ppm
- THC < 0.1 ppm

- Hydrogen FID Fuel Grade
- O_2 < 1 ppm
- H_2O < 3 ppm
- THC < 0.5 ppm

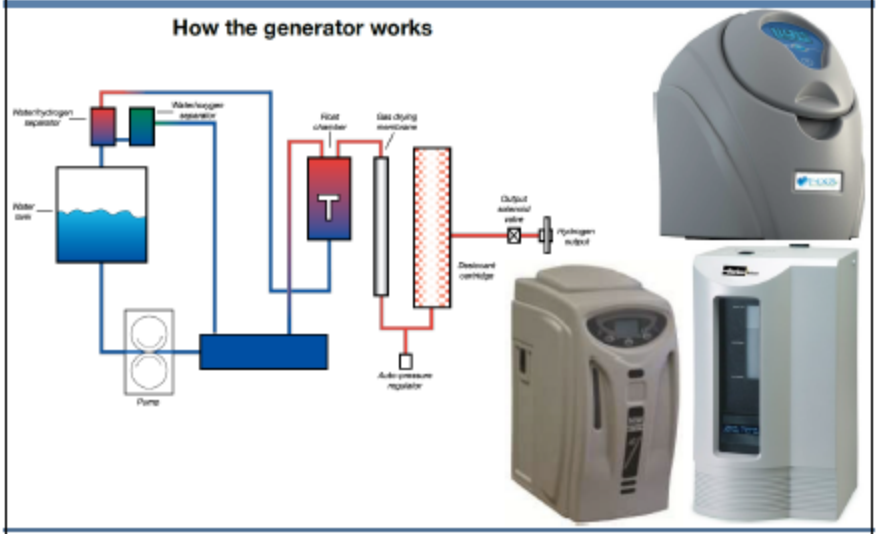
- Hydrogen Grade 6.0 UHP
- O_2 < 0.1 ppm
- H_2O < 0.5 ppm
- THC < 0.1 ppm

14

ThermoFisher SCIENTIFIC

Hydrogen Generators: Choose the Best

How the generator works

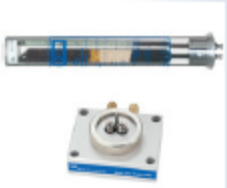


15

ThermoFisher SCIENTIFIC

Understanding Hydrogen Plumbing

- Gas Filter, triple stage



- Tubing
  - Stainless steel preferred
  - 1/8" pre-cleaned
  - New tubing is preferred over used with He

- Filter – only need with tanks
  - For removal of water, oxygen and hydrocarbons

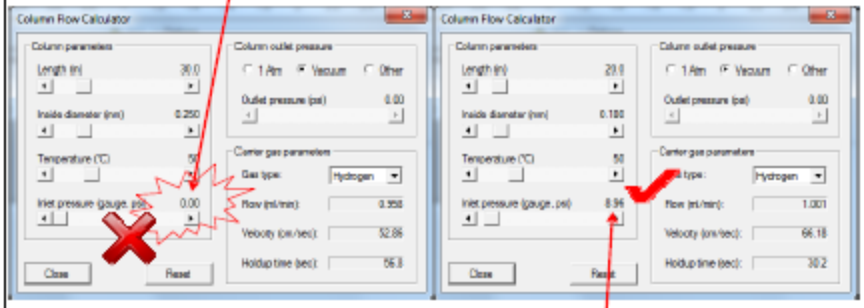
What you need to know about plumbing up hydrogen to your GC

18

ThermoFisher SCIENTIFIC

Limits on Hydrogen Flow and Column Selection

1 mL/min hydrogen on 0.25 mm × 30 m column



1 mL/min hydrogen on 0.18 mm × 20 meter column

17

ThermoFisher SCIENTIFIC

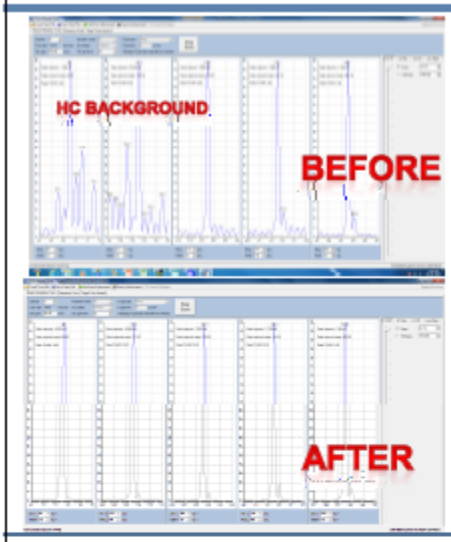
GC-MS Tuning

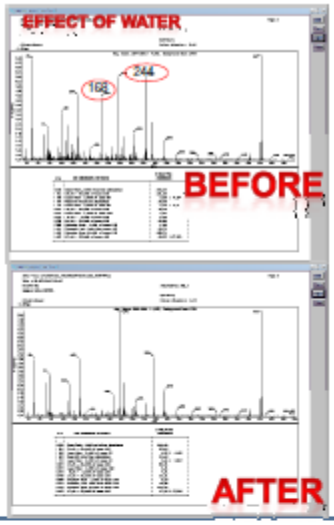
- Dealing with HC background ions and water
- Bake out at 350° C with hydrogen flow at 4 mL/min
- Mass Resolution: good
- Shows similar tune to that with helium
- Target Tuning for DFTPP and BFB
- Special tuning sequence to meet EPA tuning criteria

18

ThermoFisher SCIENTIFIC

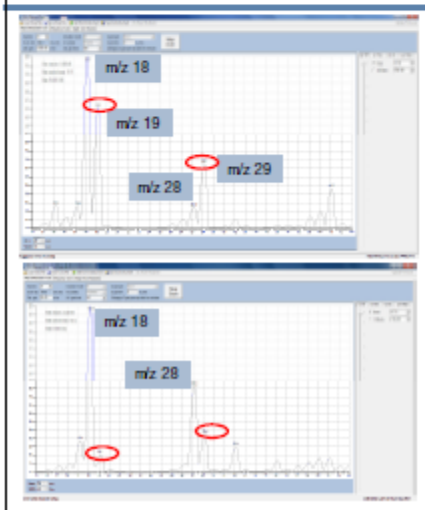
Bake-out at 350 ˚C with H_2 @ 4 mL/min for 1 hr





19 FC-43 n-$(C_4F_9)_3N$ DFTPP ThermoFisher SCIENTIFIC

Air Water Spectra: *m/z* 29 and *m/z* 19

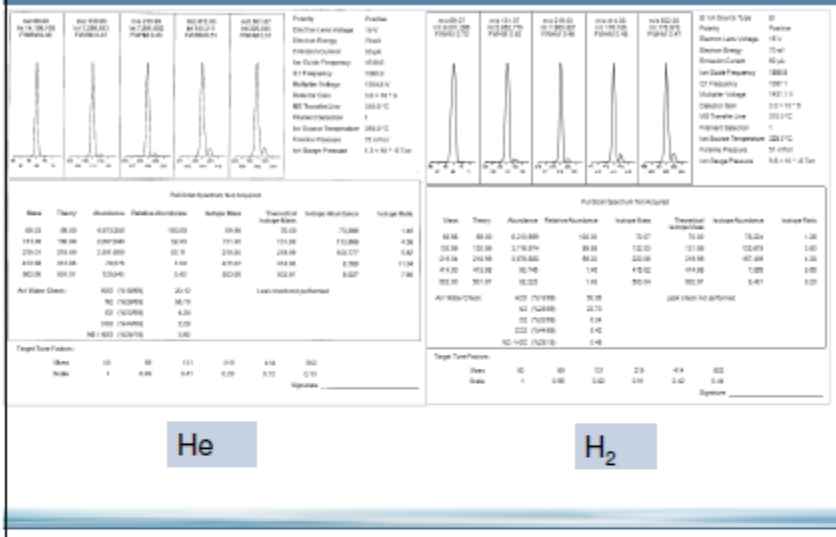


BEFORE

AFTER

20 ThermoFisher SCIENTIFIC

Tuning Report: He vs. H_2

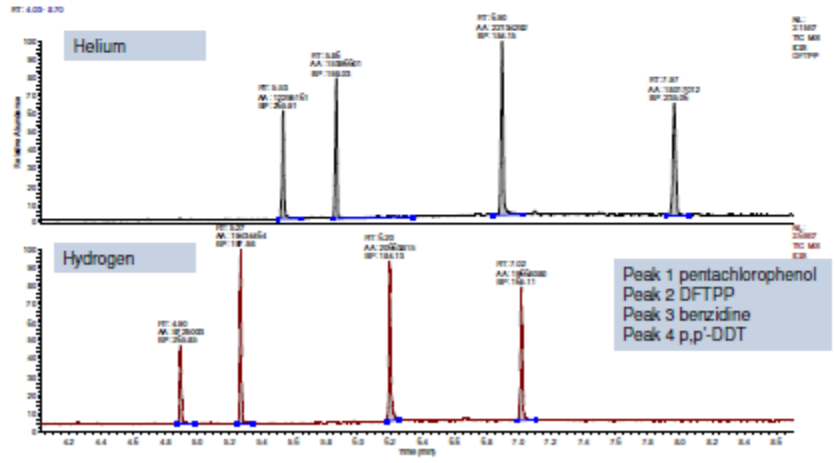


He H_2

21

ThermoFisher SCIENTIFIC

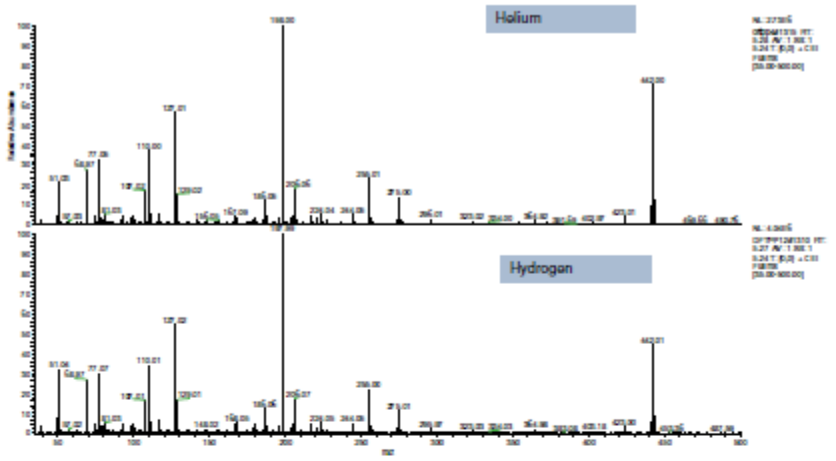
EPA Method 8270 Performance Mix (DFTPP)



22

ThermoFisher SCIENTIFIC

DFTPP (Decafluorotriphenylphosphine) Spectrum



23

ThermoFisher SCIENTIFIC

EPA Method 8270

- **EPA Method 8270**
  - Direct 1 µL liquid injection
  - Calibration (1 – 200 ppm)
  - More than 120 compounds
  - Surrogates = 40 ppm
  - Internal Standards = 40 ppm
- **Goals**
  - Improve peak shape and resolution
  - Improve method runtime (<15 minutes)



Semi-volatile Organics

24

ThermoFisher SCIENTIFIC

Method Parameters: EPA Method 8270D

- **Standards**
  - Prepared in ethyl acetate
  - Calibration curve (1.0, 2.0, 5.0, 10, 50, 100, 200 ug/mL)
- **Inlet**
  - S/SL: 325° C
  - Split Mode: 15:1
- **Carrier: 1 mL/min H_2**
- **Column**
  - TG-5 SilMS 20m x 0.18mm x 0.36 µm

- **Oven:**

50°	1 min.	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	20°/min
350°	0.5 min	

- **MS**

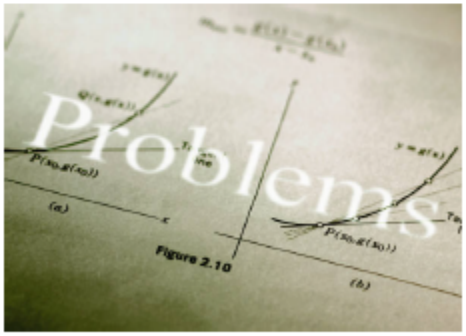
Source	325°
EC	15 uamps
Full Scan	35-500
Scan speed	4,650 amu/ sec

25

ThermoFisher SCIENTIFIC

EPA Method Criteria

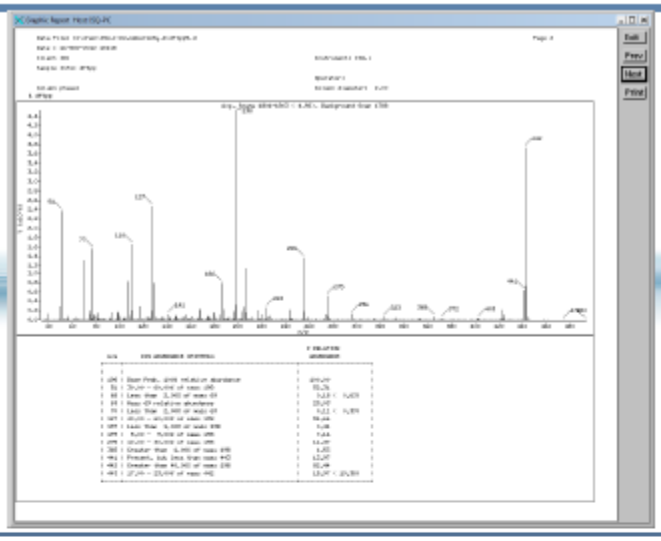
- **Tuning**
  - EPA Method 525/8270: DFTPP
  - EPA Method 524: BFB
- **Calibration**
  - Establish working range for each method (measurement of accuracy)
  - Method Detection Limits (MDLs)



26

ThermoFisher SCIENTIFIC

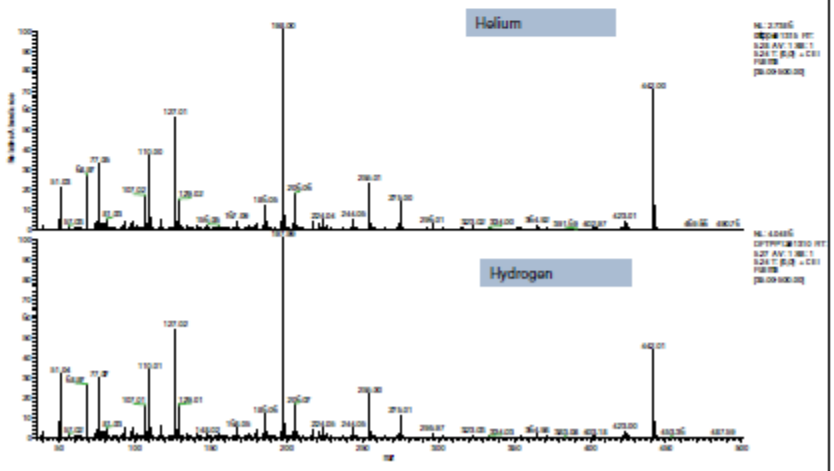
Target DFTPP H_2 Tuning Report in Target Software



27

ThermoFisher SCIENTIFIC

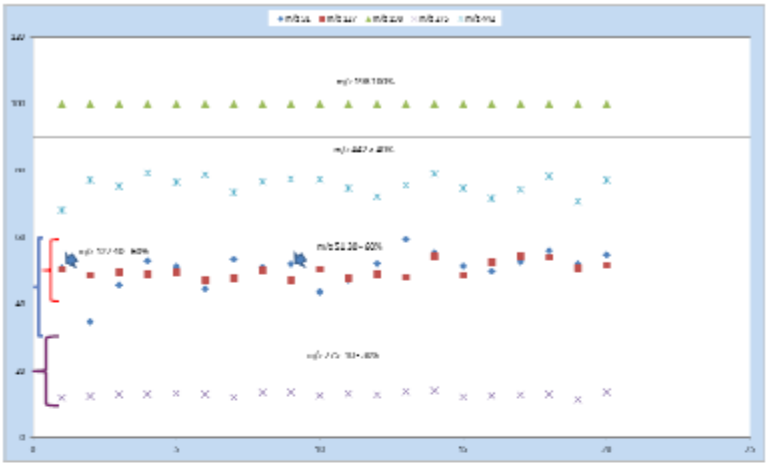
DFTPP (Decafluorotriphenylphosphine) Spectrum



28

ThermoFisher SCIENTIFIC

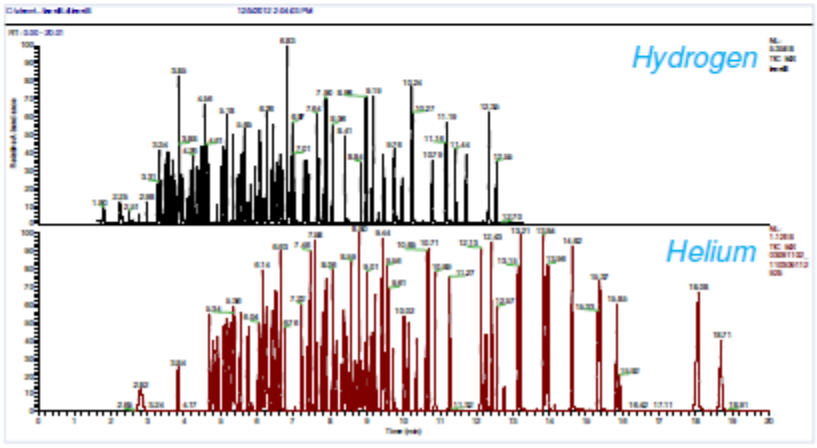
Ion Ratio Stability for DFTPP



29

ThermoFisher SCIENTIFIC

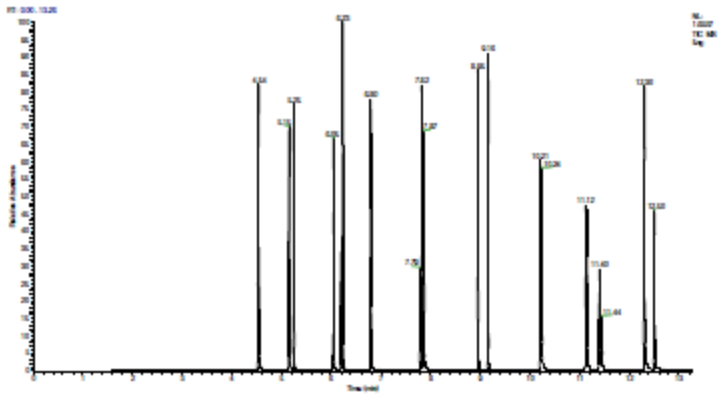
8270: Comparison of Hydrogen to Helium Run Times



30

ThermoFisher SCIENTIFIC

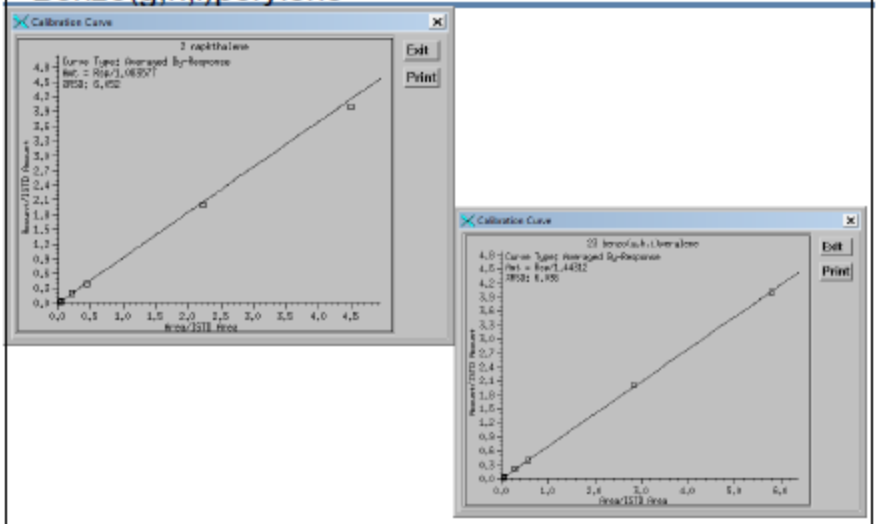
Low Level PNAs in SIM



31

ThermoFisher SCIENTIFIC

Calibration Curves: Naphthalene & Benzo(g,h,i)perylene



32

ThermoFisher SCIENTIFIC

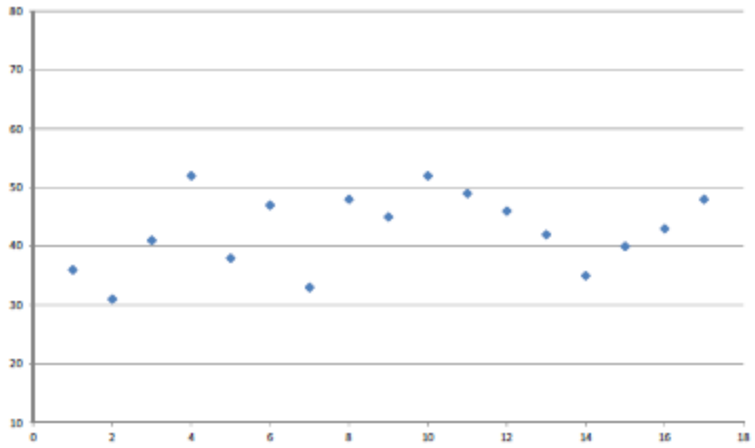
Linear Fit of Low Level PNAs in SIM (0.05 to 10 ppm)

Compound	%RSD	Compound	%RSD
naphthalene	6.1	flouranthene	6.7
2-methylnaphthalene	8.7	benzo(a)anthracene	8.2
1-methylnaphthalene	7.7	chrysene	5.9
acenaphthylene	8.5	benzo(b)fluoranthene	8.6
acenaphthene	8.5	benzo(k)fluoranthene	9.2
flourene	8.5	benzo(a)pyrene	7.8
phenanthene	3.8	indeno(1,2,3,c,d)pyrene	5.1
anthracene	7.0	dibenz(a,h)anthracene	5.4
pyrene	3.6	benzo(g,h,i)perylene	6.0
acenaphthene-d10	4.6	phenanthene-d10	4.5
chrysene-d12	9.7	perylene-d12	7.4

33

ThermoFisher SCIENTIFIC

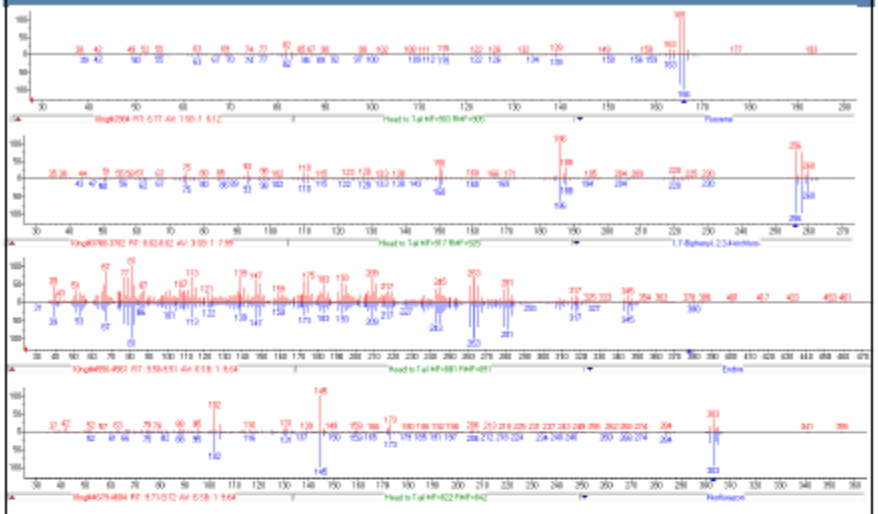
Low Level PNAs 50 ppb (+/- 50%) Accuracy



34

ThermoFisher SCIENTIFIC

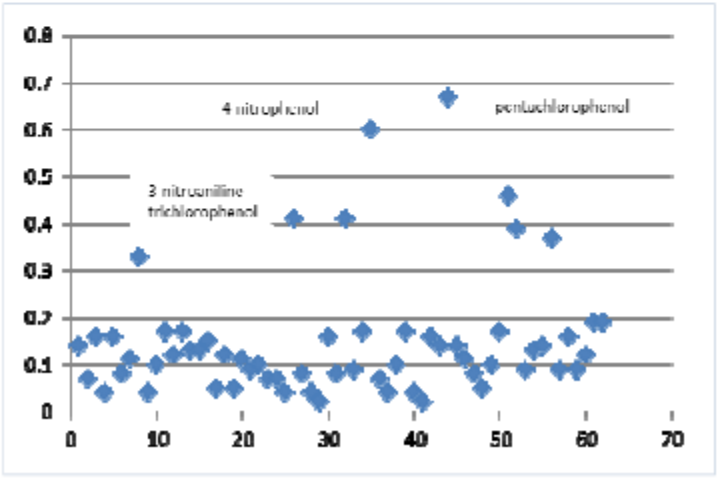
Spectral Purity: NIST Library Match



35

ThermoFisher SCIENTIFIC

8270 Sensitivity and IDLs



38

ThermoFisher SCIENTIFIC

EPA Methods 524 and 525 – Drinking water

- **EPA Method 524**
  - Purge & Trap
  - 5 mL sample volume
  - Calibration (0.4 – 200 ppb)
- **EPA Method 525**
  - Direct 1 µL liquid injection
  - 1 liter sample volume
  - Calibration (0.1 – 10 ppm)



Volatile and Semi-volatile Organics

37

ThermoFisher SCIENTIFIC

Method Parameters: EPA Method 524.2

- **Purge & Trap: 5 mL sample**

VOCARB	Purge	11 min
	Dry Purge	1 min
Desorb	240°	2 min

- **Oven**

50°	1 min.	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	

- **Inlet**
  - S/SL: 200°
  - Split : 40:1
- **Carrier: 0.7 mL/min H_2**
- **Column: TG VMS 0.18 mm x 20 m x 1.0 µm**

- **MS**

Source	275°
EC	25 uamps
FS 0.8-1.6 1.6- 15 min	47-300 35-300
Scan Speed	1,687 amu/sec

38

ThermoFisher SCIENTIFIC

Method Parameters: EPA Method 525.2

- **Standards**
  - Prepared in ethyl acetate
  - Calibration curve (0.1, 0.5, 1.0, 2.0, 5.0, 10 ug/mL)

- **Oven:**

50°	1 min	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	20°/min

- **Inlet**
  - S/SL: 325° C
  - Split Mode: 15:1
- **Carrier: 1 mL/min H_2**
- **Column**
  - TG-5 SilMS 20m x 0.18mm x 0.36 µm

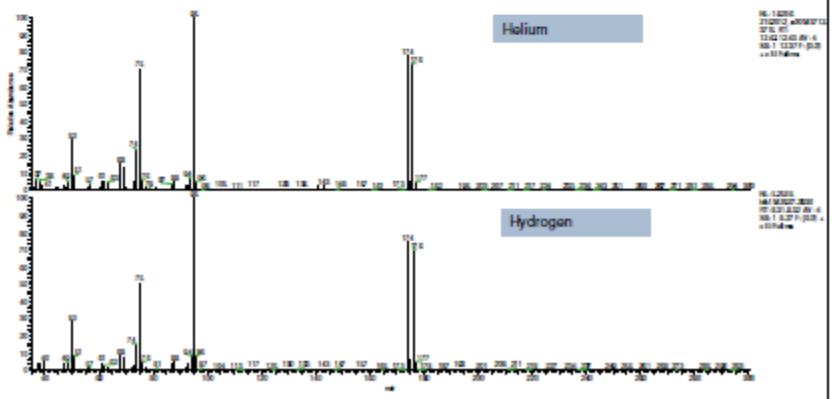
- **MS**

Source	325°
EC	15 uamps
Full Scan	35-500
Scan speed	4,650 amu/ sec

39

ThermoFisher SCIENTIFIC

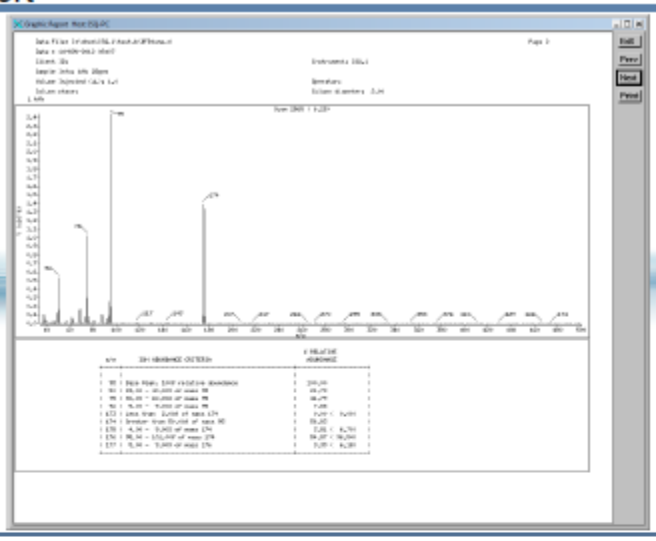
BFB (1-bromo-4-fluorobenzene)



40

ThermoFisher SCIENTIFIC

Target BFB (4-Bromofluorobenzene) H_2 Tuning Report



41

ThermoFisher SCIENTIFIC

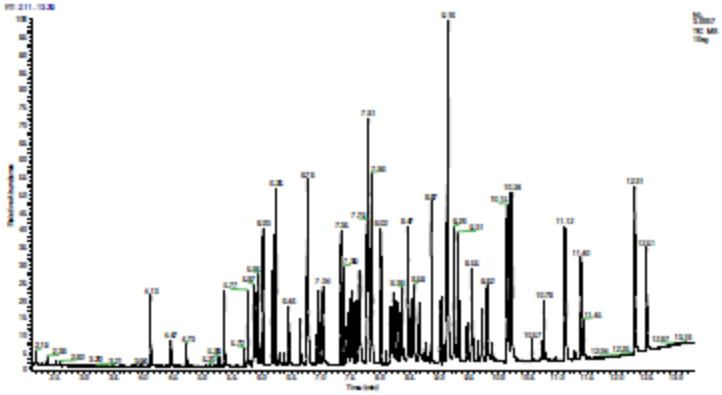
BFB Ion Ratio Stability

m/z	Criteria	run01	run02	run03	run04	run05	run06	run07	run08	run09	run10	run11
50	15-40%	28	26	26	24	27	26	25	26	28	25	25
75	>30%	52	51	48	48	51	52	49	48	48	50	53
95	100%	100	100	100	100	100	100	100	100	100	100	100
96	5-9%	8.0	7.3	7.9	7.7	8.2	7.2	7.7	7.4	7.8	7.5	7.7
173	< 2% of 174	0.4	0.6	0.7	1.5	0.4	0.4	0.8	0.7	0.5	1.1	0.3
174	>50%	76	75	69	69	75	70	72	72	71	74	72
175	5-9% of 174	7.3	7.4	7.4	5.9	7.6	8.5	6.4	7.7	6.8	6.4	6.7
176	93-101% of 174	96	95	100	96	93	96	98	95	96	101	96
177	5-9% of 176	5.1	6.3	6.6	5.2	6.4	6	5.1	5.5	6.6	6.5	6

42

ThermoFisher SCIENTIFIC

Performance: EPA Method 525 10 ppm Standard



43

ThermoFisher SCIENTIFIC

Performance: EPA Method 524.2

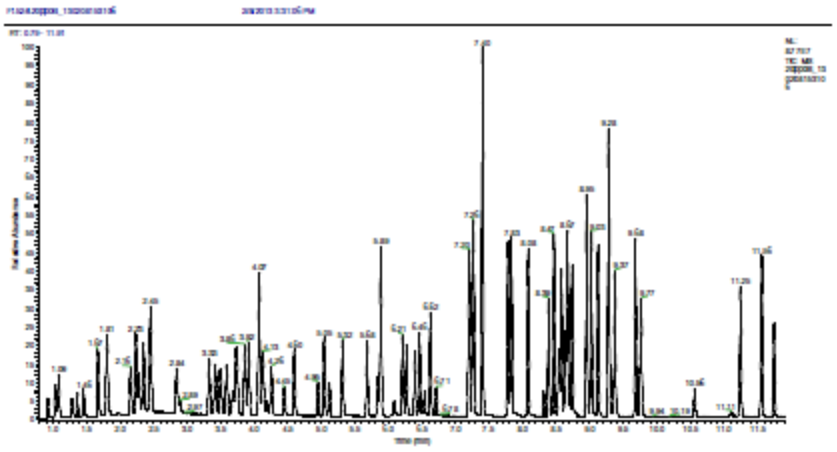
- Method parameters
- Spectral integrity
  - #1 Match to NIST
- Accuracy(0.4 – 200 ppb):
  - Passed at all levels
- **Average MDL: 0.074 ppb vs 0.048 ppb in helium**
- BFB Ion ratio stabile

Passes QC for EPA Method 524.2

44

ThermoFisher SCIENTIFIC

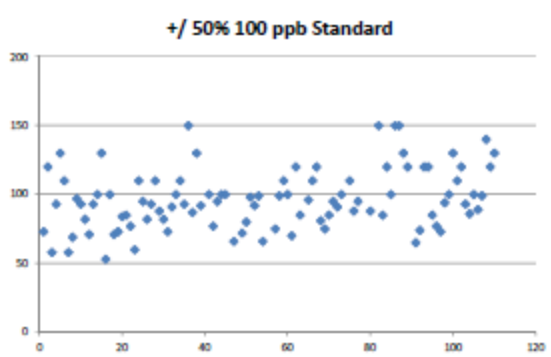
Performance: EPA Method 524 - 20 ppb Standard



45

ThermoFisher SCIENTIFIC

EPA Method 525: Measurement of Accuracy (+/- 50%)

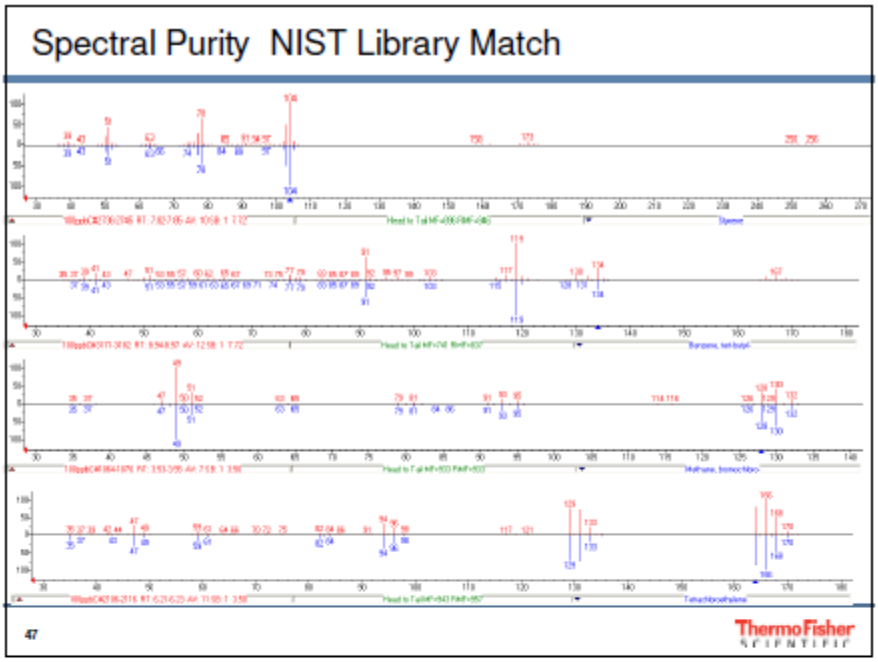


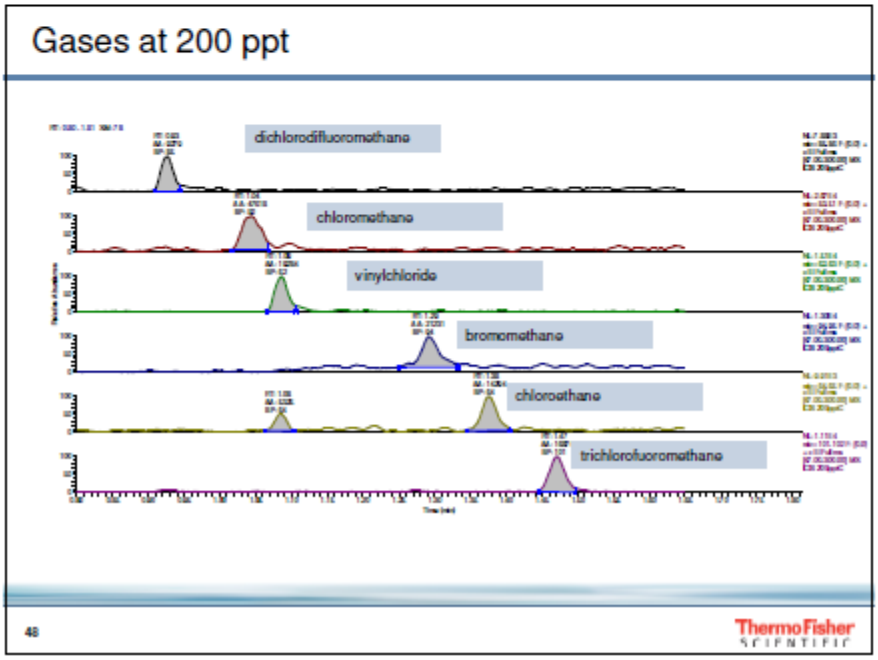
Failed
pentachlorophenol
terbacil
metribuzin
bromacil
chlorpyrifos
trans-nonachlor
carboxon
Dieldrin
tricyclazole

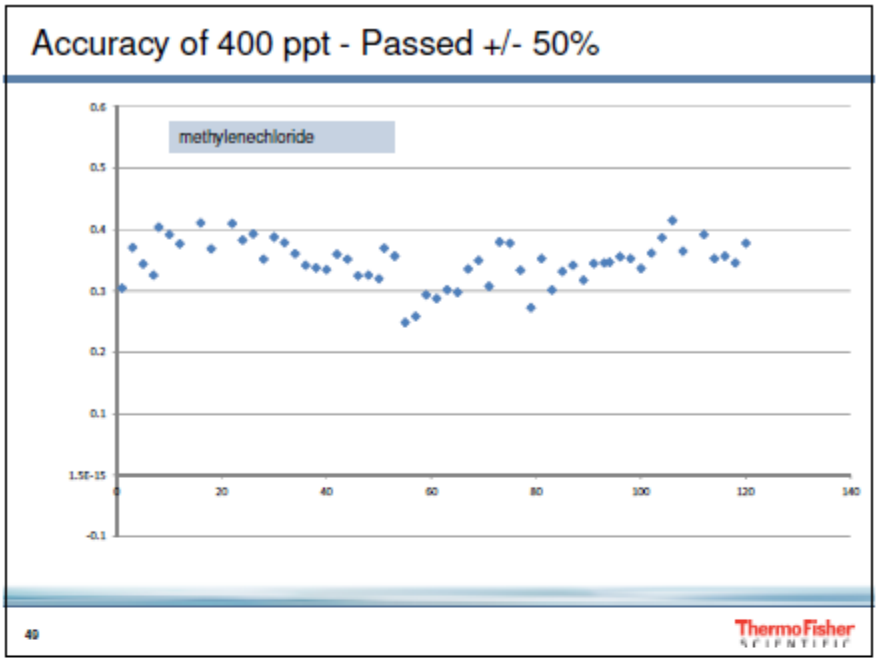
Calibration: 0.1,0.5,1,2,5,10 ppm in Full Scan

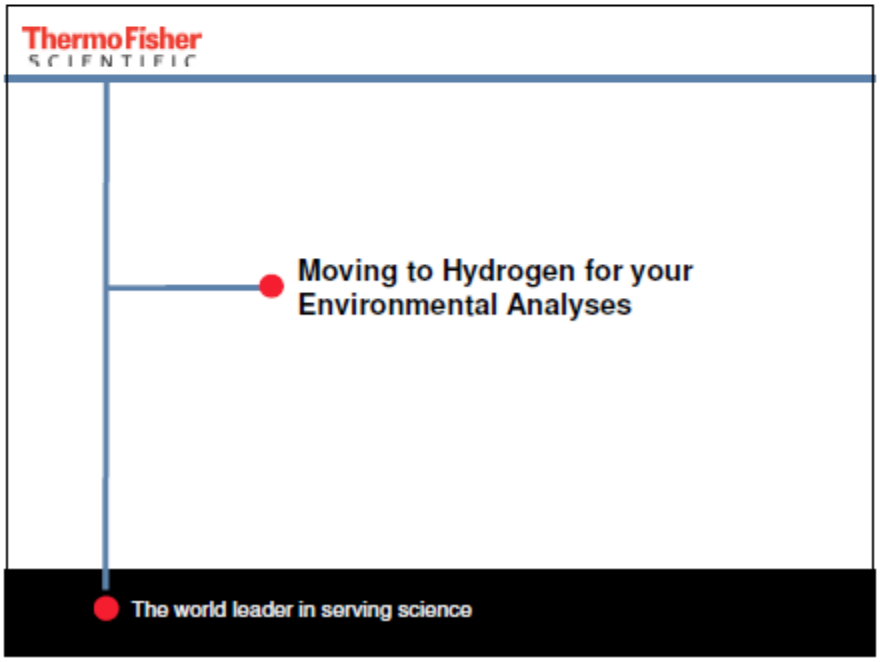
48

ThermoFisher SCIENTIFIC


Spectral Purity NIST Library Match
47
ThermoFisher
SCIENTIFIC


Gases at 200 ppt
dichlorodifluoromethane
chloromethane
vinylchloride
bromomethane
chloroethane
trichlorofluoromethane
48
ThermoFisher
SCIENTIFIC


Accuracy of 400 ppt - Passed +/- 50%
methylenechloride
0.6
0.5
0.4
0.3
0.2
0.1
1.5E-15
-0.1
0
20
40
60
80
100
120
140
49
ThermoFisher
SCIENTIFIC


ThermoFisher
SCIENTIFIC
Moving to Hydrogen for your Environmental Analyses
The world leader in serving science

Moving To Hydrogen on the GC Side

- **Hydrogen Sensor is a *Must***
  - In GC oven
  - Possible on the hydrogen generator
  - May also be required at the ceiling of the lab
- **Expect Lower Inlet Pressure**
  - Due to viscosity differences of H_2 and He
  - Move to a smaller id column



51

ThermoFisher SCIENTIFIC

Moving to Hydrogen on the MS Side

- ***NO*** **MS hardware change required to meet H_2 Installation Specs**
- **Maintain good vacuum**
  - Extended performance turbomolecular pumps
  - 9.8 x 10 $^{-6}$ Torr (1 ml/min hydrogen flow)
- **Higher initial background**
  - Minimized with stainless steel pre-cleaned tubing
  - UHP Grade 5.0 or better Hydrogen Source
  - Bake out source at 350° C for one hour with filament on
- **CI Effect on some compounds**
  - Require linear or quadratic fit
  - Reduce flow rate of H_2 into MS
- **Pressure dependency:**
  - Minimize solvent vapor with smaller id columns



ISQ Off-Axis Single Quadrupole GC-MS

52

ThermoFisher SCIENTIFIC

Conclusion: Moving to Hydrogen Carrier Gas

- Considerations
  - Gas purity
  - Safety
  - Column selection
  - Column flow rate
  - Mass spectrometer modifications:
    - Hydrogen kit



Meets QC requirements for EPA Method 524 and 525

53

ThermoFisher SCIENTIFIC

Thank you for your attention!



Questions?

Stay connected with us!

Twitter
@ChromSolutions

Chromatography Solutions Blog
http://chromblog.thermoscientific.com/blog

YouTube
http://www.youtube.com/ChromSolutions

Facebook
http://www.facebook.com/ChromatographySolutions

Pinterest
http://pinterest.com/chromsolutions/

54

ThermoFisher SCIENTIFIC

SECTION 10

AIR METHODS/MONITORING: COMPLIANCE MONITORING AND REGULATORY ISSUES

USEPA's Technology Innovation Network: Evaluating Pilot Projects on Air Sensors and Monitoring

Anand Mudambi, Martha Otto, Matt Hoagland
USEPA

Abstract

EPA has developed a Technology Innovation Network to help promote innovative environmental technologies along the continuum of technology development and deployment. The Network is a working group comprised of senior representatives across EPA programs and offices. One of the initial tasks of the Network is to pursue technology innovation opportunities in cross-program areas, one of which is air sensors. The Network will showcase pilot projects on air sensors and monitoring that employ innovative ideas on practices, tools, and methods that can be beneficially replicated elsewhere. In evaluating these pilot projects, the Agency will identify barriers to progress, how those barriers were overcome, and lessons learned, including recommended policy options that could be applied in other situations. The Agency also is finding new ways to reach out to the technology development community and, as a first step, is identifying priority environmental technology needs where innovation could lead to major improvements, efficiencies, and private sector opportunities.

US EPA's Technology Innovation Network: Evaluating Pilot Projects on Air Sensors and Monitoring

Martha Otto
Matt Hoagland,
Anand Mudambi
US EPA

NEMC
San Antonio, Texas
August 2013

Outline

- Technology Innovation and Environmental Protection
- Technology Innovation at US EPA
- Evaluating Air Sensor and Monitoring Projects
- Preliminary Findings and Recommendations
- Next Steps

*NOTE: Reference herein to any specific commercial product, process, or service by trademark, manufacturer, or otherwise, does not imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

2

Technology Innovation and Environmental Protection

Innovative Technologies

- Advance protection of human health and the environment, while furthering economic growth
- Help businesses reduce costs, expand markets, increase profitability

Smart environmental protection creates jobs.

3

EPA Vision for Technology Innovation

- Promote innovation that eliminates or significantly reduces the use of toxic substances and exposure to pollutants
- Seek prospective technological advances that have the greatest potential to achieve multiple environmental goals
- Partner with a diverse set of new and existing stakeholders to speed the design, development and deployment of the next generation of environmental technologies

4

EPA Objectives

- Design EPA policies, regulations, standards, permits, and procedures to leverage technology innovation
- Catalyze technology design, development, finance, commercialization and adoption through partnerships with stakeholders
- Stimulate cross-Agency consideration, development, commercialization, and adoption of breakthrough technologies
- Develop new relationships with the investment community

5

Facilitating Technology Innovation at US EPA

- Science and Technology Policy Council
  - Senior Managers who review select science issues that have relevance across Programs and Regions
- Technology Innovation Steering Committee
  - Senior level managers who guide EPA efforts to promote innovation from development to deployment
- Technology Innovation Network (TIN)
  - Includes representatives across programs and regions
  - Promotes cross-Agency engagement

6

Initial Project Areas Evaluated by the TIN

Air Sensors



Biodigesters and biogas



Automotive Supply Chain



Energy efficiency and wastewater treatment



7

The TIN's Goals in Project Evaluation

- Observe current activities
- Promote visibility of projects
- Identify barriers; how they were overcome; lessons learned
- Raise issues to senior leadership
- Facilitate progress
- Share best practices

8

Project Evaluation Process

- Reach out to EPA leaders in each topic area
- Collect essential information about the pilot project
  - Goals
  - Objectives
  - Timelines
  - Internal and external participants
  - Innovations
  - Barriers

9

Air Sensor and Monitoring Projects Evaluated

- Office of Air and Radiation's AirNOW program
- Office of Enforcement and Compliance's Next Generation compliance program
- EPA Region 2 community grants for participatory monitoring

10

Air Sensor and Monitoring Projects Evaluated (Cont.)

- EPA Region 6 sensor technology initiatives
- Open source challenge: benzene monitor
- "Open House" for air sensor evaluation and collaboration
- Village Green project

11

Preliminary Findings

- Challenges for cross-Agency projects
- Technical issues
- Regulatory hurdles
- The need for collaboration

12

Cross-Agency Projects

Finding:

- Many of the most promising technology innovation efforts are cross-program, but have varying levels of support for funding, staffing commitments, accountability

Preliminary Recommendations:

- Senior level champions
- Matrix management
- Ongoing commitment to technology innovation for the long term, especially when regulations are not the driving forces

13

Technical Issues

Findings:

- Sensor evaluation and calibration
- Management and analysis of increasing amounts of data
- Externally generated data quality and reliability

Preliminary Recommendation:

- Work (across Agency program and regional offices) to develop a unified and consistent approach to addressing technology verification and data management issues

14

Regulatory Hurdles

Findings:

- Regulations that are based on a specific technology might preclude the use of innovative technologies
- Difficulties in crafting regulations to ensure flexibility

Preliminary Recommendation:

- Develop Cross-Agency workgroup to focus on overcoming identified regulatory hurdles, with a clear understanding of potential legal and health-related risks

15

The Need for More Collaboration

Finding:

- Various stakeholders working on similar projects, with limited resources

Preliminary Recommendations:

- Increase communication and collaboration across the Agency programs and offices
- Leverage resources by collaborating with other Federal agencies, states, businesses, associations
- Engage the community (citizen science)

16

Epifunnies by Blazek



17



Martha Otto
USEPA/ Office of the Science Advisor
(202)564-2782
Otto.martha@epa.gov

Matt Hoagland
USEPA/Region 1
(617) 918-1361
Hoagland.matt@epa.gov

18

RADNET
Tracking Environmental Radiation Nationwide

National Radiation Air Monitoring Network

National Environmental Monitoring Conference

San Antonio -- August 6, 2013

Dan Askren & Scott Telofski
National Analytical Radiation Environmental Laboratory
Montgomery, Alabama
US EPA, Office of Radiation and Indoor Air

RADNET

Overview

- Introduction to EPA's Radiation Monitoring Program
  - RadNet's mission and objectives
  - RadNet as an upgrade to the existing ERAMS system
    - Air, Milk, Precipitation, Drinking Water
- RadNet's Air Monitoring Functional Capabilities
  - Fixed and Deployable Monitors
    - Detection, Usage and Siting
  - Data Sharing
- Response to Fukushima Nuclear Incident

RadNet's Mission

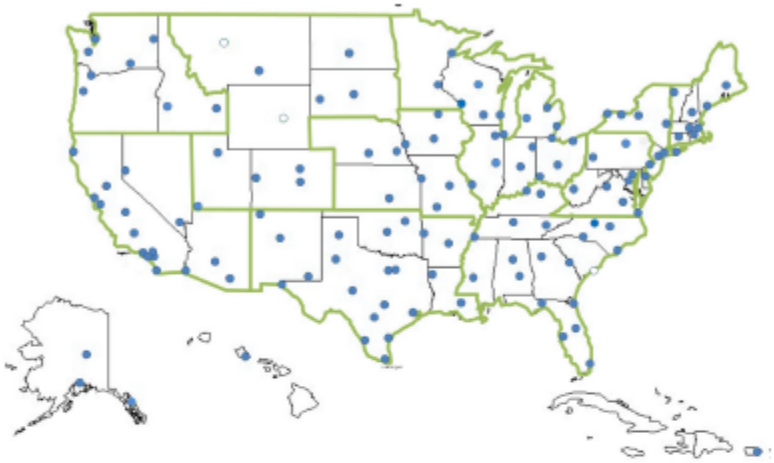
- EPA has developed a nationwide environmental radiation monitoring system known as RadNet
  - To track national / regional ambient radiation levels
  - To identify the degree and extent of contamination in the event of an emergency
- RadNet
  - supports EPA's role in incident assessment
  - focuses on monitoring potential impacts to population and public health

RadNet Objectives

- RadNet provides data quickly in the event of a radiation incident to
  - Decision makers for use concerning potential actions to protect public health
  - Dispersion modelers to assist in predicting/refining source term and dispersion characteristics
  - Nuclear/rad health experts to enable further assessment of national impact
- RadNet, for the most part, provides data related to a known radiological incident such as Fukushima
  - There may be instances where RadNet provides initial information (e.g., a foreign incident, pre-deployment)

RADNET

Fixed Air Monitor Sites



RADNET

RadNet Objectives (continued)

- RadNet data helps
  - Determine large scale national impact of a radiological incident
  - Provide better and timely data to modelers for long distance transport estimates
  - Provide exposure data for large areas of population to assist in protective action recommendations, follow-up monitoring and assessment, and population dose reconstruction

RadNet Objectives (continued)

- RadNet is not intended to
  - Be regulatory
  - Monitor nuclear facilities
  - Provide an early warning system for nuclear accidents
  - Provide a means to monitor in the immediate locality of the incident – this is addressed by other assets.

RadNet Builds Upon ERAMS

- RadNet built upon an existing ambient monitoring network known as Environmental Radiation Ambient Monitoring System (ERAMS)
- Like ERAMS, RadNet is multimedia:
  - air particulates, precipitation, drinking water and milk
- RadNet monitors and sampling efforts are operated by volunteers from EPA Regions, State and County programs
- Information collected by RadNet is publicly available
- Attributes of RadNet high-volume air samplers

RADNET

Monitoring of Other Media

- Precipitation
- Drinking Water
- Milk

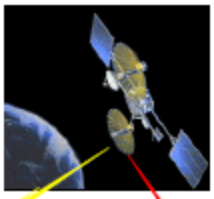
RADNET

Fixed Monitor Installations



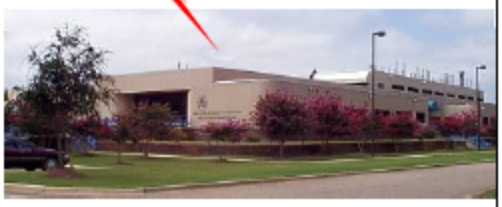
RADNET

Each fixed air monitor provides real-time capability and sends data directly to the NAREL facility automatically- a feature shared with RadNet's deployable air monitors.



Data are transmitted by satellite telemetry, cell phone, telephone modem, and internet communications.





RADNET

Fixed Monitors

- First installation 2006
- 131 Installed
- Tested to withstand temperature extremes
- Tested to evaluated sampling efficiency
- Data publically available



RADNET

Wind Tunnel Testing





RADNET

Wind Tunnel Testing





RADNET

Fixed radiation air monitoring stations have a high volume air sampler and a gamma spectrometry detector, allowing for continuous monitoring of radiation emanating from particles collected on the air filter.





In addition, the air filters are sent to the EPA's lab in Montgomery, AL (NAREL) for more sensitive analysis and further identification of radionuclides.



RADNET

The fixed monitor's gamma (sodium iodide) detector is positioned above a 4" polyester filter, which samples at 60 m^3/hr.





RADNET

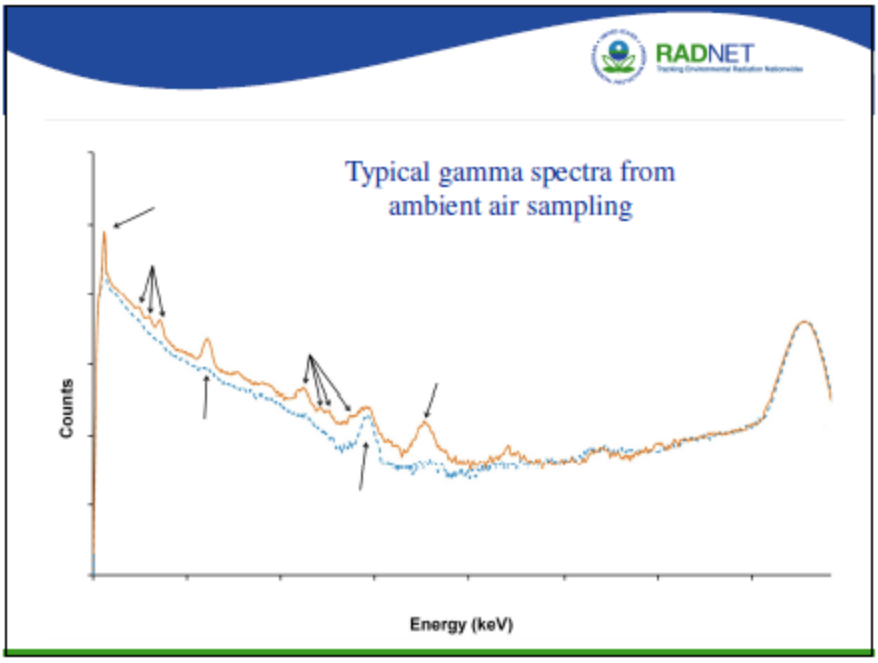
Fixed Monitors Usage

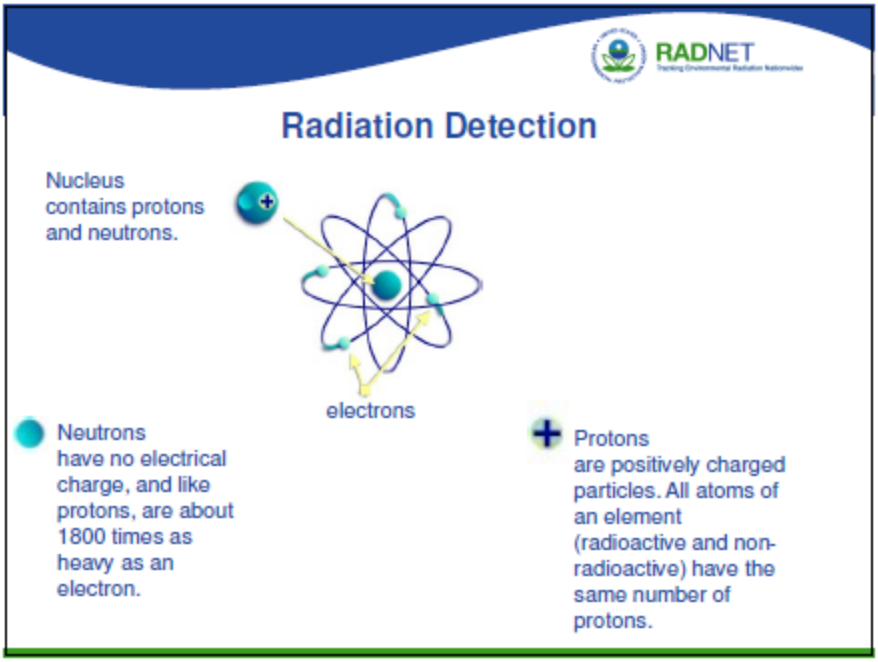
- Collect air sample continuously
- Transmit gamma count rates to the National Analytical Radiation Environmental Laboratory (NAREL) in Montgomery, AL and store spectra locally
- Receive and store data at NAREL, assess incoming data for upper and lower limits, notifies staff with "alarm" for out of range
- Supplement real-time data with analysis on filter

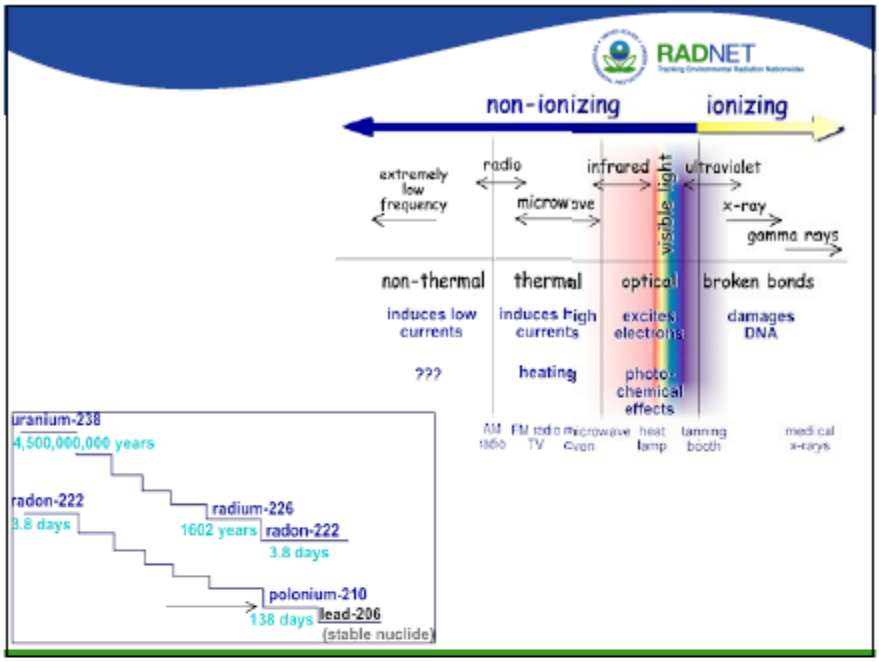
RADNET

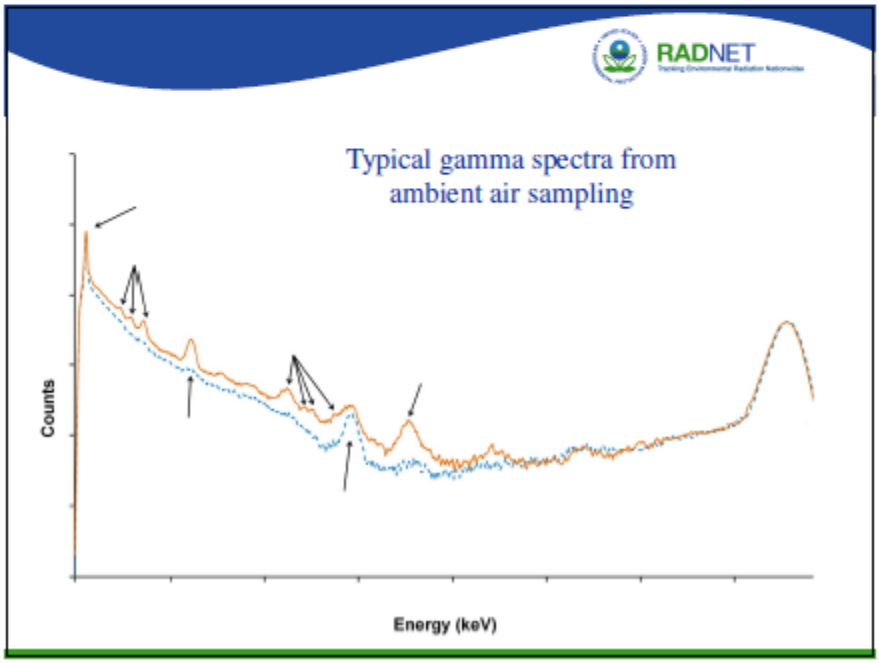
RadNet Control Room Operations

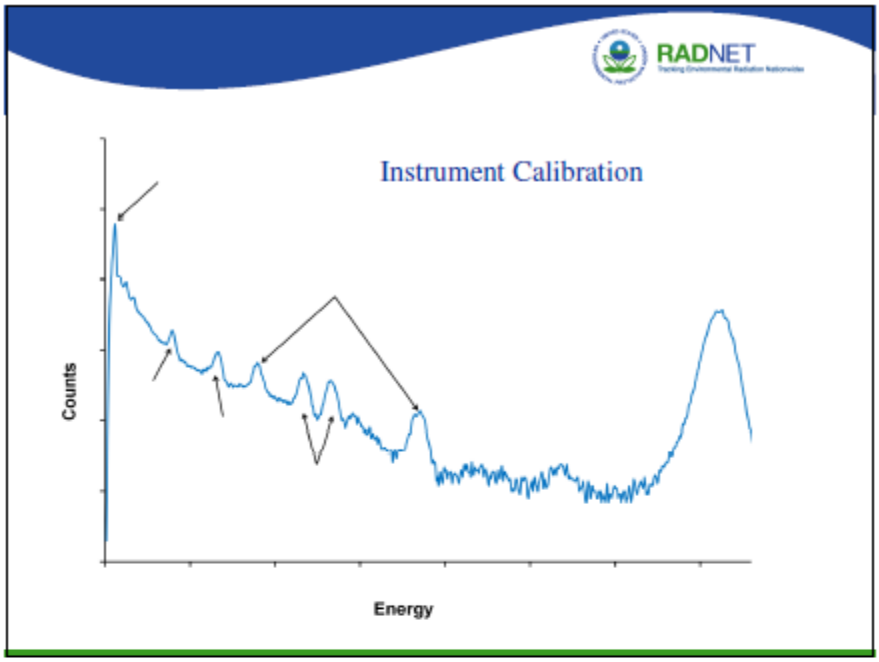


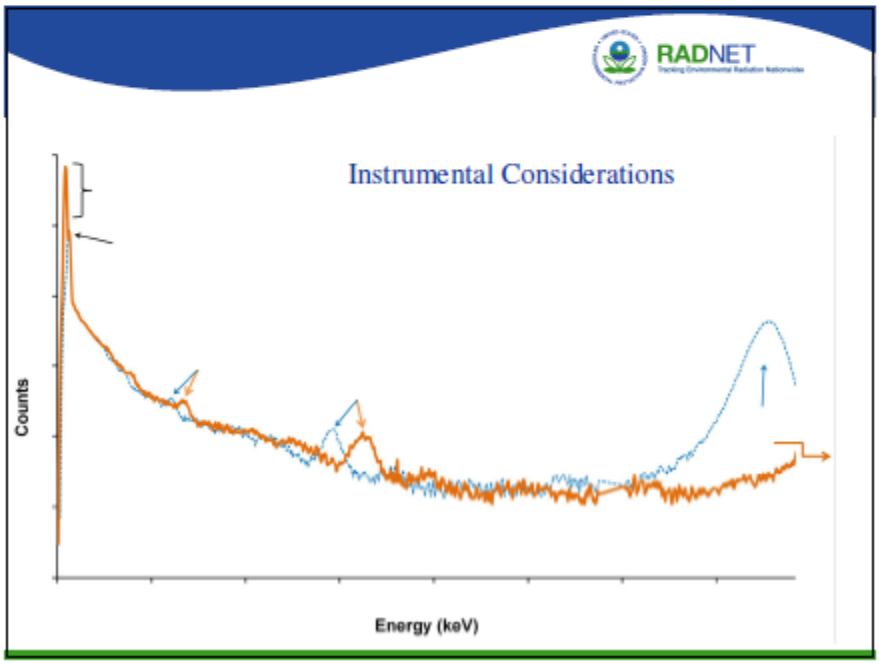

RADNET
Typical gamma spectra from ambient air sampling
Counts
Energy (keV)

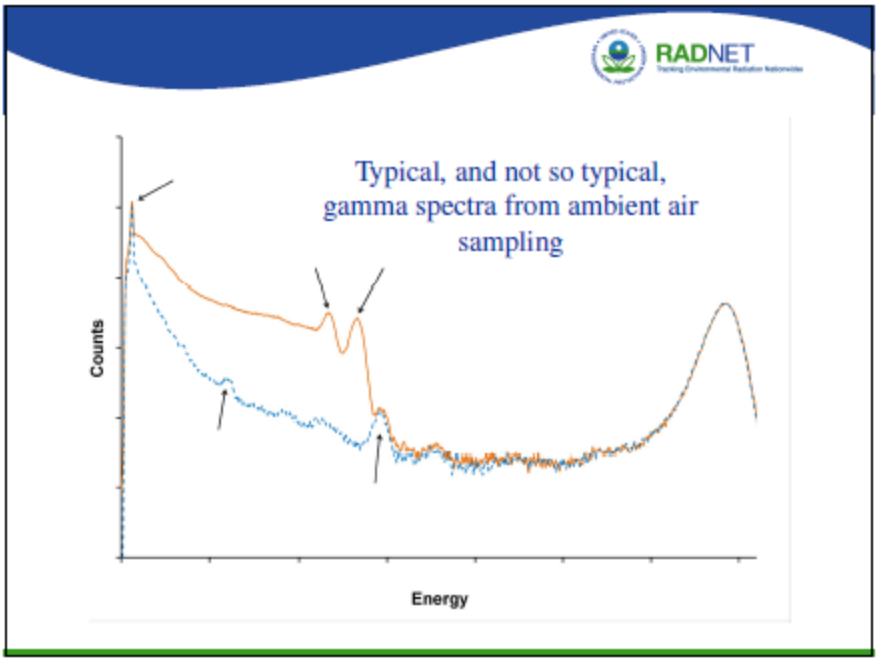

RADNET
Radiation Detection
Nucleus contains protons and neutrons.
electrons
Neutrons have no electrical charge, and like protons, are about 1800 times as heavy as an electron.
Protons are positively charged particles. All atoms of an element (radioactive and non-radioactive) have the same number of protons.

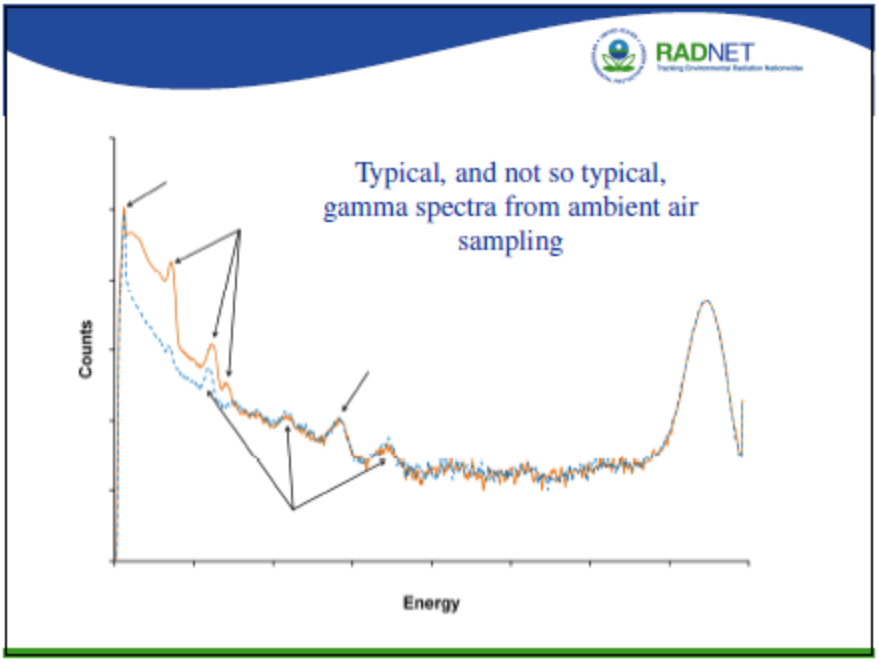

RADNET
non-ionizing
ionizing
extremely low frequency
radio
microwave
infrared
visible light
ultraviolet
x-ray
gamma rays
non-thermal
thermal
optical
broken bonds
induces low currents
induces high currents
excites elections
damages DNA
???
heating
photo-chemical effects
AM radio
FM radio TV
microwave oven
heat lamp
tanning booth
medical x-rays
uranium-238
4,500,000,000 years
radon-222
3.8 days
radium-226
1602 years
radon-222
3.8 days
polonium-210
138 days
lead-206
(stable nuclide)


RADNET
Typical gamma spectra from ambient air sampling
Counts
Energy (keV)


RADNET
Instrument Calibration
Counts
Energy

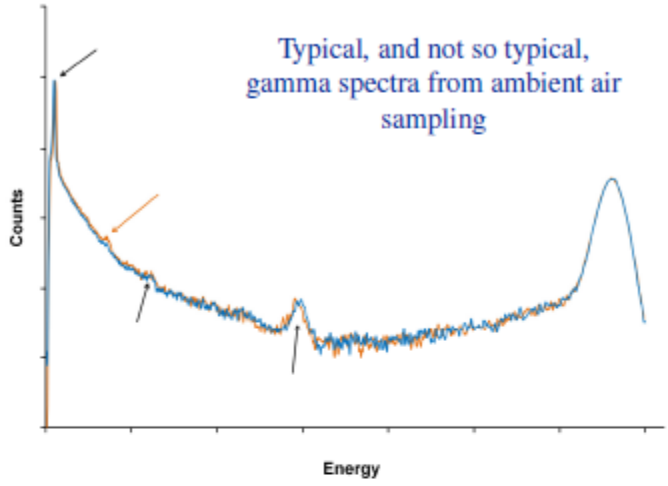

RADNET
Instrumental Considerations
Counts
Energy (keV)


RADNET
Typical, and not so typical, gamma spectra from ambient air sampling
Counts
Energy


RADNET
Typical, and not so typical, gamma spectra from ambient air sampling
Counts
Energy

RADNET

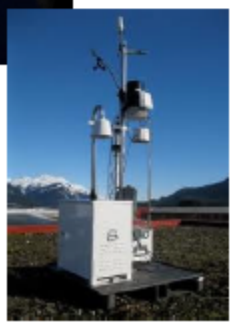
Typical, and not so typical, gamma spectra from ambient air sampling



RADNET

Deployable Monitor Sites







RADNET

RadNet's Deployable Monitors

- A Deployable monitor is a transportable unit that measures ambient gamma radiation levels in near real-time, and also collects airborne radioactivity with high and low-volume air samplers
- The *deployables* are stored in a state of readiness at the Montgomery, Alabama and Las Vegas, Nevada facilities and can be deployed to the scene of a radiological incident or pre-deployed to an event (e.g., Nationally Significant Security Event)

RADNET

Deployable Monitors



- High Volume Air Sampler
- Low Volume Air Sampler
- Gamma Exposure Instrument
- Power Distribution Panel
- Satellite Telemetry
- Data Logger
- PDA
- Platform

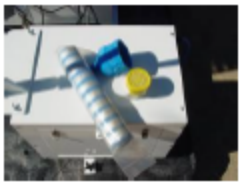
RADNET

Deployable Monitors



Deployable air monitors utilize a glass 4"filter and a glass 2" filter. Alternatively, 2" silver zeolite or charcoal cartridges may be substituted for sampling select nuclides.





RADNET

Deployable Monitor Usage

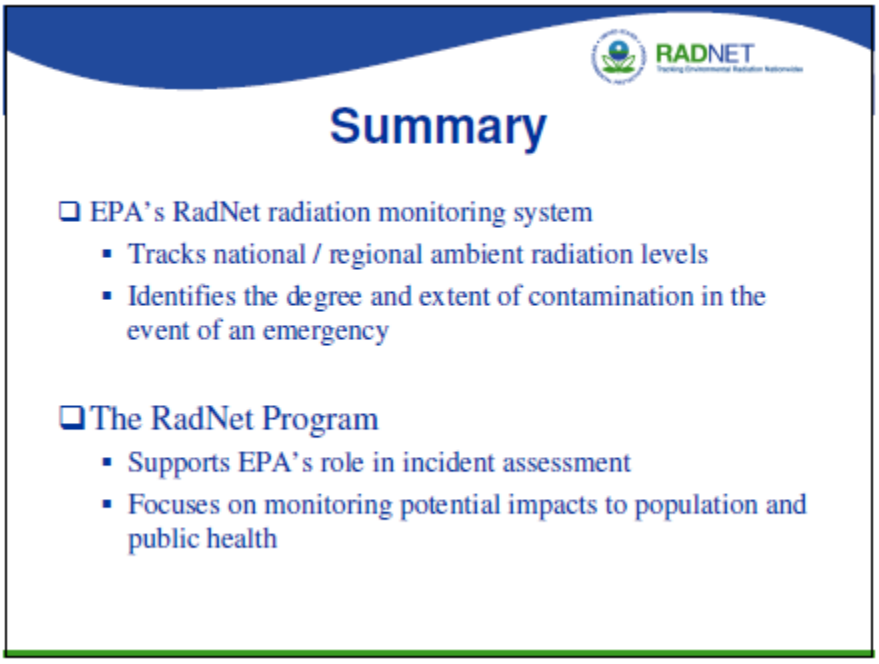
- Air sample operations
  - high volume and low volume air samples
  - charcoal or silver zeolite for iodine vapor capture
- Transmit stored information utilizing an encrypted telemetry system with redundant telecommunications capabilities:
  - Iridium Satellite modem
  - Analog modem
  - PDA download and storage
- Receive and store data at NAREL, assesses incoming data for upper limits, notifies staff with "alarm" for out of range
- Supplement near real-time data with analysis on filter

RadNet Data Sharing

- EPA shares data through CDX & Envirofacts
  - Data are available to the responder community as a priority
  - Data are given sufficient context to be understood by its audience
  - Data sharing remains consistent with Federal policies and the overall Federal response
- EPA's approach to data sharing
  - Provided data and information on the internet with appropriate context and explanation
  - Public Affairs improved public access and messaging during Fukushima response

Fukushima Results

- Reviewed more than 250,000 sets of data
- Analyzed several hundred air, milk, rain, and drinking water samples
- Established deployable monitors in Alaska, Hawaii, Guam, and Saipan
- Real Time monitoring saw one indication for a few hours
- 1,000 to 3,000 minute laboratory counts to see other isotopes in sampled media


RADNET
Summary
EPA's RadNet radiation monitoring system
Tracks national / regional ambient radiation levels
Identifies the degree and extent of contamination in the event of an emergency
The RadNet Program
Supports EPA's role in incident assessment
Focuses on monitoring potential impacts to population and public health

Evolution of Ozone Precursor Measuring and the PAMs Project from 1992 to Present

Lee Marotta
PerkinElmer

Abstract

One of the regulations of the US Clean Air Act of 1992 mandated that States in non-attainment (exceed the allowable level) of ozone precursors monitor these analytes hourly during four months in the summer. The target analyte list contains 55 non-polar compounds in the boiling point range C2 to C11. There were detailed planned points of sampling mostly from city centers or points of emission; for instance, refineries.
In 1998, most of the areas affected were the northeast corridor, the gulf coast, Illinois and Wisconsin. Some sampling sites needed to be at remote locations which required unattended operation.

This presentation will discuss the following:

- Intro to Thermal Desorption
- The initial challenges of this project and how these challenges were successfully overcome from a technical;
- The improvements made in sampling and technology;
- What states have done to make this program more successful;
- How to handle the overwhelming amount of data;
- What has been learnt from this data, and what changes have been implemented to improve the environment;
- Suggestions for the future.

The PAMS program has been beneficial and successful. All aspects including technical, data (information) and logistic, will be covered.

HUMAN HEALTH | ENVIRONMENTAL HEALTH



Ozone Precursor Analyzer

Evolution of Ozone Precursor Measuring and the PAMs Project from 1992 to Present

Carol Mayer, Orsat, LLC
Lee Marotta, PerkinElmer

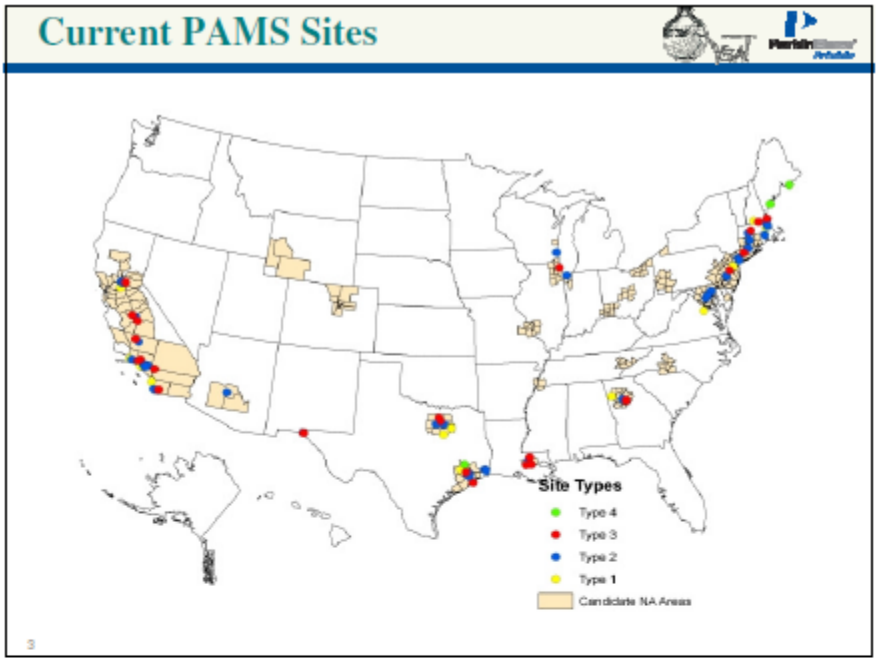
US Clean Air Act of 1992

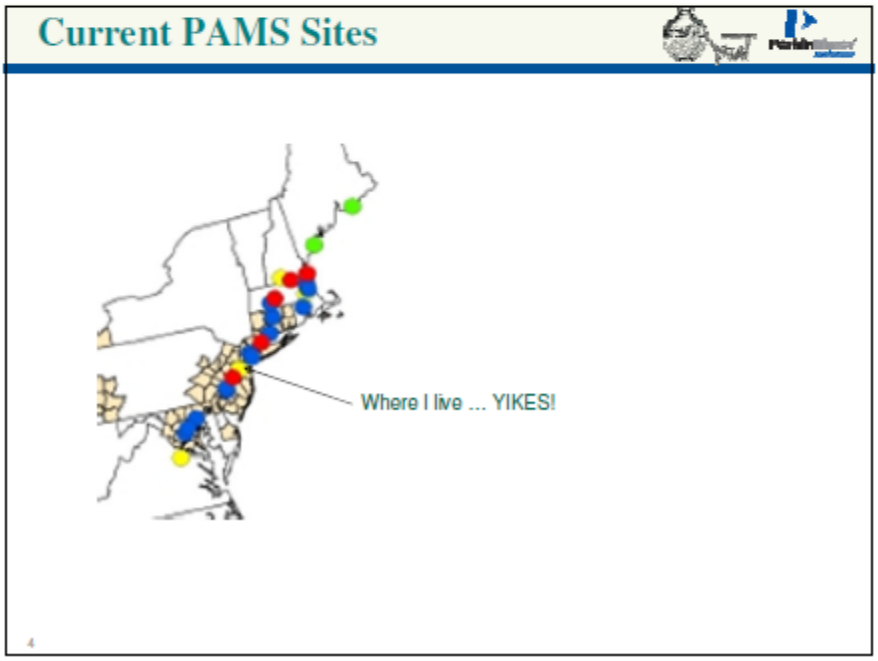


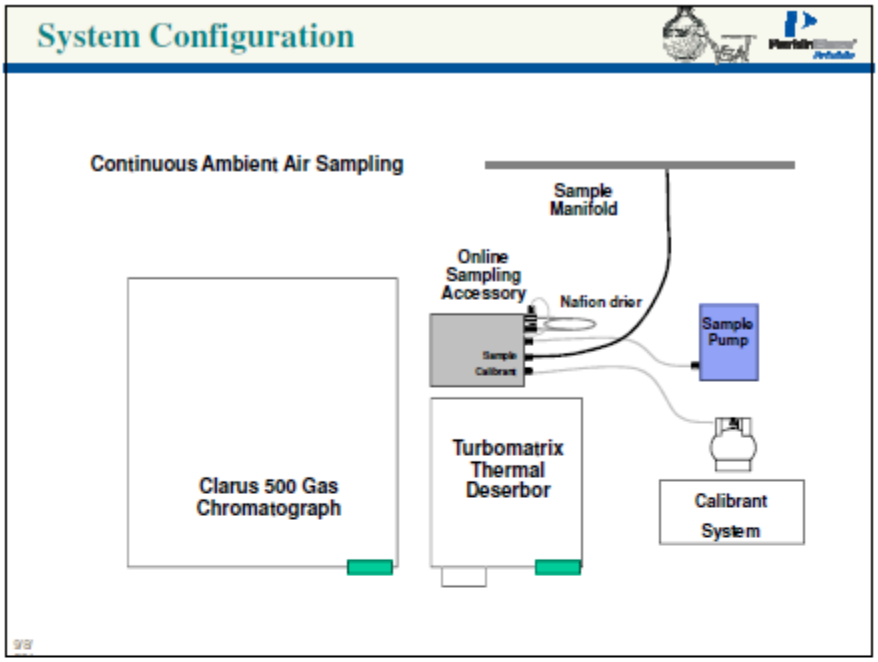
US Mandated to the states in non-attainment of their ozone precursors that they monitor for four summer months a sample every hour.

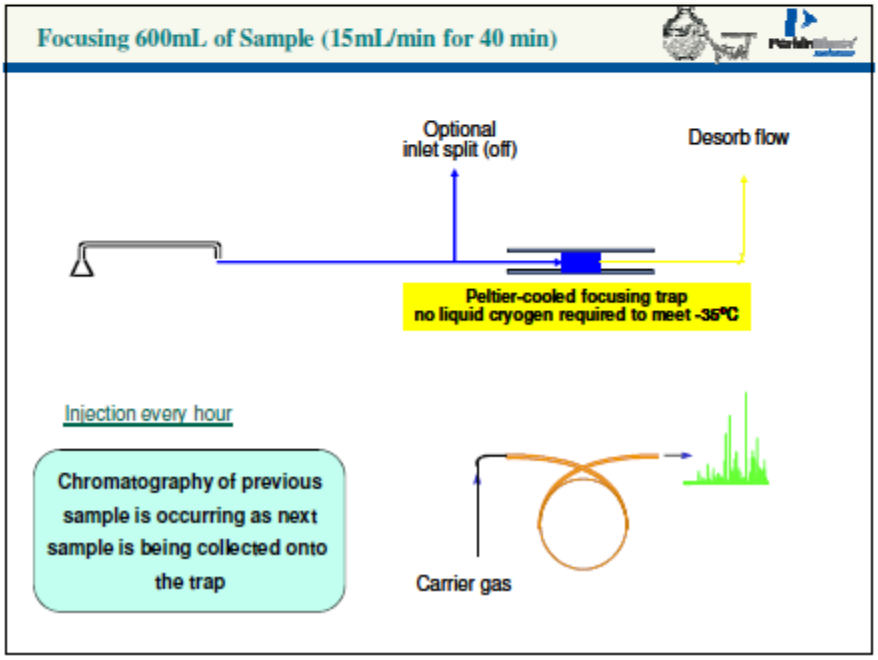
Essentially unattended operation: generators for combustion gases, controlled off-site to both collect data and to control system. A visit to the site every month to change carrier and fuel gases.

An Ozone Precursor?

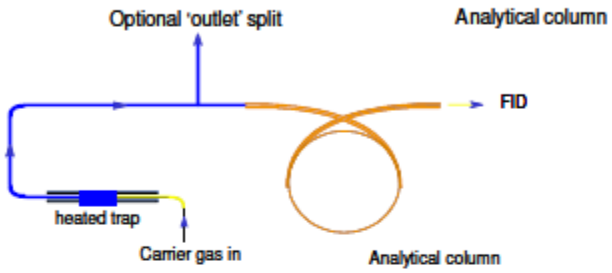

Current PAMS Sites
Site Types
Type 4
Type 3
Type 2
Type 1
Candidate NA Areas
3


Current PAMS Sites
Where I live ... YIKES!
4


System Configuration
Continuous Ambient Air Sampling
Sample Manifold
Online Sampling Accessory
Nafion drier
Sample Pump
Clarus 500 Gas Chromatograph
Turbomatrix Thermal Deserbor
Calibrant System


Focusing 600mL of Sample (15mL/min for 40 min)
Optional inlet split (off)
Desorb flow
Peltier-cooled focusing trap
no liquid cryogen required to meet -35°C
Injection every hour
Chromatography of previous sample is occurring as next sample is being collected onto the trap
Carrier gas

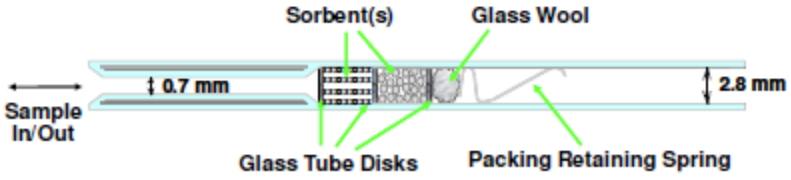
Trap desorption in opposite direction of sampling

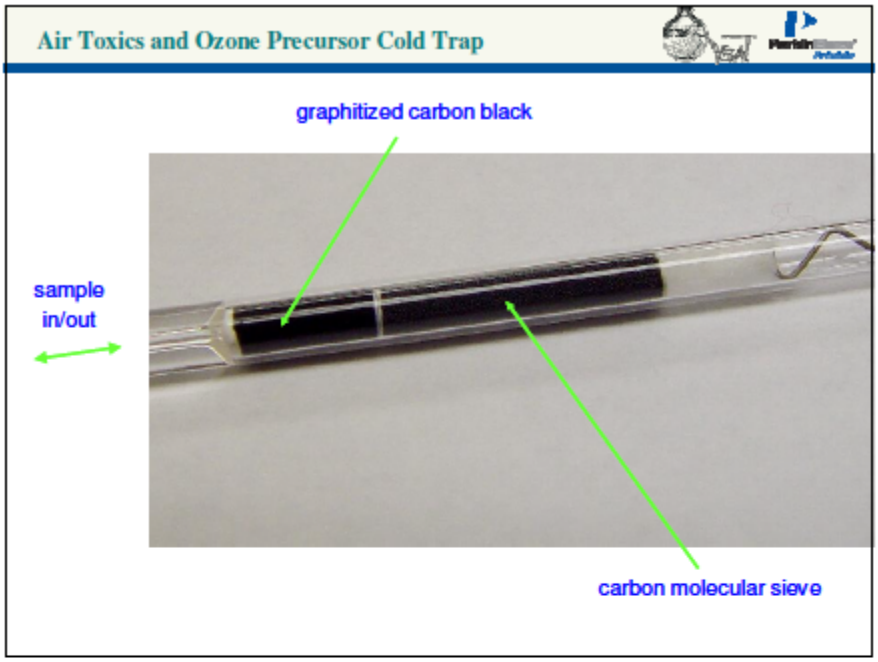


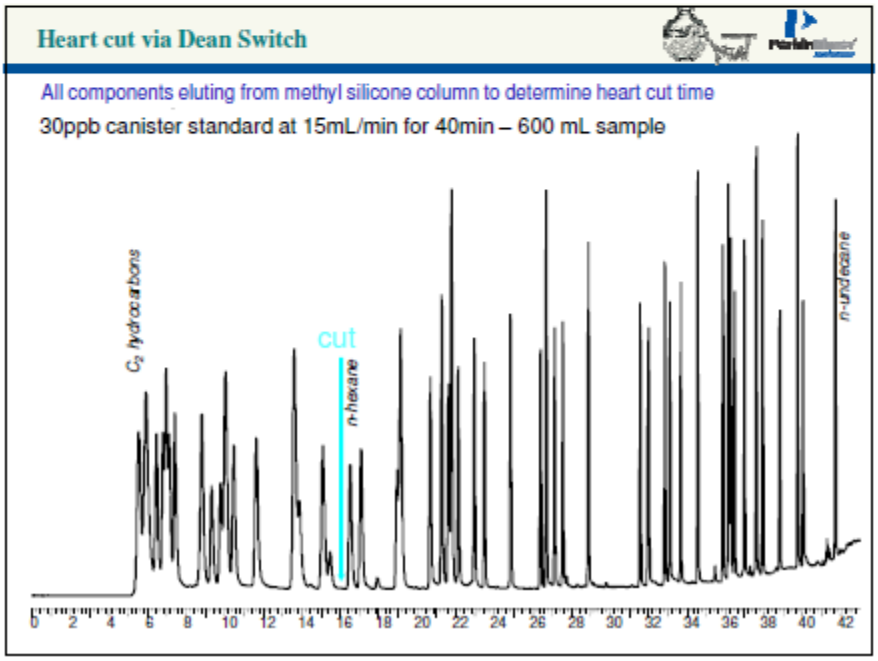
Trap heats at 99 degrees / sec to efficiently desorb cold trap

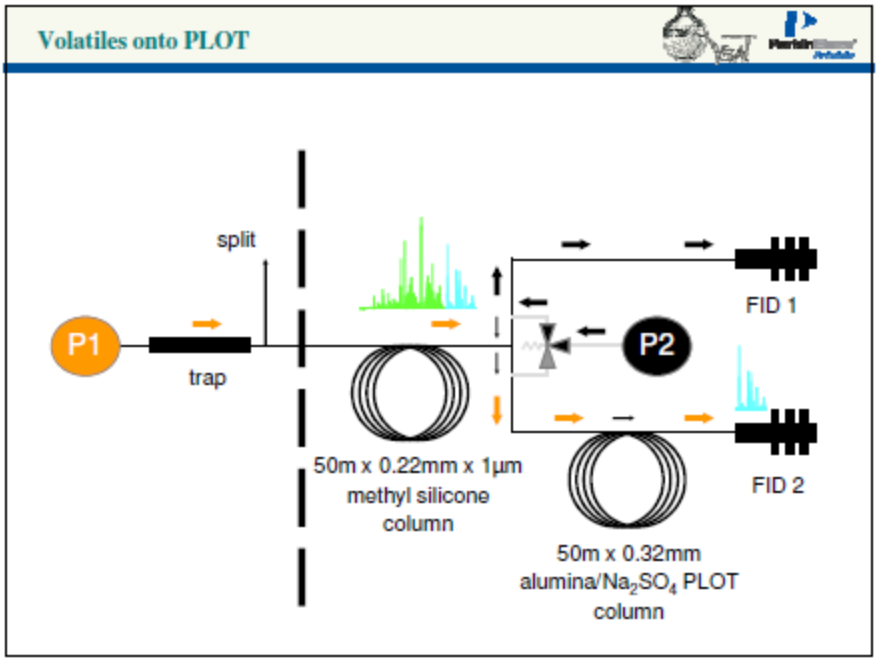
Cold Trap

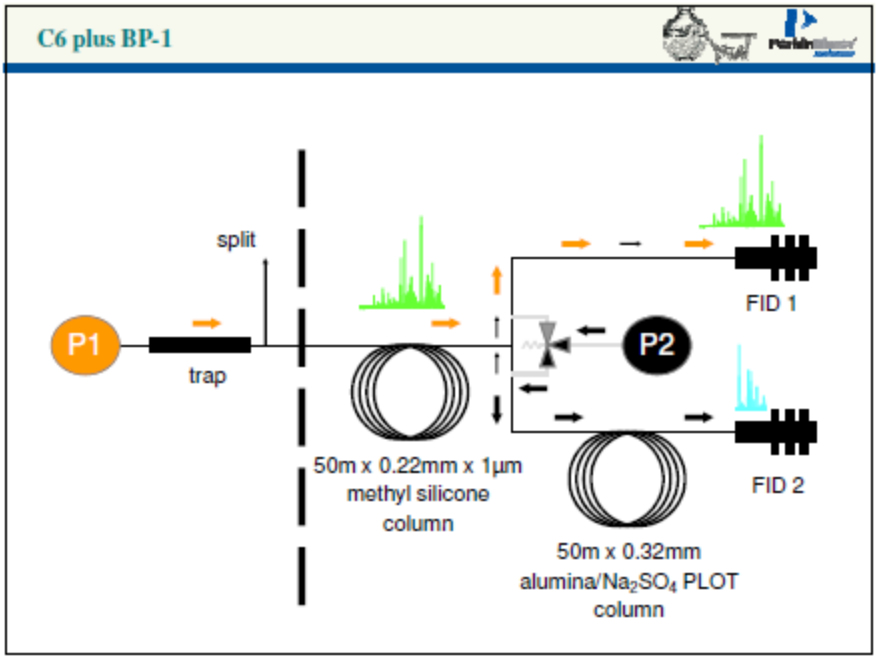
- Reduced diameter outlet reduces analyte dispersion or band broadening for narrower, focused peaks
- Trap is backflushed during desorption to recovery components



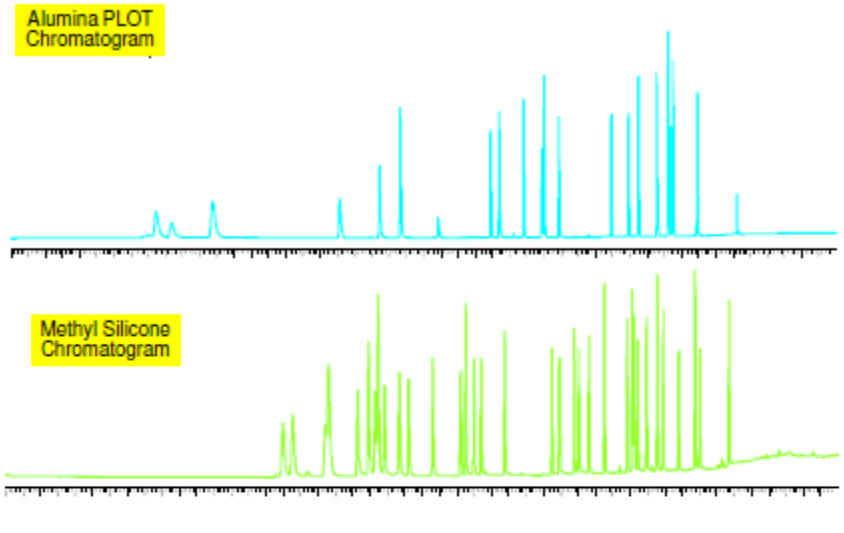

Air Toxics and Ozone Precursor Cold Trap
graphitized carbon black
sample
in/out
carbon molecular sieve


Heart cut via Dean Switch
All components eluting from methyl silicone column to determine heart cut time
30ppb canister standard at 15mL/min for 40min – 600 mL sample
C2 hydrocarbons
cut
n-hexane
n-undecane
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42


Volatiles onto PLOT
split
P1
trap
P2
FID 1
FID 2
50m x 0.22mm x 1µm
methyl silicone
column
50m x 0.32mm
alumina/Na2SO4 PLOT
column


C6 plus BP-1
split
P1
trap
P2
FID 1
FID 2
50m x 0.22mm x 1µm
methyl silicone
column
50m x 0.32mm
alumina/Na2SO4 PLOT
column

Chromatography



Target Analyte List

PLOT Column		BP1 Column		
Methane**	1,3-Butadiene	n-Hexane	2-Methylheptane	n-Decane
Ethane	2-Methyl-1-Butene*	Trans-2-Hexene*	3-Methylheptane	1,2,3-trimethylbenzene
Ethylene	Cyclopentene	Cis-2-Hexene*	N-Octane	m-Diethylbenzene*
Propane	Trans-2-Pentene	Methylcyclopentane	Ethyl Benzene	p-Diethylbenzene*
Propylene	2-Methyl-2-Butene*	2,4-Dimethylpentane	m + p-Xylene	n-Undecane*
Isobutane	1-Pentene	Benzene	Styrene	α-Pinene*
n-Butane	Cis-2-Pentene	Cyclohexane	o-Xylene	β-Pinene*
Acetylene	2,2-Dimethylbutane	2-Methylhexane	n-Nonane	
Trans-2-Butene	2,3-Dimethylbutane*	2,3-Dimethylpentane	Isopropyl Benzene	
1-Butene	2-Methylpentane	3-Methylhexane	n-Propylbenzene	
Isobutene	3-Methylpentane*	2,2,4-Trimethylpentane	m-Ethyltoluene*	
Cis-2-Butene	Isoprene	n-Heptane	p-Ethyltoluene*	
Cyclopentane	4-Methyl-1-Pentene*	Methylcyclohexane	1,3,5- trimethylbenzene	
Isopentane	2-Methyl-1-Pentene*	2,3,4-Trimethylpentane	o-Ethyltoluene*	
n-Pentane	1-Hexene*	Toluene	1,2,4-trimethylbenzene	

* Components no longer reported by TCEQ
** not quantitatively trapped

1994 C.O.A.S.T Project



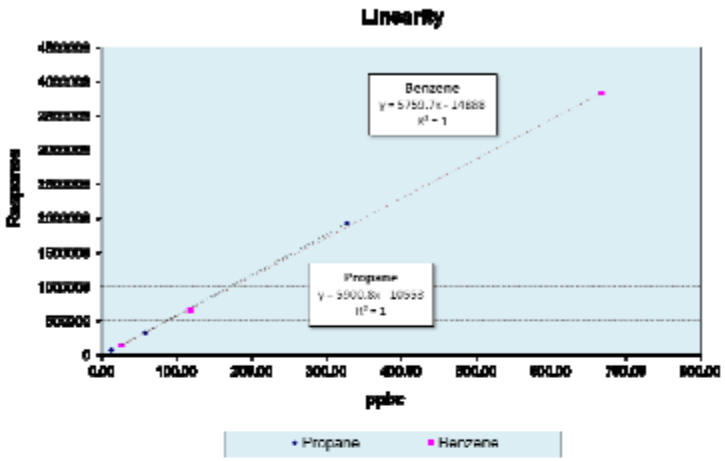
HUMAN HEALTH | ENVIRONMENTAL HEALTH

State of Texas Program Supported by Orsat

Several Requirements

- Capable of separating 56 hydrocarbon species each hour.
- Fully automated to allow automatic introduction of a daily check standard and system blank
- Daily Calibration Verification Standard (CVS)
  - 15 components across boiling point range
  - 3-point calibration curve
- Additional second source standards and retention time standards run weekly
- Automated file handling – generating 144 data files each day/site
- Current Network of 35 sites reporting hourly data (31 public)
- Current Target list of 46 compounds
- Concentrations reported as ppbC

Multi-point Calibration – Propane and Benzene



Air Monitoring Stations in Texas

Region 4 - Dallas - Fort Worth			
Dallas Hinton	Dallas	PAMS	1999
Fort Worth Northwest	Fort Worth	PAMS	2003
Eagle Mountain Lake	Fort Worth - Barnett Shale	CATMN	2010
DISH	Fort Worth - Barnett Shale	CATMN	2010
Decatur	Fort Worth - Barnett Shale	CATMN	2010
Flower Mound	Fort Worth - Barnett Shale	CATMN	2010
Everman	Fort Worth - Barnett Shale	CATMN	2011
Kennedale	Fort Worth - Barnett Shale	CATMN	2012
Mansfield	Fort Worth - Barnett Shale	CATMN	2012
Rhome (TBD)	Fort Worth - Barnett Shale	CATMN	2012
OD Wyatt (TBD)	Fort Worth - Barnett Shale	CATMN	2012
UT Arlington Campus	Fort Worth - Barnett Shale	CATMN	2012
Dallas County (TBD)	Fort Worth - Barnett Shale	CATMN	2013
Johnson County (TBD)	Fort Worth - Barnett Shale	CATMN	2013
Tarrant County (TBD)	Fort Worth - Barnett Shale	CATMN	2013
Region 46 - El Paso - Juarez			
El Paso Chamizal	El Paso	PAMS	1997
El Paso Delta	El Paso	CATMN	2011
Region 7 - Odessa - Midland			
Odessa Hays	Odessa	CATMN	1999

Dallas/Ft. Worth: 15
Houston/Galveston/Brazoria: 12
Corpus Christi: 3
Beaumont/Pt. Arthur: 2
El Paso: 2
Odessa : 1

Air Monitoring Stations in Texas, continue

Region 10 - Beaumont - Port Arthur			
Nederland	Beaumont-Pt. Arthur	PAMS	2006
Beaumont Downtown	Beaumont-Pt. Arthur	PAMS	2006
Region 12 - Houston - Galveston - Brazoria			
Clinton	Houston	PAMS	1997
Deer Park	Houston	PAMS	1997
Channelview	Houston	PAMS	2001
HRM3	Houston	EIMS	2003
Lynchburg Ferry	Houston	EIMS	2003
Wallisville	Houston	EIMS	2003
Texas City	Texas City	EIMS	2003
Lake Jackson	Lake Jackson	EIMS	2003
Danciger	Danciger	EIMS	2003
Cesar Chavez	Houston	CATMN	2004
Milby Park	Houston	CATMN	2005
HRM16	Houston	Industry	2010
Region 14 - Corpus Christi - Victoria			
Oak Park	Corpus Christi	CATMN	2005
Solar Estates	Corpus Christi	CATMN	2005
CC Palm	Corpus Christi	CATMN	2010

PAMS	8
EIMS/Industry	7
CATMN	20
Total	35

EIMS – Extended Industry Monitoring Site
CATMN – Community Air Toxics Monitoring Site

11

Automated file handling !!!



PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

… generating 144 data files each day/site!

Managing the data

TCEQ Web Based Data Reporting and Validation

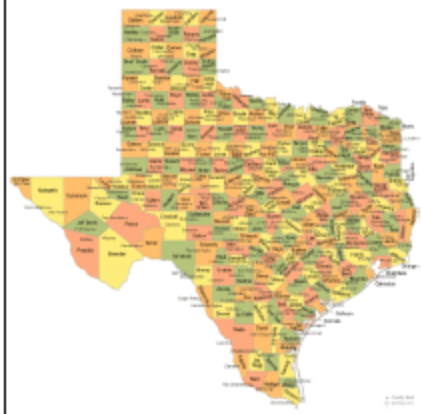
The key to handling large amounts of data consistently over long periods of time is...

Automation of Data Handling

Consistent Application of Validation Rules

Control of System Performance

What's different about Texas … sampling?



- Year round sampling
- The use of two data bases for information
  - LEADS
  - Oracle

TCEQ Web Based Data Reporting and Validation

- LEADS® Database*
  - Repository of hourly data collected directly from monitoring sites
  - Updated with data which has been validated
  - Database used for real-time Public Display of monitoring values
- Oracle Database
  - Data is "loaded" daily by QC Validation staff
  - System for the display and review of all quality control data
  - Allows "reload" of reprocessed data
  - Allows for "flagging" invalid data
  - Allows calculation of Data Recovery
  - Generation of EPA AQS files
  - Review of operator and validator logs
  - Other miscellaneous database management functions

* LEADS - Leading Environmental Analysis & Display software developed by IPS Meteostar

TCEQ Web Based Data Reporting and Validation

- System for Display and Review of Quality Controls
  - Display CVS, LCS, RTS and Blank Data
    - Shows QC failures
    - Shows "Status" Information
      - Calibration Standards (LCS and CVS) with Dilution Factors
      - Operator and Validator contact information
    - Generation of Control Charts for LCS and CVS data
  - Indicators for Audit Samples which have been run
  - Shows Precision
    - Each Sunday two CVS runs
    - Day-to-day precision calculations
  - Comparative results for CVS/LCS

Will go through these quickly

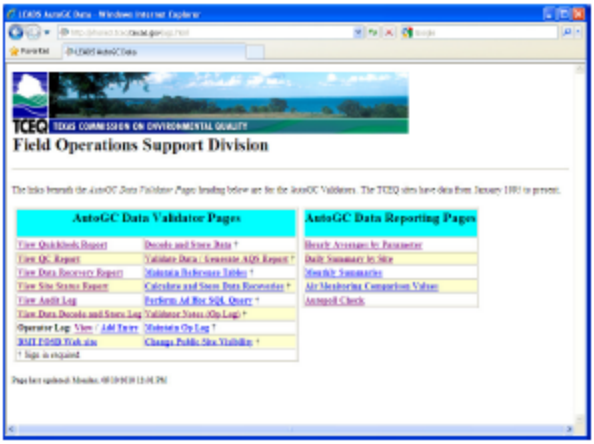
PerkinElmer
For the Better

HUMAN HEALTH | ENVIRONMENTAL HEALTH

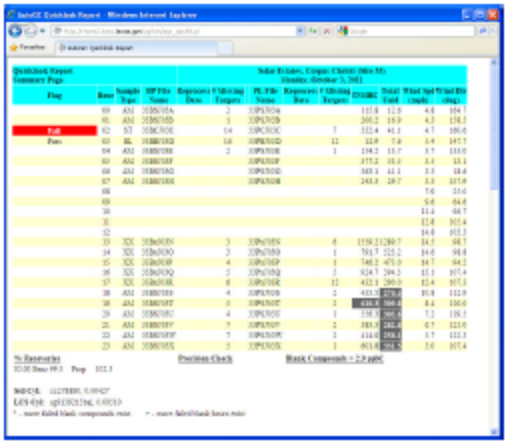
… Example of reports from oracle

The results!

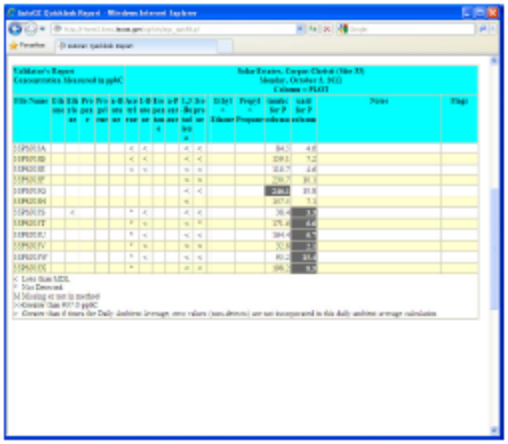
TCEQ Web Based Data Reporting and Validation



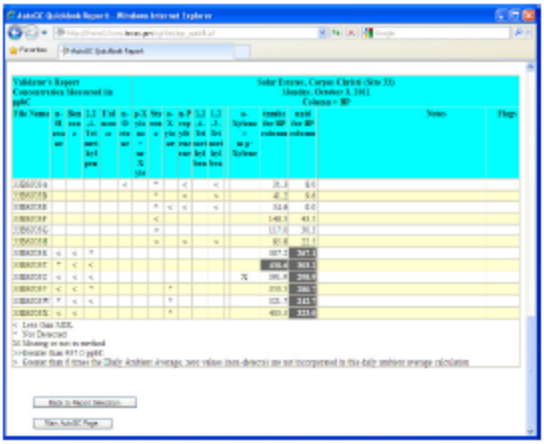
Quicklook Daily Data Report



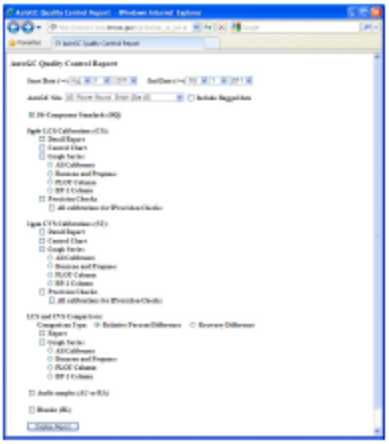
Quicklook Daily Data Report



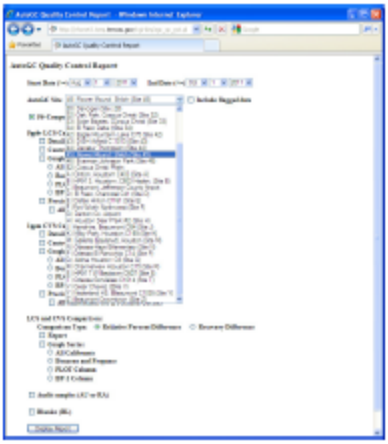
Quicklook Daily Data Report



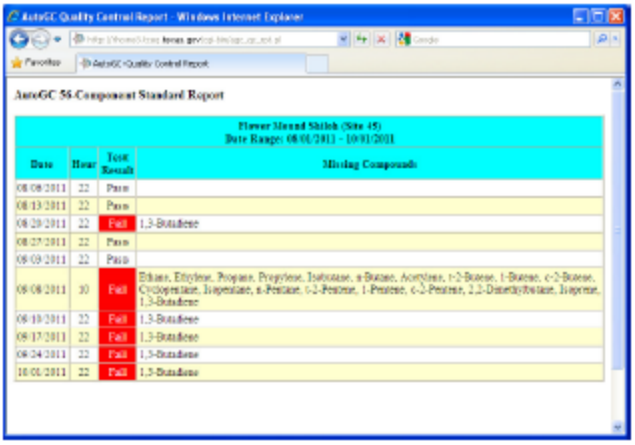
Quality Control Reports



Quality Control Reports



Quality Control Reports – Weekly RTS

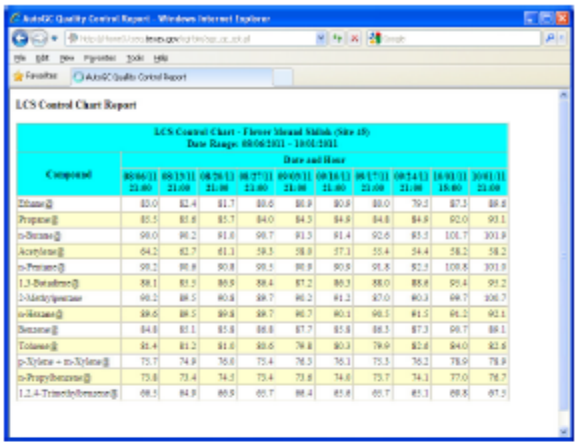


AutoGC 56-Component Standard Report

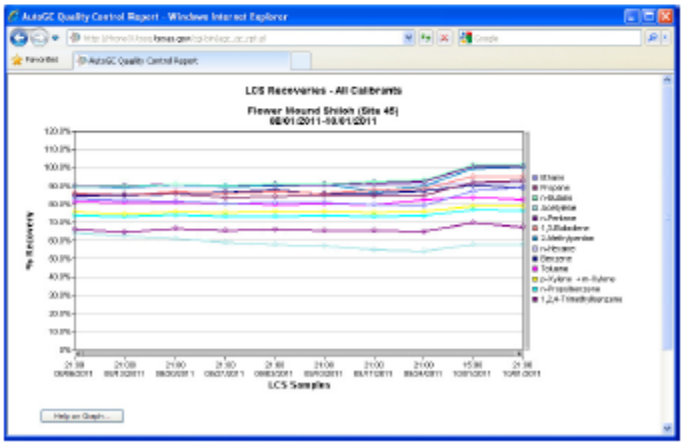
Flower Mound Shiloh (Site 45)
Date Range: 08/01/2011 - 10/01/2011

Date	Hour	Test Result	Missing Compounds
08/06/2011	22	Pass	
08/13/2011	22	Pass	
08/20/2011	22	Fail	1,3-Butadiene
08/27/2011	22	Pass	
09/03/2011	22	Pass	
09/08/2011	10	Fail	Ethane, Ethylene, Propane, Propylene, Isobutane, n-Butane, Acetylene, t-2-Butene, 1-Butene, c-2-Butene, Cyclopentane, Isopentane, n-Pentane, t-2-Pentene, 1-Pentene, c-2-Pentene, 2,2-Dimethylbutane, Isoprene, 1,3-Butadiene
09/10/2011	22	Fail	1,3-Butadiene
09/17/2011	22	Fail	1,3-Butadiene
09/24/2011	22	Fail	1,3-Butadiene
10/01/2011	22	Fail	1,3-Butadiene

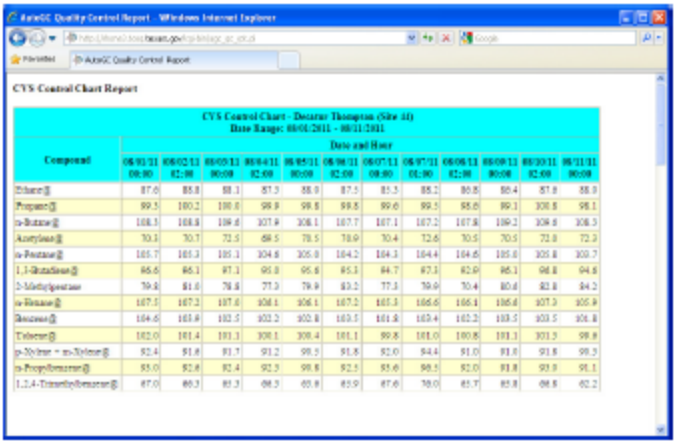
Quality Control Reports – Weekly LCS



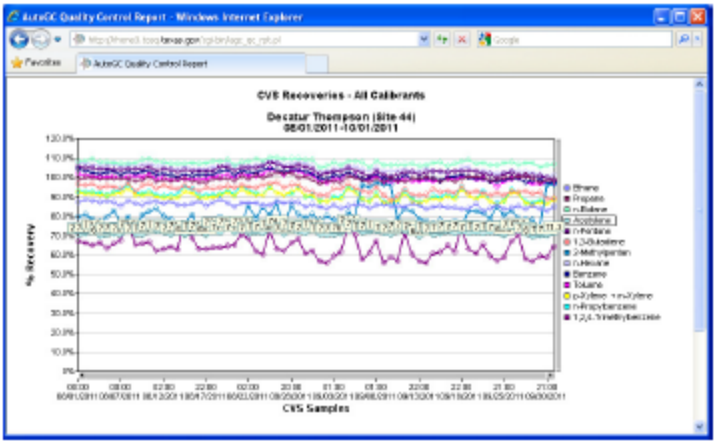
Quality Control Reports – Graph Weekly LCS



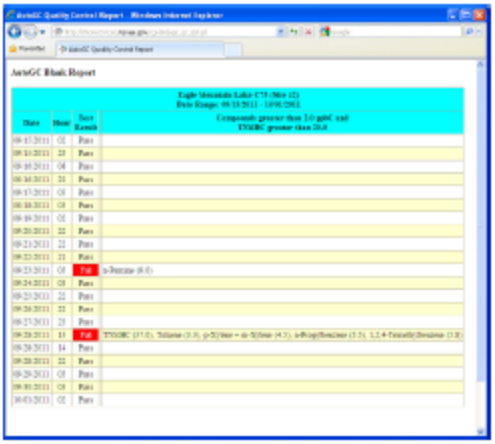
Quality Control Reports – Daily CVS



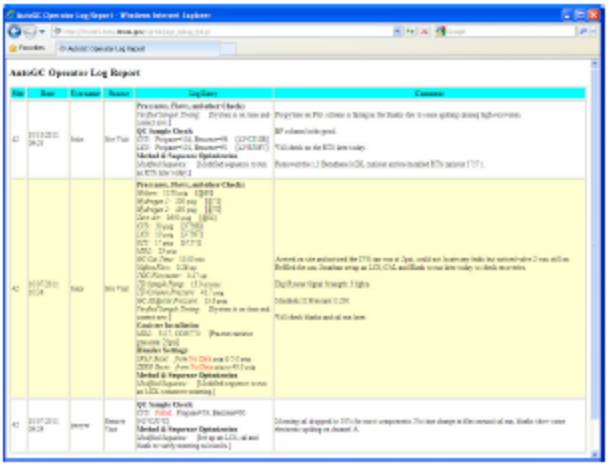
Quality Control Reports – Graph Daily CVS



Quality Control Reports – Daily Blanks



Site Operator Log Reports



Summary

- Automated Online Sampling - for sample and calibrant
- Remote Access Control
- Overlapping - Analytical Run Time
- Low Volume Cold Trap
- Auto Log - data integrity
- Automatic Leak Check per Injection
- Focusing and Chromatography without liquid cryogen
- Get info on web when you want it
- Total Solution

HUMAN HEALTH | ENVIRONMENTAL HEALTH

Thank you

???



Ozone Precursor Analyzer

Carol Meyer, Orsat, LLC
Lee Marotta, PerkinElmer
lee.marotta@perkinelmer.com

A Comparison of Various Design and Operational Approaches to Site Remediation Perimeter Air Monitoring Programs

Melissa Wellman
AECom

Abstract

AECOM has been designing, installing and operating perimeter/fenceline ambient air quality and meteorological programs for over 30 years. AECOM's more recent experience includes many monitoring programs around hazardous waste sites, landfill excavation projects plus former Manufactured Gas Plant (MGP) and Hex Chrome (Cr6) site remediation projects. Over the years, we have designed, implemented and operated many different types of perimeter Air Monitoring (AM) programs. The AM programs typically ranged from the very conservative to the much less conservative design and styles. This presentation will focus on and present information and comparisons concerning the various approaches AECOM has encountered in the design and operation of site remediation perimeter monitoring programs. All of the various AM system design and operational approaches to be discussed will be programs designed and operated by AECOM under the scrutiny of the various regulatory bodies overseeing the site-specific remediation activities.

The presentation will focus on the various design specification and operational protocol comparisons, with an assessment of the various advantages and disadvantages of each perimeter monitoring approach including the following design and operational comparisons:

- Monitoring and data quality objectives
- Parameters measured
- Parameter-specific action levels
- Instrumentation
- Data telemetry/ Action Level Alarms
- Frequency of sampling/ Length of Monitoring Programs
- Number and placement of monitoring locations
- Cost of Perimeter Monitoring Program.



A Comparison of Fence Line Air Monitoring Approaches Associated with Site Remediation

NEMC 2013 Conference – San Antonio, TX – August 2013

Melissa Wellman -- Chelmsford, MA
Leo Gendron -- Chelmsford, MA

LG1 AECOM

Introduction

- Presentation Focus
  - Comparison of design and operational approaches for several fence line air monitoring (AM) programs
  - Look at each program's:
    - AM Approach
    - Parameters measured
    - Instrumentation / telemetry
    - Long term exposure levels / real-time action levels
    - Frequency and duration for monitoring and sampling
    - Number of monitoring and sampling locations
    - Program costs
    - Advantages / Disadvantages

Slide 1

LG1 Gendron, Leo, 7/15/2013

Components of a Successful AM Program

- Design perimeter AM program plan
  - Determine measurement and analytical methods to measure specific parameters
  - Determine site-specific and risk-based action levels
  - Generate site-specific AM Plans (AMPs)
- Assist with agency and / or public interface and negotiations
- Engineer / fabricate monitoring systems, data acquisition and alarm system to meet AM needs or Lease / purchase of equipment and AM systems
- Installation and technician training
- Perform routine operation of monitoring systems
- Data Collection / QA and QC / Analysis / Reporting

AM Program Objectives

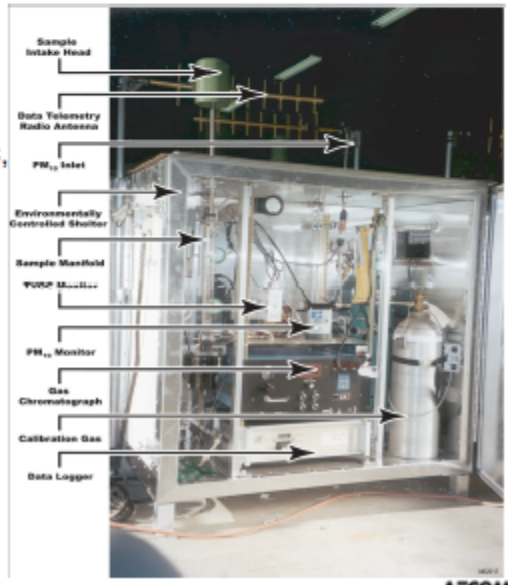
- Establish baseline levels of target compounds prior to remedial activities
- Ensure protection of public health and environment
- Coordinate fence line monitoring with worker health and safety exposure programs (separate issues)
- Document fence line air quality during remediation activities
- Evaluate the need for vapor and / or dust suppression
- Provide risk management and public confidence
- Reduce owner's potential liability
- Maintain owner's Budgets ($$$)

Program Design Options

- Determination of parameters to be monitored
- Determination of action levels
  - Based on a health / risk-based analysis
  - State established guidelines
- Equipment selection
  - Continuous (24/7) monitoring devices
  - Portable (work hours only) monitoring devices
  - Integrated samplers
  - Hand-held AM devices
- Frequency and duration of monitoring and sampling
- Number of monitoring and sampling locations
- Sophistication of data telemetry / alarm or paging systems

Fixed Air Monitoring (FAM) Unit

- Continuous real-time monitoring (24/7)
  - Particulates, TVOC, H_2S or etc.
- Automatic GC speciation for VOCs
- Sample manifold
- Requires line power
- Environmentally controlled
- Internal data logger
- Radio telemetry
- Interfaces with central computer
- Programmable alarm notification system



Portable Air Monitoring (PAM) Unit

- Real-time monitoring (work hours only)
  - Particulates, TVOC, H_2S or etc.
- Battery operated
- Internal data logger
- Radio telemetry
- Visual alarms (lights) available upon selection
- Interfaces with central computer
- Programmable alarm notification system



Recent Fence Line AM Programs

- **Program A:** MGP site in Rhode Island
  - **Utilized Hand-held and Integrated AM (at fence line)**
- **Program B:** MGP site in Ohio
  - **Utilized PAMs, Hand-held, and Integrated AM (at fence line)**
- **Program C:** MGP site on Long Island, NY
  - **Utilized FAMs (with GCs), PAMs, Hand-held, onsite Naphthalene GC, and Integrated AM (at fence line)**
- **Program D:** Combination MGP and Hex Chrome site in NJ
  - **Utilized FAMs (with GCs), PAMs, Hand-held, and Integrated AM (at fence line plus perimeter exclusion zone)**

Number & Placement of Monitoring Locations

- Each site was evaluated for the following:
  - Regulatory requirements and state guidance
  - Availability of electrical services
  - Extent and length of perimeter boundaries / security of site perimeter
  - Toxicity of contaminated soils
  - Risk Analysis for nearby sensitive receptors
  - Time schedule for installation
  - Budgetary considerations



Number & Placement of Monitoring Locations (continued)

- Proximity of remedial activities to local residents and other sensitive receptors (e.g., day care centers, schools, hospitals, housing, businesses, etc.)
- Directional location of remedial activities with respect to sensitive receptors
- Predominant wind directions, based on climatological analyses
- Remedial plans (e.g., one location at a time vs. multiple locations at a time)
- Need and ability to mobilize AM stations from one location to another

Monitoring Locations and Parameters



- **Program A: Rhode Island**
  - 4 fence line AM locations
  - periodic **hand-held** monitoring for TVOCs, particulates, and odor
  - periodic **integrated** sampling for VOCs (TO-15)
  - Manual data collection to central data base
- **Program B: Ohio**
  - 4 fence line AM locations
  - 4 PAMs (continuous **TVOC & particulates**)
  - periodic **hand-held** monitoring for TVOCs, particulates, and odor
  - periodic **integrated** sampling for VOCs (TO-15)
  - Automatic data telemetry to onsite central / alarms / paging

Monitoring Locations and Parameters (continued)



- **Program C: New York**
  - 8 fence line AM locations
  - 4 FAM and 4 PAM (continuous **TVOC & particulates**) fence line
  - Automatic **BTEX** sampling (when TVOC exceed Action Level)
  - Periodic **hand-held** sampling for TVOC , particulates, noise and odor/naphthalene
  - periodic **integrated** sampling for VOCs (TO-15)
  - Automatic data telemetry to onsite central / alarms / paging

Monitoring Locations and Parameters (continued)

- **Program D: New Jersey**
  - 11 fence line AM locations & 4 perimeter of the exclusion zone locations
  - 7 FAM and 4 PAM (continuous **TVOC & particulates**)
  - 4 PAM exclusion zone locations
  - Continuous **H_2S** sampling at 3 of the FAM locations
  - Automatic **BTEX** sampling (when TVOC exceed Action Level)
  - Periodic **hand-held** sampling for TVOC , particulates, and H_2S
  - Daily **integrated** sampling for particulates / Hex Chrome (Cr_6).
  - Automatic data telemetry to onsite central / alarms / paging

Instrumentation

- **Program A: Rhode Island**
  - Used a manual AM approach
  - VOCs … RAE PID plus SUMMA™ Canisters (TO-15 analyses)
  - Particulates … DustTrak
  - Met Data … wind speed, wind direction, ambient temperature, dewpoint
- **Program B: Ohio**
  - Used battery-operated PAM units plus automated / continuous radio telemetry of data to central computer / alarm system
  - VOC … RAE PIDs plus SUMMA™ Canisters (TO-15 analyses)
  - Particulates … DustTraks
  - Met Data … wind speed, wind direction, ambient temperature, dewpoint

Instrumentation (continued)

- **Program C: New York**
  - Used environmentally-controlled FAM units and battery-operated PAM units, plus automated / continuous radio telemetry of data to central computer / alarm system
  - VOC … RAE PIDs / Baseline GCs for BTEX / onsite GC for naphthalene / SUMMA™ Canisters (TO-15 analyses)
  - Particulates … DustTraks
  - Met Data … wind speed, wind direction, ambient temperature / dewpoint
- **Program D: New Jersey**
  - Used environmentally-controlled FAM units and battery-operated PAM units, plus automated / continuous radio telemetry of data to central computer / alarm system
  - VOC … RAE PIDs / Baseline GCs for BTEX / SUMMA™ Canisters (TO-15 analyses)
  - H_2S … Jerome H_2S Samplers (3 fixed locations plus hand-held)
  - Particulates … DustTraks / Airmetrics integrated samplers for PM_{10} and CR_6
  - Met Data … wind speed, wind directions, ambient temperature / dewpoint

Program Comparisons / Advantages / Disadvantages

Feature	Program A (Manual AM)	Program B (4 PAMs)	Program C (4 PAMs + 4 FAMs + onsite naphthalene GC)	Program D (7 FAMs + 4 PAMs + 4 PAMs (Exclusion) + H2S samplers)
Installation Issues	NA	Battery-operated PAMs Electrical Service for Central AM Trailer	Battery-operated PAMs but need Electrical Service to FAMs plus Central AM Trailer	Battery-operated PAMs but need Electrical Service to FAMs plus Central AM Trailer
Ability to Continuously Monitor at Multiple Locations - Simultaneously	No	Yes	Yes	Yes
Continuous Data Telemetry, Automatic Alarms, Paging System, and Ability to Take Immediate Corrective Actions	No	Yes	Yes	Yes
Ability to Monitor 24/7	No	Yes (with limits)	Yes	Yes
Ability to Continuously Speciate (BTEX)	No	No	Yes (FAMs)	Yes (FAMs)
Ability to Relocate AM Units Quickly	No	Yes	Yes (PAMs only)	Yes (PAMs only)
On-Site PC Display of Current Data	No	Yes	Yes	Yes
Ability to Measure Naphthalene (on-site)	No	No	Yes	No
Exclusion Zone AM Performed (early warning tool)	No	No	No	Yes
Approximate Costs: - Installation -Eq. Lease and Operations	$5k - $5k $10k-$12k/month	$10k - $20k $15k-$20k/month	$50k - $70k $30k-$40k/month	$100k - $150k $60k-$80k/month

Summary

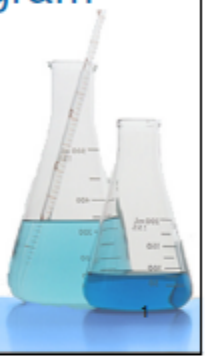
- The 4 fence line AM programs presented include AM programs that range from the fairly simplistic (**Program A**) to the very conservative and comprehensive (**Program D**).
- Many issues should be addressed in the design of a fenceline monitoring program for any site.
- Must clearly define program objectives (internal and external).
- Goal should always be to design the most technically-defensible *and* cost-effective program possible.
- Neglect of some key design issues could result in liabilities for site owner or more elaborate and costly air monitoring programs than needed.

Questions?


Thank You
Melissa Wellman
Air Quality Services / Air Monitoring & Measurements
Chelmsford, MA 01824
978-905-2454
Melissa.Wellman@aecom.com
AECOM

TNI Stationary Source Audit Sample (SSAS) Program Central Database

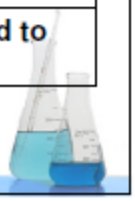
Presented By: Maria Friedman
San Antonio, Texas
August 6, 2013



1

Milestones

Date	Milestone
08-11-2008	SSAS Expert Committee 1st Meeting
10-09-2009	Final TNI SSAS Standard Adopted
09-13-2010	EPA Final Rule Published (75 FR 55636)
05-18-2011	EPA Approved TNI SSAS Program
06-16-2013	**Audit Samples Commercially Available**
07-09-2013	**First Audit Sample Results Submitted to Central Database**



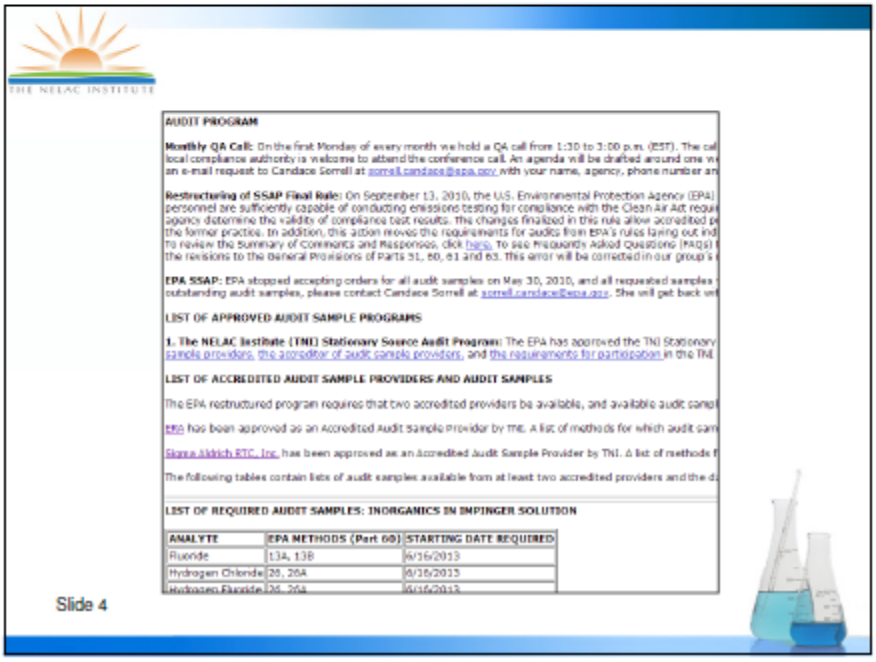
Slide 2

For More Information

- EPA website: http://www.epa.gov/ttn/emc/email.html
  - Summarizes the restructuring of the Stationary Source Audit Program (SSAP)
  - Provides lists of available audit samples and accredited Audit Sample Providers
  - Provides links to the Final Rule, Public Comments and Responses, EPA Contact Information, EPA SSAP Rule FAQ, and TNI SSAS Standard

Slide 3





AUDIT PROGRAM

Monthly QA Call: On the first Monday of every month we hold a QA call from 1:30 to 3:00 p.m. (EST). The call
local compliance authority is welcome to attend the conference call. An agenda will be drafted around one w
an e-mail request to Candace Sorrell at sorrell.candace@epa.gov with your name, agency, phone number an

Restructuring of SSAP Final Rule: On September 13, 2010, the U.S. Environmental Protection Agency (EPA)
personnel are sufficiently capable of conducting emissions testing for compliance with the Clean Air Act requi
agency determine the validity of compliance test results. The changes finalized in this rule allow accredited p
the former practice. In addition, this action moves the requirements for audits from EPA's rules laying out ind
To review the summary of Comments and Responses, click here. To see Frequently Asked Questions (FAQs)
the revisions to the General Provisions of Parts 51, 60, 61 and 63. This error will be corrected in our group's

EPA SSAP: EPA stopped accepting orders for all audit samples on May 30, 2010, and all requested samples
outstanding audit samples, please contact Candace Sorrell at sorrell.candace@epa.gov. She will get back wi

LIST OF APPROVED AUDIT SAMPLE PROGRAMS

1. The NELAC Institute (TNI) Stationary Source Audit Program: The EPA has approved the TNI Stationary
sample providers, the accreditor of audit sample providers, and the requirements for participation in the TNI

LIST OF ACCREDITED AUDIT SAMPLE PROVIDERS AND AUDIT SAMPLES

The EPA restructured program requires that two accredited providers be available, and available audit samp

ERA has been approved as an Accredited Audit sample Provider by me. A list of methods for which audit sam

Sigma Aldrich RTC, Inc. has been approved as an Accredited Audit Sample Provider by TNI. A list of methods f

The following tables contain lists of audit samples available from at least two accredited providers and the d

LIST OF REQUIRED AUDIT SAMPLES: INORGANICS IN IMPINGER SOLUTION

ANALYTE	EPA METHODS (Part 60)	STARTING DATE REQUIRED
Fluoride	13A, 13B	6/16/2013
Hydrogen Chloride	26, 26A	6/16/2013
Hydrogen Fluoride	26, 26A	6/16/2013

Slide 4

FAQ

1. **What is the Central Database?**

The Central Database is an online repository of audit sample results collected under the TNI SSAS Program. The data in the Central Database will be used by TNI and Audit Sample Provider Accreditors to monitor performance of the SSAS Program. Regulators and other participants will also be able to use the Central Database to conduct statistical queries on the data. The Central Database does not store the results of stack samples; it is for audit sample results only.



Slide 5

FAQ

2. **Do Regulatory Agencies use the Central Database to Approve Audit Sample Orders for Facilities?**

No. The Central Database has no role in the approval of audit sample orders. Regulators may refer to historical data in the Central Database during their review of the appropriateness of requested audit concentrations, however this is not a requirement of the TNI SSAS Standard.



Slide 6

FAQ

3. **How is data submitted to the Central Database?**

Audit Sample Providers (currently, ERA and Sigma-Aldrich RTC) submit results to the Central Database within 3 business days after reporting the audit sample data.

Slide 7

FAQ

4. **As a Stack Tester, Laboratory, or Regulator, what do I need to know?**

In order for a Provider to submit audit sample results to the Central Database, they need to use unique IDs, assigned by TNI, to represent the Stack Tester, Laboratory, and Regulatory Agency involved with the audit sample. An ID is a unique code that will be permanently associated with your organization in the TNI SSAS Program.

Slide 8

FAQ

5. **How do I receive an ID for the TNI SSAS Program?**

Simply visit the online form and answer a few basic questions about your organization. You should receive an e-mail response with your assigned ID within 24 hours. Audit Sample Providers will ask for your assigned TNI ID when placing an order, so it is best to obtain your ID in advance. Note that the ID is specific to an organization, not an individual; you do not need an ID for an employee.

Slide 9



FAQ

6. **I represent a Laboratory and we already have a TNI Code in LAMS (e.g., TNI01234). Is that my ID for the TNI SSAS Program?**

No. The ID assigned by TNI to your Laboratory for SSAS is unique. TNI Codes from LAMS cannot be used. Likewise, EPA IDs are also not applicable to SSAS.

Slide 10



FAQ

7. **I represent a Facility undergoing Stack Testing. Do I need an ID?**

No. Only Stack Testers, Laboratories, and Regulators must obtain IDs from TNI.

Slide 11

FAQ

8. **How can I see the data that has been submitted to the Central Database?**

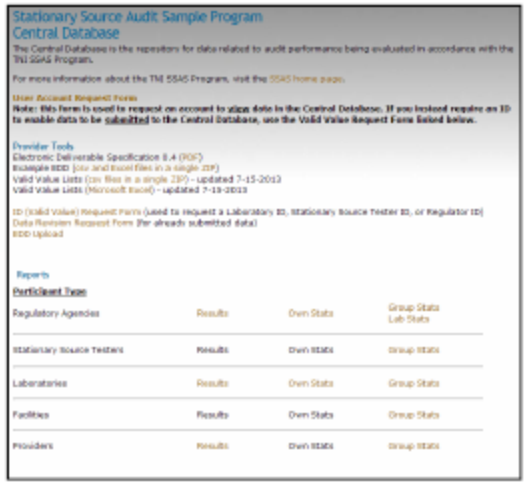
To see data in the Central Database, you must have a secure user account. At this time, user accounts are being granted only to Regulatory Agencies. Early in 2014, it is anticipated that user accounts will be available for Stack Testers and Laboratories as well. Note that having a user account is optional; you are not required to have a user account in order to participate in the TNI SSAS Program.

Slide 12

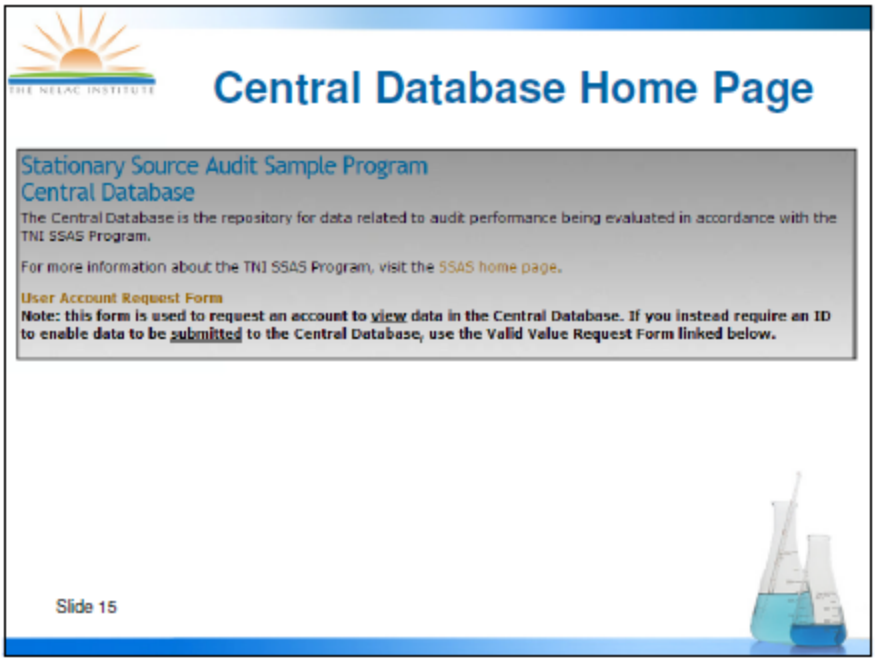
Live DEMO

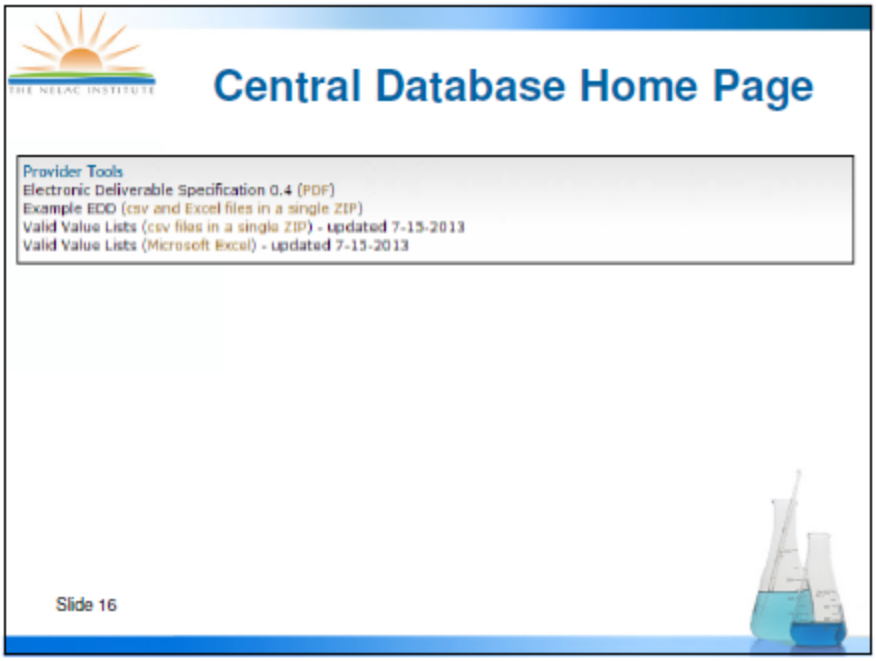
Slide 13

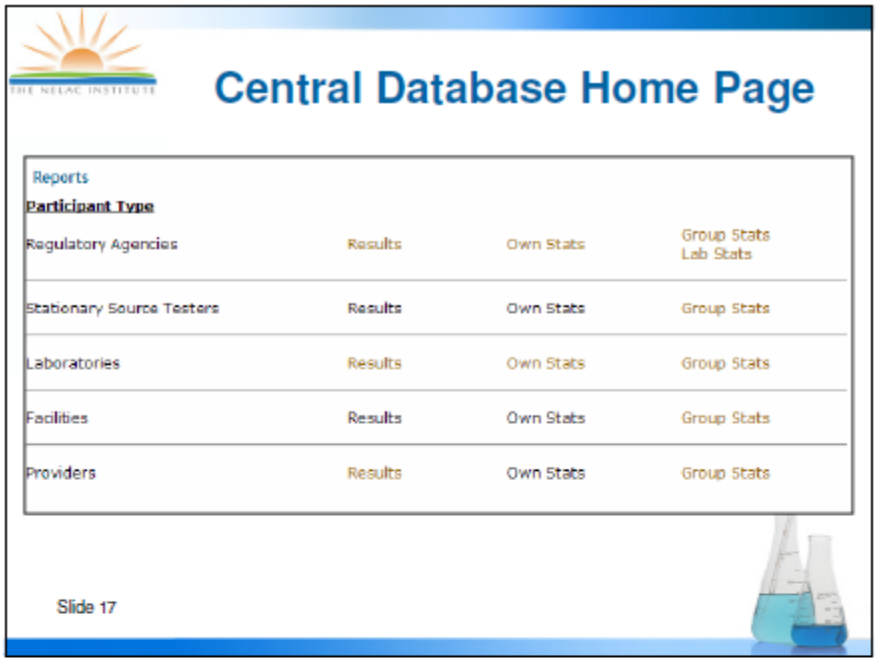
Central Database Home Page

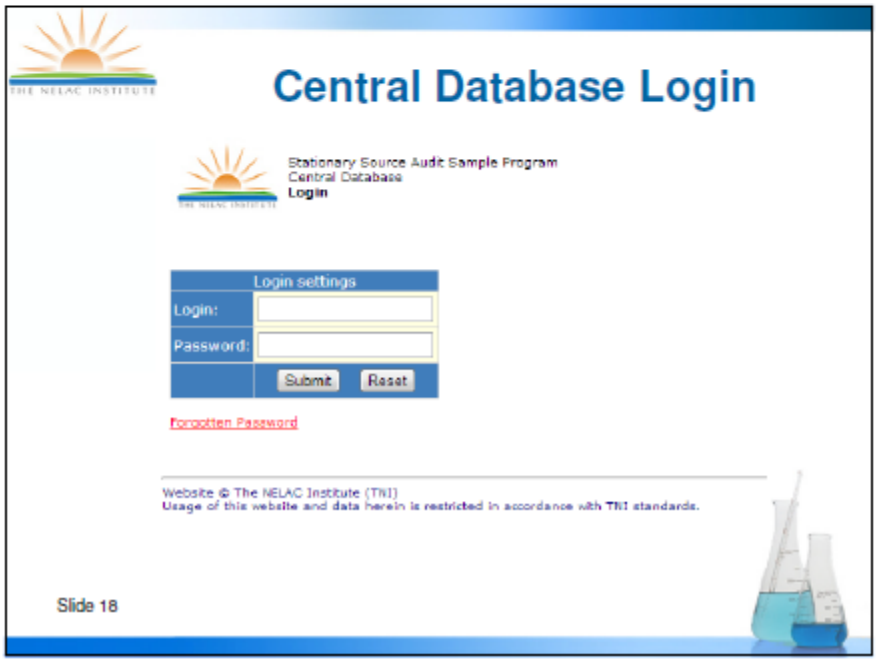


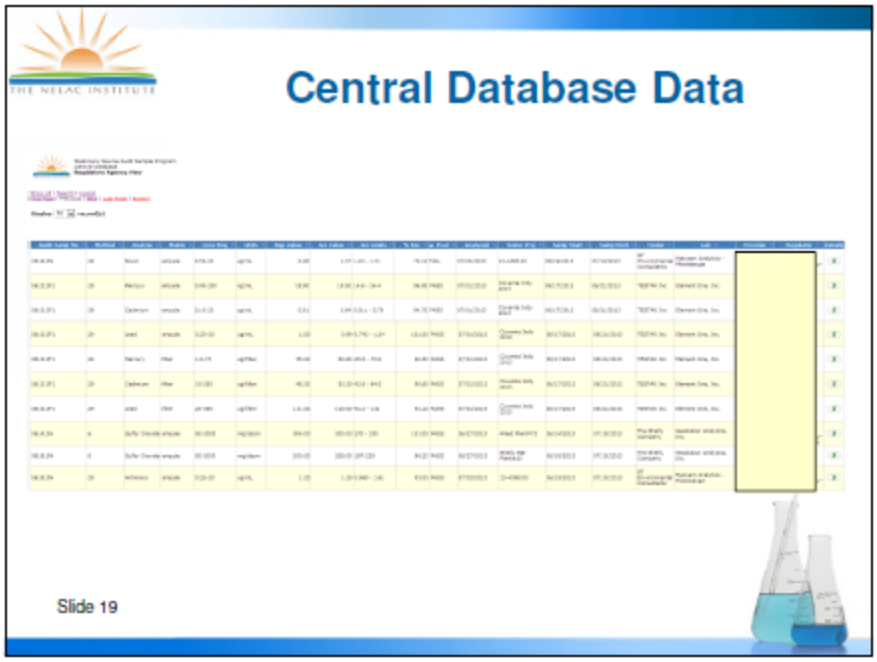
Slide 14

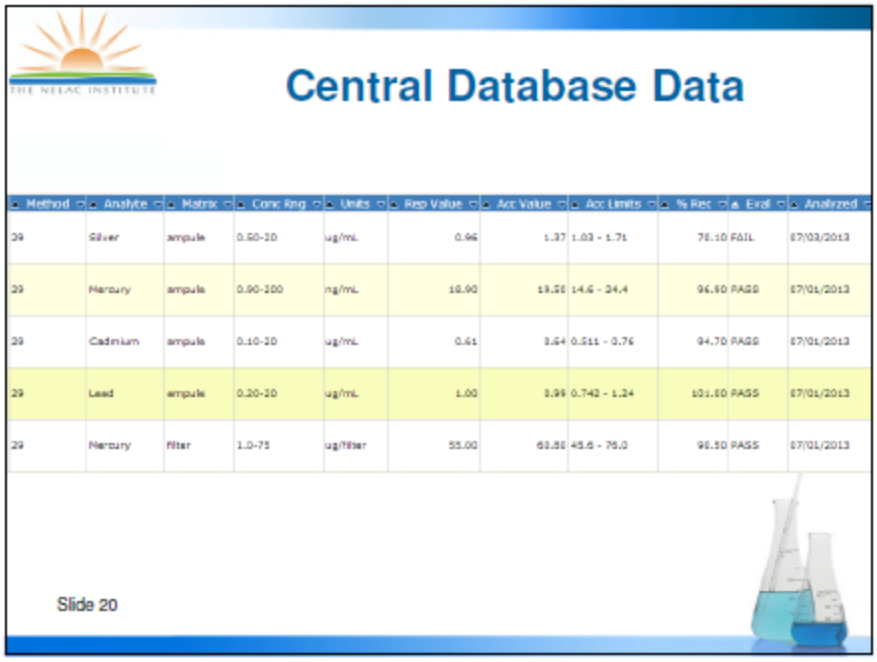

Central Database Home Page
Stationary Source Audit Sample Program
Central Database
The Central Database is the repository for data related to audit performance being evaluated in accordance with the TNI SSAS Program.
For more information about the TNI SSAS Program, visit the SSAS home page.
User Account Request Form
Note: this form is used to request an account to view data in the Central Database. If you instead require an ID to enable data to be submitted to the Central Database, use the Valid Value Request Form linked below.
Slide 15

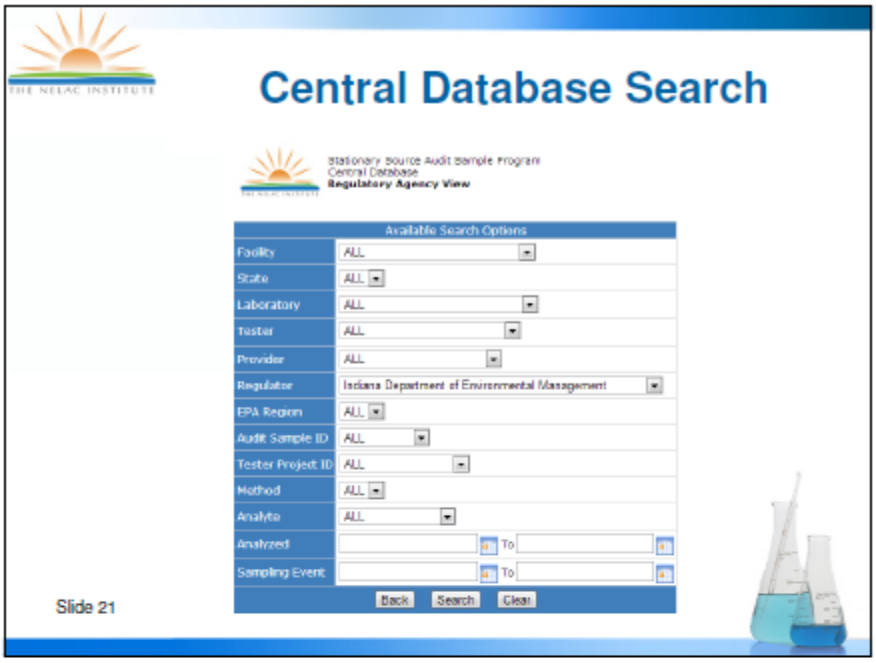

Central Database Home Page
Provider Tools
Electronic Deliverable Specification 0.4 (PDF)
Example EDD (csv and Excel files in a single ZIP)
Valid Value Lists (csv files in a single ZIP) - updated 7-15-2013
Valid Value Lists (Microsoft Excel) - updated 7-15-2013
Slide 16

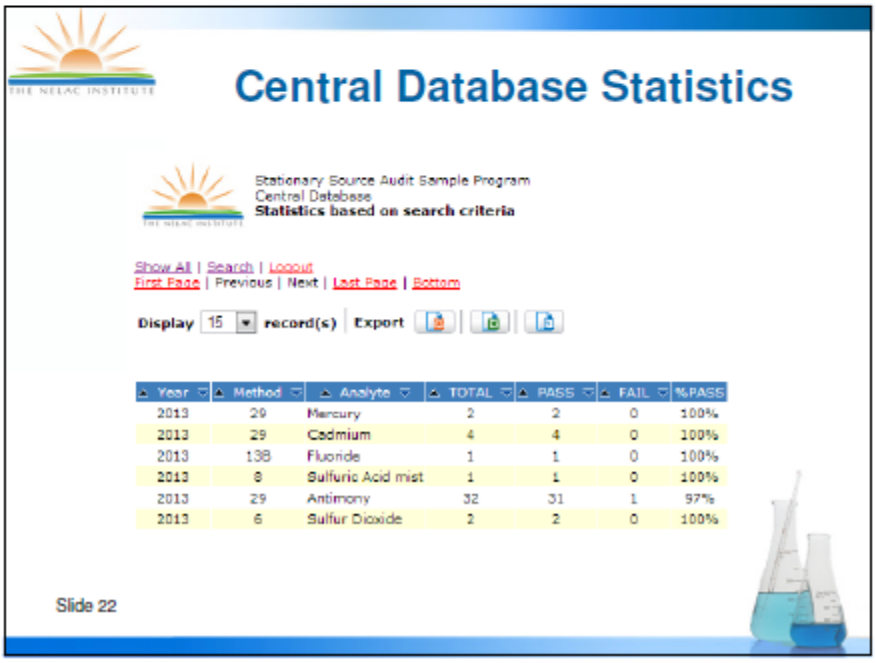

Central Database Home Page
Reports
Participant Type
Regulatory Agencies
Results
Own Stats
Group Stats
Lab Stats
Stationary Source Testers
Results
Own Stats
Group Stats
Laboratories
Results
Own Stats
Group Stats
Facilities
Results
Own Stats
Group Stats
Providers
Results
Own Stats
Group Stats
Slide 17


Central Database Login
Stationary Source Audit Sample Program
Central Database
Login
Login settings
Login:
Password:
Submit
Reset
Forgotten Password
Website © The NELAC Institute (TNI)
Usage of this website and data herein is restricted in accordance with TNI standards.
Slide 18


THE NELAC INSTITUTE
Central Database Data
Slide 19


THE NELAC INSTITUTE
Central Database Data
Method
Analyte
Matrix
Conc Rng
Units
Rep Value
Acc Value
Acc Limits
% Rec
Eval
Analyzed
29 Silver ampule 0.50-10 ug/mL 0.96 1.37 1.03 - 1.71 78.10 FAIL 07/03/2013
29 Mercury ampule 0.00-200 ng/mL 18.00 19.50 14.6 - 24.4 96.50 PASS 07/01/2013
29 Cadmium ampule 0.10-10 ug/mL 0.61 0.64 0.511 - 0.76 94.70 PASS 07/01/2013
29 Lead ampule 0.20-20 ug/mL 1.00 0.99 0.742 - 1.24 101.00 PASS 07/01/2013
29 Mercury filter 1.0-75 ug/filter 55.00 60.50 45.6 - 76.0 90.50 PASS 07/01/2013
Slide 20





Year	Method	Analyte	TOTAL	PASS	FAIL	%PASS
2013	29	Mercury	2	2	0	100%
2013	29	Cadmium	4	4	0	100%
2013	13B	Fluoride	1	1	0	100%
2013	8	Sulfuric Acid mist	1	1	0	100%
2013	29	Antimony	32	31	1	97%
2013	6	Sulfur Dioxide	2	2	0	100%

Next Steps

- Stationary Source Testers and Laboratories
  - Obtain your SSAS ID to identify your organization in the Central Database
- Regulators
  - Obtain your SSAS ID to identify your agency in the Central Database
  - (optional) Apply for a user account to access the Central Database
    http://nelac-institute.org/ssas/request-user-account.php

23



Comments – Questions?

Maria Friedman
TestAmerica
949-260-3201
maria.friedman@testamericainc.com

Gregg O'Neal
North Carolina DENR
919-715-0251
gregg.oneil@ncdenr.gov

Michael Klein
New Jersey DEP
609-530-4041
michael.klein@dep.state.nj.us

Stanley Tong
EPA Region IX
415 947-4122
tong.stanley@epa.gov

24




Thank you to all who participate and contribute to the TNI SSAS Program!
Slide 25

Implementation Experience with ASTM D7036: What Emission Testing Firms, Accreditation Bodies, Regulators, and the Regulatory Community Need to Know

David L. Elam, Jr.
Summa Consultants, Inc./Stack Testing Accreditation Council, Inc.

Abstract

Beginning March 27, 2012, each Part 75 stack test or relative accuracy test audit (RATA) must be performed by an "Air Emission Testing Body" (AETB), as defined in 40 CFR 72.2 (i.e., the "Minimum Competency Rule", and at least one "Qualified Individual" (QI), as defined in §72.2, must be on-site during the testing (see Part 75, Appendix A, Section 6.1.2). By definition, an AETB is a source testing firm that conforms to ASTM D7036, Standard Practice for Competence of Air Emission Testing Bodies.

Although the Minimum Competency Rule allows an AETB to limit the scope of ASTM D7036 conformance to Part 75 test programs, the ASTM standard is intended to apply to all work that an AETB performs, including Part 60 and performance engineering test programs. Further, the Source Evaluation Society (SES) awards the Qualified Source Testing Individual (QSTI) credential, which can satisfy the QI requirement of ASTM D7036; however, there are timing differences in QI and QSTI requirements, which can be challenging to differentiate. The result is that a seemingly straightforward regulatory requirement can be confusing and challenging.

This presentation examines three key areas.

1. The requirements of ASTM D7036 and the Minimum Competency Rule and the relationship between the two.
2. The experience of the Stack Testing Accreditation Council (STAC), an Accreditation Body focused on ASTM D7036, with assessments of AETB's.
3. The results of queries of EPA's Emission Collection and Monitoring Plan System (ECMPS) database, the system that Part 75 sources use to report Part 75 test programs.

The presentation will shed light on the challenges associated with the proper implementation of ASTM D7036, providing valuable insights to regulators, the regulated community, AETBs, and other Accreditation Bodies. These insights will enable all parties to develop strategies to quickly identify problems with ASTM D7036 conformance. Such information will allow the selection of properly qualified AETBs and when necessary, be helpful in the establishment and evaluation of effective correction action plans.

Implementation Experience with ASTM D7036

National Environmental Monitoring Conference
San Antonio, TX
6 August 2013

David L. Elam, Jr.
Summa Consultants, Inc./Stack Testing Accreditation Council, Inc.
100 Deerfield Trail
Chapel Hill, NC 27516
919.967.0500
delam@summaconsultants.com

Presentation Covers Five Key Areas

1. Review Minimum Competency Rule History, Requirements, and Purpose
2. Present the Essentials of ASTM D7036-04 Conformance
3. Discuss AETB's Options for Affirming Conformance
4. Examine EPA's ECMPS Database and AETB's Performing Part 75 Test Programs
5. Provide Guidance on Evaluating AETB Conformance

2

Copyright Summa Consultants, Inc. 2013
Reproduction permission issued to STAC

EPA Reports Problems with Source Test Data Quality (1/2)

Preamble to Final Rule for Minimum Competency Requirements for Air Emission Testing:

- "EPA believes the evidence is strong that unqualified, under-trained and inexperienced testers are routinely deployed on testing projects."
- "There are many reasons why voluntary compliance has not worked, including disagreement among stack test companies on a minimum competency standard, and the sources' often used practice of hiring the lowest bidder."

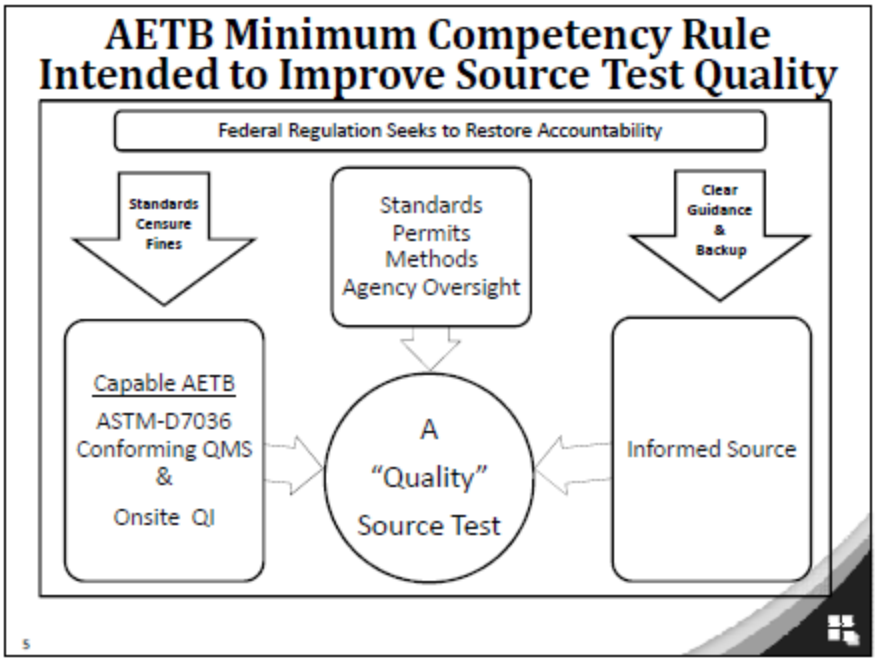
3

EPA Reports Problems with Source Test Data Quality (2/2)

But regulatory oversight has changed too.

- Shrinking budgets mean:
  - Less observation, electronic reporting
  - Delayed, and less critical report reviews

4



Long Path to Minimum Competency Rule Promulgation

Date	Scope & Federal Register Reference
8/22/06	EPA Proposed Amendments to Part 75 Regulations to Require Source Testing Firms Meet ASTM D7036-04 (FR 71, 49254)
1/24/08	Final Rule Initially Promulgated with Effective Date of 1/1/09 (FR 73, 4311)
11/4/08	Rule was Stayed (FR 73, 65554)
6/11/10	Rule was Re-proposed (FR 75, 33397)
3/28/11	Rule was Promulgated with Compliance Date 12 Months after Publication in FR (FR 76, 17288)
3/27/12	Part 75 Test Programs Must be Performed by AETBs that Conform to ASTM D7036-04[1]

[1]Minimum Competency Rule applies to all Part 75 RATAs, Appendix E, and LME stack tests. Routine CEMS operations & maintenance activities, including CGAs, are exempted from requirement.

6

Minimum Competency Rule Requirements

- AETB Statement of Conformance to ASTM D7036-04
  - Can be limited to only Part 75 work, but this is not Stack Testing Accreditation Council (STAC) policy
  - Conformance to the ASTM D 7036-04 can be demonstrated in two ways:
    - Management certification letter (self-declaration, self-certification)
    - Certificate of accreditation (or interim accreditation) issued by recognized, national accreditation body
- Qualified Individual on Site
  - Proof of QI claim
  - Endorsement of SES Exams

7

What is ASTM D 7036?

1. A quality management standard applicable to firms that conduct source testing
2. A consensus standard based on ISO17025, *General Requirements for the Competence of Testing and Calibration Laboratories*
3. A requirement for source testing firms that perform Part 75 emission testing programs beginning 3/27/2012

Note:

- ASTM D 7036-04 is referenced in the rule
- Newer versions exist:
  - ASTM D 7036-04 (Reapproved 2011)
  - ASTM D 7036-12

8

What Does It Mean to "Conform to ASTM D 7036?"

EPA allows AETB to demonstrate ASTM D7036 Conformance in two ways:

1. Management certification letter (self-declaration)
   - AETB Management says "Our operations conform to ASTM D7036."
2. Certificate of accreditation or interim accreditation issued by recognized, national accreditation body (AB)
   - ***Interim Accreditation***: The AETB has completed a Structural Assessment and the AB has determined that the AETB has a conforming system in place.
   - ***Accreditation***: The AETB has completed a Functional Assessment and the AB has determined that the AETB is operating in accordance with the procedures of its conforming system.

9

Foundation of ASTM D7036-04 Conformance

1. The AETB must have a Quality Manual that addresses requirements of ASTM D7036
2. The AETB must have certain positions
   - Technical Manager
   - Quality Manager
   - Qualified Individual
3. Test Plans are required for all projects
4. The AETB must conduct annual internal audits
5. Confirmation by management that each test program conforms to ASTM D7036

10

AETB Is Responsible for Ensuring ASTM D7036 Conformance

- AETB must conform to ASTM D7036-04.
- Even so, the Source is responsible for obtaining certain conforming information from the AETB, and reporting it to EPA.
- If an AETB provided a Part 75 source with a false certification, regulators have the option of referring the matter to federal prosecutors for possible action against the AETB under 18 U.S.C. 1001.

See question 11 in Draft Part 75 Policy Manual

11

Part 75 Sources Must Obtain Information from AETBs (1/2)

40 CFR Part 75, Appendix A, 6.1.2(b):

"The owner or operator shall obtain from the AETB **a certification that as of the time of testing the AETB is operating in conformance with ASTM D7036–04** (incorporated by reference, *see § 75.6)*. The AETB's certification may be limited in scope to the tests identified under paragraph (a). The AETB's certification need not extend to other work it may perform. This certification shall be provided in the form of either:

(1) A certificate of accreditation or interim accreditation for the relevant test methods issued by a recognized, national accreditation body; or

(2) A letter of certification for the relevant test methods signed by a member of the senior management staff of the AETB."

12

Part 75 Sources Must Obtain Information from AETBs (2/2)

40 CFR Part 75, Appendix A, 6.1.2(c), [75.59(a)(15), (b)(6), (d)(4)]:

- Name, phone number, email address of AETB
- Name of each QI, date QI took exam, name & email of exam provider
- (1) A certificate of accreditation or interim accreditation for the relevant test methods issued by a recognized, national accreditation body; or
- (2) A letter of certification for the relevant test methods signed by a member of the senior management staff of the AETB.

13

Part 75 Sources Are Advised to Obtain Additional Info from AETBs

40 CFR Part 75, Appendix A, 6.1.2(c)

- AETB's Quality Manual
- The results of any internal and external audits performed during the preceding 12 months
- Performance data and corrective actions implemented during preceding 12 months
- Training records for **all** on-site personnel, including QIs, for the preceding 12 months

14

Part 75 Sources Use ECMPS to Report Test Program Data

Emissions **C**ollection and **M**onitoring **P**lan **S**ystem supports reporting of:

- Monitoring Plan
- Quality Assurance and Certification Data
- Emissions Data
  - AETB Information
    - Name of QI
    - AETB Name & Contact Info
    - QI Exam Date & Exam Provider

15

ECMPS Database Review (3/27/12 - 3/26/13)[1]

Criteria	Value
Part 75 RATA Tests Performed	5898 on 2772 Units
Identified QIs Performing Part 75 Tests	437
Identified AETBs Performing Part 75 Tests	139
Accredited or Interim Accredited AETBs Performing Part 75 Tests[2]	18
Part 75 RATA Tests Performed by Accredited or Interim Accredited AETBs	1812
Percentage of AETBs Performing Part 75 Tests that are Accredited or Interim Accredited	13%
Percentage of Part 75 Tests Performed by Interim Accredited or Accredited AETBs	31%

[1]Raw Data provided by EPA CAMD.
[2]There are 22 STAC Accredited or Interim Accredited AETBs.

16

Which is Better?

Self-Certification or Third Party Accreditation? 1/3

- The Apparent Answer:
  - The Minimum Competency Rule says either is ok.

17

Which is Better?

Self-Certification or Third Party Accreditation 2/3

- The Apparent Answer:
  - The Minimum Competency Rule says either is ok.
- The Real Answer:
  - The one that stands up to scrutiny.

18

Which is Better?

Self-Certification or Third Party Accreditation? 3/3

- Submittal of an application for accreditation begins with self-certification of conformance.
- Third party accreditation will evolve as the preferred option when:
  - The assessment process is completely and credibly established
  - There are multiple accreditation bodies
  - The business value of accreditation is established

  and/or if:
  - There is misrepresentation of self-certification status

19

Verifying ASTM D7036 Implementation (1/2)

Element	Value	Comments
QI Credential	High Required by MCR	MCR requires credentials but there have been instances of confusion about the exam date and QSTI award date. Verify methods and actual exam date, not QSTI date.
Site-specific Test Plan	High Not Mentioned in MCR	Not specifically mentioned in MCR, but a requirement for all test projects per ASTM D7036-04, conformance to which is required by MCR.
QM	Low Suggested by MCR	MCR advises source to obtain. But the QM provides no evidence of implementation, plus AETB can requests treatment of QM as CBI. Instead, request copy of table of contents and completed ASTM D7036-04 Checklist. ASTM D7036-04 Checklist is available at: http://www.betterdata.org/getaccredited.htm
MCR = Minimum Competency Rule		

20

Verifying ASTM D7036 Implementation (2/2)

Element	Value	Comments
Corrective Action Log	High Suggested by MCR	MCR advises source to obtain performance data and corrective actions for past 12 months. Corrective action tracking demonstrates implementation of ASTM D7036 requirements.
Training Log	Low Suggested by MCR	MCR advises source to obtain records for past 12 months. The exam for the QI is valid for 5 years. The absence of training during the past 12 months may not indicate a problem.
Internal and External Audit Results	High Suggested by MCR	MCR advises source to obtain data for past 12 months. ASTM D7036 requires annual internal audits. Demonstrates implementation of ASTM D7036 requirements.
MCR = Minimum Competency Rule		

21

Summary

- Minimum Competency Rule compliance is more than a Quality Manual and QI on site
- Conformance means that the AETB is implementing ASTM D7036
- Verification of conformance can be as simple as looking at key evidence of ASTM D7036 implementation:
  - QI exam date and methods
  - QM Table of Contents and ASTM D7036 checklist
  - Continual improvement documentation (corrective action logs, audit results)

22

Web Resources

Stack Testing Accreditation Council (STAC):

http://www.betterdata.org

Draft Part 75 Policy Manual:

http://www.epa.gov/airmarkets/emissions/monitoring.html

Source Evaluation Society:

http://www.sesnews.org/index.php?q=QSTIQSTO

ASTM International:

http://www.astm.org/

23

Key ASTM D7036-04 Citations (1 of 3)

Section 4.1, sentence 3:

The Quality Manual and its implementation shall provide the sole basis for determining the conformance of the AETB with this standard.

Section 8.3.2.3:

The Qualified Individual shall sign a statement to be kept on file with the AETB, agreeing that all tests conducted under his/her supervision will conform to the quality manual and this practice in all respects.

24

Key ASTM D7036-04 Citations (2 of 3)

Section 12.3:

A site specific test plan shall be used for each test project. (note that the standard describes 11 items that the test plan shall address)

Section 12.4:

The test plan, along with the AETB's quality manual, is the document against which an assessor shall perform any on-site assessment of conformance to this practice.

25

Key ASTM D7036-04 Citations (3 of 3)

Section 15.3.19:

The test report shall include a signed statement by a responsible individual that the AETB operates in conformance with the requirements of this practice during the test project.

26

Method 0023A: A Healthier PBMS Alternative

Yves Tondeur, et al
SGS Analytical Perspective

Abstract

Method 0023A is a good example of where the proper application of a PBMS (Performance-Based Measurement System) can lower costs while significantly increasing confidence in the data relative to standard methods for polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas samples. Method 0023A was introduced in the nineties in support of CAA/RCRA regulations for specific source categories. In particular, the EPA wanted to ensure that the target analytes present in the Filter/Particulate Matter/Probe Rinse (F/PM/PR) fractions were accounted for by requiring the latter to be analyzed as a separate sample. This choice leads to two analytical runs per sampling train.

The driving force behind this decision can be explained as follows. Under M0023A's sister method (Method 23) there is a distinct possibility of underestimating the target analyte concentrations due to poor extraction efficiencies from the F/PM/PR fraction. This possibility arises from combining all of the fractions from a sampling train inside of the same Soxhlet extraction vessel and, typically, adding the labeled extraction standards to the resin only. Such a low bias is more likely when the particulate load is significant. Additionally, when the laboratory "folds" the F/PM/PR components on top of the resin/glasswool bed, with the former located above the Soxhlet apparatus' solvent return elbow, poor extraction efficiencies are expected. Such a configuration prevents the F/PM/PR components from being submerged in solvent during the extraction cycles, increasing the likelihood of lower extraction efficiencies. Noteworthy is that such losses of analytes are undocumented, and are, therefore, uncorrected since the extraction standards are not introduced in this fraction. All of these issues can be addressed by the judicious selection and use of additional labeled PCDD/F standards, removing the need for doubling-up the analytical costs.

Method 0023A: A Healthier PBMS Alternative

Y. Tondeur, B. Vining, A. Martin, H. Distel and J. Hart

2013 National Environmental Monitoring Conference
Air Methods and Monitoring
"Protecting Human Health through Environmental Measurements and Monitoring"

San Antonio, TX
August 5th - 9th

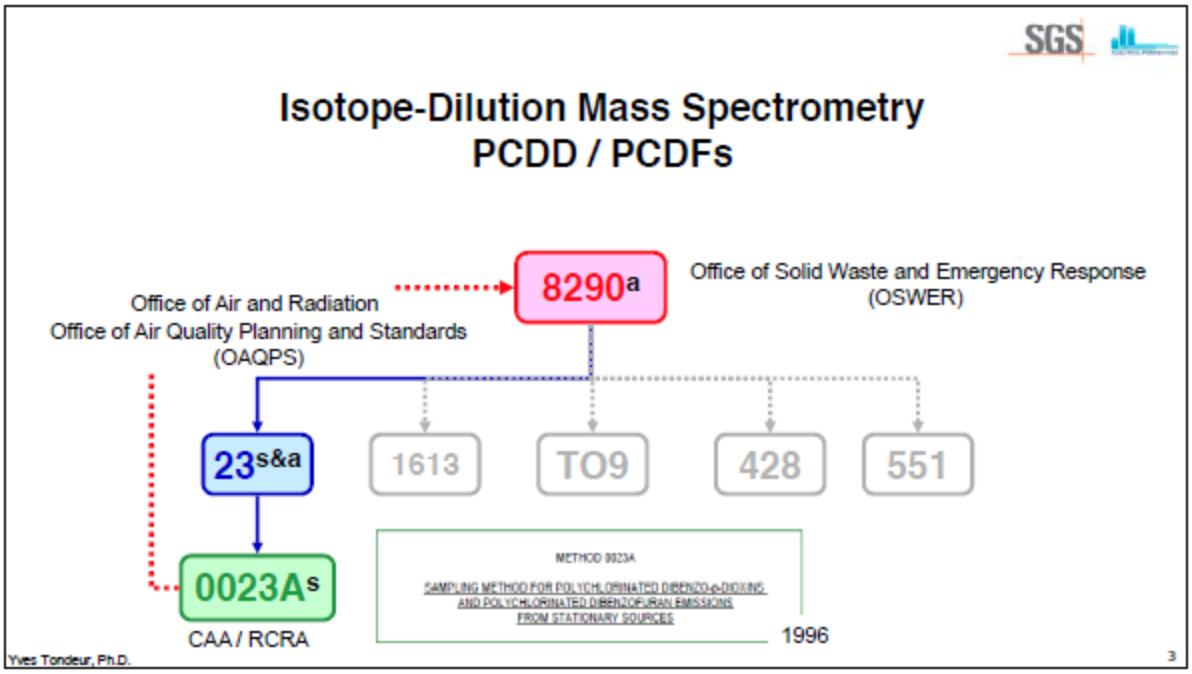
Outline

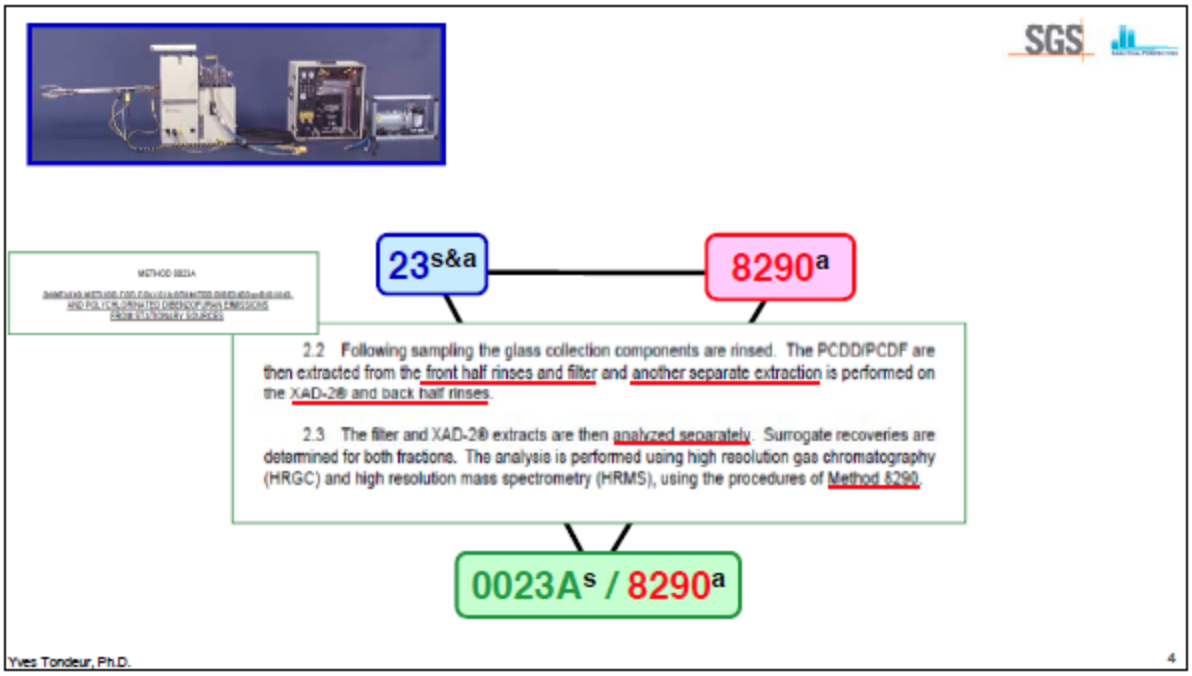
Beware of Quantitation without Representation[0023]

1. Methods' Trilogy
2. CAA / RCRA
   - Sampling Train Components
   - Why M0023A?
   - "Quick Fix"
3. PBMS Solution
   - Definition
   - Concept
   - Proof of Concept
4. Conclusions

Objective

Demonstrate the equivalency & superiority of a cost-effective alternative to Method 0023A based on Method 23[0023] for "dioxins" in stack samples


SGS
Isotope-Dilution Mass Spectrometry
PCDD / PCDFs
Office of Air and Radiation
Office of Air Quality Planning and Standards
(OAQPS)
8290a
Office of Solid Waste and Emergency Response
(OSWER)
23s&a
1613
TO9
428
551
0023As
METHOD 0023A
SAMPLING METHOD FOR POLYCHLORINATED DIBENZO-p-DIOXINS AND POLYCHLORINATED DIBENZOFURAN EMISSIONS FROM STATIONARY SOURCES
1996
CAA / RCRA
Yves Tondeur, Ph.D.
3


SGS
23s&a
8290a
2.2 Following sampling the glass collection components are rinsed. The PCDD/PCDF are then extracted from the front half rinses and filter and another separate extraction is performed on the XAD-2® and back half rinses.
2.3 The filter and XAD-2® extracts are then analyzed separately. Surrogate recoveries are determined for both fractions. The analysis is performed using high resolution gas chromatography (HRGC) and high resolution mass spectrometry (HRMS), using the procedures of Method 8290.
0023As / 8290a
Yves Tondeur, Ph.D.
4

Why M0023A?

- Emission tests "***in the past***" led to significant **PM load** compared to today's
- Existing methods unclear about "***purpose***"
- Laboratory's **practices** (*possibly*)[prep of thimble] unaligned with "***tacit purpose***"
- EPA's valid concerns
  - **incorrectly** estimating concentrations
  - due to poor extraction efficiencies of **PM's PCDD/Fs**
  - undocumented laboratory's **performance**
  - ***quantitation without representation***[2223]
- Pre-PBMS Era Solution → two analytical runs per sampling train → *Quick Fix*
  - front half (**Probe Rinses / Filter / PM**)
  - back half (**XAD-2 Resin / Rinses**)
  - circumstances, pressures, knowledge, availability of standards, PBMS timing
  - **double** analytical costs

PBMS

Performance Based Measurement System
(Federal Register Notice 62 FR 52098, October 6, 1997)

*" Set of processes wherein the data quality **needs**, mandates or limitations of a program or project are **specified**, and serve as **criteria** for selecting appropriate methods to meet those needs in a **cost - effective** manner. "*

PBMS

- Return **Flexibility**
- Imagination & Innovation
- Transfer of **Responsibility**
  - **Accurate** Demonstration of Compliance
  - Selection of **Appropriate** Method
- Data User's **Accountability**
  - **D**ata **Q**uality **O**bjectives
  - Performance Assessment
  - Measurement of **Uncertainty**
- Defensible & Scientifically-Sound Approaches
- Responsibility & Accountability
- Professionalism [PBMS is not carte blanche for chaos]

Yves Tondeur, Ph.D. 7

A Healthier PBMS Solution

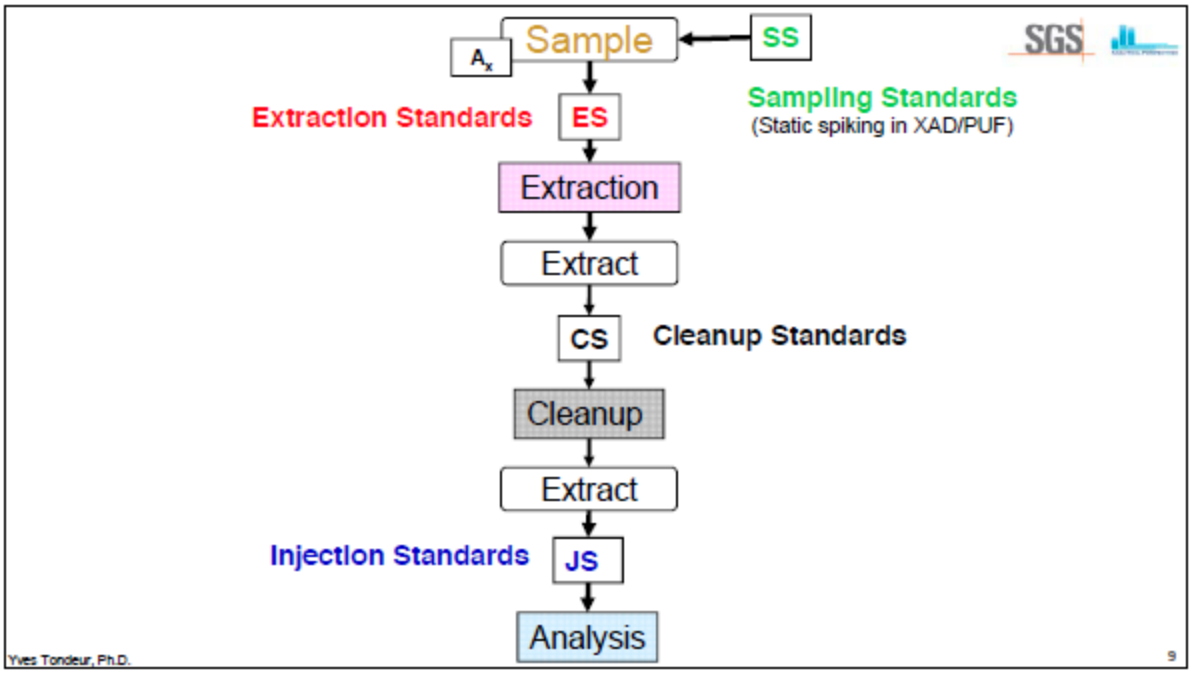
one analytical run per train *vs.* two
more reliable data

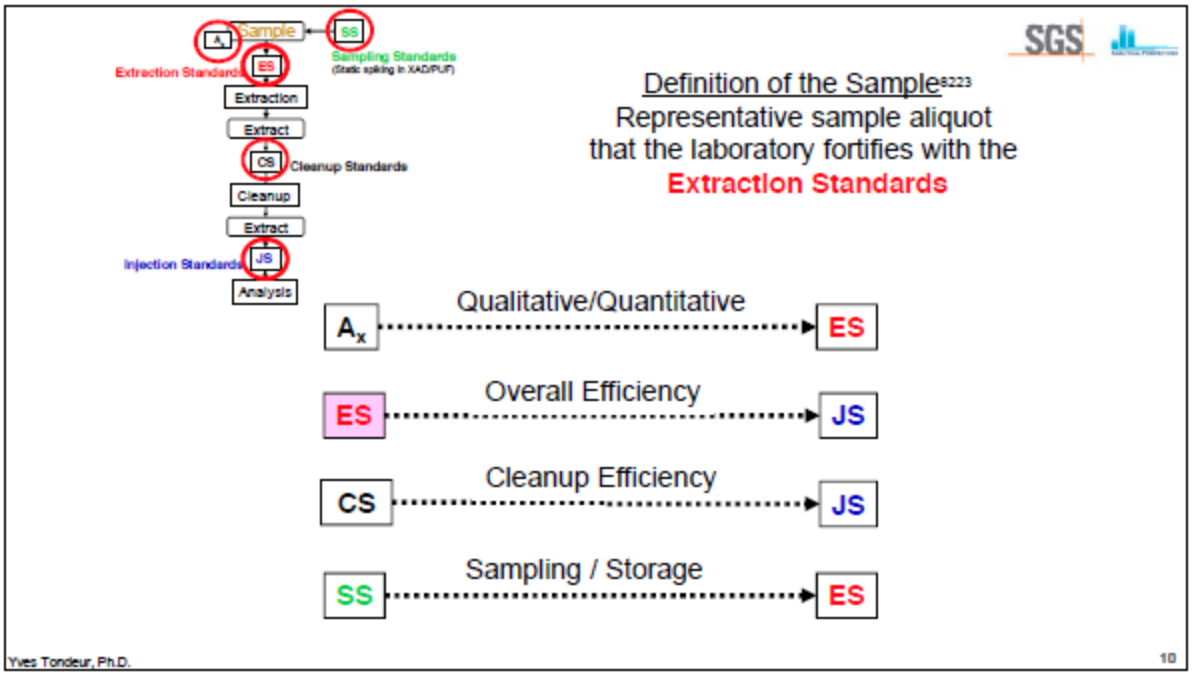
quantitation without representation

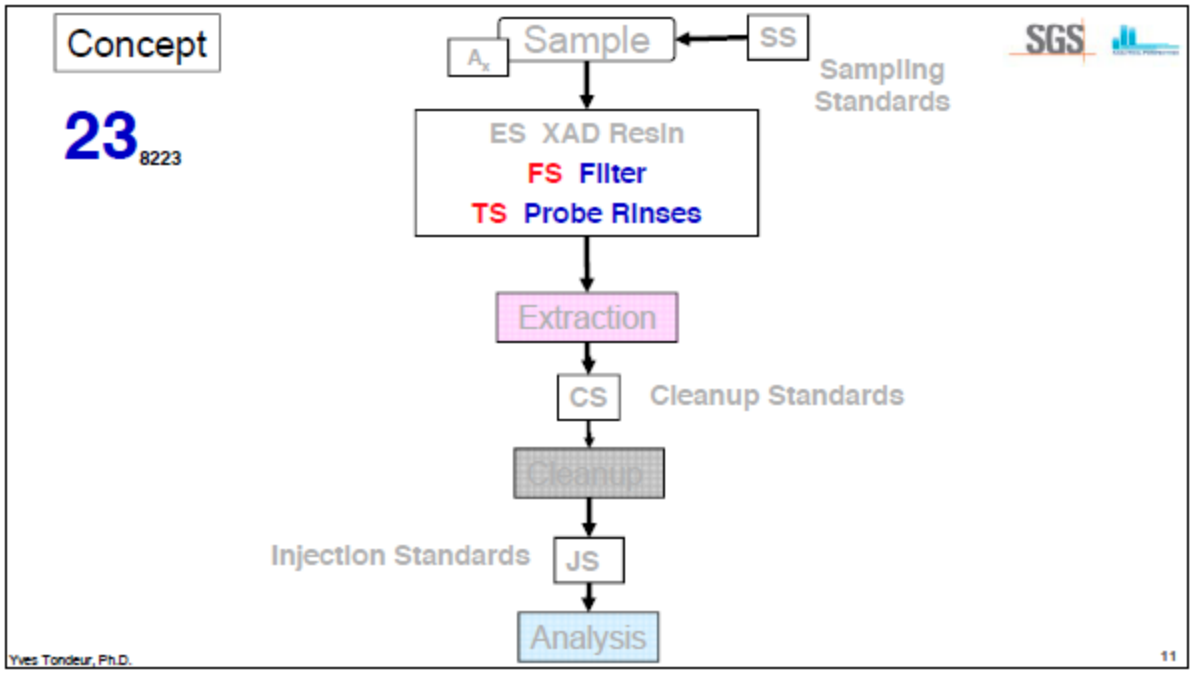
"Standards"

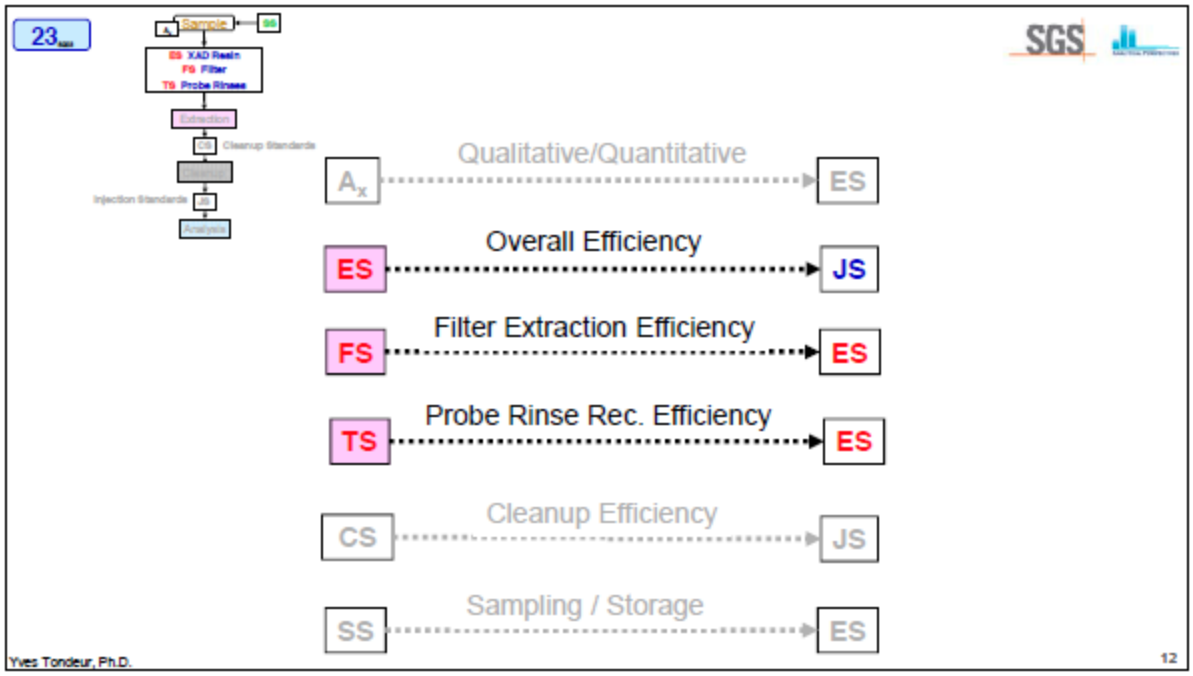
Functions & Relationships

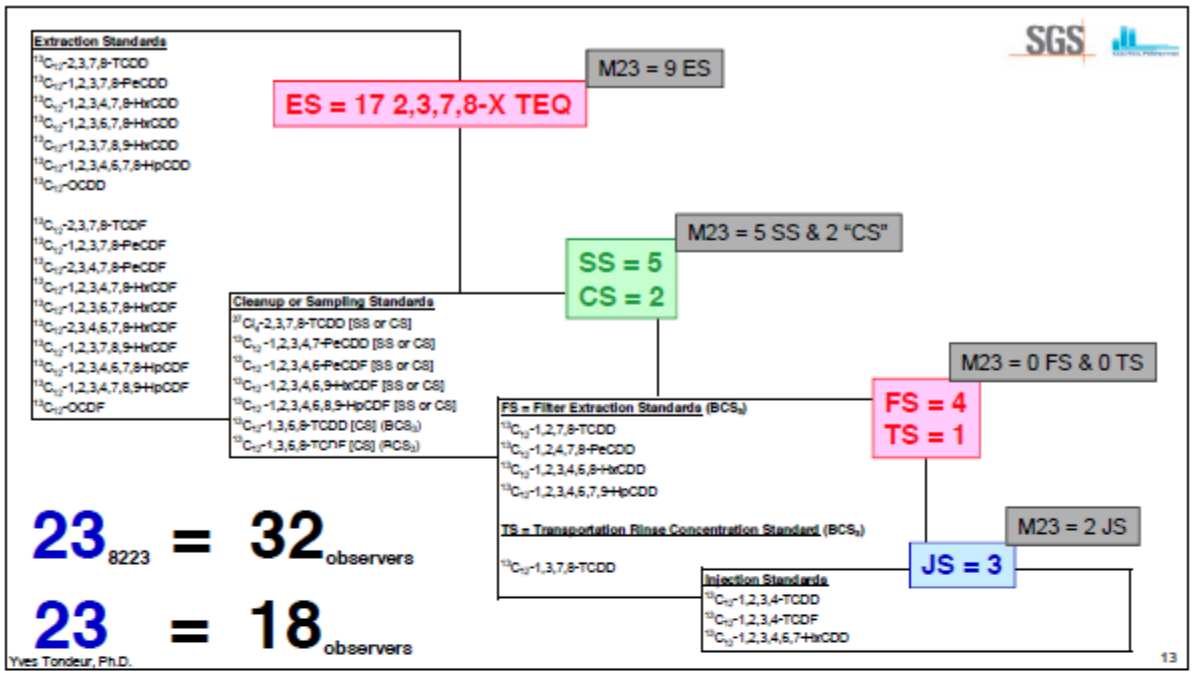
Yves Tondeur, Ph.D. 8

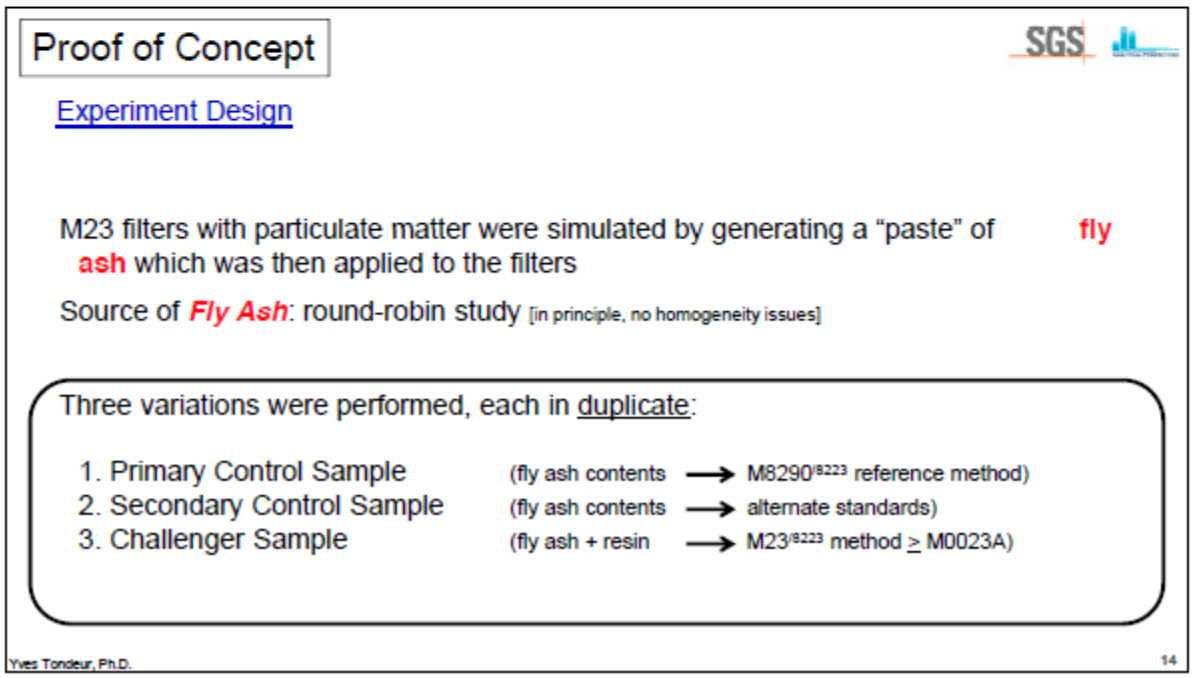

Sample
SS
A_x
Sampling Standards
(Static spiking in XAD/PUF)
Extraction Standards
ES
Extraction
Extract
CS
Cleanup Standards
Cleanup
Extract
Injection Standards
JS
Analysis
Yves Tondeur, Ph.D.
9


Definition of the Sample[8223]
Representative sample aliquot
that the laboratory fortifies with the
Extraction Standards
Qualitative/Quantitative
A_x
ES
Overall Efficiency
ES
JS
Cleanup Efficiency
CS
JS
Sampling / Storage
SS
ES
Yves Tondeur, Ph.D.
10


Concept
23 8223
Sample
SS
Sampling Standards
ES XAD Resin
FS Filter
TS Probe Rinses
Extraction
CS
Cleanup Standards
Cleanup
Injection Standards
JS
Analysis
Yves Tondeur, Ph.D.
11


Qualitative/Quantitative
ES
Overall Efficiency
JS
Filter Extraction Efficiency
Probe Rinse Rec. Efficiency
Cleanup Efficiency
Sampling / Storage
Yves Tondeur, Ph.D.
12


Extraction Standards
$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
$^{13}C_{12}$-OCDD
$^{13}C_{12}$-2,3,7,8-TCDF
$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,4,7,8-PeCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF
$^{13}C_{12}$-OCDF
ES = 17 2,3,7,8-X TEQ
M23 = 9 ES
SS = 5
CS = 2
M23 = 5 SS & 2 "CS"
Cleanup or Sampling Standards
$^{37}Cl_4$-2,3,7,8-TCDD [SS or CS]
$^{13}C_{12}$-1,2,3,4,7-PeCDD [SS or CS]
$^{13}C_{12}$-1,2,3,4,6-PeCDF [SS or CS]
$^{13}C_{12}$-1,2,3,4,6,9-HxCDF [SS or CS]
$^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF [SS or CS]
$^{13}C_{12}$-1,3,6,8-TCDD [CS] (BCS_3)
$^{13}C_{12}$-1,3,6,8-TCDF [CS] (RCS_3)
FS = 4
TS = 1
M23 = 0 FS & 0 TS
FS = Filter Extraction Standards (BCS_2)
$^{13}C_{12}$-1,2,7,8-TCDD
$^{13}C_{12}$-1,2,4,7,8-PeCDD
$^{13}C_{12}$-1,2,3,4,6,8-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,9-HpCDD
TS = Transportation Rinse Concentration Standard (BCS_4)
$^{13}C_{12}$-1,3,7,8-TCDD
JS = 3
M23 = 2 JS
Injection Standards
$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4-TCDF
$^{13}C_{12}$-1,2,3,4,6,7-HxCDD
23 8223 = 32 observers
23 = 18 observers
Yves Tondeur, Ph.D.
13


Proof of Concept
Experiment Design
M23 filters with particulate matter were simulated by generating a "paste" of fly ash which was then applied to the filters
Source of Fly Ash: round-robin study [in principle, no homogeneity issues]
Three variations were performed, each in duplicate:
1. Primary Control Sample (fly ash contents → M8290/8223 reference method)
2. Secondary Control Sample (fly ash contents → alternate standards)
3. Challenger Sample (fly ash + resin → M23/8223 method ≥ M0023A)
Yves Tondeur, Ph.D.
14

Proof of Concept

SGS

Experiment Design

1. Primary Control Sample Lab ID 005/006
   - Filter / ***Fly ash*** spiked with **ES** only followed by extraction ([A_x] = M8290/8223 reference)
2. Secondary Control Sample Lab ID 003/004
   - Filter / ***Fly ash*** spiked with **FS** only followed by extraction
3. Challenger Sample Lab ID 001/002
   - Filter / **Fly ash** spiked with **FS**, then
   - ***XAD*** was added, and **as per M23/0023A**, **ES** were spiked on the resin and extraction took place23/8223
     - ✓ Fly ash analytes [A_x] quantified using the **ES** (as per M23 & compared to M8290 reference above)
     - ✓ Recoveries of the **ES** (as per M23)
     - ✓ Recoveries of the **FS** (as per M23 SS) to document filter/PM extraction efficiency

Yves Tondeur, Ph.D. 15

Proof of Concept

SGS

Experiment Design

Samples were processed
from
extraction to analysis
as typical stack samples

- 2,3,7,8-X
- TEQ
- Homologue Groups [TMB = total mass balance]
- % ES & FS recoveries
- RPDs [A_x, TEQ, Hmlg]
- Combined Standard Uncertainties (%u_c)

Yves Tondeur, Ph.D. 16

Proof of Concept

Results

all details/breakdowns are available from proceedings' presentation (supplemental information = hidden slides)

RSD (N = 3x2) (hidden slide 18)	17	2,3,7,8-X	average: 3.5%	minimum: 1.1%	maximum[a]: 15%
	8	Homologue Groups	average: 2.6%	minimum: 1.6%	maximum: 3.8%
		TEQ	1.8%		
		TMB [PCDD/Fs]	1.5%		
RPD (Challenger/PCS[b]) (hidden slide 19)	17	2,3,7,8-X	average: 2.3%	minimum: 0.0%	maximum[a]: 15%
	8	Homologue Groups	average: 2.2%	minimum: 0.4%	maximum: 6.6%
		TEQ	1.7%		
		TMB [PCDD/Fs]	3.0%		
RPD (Challenger/PCS[b]) DUP (hidden slide 19)	17	2,3,7,8-X	average: 3.5%	minimum: 0.6%	maximum[a]: 13%
	8	Homologue Groups	average: 2.6%	minimum: 0.3%	maximum: 5.8%
		TEQ	3.4%		
		TMB [PCDD/Fs]	0.0%		

a) Maximums are all <10% except for 123789-HxCDF (lower concentration & poorly resolved peak = more variation associated with peak integration)
b) RPDs Challenger/SCS and DUP are similar and available from hidden slide 25

hidden slide 18

Proj.: V1125	Batch: 11119								
Lab ID	005	006	003	004	001	002	Ave	Nx6 sd	RSD
Name	Primary Control	Primary Control	Sec. Control	Sec. Control	Challenger	Challenger			
Analyte	Conc. (pg)	Conc. (pg)	Conc. (pg)	Conc. (pg)	Conc. (pg)	Conc. (pg)	pg	pg	
2378-TCDD	53.1	56.1	56.8	58.5	54.2	53.8	55.4	2	3.7%
12378-PeCDD	235	248	252	247	234	227	240	10	4.0%
123478-HxCDD	256	264	257	263	256	257	259	3	1.3%
123678-HxCDD	583	583	586	593	577	576	583	6	1.1%
123789-HxCDD	472	472	484	485	458	475	488	6	1.4%
1234678-HpCDD	3,030	3,100	3,210	3,090	3,050	3,070	3,092	63	2.0%
OCDD	2,230	2,340	2,110	1,930	2,270	2,300	2,197	153	6.9%
2378-TCDF	955	1,010	976	955	955	948	967	23	2.4%
12378-PeCDF	1,300	1,330	1,390	1,440	1,280	1,280	1,337	65	4.9%
23478-PeCDF	1,810	1,820	1,540	1,830	1,560	1,520	1,580	46	2.9%
123478-HxCDF	1,160	1,160	1,200	1,200	1,140	1,150	1,168	26	2.2%
123678-HxCDF	1,300	1,360	1,360	1,370	1,320	1,310	1,337	30	2.3%
234678-HxCDF	1,480	1,470	1,520	1,510	1,440	1,460	1,483	29	1.9%
123789-HxCDF	179	212	134	178	208	186	183	28	15.4%
1234678-HpCDF	2,780	2,780	2,860	2,790	2,740	2,730	2,777	47	1.7%
1234789-HpCDF	745	765	752	737	734	752	748	11	1.5%
OCDF	2,050	2,080	1,990	1,850	2,010	2,050	2,005	82	4.1%
Totals									
Total TCDD	7,070	7,090	7,250	7,580	6,940	7,270	7,200	223	3.1%
Total PeCDD	9,950	10,800	10,400	10,700	9,890	10,700	10,407	401	3.8%
Total HxCDD	10,500	10,100	10,300	10,600	10,100	10,700	10,383	256	2.5%
Total HpCDD	5,550	5,710	5,790	5,720	5,570	5,640	5,663	93	1.6%
Total TCDF	35,900	35,400	34,700	36,200	33,600	34,000	34,967	1044	3.0%
Total PeCDF	22,600	23,800	23,500	24,100	22,800	23,900	23,417	598	2.6%
Total HxCDF	13,000	12,800	12,500	12,800	12,800	13,400	12,883	299	2.3%
Total HpCDF	5,830	5,910	6,070	5,910	5,740	5,890	5,892	109	1.8%
Total PCDD/Fs	115,000	116,000	115,000	117,000	112,000	116,000	115,167	1722	1.5%
ITEF TEQs									
TEQ: ND=0	1,750	1,780	1,690	1,730	1,720	1,720	1,732	31	1.8%
TEQ: ND=DL/2	1,750	1,780	1,690	1,730	1,720	1,720	1,732	31	1.8%
TEQ: ND=DL	1,750	1,780	1,690	1,730	1,720	1,720	1,732	31	1.8%

	ave RSD	min	max
	3.5%	1.1%	15.4%
	2.6%	1.6%	3.8%

Challenger vs. PCS: PCS = ES-ref.	Challenger 001 ES-1	Primary 005 ES-1	RPD	Challenger 002 ES-2	Primary 006 ES-2	RPD
Analyte	**Conc. (pg)**	**Conc. (pg)**		**Conc. (pg)**	**Conc. (pg)**	
2378-TCDD	54.2	53.1	2%	53.8	56.1	4%
12378-PeCDD	234	235	0.4%	227	248	8%
123478-HxCDD	258	256	0.8%	257	264	3%
123678-HxCDD	577	583	1%	576	583	1%
123789-HxCDD	458	472	3%	475	472	1%
1234678-HpCDD	3050	3,080	1%	3070	3,100	1%
OCDD	2270	2,290	2%	2300	2,340	2%
2378 TCDF	955	955	0.0%	948	1,010	6%
12378-PeCDF	1280	1,300	2%	1280	1,330	4%
23478-PeCDF	1560	1,610	3%	1520	1,620	6%
123478-HxCDF	1140	1,160	2%	1150	1,160	1%
123678-HxCDF	1320	1,300	2%	1310	1,360	4%
234678-HxCDF	1440	1,460	3%	1480	1,470	1%
123789-HxCDF	208	179	15%	186	212	13%
1234678-HpCDF	2740	2,760	1%	2730	2,780	2%
1234789-HpCDF	734	745	1%	752	765	2%
OCDF	2010	2,050	2%	2050	2,080	1%
Totals						
Total TCDD	6940	7,070	2%	7270	7,090	3%
Total PeCDD	9890	9,950	1%	10700	10,800	1%
Total HxCDD	10100	10,500	4%	10700	10,100	6%
Total HpCDD	5570	5,550	0%	5640	5,710	1%
Total TCDF	33800	35,900	7%	34000	35,400	4%
Total PeCDF	22800	22,800	1%	23900	23,600	1%
Total HxCDF	12800	13,000	2%	13400	12,800	5%
Total HpCDF	5740	5,830	2%	5850	5,910	0.3%
Total PCDD/Fs	**112000**	**115,000**	**3%**	**116000**	**116,000**	**0.0%**
ITEF TEQs						
TEQ: ND=0	1,720	1,750	1.7%	1,720	1,780	3.4%
TEQ: ND=DL/2	1,720	1,750	1.7%	1,720	1,780	3.4%
TEQ: ND=DL	1,720	1,750	1.7%	1,720	1,780	3.4%

hidden slide 19

001/005	002/006
ave RPD	ave RPD
2.3%	3.5%
min	min
0.0%	0.6%
max	max
15.0%	13.1%

001/005	002/006
ave RPD	ave RPD
2.2%	2.6%
min	min
0.4%	0.3%
max	max
6.6%	5.8%

Yves Tondeur, Ph.D.

19

Challenger vs. SCS: SCS = FS-based	Challenger 001 ES-1	Secondary 003 FS-1	RPD	Challenger 002 ES-2	Secondary 004 FS-2	RPD
Analyte	**Conc. (pg)**	**Conc. (pg)**		**Conc. (pg)**	**Conc. (pg)**	
2378-TCDD	54.2	56.6	4%	53.8	58.5	8%
12378-PeCDD	234	252	7%	227	247	8%
123478-HxCDD	258	257	0.4%	257	263	2%
123678-HxCDD	577	586	2%	576	593	3%
123789-HxCDD	458	464	1%	475	465	2%
1234678-HpCDD	3050	3210	5%	3070	3090	1%
OCDD	2270	2110	7%	2300	1930	17%
2378-TCDF	955	976	2%	948	955	1%
12378-PeCDF	1280	1390	8%	1280	1440	12%
23478-PeCDF	1560	1540	1%	1520	1630	7%
123478-HxCDF	1140	1200	5%	1150	1200	4%
123678-HxCDF	1320	1380	3%	1310	1370	4%
234678-HxCDF	1440	1520	5%	1480	1510	2%
123789-HxCDF	208	134	43%	186	176	6%
1234678-HpCDF	2740	2860	4%	2730	2790	2%
1234789-HpCDF	734	752	2%	752	737	2%
OCDF	2010	1990	1%	2050	1850	10%
Totals						
Total TCDD	6940	7,250	4%	7270	7,580	4%
Total PeCDD	9890	10,400	5%	10700	10,700	0%
Total HxCDD	10100	10,300	2%	10700	10,800	1%
Total HpCDD	5570	5,790	4%	5640	5,720	1%
Total TCDF	33800	34,700	3%	34000	36,200	6%
Total PeCDF	22800	23,500	3%	23900	24,100	1%
Total HxCDF	12800	12,500	2%	13400	12,800	5%
Total HpCDF	5740	6,070	6%	5850	5,910	0%
Total PCDD/Fs	**112000**	**115,000**	**2.6%**	**116000**	**117,000**	**0.9%**
ITEF TEQs						
TEQ: ND=0	1,720	1,690	1.8%	1,720	1,730	0.6%
TEQ: ND=DL/2	1,720	1,690	1.8%	1,720	1,730	0.6%
TEQ: ND=DL	1,720	1,690	1.8%	1,720	1,730	0.6%

hidden slide 20

001/003	002/004
ave RPD	ave RPD
6.1%	5.4%
min	min
0.4%	0.6%
max	max
43.3%	17%

001/003	002/004
ave RPD	ave RPD
3.7%	2.3%
min	min
2.0%	0.0%
max	max
5.6%	6.3%

Yves Tondeur, Ph.D.

20

Proof of Concept

Results (supplemental information hidden slide 22)

$^{TEQ}u_c$ [~7.5% - 8%] > ^{TEQ}RPD [~2% – 4%]

Combined Standard Uncertainties (u_c) for TEQ

Primary Control Sample (005)	Primary Control Sample DUP (006)	Challenger (001)	Challenger DUP (002)
7.45%	7.51%	7.45%	7.73%

Yves Tondeur, Ph.D. 21

V1125	Primary Control	Primary Control DUP	Challenger	Challenger DUP
Analyte	005	006	001	002
	$\%u_c$	$\%u_c$	$\%u_c$	$\%u_c$
2,3,7,8-TCDD	13.2%	13.4%	13.6%	12.9%
1,2,3,7,8-PeCDD	8.20%	8.70%	9.50%	8.65%
1,2,3,4,7,8-HxCDD	9.90%	10.8%	9.75%	10.8%
1,2,3,6,7,8-HxCDD	6.75%	7.50%	6.65%	7.55%
1,2,3,7,8,9-HxCDD	8.15%	8.70%	8.10%	9.10%
1,2,3,4,6,7,8-HpCDD	5.50%	5.30%	5.25%	5.45%
OCDD	5.65%	5.60%	5.65%	5.80%
2,3,7,8-TCDF	7.15%	7.25%	7.40%	7.15%
1,2,3,7,8-PeCDF	9.55%	9.35%	9.60%	9.75%
2,3,4,7,8-PeCDF	6.30%	6.20%	6.20%	6.70%
1,2,3,4,7,8-HxCDF	8.55%	8.65%	8.30%	8.35%
1,2,3,6,7,8-HxCDF	8.95%	9.00%	8.60%	8.95%
2,3,4,6,7,8-HxCDF	7.95%	8.00%	7.70%	7.85%
1,2,3,7,8,9-HxCDF	55.5%	56.0%	54.0%	55.5%
1,2,3,4,6,7,8-HpCDF	5.35%	5.30%	5.60%	5.50%
1,2,3,4,7,8,9-HpCDF	7.60%	7.25%	7.90%	7.60%
OCDF	8.25%	8.10%	7.95%	8.30%
ITEF TEQ (ND=DL; EMPC=EMPC)	7.45%	7.51%	7.45%	7.73%

hidden slide 22

Yves Tondeur, Ph.D. 22

Proof of Concept

Results

Fly Ash
M23[8223] vs. Consensus Values

Round-Robin FLY ASH & SGS-AP Study	Consensus Ave pg	Consensus Median pg	V1125 SGS-AP Ave (N=6) pg	RPD Median/SGS-AP
2,3,7,8-TeCDD	50.9	51.7	55.4	7%
1,2,3,7,8-PeCDD	230	233	240	3%
1,2,3,4,7,8-HxCDD	246	248	259	4%
1,2,3,6,7,8-HxCDD	583	587	583	1%
1,2,3,7,8,9-HxCDD	439	455	468	3%
1,2,3,4,6,7,8-HpCDD	3,023	3,058	3,092	1%
OCDD	2,310	2,328	2,197	6%
2,3,7,8-TeCDF	958	976	967	1%
1,2,3,7,8-PeCDF	1,260	1,268	1,337	5%
2,3,4,7,8-PeCDF	1,345	1,363	1,580	15%
1,2,3,4,7,8-HxCDF	1,162	1,170	1,168	0%
1,2,3,6,7,8-HxCDF	1,309	1,321	1,337	1%
2,3,4,6,7,8-HxCDF	1,387	1,433	1,483	3%
1,2,3,7,8,9-HxCDF	330	170	183	7%
1,2,3,4,6,7,8-HpCDF	2,886	2,943	2,777	6%
1,2,3,4,7,8,9-HpCDF	738	760	748	2%
OCDF	2,170	2,141	2,005	7%
ITEQ (PCDD/F)	1,610	1,620	1,732	7%

2378-X	
RPD Ave	4%
min	0.2%
max	15%

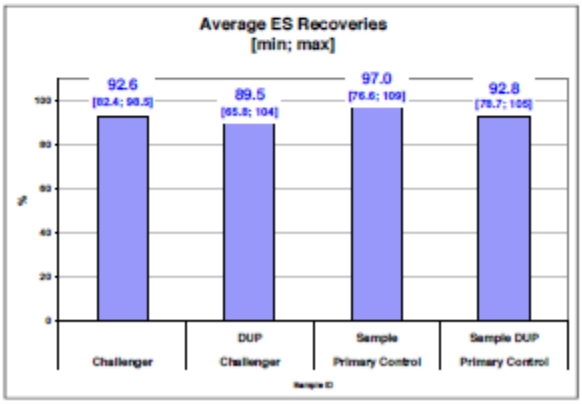
Yves Tondeur, Ph.D. 23

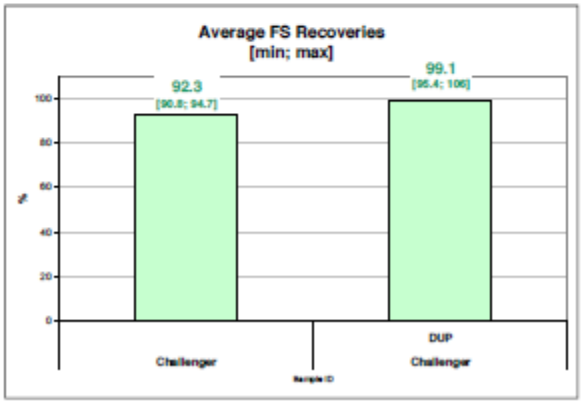
Proof of Concept

Results

(supplemental information = hidden slide 26)

Recoveries of Labeled Standards





Yves Tondeur, Ph.D. 24

Proof of Concept

Results (supplemental information = hidden slide 25)

RPD (Challenger/SCS)	17	2,3,7,8-X	average:	6.1%	minimum:	0.4%	maximum[a]:	43%
(hidden slide 20)	8	Homologue Groups	average:	3.7%	minimum:	2.0%	maximum:	5.6%
		TEQ		1.8%				
		TMB [PCDD/Fs]		2.6%				

RPD (Challenger/SCS) DUP	17	2,3,7,8-X	average:	5.4%	minimum:	0.6%	maximum:	17%
(hidden slide 20)	8	Homologue Groups	average:	2.3%	minimum:	0.0%	maximum:	6.3%
		TEQ		0.6%				
		TMB [PCDD/Fs]		0.9%				

Yves Tondeur, Ph.D.

a) Maximums are all <10% except for 123789-HxCDF (lower concentration & poorly resolved peak = more variation associated with peak integration)

25

Proof of Concept

Results

Recoveries of Labeled Standards

V1128	V1128_11118_DF_001	V1128_11118_DF_002	V1128_11118_DF_003	V1128_11118_DF_004	V1128_11118_DF_005	V1128_11118_DF_006
	Challenger	Challenger DUP	Primary Control Sample	Primary Control Sample DUP	Secondary Control Sample	Secondary Control Sample DUP
Standard	HS Recoveries	HS Recoveries	HS Recoveries	HS Recoveries	HS Recoveries	HS Recoveries
RS 2378-TCDD	95.3	95.6	104	95.9	-	-
RS 12378-PeCDD	97.8	94	104	95.7	-	-
RS 123478-HxCDD	94	97.3	102	95.7	-	-
RS 123678-HxCDD	95.6	97.5	101	95.6	-	-
RS 123789-HxCDD	94.6	94.7	101	94.2	-	-
RS 1234678-HpCDD	90.6	94.6	93.7	91.7	-	-
RS OCDD	82.4	85.8	76.8	76.7	-	-
RS 2378-TCDF	96.3	104	98.9	98	-	-
RS 12378-PeCDF	96.5	104	100	105	-	-
RS 23478-PeCDF	97	96.5	101	93	-	-
RS 123478-HxCDF	92.6	96.2	97.8	91.4	-	-
RS 123678-HxCDF	91	93.1	101	91	-	-
RS 234678-HxCDF	91.8	90	98.1	94.4	-	-
RS 123789-HxCDF	89.9	93.4	98.9	96.5	-	-
RS 1234678-HpCDF	90.8	92	93.9	95.6	-	-
RS 1234789-HpCDF	88.9	93.9	93.7	97.4	-	-
RS OCDF	86.8	88.3	93.1	93	-	-
Standard	CS/AS/FS Rec.	CS/AS/FS Rec.	CS/AS/FS Rec.	CS/AS/FS Rec.	CS/AS/FS' Rec.	CS/AS/FS' Rec.
CA 37Cl-2378-TCDD	92.8	94.6	101	91.8	95.3	93.1
CA 13C-PeCDD	92.8	93.1	98.4	95.4	94	91.9
CA 13C-PeCDF	95.1	99	99.8	93.5	97.6	96.1
CA 13C-HxCDF	97.7	94.8	97.8	98.3	93.3	98.5
CA 13C-HpCDF	98	91.3	97.2	97.1	91.4	90.7
NA 13C-TCDD	97.2	101	107	96.1	99.8	98.1
NA 13C-TCDF	101	104	104	102	102	98.4
FS 1378-TCDD	90.8	95.4	-	-	95.4	91.8
FS 12478-PeCDD	93.2	106	-	-	96.8	96.1
FS 123468-HxCDD	94.7	98.3	-	-	96.3	93.8
FS 1234678-HpCDD	91.5	96.9	-	-	96	93.3
Average HS Recoveries	92.6	89.5	97.3	92.8	-	-
Min. HS Recoveries	82.4	85.8	76.8	76.7	-	-
Max. HS Recoveries	96.5	104	100	105	-	-
Average FS Recoveries	92.3	99.1	-	-	-	-
Min. FS Recoveries	90.8	95.4	-	-	-	-
Max. FS Recoveries	94.7	106	-	-	-	-
Average FS' Recoveries	-	-	-	-	94.7	92.9
Min. FS' Recoveries	-	-	-	-	90.3	90.3
Max. FS' Recoveries			-	-	96.8	96.1
Average CS/AS Recoveries	93.2	95.4	97.6	91.7	95.8	93.8
Min. CS/AS Recoveries	86	91.3	96.4	95.4	90.3	98.5
Max. CS/AS Recoveries	101	104	107	102	102	98.4

hidden slide 26

FS recoveries in the Secondary Control Samples are computed relative to the JS rather than the ES since the latter were not used for the SCS. Effectively, the FS' represent the overall efficiencies.

Yves Tondeur, Ph.D.

26

Conclusions

- EPA's concerns (more than) adequately addressed
- Alternate Method 23/8223 ≥ Method 0023A

- Principle: ***beware of quantitation without representation***
- Philosophy: ***fitness for purpose***
- Attitude: ***performance based measurement system***

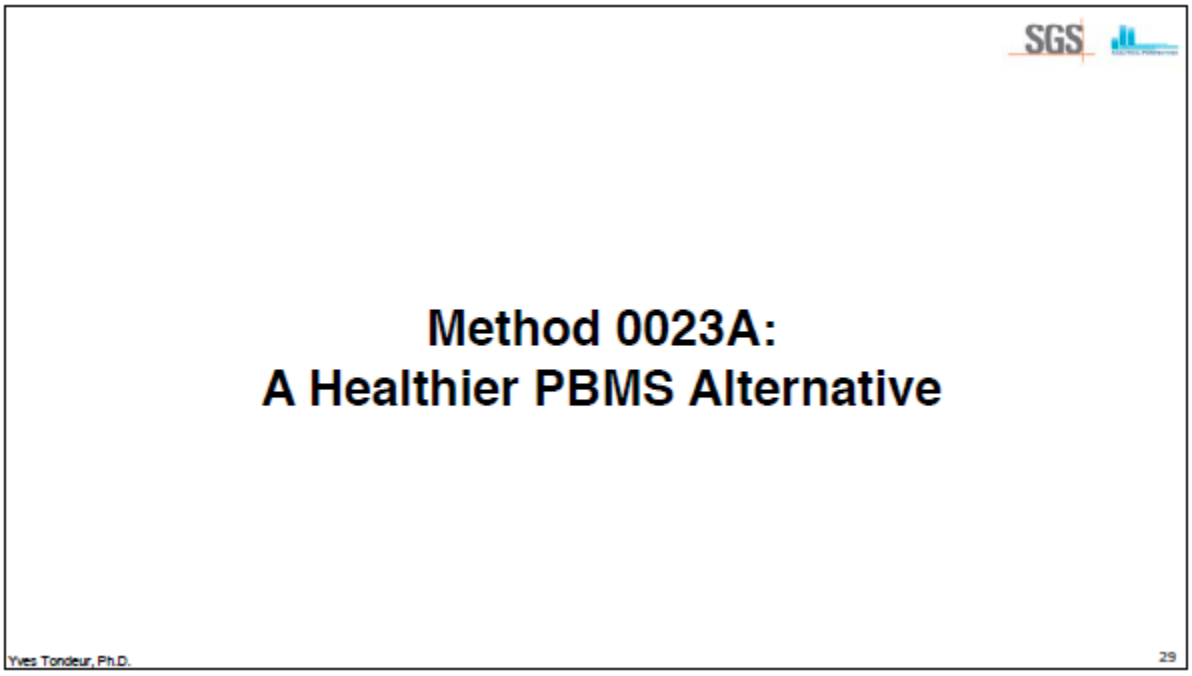
- Turning "***temporary fix***" into "***long-term effective solution***"
  - ✓ more confidence in the data
  - ✓ fit-for-purpose data (desired end-point: **Measurement of Uncertainty**)
  - ✓ reducing costs, energy, waste, pollution while "filling" the gaps in existing methods

Yves Tondeur, Ph.D. 27

Conclusions

clearly a healthier "*win-win*" alternative

Yves Tondeur, Ph.D. 28


SGS
Method 0023A:
A Healthier PBMS Alternative
Yves Tondeur, Ph.D.
29

SECTION 11

CURRENT TOPICS IN MICROBIOLOGY

Method Development for Detection of Biothreat Agents from Environmental Samples

Tonya Nichols
U.S. EPA

Abstract

In the event of an indoor, outdoor, or water system contamination with pathogenic microorganisms, it is necessary to have sampling and analytical methods that measure the concentration of the biological agent of concern in the environmental samples taken from the various environmental matrices (water, surfaces, and air). To address this need, the Homeland Security Research Program (HSRP) conducts research to select existing methods for immediate use or further refinement of the method to better fit the response community's requirements for sensitive, higher-throughput methods in a timely and cost-effective manner for risk management decisions. Our method development efforts are in direct support of the EPA's Environmental Response Laboratory Network (ERLN). The biological detection methods research includes both biological select and non-select agents with Bacillus anthracis being the highest priority. Standard Analytical Procedures (SAPs) have been developed for several biothreat agents. Few of the SAPs including those for Escherichia coli O157:H7, Vibrio cholerae, Salmonella Typhi, and Non-Typhoidal Salmonella species in water samples have been verified in a single laboratory set up. On the select agents, our efforts have been focused on combining the traditional culture method with high-throughput molecular analysis using the polymerase chain reaction (PCR) for the detection of B. anthracis spores. The Rapid Viability PCR (RV-PCR) method has been developed and optimized for air filters, wipes, water, vacuum filters, vacuum socks, and sponge-stick sampling tools. Single laboratory verification of the method demonstrated a limit of detection (LOD) at the level of 10 CFU/sample for air filters, wipes, and water samples. The method was field-tested using B. anthracis surrogate samples from a facility decontamination exercise. In a split-sample analysis, the RV-PCR method was 97.8% in agreement with traditional culture-based method. In summary, our research aims to provide rapid, high-throughput, highly sensitive, specific, time-efficient, and cost-effective methods for the detection of viable biological contaminants. This presentation will describe method development and testing for biothreat agents and the applicability to recovery from contamination incidents.

Method Development
for
Detection of Biothreat Agents
from
Environmental Samples

Tonya Nichols, PhD
Acting Director, Threat and Consequence Assessment Division
U.S. Environmental Protection Agency



National Environmental Monitoring Conference
August 2013

EPA Mission

Protect Human Health and the Environment



EPA conducts environmental sampling to detect contaminants and to determine extent of contamination to inform risk management decisions.

2

2001 – Anthrax Letters

EPA was tasked with the remediation of buildings contaminated by the anthrax letters of 2001

Sample Collection





Sample Transport

Sample Analysis





3

EPA Mission expanded – CBR* Agents

*Chemical, Biological, Radiological

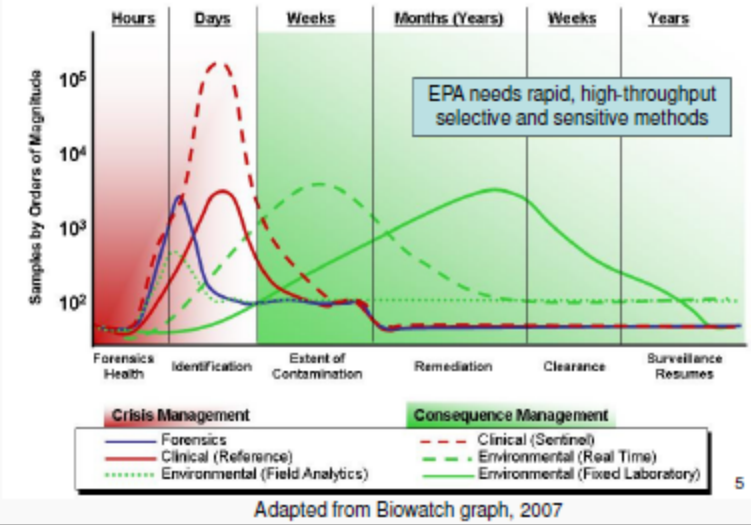
Responsibilities

- **Protect water systems from attacks and for detecting and recovering from successful attacks** affecting water systems by leading efforts to provide States and water utilities guidance, tools and strategies. *EPA is the federal government Sector Specific Agency (SSA) lead for water infrastructure.*
- **Decontaminate buildings and outdoor areas** impacted by a terrorist attack by leading efforts to establish clearance goals and clean up.
- **Develop a nationwide laboratory network** with the capability and capacity to analyze for chemical, biological and radiological agents for routine monitoring and in response to a terrorist attack.

EPA needs sensitive and selective methods for a wide variety of threat agents

4

Anticipated Sampling and Analytical Needs – Bioterrorism Event



5

Adapted from Biowatch graph, 2007

ERLN: Environmental Response Laboratory Network

Integrated Consortium of Laboratory Networks (ICLN)
- LRN, FERN, ERLN, NAHLN, NPDN, DLN
- coordination of analytical lab services in CBR events
- strive to establish methods for risk-based prioritization
- aims to improve capability for "surge" requirements

Sample Collection



Sample Transport

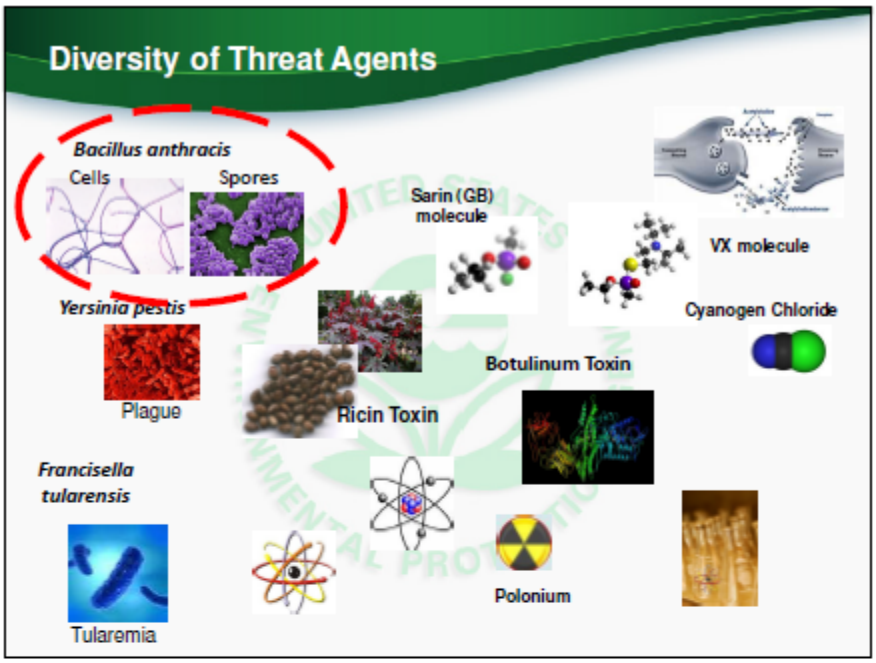
Sample Analysis

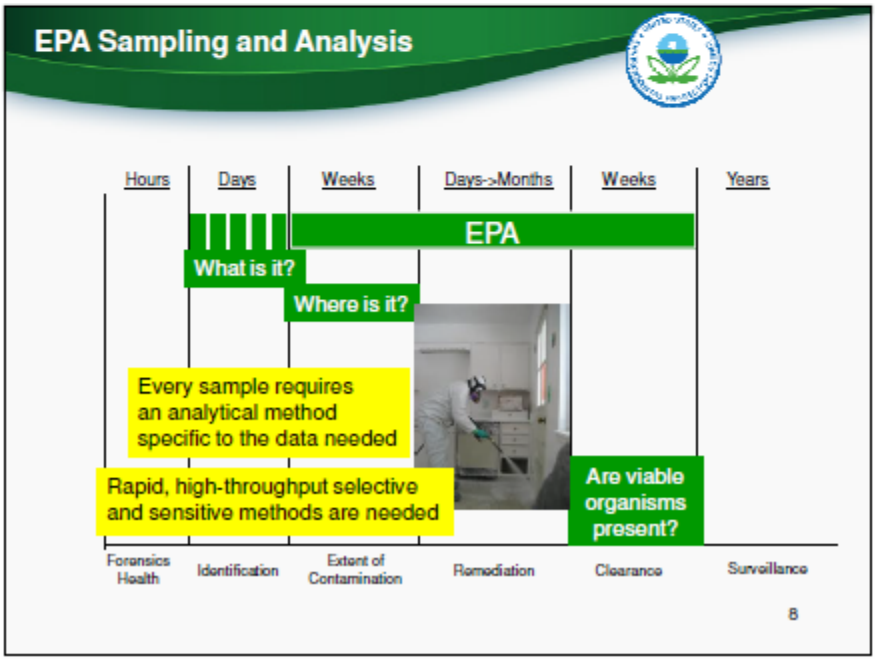


ERLN:
- All Hazards/All Environmental media laboratory network
- Enhance EPA capabilities and/or leverage other networks' capabilities
- Provide procedures/practices to support EPA responses

http://www.epa.gov/oemerln1/info.html

6

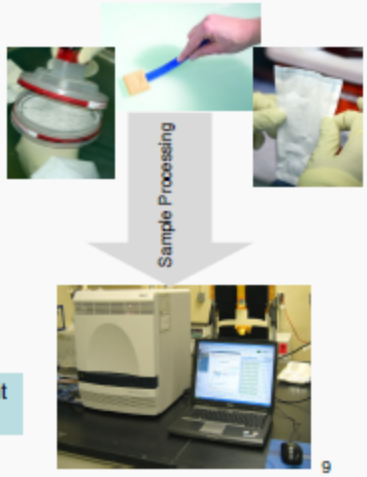

Diversity of Threat Agents
Bacillus anthracis
Cells
Spores
Yersinia pestis
Plague
Francisella tularensis
Tularemia
Sarin (GB) molecule
VX molecule
Cyanogen Chloride
Botulinum Toxin
Ricin Toxin
Polonium


EPA Sampling and Analysis
Hours
Days
Weeks
Days->Months
Weeks
Years
EPA
What is it?
Where is it?
Every sample requires an analytical method specific to the data needed
Rapid, high-throughput selective and sensitive methods are needed
Are viable organisms present?
Forensics Health
Identification
Extent of Contamination
Remediation
Clearance
Surveillance
8

EPA considerations for Biothreat Agent Method Development

- ❑ Viability
- ❑ Limit of detection
- ❑ Sample processing time
- ❑ High throughput (Automation)
- ❑ Green approach (less waste)

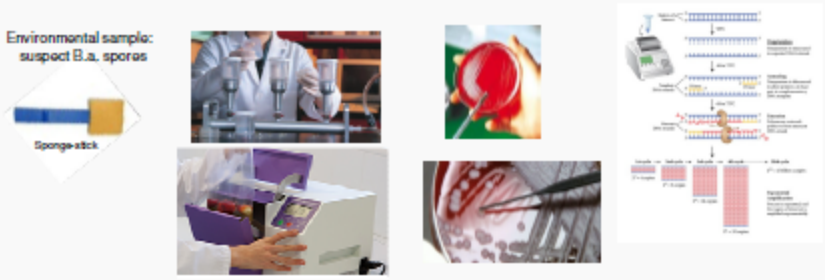
Does this require new method development or refinement of existing methods?



9

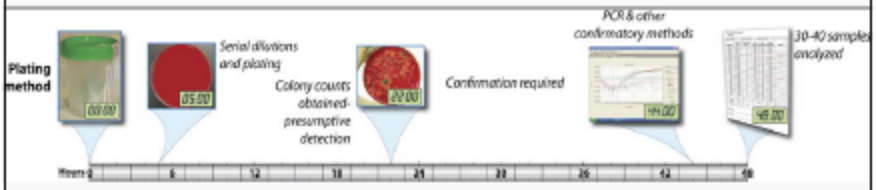
Traditional Lab Analysis for *Bacillus anthracis* (Anthrax)

Sample received in lab → Sample processed to extract spores → Sample aliquot plated on culture media → Positive culture - confirmed by PCR



Timeline for Traditional Ba Method

Average lab can process 30 - 40 samples in 48 hours.



In a bioterrorism event, hundreds to thousands of environmental samples may be taken, in addition to clinical samples.

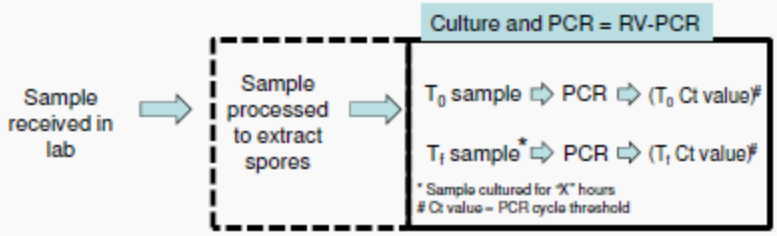
11

Enhancing *B. anthracis* Analytical Capability

#1 Priority for EPA's ERLN

EPA has developed a new method for *B. anthracis*

Rapid-**V**iability **P**olymerase **C**hain **R**eaction (RV-PCR) method



Rapid-Viability PCR Method for Detection of Live, Virulent *Bacillus anthracis* in Environmental Samples, *Appl. Environ. Microbiol.*, Vol. 77, 6570-6578, Sept 2011

12

RV-PCR Protocol

Video : http://www.epa.gov/nhsrc/video/rvpcr.html

Sample Processing and Incubation









13

RV-PCR for *B. anthracis*

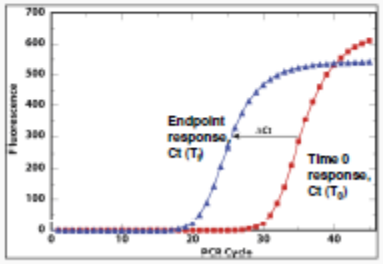
△Ct from T_0 and $T_f \geq 9$ indicates growth of viable spores

T_0 sample ⇨ PCR ⇨ (T_0 Ct value)#

T_f sample* ⇨ PCR ⇨ (T_f Ct value)#

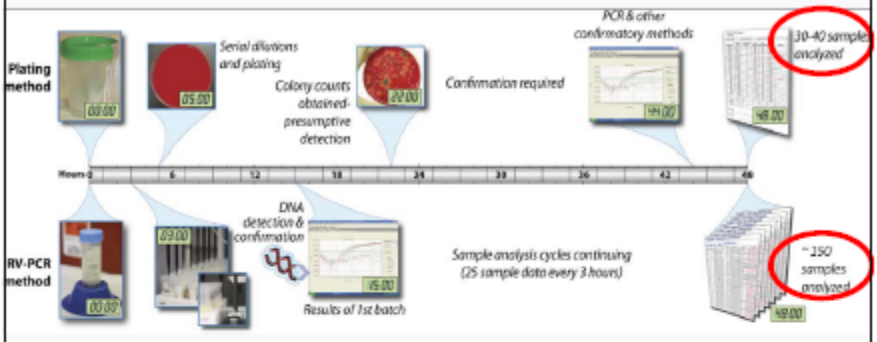
* Sample cultured for "X" hours

Ct value = PCR cycle threshold



14

Comparison of RV-PCR with Traditional Plating Method



Plating Method: 30-40 samples
RV-PCR Method: 150 samples

15

Evaluation of RV-PCR method with wipes, vacuum socks and filters

- Spore recovery from vacuum samples is lower than from wipes

Sample Type with Test Dust + Ba Spores	Spore Recovery (average of 3 replicates)
Wipe	82 ± 4 %
Vacuum Sock	55 ± 3 %
Vacuum Filter	43 ± 4 %


Vacuum filter

- The DNA extraction protocol was modified to accommodate high levels of dirt (up to 1 g)
- LOD: 10-99 CFU/sample with the 2 plasmid assays
- LOD: 100-999 CFU/sample with the chromosome assay


Vacuum sock

16

Evaluation of RV-PCR method with sponge stick sampling tools

- Spore recovery from sponge stick sampling tools is *significantly lower* than recovery from wipe samples.

Sample Type (6 replicates per treatment)	Spore Recovery after 1st Extraction	Spore Recovery after 2nd Extraction	Spore Recovery after 3rd Extraction
Clean Sponge Stick	18 ± 3 %	24 ± 6 %	25 ± 4 %
Dirty Sponge Stick	17 ± 3 %	21 ± 4 %	23 ± 2 %

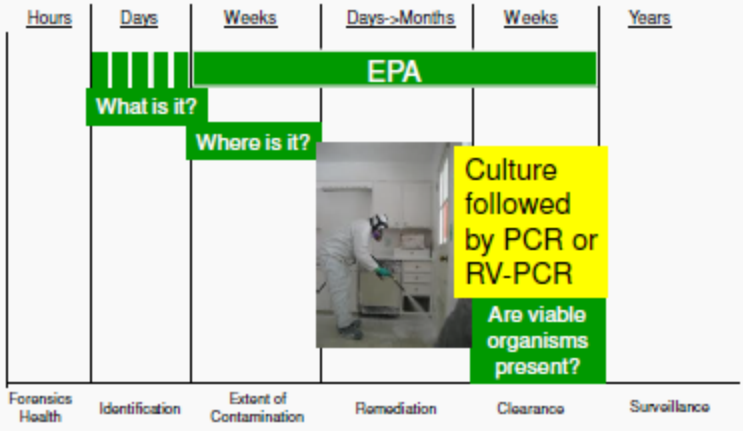


Sponge stick sampling tool

- Due to lower spore recovery from sponge-stick sampling tools, a longer incubation time (15 hours) is required to maintain an LOD at the level of 10-99 CFU/sample with this sample type.

17

EPA Sampling and Analysis



18

Field Evaluation of RV-PCR

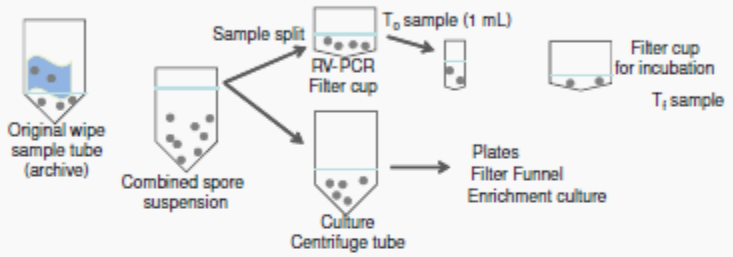
Compared to Traditional Culture/Plating Method

Bio-Response Operational Testing and Evaluation (BOTE)





Environmental samples were taken pre- and post-decon treatment of contaminated building with *B. atropheaus* (Ba surrogate).



19

Field Evaluation of RV-PCR

Compared to Traditional Culture/Plating Method

Bio-Response Operational Testing and Evaluation (BOTE)





Environmental samples were taken pre- and post-decon treatment of contaminated building with *B. atropheaus* (Ba surrogate).

BOTE Decon Event	% Agreement n= 250 samples
Pre-Contamination (Bkg)	94.7%
Pre-VHP	88.9%
Post-VHP	91%
Pre-Bleach	89.7%
Post-Bleach	100%
Pre-Clorine Dioxide	100%
Post-Clorine Dioxide	100%)
Total	95.4%

20

Timeline for BOTE Sample Processing and Analysis (20-24 samples)

RV-PCR

- Receiving (2 people): 1 hr
- RV-PCR to T0 sample (1 person): ~4 hr
- T0 aliquot processing (1 person): ~3 hr
- T9 aliquot processing (1 person): ~3 hr
- PCR (1 person): 2-3 hr
- **Overall RV-PCR (people hours): 14-16 hr**

Culture

- Receiving (2 people): 1 hr
- LRN culture protocol: 2 people 8-10 hr
- Culture (next day, 1 person): 7-8 hr
- Culture (3rd day, 1 person): 3-4 hr
- **Overall Culture (people hours): 28-32 hr**

The RV-PCR method enhances ERLN's lab capability/capacity to analyze the hundreds of environmental samples in a timely manner.

21

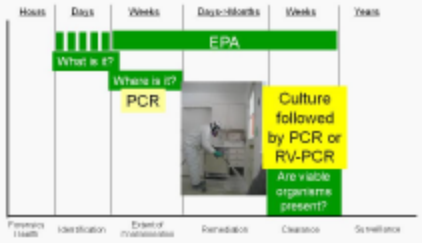
Protocol for Detection of *B. anthracis*



Response phase-appropriate methods:

Site Characterization Phase: Single gene target Real-time PCR with an option for multiple gene target real-time PCRs

Post-Decontamination Phase: Traditional Culture: serial dilution followed by plating and real-time PCR (of colonies) or RV-PCR



22

Challenges to Bioagent Method Development

- Biosafety requirements for collection, transport, and analysis
- Lack of validated methods for all matrices
  - Sensitivity
    - LOD (limit of detection)
    - Recovery from environmental media (air, water, soil, surfaces, waste)
    - Exposure dose risk levels (unknown for many)
    - Concentration techniques to facilitate detection
  - Selectivity
- Viability
  - Screening (Extent of Contamination)
  - Clearance (Following Decontamination)
- Method implementation
  - Logistics (equipment, tech expertise, transport)
  - Time

23

EPA Biothreat Method Development Team

Research for Response

National Homeland Security Research Center

Sanjiv Shah
Tonya Nichols *
Erin Silvestri
Matthew Magnuson
Frank Schaefer
Gene Rice
Hiba Ernst

Office of Emergency Management

Marissa Mullins
Erica Canzler
Dana Tulis

Office of Water

Latisha Mapp

*Tonya Nichols, PhD
nichols.tonya@epa.gov



24

EPA Resources on Biothreat Methods

ERLN http://www.epa.gov/oemerln1/info.html
SAM http://www.epa.gov/sam/



Bio Method Development Lead
Sanjiv Shah, PhD
shah.sanjiv@epa.gov

Bio Method Lead for ERLN
Marissa Mullins
mullins.marissa@epa.gov

Selected Analytical Methods for Environmental Remediation and Recovery (SAM): Methods for detection of chemical, radiological, pathogenic, and biotoxin agents from diverse environmental sample types

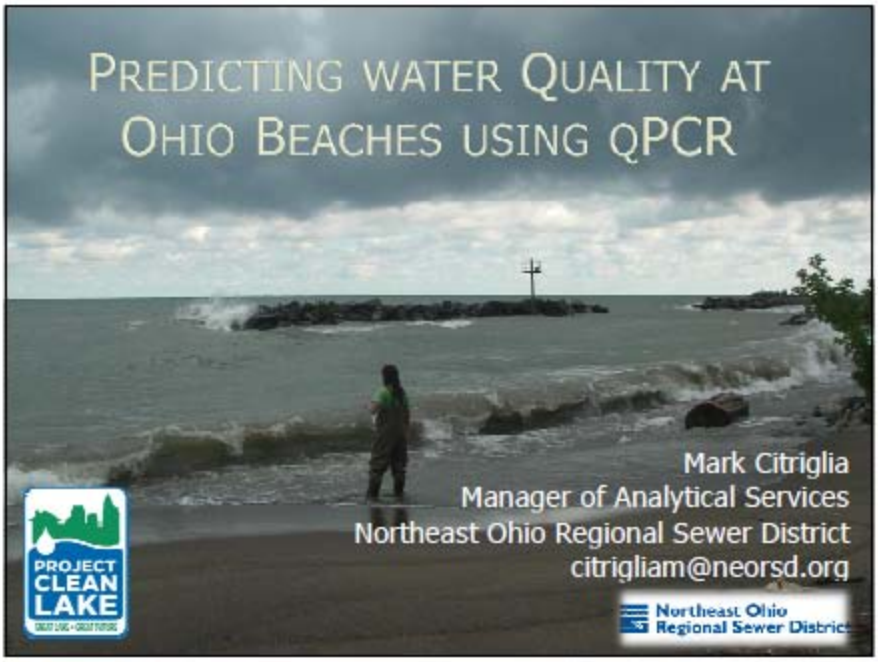
25

Predicting Water Quality at Ohio Beaches Using qPCR

Mark Citriglia
Northeast Ohio Regional Sewer District

Abstract

The Northeast Ohio Regional Sewer District (NEORSD) has two GLRI grants that parallel each other. One grant focuses on Modeling at Urban Beaches the other grant focuses on testing various rapid methods. Villa Angela (VA) beach in Cleveland Ohio has made the National Resource Defense Council's (NRDC) repeat offenders list. This list contains any beach that has had more than 25% of samples taken exceeding the Single Sample Maximum (SSM) of 235cfu/100ml from 2006 through 2011. Historical data generated by NEORSD indicates that VA beach exceeds the SSM on more than 40% of the samples taken. Additionally using the previous days E. coli results to determine water quality is only accurate 50% of the time. NEORSD has been using rapid method technology qPCR for the analysis of E. coli on samples collected at various beaches since 2007. NEORSD has compiled historical data from 2009 and 2011 and has determined that qCPR technology can be used to accurately predict the water quality at VA beach. A predictive model was created using the Virtual Beach Program created by the U.S. EPA. Samples are collected at 7:00am in the morning, delivered to the lab, processed and analyzed by qPCR. The E. coli results are determined from a standard curve and then entered into the model to predict the E. coli density for the day. The data is the entered on the Ohio Nowcast Site and used for public notification.



Recent Headlines

Cleveland. Com : "Ohio's Lake Erie beaches worst in nation for water quality, study says"

USA Today : "Beach bound? Read this before you go near the water"

"States with the highest violation rates: Ohio (21%); Wisconsin (14%) and Minnesota (12%). States with the fewest violations: Delaware (less than 1%); New Hampshire (1%); and North Carolina (2%)."

Huffington Post : "NRDC Beach Report Highlights 11 'Repeat Offenders' For Water Contamination –"

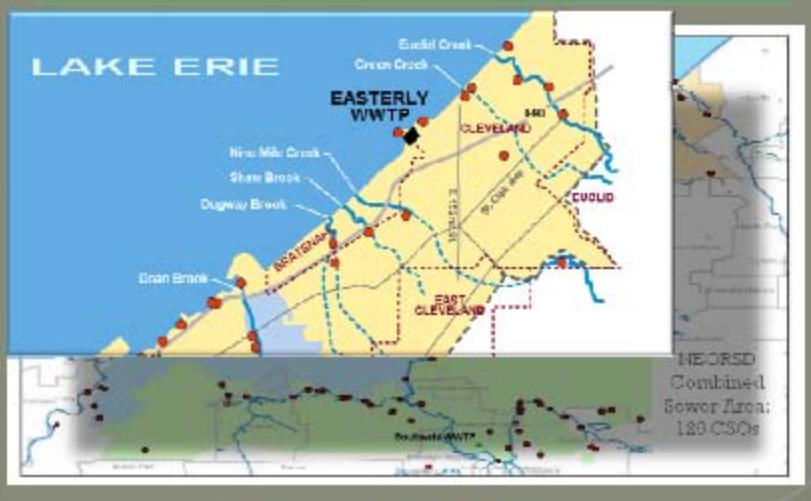
"It's no surprise that most of these destinations are near urban areas known for their pollution, including and ."

NRDC Repeat Offenders List

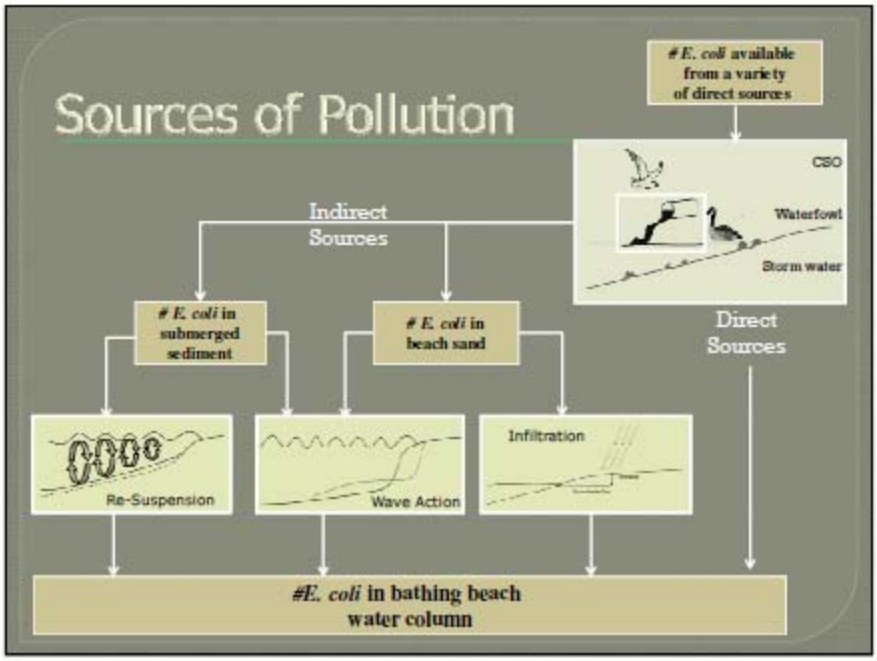
- California: Avalon Beach in Los Angeles County
- California: Doheny State Beach in Orange County
- California: Poche County Beach in Orange County
- Indiana: Jeorse Park Beach in Lake County (2 of 2 monitored sections):
- New Jersey: Beachwood Beach in Ocean County
- New York: Ontario Beach in Monroe County
- Ohio: Lakeshore Park in Ashtabula County
- Ohio: Euclid State Park in Cuyahoga County
- Ohio: Villa Angela State Park in Cuyahoga County
- Ohio: Edison Creek in Erie County
- Wisconsin: South Shore Beach in Milwaukee County

Data Provided by the National Resources Defense Council (NRDC), *Testing the Waters 2013*

NEORSD Service Area




Villa Angela and Euclid Beaches
CSO 238
WQ Station
CSO 209
Euclid Creek
Weather Station
Google

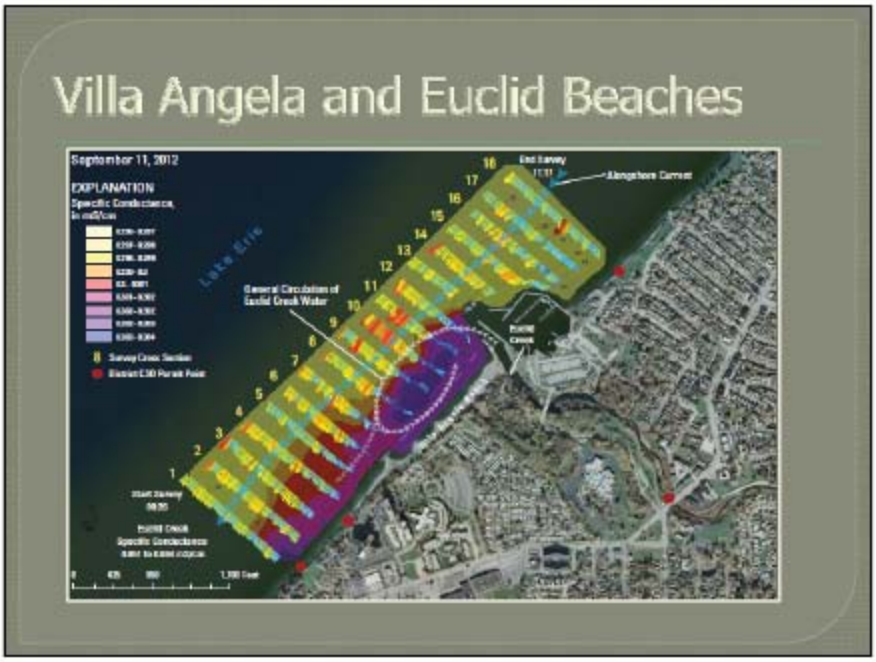

Sources of Pollution
E. coli available from a variety of direct sources
CSO
Waterfowl
Storm water
Indirect Sources
Direct Sources
E. coli in submerged sediment
E. coli in beach sand
Re-Suspension
Wave Action
Infiltration
#E. coli in bathing beach water column

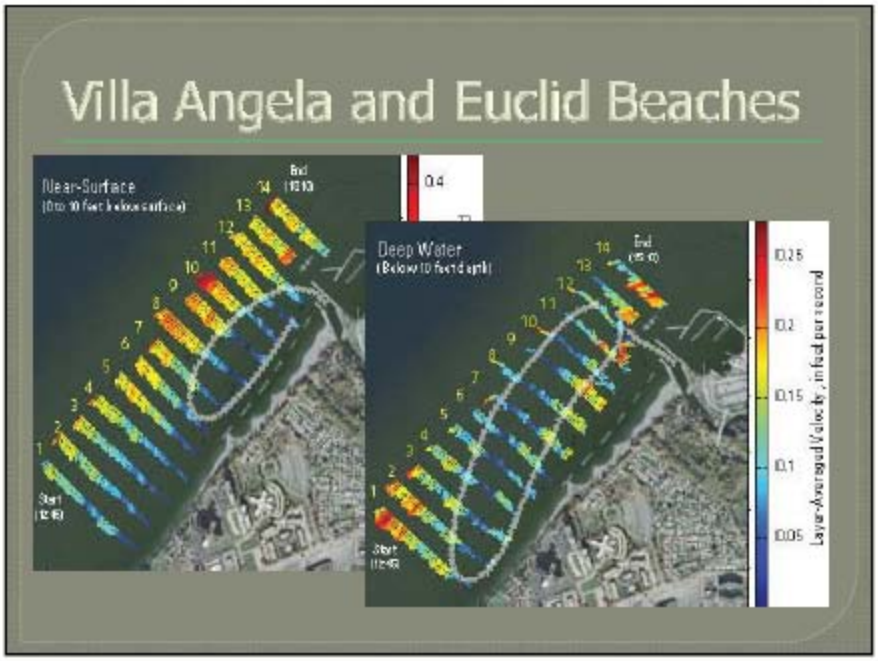
Sources of Pollution



Bird Population




Villa Angela and Euclid Beaches
September 11, 2012
EXPLANATION
Lake Erie
General Circulation of Euclid Creek Water
Euclid Creek


Villa Angela and Euclid Beaches
Near-Surface
Deep Water
0.4
0.25
0.2
0.15
0.1
0.05
Layer-Averaged Velocity, in feet per second

Combined Sewer Overflows

2011 Beach Monitoring Euclid and Villa Angela Beaches				
# CSO from Euclid Creek PS	31	Volume (MG)	97	
Beach	Euclid		Villa Angela	
Sampling Point	East	West	East	West
Total Days Samples	124	124	126	127
Number Days > SSM	55	55	62	49
% Days > SSM	44%	44%	49%	39%
% Days > SSM- CSO+24hrs	29%	32%	21%	19%
%Days > SSM - CSO+48hrs	26%	30%	20%	13%

2012 Beach Monitoring Euclid and Villa Angela Beaches				
# CSO from Euclid Creek PS	18	Volume (MG)	13	
Beach	Euclid		Villa Angela	
Sampling point	East	West	East	West
Total Days Samples	123	123	121	122
Number Days > SSM	49	57	53	54
% Days > SSM	40%	46%	44%	36%
% Days > SSM- CSO+24hrs	36%	40%	42%	33%
%Days > SSM - CSO+48hrs	34%	38%	39%	30%

PROJECT CLEAN LAKE

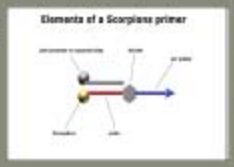
Beach Research

- 2007 -2010: IMS/ATP – qPCR with USGS
- 2011: Received two GLRI grants
  - Rapid Method Comparison at Four Ohio Beaches
  - Modeling at Villa Angela / Euclid Beaches
- 2012 – qPCR Model
- 2013 – qPCR Model + environmental factors

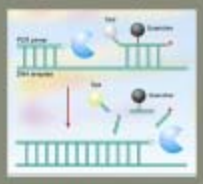


qPCR Assays

- *E. Coli* Scorpion Assay
  - Rachel Nobel Ph.D. U.N.C Chapel Hill
  - Distributed by BioGX – Sample Ready Form
  - SPC = Salmon DNA
  - Instrument = ABI 7500
  - Total Analysis Time = 2.5 Hrs.



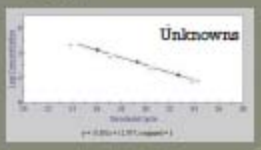
- *Enterococci* Assay
  - EPA Method 1611: *Enterococci in Water by Taqman® qPCR*
  - SPC = Salmon DNA
  - IAC = Internal Amplification Control
  - Instrument = ABI Step-One Plus
  - Total Analysis Time = 3.5 Hrs.



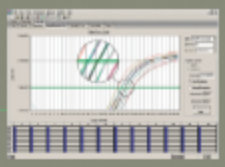
qPCR Methods of Quantitation

- **Absolute Quantitation**
  - Determine or Quantitate the unknown value based on a standard curve

- **Relative Quantitation**
  - Analyze changes in gene expression in a sample relative to another reference sample(s)
  - Two Relative Methods (ΔCt and ΔΔCt)
    - Calibrators
    - Specimen Processing Control (SPC)



qPCR Controls



- **Calibrator**
  - Known amount of target organism prepared ahead of time in large batches
  - Analyzed with each batch of samples and treated just like a sample
  - ΔCt = Sample Ct value relative to calibrator Ct value
- **Specimen Processing Control (SPC)**
  - DNA added at known concentration prior to extraction
  - Used to determine extraction efficiency and matrix inhibition
  - Δ ΔCt = Sample Ct value relative to the Calibrator Ct value and SPC CT value

2011 *Enterococci* Assay Results

Beach	Huntington	Edgewater	Euclid	Villa Angela
Total Samples Collected	131	242	234	234
# of Samples > SSM	43	72	112	107
# of Samples < SSM	83	170	122	127
# of Samples w/ Inhibition	3	5	2	4
# of Samples Reported as ND	11	9	7	7
# of Correct Non Exceedence	78	108	75	75
# of False Positive	5	62	47	52
# of Correct Exceedence	35	54	103	100
# of False Negative	9	18	9	7
Accuracy	86%	67%	76%	76%
Sensitivity	81%	75%	92%	93%
Specificity	90%	64%	61%	59%

2011 *E. coli* Assay Results

Beach	Huntington	Edgewater	Euclid	Villa Angela
Total Samples Collected	125	241	241	241
# of Samples > SSM	23	77	102	105
# of Samples < SSM	102	164	139	136
# of Samples w/ Inhibition	45	59	38	39
# of Samples w/ Inhibition > SSM	20	20	29	26
# of Samples Reported as ND	59	76	30	27
# of Correct Non Exceedence	99	147	116	106
# of False Positive	2	16	23	29
# of Correct Exceedence	18	68	93	91
# of False Negative	6	10	9	12
Accuracy	94%	89%	87%	83%
Sensitivity	78%	88%	91%	90%
Specificity	98%	90%	83%	78%

Methods of Quantitation 2011

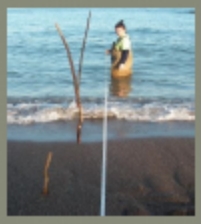
Villa Angela Beach *Enterococci* qPCR Summary			
	Standard Curve	ΔΔCt	ΔCt
Total Samples Collected	234	234	234
# of Samples > SSM	112	112	112
# of Samples < SSM	122	122	122
# of Correct Non Exceedence	75	99	101
# of False Positive	47	29	27
# of Correct Exceedence	103	83	84
# of False Negative	9	70	72
Accuracy	76%	58%	58%
Sensitivity	92%	34%	32%
Specificity	61%	78%	80%

Methods of Quantitation 2011

Villa Angela Beach *E. coli* qPCR Summary			
	Standard Curve	ΔΔCt	ΔCt
Total Samples Collected	241	241	241
# of Samples > SSM	105	105	105
# of Samples < SSM	136	136	136
# of Correct Non Exceedence	100	95	109
# of False Positive	29	40	26
# of Correct Exceedence	94	84	74
# of False Negative	12	22	32
Accuracy	83%	74%	76%
Sensitivity	70%	80%	70%
Specificity	78%	72%	80%

Sampling Schedule 2012

- Sample Collection (1 hour 15 minutes)
  - Start time 06:30 AM
  - Sample Collection ~ 07:00 AM
  - Sample received at lab ~ 07:45 AM
- qPCR Analysis (~ 2.0 Hours)
  - Filtration ~ 14 minutes (max 30 min)
  - Extraction ~11 minutes (max 28 min)
  - Pre analysis work ~ 20 minutes
  - Analysis time 65 minutes
  - data review ~ 20 minutes



Ohio Nowcast

2012 qPCR Model

Virtual Beach Software

- Model: LOG10[EColiMF] = 64.2763e-01 - 11.1998e-02*MeanSampleCt
- Probability Threshold of 45%

	# Samples	CNE	False +	CE	False -	Accuracy	Sensitivity	Specificity
VB Model	87	47	1	24	15	82%	62%	98%
Delta Delta Ct	87	46	2	31	8	89%	80%	96%
Previous Day *E. coli*	69	24	13	14	18	55%	44%	65%

Ohio Nowcast

2013 Beach Models

Villa Angela Euclid Beach

- qPCR Model (Δ ΔCt value)
  - Air temperature
  - Wave height
  - Sample pH
- Backup Model
  - Day of the year
  - 24 hour rainfall
  - Air temperature
  - Turbidity
  - Wave height

qPCR Model				
CNE	False +	CE	False -	Accuracy
17	15	33	2	75%
Backup Model				
CNE	False +	CE	False -	Accuracy
24	8	27	8	76%
Previous Days E. coli				
CNE	False +	CE	False -	Accuracy
19	12	25	12	64%
qPCR Absolute Quantification				
CNE	False +	CE	False -	Accuracy
29	3	32	4	89%
qPCR Relative Quantification /\ Ct				
CNE	False +	CE	False -	Accuracy
18	14	34	2	76%
qPCR Relative Quantification /\ /\ Ct				
CNE	False +	CE	False -	Accuracy
25	7	32	1	93%

2013 Beach Models

Ohio Nowcast

- Edgewater Beach
  - qPCR Model (Δ Ct value)
    - Water temperature
    - Turbidity
    - 72 Hr rainfall
  - Backup Model (Inhibition)
    - Day of the year
    - pH
    - Wave + Turbidity
    - 48 Rainfall (Hopkins+USGS)

qPCR Model				
CNC	False +	CE	False -	Accuracy
43	11	11	2	81%
Backup Model				
CNE	False +	CE	False -	Accuracy
47	7	8	5	82%
Previous Days E. coli				
CNF	False +	CF	False -	Accuracy
42	11	2	11	67%
qPCR Absolute Quantification				
CNC	False +	CC	False -	Accuracy
57	7	9	4	91%
qPCR Relative Quantitation ΔCt				
CNF	False +	CF	False -	Accuracy
49	5	9	4	87%
qPCR Absolute Quantitation ΔΔCt				
CNC	False +	CC	False -	Accuracy
43	11	11	2	81%

2013 – 2014 Additional Work

- EPA Method 1611
  - Continue to collect data
- E. Coli Assay
  - Comparative study with new TaqMan assay
- MST Bacteroidales
  - General Marker
  - Human HF183
  - Human BacHum
  - Bird Catellicoccus marimammalium
- Evaluate Models based on 2013 data set


Contact Information
Mark Citriglia
Northeast Ohio Regional Sewer District
citrigliam@neorsd.org
216-641-6000 ext. 2514

Approaches to the Detection of Fecal Coliforms

Colin Fricker
CRF Consulting Ltd.

Abstract

While the term “fecal coliform” is misinterpreted by many, the examination of materials for the presence of fecal coliforms remains a widely applied test for some waters and biosolids. Fecal coliforms are generally defined as total coliform organisms that are able to grow at elevated temperature (e.g. 44oC) and the group was first used as a surrogate for E. coli. Now that robust methods are available for the detection of E. coli specifically the use of fecal coliforms as indicators has declined. Nonetheless, there remain regulations that rely upon the detection of fecal coliforms.

Traditionally, fecal coliforms have been detected using membrane filtration techniques that utilise fermentation of lactose as the indicator pathway with elevated temperature of incubation inhibiting those coliforms thought not to be of fecal origin. Unfortunately there are many coliforms that are not of fecal origin that are able to ferment lactose at 44oC. However, until regulations are changed there is still a requirement to test. Membrane filtration techniques are being utilized less and less due to the high labor requirement and the time taken to obtain a confirmed result and other methods that utilize ?-D-galactosidase as the indicator nutrient are being used more frequently.

Membrane filtration suffers, in particular when samples with high particulate concentrations are examined as the membranes can block and reading of membranes containing high numbers of large particles can be problematic. For this reason, most probably number techniques are often favoured. A comparison of the two approaches will be presented together with discussion on the relative merits of both and guidance on the interpretation of both. The benefits and cost savings of utilizing most probable number techniques will be highlighted.

Approaches to the Detection of Fecal Coliforms

Colin Fricker
CRF Consulting Ltd
Analytical Services Inc.
University of Kingston

What is a fecal coliform?

- EPA states that fecal coliforms are composed of the genera:
  - *Escherichia*
  - *Klebsiella*
  - *Enterobacter*
  - *Citrobacter*
- Recognises that "*Klebsiella* may not be fecal in origin"

Method 1680

- Fecal coliform bacteria are Gram-negative, non-spore-forming rods that are found in the intestines and feces of humans and other warm-blooded animals.
- Does this include *Proteus, Serratia, Yersinia*??

Fecal coliforms in practice

- Are method defined
- Traditional methods rely on bile salts (or similar) and elevated temperature for selectivity
- Rely on lactose fermentation and production of gas for specificity

Methods based on β-galactosidase

- β-galactosidase used for widely than lactose for total coliforms
- Some methods have been adapted for detecting fecal coliforms
- Comparing the methods is a challenge!!

Comparing Colilert-18 with mFC

- USEPA Alternative Test Procedure
- Compare mFC agar with Colilert-18 Qtray
- Fecal coliforms defined as *Escherichia, Enterobacter, Klebsiella, Citrobacter*
- Samples prepared from disinfected sewage effluent
- Target concentration 20-50 cfu/ 100 mL

Study protocol

- Analyse samples by reference procedure and test procedure
- "Confirm positives" by inoculation into LTB (35°C) followed by EC medium (44.5°C)
- Isolates which produced gas in both media were considered true positives
- Isolates that did not produce gas were considered to be presumptive false positives (protocol)

"Confirmed" recovery of fecal coliforms

Sample	CL18 mean	mFC mean	CL18 range	mFC range
1	53.6	27.9	31-68	18-42
2	40.5	23.6	23-57	16-34
3	58.0	37.1	41-79	28-44
4	50.9	43.5	33-75	31-57
5	37.2	44.6	26-47	26-58
6	58.0	46.0	40-73	35-61
7	58.4	40.8	39-75	31-55
8	65.8	39.6	52-93	17-61
9	52.1	31.9	33-72	9-42
10	42.0	43.4	27-50	16-59
Mean	51.7	37.8		

"False positive" rates

Description	Colilert-18®	m-FC
Number of colonies tested	200	200
Number confirmed by EC broth	175	166
Number confirmed by Vitek	+25	+33
"False positive" by EC	25	33
"False positive" by Vitek	0	1
% False positive by EC	12.5	17.0
% False positive by Vitek	0	0.5

False negative rates

Description	Colilert-18®	m-FC
Number of colonies tested	200	205
Confirmed negative by EC broth	186	161
Number confirmed positive by Vitek	14	44
"False negative" results	14	44
Percentage "false negative"	7.0	21.5

Assessment of results

- Colilert-18 detected significantly more fecal coliforms than did the reference method
- Many contributing factors
- Inherent lack of sensitivity of mFC (harsh inhibitors, lactose)
- Difference in target reaction
- Poor confirmation procedures

Design of comparison studies

- Must be consistent with definition of target
- e.g. If target definition is four genera then all isolates MUST be identified to genus level
- Therefore appropriate confirmation procedures are required
- Difficult to truly compare two methods with different target groups

Some take home messages

- Not all coliforms (fecal or otherwise) ferment lactose rapidly
- The same is true for *E. coli* (particularly in EC medium)
- Gram negative bugs that produce β-galactosidase at 44.5°C can be considered as fecal coliforms
- Study design affects the outcome!!

OMG…. I got a finding! Now what?

Robin Cook
City of Daytona Beach EML

Abstract

Sharing practical information to meet the intent of the standard. Building a bridge to bring good science, common sense and the bench analyst together.

OMG, I Got a Finding…..Now What?

Robin Cook
City of Daytona Beach EML
August 2013

General Requirements

- Incubator temps, 2 X day, 4 hours apart
- Stability/ uniformity check - one time study
- Equilibrium Check – one time study
- Thermometers - Must be checked when temperature has a direct effect on result
  - NIST traceable
  - Proper Graduations
  - For SM methods verify, 2X year not just once

Uniformity Check

- Standard does not give a frequency – At least at initial set up or if moved.
- Procedure:
  - Calibrated thermometer in different areas of the incubator
  - Check different shelves, corner and the middle of the unit.
  - Document temps and locations

Equilibrium Check

- Document temp of the unit prior to sample addition.
- Add a normal sample load at minimum, max load if you can
- Check temp over time and document the time and temp when proper incubation temp is regained.
- Ok if it takes hours.

Now What ?

- Adjust incubation time
- Reduce the number of samples incubated at one time
- Better unit
- Save the info – maintenance log maybe.

General Requirements

- Organisms
  - Appropriate for use
  - Not expired
  - Traceable – Have a procedure for subculturing
  - Verify– How might you verify a negative organism?

Track Your Supplies

- Micro Supplies - One way of tracking
  - Sterility check
  - Volume check
  - Container chlorine check
  - Media Checks

City of Daytona Beach EML

Micro supplies

Tracking No: M_____

Description: _____

Date Rec'd: _____ Date Open:_____ Date Consumed/Disposed:_____

Vendor:_____ Lot #:_____ # of pieces: _____

Sterility Check:

Ph check:

Performance Check:

25

Additional info on reverse

Media QC

TESTS:

- (1) Sterility
- (2) pH
- (3) + Control
- (4) – Control (if applicable)

- Buy ready to use: test per lot
  - Lab must check even if certificate was supplied.
- Make in lab: test per batch

Student t test:

- Required by SM
- Demonstrates consistent uniform results
- Compares a lot/batch of known quality with one of unknown quality
- DI is used in media prep or for making serial dilutions

Student t How To:

- Best time to check is during a tank change of the DI water.
- Sample before change and again after
- Sample like a bacti sample in a sterile container.
- May want to get extra volume for extra dilutions
- High Purity water will substitute as control

More Student t:

- Prepare Stock Solution: Loopful usually enough
- Use organisms that are relevant
- Make additional solutions using a serial dilution with DI as diluent.
- Place 0.1 ml of approx 10^{-4} dilution into 3 to 5 plates
- Place 1 ml of approx. 10^{-4} dilution into 3 to 5 plates
- Use either Pour Plate Method (SM 9215B) or membrane filtration
- Incubate appropriately for the type of testing.

Student t Results:

- Count both sets then use the best fit for the method.
- Total by MF 20-80 cfu/ 100ml
- Fecal by MF 20-60 cfu/100 ml
- HPC by Pour Plate 30-300 cfu/ml
- NOTE : Being outside the range does not negate the test.
- Calc is based on $\log_{10}$
- Do not drop the signs
- A negative number is below 2.78

Test run 2/25/09

Instrument: 35C Incubator

Matrix: DI Water before and after tank change

City of Daytona Beach Environmental Monitoring Lab

Analyst: Robin Cook

Sample Before change	CFU/ 100ml	Sample After change	CFU 100mL	Range of Log of result
Replicate 1	80	Replicate 1	102	0.105510
Replicate 2	107	Replicate 2	95	-0.051660
Replicate 3	98	Replicate 3	101	0.013095
Replicate 4	69	Replicate 4	82	0.074965
Replicate 5	83	Replicate 5	67	-0.093003
Standard Deviation S of range				**0.08331**

Mean Recovery of range:	0.00978	Serial dilution of culture to yield final conc approx (10)-4
t = Mean range/(S_d/Square rt of incidents)	0.2625	Positive Culture # E07020409C
If t < 2.78 Not Significantly different	PASS	Before Sampled 012009 by DM After Sampled 022509 by BP

Dechlorination Study

How do I check a container? One Approach

- Assume $C_1V_1=C_2V_2$
- Use the same amount as you would for samples
- Put solution into a randomly selected container
- Check with the correct amount of DPD.
  - Pink? Still has CL2 so not enough sodium thio.

General Requirements

- Autoclaves
  - Heat Distribution, one time study
  - Pressure check
  - Verify the timer

Internal Autoclave Checks

- Pressure Check-
  - Check the seals. Any leaks, cracks, wear. Write it down!
  - Acceptable pressure readings typically 15 – 18 psi
  - Interpretation has been published.
    - PV=nRT
    - www.nelac-institute.org/interpret.php#pab_6 for the body of the interpretation

Autoclave Annual Maintenance

- Internally or by service contract – performed annually
- Include a pressure check and calibration of temperature device.
- Service contract – keep the records
- So how do we do this internally?

Internal Autoclave Checks

- Temperature Calibration- most critical is for media prep
  - Internal thermometer- check against NIST traceable calibrated max-min thermometer
  - External thermometer (i.e. max-min) check with NIST traceable reference thermometer in boiling water.
  - www.sterilizers.com/autoclave-time-temperature-pressure-chart.html

More General Requirement Challenges

- ALL Activities need SOP
- Washing Glassware- Have an SOP
- Maintaining cultures – Have an SOP
- Follow Your SOP

SOP for Inhibitory Residue Test ?

TNI std M5 1.7.3.7 (b)(vi) - Does the laboratory have a **documented** [written] procedure for washing labware?

TNI std M5 1.7.3.7 (b)(vi) Does the laboratory use **detergents** [Alconox, Liquinox] designed for laboratory use for washing labware?

Inhibitory Residue Test

- Using glass petri dishes wash as follows
  - Group A : use your lab procedure
  - Group B : lab procedure then rinse 12 X with DI
  - Group C : wash but **DO NOT RINSE**

Group D: plastic ready to use acceptable lot of petri dishes.

IRT CONT

- Once washed and dried, label appropriately
- Autoclave using normal procedures as a single unit. **NOT THE PLASTIC DISHES**
- Use E. aerogenes range of 50 to 250 cfu/ml.
- Inoculate 3 plates for each set with 0.1 ml of culture mix. Then inoculate 3 plates with 1 ml of culture mix.
- Use SM 9215 pour plate method at 35° C for 48 hrs.

QC for Quantitative Tests (Precision Criteria):

- Does not specify frequency in SM
- Based on the $\log_{10}$ of the results
- At least 15 sets of duplicates
- Maybe seasonal depending on the samples (warm vs. cold)
- What do you do if the duplicates are outside this range?

Precision Criterion for Fecal Coliform by MF 3rd Quarter 2008					
Date/ Replicate number	replicate 1	replicate 2	log replicate 1	log replicate 2	diff inlog
1	1	2	0	0.301029996	-0.301029996
2	1	1	0	0	0
3	12	19	1.079181246	1.278753601	-0.199572355
4	1	1	0	0	0
5	25	18	1.397940009	1.255272505	0.142667504
6	1	1	0	0	0
7	1	2	0	0.301029996	-0.301029996
8	1	1	0	0	0
9	1	1	0	0	0
10	1	1	0	0	0
11	1	1	0	0	0
12	10	1	1	0	1
13	1	1	0	0	0
14	1	1	0	0	0
15	1	1	0	0	0
				ave of logs =	0.022735677
				precision criterion=	0.074345664

Method Requirements –SM 9223 B

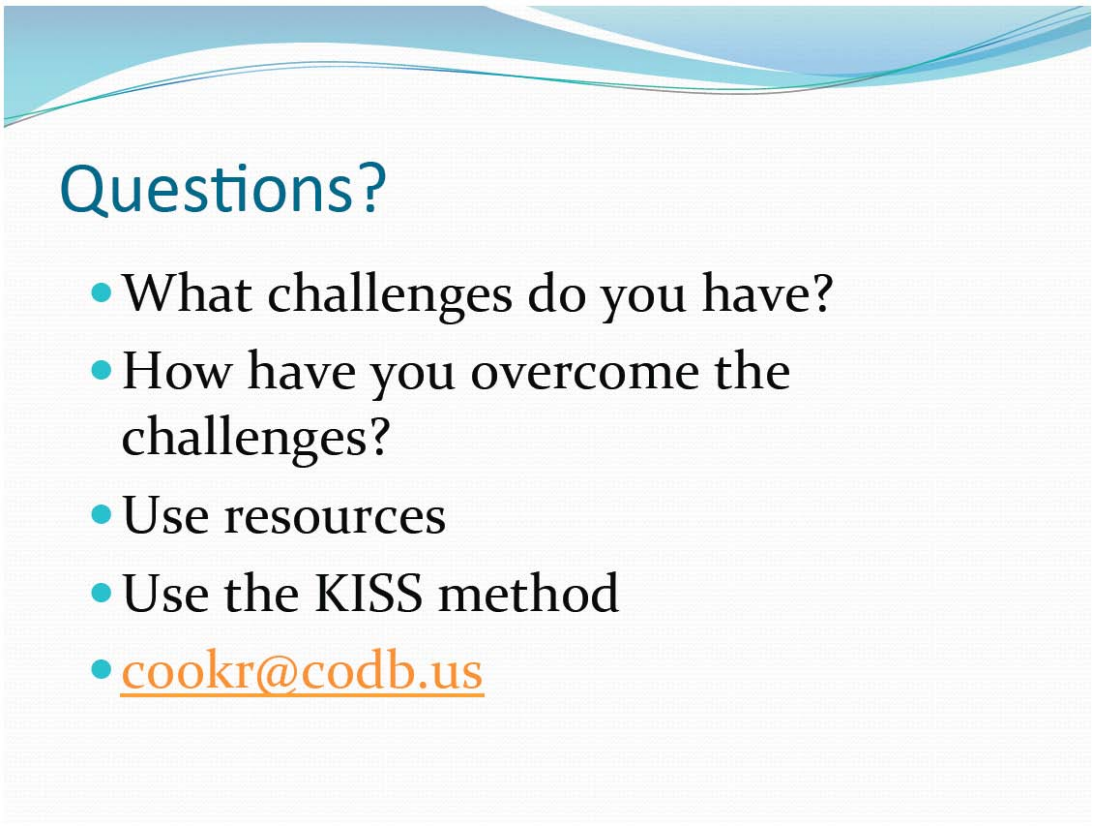
- SM 9223 B **certification** includes ONLY:
  - Colilert and Colilert-18
- SM 9223 B certification does not include:
  - Readycult [Verifications no longer required]
  - Colisure
  - Quantitray
    - Lab must apply for certification (equivalent technology PTs, iDOC, SOP, etc.)
- Are samples **100 ml** if performing Presence/ Absence?
- **Verifications** not required if tests are P/A.

SM 9223 B

- Storage? Protect the reagent from the light
- Do you use **reagent water** for Colilert controls? Don't use dilution water.
- How do you check the pH?

Method Requirements- Common Problems

- Drinking Water- 100 ml sample
  - Is your sample 100 ml (+/- 2.5 ml)?
  - How do you subsample appropriately?
- Membrane Filtrations
  - Do dilutions yield the appropriate number of colonies?
  - Do you verify typical AND atypical colonies, if required by the method?


Questions?
What challenges do you have?
How have you overcome the challenges?
Use resources
Use the KISS method
cookr@codb.us

What Are the Critical Elements in the Microbiology Laboratory?

Margo E. Hunt

Abstract

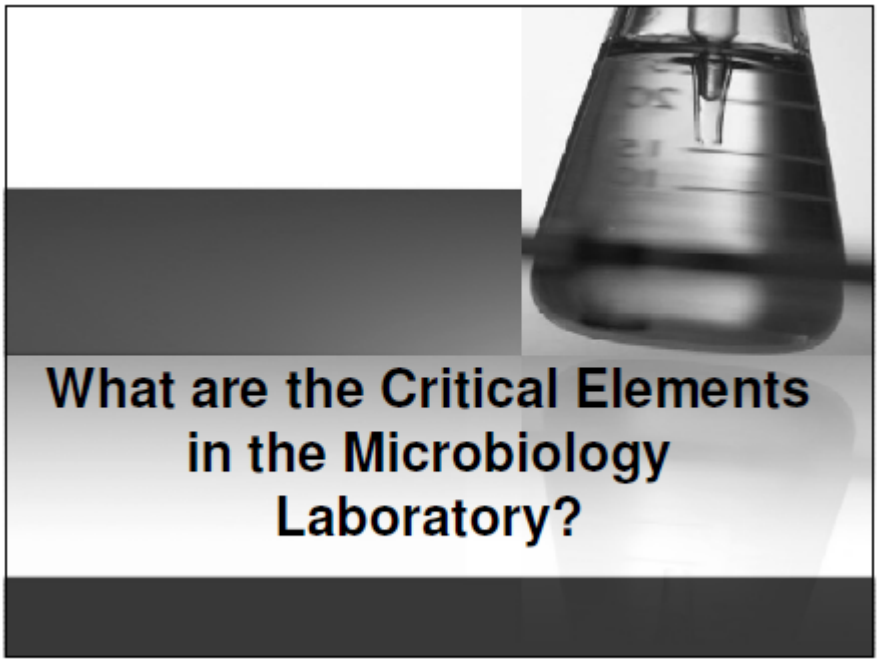
Microbiology is the study of dynamic biological processes involving bacteria, fungi, viruses, and protozoa. In terms of microbiology, the US Food and Drug Administration (FDA) talks about Quality by Design (QbD) where quality is built into the product with an understanding of the final product and the process by which it is developed based on a systematic approach of sound science and risk management. In the water testing industry, the quality process design is set in place to prove that appropriate regulations are being followed and that the water is safe. The process design is formulated into a Quality Management Plan that is supported by both management and analysts. It is their efforts to maintain a system where all activities are supported by appropriate quality control activities and fully documented.

Microbiological analytical methods must be scientifically sound (e.g., specific, sensitive, and accurate) and provide results that are reliable. There should be assurance of proper equipment function for laboratory experiments. Procedures for analytical method and equipment maintenance, documentation practices, and calibration practices supporting process-development efforts must be documented. The microbiological process is reviewed both within the laboratory on a routine basis and by external reviewers (auditors, accreditation officials) at periodic intervals such as annually or biannually.

The critical elements in the microbiology laboratory are the following:

1. Facility,
2. Equipment and supplies,
3. Personnel, both management, supervisors, and analysts,
4. Analytical Methods, and
5. Documentation

Each will be discussed with an emphasis on analytical methods in response to both the US Environmental Protection Agency's (EPA) final rule, published in 2012, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Analysis and Sampling Procedures (77FR: 29758) and the draft AOAC International's "Microbiology Water Methods, Quality Assurance and Quality Control."



Margo E. Hunt, Ph.D.
Part 9000 Coordinator, Microbiology
Standard Methods for the Examination of Water and Waste Waters (SM)

APHA, WEF, AWWA

Daubert vs. Merrell Dow

- Supreme Court decision in 1993
- Trial judges must ensure scientific evidence is relevant and reliable.

Illustrative, not definitive, list:

- Theory or technique can be or has been tested
- Peer review and publication of theory or technique
- Known or potential rate of error
- Existence and maintenance of standards controlling the technique in the scientific community
- General acceptance of the methodology or technique in the scientific community

Quality by Design (QBD)

- FDA term – process design
- EPA term – quality system

FDA

- Bacteriological Analytical Manual (BAM)
- Microbiological Best Practices, USP <11177>

USP <11177>

Personnel training
Cultures
Media preparation
Laboratory records
Laboratory layout
Interpretation of results
QC testing
Sample Handling
Laboratory equipment
Documentation
Media preparation

EPA

- 1978 Microbiological Methods for Monitoring the Environment, Water and Wastes
- Manual for the Certification of Laboratories Analyzing Drinking Water, fifth edition + 2 supplements

Standard Methods 9020

- Discusses critical elements in the microbiology laboratory and for analytical methods
- Basic Quality Assurance and Quality Control elements with minimal frequency of QC checks for most processes.

Standard Methods 9020A

- Discusses importance of Quality Assurance and the Quality Assurance Manual

9020B and 9020C

1. Facility
2. Personnel, both management and staff
3. Equipment and Supplies
4. Documentation
5. Analytical Methods
6. PT/PE (collaborative)Testing

1. Facility

- Ventilation
- Space Utilization
- Laboratory bench areas
- Walls and floors
- Cleanliness
- Electricity

2. Personnel

- Experienced in the science
- Organized
- Takes responsibility
- DOC – initial and on-going for each analyst

3. Equipment and ...

- Temperature sensing devices
- Balances
- Meters
- Autoclaves and ovens
- Incubators
- Etc.

3. Supplies

- Glassware
- Reagent water
- MF filters
- Media – purchase, storage, preparation, storage

4. Documentation

- Record everything
- Write down what you are going to do and how you are going to do it
- Follow what you said you were going to do
- SOPs
- Analytical results

5. Analytical Methods

- Run positive and negative culture controls
- Blanks
- Sterility Checks

5. Analytical Methods

- Establish analyst variability in counting
- Run duplicates at set frequency, e.g., one per batch or test run

5. Analytical Methods

- Verification – established methods
- Validation – new or non-standard methods

5. Analytical Methods

Qualitative Methods – presence/absence

1 Accuracy and precision
2. Specificity/Selectivity
3. Detection Limit
4. Robustness
5. Repeatability

5. Analytical Methods

Quantitative Methods

1. Accuracy
2. Precision/Repeatability
3. Precision/Reproducibility
4. Recovery/sensitivity
5. Detection Limit
6. Upper counting limit
7. Range

6. PE/PT Testing

- Collaborative testing

EPA and 40 CFR 136.7

- EPA's final rule, 2012, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Analysis and Sampling Procedures"

12 Critical Quality Control Elements

- These elements must be clearly documented in the written SOP for each analytical method not containing QA/QC procedures,
- Unless a written rationale is provided to explain why these elements are inappropriate.

12 Critical Elements for Chemistry

1. Demonstration of Capability (DOC)
2. Method Detection Limit (MDL)
3. Laboratory reagent blank (LRB), also referred to as a method blank (MB)
4. Laboratory fortified blank (LFB), also referred to as spiked blank or laboratory sample control (LCS)

12 Critical Elements for Chemistry

5. Matrix spike (MS) and matrix spike duplicate (MSD) or laboratory fortified matrix (LFM)
6. Internal standards, surrogate standards, or tracers
7. Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV)
8. Control charts or other trend analysis of QC results

12 Critical Elements for Chemistry

9. Correction active (root cause analysis)
10. QC acceptance criteria
11. Definitions of preparation and analytical batches that may drive QC frequencies
12. Minimum frequency for conducting all QC elements

Are these terms applicable to microbiology?

- Some QC elements are universal, but not all chemistry QC elements are applicable to microbiology.

Are these terms applicable to microbiology?

- Microbiology has greater variability in analytical testing:

analyst	equipment used
calibration of equipment	environment
materials used	sample matrix
storage conditions	

The microorganisms themselves!

AOAC – Micro. committee

- Patsy Root, Senior Regulatory Affairs Specialist, IDEXX
- Laurie Kundrat, Technical Support Specialist, Microbiologics
- Karla I. Ziegelmann-Fjeld, Technical Manager, Microbiologics
- Margo Hunt, Part 9000 Coordinator, Standard Methods

10 Critical Elements - Microbiology

1. Demonstration of Capability (DOC), initial and on-going*
2. Method blanks and sterility checks*
3. QC samples and laboratory fortified blanks*
4. Matrix spike and matrix spike duplicates*
5. Calibration*

10 Critical Elements - Microbiology

6. Control charts – trend analysis*
7. Corrective actions*
8. QC acceptance criteria*
9. Definition of a batch or test run*
10. Minimum frequency of QC checks*

1. DOC

- Each analyst must demonstrate initial and ongoing capability for each analytical they perform.
- The intent is to prove both reliability and integrity of the laboratory's test results.

2. Method Blanks & Sterility Checks

- Ensure that unknown samples have not been compromised, contaminated or invalidated due to
  - improper handling or preparation,
  - inadequate sterilization or
  - environmental exposure.

3. QC Samples & Laboratory Fortified Blanks

- Ensure that growth media, or other method reagents/materials, are capable of supporting proper growth and/or analytical results.
- Positive and Negative Culture Controls

4. Matrix Spike & Matrix Spike Duplicates

- For difficult matrices or new methods

5. Calibration

- Calibration of microbiological equipment (initial and continuing) Performance Qualification

6. Control Charts/Trend Analyses

- and Trend Analyses of Quality Control Results

7. RCA/Correction Action

- RCA = Root Cause Analysis

8. QC Acceptance Criteria

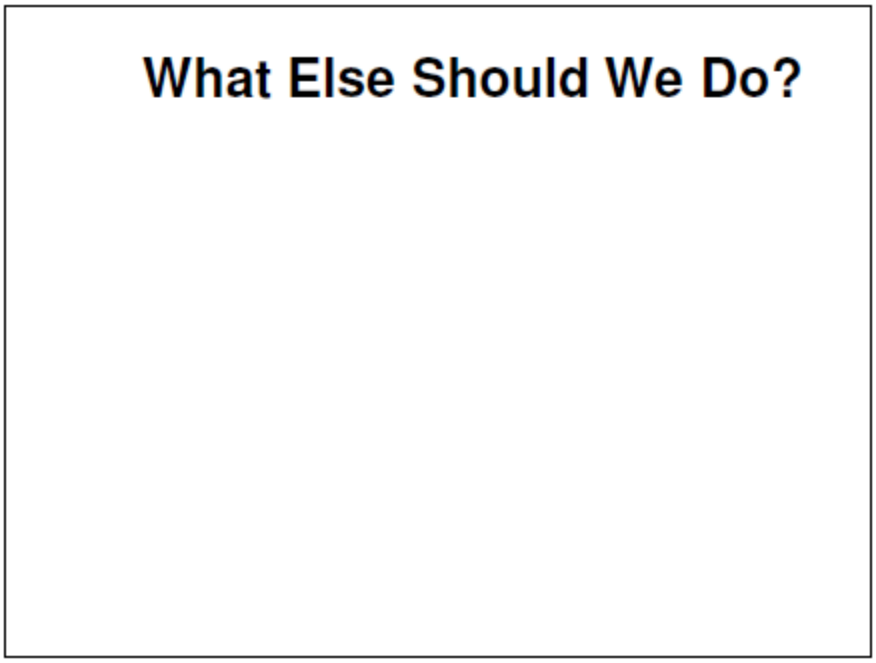
- Used to determine if test results are acceptable
- Must be established prior to testing

9. Definitions of a Batch

- Preparation
- Analytical

10. Minimum Frequency QC Checks Lab Equipment

- Ensure precise and consistent results


What Else Should We Do?

Auditing Laboratories for Cryptosporidium and Giardia

Debra Waller
NJDEP – Office of Quality Assurance

Abstract

Debra Waller, Research Scientist at the NJDEP, will present an informational session on the protocols for conducting an assessment of a laboratory performing Cryptosporidium and Giardia testing. Debra will include information on the State of New Jersey's developing protozoan testing protocols. The presentation will include how to prepare for and perform an assessment. A hands-on workshop is planned for the class.

Auditing Cryptosporidium/ Giardia Laboratories

Debra Waller
NJDEP-Office of Quality Assurance
debra.waller@dep.state.nj.us
August 2013

Note:

This presentation does not address all of the requirements of the analytical methods (1623 or 1623.1)

For example the presentation does not address microscopic calibration, the IMS portion and only refers to some of the portions of the examination phase (typical size, shape and magnification used).

Note:

This presentation is also based on the use of an *Envirocheck® HV filter for sample filtration, *Easy Stain®, and that the laboratory has performed the required Initial Demonstration of Capability (IDC). Also all negative and positive staining controls were acceptable and monthly analyst verifications are performed as required and a digital photo library is retained by the single Principal Analyst for the purposes of this presentation. Control charts are retained for OPR and MS data as required.

*Inclusion of these products are for example only and not as an endorsement.

Sample Volumes

- Must collect and filter at least 10L of sample (method verified for 10L and 50L samples only).
- Volume must be noted in the bench sheet to the nearest 0.25L.

Note: A laboratory can use other sample volumes provided that the laboratory demonstrates equivalent or superior performance through an approved initial demonstration of capability (IPR, MS/MSD for 1623.1, OPR and MB) prior to changes being made for the analysis of regulatory samples. For the purposes of this presentation the laboratory has not performed an IDC for alternative volumes.

Sample Collection and Filtration Records

- Must maintain a record of:
  - Sample number or ID
  - Sample turbidity (if not provided, must be tested)
  - Sample type and date and time of collection
  - Date and time of receipt in the laboratory
  - Temperature at receipt (<20°C and not frozen)
  - Sample filtration start date and time
  - Name/initials of the person that filtered the sample (client or lab)
  - Lot number and number of filters used for the sample filtration

Holding Times

- 4 days (96 hours) between collection/filtration and elution
- 1 working day between elution and application of sample to slide
- 3 days (72 hours) between application to slide and staining
- 7 days (168 hours) between staining and examination

Example Required QC Samples Ongoing Precision and Recovery (OPR)

- Must be tested at a frequency of 1 per every 20 samples tested or portions thereafter if more than 20 samples are analyzed in a week.
- Must be spiked with ~100-500 oocysts/cysts (o/c) each week that samples are tested.

Example (Con't)

- More than 50% of the o/c must appear undamaged and morphologically intact
- Must meet %R for C in the range of 33-100% and 22-100% for G.
- OPR is to be processed through the entire procedure.

Method Blank

- To be processed after the OPR.
- Must be analyzed each week (7 days or 168 hours, time period begins with the processing the OPR).
- Must be free of o/c and any potentially interfering organism or material.
- Every field sample must be associated with an acceptable OPR and MB.

Matrix Spike (MS) Sample Analysis

- Must be performed for one of every twenty field samples tested from the same individual sources analyzed.
- Volume of original sample to sample volume used for the MS must be within 10%.
- Must be associated with an acceptable OPR and Method Blank (MB) analysis.
- Recovery must meet 32-100% for C and 8-100% for G.

Sample #	MS %Recovery C/G	S. Vol.	MS. Vol.
MS-1	10/12	10.0	12.0
1		N/A	N/A
2		N/A	N/A
3		N/A	N/A
4		N/A	N/A
5		N/A	N/A
6		N/A	N/A
7		N/A	N/A
8		N/A	N/A
9		N/A	N/A
10		N/A	N/A
11		N/A	N/A
12		N/A	N/A
13		N/A	N/A
14		N/A	N/A
15		N/A	N/A
16		N/A	N/A
17		N/A	N/A
18		N/A	N/A
19		N/A	N/A
20		N/A	N/A
21		N/A	N/A
22		N/A	N/A
23		N/A	N/A
24		N/A	N/A
25		N/A	N/A
MS-2	11/15	10.0	11.5

What problems do we see with this MS data?

*MS samples are not being performed at the correct frequency.

*The acceptance criteria is outside range.

*The sample volume to MS volume is not within 10%.

Reagents

- 1.0 NaOH and 0.1N HCl solutions must be purchased with a lot specific certificate of analysis retained, and the lot number in use noted in the raw data records (tracking of the origin of use). Normality cannot be adjusted.
- Working elution buffer solutions must be used within one week of preparation.
- Reagents cannot be frozen including bead suspensions. Light sensitive materials need to be stored in the dark between 1 to 10 degrees C.
- Working DAPI solution is to be made daily with 50µl of 2mg/ml into 50ml of phosphate buffer (PBS) solution.
- PBS (pH 7.4 defined in 1623.1, no final pH in 1623) is to be made with saline.

Reagents

- Diluted and unused working reagents must be discarded after 48 hours or following manufacturer's instructions. Working elution buffer can be stored for one week.
- Several manufacturer's have been approved for use, any alternative would require an acceptable IDC prior to use with regulatory samples.
- The same elution buffer batch must be used for all samples associated in the sample set. Prepare enough working elution solution to process all samples including the original OPR and MB that was run for the sample set and any additional OPR samples that would be required for >20 samples in the same day of analysis.
- Reagent water must not contain Cd, Cr, Cu, Pb, Ni or Zn in concentrations of >0.05mg/L to be acceptable for use.

What is wrong with this Reagent Prep information?

Name	Lot or Batch ID	Final pH	Prep Tech.	Exp. Date	Storage	Prep. Date.
Working DAPI	Batch 1-10-13	NA	DW	1-15-13	Freezer	1-10-13
PBS	Batch 1-10-13	7.6	DW	1-10-14	4 C	1-10-13
1.0N NaOH	Batch 1-10-13	NA	DW	5-10-13	Room temp	1-10-13
0.1N HCl	Batch 1-10-13	NA	DW	5-10-13	Room temp	1-10-13
Working DAPI	Batch 2-3-13	NA	DW	2-8-13	On bench in the light	2-2-13
PBS		7.7	DW		4 C	3-10-13
Working DAPI	Batch 1	NA	DW	3-15-14	freezer	3-10-13
Easy Stain	Batch 4	NA	DW	3-15-13	100 µl of 2 mg/ml stock in 50ml PBS-freezer	3-10-13
Elution Buffer	Batch 1	NA	DW	4-6-13	4 C	3-29-13
Bead Suspensions	Lot number in receipt file	NA			Freezer	

Reagents are inappropriately stored in the freezer.
Storage is beyond one week .
The pH for the PBS is >7.4 (1623.1) and information is missing for the 3/10/13 batch
The lab is preparing the 1.0N NaOH and 0.1N HCl solutions.
The working DAPI solution is not made daily and is being stored in the light.

What is wrong with this reagent water testing information?

Date	Single Limit	Cadmium	Copper	Lead	Nickel	Zinc
Jan. 2005	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.02mg/L	0.01 mg/L	0.01 mg/L
Jan. 2006	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.03 mg/L	0.01 mg/L	0.01 mg/L
Jan. 2007	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.03 mg/L	0.01 mg/L	0.01 mg/L
Jan. 2008	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.02mg/L	0.01 mg/L	0.01 mg/L
Jan. 2009	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.02mg/L	0.01 mg/L	0.01 mg/L
Jan. 2010	<0.05 mg/L	0.005 mg/L	0.001 mg/L	0.02mg/L	0.01 mg/L	0.01 mg/L
Jan. 2011	<0.05 mg/L	0.005 mg/L	0.07 mg/L	0.04 mg/L	0.01 mg/L	0.01 mg/L
Jan. 2012	<0.05 mg/L	0.005 mg/L	0.09 mg/L	0.05 mg/L	0.01 mg/L	0.05 mg/L
Jan. 2013	<0.05 mg/L	0.005 mg/L	0.10 mg/L	0.06 mg/L	0.05 mg/L	0.10 mg/L

Results for some are <0.05mg/ L and collectively are >0.10 mg/L.
The lab is not testing the water for chromium as required.

General Record Keeping

- The FITC, DAPI and DIC characterizations and size measurements must be recorded for all positive results for field samples tested.
- Report zero organisms if no oocysts or cysts are observed.
- Final results are to be reported as oocycts or cysts per liter and are to be adjusted to reflect the number resulting form the analysis of a 10 or 50L sample (or other approved volume).
- Processed packed pellet volume cannot exceed 0.5ml. If total is >0.5 ml then separate 0.5 ml sub-samples must be tested.
- Record the number of subsamples on the bench sheet.

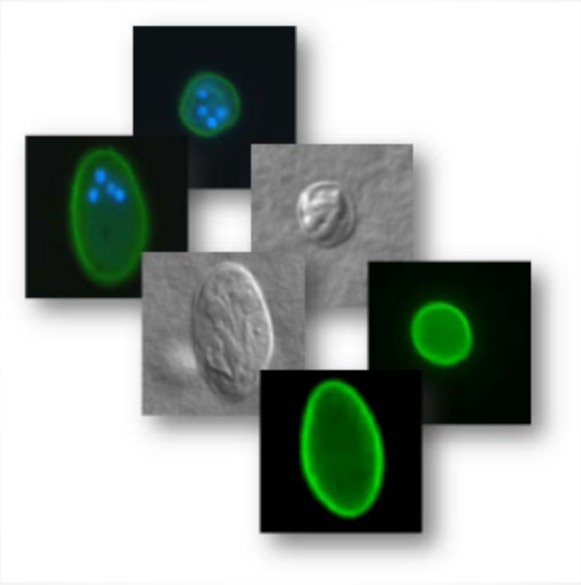
Magnification Required

Procedural Step:	Minimum Mag.	Preferred or Required Mag.
• FITC and counting	200X	200X
• DAPI	400X	1000X (Note in 15.2 of 1623/1623.1)
• DIC	1000X	1000X
• Measurement	1000X	1000X

Typical Size and Shape for Test Organisms

Cryptosporidium 4 to 6 µm round to oval
Giardia 8 to 18 µm long by 5 to 15 µm wide, oval to round

*Measurements to be recorded to the nearest 0.5 µm.



Improvement to Method 1623 to Detect Cryptosporidium and Giardia

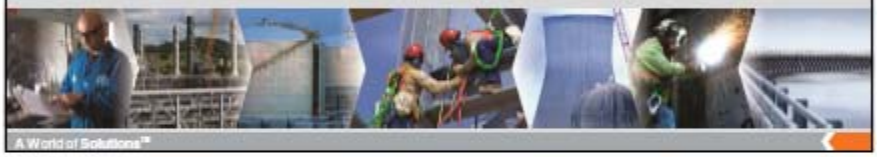
Leah Villegas
CB&I Federal Services

Abstract

One global public health challenge is detecting pathogens in water. Advances in laboratory procedures are allowing for better detection of pathogens. Like Cryptosporidium—which can cause gastrointestinal illness. The illness may be severe and sometimes fatal for people with weakened immune systems. The U.S. Environmental Protection Agency developed and validated Method 1623.1 as an effective procedure to improve Cryptosporidium recovery from challenging matrices using Filtration/IMS/FA. The substantial changes from the current Method 1623 are the addition of sodium hexametaphosphate, and a rinse to remove excess debris during immunomagnetic separation of the organisms. The Method 1623.1 inter-laboratory validation study consisted of 14 laboratories analyzing 4 reagent water and 4 source water samples. The Cryptosporidium mean recovery represented a ?20 percentage point increase compared to the previous validation of Method 1623. The Giardia mean recoveries of approximately 40% were similar to the previous method validation. Laboratories performing Method 1623.1 are expected to see improved Cryptosporidium recoveries from challenging matrices and higher analytical confidence knowing they are meeting more stringent quality control.

Improvement to Method 1623 to Detect *Cryptosporidium* and *Giardia*

Leah Fohl Villegas Ph.D.
CB&I Federal Services



A World of Solutions™

More than 400,000 people sick from 1993 Milwaukee *Cryptosporidium* outbreak

Milwaukee marks 20 years since Cryptosporidium outbreak





Journal Sentinel files

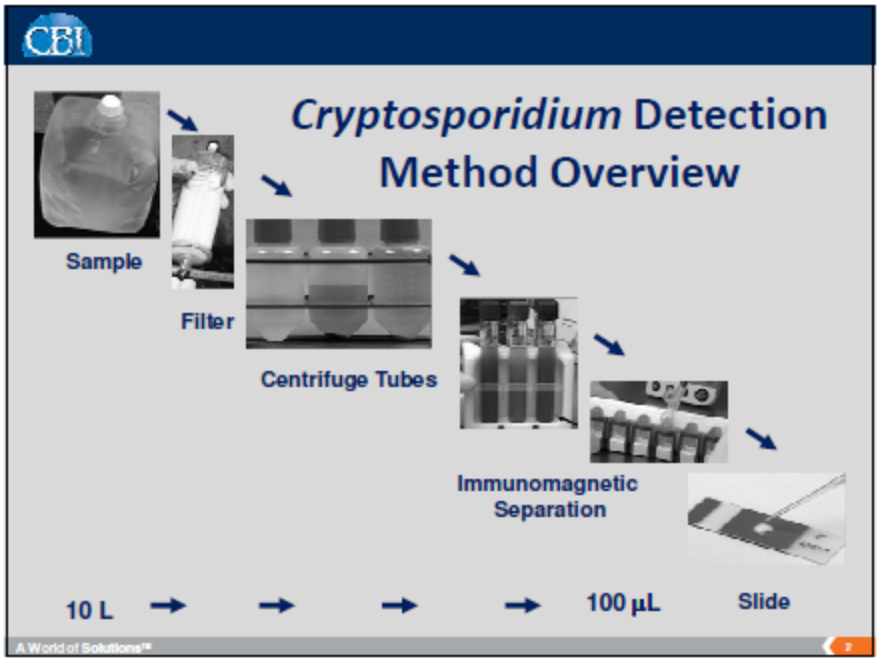
Waitress Barbara Franke ladles boiled water into a pitcher for customers at Miss Katie???s Diner in 1993.

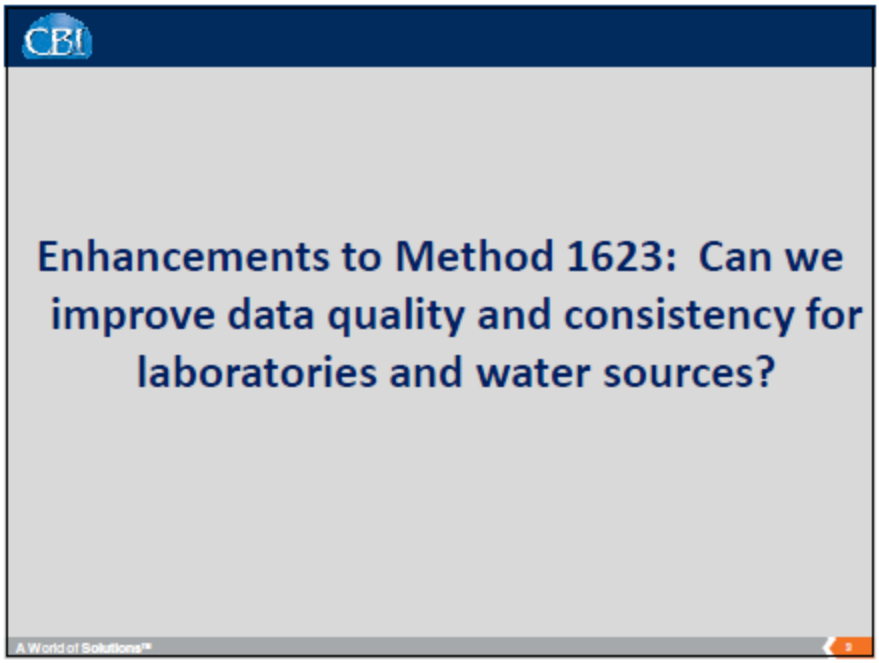
City water remains free of parasite, frequent testing shows

By Don Behm of the Journal Sentinel

April 6, 2013

A World of Solutions™


CBI
Cryptosporidium Detection Method Overview
Sample
Filter
Centrifuge Tubes
Immunomagnetic Separation
10 L
100 µL
Slide
A World of Solutions™


CBI
Enhancements to Method 1623: Can we improve data quality and consistency for laboratories and water sources?
A World of Solutions™

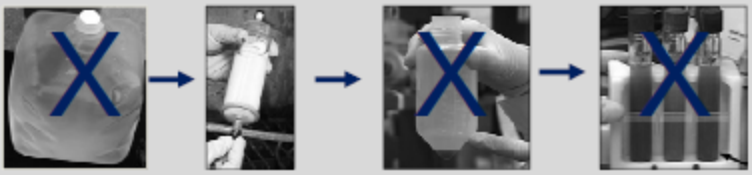
Start with collecting the oocysts

Filtration
Elution
Centrifugation
IMS
Detection

- Sodium hexametaphosphate dispersant is used to facilitate recoveries for finished water and waste water

A World of Solutions™

Cryptosporidium recovery in clay matrix with NaHMP treatments

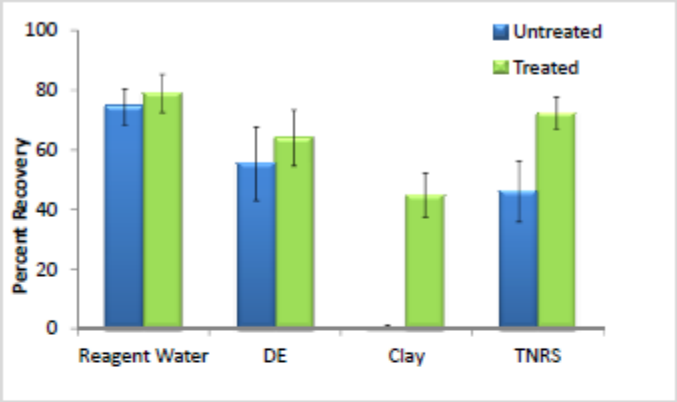


Sample → Filter → Centrifuge Tubes → IMS

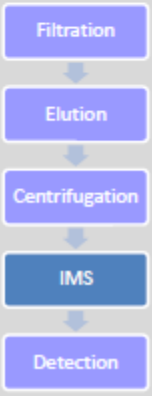
NaHMP addition	Cryptosporidium % Recovery
Untreated	0.6
0.01% to sample	40.6
0.01% pre-elute	32.2
5.0% pre-elute	48.2

A World of Solutions™

Cryptosporidium recovery in artificial matrices using 5.0% NaHMP pre-elution treatment



What about the secondary concentration steps?

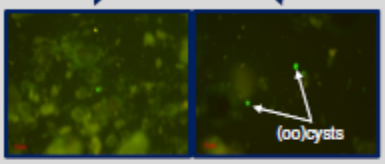


- Secondary concentration requires reducing the 250 mL eluate containing debris and oocysts to microliter volumes

IMS rinse



No Wash Wash



200X Total magnification

- Performed on over 1000 samples with no adverse impact on recovery
- Reduced scope time an average of 10 min/slide

A World of Solutions™

Testing the Concept: Side-by-side analysis

Filtration

Elution ← with & without NaHMP

Centrifugation

IMS ← Rinse all samples

Detection

A World of Solutions™

Side-by-side studies on raw surface water samples

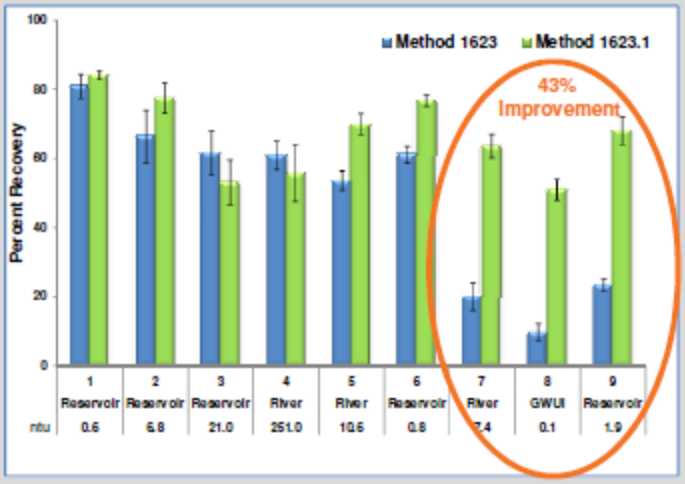
- Sites had reported low recoveries



- Reservoir
- River
- Ground water under the influence

A World of Solutions™

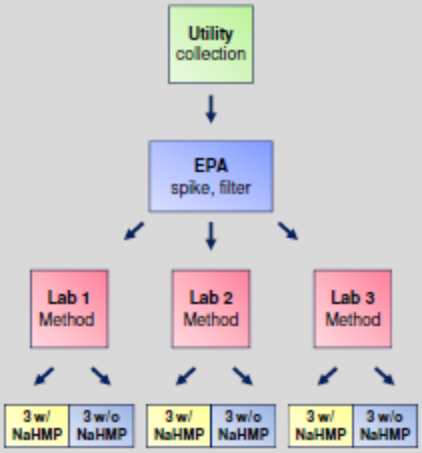
Improved Recovery in Challenging Surface Waters



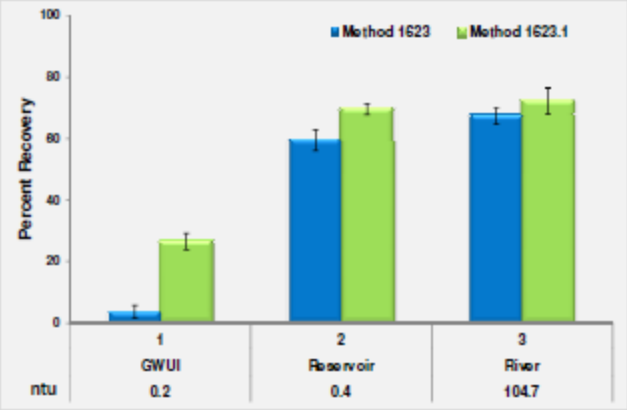
A World of Solutions™

Multiple labs

- 3 LT2 labs & EPA lab
- 4 reagent water samples
- Same 3 raw waters
- Same reagents
- Side by side samples



Multi-Laboratory Improvement with Challenging Matrix



Summary of side-by-side studies

- A pre-elution step using 5% NaHMP was practical and effective
- In those waters where recoveries were low, *Cryptosporidium* recoveries improved with dispersant addition
- In those waters where recoveries were high, the dispersant did not interfere
- NaHMP treatment did not affect reagent water or *Giardia* recoveries

Building Method 1623.1:

The validation process



Small changes that improve oocyst recovery



- Pre-elution treatment with NaHMP
- IMS rinse to reduce analyst fatigue
- More rigorous QA/QC

A World of Solutions™

Method 1623.1 Validation: study plan

- 14 laboratories
- 14 public water utilities
- 4 reagent water & 4 source water for each lab
- Variation in source water samples
  - Turbidity: 1 to 53 NTU
  - Conductivity: 33 to 885 µS
  - pH: 6.5 to 8.5



River
Reservoir/Lake
Ground

Reagent Water Results

- 20 percentage point improvement in *Cryptosporidium* recovery

Statistic	Method 1623	Method 1623.1
Mean % Recovery	40	60
Standard deviation	9	9
Mean RSD	24	16
n	29	56

Source Water Results

- 23 percentage point improvement in *Cryptosporidium* recovery

Statistic	Method 1623	Method 1623.1
Mean % Recovery	38	61
Standard deviation	9	7
Mean RSD	25	13
n	14	53

Method 1623.1 *Cryptosporidium* Acceptance Criteria

	Method 1623	Method 1623.1
Reagent Water	22 – 100	33 – 100*
Raw Source Water	13 – 111 (61)	32 – 100 (46)

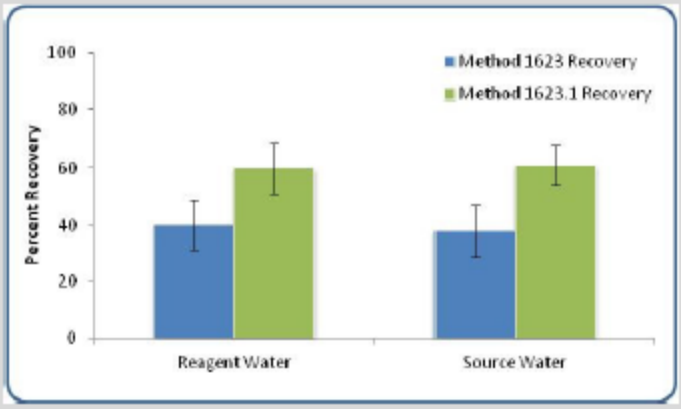
*Same criteria as an update based on 5 reagent water PT rounds

A World of Solutions™ 20

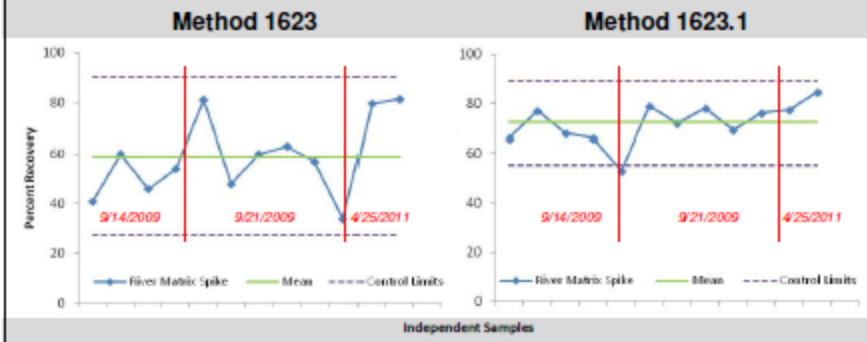
Advantages of Method 1623.1

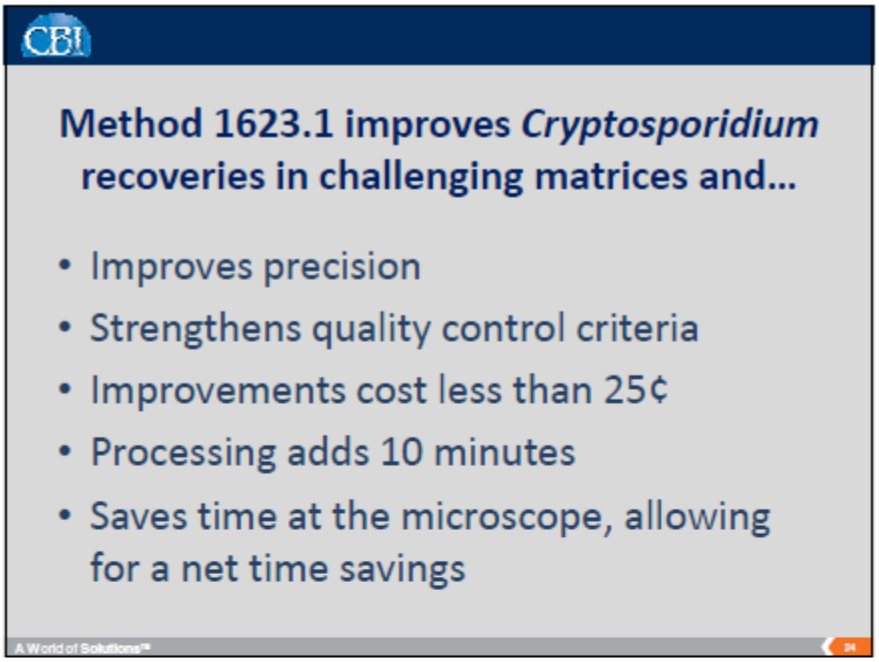
A World of Solutions™ 21

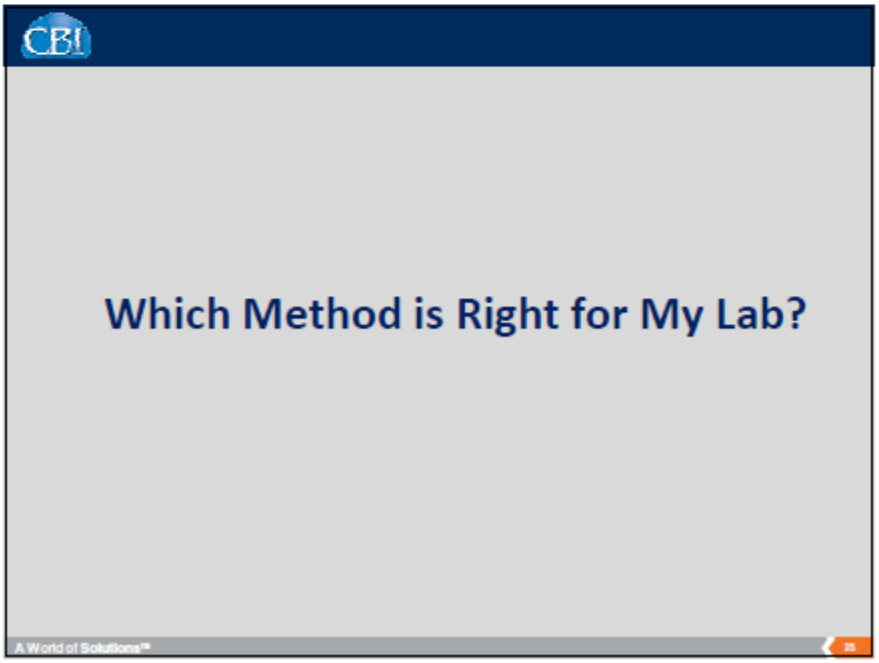
Method 1623 vs. Method 1623.1



Improved Accuracy in River Matrix




CBI
Method 1623.1 improves *Cryptosporidium* recoveries in challenging matrices and...
• Improves precision
• Strengthens quality control criteria
• Improvements cost less than 25¢
• Processing adds 10 minutes
• Saves time at the microscope, allowing for a net time savings
A World of Solutions™
24


CBI
Which Method is Right for My Lab?
A World of Solutions™
25

Who Benefits by Switching to 1623.1?

- Labs testing any water source giving low recoveries in matrix spikes
- Labs testing multiple water sources



Initial Demonstration of Capability

- 4 spiked reagent water samples with ≥38% recovery
- 3 matrix samples (2 spiked & 1 unspiked)
- One method blank
- Don't forget PT samples for 1623.1



Summary

- Method 1623.1 significantly improves recoveries for challenging water sources
- Only 8 samples are needed to demonstrate capability
- Everyone is encouraged to adopt the 33% acceptance criteria
- Everyone is encouraged to use the IMS rinse



A World of Solutions™

Thank You!!

- For more information contact:
  - Miller.Carrie@epa.gov
- Contact Information, Method 1623.1 and video are found on LT2 Lab Quality Assurance Program page: http://water.epa.gov/lawsregs/rulesregs/sdwa/lt2/lab_home.cfm

SECTION 12

LEGAL DEFENSIBILITY OF DATA

Legal Defensibility Is an Oxymoron

Jerry Parr
Catalyst Information Resources

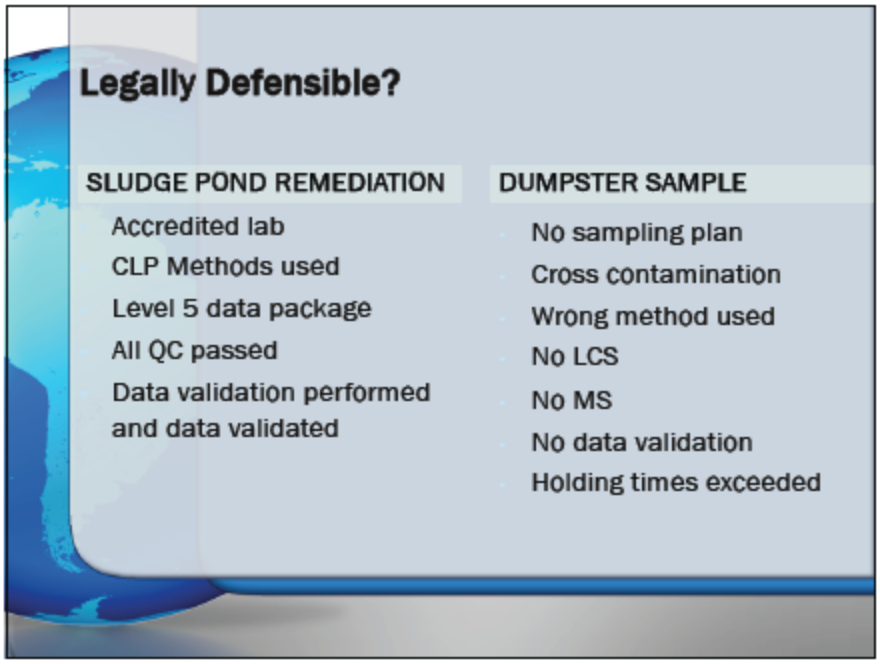
Abstract

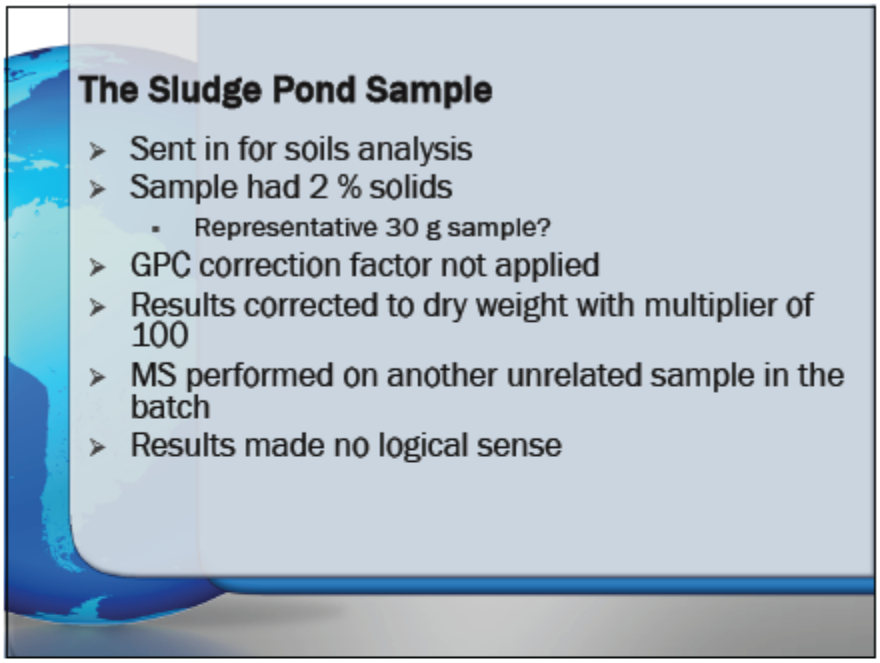
How laboratory data is used in the courts is a function of the skill of the opposing attorneys, the credibility of the witnesses, and the opinion of the jury. In the court's opinion, what is important is not the defensibility of data, but its admissibility. In 1993, in Daubert vs Merrell Dow Pharmaceuticals, the US Supreme Court established 4 foundational principles that relate to the admissibility of scientific evidence:

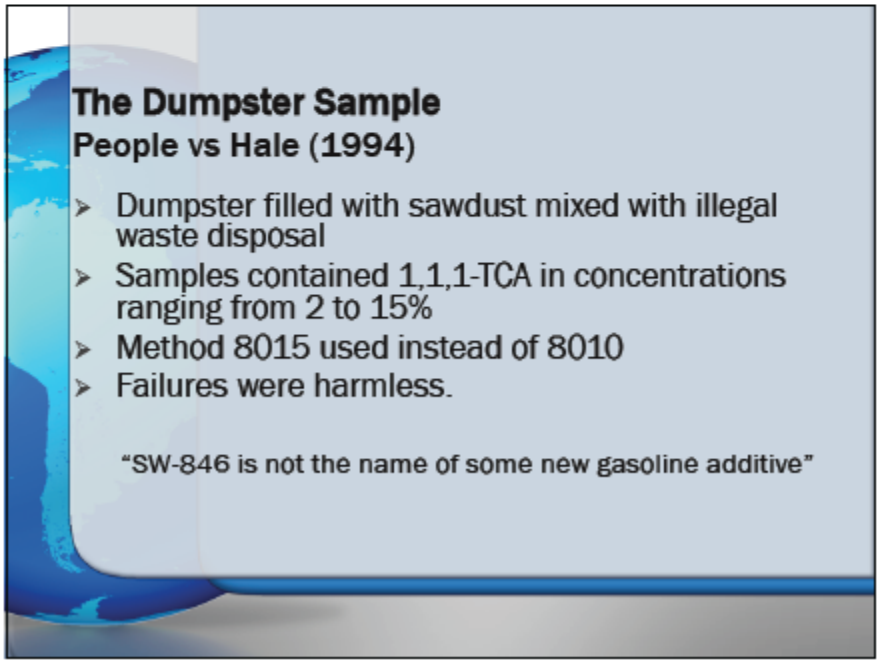
- Whether a theory or technique can be (and has been) tested,
- Whether it has been subjected to peer review and publication,
- Whether there is a high known or potential rate of error,
- Whether there are professional standards controlling the technique's operation, and
- Whether the technique has been accepted within the scientific community.

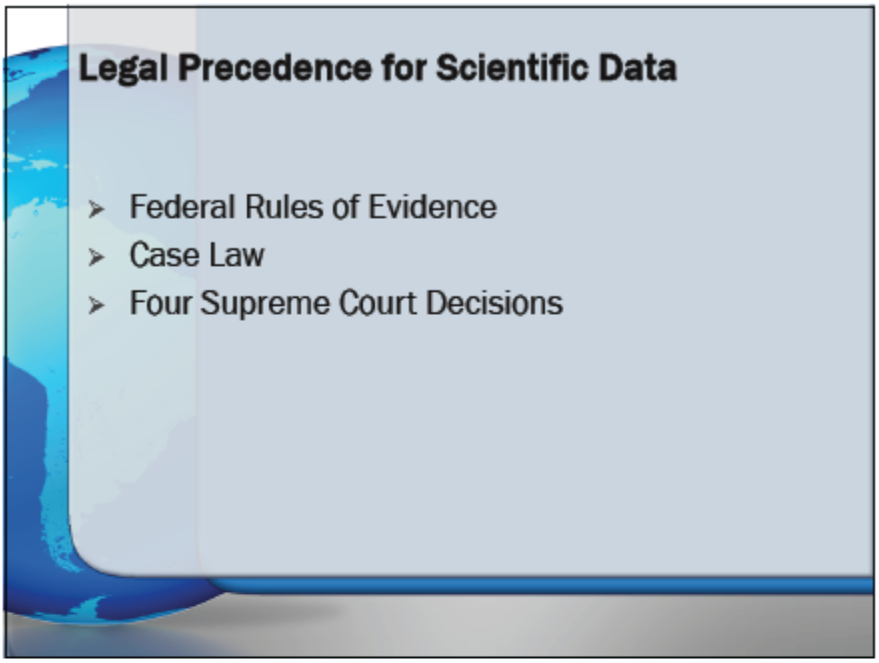
These principles have been upheld in 2 other resent Suprem Court decisions. This presentation will review the Daubert principles and how how they relate to method validation, quality control, and laboratory accreditation.

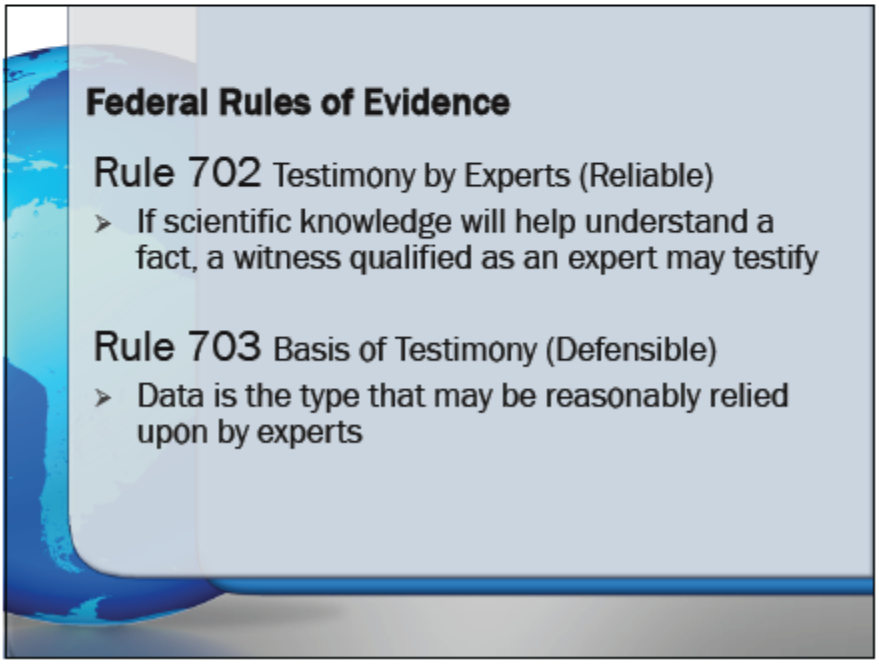

Ensuring Legal Standing
Legally defensible data is an oxymoron.
Jerry Parr
Catalyst Information Resources


Legally Defensible?
SLUDGE POND REMEDIATION
Accredited lab
CLP Methods used
Level 5 data package
All QC passed
Data validation performed and data validated
DUMPSTER SAMPLE
No sampling plan
Cross contamination
Wrong method used
No LCS
No MS
No data validation
Holding times exceeded


The Sludge Pond Sample
Sent in for soils analysis
Sample had 2 % solids
Representative 30 g sample?
GPC correction factor not applied
Results corrected to dry weight with multiplier of 100
MS performed on another unrelated sample in the batch
Results made no logical sense


The Dumpster Sample
People vs Hale (1994)
Dumpster filled with sawdust mixed with illegal waste disposal
Samples contained 1,1,1-TCA in concentrations ranging from 2 to 15%
Method 8015 used instead of 8010
Failures were harmless.
"SW-846 is not the name of some new gasoline additive"


Legal Precedence for Scientific Data
Federal Rules of Evidence
Case Law
Four Supreme Court Decisions


Federal Rules of Evidence
Rule 702 Testimony by Experts (Reliable)
If scientific knowledge will help understand a fact, a witness qualified as an expert may testify
Rule 703 Basis of Testimony (Defensible)
Data is the type that may be reasonably relied upon by experts

Frye vs. United States (1923)

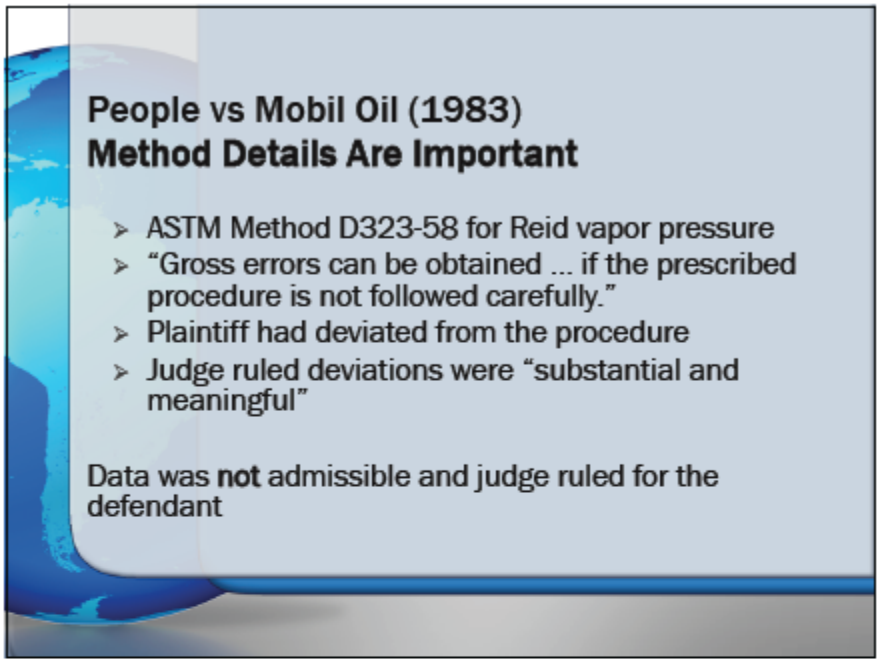
Scientific evidence "must be sufficiently established to have gained general acceptance in the particular field in which it belongs."

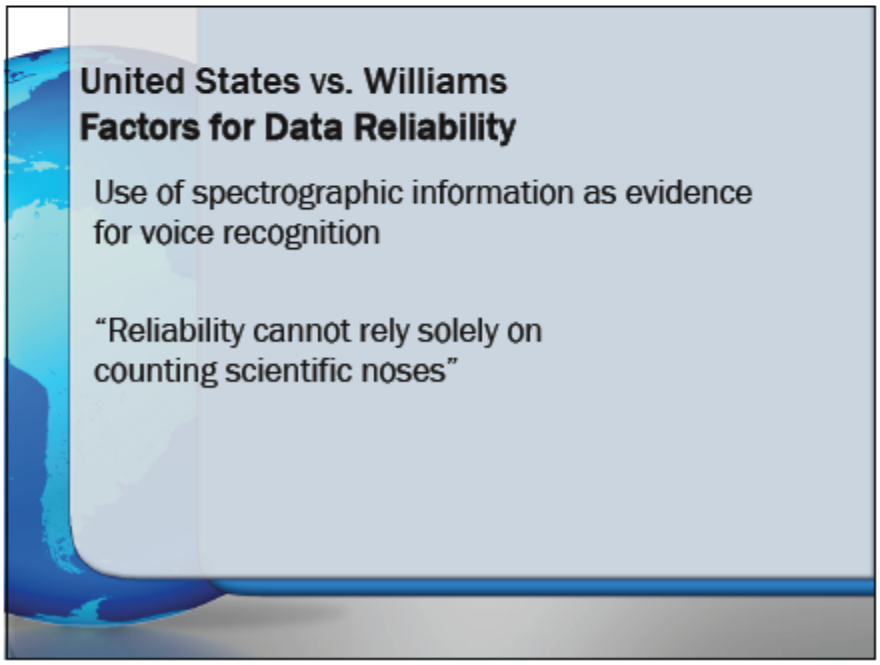


Paoli Railroad Yard PCB Litigation (1992)
Data Reliability is Important

- No written SOP
- Blank results > sample results
- MS 1000 X sample concentrations
- Sample results below low standard

Data was **not** admissible


People vs Mobil Oil (1983)
Method Details Are Important
ASTM Method D323-58 for Reid vapor pressure
"Gross errors can be obtained ... if the prescribed procedure is not followed carefully."
Plaintiff had deviated from the procedure
Judge ruled deviations were "substantial and meaningful"
Data was not admissible and judge ruled for the defendant


United States vs. Williams
Factors for Data Reliability
Use of spectrographic information as evidence for voice recognition
"Reliability cannot rely solely on counting scientific noses"

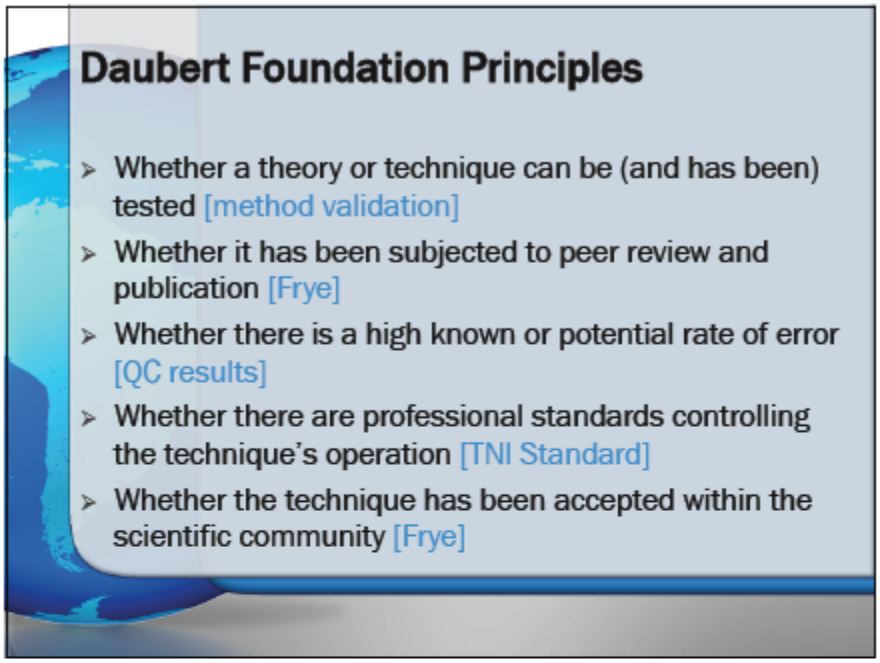
Williams Reliability Factors

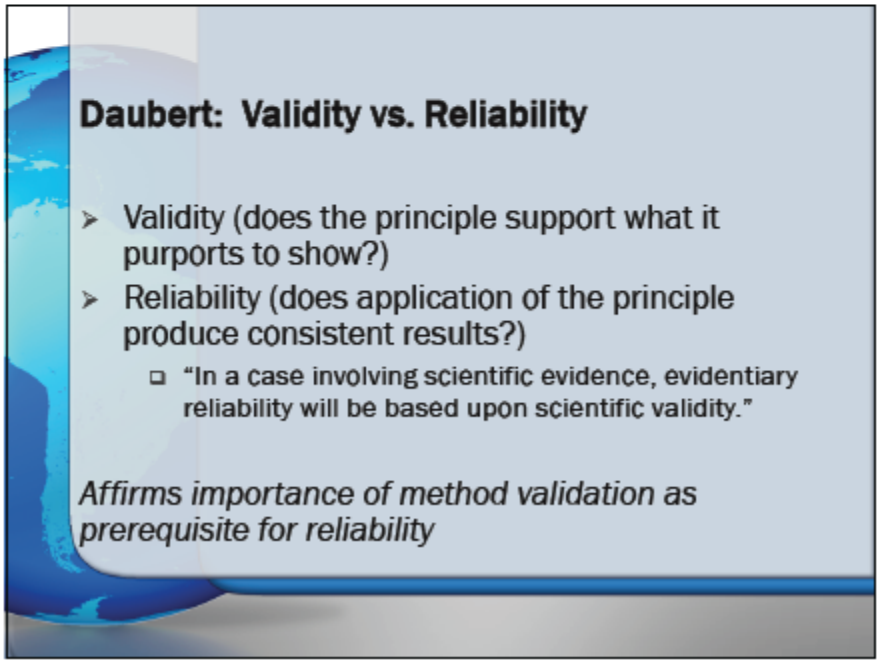
- Potential rate of error
- Existence and maintenance of standards
- Accepted industry practice
- Certification
- Care and concern over use
- Potential for abuse
- Fail-safe characteristics

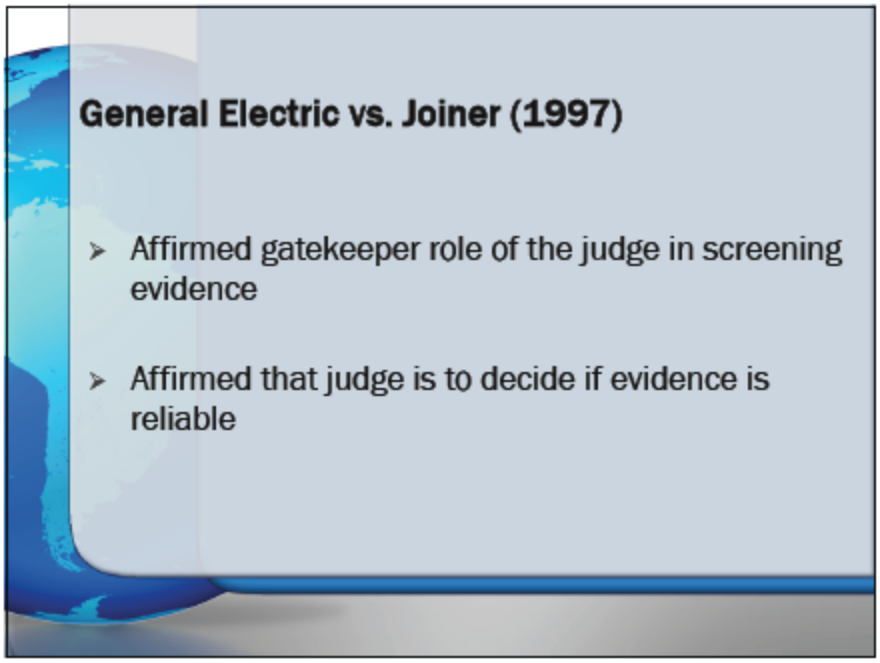
Daubert vs. Merrell Dow Pharmaceuticals (1993)

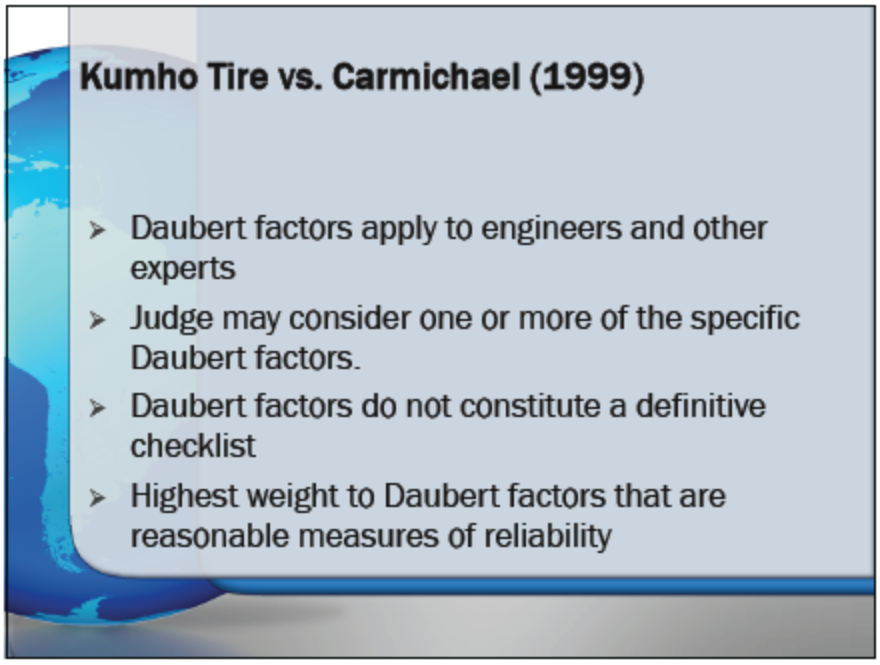
Federal Rules of Evidence, not Frye, provide the standard for admitting expert scientific testimony

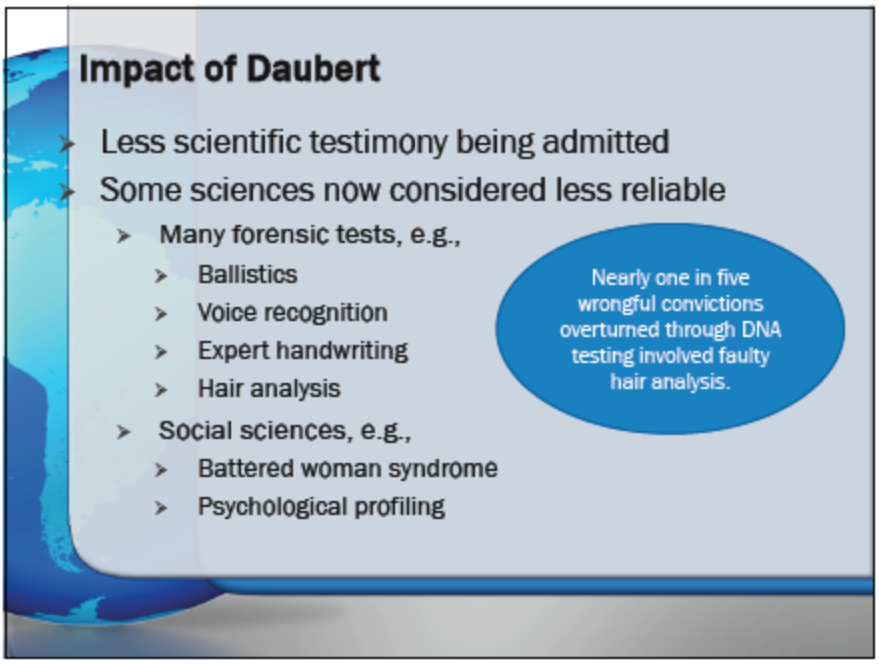


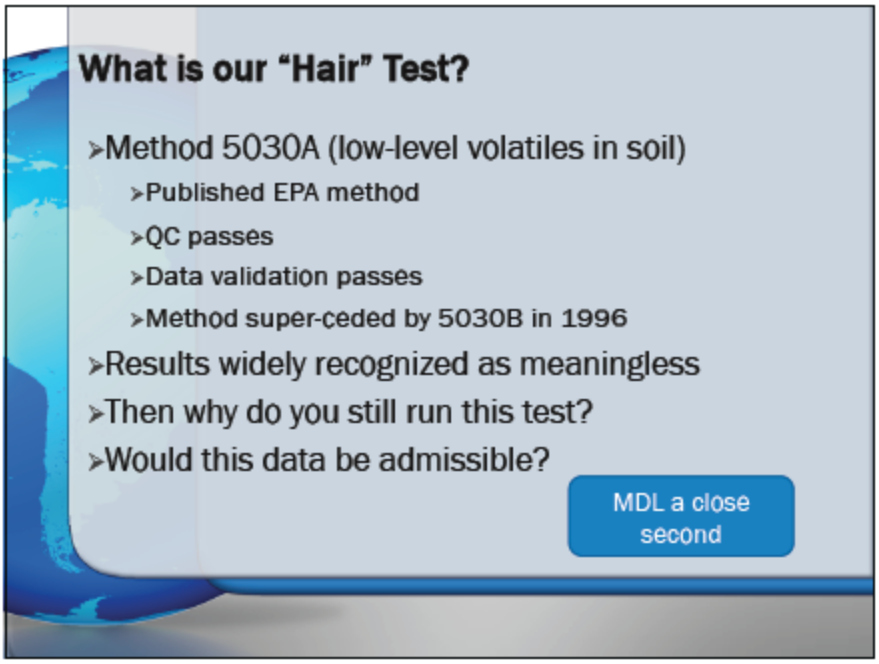

Daubert Foundation Principles
Whether a theory or technique can be (and has been) tested [method validation]
Whether it has been subjected to peer review and publication [Frye]
Whether there is a high known or potential rate of error [QC results]
Whether there are professional standards controlling the technique's operation [TNI Standard]
Whether the technique has been accepted within the scientific community [Frye]

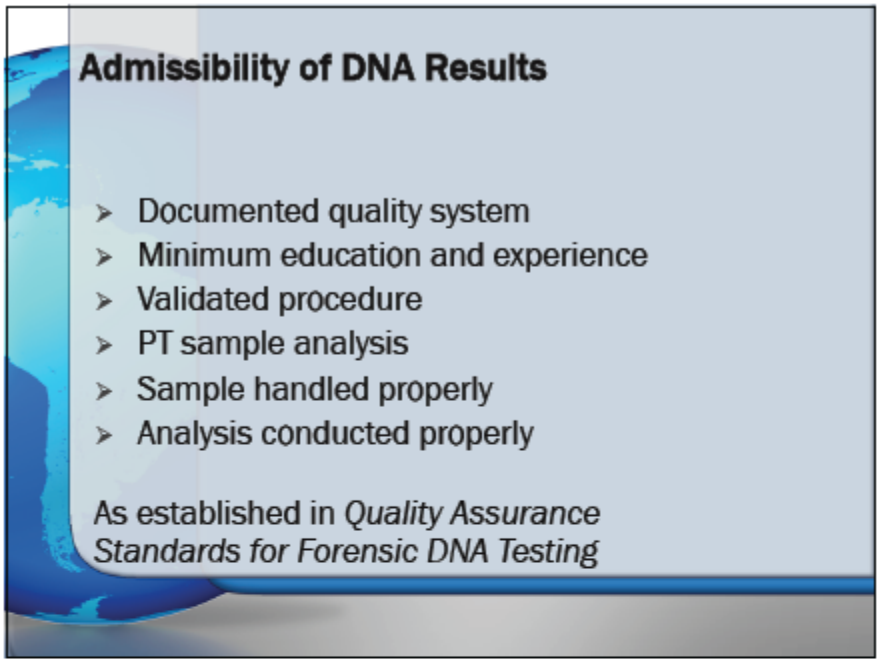

Daubert: Validity vs. Reliability
Validity (does the principle support what it purports to show?)
Reliability (does application of the principle produce consistent results?)
"In a case involving scientific evidence, evidentiary reliability will be based upon scientific validity."
Affirms importance of method validation as prerequisite for reliability

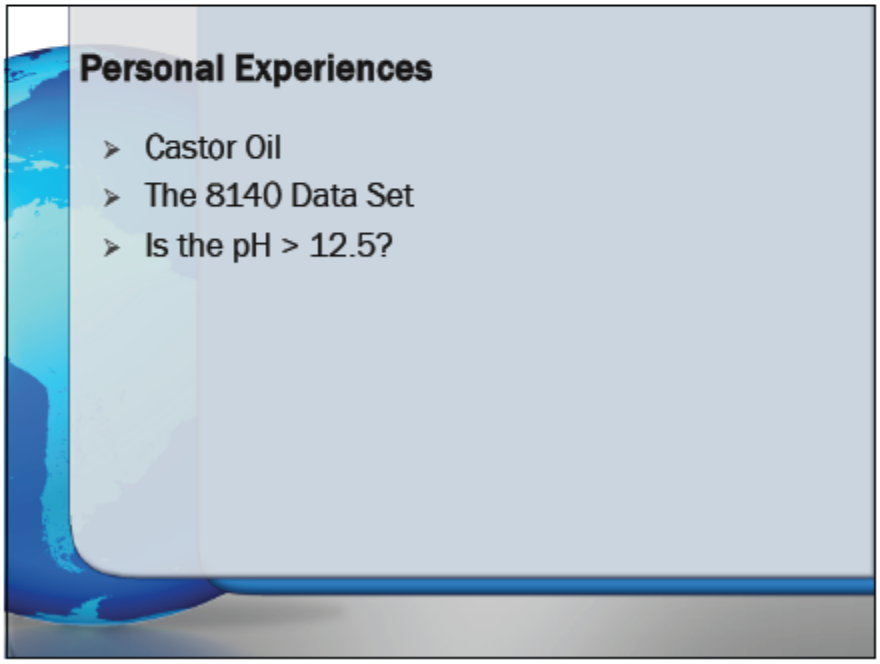

General Electric vs. Joiner (1997)
Affirmed gatekeeper role of the judge in screening evidence
Affirmed that judge is to decide if evidence is reliable

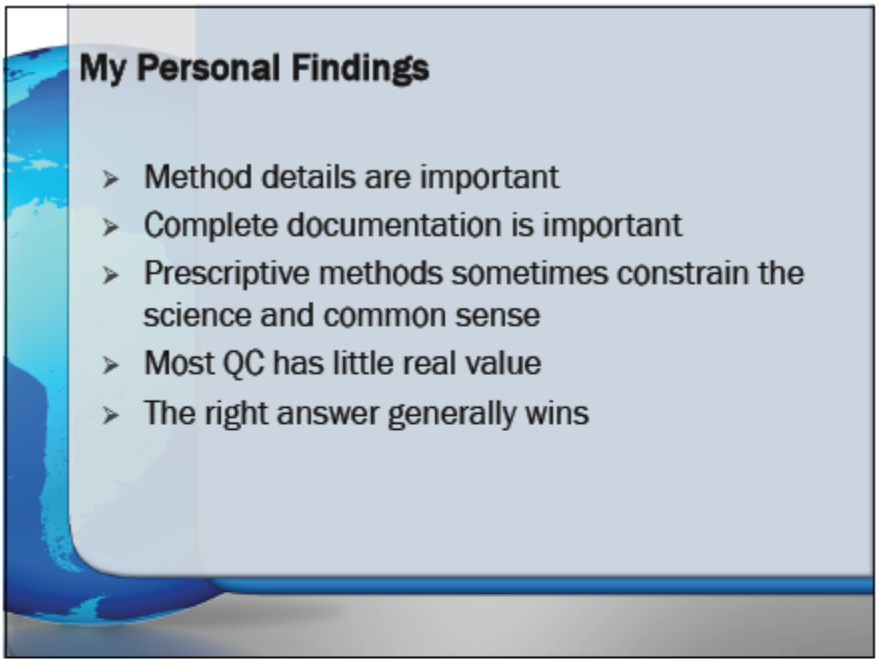

Kumho Tire vs. Carmichael (1999)
Daubert factors apply to engineers and other experts
Judge may consider one or more of the specific Daubert factors.
Daubert factors do not constitute a definitive checklist
Highest weight to Daubert factors that are reasonable measures of reliability

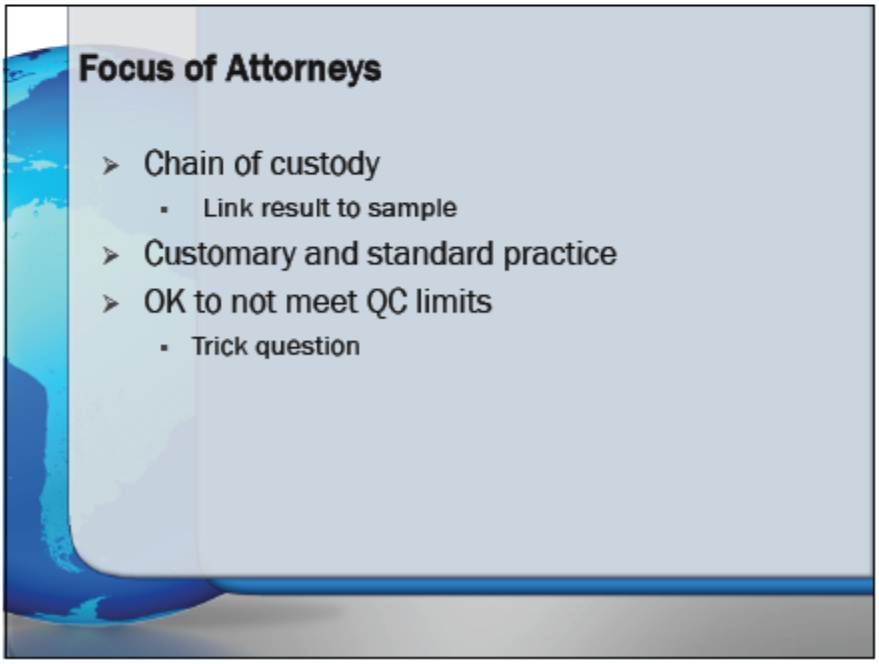

Impact of Daubert
Less scientific testimony being admitted
Some sciences now considered less reliable
Many forensic tests, e.g.,
Ballistics
Voice recognition
Expert handwriting
Hair analysis
Social sciences, e.g.,
Battered woman syndrome
Psychological profiling
Nearly one in five wrongful convictions overturned through DNA testing involved faulty hair analysis.

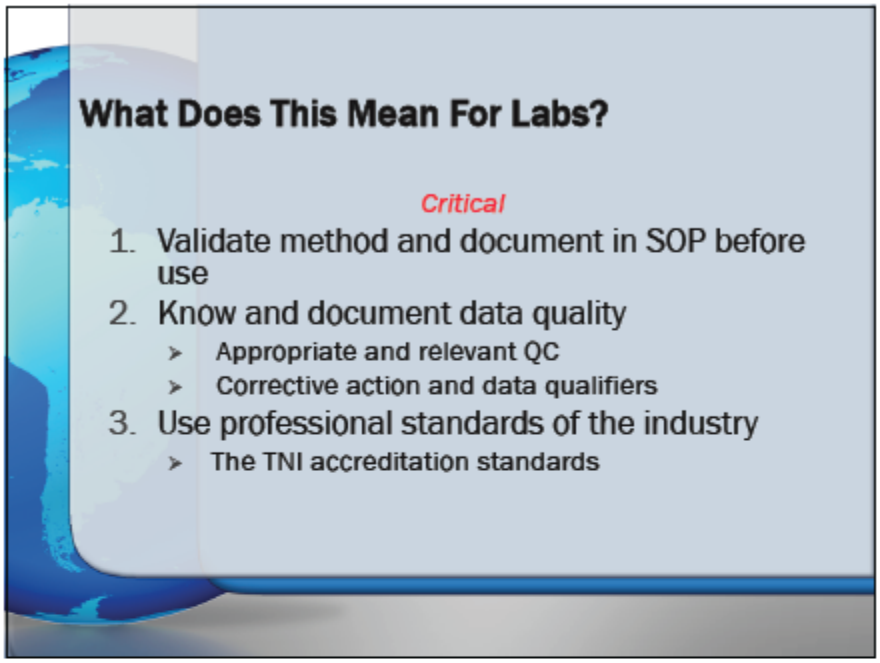

What is our "Hair" Test?
Method 5030A (low-level volatiles in soil)
Published EPA method
QC passes
Data validation passes
Method super-ceded by 5030B in 1996
Results widely recognized as meaningless
Then why do you still run this test?
Would this data be admissible?
MDL a close second

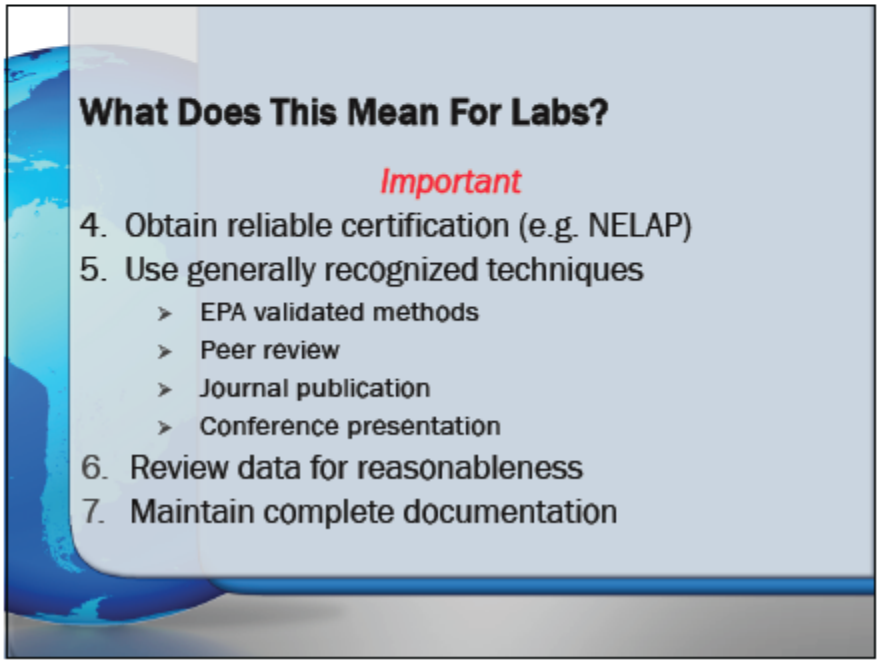

Admissibility of DNA Results
Documented quality system
Minimum education and experience
Validated procedure
PT sample analysis
Sample handled properly
Analysis conducted properly
As established in Quality Assurance Standards for Forensic DNA Testing


Personal Experiences
Castor Oil
The 8140 Data Set
Is the pH > 12.5?


My Personal Findings
Method details are important
Complete documentation is important
Prescriptive methods sometimes constrain the science and common sense
Most QC has little real value
The right answer generally wins


Focus of Attorneys
Chain of custody
Link result to sample
Customary and standard practice
OK to not meet QC limits
Trick question


What Does This Mean For Labs?
Critical
1. Validate method and document in SOP before use
2. Know and document data quality
➢ Appropriate and relevant QC
➢ Corrective action and data qualifiers
3. Use professional standards of the industry
➢ The TNI accreditation standards


What Does This Mean For Labs?
Important
4. Obtain reliable certification (e.g. NELAP)
5. Use generally recognized techniques
➢ EPA validated methods
➢ Peer review
➢ Journal publication
➢ Conference presentation
6. Review data for reasonableness
7. Maintain complete documentation

Conclusions

- The right answer, "scientific validity", should always be admissible
- Everything does not have to be perfect for data to be admissible
- Methods used within a sound quality systems framework should have strong legal standing
- Differences in data on split samples are likely due to other factors

Finally, What Is A "Defensible" Result?

- Method used is appropriate for the measurement need
- Method performance validated
- Laboratory QC demonstrated control
- Quality is known and documented
- Laboratory has a quality system
- Quality system is independently verified
- Documentation is sufficient to reconstruct result


THANK YOU!
Jerry Parr
Catalyst Information Resources
jparr@catalystinforesources.com
817-598-1155

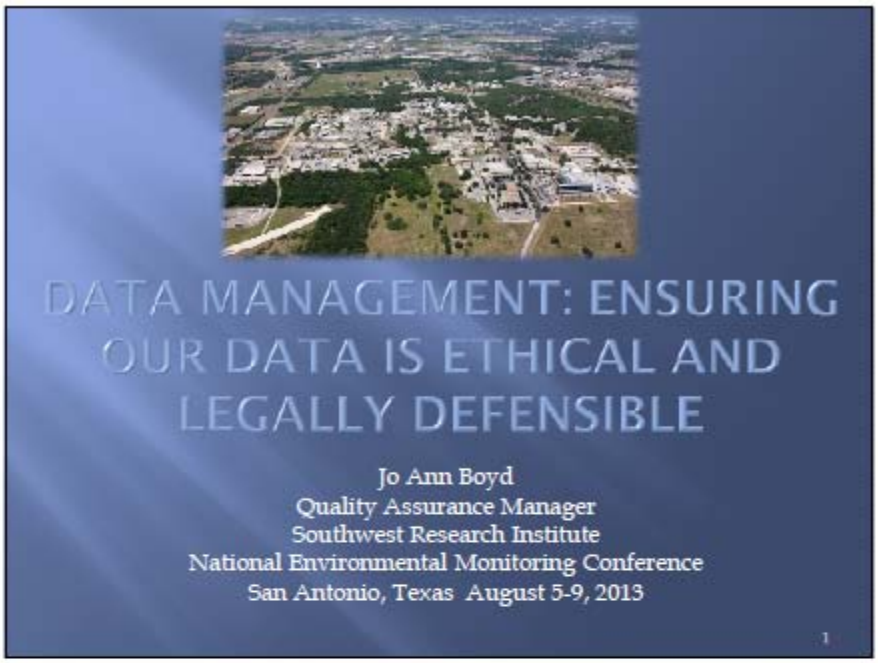
Data Management: Ensuring Our Data Is Ethical and Legally Defensible

JoAnn Boyd
Southwest Research Institute

Abstract

Are we ensuring that each set of data produced are competent to meet the legal defensibility of potential litigation? What is wrong with the data? Measures must be taken to ensure that data meets compliance for any regulatory agency or consumer. Data submitted for litigation is not always reviewed by someone who is knowledgeable in that area. The areas of concern are; do we do and report what we say we do. Are we meeting the regulations, statements of work, internal procedures, and quality control measures for the process? Are we meeting the review requirements to verify and validate the work performed? This presentation will provide examples of repeated problems in the industry and how to document properly to ensure that data will meet litigation requirements.

Data integrity and defensibility are critical factors for regulatory work. Most analytical or testing data for government or commercial aspects is subject to litigation. The highest quality data establish documents that provide repeatability of the work and legally defensible data. Litigation looks for questionable data, loopholes that prompt questions to the data, and missing information that was critical to the completion of the data report or package. In making decisions regarding integrity of the testing and results to be reported, ethical dilemmas can be critical judgments in business today.


DATA MANAGEMENT: ENSURING OUR DATA IS ETHICAL AND LEGALLY DEFENSIBLE
Jo Ann Boyd
Quality Assurance Manager
Southwest Research Institute
National Environmental Monitoring Conference
San Antonio, Texas August 5-9, 2013
1


GOALS
2

What is Data Quality?

Concise, high-value definitions of Data Quality by expert users, analysts, and end users.

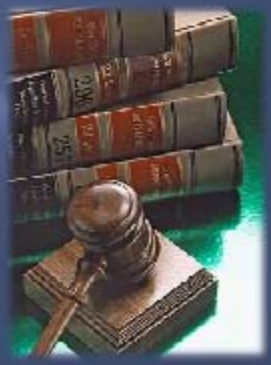
Data has quality if it satisfies the requirements of its intended use.



Good Documentation Archived for Required Contract







Legally Defensible Data to Meet Intended Use & Potential Litigation

Legal Defensibility



Documentation
- Document all correct and incorrect results
- Identify staff and date of documentation



Evaluation
- Provide any effects of the testing or reporting situation
- Ensure staff can support the information



Reporting
- Report all information and do not omit data



Exceptions
- Report the out of ordinary, why, when, where, who, etc.



Evidentiary
- Provide evidence to support all issues

5

Legal Loopholes

Lawyers may not be chemists
- *They may hire chemists as expert witness*

Lawyers look for loop holes
- *Missing QC*
- *Missing signatures*
- *Missing data*
- *Expired Standards*
- *Question staff for expertise*
- *Many more items……*



6


Problems Linked to Poor Data Quality
Poor project cost and scheduled tracking
Inappropriate staffing levels
Flawed methods and decisions
Ineffective and inefficient testing
Lack of or insufficient procedure and training
Inadequate/improper quality controls/materials
Lack of project/data monitoring
7


CONSEQUENCES OF POOR QUALITY
Liability
Repeating the tests
• Costs money
• Wastes time
Rejecting the work
• Not getting paid for the work
• Throwing money away
Liability Claims
• Paying individual health claims
• Paying claims for a city
Poor Science and/or Documentation
• Not getting work from other clients
• Reputation affected
8


REVIEW/INSPECTIONS REQUIRED
Quality Assurance
• procedures
• training
• systems operations
• lab notebooks
• quality control
• operations documentation
• materials
• raw data
• final report


CRITICAL AREAS
Any step or measurement in the process or procedure that can change the outcome.
Weighing
Spiking
Sample Prep
Analysis
Secondary Solutions
10

Environmental Needs

- Environmental Protection Agency
  - RCRA
  - CERCLA
  - SDWA
  - CWA
  - Homeland Security
- State Departments
- Department of Defense
- Department of Energy



11

Legal Defensibility



- Documented evidence
- Compliance criteria
- Traceability
- Custody
- Ethics
- Cradle to grave
- Secondary review



12

Lack of Defensible Data

Is a cost to	• Government • Companies • Taxpayers
The only people making money in poor quality data are the lawyers	• They find reasons to win cases and large fees leaving little to those they represent

13



14

Defining Ethics

Ethics defined in the Merriam-Webster Dictionary

"The discipline dealing with what is good and bad and with moral duty and obligation".

- Simply put… learning what is right or wrong, and then doing the right thing.
- Stress or confusion is not an excuse for unethical actions.

15

Personal Moral code

Each person develops growth and moral code as a child through lessons in hygiene, safety, honesty, fairness by:

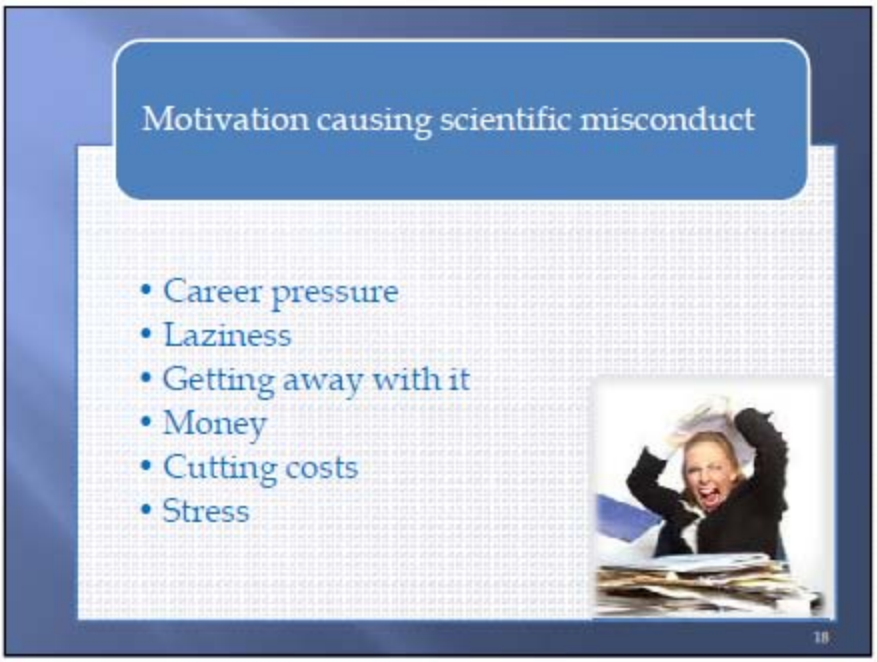
- Parents
- Teachers
- Friendships
- Clergy
- Supervisor
- Work relationships

Telling the truth when a mistake is made

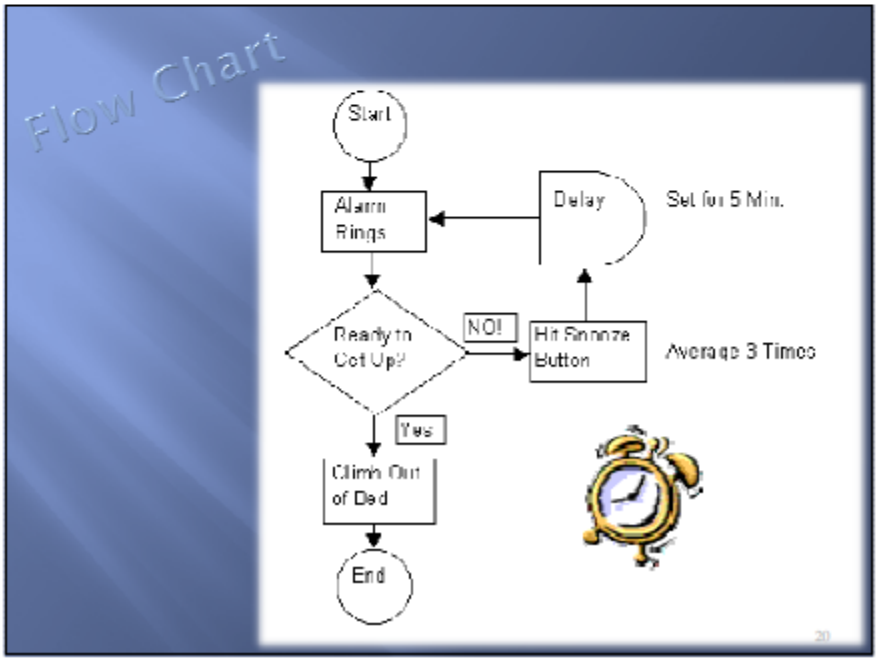
Provide what happened and the consequences

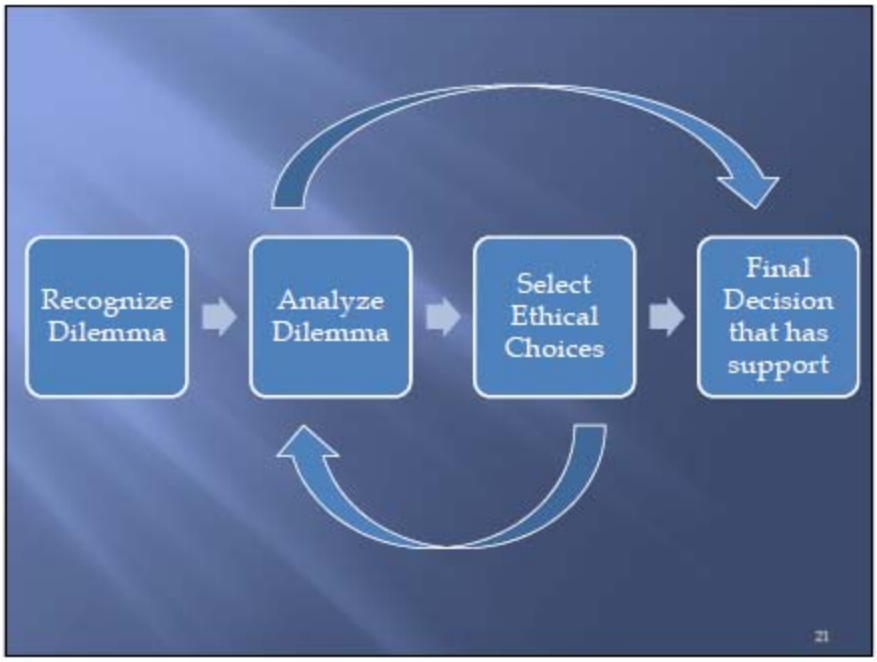



It is okay to make mistakes: Document them
"Anyone who has never made a mistake has never tried anything new." —Albert Einstein
"Freedom is not worth having if it does not include the freedom to make mistakes." —Mahatma Gandhi
Mistakes are always forgivable, if one has the courage to admit them. Bruce Lee
The successful man will profit from his mistakes and try again in a different way. Dale Carnegie
Success does not consist in never making mistakes but in never making the same one a second time. George Bernard Shaw
17


Motivation causing scientific misconduct
• Career pressure
• Laziness
• Getting away with it
• Money
• Cutting costs
• Stress
18


Areas of Potential Concern
Risk Analysis of the scope
Sampling Issues
Instrumentation
Support Equipment & Computers
Quality control materials
Out of control situations
Method accountability
Reporting of all pertinent information
19


Flow Chart
Start
Alarm Rings
Delay
Set for 5 Min.
Ready to Get Up?
NO!
Hit Snooze Button
Average 3 Times
Yes
Climb Out of Bed
End


Recognize Dilemma
Analyze Dilemma
Select Ethical Choices
Final Decision that has support
21


Agriculture problems
22

Arsenic in Agriculture

In the past, inorganic arsenic compounds were used as pesticides on cotton fields and in orchards.

- Inorganic arsenic compounds can no longer be used in agriculture
  - cannot be destroyed in the environment.
- Arsenic only changes its form, or becomes attached/separated from particles.

23

Arsenic in Embalming

From the Civil War until about 1910, arsenic was the main ingredient in the embalming fluids

- Arsenic is toxic will never degrade into harmless by-products
- Progress in embalming practices during the late 1880s has left a legacy
- Potential health harm of archeologists, cemetery workers
- Impacts the environment
- Potential amounts of arsenic seeping into water systems





24


Building/Factory Contaminations
Public Facility from previous industrial organizations
Pollution effects global climate changes and local residents
25


Environmental Support
Oil Spills
TEXAS DROUGHT
Tornados/Tsunamis
Floods
Burned Buildings
Fires
Nuclear Explosions
Hurricanes
26


River Dioxin Contamination
Dioxin contamination was found in animal feeds distributed to over 3,400 consignees throughout the country. (1997)
Ball Clay slurry


Fracking: Good or Bad

Resolutions for Disaster Analysis

Decisions in testing and reporting that:

- Ensure the safety of communities
- Verify legal defensibility
- Support for all stakeholders
- Confidence that the work you perform and report identifies integrity

29

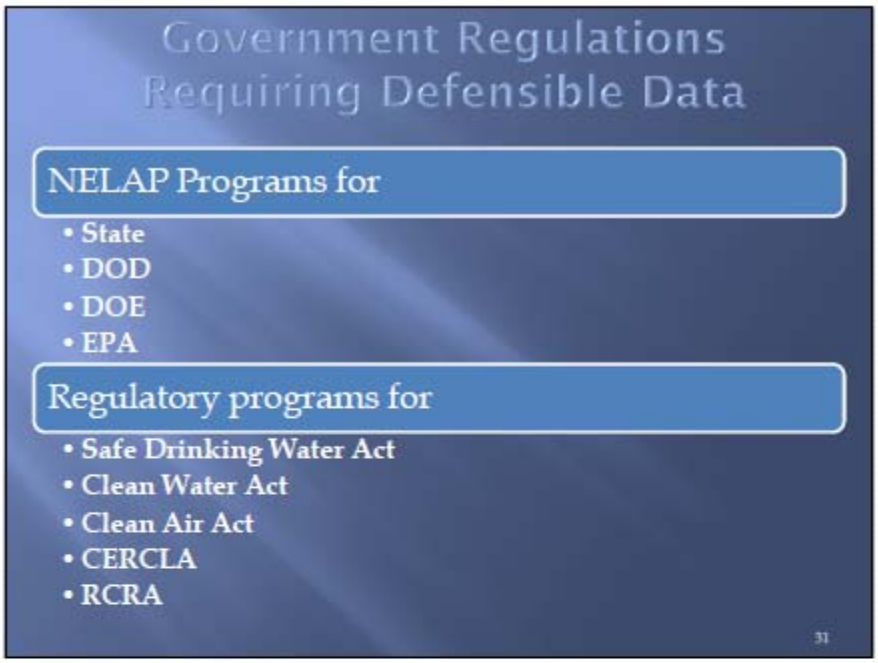
Standards of Personal Conduct



Expectations?

- Reporting Improper, Unreliable or Suspicious Behavior
- Reporting behaviors of potential security concerns
- Reporting activities that seriously deviate from accepted scientific practices

30


Government Regulations Requiring Defensible Data
NELAP Programs for
• State
• DOD
• DOE
• EPA
Regulatory programs for
• Safe Drinking Water Act
• Clean Water Act
• Clean Air Act
• CERCLA
• RCRA
31


Regulatory Programs
NELAP
• Laboratory Accreditation
• Field Monitoring Accreditation
DOE with NELAP
DOD with NELAP
GLP EPA Registration
NQA1
32

Providing Defensible Data

- Define the methods of testing
- Provide all data involved
- Describe out of criteria situations
- Define the corrective actions taken
- Evaluate the effect of problems on data
- Ensure that the proper controls are implemented
- Document, Document, Document

33

Assurance for Final Data



Assure that data are scientifically sound

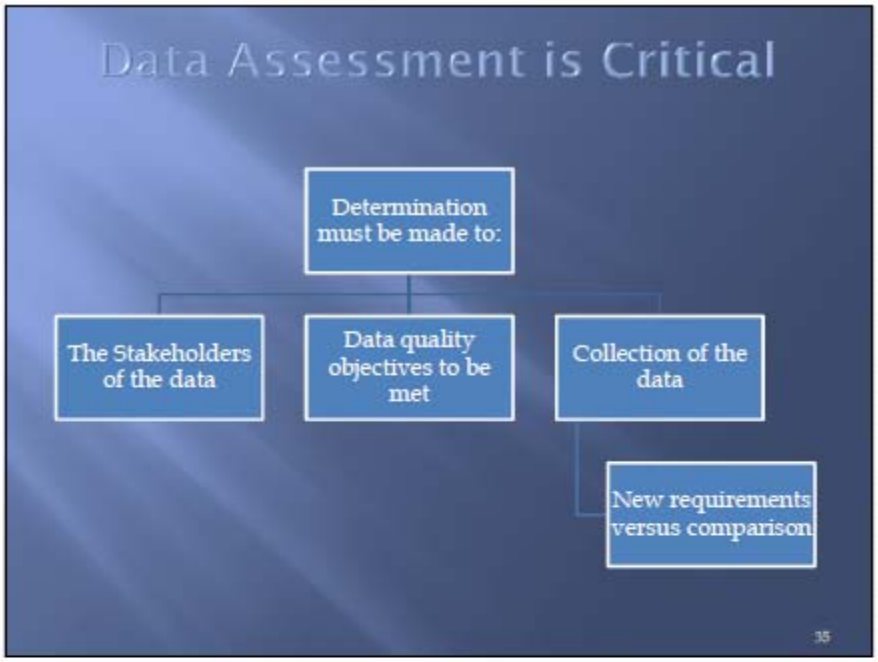
- Have you have done what you said in the procedures and do the procedures provide what you did.
- Through equipment calibration and checks, QC checks, periodic maintenance, data qualification, and explanations where necessary.

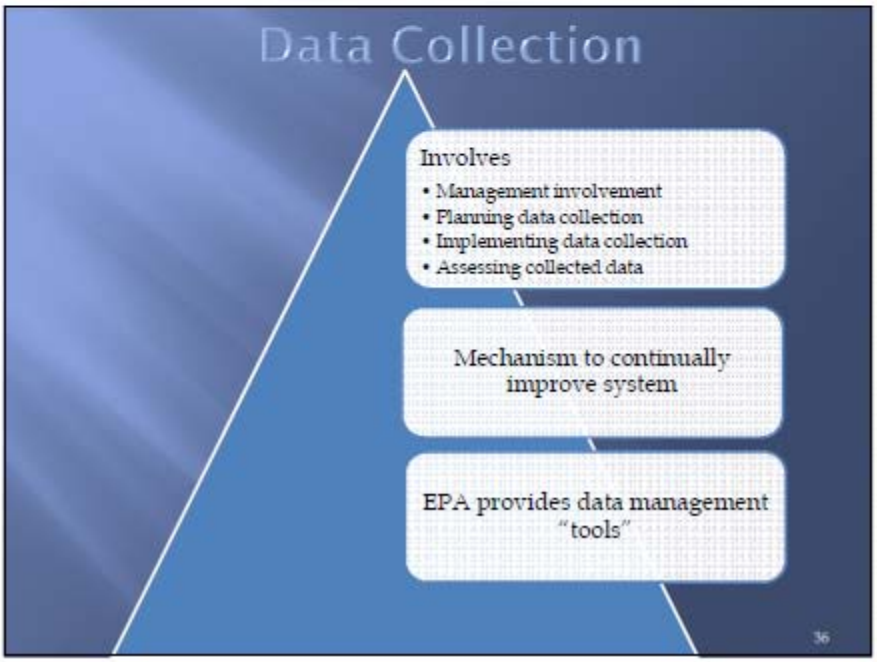


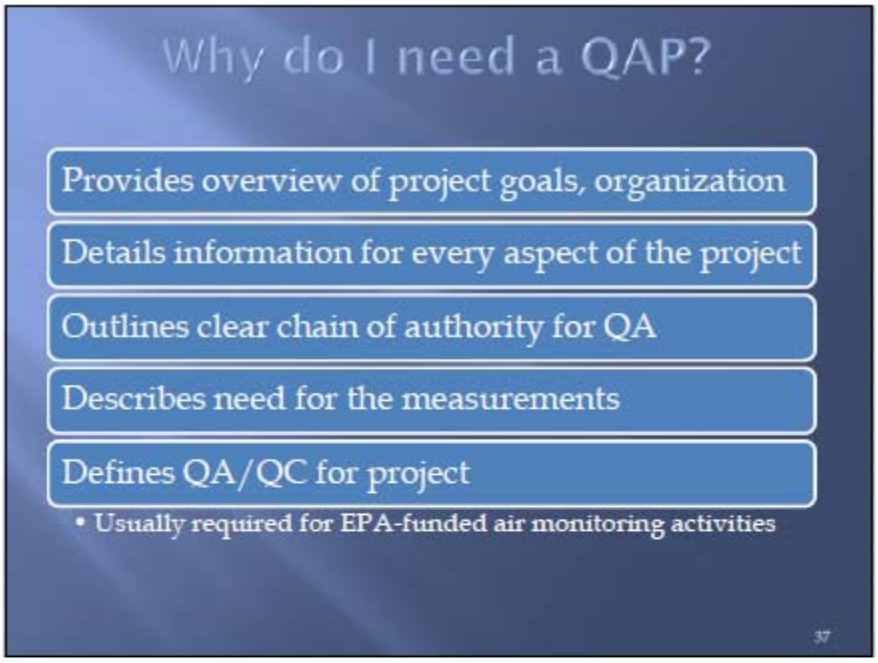
Assure that data are legally defensible

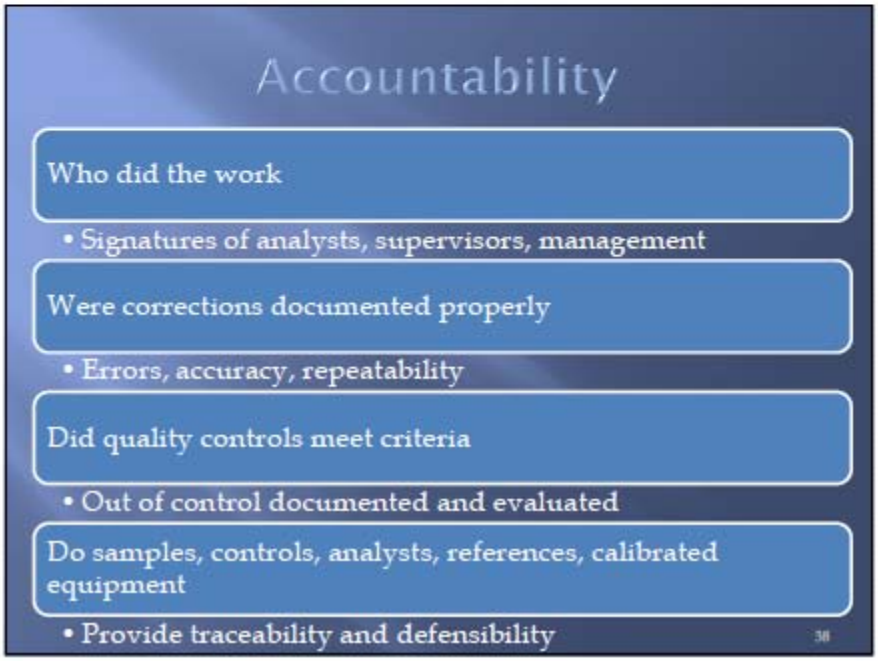
- Does your evidence back up your data and claims
- Is all pertinent material available such as chain of custody, logbooks, raw data, inspections and reports, corrective measures for out of control situations.
- Remember: If you didn't document it, it didn't happen

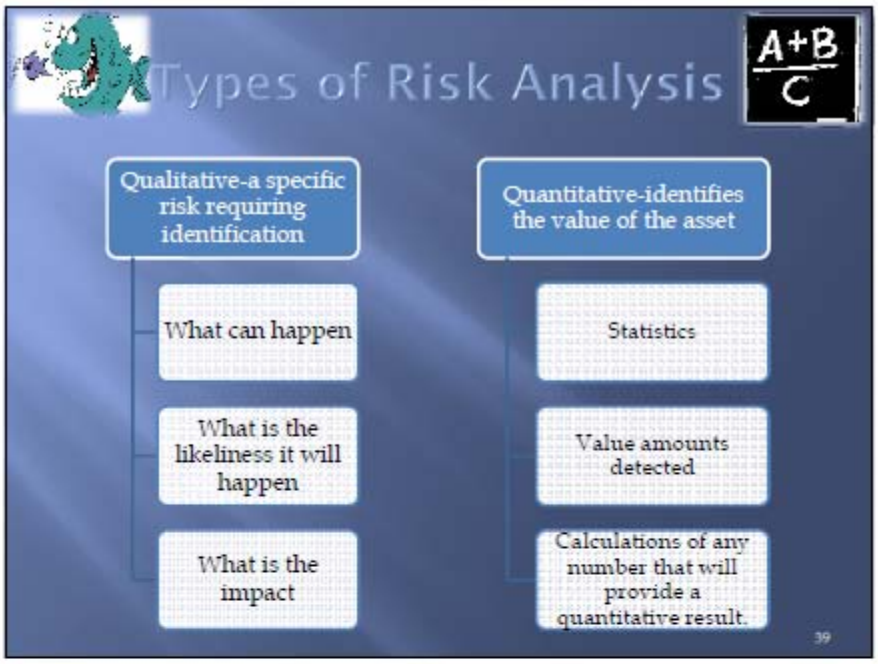
34

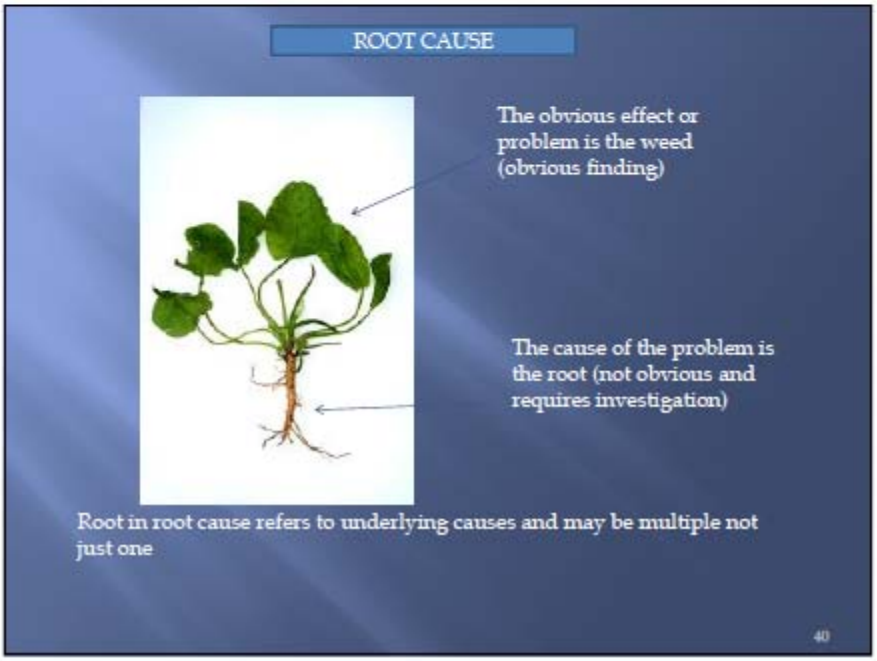

Data Assessment is Critical
Determination must be made to:
The Stakeholders of the data
Data quality objectives to be met
Collection of the data
New requirements versus comparison
35

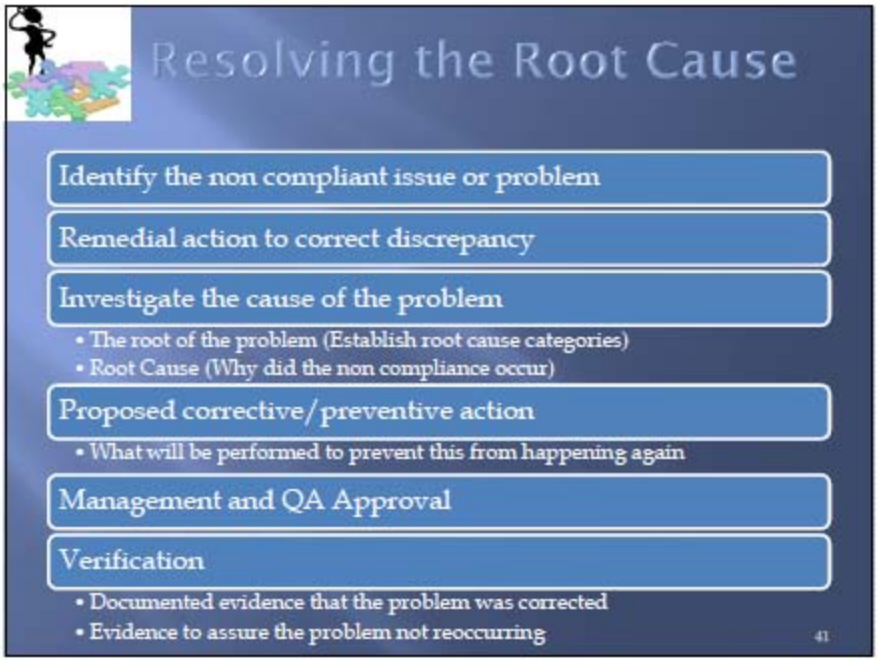

Data Collection
Involves
• Management involvement
• Planning data collection
• Implementing data collection
• Assessing collected data
Mechanism to continually improve system
EPA provides data management "tools"
36

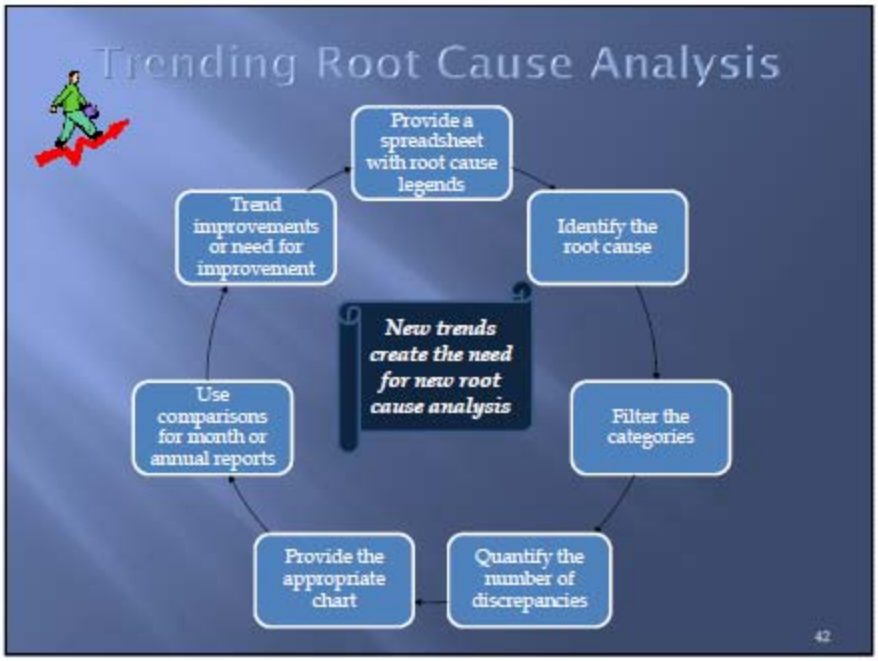

Why do I need a QAP?
Provides overview of project goals, organization
Details information for every aspect of the project
Outlines clear chain of authority for QA
Describes need for the measurements
Defines QA/QC for project
• Usually required for EPA-funded air monitoring activities
37

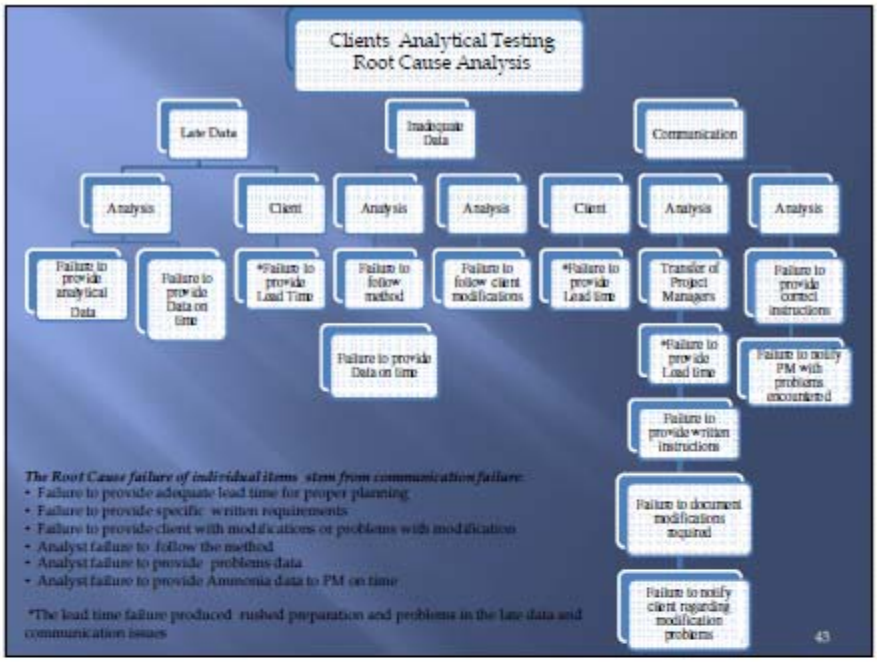

Accountability
Who did the work
• Signatures of analysts, supervisors, management
Were corrections documented properly
• Errors, accuracy, repeatability
Did quality controls meet criteria
• Out of control documented and evaluated
Do samples, controls, analysts, references, calibrated equipment
• Provide traceability and defensibility
38

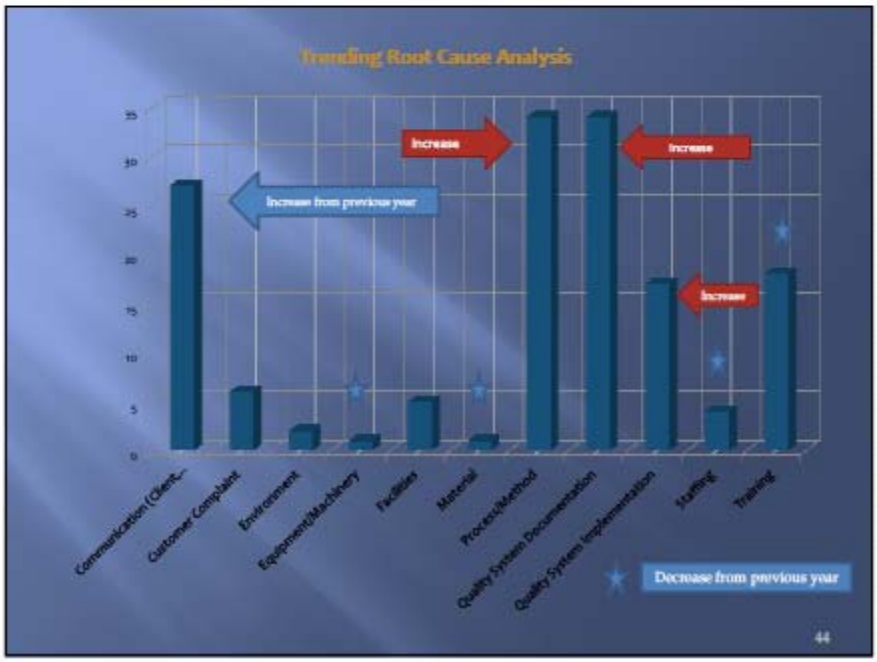

Types of Risk Analysis
A+B
C
Qualitative-a specific risk requiring identification
What can happen
What is the likeliness it will happen
What is the impact
Quantitative-identifies the value of the asset
Statistics
Value amounts detected
Calculations of any number that will provide a quantitative result.
39


ROOT CAUSE
The obvious effect or problem is the weed (obvious finding)
The cause of the problem is the root (not obvious and requires investigation)
Root in root cause refers to underlying causes and may be multiple not just one
40


Resolving the Root Cause
Identify the non compliant issue or problem
Remedial action to correct discrepancy
Investigate the cause of the problem
• The root of the problem (Establish root cause categories)
• Root Cause (Why did the non compliance occur)
Proposed corrective/preventive action
• What will be performed to prevent this from happening again
Management and QA Approval
Verification
• Documented evidence that the problem was corrected
• Evidence to assure the problem not reoccurring
41


Trending Root Cause Analysis
Provide a spreadsheet with root cause legends
Identify the root cause
Filter the categories
Quantify the number of discrepancies
Provide the appropriate chart
Use comparisons for month or annual reports
Trend improvements or need for improvement
New trends create the need for new root cause analysis
42


Clients Analytical Testing
Root Cause Analysis
Late Data
Inadequate Data
Communication
Analysis
Client
Analysis
Analysis
Client
Analysis
Analysis
Failure to provide analytical Data
Failure to provide Data on time
*Failure to provide Lead Time
Failure to follow method
Failure to follow client modifications
*Failure to provide Lead time
Transfer of Project Managers
Failure to provide correct instructions
Failure to provide Data on time
*Failure to provide Lead time
Failure to notify PM with problems encountered
Failure to provide written instructions
Failure to document modifications required
Failure to notify client regarding modification problems
The Root Cause failure of individual items stem from communication failure:
• Failure to provide adequate lead time for proper planning
• Failure to provide specific written requirements
• Failure to provide client with modifications or problems with modification
• Analyst failure to follow the method
• Analyst failure to provide problems data
• Analyst failure to provide Ammonia data to PM on time
*The lead time failure produced rushed preparation and problems in the late data and communication issues
43


Trending Root Cause Analysis
Increase
Increase
Increase from previous year
Increase
Communication (Client...
Customer Complaint
Environment
Equipment/Machinery
Facilities
Material
Process/Method
Quality System Documentation
Quality System Implementation
Staffing
Training
Decrease from previous year
44

Data Quality Considerations

- Is the quality of the data known?
- Are errors within acceptable limits?
- Are the data usable?
- Were enough data collected?



45



46

The Data User's Guide to Producing Legally Defensible Environmental Data

Christina Hiegel
Trihydro Corporation

Abstract

Key Words: Data Validation, Data Defensibility, Data Quality, Environmental Data, Legally Defensible Data
Frequently, planning for defensible data that may be used in litigation is not the first element that is considered when organizing for a project sampling or data collection event. However, when the data are in error, the defensibility of the data becomes the most important aspect of the project as the opposing council work to discredit the data. Data defensibility, like safety, should not be left to luck.

Devoting significant time to plan and prepare for a complex project can be daunting and when regulatory requirements do not require specific planning documents, determining what is really important can be difficult. In addition, each project, state, and client has different requirements for planning for defensible data. Budget considerations do not always allow for development of Sampling and Analysis Plans (SAPs), Quality Assurance Project Plans (QAPPs), Data Management Plans (DMPs), Standard Operating Procedures (SOPs), and other plans. The following steps will be discussed in determining to help determine what is really important when producing defensible data:

DEFINE DEFENSIBILITY: The first step in planning for legally defensible data is determining how the success of the project will be defined.

PLANNING: Once the goals of the project are defined, the second step is to choose what tools the project will need to be successful.

PREPARATION: When the planning is complete, the preparations of the tools that will be used to measure the defensibility are initiated. The most important aspect of planning will be effectively communicating to the laboratory, managers, and sample crew what is required for the success of the project.

EXECUTE: Execution of the project should result in the samples being collected in accordance with the planning documents; chain-of-custody should be properly maintained; and the laboratory should analyze the data in accordance with the methods.

REVIEW: The review process ensures that the project planning and execution was effective.

MANAGE: Finally, once the data are reviewed and approved or rejected, the data should be maintained with any data validation qualifiers, laboratory data qualifiers, and notes.

Due to the increased awareness of environmental risk factors affecting human and ecological receptors, the quality of the procedures involved in the defining, planning, preparation, execution, review, and management of data is under heavier scrutiny than ever before. Therefore, the goal of this user's guide is to provide guidance in understanding what the critical steps are to producing defensible data will help to improve the quality of the data results and the assist end users in defending their data in court.

Data Defensibility

The Data User's Guide to Producing Legally Defensible Environmental Data

By Christina Hiegel, P.E.
Civil/Environmental Engineer

Introduction

Christina has over 11 years' experience in the environmental industry. She is a registered Civil/Environmental Engineer and manages the chemistry group at Trihydro. Her primary responsibilities include providing technical support for projects in data defensibility, data quality, and leading data quality efforts.



Christina Hiegel

Overview

Define → Plan → Prepare → Execute → Review → Manage

Trihydro

Definition of Defensible Data

Define → Plan → Prepare → Execute → Review → Manage



Trihydro

What is Your Final Goal?

Short Term



Long Term

To reach your "Final Goal", the supporting data will have to be measured in both extent and quality.

Trihydro

Developing Data Quality Objectives

- Step 1: State the Problem
- Step 2: Identify the Decision
- Step 3: Identify Information Inputs
- Step 4: Define the Boundaries of the Study
- Step 5: Develop the Analytical Approach
- Step 6: Specify the Performance or Acceptance Criteria
- Step 7: Develop the Plan for Obtaining Data

USEPA, 2006a. Guidance on Systematic Planning Using the Data Quality Objectives Process (EPA QA/G-4). (EPA/240/B-06/001). Available from http://www.epa.gov/QUALITY/qs-docs/g4-final.pdf

Trihydro

Planning Defensible Data

Define → Plan → Prepare → Execute → Review → Manage



Bad Idea – Spending money without a plan

Trihydro

Choose Your Resources Wisely



Trihydro

Organizational Chart



Trihydro

Contracting with the Laboratory

- Certifications
- Capabilities
- Capacities
- Methodology
- Reporting Limits

STANDARDMETHODS

ASTM INTERNATIONAL

Trihydro

Plans for the Future – Looking Ahead

- QAPP
- DMP
- SAP
- SMP
- DQO



Trihydro

Preparing

Define → Plan → Prepare → Execute → Review → Manage



Trihydro

Laboratory Preparation



Trihydro

Field Preparation



Trihydro

Executing Defensible Data…

Define → Plan → Prepare → Execute → Review → Manage



BAD DATA

Bad Idea – Collecting/Analyzing data that is not usable

Trihydro

…In the Laboratory



- Following Methods
- Following SOPs
- Quality Assurance Samples
- Documentation
- Sample Custody
- Quality Assurance Review

Trihydro

...In the Field



- Collection Methods
- Collection Order
- Decontamination
- Quality Assurance Samples
- Documentation
- Sample Custody
- Packing/Shipping

Trihydro

Quality Assurance Samples

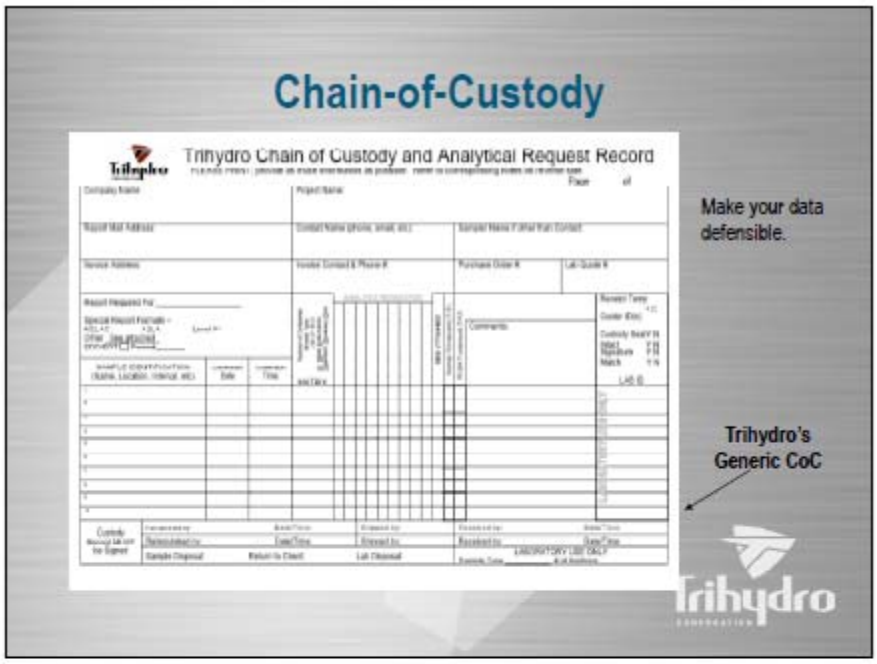
HOW MANY SHOULD I COLLECT??

Check your sample plans!

RULE OF THUMB

QA Sample	How Many	Percentage
Field Duplicate	1 per 10	10%
Field Blank	1 per day	--
Equipment Blank	1 per day	--
Trip Blank	1 per cooler with VOCs	--
MS/MSD	1 per 20	5%

Trihydro


Chain-of-Custody
Trihydro Chain of Custody and Analytical Request Record
Make your data defensible.
Trihydro's Generic CoC
Trihydro


Why Validate Data?
Define
Plan
Prepare
Execute
Review
Manage
Trihydro

Choosing Validation Levels

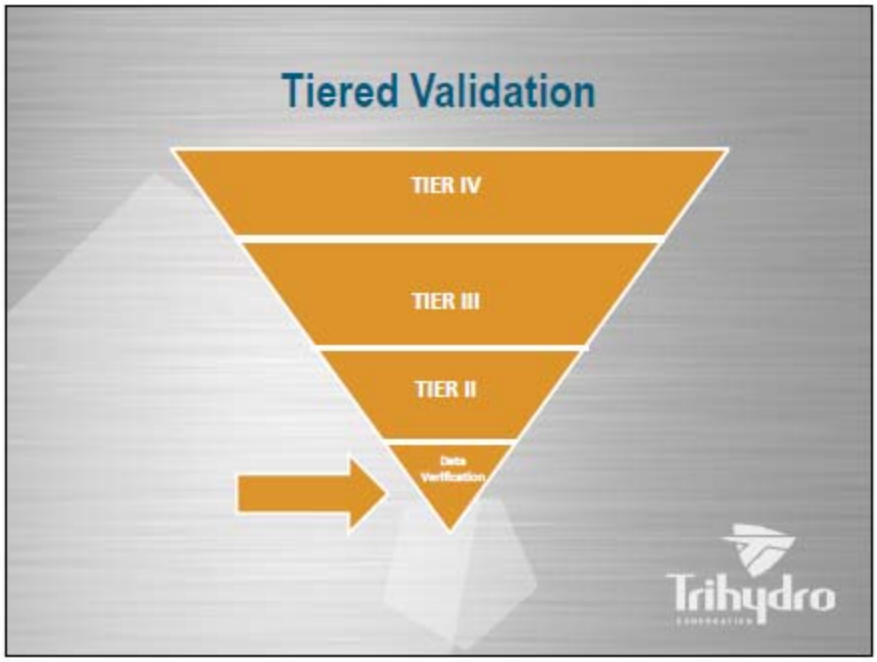


Trihydro

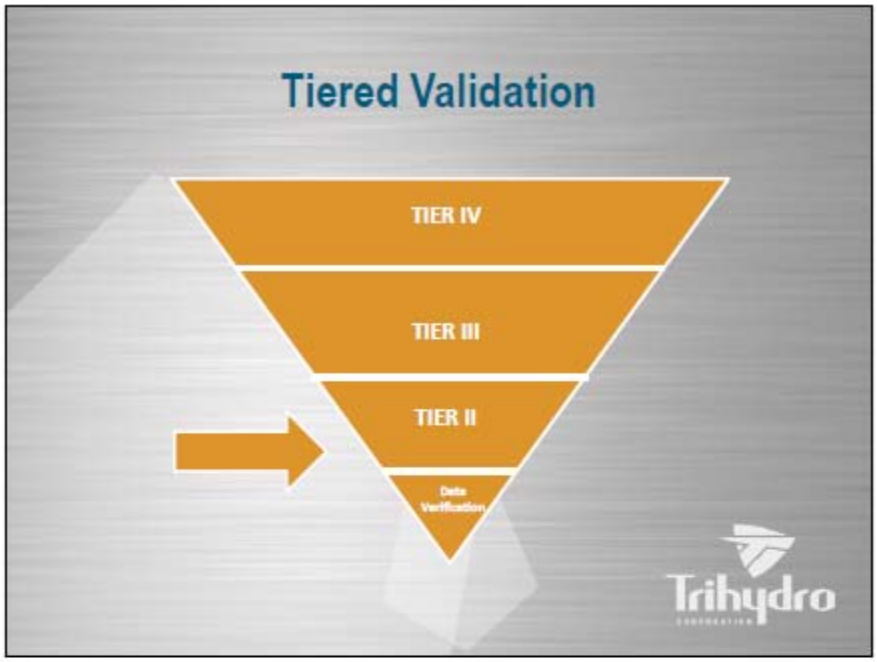
Tiered Validation

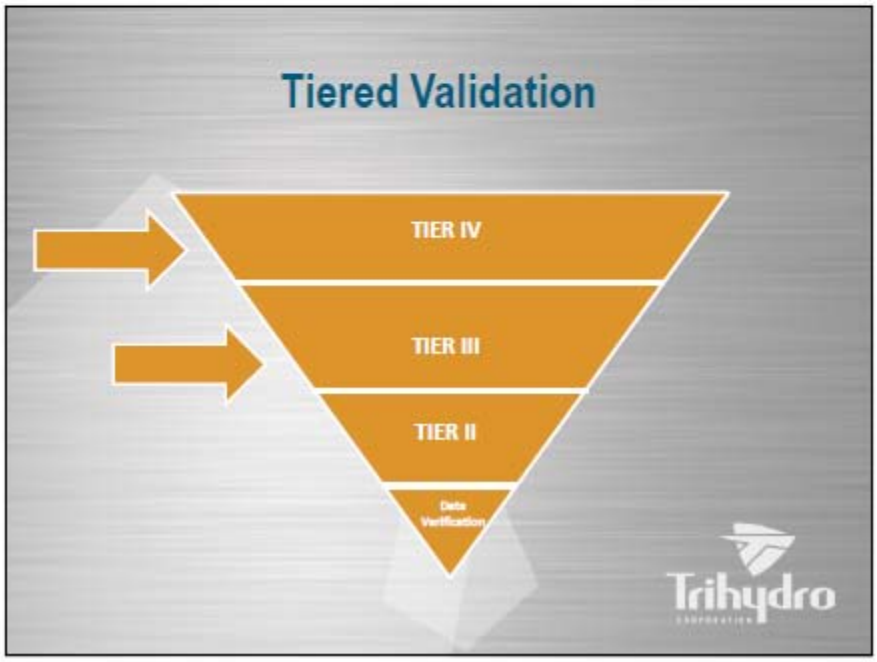


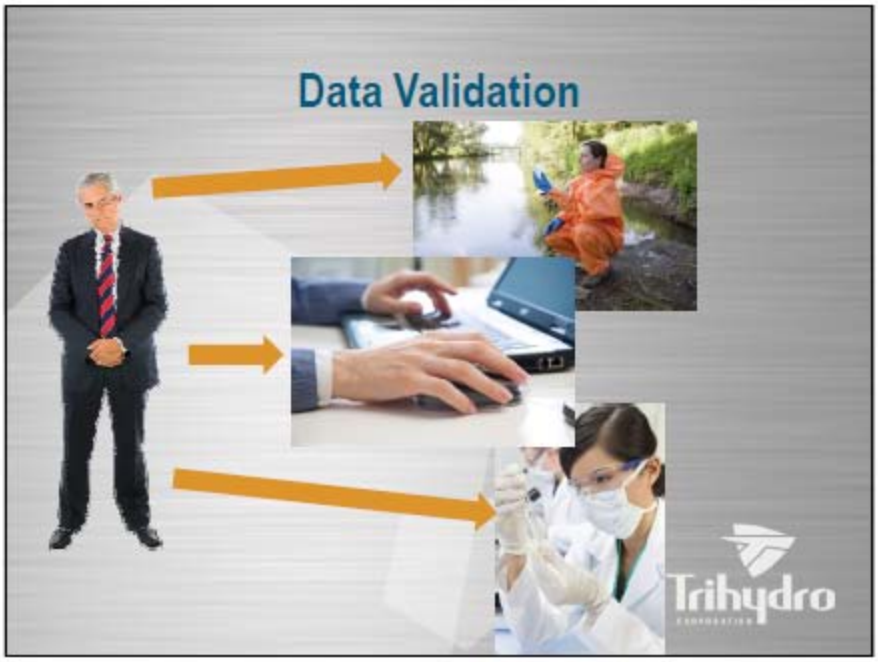
Trihydro

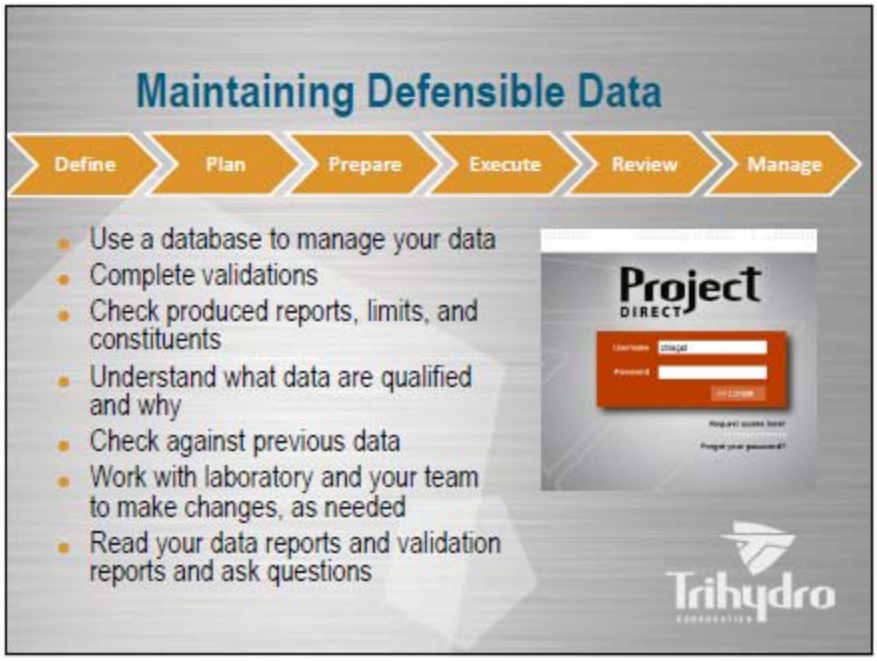

Tiered Validation
TIER IV
TIER III
TIER II
Data Verification
Trihydro


Data Verification
Trihydro


Tiered Validation
TIER IV
TIER III
TIER II
Data Verification
Trihydro


Tiered Validation
TIER IV
TIER III
TIER II
Data Verification
Trihydro


Data Validation
Trihydro


Maintaining Defensible Data
Define
Plan
Prepare
Execute
Review
Manage
Use a database to manage your data
Complete validations
Check produced reports, limits, and constituents
Understand what data are qualified and why
Check against previous data
Work with laboratory and your team to make changes, as needed
Read your data reports and validation reports and ask questions
Project
DIRECT
Trihydro

I Messed Up! What Do I Do?

- Don't panic
- Don't cover-up or hide your mistake



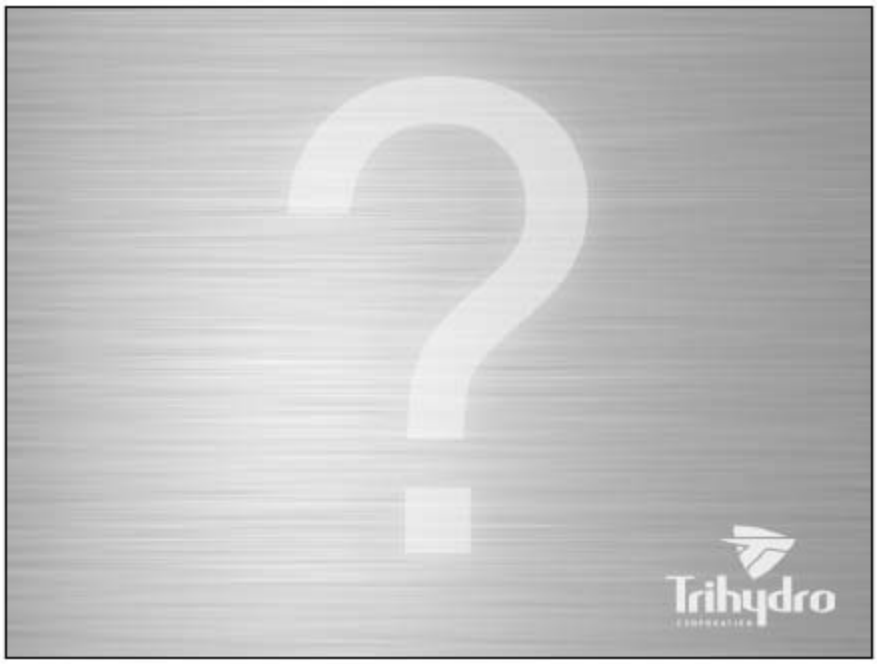
Trihydro

Defensible Data

Define → Plan → Prepare → Execute → Review → Manage



Trihydro


Trihydro

Enabling Data Defensibility and Laboratory Productivity Using a Laboratory Execution System

Kathy Smith
The Narragansett Bay Commission

Abstract

Data defensibility demands that environmental monitoring laboratories provide full traceability of its data from field sample collection, the execution of the analytical procedures to final result reporting.

To ensure labs can meet these increasing requirements, procedure control and data traceability must be available in a cost effective manner. Recent advances in laboratory informatics technology including the Laboratory Execution System or LES, have made this not only feasible, but flexible enough not to compromise a lab's operational requirements.

See how one laboratory is implementing a comprehensive Laboratory Execution System based informatics system that provides a comprehensive solution from field sample collection to final result reporting.



Enabling Data Defensibility and Laboratory Productivity Using a Laboratory Execution System"

Narragansett Bay Commission

Providence, RI

Challenges in the QA/QC Space

Public and Private labs need to reduce costs without compromising quality

- Our customers need solutions that let QA/QC maintain their high attention to detail, but that shorten the time and cost required to qualify an area or material for use, and communicate that information quickly to the right people
- Solutions that can deliver metrics on operational effectiveness and drive the reduction/elimination of non-value added tasks are critical to meeting their business objectives
- A key factor includes **traceability and defensibility**, quickly and easily finding your results, raw data, audit trail, approval process, etc.

With our New LES – Laboratory Execution System

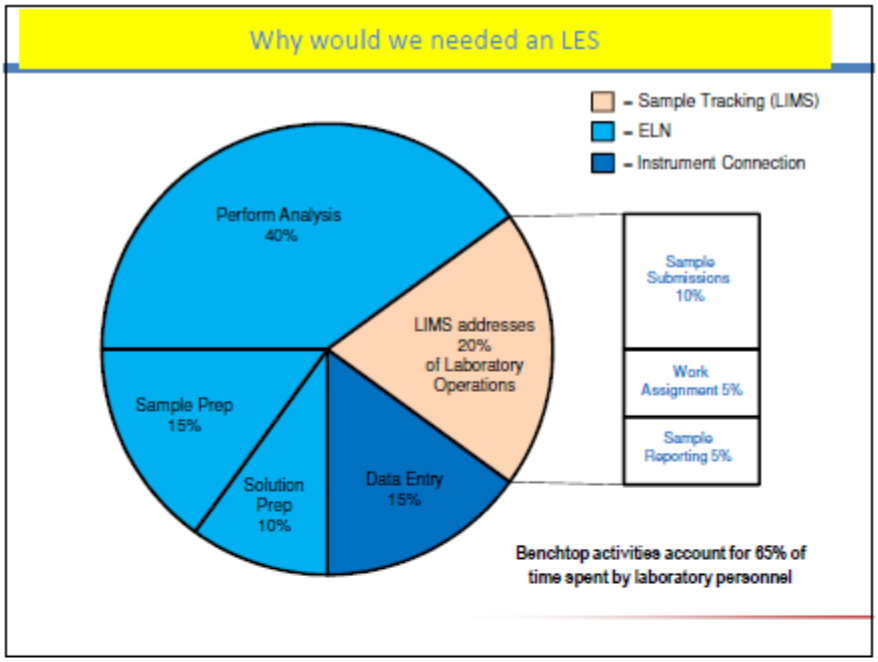
- Automatically
  - Enforce all SOPs and Methods
  - Connect field samplers directly to the lab
  - Verify instrument calibration
  - Check reagent expiry and reorder
  - Verify Analyst Certifications
  - Store worksheets electronically
  - Check Specs before committing to LIMS
  - e-Signatures on all transactions if desired
- Enable the lab to become paperless
- Facilitate TNI/ISO 17025 Certification

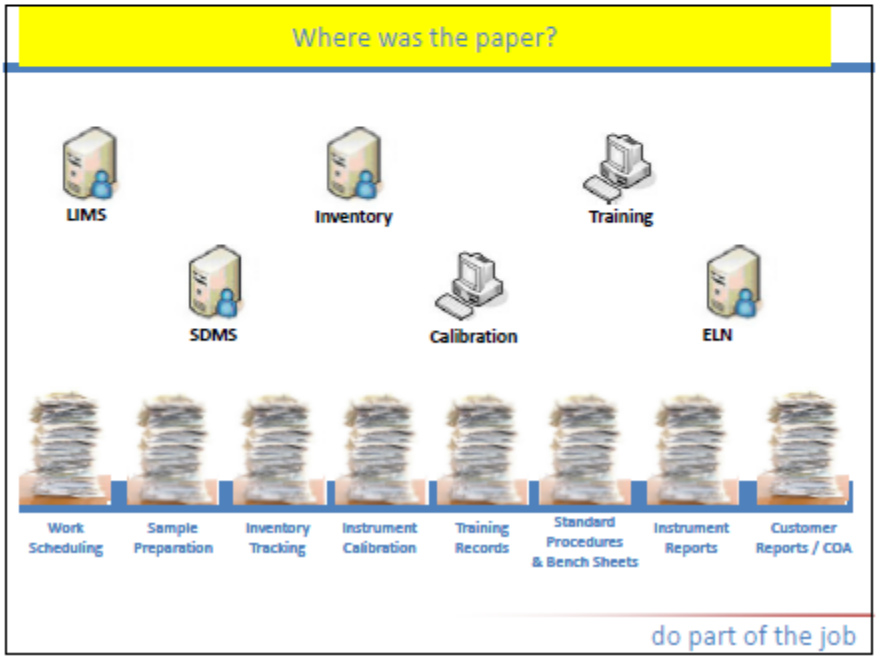
Narragansett Bay Commission

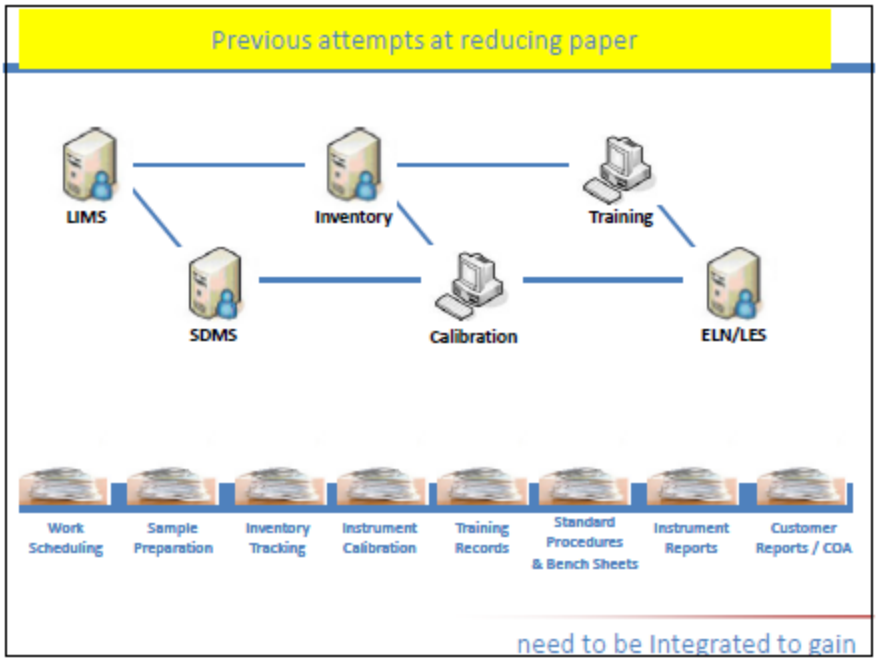
NBC addressed these challenges and the solution integrates..

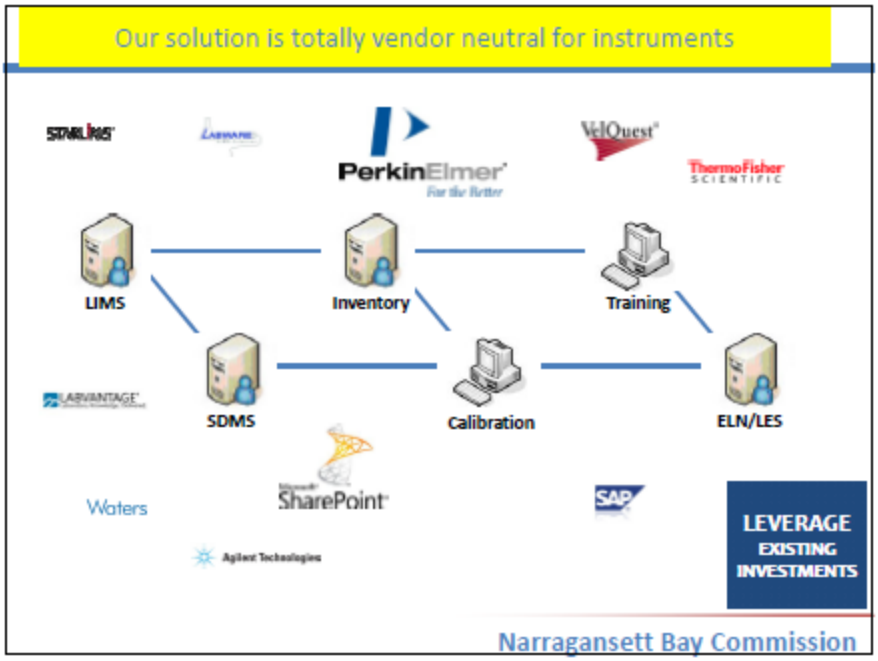
- Electronic Worksheets to replace all paper in the laboratory
- iPads to collect field sampling information and metadata
- Touch screen monitors for sample receipting
- Automated bi-direction instrument interfacing for all lab equipment
- SharePoint as the document management system and to capture all lab worksheets
- HachWIMS software to integrate lab and plant data, and generate reports
- Integration of 3 wind turbines provide around half of the site's power needs – also interfaced to the WIMDS
- Publishing data to our customers through a web portal

Narragansett Bay Commission


Why would we needed an LES
– Sample Tracking (LIMS)
– ELN
– Instrument Connection
Perform Analysis
40%
LIMS addresses
20%
of Laboratory
Operations
Sample Prep
15%
Solution
Prep
10%
Data Entry
15%
Sample
Submissions
10%
Work
Assignment 5%
Sample
Reporting 5%
Benchtop activities account for 65% of
time spent by laboratory personnel


Where was the paper?
LIMS
Inventory
Training
SDMS
Calibration
ELN
Work
Scheduling
Sample
Preparation
Inventory
Tracking
Instrument
Calibration
Training
Records
Standard
Procedures
& Bench Sheets
Instrument
Reports
Customer
Reports / COA
do part of the job


Previous attempts at reducing paper
LIMS
Inventory
Training
SDMS
Calibration
ELN/LES
Work Scheduling
Sample Preparation
Inventory Tracking
Instrument Calibration
Training Records
Standard Procedures & Bench Sheets
Instrument Reports
Customer Reports / COA
need to be Integrated to gain


Our solution is totally vendor neutral for instruments
PerkinElmer
VelQuest
ThermoFisher SCIENTIFIC
LIMS
Inventory
Training
SDMS
Calibration
ELN/LES
LABVANTAGE
Waters
SharePoint
SAP
Agilent Technologies
LEVERAGE EXISTING INVESTMENTS
Narragansett Bay Commission

How does paper impact our lab?

- Paper based processes introduce risk areas, bottlenecks and costs:
- Risks
  - Transcription errors (3%-5%)
  - Procedural errors - Deviation from SOP
  - Calculation errors – miscalculations (ex. 1+1=3)
  - Transcription errors – Illegibility (ex. Was that 3 or 8?)
  - Omissions of data/information
  - Loss / destruction of paper / Illegibility
- Bottlenecks
  - Data transcription, double and triple transcription of information that already exists
  - Manual calculations
  - Lack of real-time feedback, delays in decisions and actions
- Costs
  - Hard Costs – paper, notebooks, storage, consumables
  - Soft Costs – human errors, investigations, corrective actions



Paper forms are easy to use, but disconnected and impede data flow



LIMS/ERP/SAP/ Other Informatics System

Example Form





Record Retention
$1600 per month/month



Analyst
Qualified ?
Certified ?
Training ?
Present?



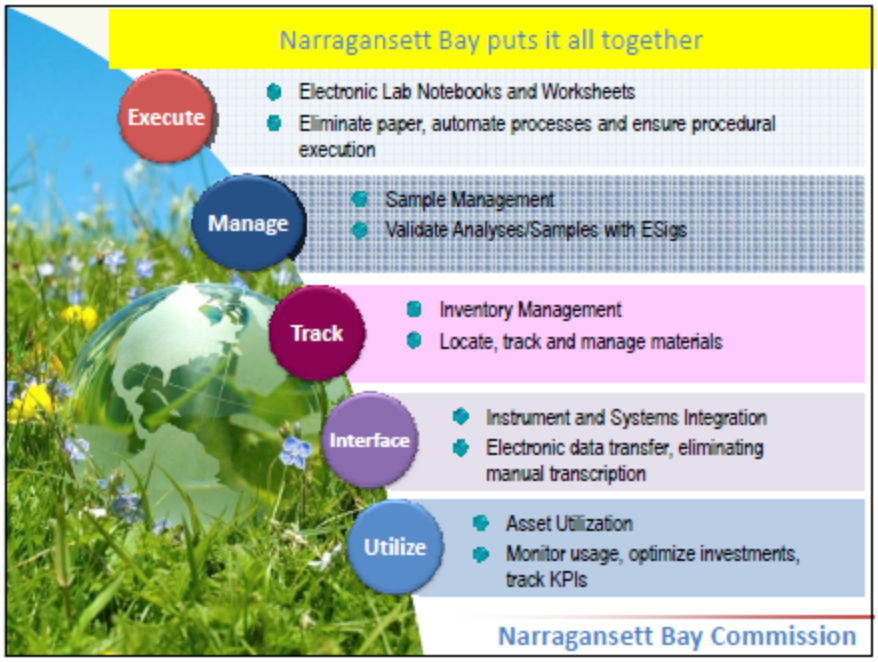
Inventory
Expired ?
Reorder?

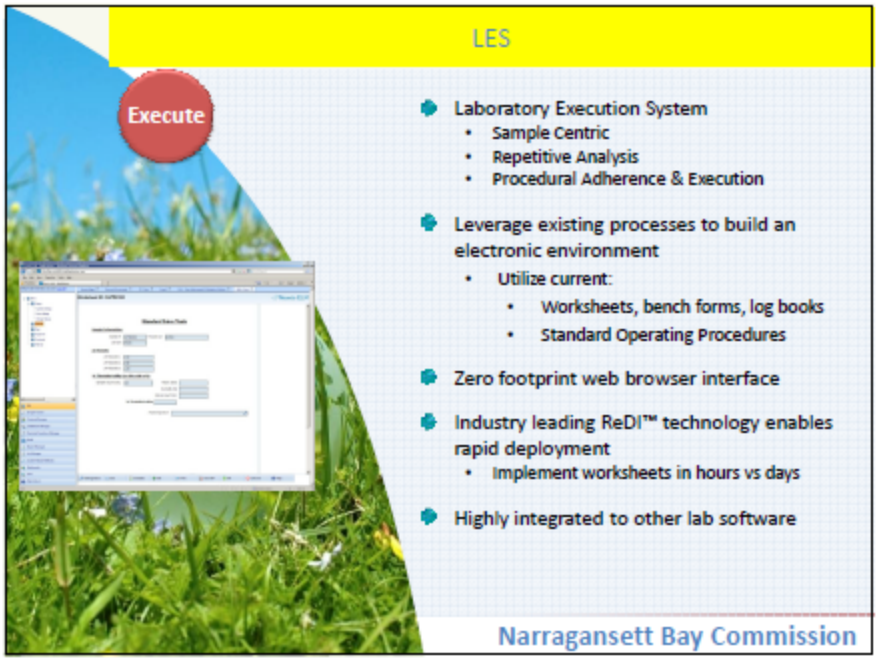


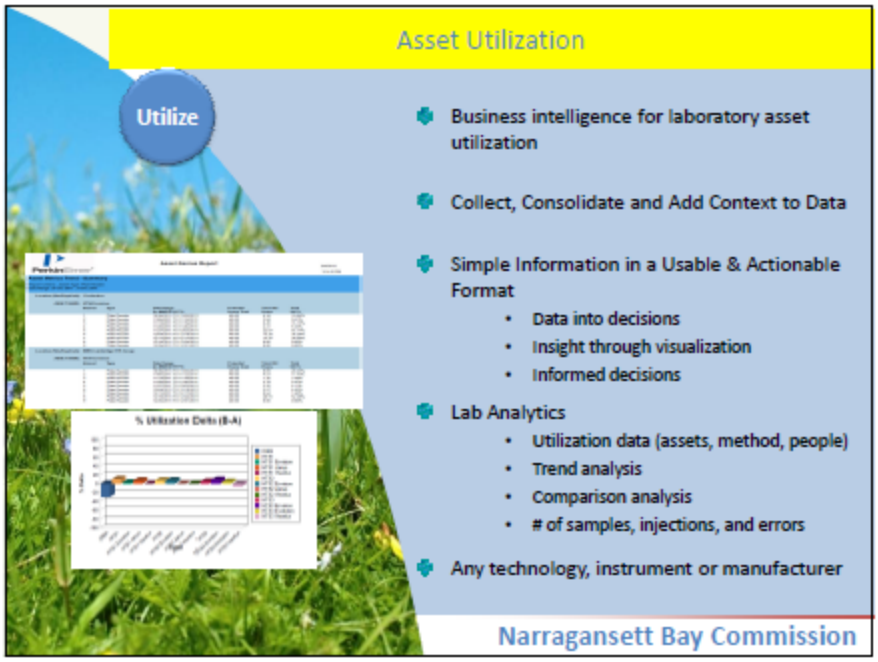
Instrument
Calibrated ?

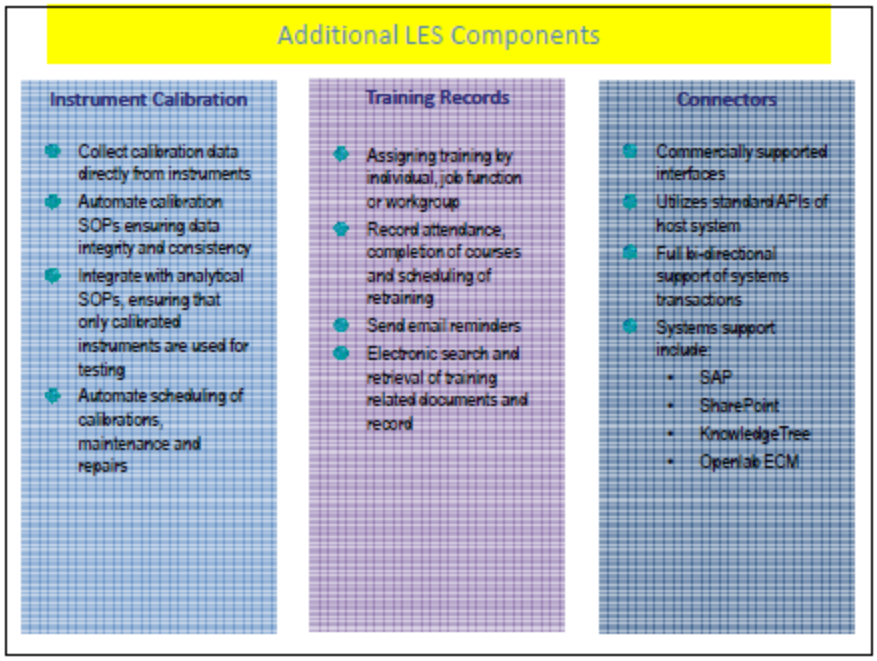


Instrument Data


Narragansett Bay puts it all together
Execute
Electronic Lab Notebooks and Worksheets
Eliminate paper, automate processes and ensure procedural execution
Manage
Sample Management
Validate Analyses/Samples with ESigs
Track
Inventory Management
Locate, track and manage materials
Interface
Instrument and Systems Integration
Electronic data transfer, eliminating manual transcription
Utilize
Asset Utilization
Monitor usage, optimize investments, track KPIs
Narragansett Bay Commission


LES
Execute
Laboratory Execution System
Sample Centric
Repetitive Analysis
Procedural Adherence & Execution
Leverage existing processes to build an electronic environment
Utilize current:
Worksheets, bench forms, log books
Standard Operating Procedures
Zero footprint web browser interface
Industry leading ReDI™ technology enables rapid deployment
Implement worksheets in hours vs days
Highly integrated to other lab software
Narragansett Bay Commission


Asset Utilization
Utilize
Business intelligence for laboratory asset utilization
Collect, Consolidate and Add Context to Data
Simple Information in a Usable & Actionable Format
Data into decisions
Insight through visualization
Informed decisions
Lab Analytics
Utilization data (assets, method, people)
Trend analysis
Comparison analysis
# of samples, injections, and errors
Any technology, instrument or manufacturer
Narragansett Bay Commission

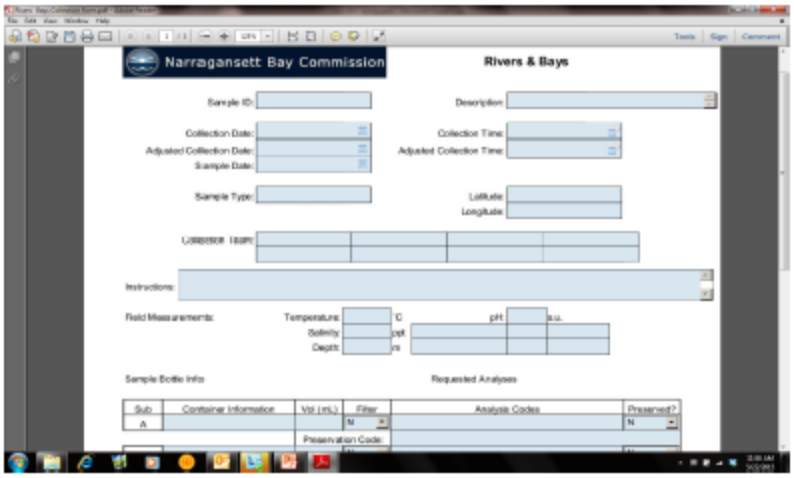

Additional LES Components
Instrument Calibration
Collect calibration data directly from instruments
Automate calibration SOPs ensuring data integrity and consistency
Integrate with analytical SOPs, ensuring that only calibrated instruments are used for testing
Automate scheduling of calibrations, maintenance and repairs
Training Records
Assigning training by individual, job function or workgroup
Record attendance, completion of courses and scheduling of retraining
Send email reminders
Electronic search and retrieval of training related documents and record
Connectors
Commercially supported interfaces
Utilizes standard APIs of host system
Full bi-directional support of systems transactions
Systems support include:
SAP
SharePoint
KnowledgeTree
OpenLab ECM

Field Inspectors

- "The purpose of The NELAC Institute (TNI) National Environmental Field Activities Program (NEFAP) is to establish and implement an accreditation program for field sampling and measurement organizations (FSMOs)."

Narragansett Bay Commission

Sample Collection on iPads



How did we convert our paper forms to electronic?



Automated Worksheet = PDF + Automation / Integration Controls

Current paper forms become

Procedures-based ELN dramatically enhances lab productivity

Problems with paper

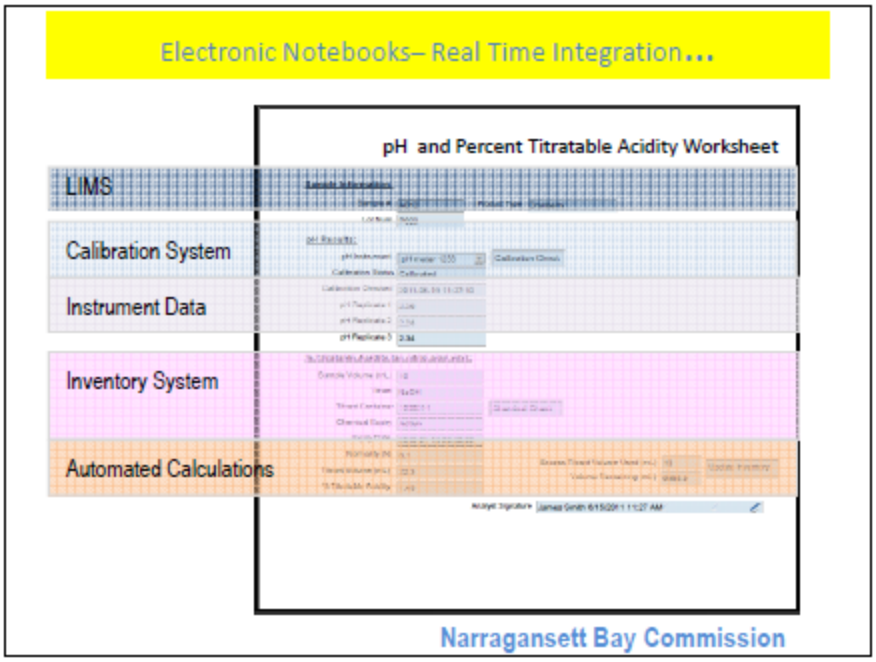


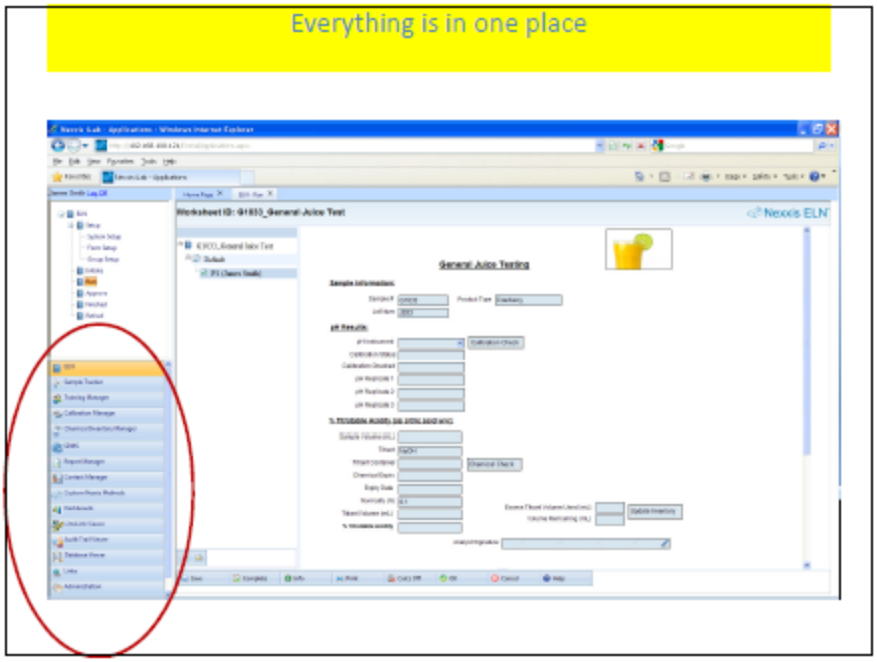
- Illegible handwriting/transcription errors
- Information recorded where it should not be
- Image printed/pasted onto page
- Ultimately no control

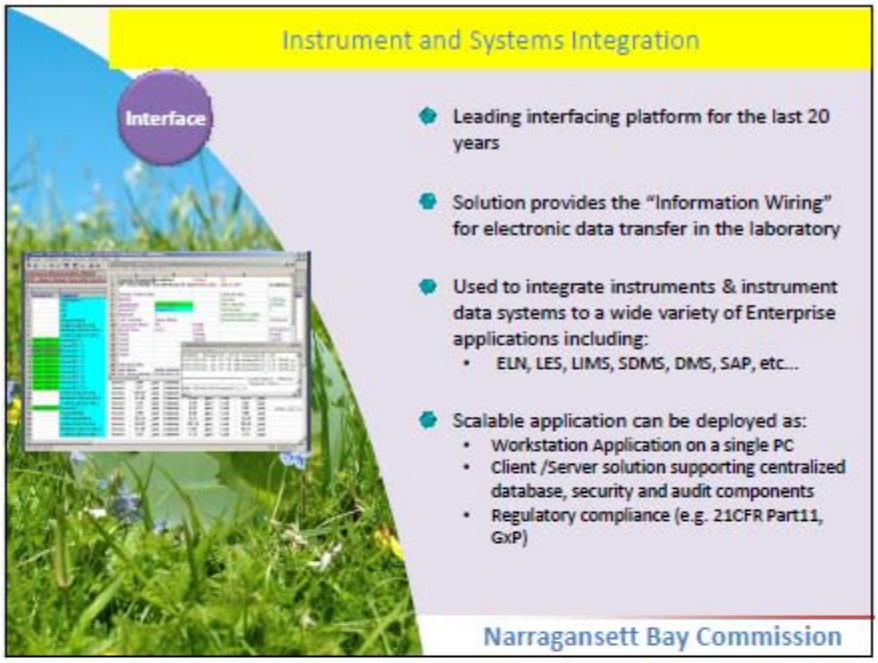
Benefits of Automation

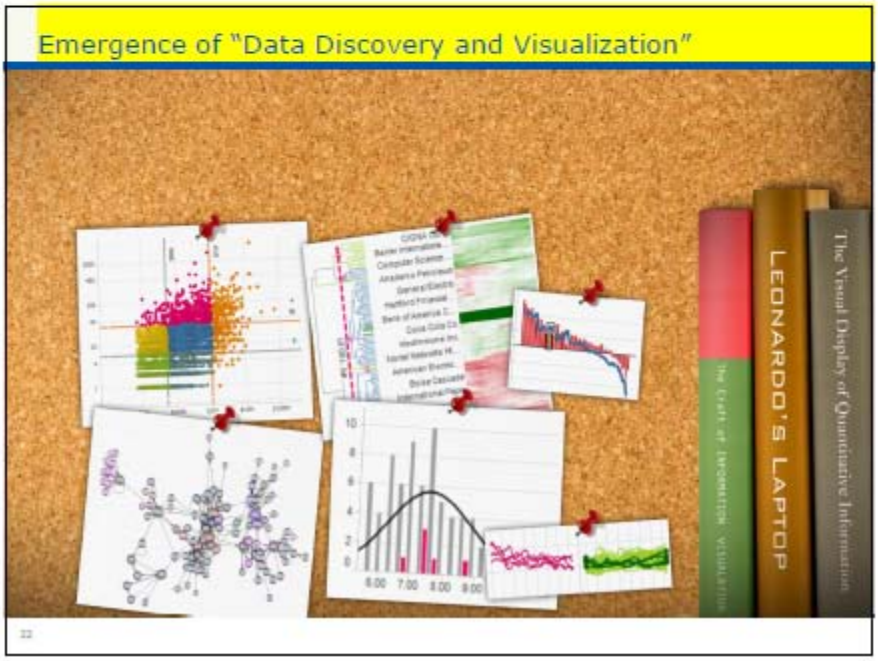


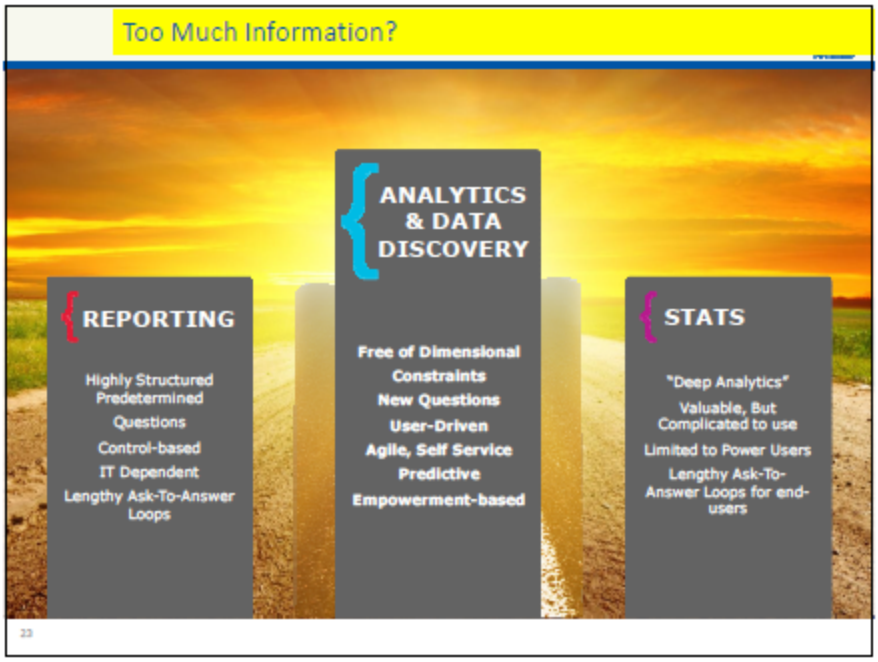
- Legible text
- All information electronically traced
- Selection from pre-defined lists
- Electronic signature
- Insert image electronically
- Controlled execution –step by step

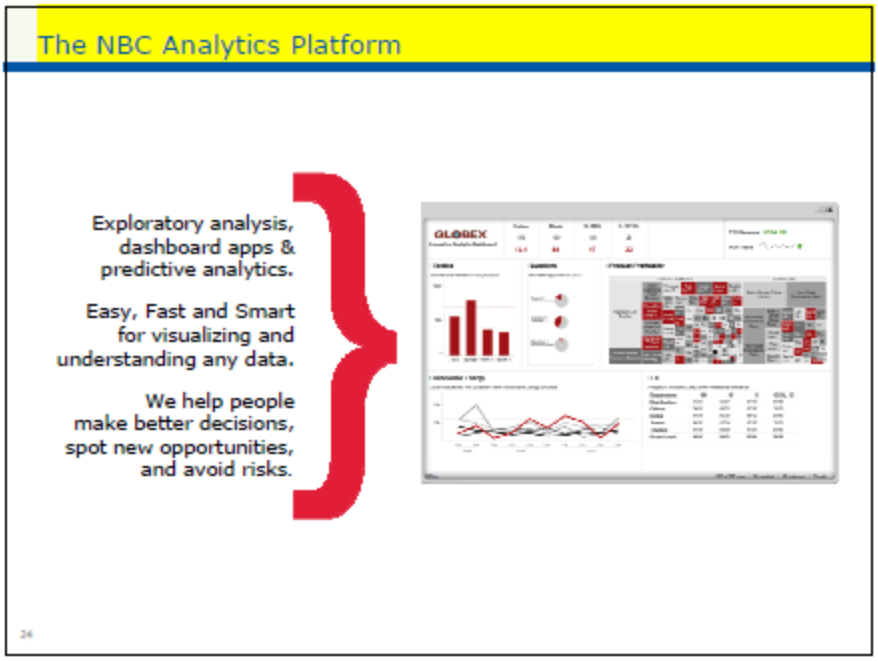

Electronic Notebooks– Real Time Integration…
pH and Percent Titratable Acidity Worksheet
LIMS
Calibration System
Instrument Data
Inventory System
Automated Calculations
Narragansett Bay Commission

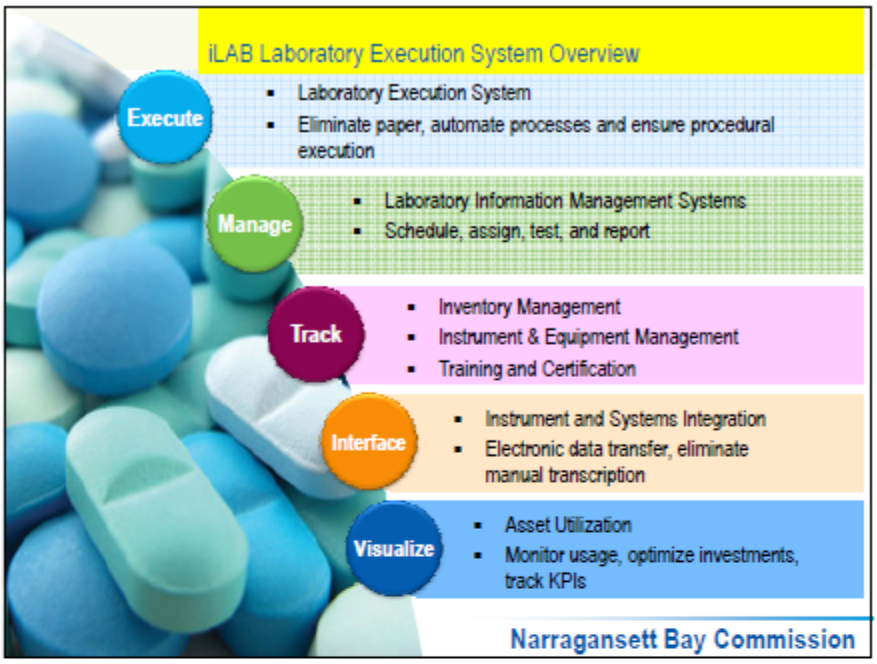

Everything is in one place
Nexus ELN
General Juice Testing

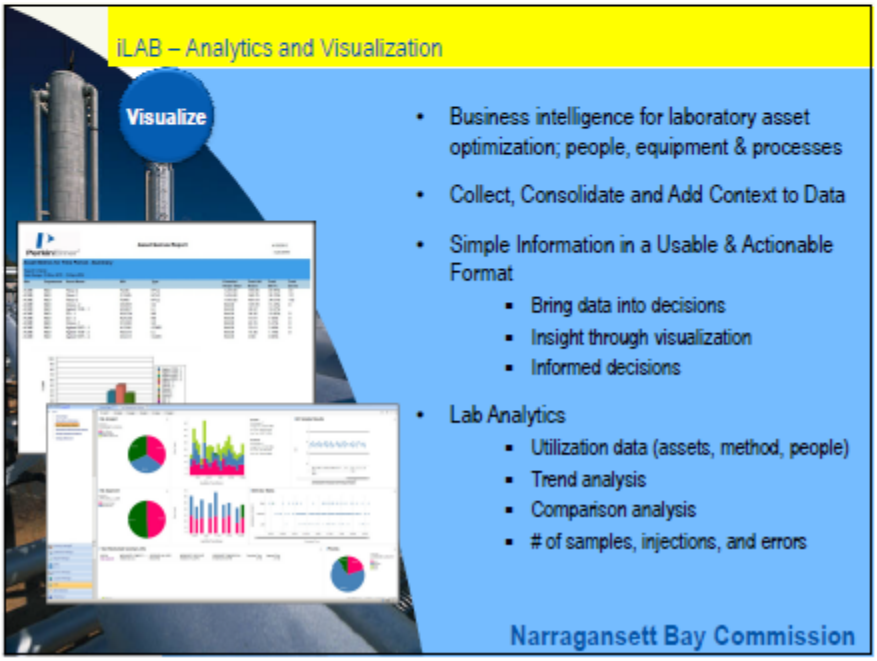

Instrument and Systems Integration
Interface
Leading interfacing platform for the last 20 years
Solution provides the "Information Wiring" for electronic data transfer in the laboratory
Used to integrate instruments & instrument data systems to a wide variety of Enterprise applications including:
ELN, LES, LIMS, SDMS, DMS, SAP, etc...
Scalable application can be deployed as:
Workstation Application on a single PC
Client /Server solution supporting centralized database, security and audit components
Regulatory compliance (e.g. 21CFR Part11, GxP)
Narragansett Bay Commission

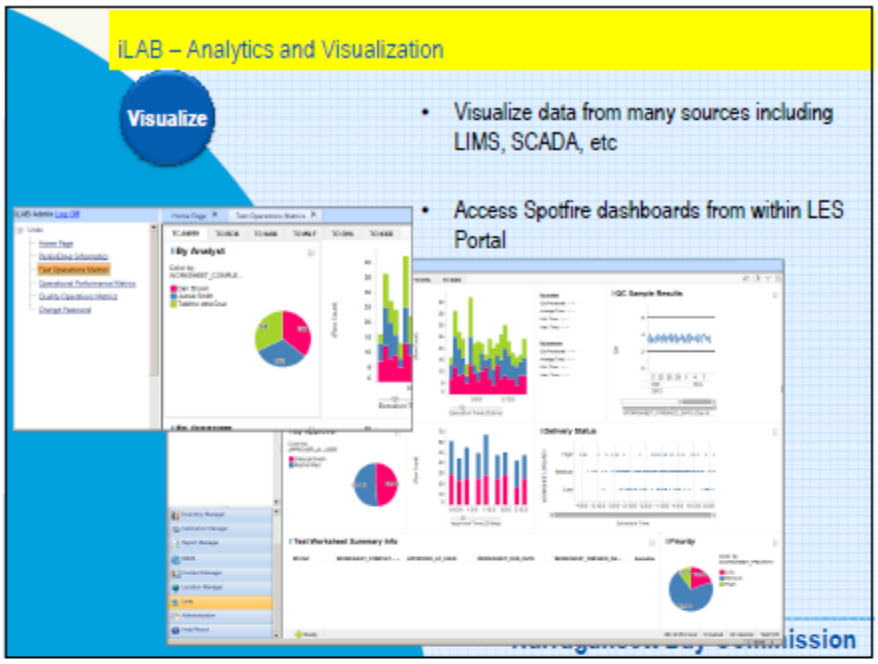

Emergence of "Data Discovery and Visualization"
LEONARDO'S LAPTOP
The Visual Display of Quantitative Information

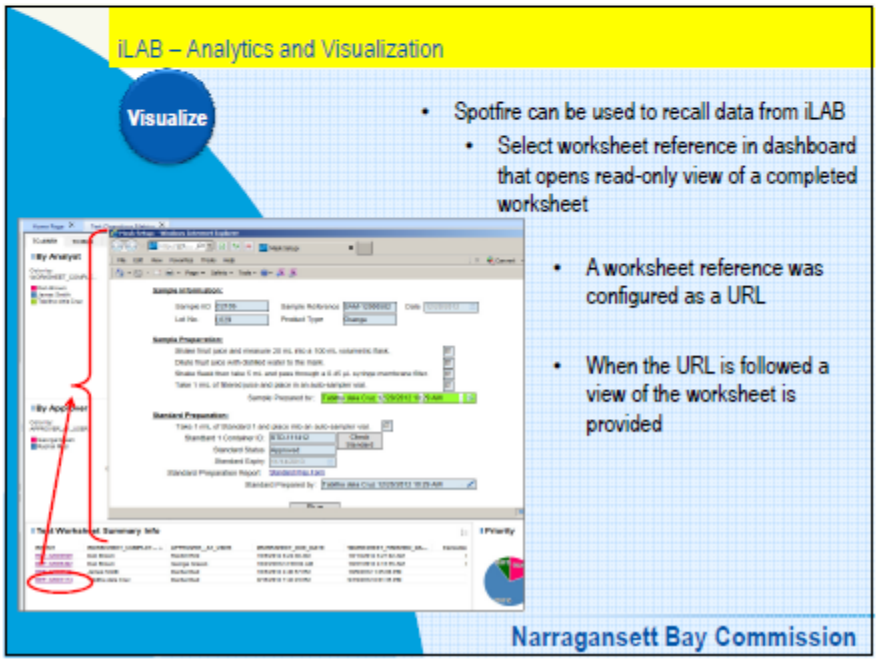

Too Much Information?
REPORTING
Highly Structured Predetermined Questions
Control-based
IT Dependent
Lengthy Ask-To-Answer Loops
ANALYTICS & DATA DISCOVERY
Free of Dimensional Constraints
New Questions
User-Driven
Agile, Self Service
Predictive
Empowerment-based
STATS
"Deep Analytics"
Valuable, But Complicated to use
Limited to Power Users
Lengthy Ask-To-Answer Loops for end-users
23


The NBC Analytics Platform
Exploratory analysis, dashboard apps & predictive analytics.
Easy, Fast and Smart for visualizing and understanding any data.
We help people make better decisions, spot new opportunities, and avoid risks.
GLOBEX
24


iLAB Laboratory Execution System Overview
Execute
Laboratory Execution System
Eliminate paper, automate processes and ensure procedural execution
Manage
Laboratory Information Management Systems
Schedule, assign, test, and report
Track
Inventory Management
Instrument & Equipment Management
Training and Certification
Interface
Instrument and Systems Integration
Electronic data transfer, eliminate manual transcription
Visualize
Asset Utilization
Monitor usage, optimize investments, track KPIs
Narragansett Bay Commission


iLAB – Analytics and Visualization
Visualize
Business intelligence for laboratory asset optimization; people, equipment & processes
Collect, Consolidate and Add Context to Data
Simple Information in a Usable & Actionable Format
Bring data into decisions
Insight through visualization
Informed decisions
Lab Analytics
Utilization data (assets, method, people)
Trend analysis
Comparison analysis
# of samples, injections, and errors
Narragansett Bay Commission


iLAB – Analytics and Visualization
Visualize
• Visualize data from many sources including LIMS, SCADA, etc
• Access Spotfire dashboards from within LES Portal


iLAB – Analytics and Visualization
Visualize
• Spotfire can be used to recall data from iLAB
• Select worksheet reference in dashboard that opens read-only view of a completed worksheet
• A worksheet reference was configured as a URL
• When the URL is followed a view of the worksheet is provided
Narragansett Bay Commission

iLAB – Analytics and Visualization

Visualize

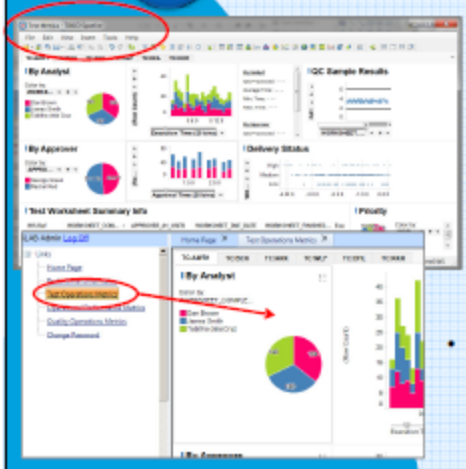


- All data is cross-linked to help the user analyze the data more effectively
  - Facilitates rapid data drill down
- Typical scenario: Find reason for testing delays in laboratory
  - Select one an area in one chart and highlight those selections in others…
  - Reduce data in table to the selected items only..
- Initial finding; Analysts completing work in timely fashion but approvers appear to be the cause of the delays.
  - Is it one approver?
  - Why the delay? Procedural issue?

Narragansett Bay Commission

iLAB – Analytics and Visualization: Setup

Visualize

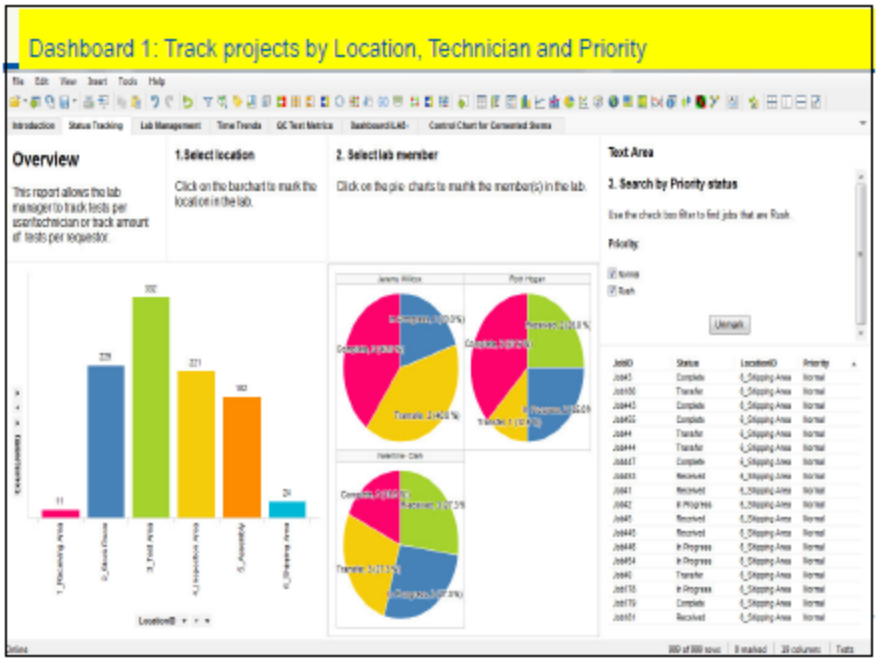


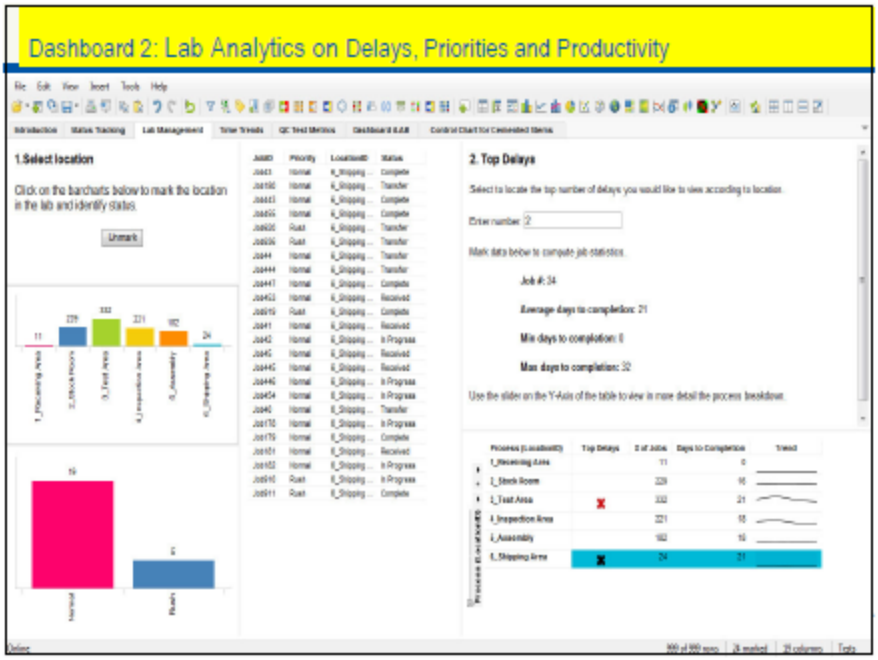
- New dashboards configured as needed
  - Dashboard can "mash up" data from external sources in addition to iLAB
  - Dashboard can be configured to provide "guided" analytics for infrequent users
  - Dashboards can be used outside of iLAB environment when appropriate

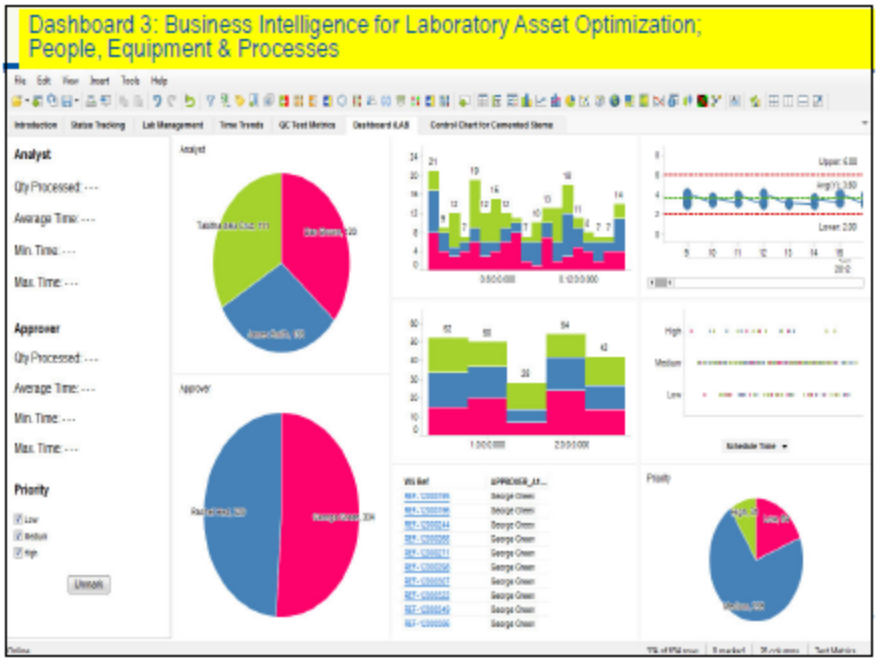
Dashboard is stored in Webplayer and accessible through URL

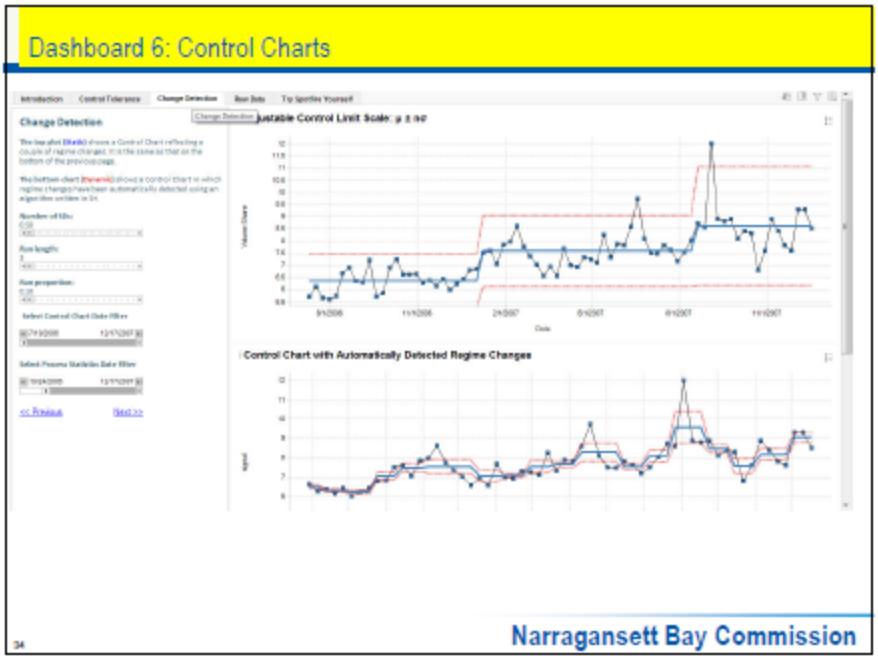
- iLAB Portal is configured to load new dashboard

Narragansett Bay Commission


Dashboard 1: Track projects by Location, Technician and Priority
Overview
This report allows the lab manager to track tests per user/technician or track amount of tests per requestor.
1.Select location
Click on the barchart to mark the location in the lab.
2. Select lab member
Click on the pie charts to mark the member(s) in the lab.
Text Area
2. Search by Priority status
Priority:
Unmark

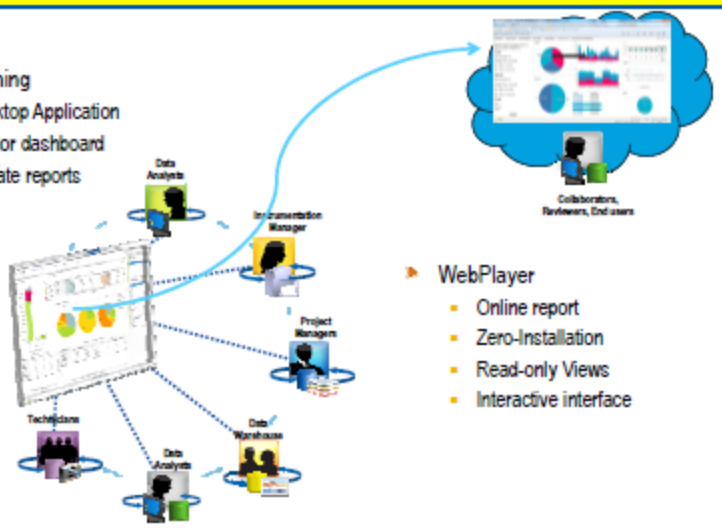

Dashboard 2: Lab Analytics on Delays, Priorities and Productivity
1.Select location
Click on the barcharts below to mark the location in the lab and identify status
Unmark
2. Top Delays
Select to locate the top number of delays you would like to view according to location
Enter number: 2
Mark data below to compute job statistics
Job #: 34
Average days to completion: 21
Min days to completion: 0
Max days to completion: 32
Use the slider on the Y-Axis of the table to view in more detail the process breakdown


Dashboard 3: Business Intelligence for Laboratory Asset Optimization; People, Equipment & Processes
Analyst
Qty Processed: ---
Average Time: ---
Min. Time: ---
Max. Time: ---
Approver
Qty Processed: ---
Average Time: ---
Min. Time: ---
Max. Time: ---
Priority
Low
Medium
High
Unmark


Dashboard 6: Control Charts
Change Detection
Control Chart with Automatically Detected Regime Changes
<< Previous
Next >>
Narragansett Bay Commission

Easy Collaboration and Report Generation All-in-One Solution

- Data Mining
  - Desktop Application
  - Author dashboard
  - Update reports



- WebPlayer
  - Online report
  - Zero-Installation
  - Read-only Views
  - Interactive interface

35

Narragansett Bay Conclusions

- LES integrates people, procedures and lab systems to provide real time workflow control at the bench level and assure defensible data
  - Maintain high attention to detail while reducing the time and cost required to qualify an area or material for use
  - Quickly communicate critical information to support business decisions
  - Deliver metrics on operational effectiveness and drive the reduction/elimination of non-value added tasks
  - Reduce the time and effort needed to capture, document, and manage data



36

Narragansett Bay Commission

The Other Half of Your Lab Result

Bryan Vining
SGS Analytical Perspectives

Abstract

Consumers of laboratory data – facilities being tested, regulators, risk assessors, and others – often are quite content to receive a single, simple number as the result of the lab's efforts. Based on this number, one or more individuals will make decisions about human health. Perhaps a facility will be forced to stop operations. Conversely, an area previously deemed unsafe for human habitation may be made into a playground. These decisions frequently occur based on a number that is missing its complete context – the measurement uncertainty. Without this key attribute, the data is incomplete and potentially misleading – especially in cases of significant error.

Many publications exist regarding the estimation of measurement uncertainty, advocating many different means for determining it. Most of these methods proceed from backwards-looking approaches. For example, one may perform a retrospective analysis of proficiency testing data to obtain a static uncertainty interval to apply to future measurements. Not only must one be careful to use appropriate statistics in such cases, but these methods inherently fail to inform the data users about the impact of any changes in the analytical system from the state in which such data were acquired to the state in which the data for their samples. For instance, if an instrument exhibits unusually poor response, the uncertainty may change. We will demonstrate how a system that estimates uncertainty for each measurement – that is, where and when it is needed – works. We will briefly delve into applications for such a system and the value it brings to data users. Most importantly, we will show that uncertainty is not a constant and approaches that respect this fact are needed.

"The Other Half of your Measurement"

06 AUG 2013

Bryan Vining, Ph.D.
SGS-Analytical Perspectives



This is Emily. She's on her way to oversee an environmental sampling event.

Samples are collected and sent to a lab.





The lab analyzes the sample using a published, trusted method…

38.5 PPM

The lab sends Emily a number beneath the regulatory limit.
All is well!!

It's a story with a happy ending…

Or is it?

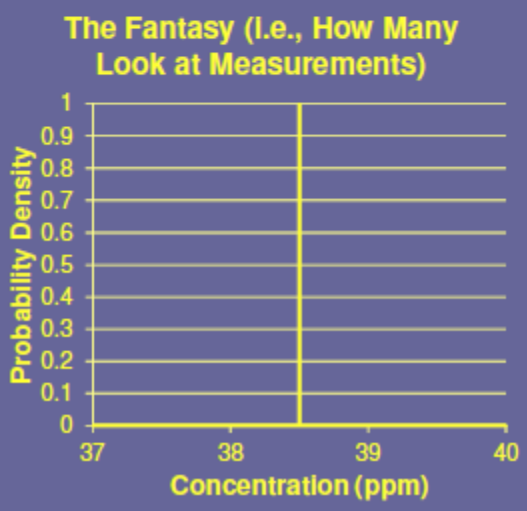
It's also a fairy tale, full of things as imaginary as elves and dragons

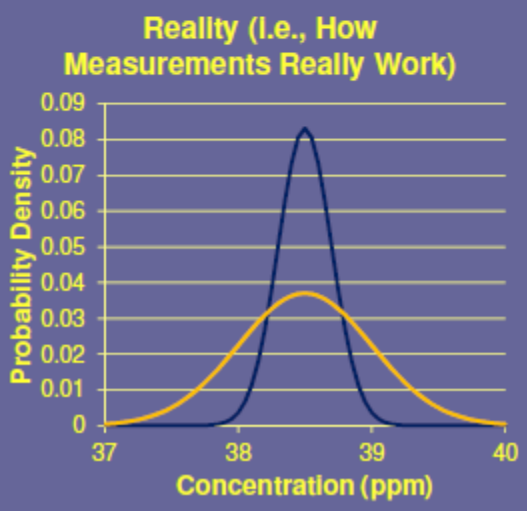




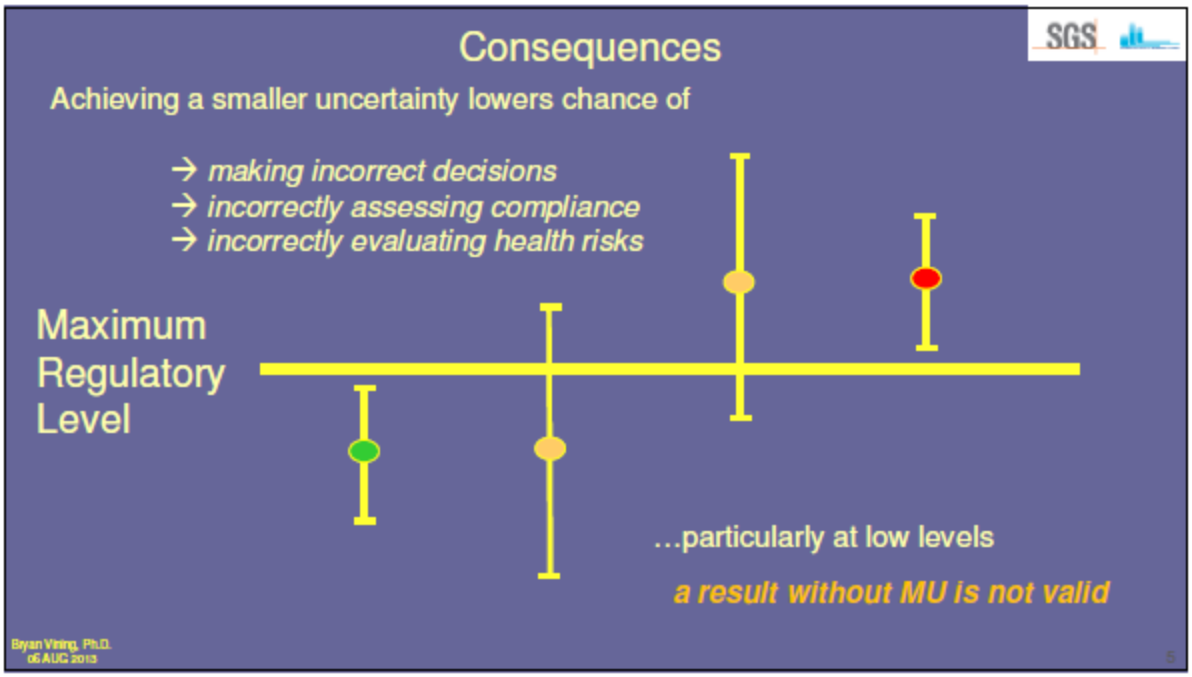
Bryan Vining, Ph.D.
06 AUG 2013

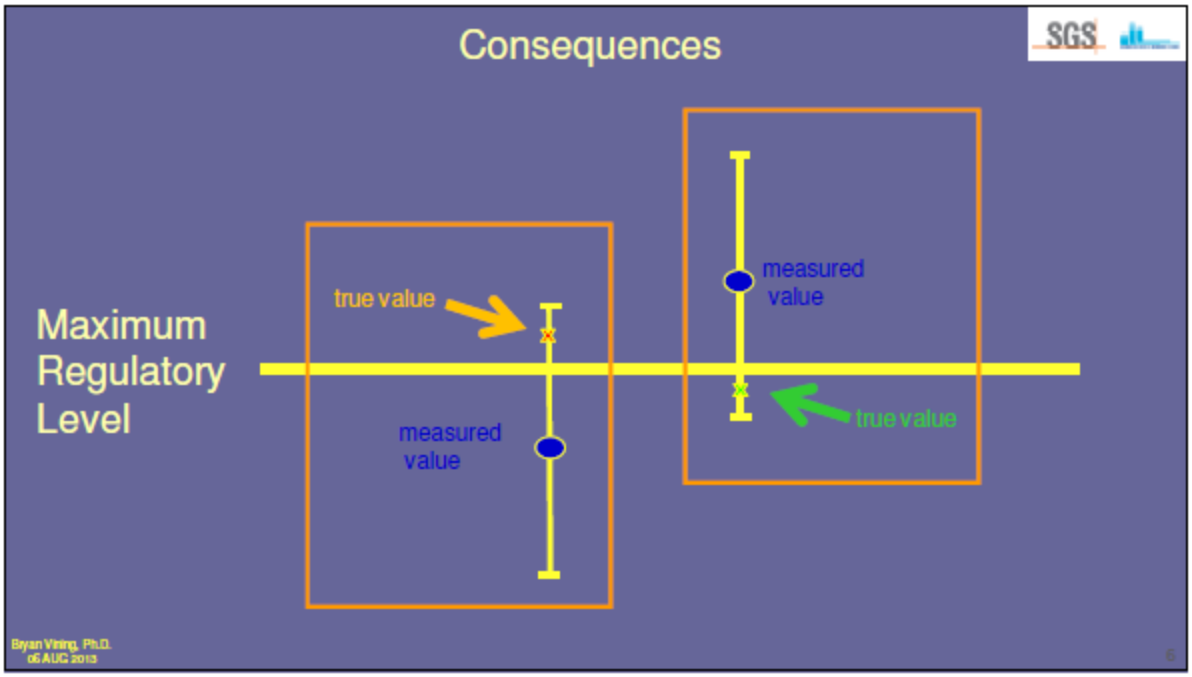
38.5 PPM





Bryan Vining, Ph.D.
06 AUG 2013


Consequences
SGS
Achieving a smaller uncertainty lowers chance of
→ making incorrect decisions
→ incorrectly assessing compliance
→ incorrectly evaluating health risks
Maximum Regulatory Level
…particularly at low levels
a result without MU is not valid
Bryan Vining, Ph.D.
06 AUG 2013
5


Consequences
SGS
Maximum Regulatory Level
true value
measured value
measured value
true value
Bryan Vining, Ph.D.
06 AUG 2013
6

Consequences



1. US Regulations might not consider the **error bar**
2. US Regulatory Limits might have the **uncertainty** built in
3. Users' **decisions** should incorporate measurement of uncertainty

→ Importance of DQO (acceptable sample data *vs.* compliant sample)
→ Enhance clarity on actual performance

Bryan Vining, Ph.D.
06 AUG 2013

How to estimate combined standard uncertainty (u_c)

$$u_c = \sqrt{\sum_{i=1}^{n} u_i^2}$$

Agreement begins and ends here. Multiple approaches to estimating individual u_i exist.
Most notable approaches are:

- "Top Down"
- "Bottom Up"
- "Hybrid"

Bryan Vining, Ph.D.
06 AUG 2013

SGS

"Top Down" estimate of combined standard uncertainty (u_c)

Uses multiple measurements of CRMs to determine bias and precision.

$$u_c = \sqrt{u_b^2 + u_p^2}$$

u_b = Uncertainty due to bias
u_p = Uncertainty due to precision

Problems:
- Significance test of bias often statistically incorrect
- Bias handled in various, sometimes improper ways

Bryan Vining, Ph.D.
06 AUG 2013

9

SGS

"Bottom Up" estimate of combined standard uncertainty (u_c)

Estimates uncertainty of individual contributions and "builds up" an uncertainty estimate

$$u_c = \sqrt{u_1^2 + u_2^2 + u_3^2 + \cdots}$$

u_1 = Uncertainty due to factor 1
u_2 = Uncertainty due to factor 2
u_3 = Uncertainty due to factor 3
Factors could include, e.g., calibration, uncertainty in standards, pipetting error, etc.

Problems:
- Identifying and correctly determining all contributions
- Frequently yields lowest estimate of all techniques

Bryan Vining, Ph.D.
06 AUG 2013

10

"Hybrid" estimates of combined standard uncertainty (u_c)

As the name suggests, these use some combination of top-down and bottom-up approaches.

$$u_c = \sqrt{u_p^2 + u_1^2 + u_2^2 + \cdots}$$

u_p = Uncertainty due to precision
u_1 = Uncertainty due to factor 1
u_2 = Uncertainty due to factor 2

Problems:
This approach can have some or all of the issues that the other two approaches have.

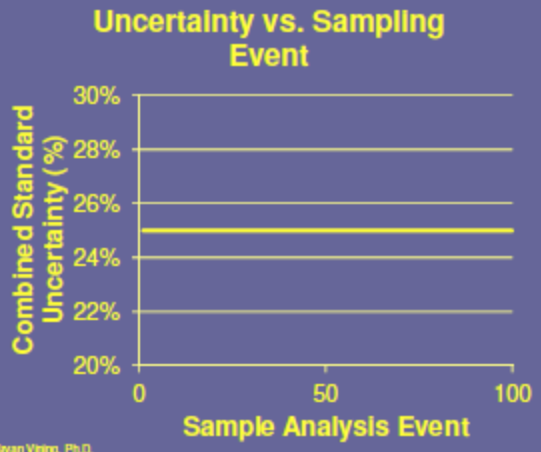
Bryan Vining, Ph.D.
06 AUG 2013

11

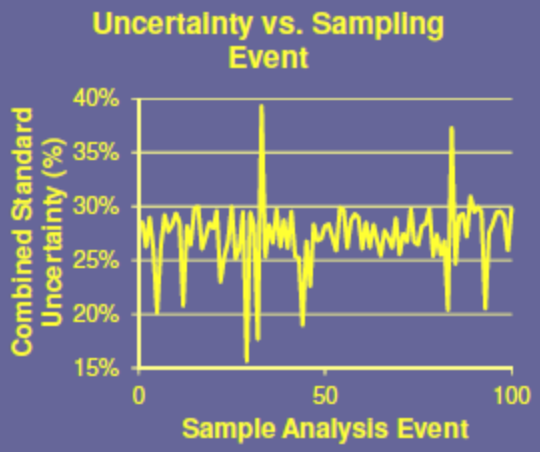
One overarching problem

Uncertainty is treated as a…

Constant = Fantasy

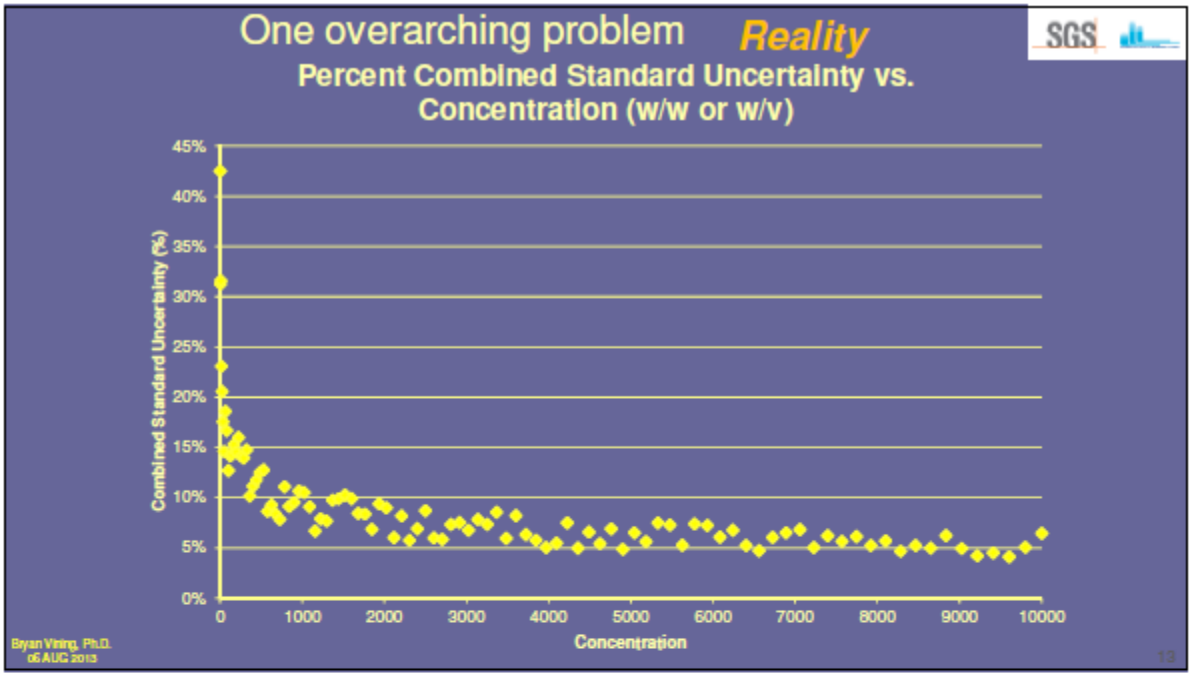


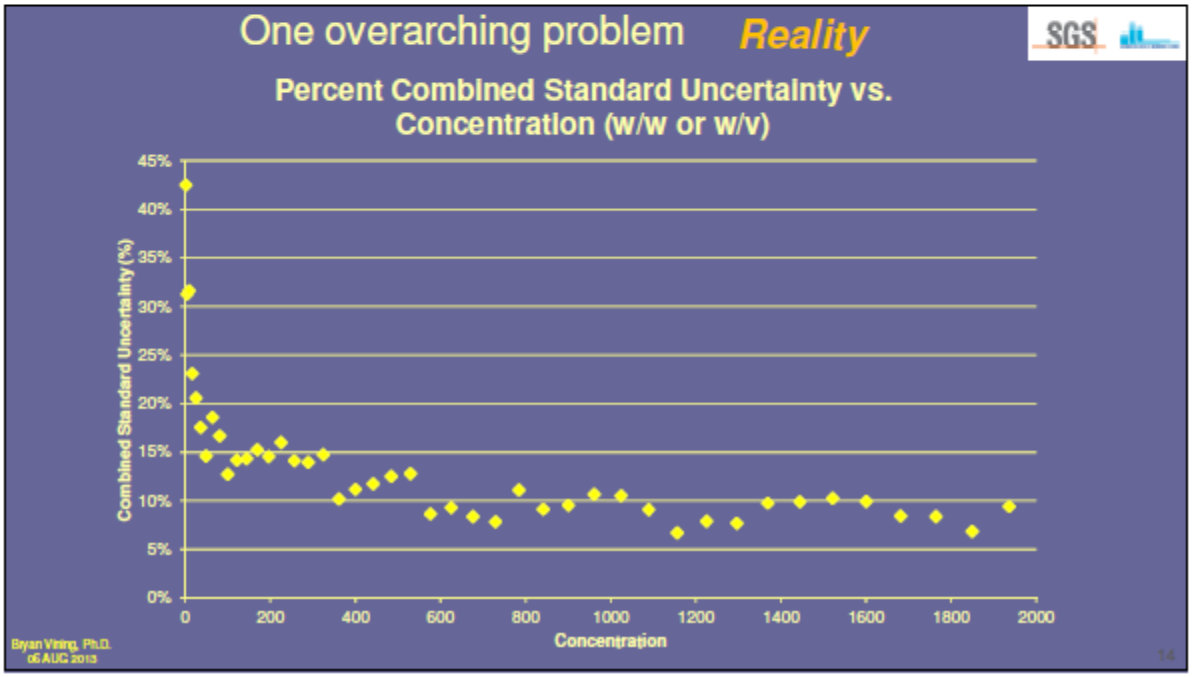
Reality (sort of)

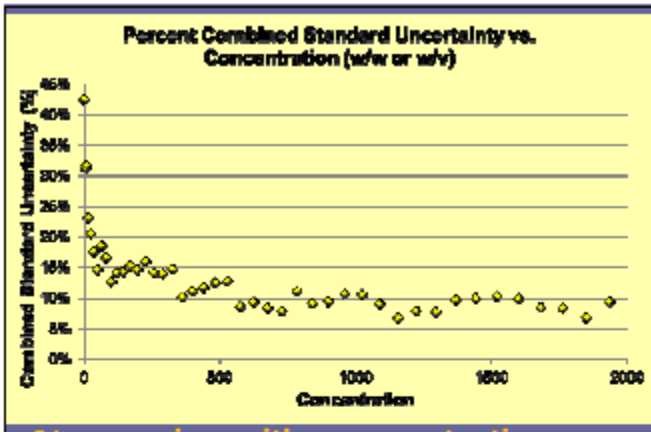


Bryan Vining, Ph.D.
06 AUG 2013

12


One overarching problem
Reality
SGS
Percent Combined Standard Uncertainty vs. Concentration (w/w or w/v)
Combined Standard Uncertainty (%)
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
Concentration
Bryan Vining, Ph.D.
06 AUG 2013
13


One overarching problem
Reality
SGS
Percent Combined Standard Uncertainty vs. Concentration (w/w or w/v)
Combined Standard Uncertainty (%)
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Concentration
Bryan Vining, Ph.D.
06 AUG 2013
14



If $\%u_c$ doesn't vary with concentration, the uncertainty does not reflect reality.

If $\%u_c$ is always the same at the same concentration, it doesn't reflect reality.

%uc varies with concentration.

It also varies at a given concentration because of a number of factors.

Bryan Vining, Ph.D.
06 AUG 2013

15

Causes of $\%u_c$ variance:

Variance in

- Extraction efficiency
- Instrument response
- Instrument noise
- Analyst spiking of standards
- %solids/%lipids determination
- Lab method blank response

These factors affect the signal-to-noise ratio of the measurement

This list is not exhaustive, but it shows many common sources of variance in uncertainty.

Bryan Vining, Ph.D.
06 AUG 2013

16

Solution: *Determine u_c where and when needed*

From the Guide to Expression of Uncertainty in Measurement:
"…it is imperative that the method for evaluating the expressing uncertainty be uniform throughout the world so that measurements performed in different countries can be easily compared."

What matters isn't the method…

What matters is getting the best estimate of u_c possible.

We don't need a uniform way to estimate uncertainty.
We need a uniform way to *assess* the *quality* of uncertainty estimates.

Bryan Vining, Ph.D.
06 AUG 2013
17

Isotope Dilution Example

- Systematic Errors
  - identification, correction/elimination, compensation (self-correction)
  - "***all we have left are random errors***"
- What we want **MU** to be
  - realistic
  - situational
  - timely
  - accurately reflect actual performance

Bryan Vining, Ph.D.
06 AUG 2013
18

Isotope Dilution Example

SGS

$$\%u_c = \sqrt{RSD_{BCS_3}^2 + RPD_{BCS_3}^2 + (\lambda \times RSD_{LOD}^2) + RSD_{J\&E}^2 + RSD_{PS/PL}^2} + [A_x] * RSD_{LMBs}^2$$

RSD_{BCS3} RSD obtained from a large number of BCS_3's and representing the variation from day to day, from chemist to chemist, from standard solution to standard solution (long term) of the spiking

RPD_{BCS3} sample extraction batch RPD for the BCS_3 analyses (short-term effect of the instrumentation)

RSD_{LOD} RSD associated with the annual determination of the LOD; i.e., the RSD from the mean EDL.

λ unitless analytical factor representing the contribution of the individual sample preparation efficiencies as well as the presence of chemical noise or other factors contributing to S/N.

"LMB" capturing the random nature of background contamination temporary → evaluation → refinement → "final"

Bryan Vining, Ph.D.
06 AUG 2013

19

Isotope Dilution Example

SGS

- The lambda scaling term is defined by:

$$\lambda = \frac{EDL}{LOD_{adj.} + [A_x]}$$

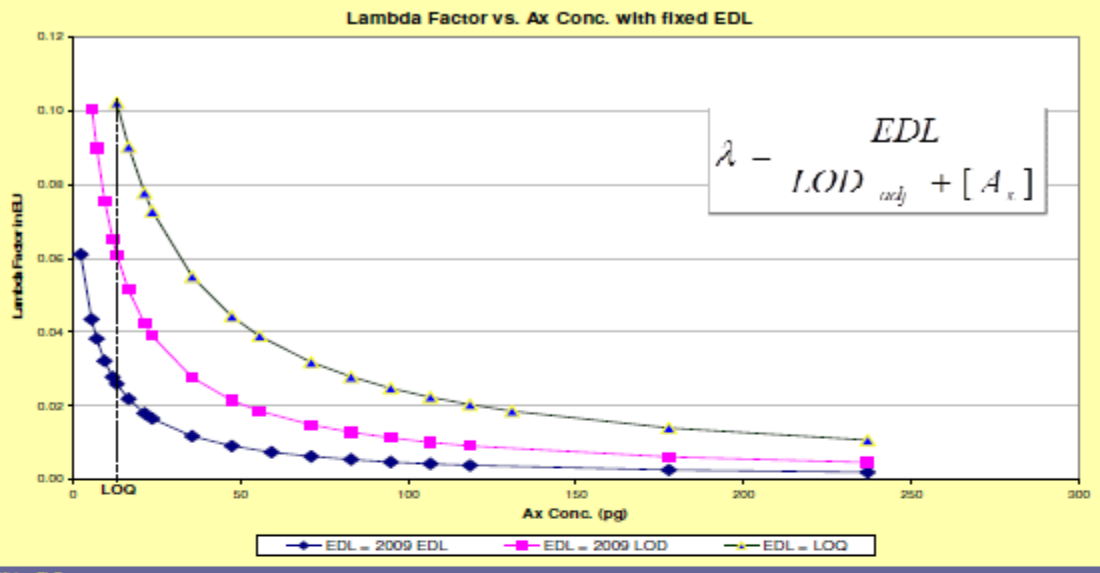
In which,

- EDL = actual sample- and analyte-specific detection limit
- $[A_x]$ = Concentration of native analyte or EDL in the case of a non-detect
- $LOD_{adj.}$ = The LOD adjusted for sample weight, split factor, and dilution factor

Bryan Vining, Ph.D.
06 AUG 2013

20

Isotope Dilution Example



Bryan Vining, Ph.D.
06 AUG 2013

21

Isotope Dilution Example

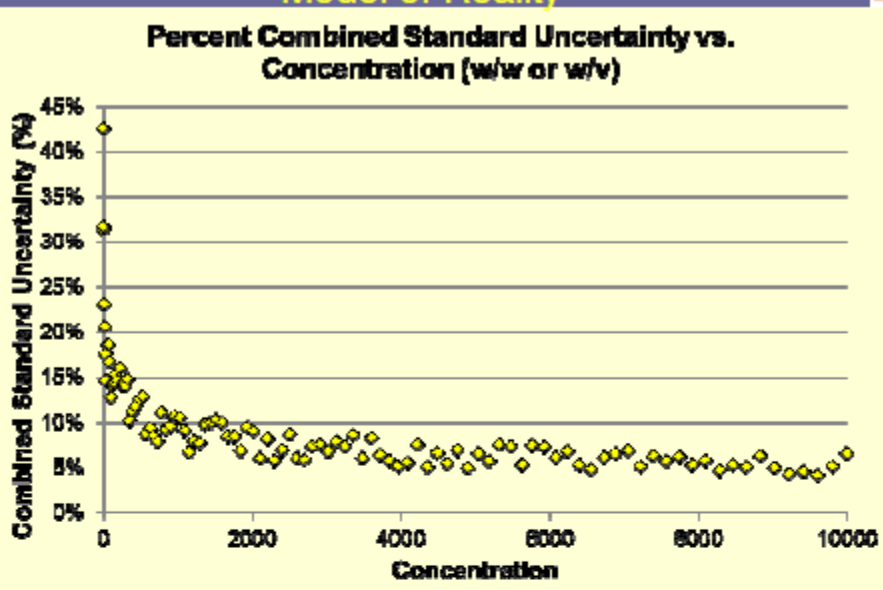
$$\%u_c = \sqrt{RSD^2_{BCS_3} + RPD^2_{BCS_3} + (\lambda \times RSD^2_{LOD}) + RSD^2_{J\&E} + RSD^2_{PS/PL}} + [A_x] * RSD^2_{LMBs}$$

So, how realistic is it?

Bryan Vining, Ph.D.
06 AUG 2013

22

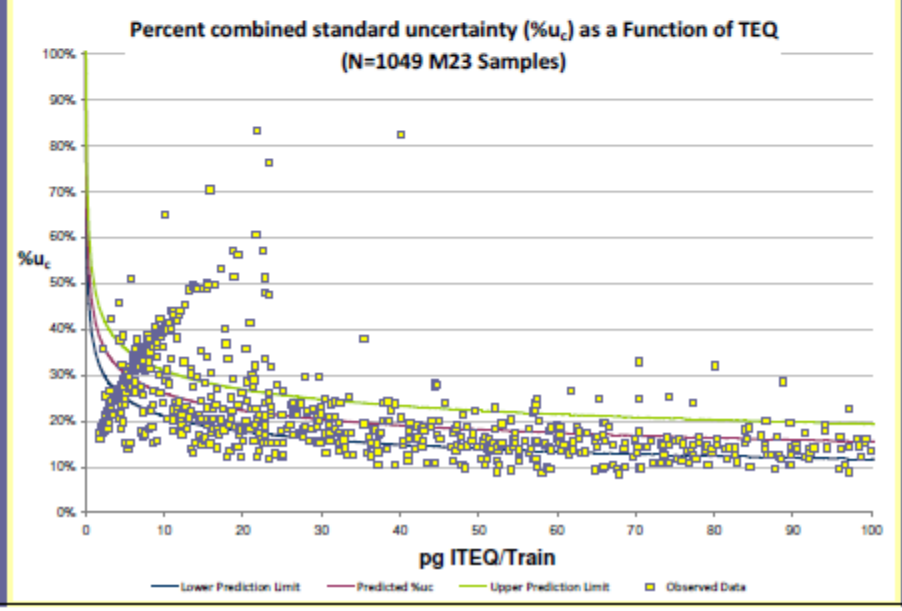
Model of Reality



Bryan Vining, Ph.D.
06 AUG 2013

23

Results from the ID Equation



Bryan Vining, Ph.D.
06 AUG 2013

24

Other ways to deal with S/N for non-ID methods

SGS

For a given noisy signal (e.g., a chromatogram), the uncertainty of the signal may be determined as:

$$u_{S/N} = \int_{-T}^{T} (T - |\tau|) \lim_{N\to\infty} \frac{1}{N} \sum_{k=1}^{N} x_k(t_1) x_k(t_2)\, dt_1 dt_2$$

In which,

T = Integration time

N = number of data points in the signal

$x_k(t)$ = individual data points in the signal

t_1 = data point at time 1

t_2 = data point at time 2

$\tau = t_1 - t_2$

Bryan Vining, Ph.D.
06 AUG 2013

25

Conclusion

SGS

- Reality is not as pretty as the fantasy world of no uncertainty, but we must strive to cope with it.
- Uncertainty estimates should match reality – if they don't, the method of estimation is incorrect
- Uncertainty is not a constant nor a constant percentage of a result. It changes with each measurement, and we must devise a way to capture that change.
- Finally, we must learn to be comfortable with uncertainty and embrace it.

Bryan Vining, Ph.D.
06 AUG 2013

26

Conclusion

"I can live with doubt and uncertainty. I think it's much more interesting to live not knowing than to have answers which might be wrong"
- Richard Feynman, Nobel Prize in Physics, 1965

"The supreme triumph of reason is to cast doubt on its own validity"
- Miguel de Unamuno, poet and philosopher

How to Choose a Laboratory that Will Meet Your Data Assessment and Testing Needs?

Kim Watson
Stone Environmental, Inc.

Abstract

Engineers are often faced with the dilemma of choosing a new or additional laboratory for their environmental testing needs when they begin a project in a new geographical location, or embark on a project with a more extensive list of test methods than their current "favorite" laboratory offers. Theoretically, the law of environmental analytical work allows for the purchase of two of the following three characteristics: good quality, fast turnaround or low cost. However, more importantly, clients must look at a broader set of criteria for choosing a new laboratory such as: can they create data deliverables for both electronic and manual data assessment; do they offer the tests we need; are they NELAP and/or DOD accredited; and finally, is the price within the projected budget?

One question that is not asked often enough is: if a laboratory can meet all of the above criteria, does that guarantee that the data produced will satisfy the data assessment requirements and the data quality objectives of the project?

In the best of circumstances, the data assessor, the client and the testing laboratory should be in full partnership in an environmental investigation or monitoring project. In this paper, we will examine what an extended list of criteria ought to include, ways to evaluate a laboratory that go beyond these simple questions, and ways in which the accrediting bodies can increase the value of the accreditations awarded, especially in a time of decreased travel budgets and over-full schedules.

Additional Author: Deborah H. Gaynor, Ph.D.



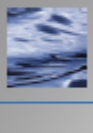
How to Choose a Laboratory that Will Meet Your Data Assessment and Testing Needs?

2013 NEMC
Legal Defensibility of Data

Prepared by Kim Watson, RQAP-GLP
Deborah Gaynor, Ph.D, Phoenix

1

STONE ENVIRONMENTAL INC



Where We've Been – 1970's

Selecting a Laboratory:

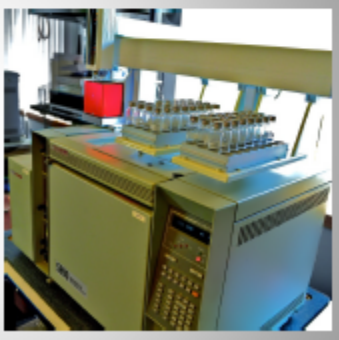
Location, Price, Size

Preference, Performance

Law of Environmental Services--

Purchase any two:

- QUALITY
- COST
- TURNAROUND TIME



2

STONE ENVIRONMENTAL INC

Where We Are Now - 2013

Selecting a Laboratory:

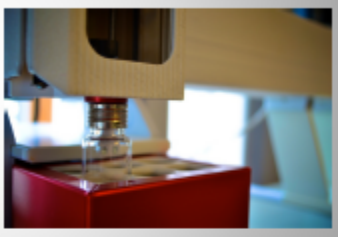
Location, Price, Size

Preference, Performance

Law of Environmental Services--

Purchase any two:

- QUALITY
- COST
- TURNAROUND TIME
- MULTIPLE ACCREDITATIONS



3

STONE ENVIRONMENTAL INC

Are We Evaluating Laboratories Effectively?

- What is the cost of accurate, defensible, analytical measurements??
- If it isn't worth it, don't buy it.
- If it isn't written down, it didn't happen.
- Why do sampling and analysis if resulting data isn't traceable, defensible, and good science.



4

STONE ENVIRONMENTAL INC

Are We Evaluating Laboratories Effectively?

- SCIENCE – WHAT IS IT ALL ABOUT?

-Lord KelvinQuote.pdf



5

STONE ENVIRONMENTAL INC

Where We Need To Be

Extended List of Criteria Should Include the Following

- QAPP – Value of the UFP QAPP, Standard Formats and Consistency
- **SOPs – Read them – Don't Just Collect them**
- **Data Quality Objectives**
  - Measurement Performance Criteria
  - Accuracy and Precision
- DOCs – Performed with modifications
- **Calibrations – How are they performed?** per method.
- Full Data Packages – Organization as per CLP with Bookmarks

6

STONE ENVIRONMENTAL INC



Where We Need To Be – (con't)

- Internal Data Review - Policy and procedures for data package review and manual integration review.
- EDDs – What's your favorite format?
- Chromatography (Signal/Noise), Interpretation of TICs
- Reporting Error Rate
  - Including Sample Login
- **Non Analytical Services**
  - Shipping Services
  - Bottle Orders
- **PE Performance – Policy for suspending an analyte**

7

STONE ENVIRONMENTAL INC



Where We Need To Be-Examples

- **SOPs: Read them – Don't Just Collect them**
  - **Examples: Hexavalent Chromium and Method 8151A Extraction Modification**
- **Data Quality Objectives: Setting Appropriate Data Quality Objectives**
  - **Measurement Performance Criteria**
  - **Accuracy and Precision**
- **Calibrations – How are they performed**
- **Non Analytical Services**
  - **Shipping Services**
  - **Bottle Orders**

8

STONE ENVIRONMENTAL INC



Ask for and Examine SOPs

Ask for the laboratory' s SOPs for the methods they will run for you. Include the sample preparation SOPs as well as the analytical SOPs.

- Example 1:

  The laboratory will be analyzing hexavalent chromium in soils. At the validator' s request, they provided the SOPs for not just analysis of hexavalent chromium, but also for measurement of pH and oxidation-reduction potential (ORP).

  Guess what: the ORP SOP did not list a platinum (or other noble metal) electrode in the materials section, and the procedure did not include instructions for using an indicator electrode as well as a reference electrode. This opens up the question whether or not the laboratory actually is measuring ORP, or just obtaining erroneous readings from their pH meter.

9



STONE ENVIRONMENTAL INC



Ask for and Examine SOPs

Ask for the laboratory' s SOPs for the methods they will run for you. Include the sample preparation SOPs as well as the analytical SOPs.

- Example 2: The laboratory provided their preparation and analysis SOPs for Method 8151A (chlorinated acid herbicides).

  Here' s what the validator found upon comparing the soil extraction SOP to the method:

  Method 8151A example

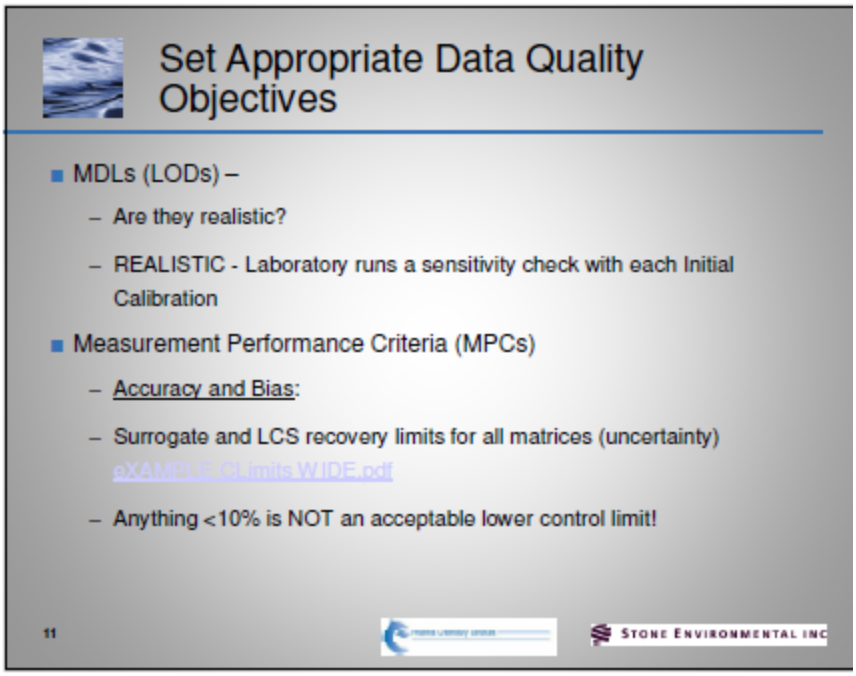
- Example 3: A welcomed way to reference the differences between a Method to the Lab SOP.
- MADEP EPH/PAH

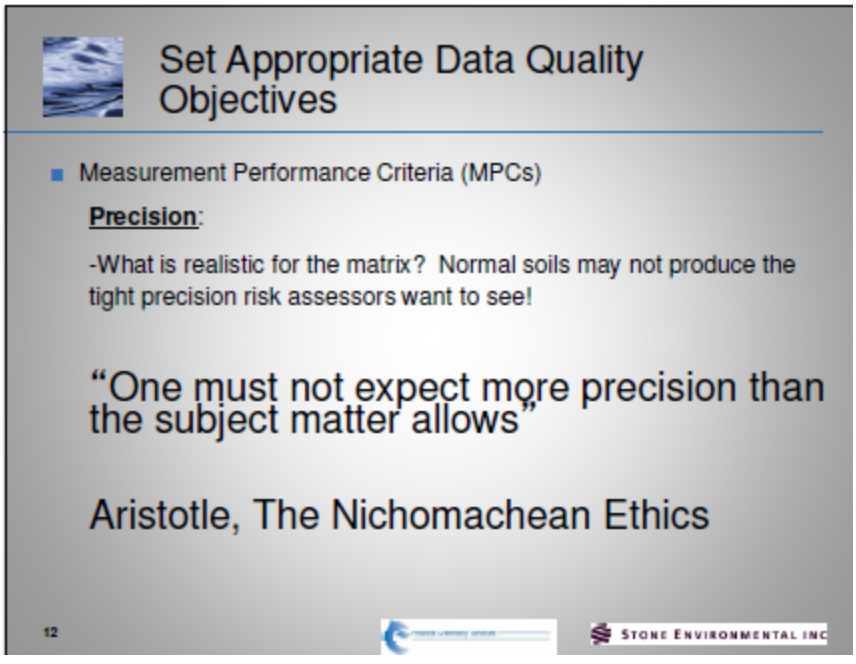
  Pages from 3-OL-2005 EPH_rev1_1_SOP.pdf

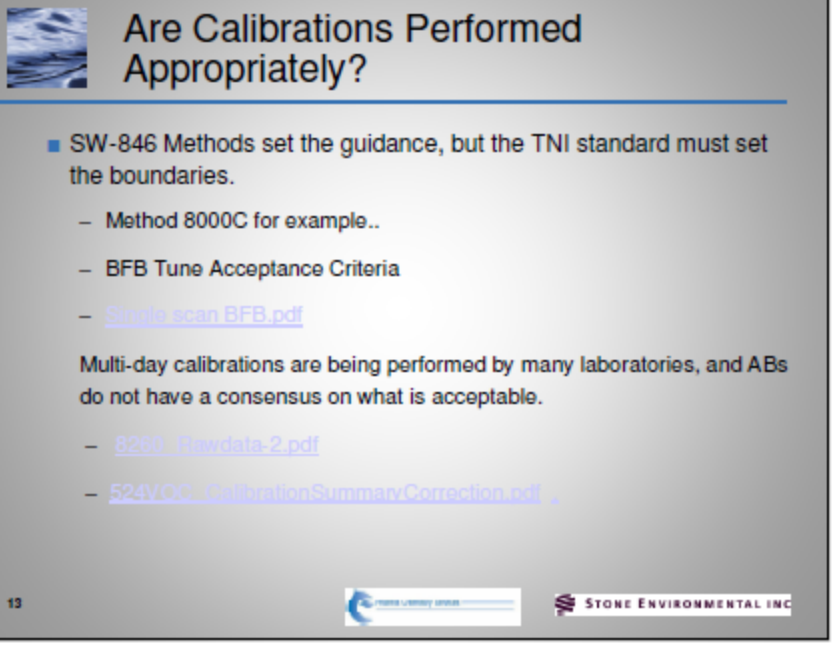
10

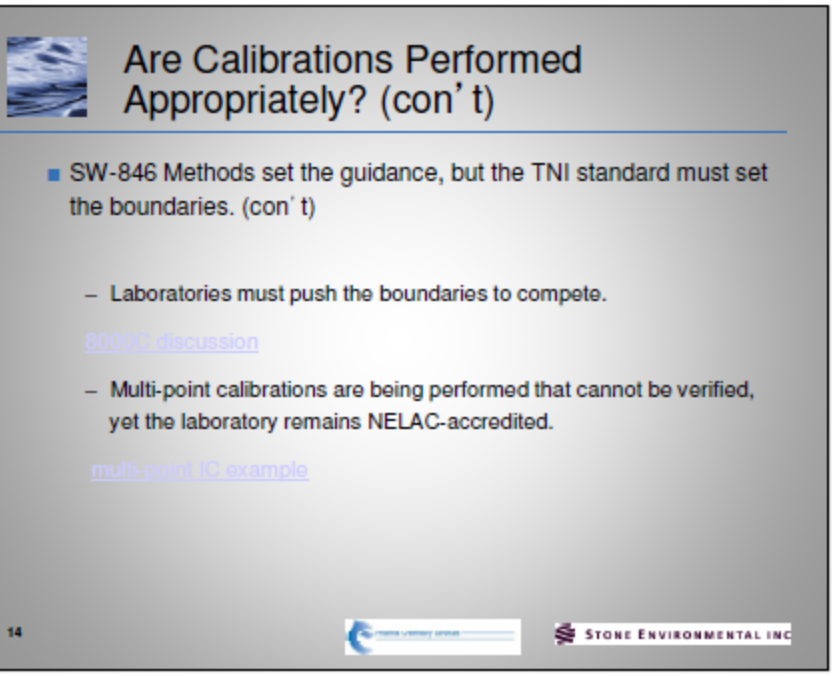


STONE ENVIRONMENTAL INC


Set Appropriate Data Quality Objectives
MDLs (LODs) –
Are they realistic?
REALISTIC - Laboratory runs a sensitivity check with each Initial Calibration
Measurement Performance Criteria (MPCs)
Accuracy and Bias:
Surrogate and LCS recovery limits for all matrices (uncertainty)
eXAMPLE CLimits WIDE.pdf
Anything <10% is NOT an acceptable lower control limit!
11
STONE ENVIRONMENTAL INC


Set Appropriate Data Quality Objectives
Measurement Performance Criteria (MPCs)
Precision:
-What is realistic for the matrix? Normal soils may not produce the tight precision risk assessors want to see!
"One must not expect more precision than the subject matter allows"
Aristotle, The Nichomachean Ethics
12
STONE ENVIRONMENTAL INC


Are Calibrations Performed Appropriately?
SW-846 Methods set the guidance, but the TNI standard must set the boundaries.
Method 8000C for example..
BFB Tune Acceptance Criteria
Single scan BFB.pdf
Multi-day calibrations are being performed by many laboratories, and ABs do not have a consensus on what is acceptable.
8260_Rawdata-2.pdf
524VOC_CalibrationSummaryCorrection.pdf
13
STONE ENVIRONMENTAL INC


Are Calibrations Performed Appropriately? (con't)
SW-846 Methods set the guidance, but the TNI standard must set the boundaries. (con't)
Laboratories must push the boundaries to compete.
8000C discussion
Multi-point calibrations are being performed that cannot be verified, yet the laboratory remains NELAC-accredited.
multi-point IC example
14
STONE ENVIRONMENTAL INC



Expect the Best Non-Analytical Services

- Shipping Services –
  - Bottle orders, packing materials included, field packs, courier service.
- Sample Receiving –
  - Immediate log-in.
  - COCs emailed back to sampler or field project manager within 48 hours of receipt.
  - Sample Acceptance criteria are scientifically defensible.
  - SampleTemperatureAcceptancePolicy.pdf

15

STONE ENVIRONMENTAL INC



Expect the Best Non-Analytical Services

- Data Deliverables
  - Full Data Package as described in the CLP SOW (for full validation) or or find out what "CLP like" looks like…
  - Choice of EDD formats—done correctly!
- Responsiveness
  - Laboratory Project Manager is always available by phone or email
  - Corrective Actions are performed if needed
  - Revisions are received promptly

16

STONE ENVIRONMENTAL INC



What Can the Accreditation Sector Do?

- What can the Laboratory Accreditation Industry do to increase the value of laboratory services?
- Is it appropriate to expect more from an accredited laboratory?
  - What are the differences between accredited and non-accredited laboratories?
  - Does consistency of performance matter to purchasers of laboratory services?
  - Does accreditation contribute to marketing success?

17



STONE ENVIRONMENTAL INC



What Can the Accreditation Sector Do?

- What is the role of cost in laboratory selection?
  - If results are rejected due to laboratory deficiencies, what is the cost to the data user?
  - If data results end up in litigation, are they robustly defensible?
  - Is there a cost differential (and how big is it?) between accredited and non-accredited laboratories?
- Are expectations set appropriately?
  - Impact on protection of human health.
  - Impact on protection of ecosystem health and viability.

18



STONE ENVIRONMENTAL INC

Value Added by Accreditation

- PE Performance Tracking
  - Notification of failures and suspicions
  - Passing 2 out of 3 consecutive PEs
- Hands and Eyes on Laboratory's Quality System *and* Technical Performance!



19

STONE ENVIRONMENTAL INC

Value Added by Accreditation

- Accreditation by Matrix, Technology, Analyte
- Accreditation by Matrix & Technology (NEFAP)



20

STONE ENVIRONMENTAL INC

Value Added by Accreditation

- Third Party Assessors and Assessments
  - Technically Sound Science
  - Strong understanding of analytical systems and software
  - Strong understanding of management systems



21

STONE ENVIRONMENTAL INC

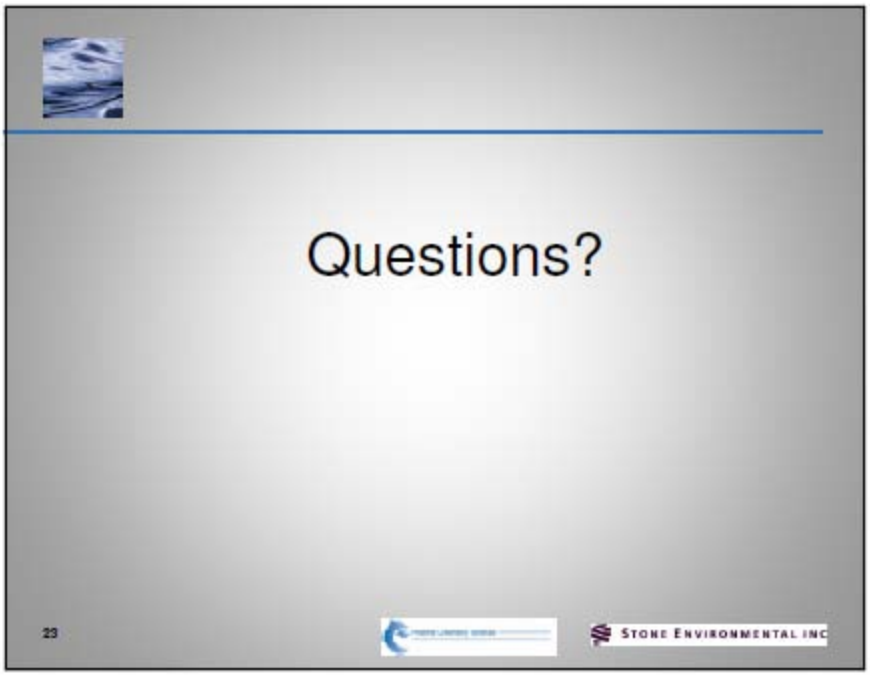
ACKNOWLEDGMENTS

Stone Environmental Inc.
and
Phoenix Chemistry Services

Would like to thank all the laboratories that provided examples!

22

STONE ENVIRONMENTAL INC


Questions?
23
STONE ENVIRONMENTAL INC

Data Validation, Usability and Defensibility

Kesavalu Bagawandoss
Accutest Laboratories

Abstract

Data validation is the heart and soul of data usability and defensibility of environmental laboratory data. Data from laboratories are submitted in several forms. Namely, Level I, Level II, Level III and Level IV. There are three steps in determining if the data is complete, valid and usable for a specific project and objective. The three steps are data verification, data validation and data usability. This presentation would outline the steps involved in obtaining defensible data from the laboratories based on the project requirements and the defined data quality objectives such as risk assessment. The qualification of data using the guidance provided in the USEPA National Functional Guidelines and Professional Judgment will be discussed. The selection of data validators and their qualifications will be discussed in terms of defending data when legal challenges are posed. A discussion of when does one need to validate data using a third party validator will be addressed. An example data validation report will be presented. The role of professional judgment of a data validator will be discussed. The need for consistent application of Professional Judgment will be addressed.

NEMC 2013

Data Validation, Usability & Defensibility

Kesavalu M. Bagawandoss Ph.D., J.D.
August 6, 2013



Data Validation

- Data Validation consists of an analyte and sample specific process of evaluating compliance of the laboratory data with methods, procedures or contract requirements.
- Guidance document for Data Validation is from the USEPA CLP Program
- http://www.epa.gov/superfund/programs/clp/guidance.htm

2

Data Validation

What is required for validation?

- Level 4 Data package is a mandatory deliverable
- EDD depending on format of validation software
- SOP's, QAP's and Methods
- Specific contracts or SOW's provided to the laboratory or required by client

3

Data Validation

Two Criteria must be measured:

1. Does the data meet the specific technical and QC criteria established
2. Usability of the data not meeting the technical and QC criteria established

If the data does not meet criteria how does one handle the data.

4

Data Validation

- Data Validation requires extensive laboratory systems knowledge and the ability to apply consistent professional judgment during the process.
- In other words the same data package cannot be validated differently on a different day by the same person.

5

Data Validation

How to select Data Validators

- Knowledge, Technical Background
- Experience (history of prior validation and challenges)(check references)
- Will the validator stand the legal challenge
- Can the validator defend the data on your behalf
- History on legal challenges and background of company
- 3rd party data validation vs. internal validation

6

Data Validation

When do you need validation?

- Laboratory quality is unknown
- Laboratory has a history of errors
- Data is used for litigation
- Data is used for Risk Assessment (agency requirements need to be adhered to)
- Project plan requires full validation
- Routine Monitoring???(under the microscope?)
- Agency spilt samples

7

Data Validation

Tools available for data validation

- Commercial software
- Databases developed by validators
- Guidance documents from public sources (validation guidelines established by EPA CLP and others)
- Most tools are semi-automatic due to professional judgment assessments
- Establishing standard codes- explanations for each situation of qualification (data qualifier codes)

8

Data Validation

Discussions

- Look for trends in Lab performance
- Formats and requirements of data validators
- Ethics in data validation and relationships
- Judgment of Data validators vs. defense of data
- QA/QC issues and how to handle data
- Consistency in Data Validation

9

Data Validation

Discussions (contd.)

- Under what circumstances do you as a data validator choose to accept data where there were problems with the QA/QC, method selection or sample integrity.
- "Analyst/validators discretion", all data deficiencies are not created equal, where do you draw the lines.

10

Data Usability

- Data usability is an executive summary report of the data based on the validation performed with comments and comparison of site specific analytes and plausibility
- TCEQ provides guidance for TX as to how the data usability report should be prepared
- DV report + Narrative = Data Usability Summary

11

Data Usability

- Based on the data usability summary, risk assessment can be performed
- Data validation coupled with the data usability provides a strong platform for risk assessment with ruggedness
- Further, the defensibility of data is enhanced due to the rigorous scrutiny of the data from inception to conclusion of the project and beyond

12

Data Defensibility

- Data defensibility starts with the initiation of sampling in the field
- Prior to sampling a solid sampling and analysis plan must be prepared and approved
- All parties must be involved with the conception of the project
- Parties must include both the stake holders and all other players including data validators

13

Data Defensibility

- The standard for defensibility is based on the Daubert case, wherein the US Supreme Court outlines a list of factors
- The Code of Evidence also spells out expert qualifications as well as individual State rules
- Any method could be defended as long as they can confirm to the Daubert factors outlined by the Court
- Daubert v. Merrel Dow Pharmaceuticals, Inc., 509 U.S. 579, 1993

14

Data Defensibility

The Daubert factors are:

(1) whether the expert's theory has been tested;

(2) whether the theory has been subject to peer review and publication;

(3) the known or potential rate of error of a technique or theory when applied;

(4) the existence and maintenance of standards and controls; and

(5) the degree to which the technique or theory has been generally accepted in the scientific community. *See Moore v. Ashland Chem. Inc.*, 151 F.3d 269, 275 (5th Cir.1998) (citing *Daubert*, 509 U.S. at 593-95, 113 S.Ct. at 2796-97 (1993)).

15

Data Defensibility

- In general an expert identified must have knowledge of the data as well as the project requirements and the expertise required for the analytical methods utilized
- The ideal person would be someone with experience in the subject matter and has validated the data and understands the intricacies of the data subject to cross examination providing the trier of facts the evidence to gain the truth in the matter

16

Data Defensibility

- Just because a person has been qualified as an expert in another case does not mean that he can be qualified as an expert in the case at hand
- The expert is still subject to challenges before trial to be qualified as an expert
- Louisiana Law allows for the opponent to challenge the qualifications of an expert 30 days prior to trial before the trial judge in any case.

17

References

- http://www.epa.gov/superfund/programs/clp/guidance.htm
- http://www.epa.gov/superfund/programs/clp/download/somnfg.pdf
- http://www.epa.gov/superfund/policy/pdfs/Transmittal%20Memo-%20SF%20Data%20Validation%20Guidance.pdf
- http://www.epa.gov/quality/qs-docs/r5-final.pdf
- http://www.epa.gov/quality/qs-docs/q8-final.pdf
- www.TerraBase.com
- www.Envstd.com
- Daubert v. Merrel Dow Pharmaceuticals, Inc., 509 U.S. 579, 1993.
- TCEQ data usability guidelines TCEQ publication RG-366/TRRP-13, May 2010.

18

SECTION 13

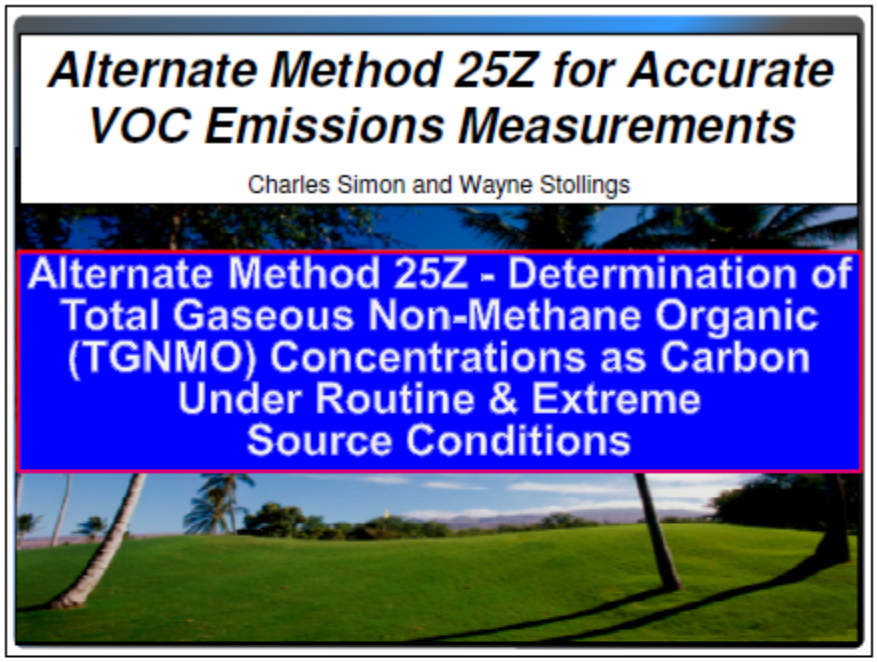
AIR METHODS/MONITORING: MONITORING, METHODS, AND TECHNOLOGY

Alternate Method 25Z for Accurate VOC Emission Measurements

Charles Simon
VOC Reporting, Inc.

Abstract

How is your facility classified? Major Source? True Minor Source? Correctly permitted Synthetic Minor Source? When did/will your facility exceed a PSD increment? These are some pretty important questions for both operators and regulators. The accuracy of emission test results cannot be understated since they provide the answers to these critical questions. Determining accurate emission rates of Volatile Organic Compounds (VOC) has historically been the most difficult of the criteria pollutant source emission tests. Method 25 has been used since 1980 to define the organic carbon emission rates of a broad spectrum of industrial sources. After collecting and analyzing thousands of Method 25 samples, the authors are in the unique position to provide an update to this Method that substantially improves its accuracy in extreme, non-traditional, applications. The prescriptive nature of the original Method 25 is altered to include a selection of modifications appropriate for each source category. These changes define equipment cleaning, quality assurance and audit sample collection procedures; remove interference from carbon dioxide; permit accurate determination of VOC emissions in a host of non-traditional sources including those with ultra-high VOC concentration (>1,000,000 ppmC), those with aerosolized VOC and organic-laden droplets, and even steam vents! Modifications to laboratory procedures assure complete recovery of organic compounds that are collected in the cryogenic trap, even thermally reactive compounds.

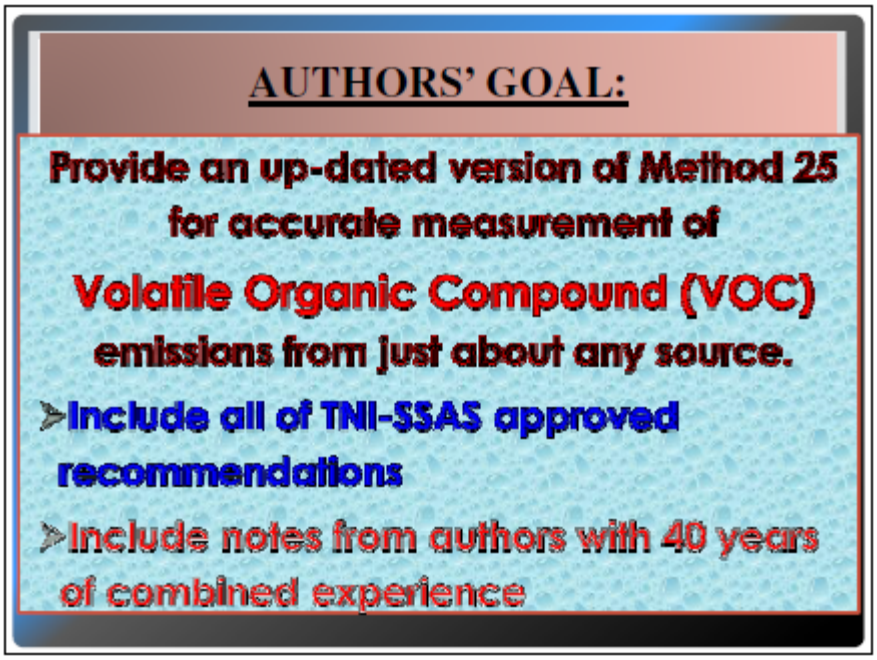

Alternate Method 25Z for Accurate VOC Emissions Measurements
Charles Simon and Wayne Stollings
Alternate Method 25Z - Determination of Total Gaseous Non-Methane Organic (TGNMO) Concentrations as Carbon Under Routine & Extreme Source Conditions

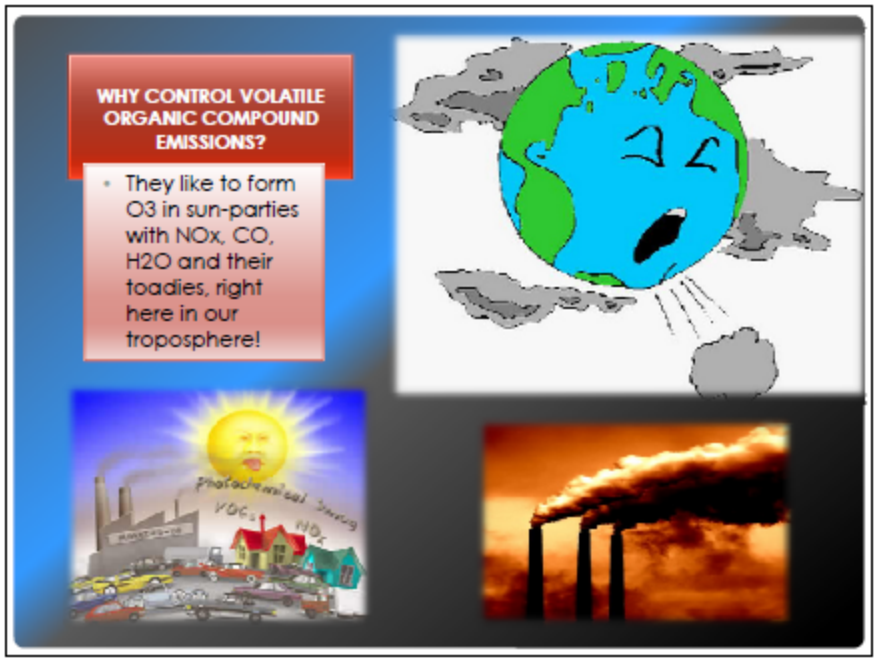

TNI Stationary Source Audit Sample Expert Committee (TNI-SSAS)
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Logic Tree
ACCREDITED IN ACCORDANCE WITH
nelac
Mission Statement:
Development and implementation of TNI consensus standards that enable the externalization of the EPA's Stationary Source Audit Program (SSAP), that includes the following elements:

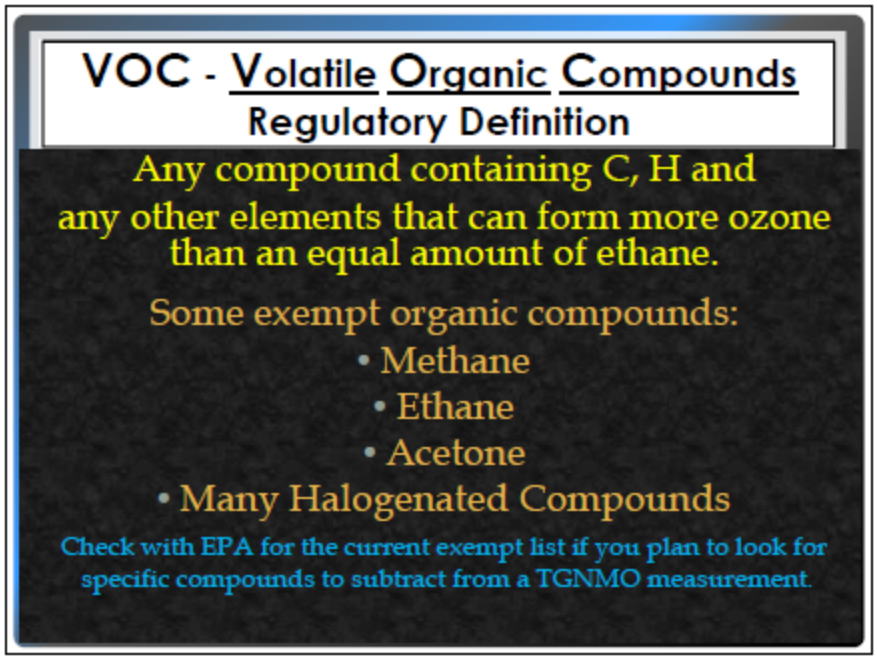

o Roles and responsibilities of program participants
o Manufacture of audit samples
o Oversight of audit sample providers
o Management of audit sample results
o Acceptance criteria

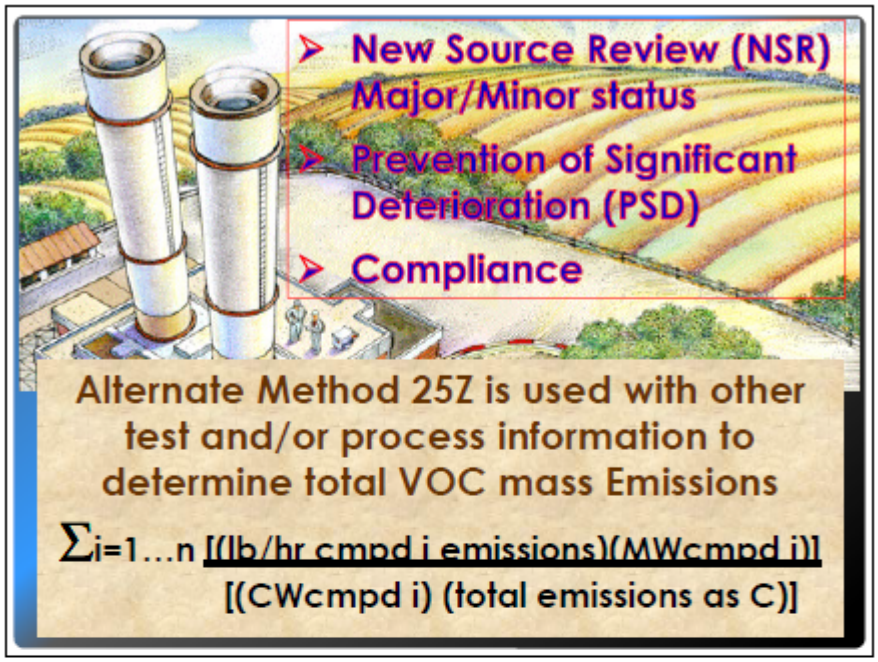

THE PROBLEM
Regression-Based M25 Audit Acceptance Criteria:
ppmC >1,000 ±15-20%
500 ±25
200±40%
100±70%
USE Clean Equipment, Advise Blank-Correct if <150 ppmC

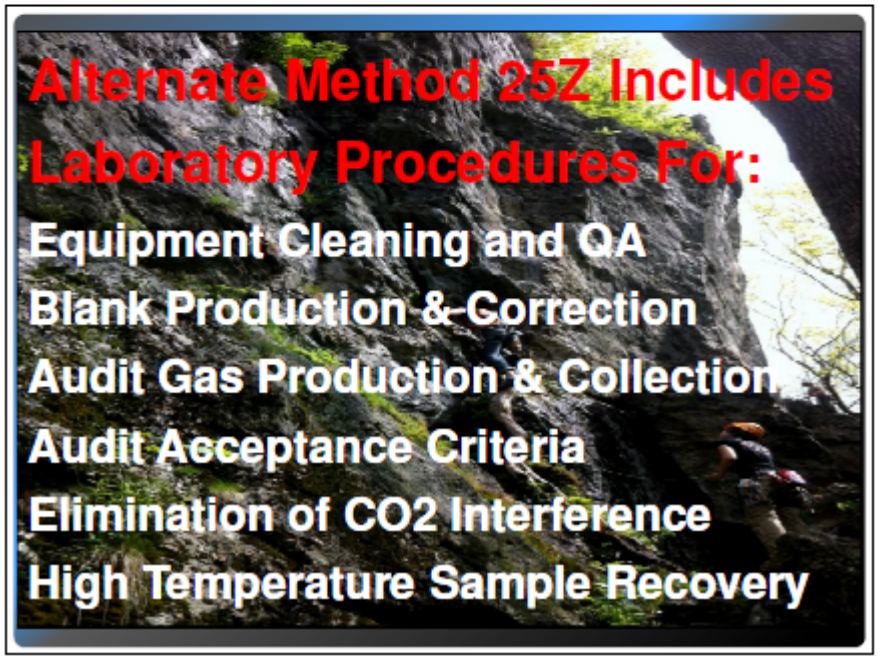

Alternate Method 25Z was developed as a response to an EPA request to improve Reference Method 25.
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
EXCUSES
The development effort was performed under the authority of the TNI Stationary Source Audit Sample Committee


AUTHORS' GOAL:
Provide an up-dated version of Method 25 for accurate measurement of
Volatile Organic Compound (VOC)
emissions from just about any source.
Include all of TNI-SSAS approved recommendations
Include notes from authors with 40 years of combined experience


WHY CONTROL VOLATILE ORGANIC COMPOUND EMISSIONS?
• They like to form O3 in sun-parties with NOx, CO, H2O and their toadies, right here in our troposphere!

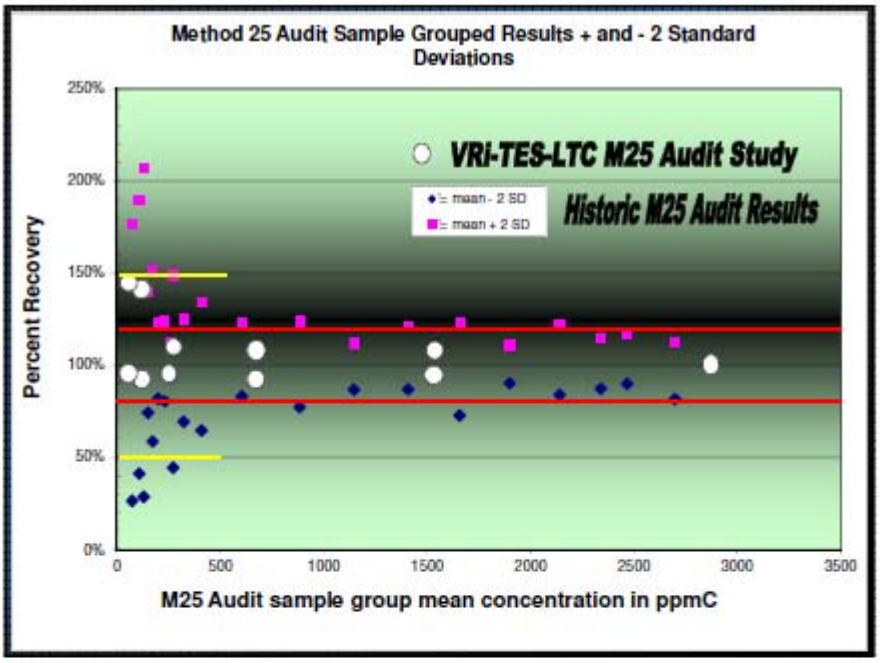

VOC - Volatile Organic Compounds
Regulatory Definition
Any compound containing C, H and any other elements that can form more ozone than an equal amount of ethane.
Some exempt organic compounds:
• Methane
• Ethane
• Acetone
• Many Halogenated Compounds
Check with EPA for the current exempt list if you plan to look for specific compounds to subtract from a TGNMO measurement.

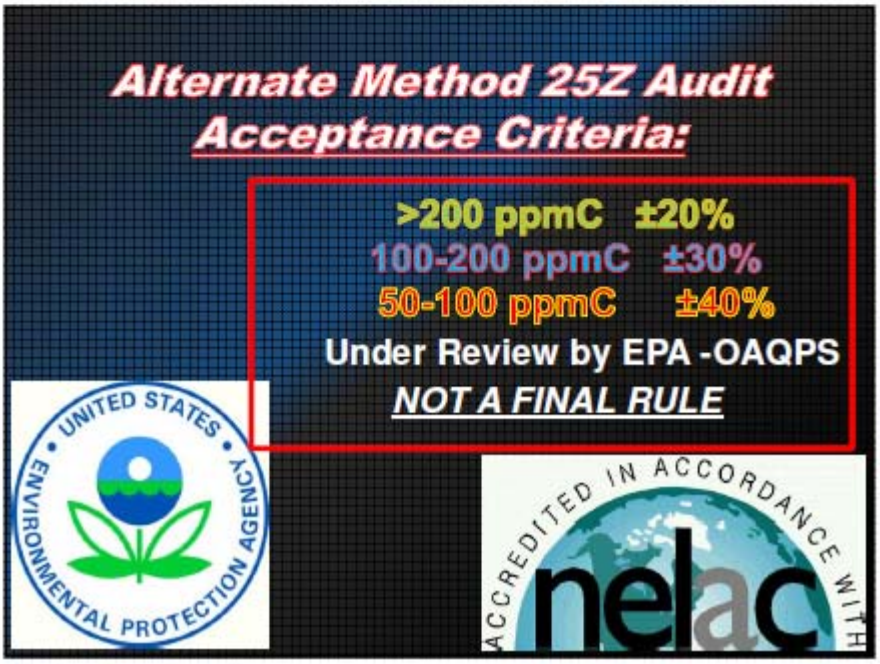

New Source Review (NSR) Major/Minor status
Prevention of Significant Deterioration (PSD)
Compliance
Alternate Method 25Z is used with other test and/or process information to determine total VOC mass Emissions
$\sum_{i=1...n}$ [(lb/hr cmpd i emissions)(MWcmpd i)]
[(CWcmpd i) (total emissions as C)]


Alternate Method 25Z Includes Laboratory Procedures For:
Equipment Cleaning and QA
Blank Production & Correction
Audit Gas Production & Collection
Audit Acceptance Criteria
Elimination of CO2 Interference
High Temperature Sample Recovery

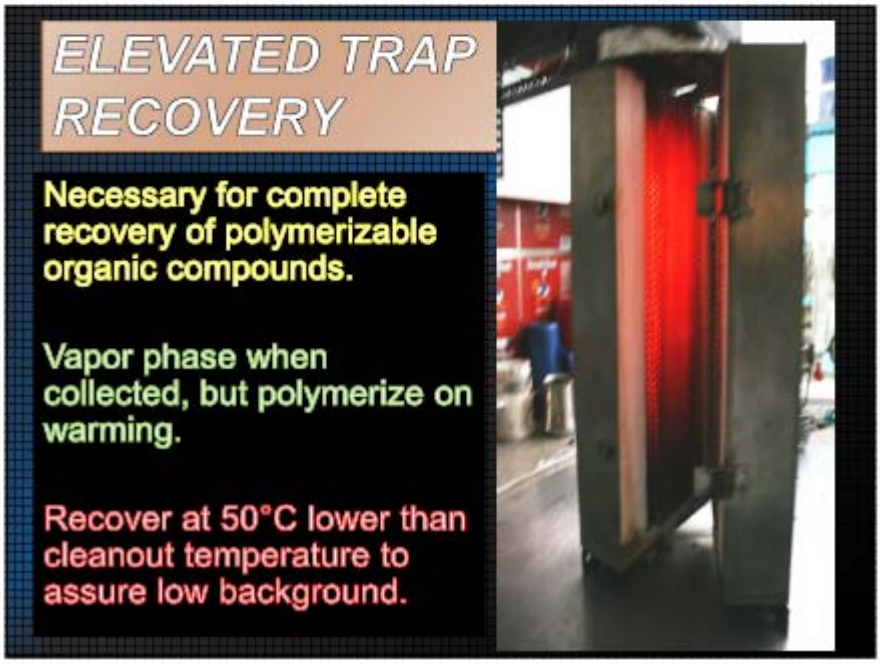

High-Temperature Gas (>500°F)
High-Moisture Gas (up to 99%)
Ultra-High Concentration VOC (>1,000,000 ppmC)
Gas with VOC-containing aerosols and/or droplets
Measuring & Reporting CH4 and CO concentrations

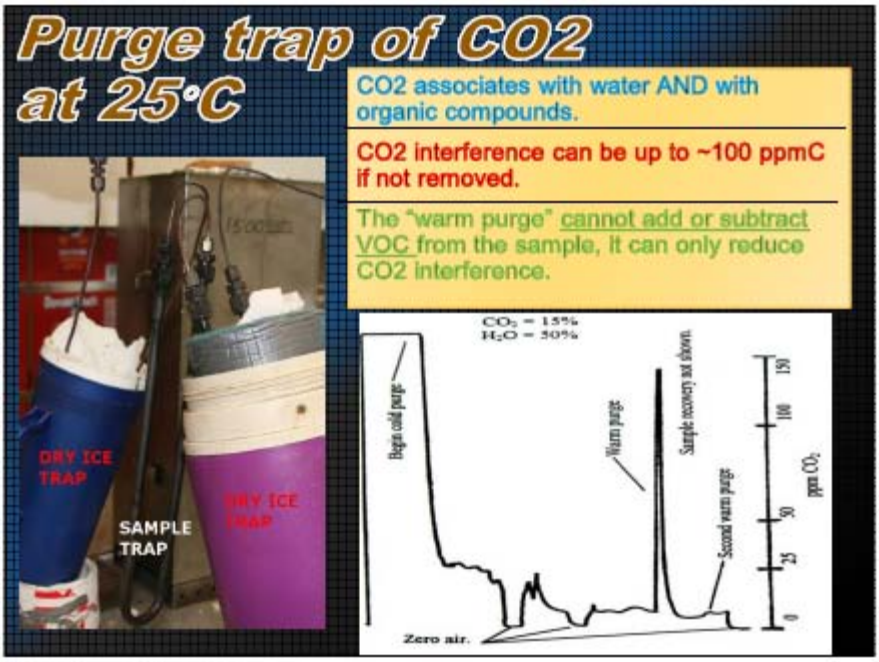

LABORATORY M25 AUDIT ANALYSES RESULTS
TES
VRI
TES
257-3046 ppmC
101±2%
104±5%
61-122 ppmC
94±1%
108±4%
Ethane, Propane, MEK + 2-8% CO2


Method 25 Audit Sample Grouped Results + and - 2 Standard Deviations
VRI-TES-LTC M25 Audit Study
Historic M25 Audit Results
= mean - 2 SD
= mean + 2 SD
Percent Recovery
250%
200%
150%
100%
50%
0%
0
500
1000
1500
2000
2500
3000
3500
M25 Audit sample group mean concentration in ppmC

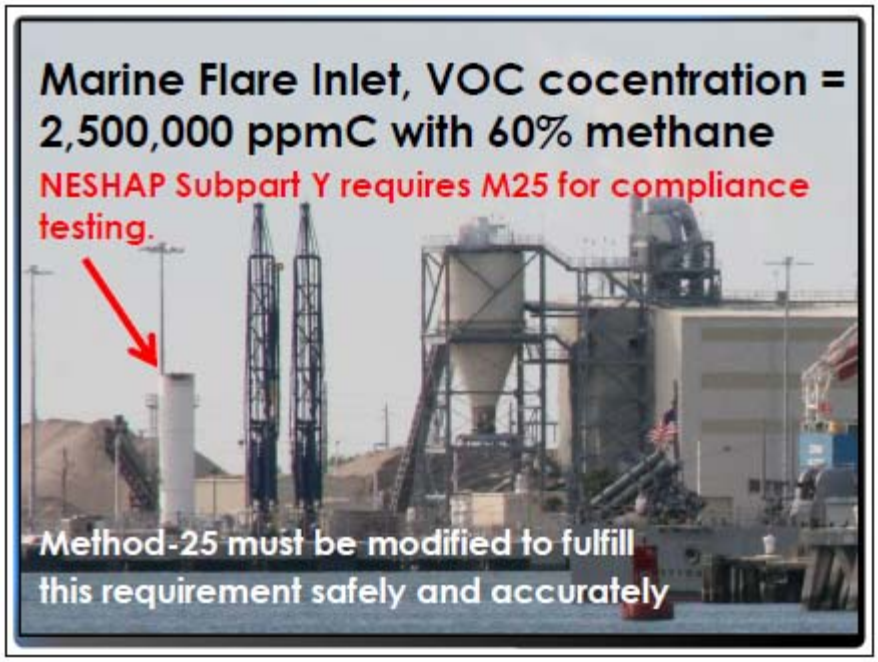

Alternate Method 25Z Audit Acceptance Criteria:
>200 ppmC ±20%
100-200 ppmC ±30%
50-100 ppmC ±40%
Under Review by EPA -OAQPS
NOT A FINAL RULE
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ACCREDITED IN ACCORDANCE WITH
nelac

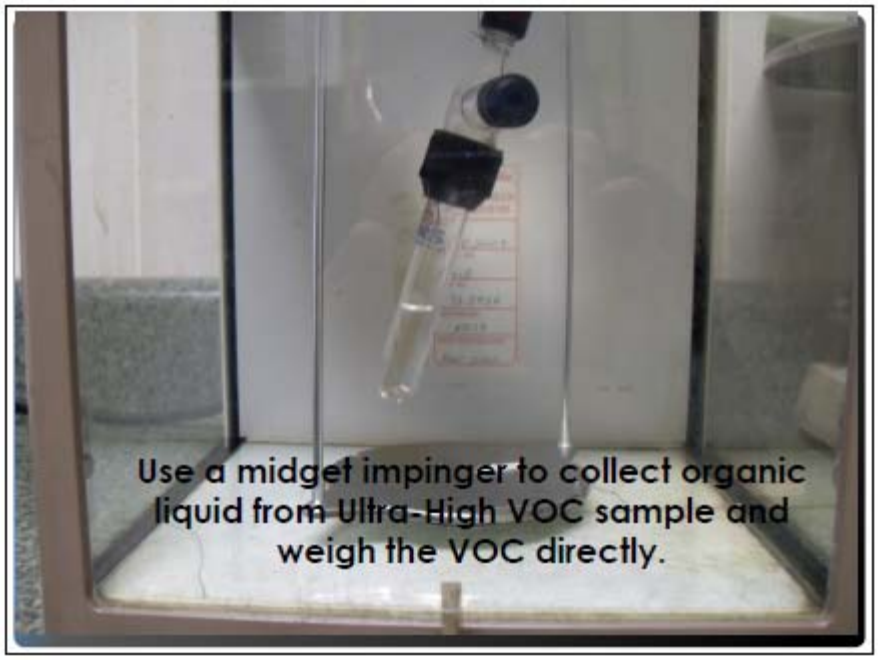

METHOD 25
IMPROVEMENTS
0.3 micron glass fiber filter.
2.0 micron gff for inlets
Elevated trap recovery temperature.
Purge CO2 interference at 25°C with cold trap in line.

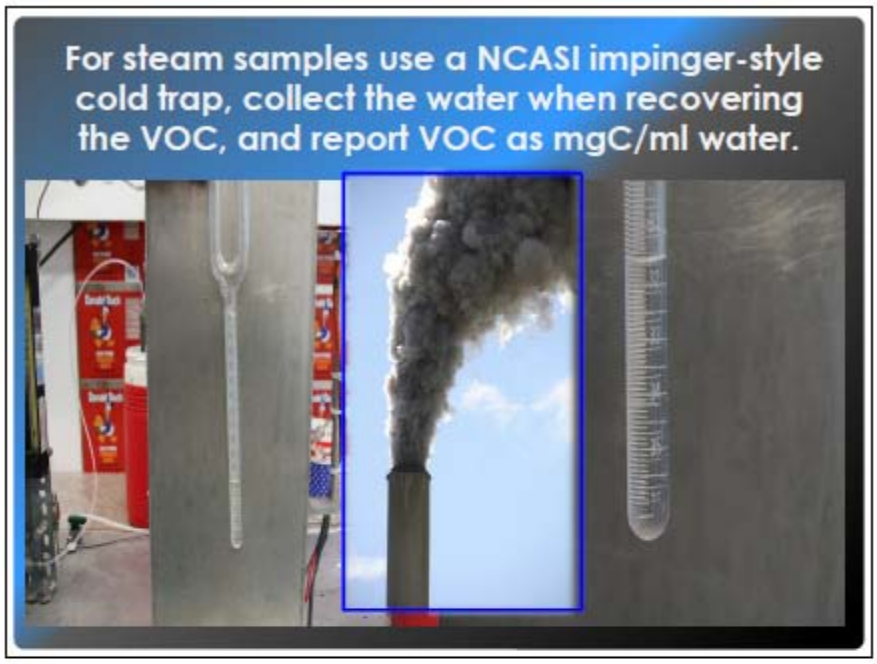

ELEVATED TRAP RECOVERY
Necessary for complete recovery of polymerizable organic compounds.
Vapor phase when collected, but polymerize on warming.
Recover at 50°C lower than cleanout temperature to assure low background.

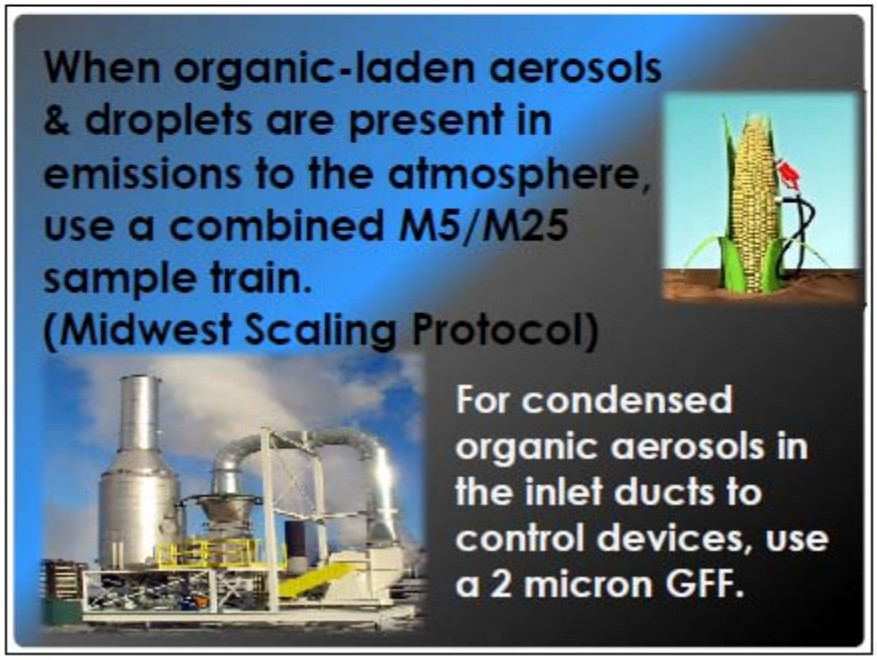

Purge trap of CO2 at 25°C
CO2 associates with water AND with organic compounds.
CO2 interference can be up to ~100 ppmC if not removed.
The "warm purge" cannot add or subtract VOC from the sample, it can only reduce CO2 interference.
DRY ICE TRAP
SAMPLE TRAP
DRY ICE TRAP
CO_2 = 15%
H_2O = 30%
Begin cold purge
Warm purge
Sample recovery not shown
Second warm purge
Zero air.
150
100
50
25
0
ppm CO_2

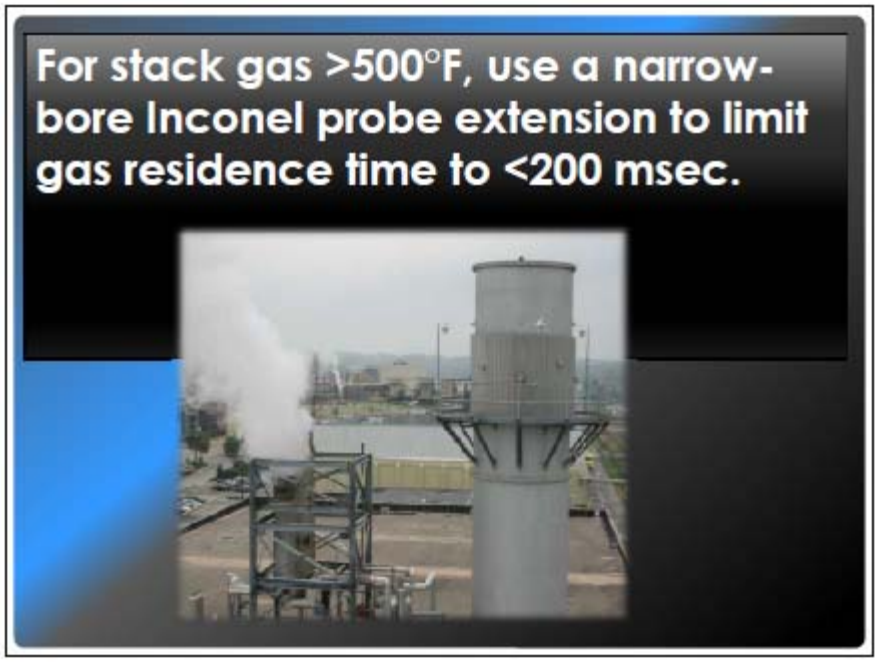

Ultra-High VOC testing:
Marine Flares


Marine Flare Inlet, VOC cocentration = 2,500,000 ppmC with 60% methane
NESHAP Subpart Y requires M25 for compliance testing.
Method-25 must be modified to fulfill this requirement safely and accurately

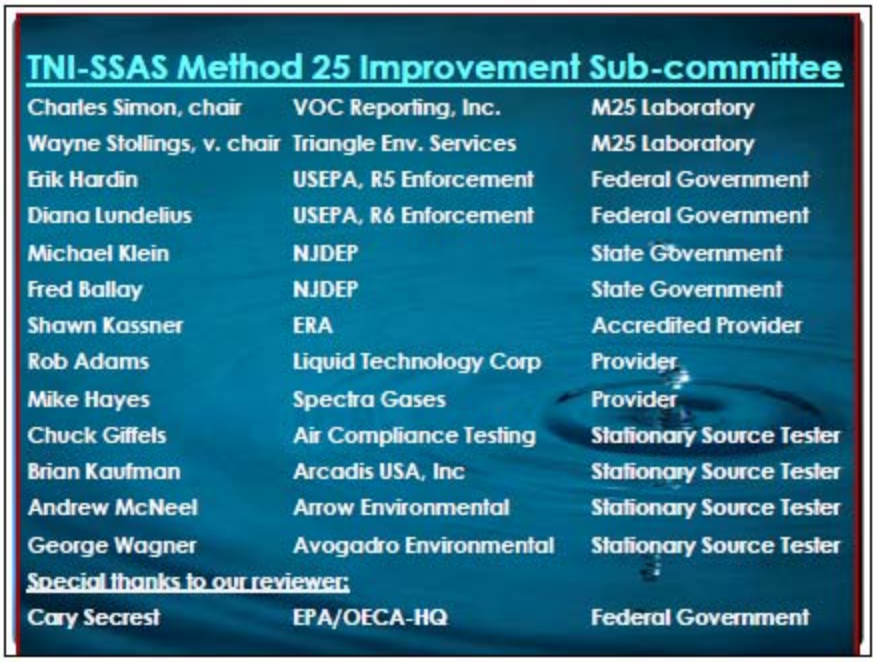

Use a midget impinger to collect organic liquid from Ultra-High VOC sample and weigh the VOC directly.


For steam samples use a NCASI impinger-style cold trap, collect the water when recovering the VOC, and report VOC as mgC/ml water.


When organic-laden aerosols & droplets are present in emissions to the atmosphere, use a combined M5/M25 sample train.
(Midwest Scaling Protocol)
For condensed organic aerosols in the inlet ducts to control devices, use a 2 micron GFF.


For stack gas >500°F, use a narrow-bore Inconel probe extension to limit gas residence time to <200 msec.


There are still unregulated and new VOC emission sources that present a challenge to the testing and regulatory communities.



TNI-SSAS Method 25 Improvement Sub-committee

Charles Simon, chair	VOC Reporting, Inc.	M25 Laboratory
Wayne Stollings, v. chair	Triangle Env. Services	M25 Laboratory
Erik Hardin	USEPA, R5 Enforcement	Federal Government
Diana Lundelius	USEPA, R6 Enforcement	Federal Government
Michael Klein	NJDEP	State Government
Fred Ballay	NJDEP	State Government
Shawn Kassner	ERA	Accredited Provider
Rob Adams	Liquid Technology Corp	Provider
Mike Hayes	Spectra Gases	Provider
Chuck Giffels	Air Compliance Testing	Stationary Source Tester
Brian Kaufman	Arcadis USA, Inc	Stationary Source Tester
Andrew McNeel	Arrow Environmental	Stationary Source Tester
George Wagner	Avogadro Environmental	Stationary Source Tester

Special thanks to our reviewer:

Cary Secrest	EPA/OECA-HQ	Federal Government



TNI-SSAS Committee Members, Associate Members and Guests

Maria Friedman, chair	TestAmerica	Laboratory
Stanley Tong	USEPA R9	Federal Government
Richard Swarz, v. chair	Missouri DNR	State Government
Michael Klein	New Jersey DEP	State Government
Greg O'Neal	North Carolina DAQ	State Government
Michael Schapira	Enthalpy	Laboratory
Jim Serne	TRC Solution	Stationary Source Tester
Theresa Lowe	CCI Environmental	Stationary Source Tester
Paul Meeter	Weston Solutions	Stationary Source Tester
Michael Hayes	Linde	Provider
Ty Garber	Phenova	Provider
Shawn Kassner	Phenova	Provider
Mike Miller	Member at large	
Ken Jackson	TNI	Program Administrator
William Daystrom	TNI	Webmaster
Rob Knake	A2LA	Provider Accreditor
William (Bill) Hirt	ACLASS	Provider Accreditor
Geneva Powman	ACLASS	Provider Accreditor
Tom Waderra	ERA	Accredited Provider
Bob O'Brien	Sigma-Aldrich	Accredited Provider
Charles Simon	VOC Reporting, Inc.	M25 Laboratory
Wayne Stollings	Triangle Env. Services	M25 Laboratory
DeAnna Oser	Georgia DNR	State Government

Recent Developments in SO3 Source Emission Testing Methods

David Ostaszewski
O'Brien and Gere

Abstract

Source emission testing to evaluate emissions of sulfur trioxide (SO3) is one of the more complex source emission field test programs that can be performed. Adding to the uncertainty is the wide variety of both manual field test methods and continuous emission monitoring approaches available and currently being used. This presentation will provide a brief history of SO3 testing methodologies and outline the various manual and instrumental methods in use today. Advantages and disadvantages of each sampling approach will also be discussed. Recent development of new ASTM test methods that will hopefully help standardize SO3 source emission test programs will also be reviewed.

SO_3 Emission Monitoring Method Overview and Update

David Ostaszewski, PE



O'BRIEN & GERE

SO_3 Emissions Issues

- The formation of sulfur trioxide (SO_3) and sulfuric acid mist (H_2SO_4) in flue gas streams has long been a major concern for coal-fired combustion units
- The presence of SO_3 and acid mists in the flue gas results in several process operational issues such as:
  - Visible plume problems and PM-2.5 precusor
  - Ductwork corrosion
  - Plugging of equipment including turning vanes, economizers, air heaters and baghouse units due to ammonium bisulfate formation
  - Combustion device efficiency reductions due to higher back-end temperatures required to limit acid gas formation and condensation
  - SCR catalyst degradation

© 2013 O' Brien & Gere

SO_3 Acid Gas Measurement Challenges

- SO_3 and H_2SO_4 measurement is one of the more difficult source emission testing challenges
  - SO_3 typically present in low concentrations
  - Very hygroscopic, tends to condense very quickly
  - SO_3 tends to absorb onto surfaces and flyash
  - Can exist in several states or phases simultaneously – SO_3 vapor, H_2SO_4 vapor, H_2SO_4 aerosol, droplets.
  - Equilibrium between phases varies with temperature, concentration, and flue gas moisture
  - Many sources of interference and bias in traditional test methods.
  - High levels of SO_2 present in coal-fired sources cause bias

© 2013 O'Brien & Gere

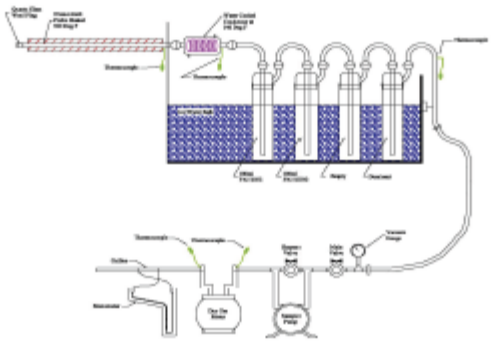
Traditional SO_3 Test Methods

- There are several sampling methods and analytical techniques for SO_3 measurement
  - ASTM D-3226-73T – The "Granddaddy" of SO_3 measurement methods
    - Original controlled condensation method developed in the 1960s
    - Glass wool plug in probe tip used for particulate removal
    - Probe temperature maintained at >500 Deg. F
    - Condenser temperature maintained at 140 Deg. F
  - USEPA Reference Method 8
    - Isokinetic method using USEPA Method 5 type probe
    - No controlled condensation, SO_3 is absorbed into isopropyl alcohol (IPA) solution. Barium perchlorate titration or IC analysis
    - Not suitable for measurements from coal fired boilers due to high SO_2 levels – portion of the SO_2 is adsorbed in the IPA biasing the sample.

© 2013 O'Brien & Gere

Manual SO_3 Sample Train Schematic

ASTM D-3226-73T CONTROLLED CONDENSATE METHOD

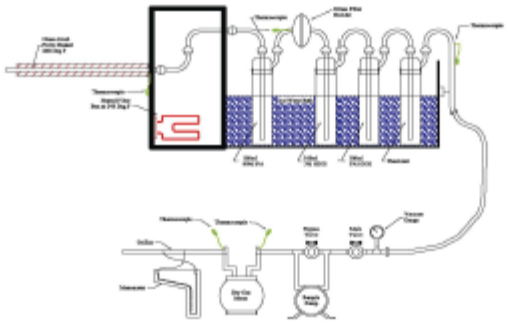


© 2013 O'Brien & Gere

O'BRIEN & GERE

Manual SO_3 Sample Train Schematic

USEPA REFERENCE METHOD 8



© 2013 O'Brien & Gere

O'BRIEN & GERE

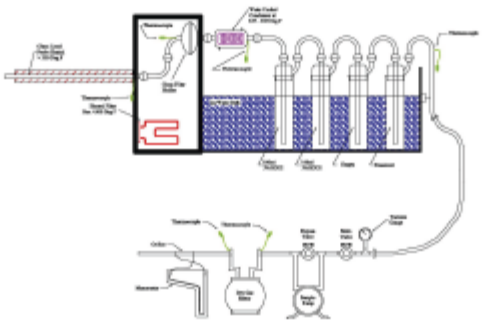
Traditional SO_3 Test Methods (Cont.)

- USEPA Reference Method 8A (Conditional Test Method 13)
  - Commonly used SO_3 test method promulgated by USEPA in 1996
  - Attempts to address sulfate and particulate matter interference issues associated with Method 8
  - Non-isokinetic, single point sample method
  - Heated sample probe and quartz filter upstream of condenser maintained at >500 Deg. F
  - Controlled condensation using modified Graham condenser maintained between 167 to 185 Deg. F
  - SO_3 sample recovered from condenser using water or IPA (recommended) rinse. Barium perchlorate titration or IC analysis on rinsate

© 2013 O'Brien & Gere

Manual SO_3 Sample Train Schematic

USEPA/NCASI METHOD 8A



© 2013 O'Brien & Gere

Traditional SO_3 Test Methods (Cont.)

- USEPA Modified Reference Method 8
  - Isokinetic method using Method 5 type probe
  - No controlled condensation
  - Cyclone separator used on the end of the sample probe to knock out water droplets
- USEPA Conditional Test Methods 13A and B
  - Developed by USEPA as an alternative to Method 8
  - Method 13A is a non-isokinetic method that uses a filter (heated to > 500 Deg. F) upstream of impinger train
  - Method 13B is similar to 13A, only isokinetic for sampling sources equipped with wet scrubbers that may have water droplets present in exhaust stream
  - No controlled condensation, SO_3 is absorbed into IPA impinger

© 2013 O' Brien & Gere

SO_3 Test Method Enhancements

- There are several modifications that can be made to manual SO_3 measurement methods to improve method performance
  - Use alternate means to remove particulate matter to reduce SO_3 sample loss in high PM locations(due to SO_3 absorption onto flyash or SO_2 oxidation)
    - inertial separation probes (coated)
    - electrostatic precipitation
    - cyclonic separation
  - Dynamic sample train spiking
  - Oxygen measurements taken at probe tip and from sample train
  - Change location - Sample downstream of particulate or acid gas control device and at multiple points whenever possible

© 2013 O' Brien & Gere

SO_3 Test Method Enhancements (Cont.)

- Use filter in backend of condensation coil to collect acid aerosols
- Be sure to condition PM filter or thimble prior to sampling
- Use a sample probe of at least 5 feet in length when sampling downstream of FGD to ensure acid droplets are vaporized. Maintain probe temperature at ≥600 Deg. F if possible (can lower temperature if longer sample probe is used)
- Verify on-site titration results with ion chromatography (IC)
- Adjust condenser coil temperature as stack gas moisture levels increase

© 2013 O' Brien & Gere

Condenser Coil Temperature Adjustment

Condenser Coiler Operating Temperature versus Moisture	
Percent Moisture	Condenser Coil Temperature Increase (°F)
≤ 16	Baseline
17	+2
18	+4
19	+6
20	+8

© 2013 O' Brien & Gere

Continuous SO_3 Monitoring Methods

- Acid deposition probes (Breen, EES, Land)
  - In-situ measurement, acid dew point measurement procedure
  - Uses temperature controlled plate inserted into the flue gas stream to repeatedly condense and evaporate acid material
  - H_2SO_4 concentrations are evaluated using the formation and evaporation temperatures of the acid material.
- Can also potentially quantify other sulfate compounds
  - ammonium bisulfate
  - ammonium sulfate
  - sodium bisulfate



© 2013 O' Brien & Gere

O'BRIEN & GERE

Continuous SO_3 Monitoring Methods (Cont.)

- FTIR -
  - Under development, in-situ cross duct measurement, therefore no issues with sample loss or bias
  - Issues to resolve include - long term reliability, probe design, detection limit, interferences
- Continuous wet-chemical approach – EES/Pentol
  - Semi-extractive sample system using heated probe
  - Sample diluted in IPA and water in the probe head
  - Sample transported to instrument where analysis occurs, typically a reaction with bariumchloranilate measured with a photometer or equivalent.



© 2013 O' Brien & Gere

O'BRIEN & GERE

Continuous SO_3 Monitoring Methods (Cont.)

- Tunable Diode Laser
- Differential Optical Absorption Spectroscopy - (DOAS)
- Quantum Cascade Laser Spectroscopy – Thermo Scientific Arke SO3
  - Dilution-extractive sample system
  - Particulate removal via inertial particulate removal technique
  - SO3 generation at the probe location
- Cavity Enhanced Absorption Spectroscopy – Cemtek



© 2013 O' Brien & Gere

SO3 Measurement Developments - Stay Tuned for:

- There is significant activity in both manual and instrumental SO3 method development
- SO_3 instrumental method is currently under development by ASTM (WK34495)
  - Quantum cascade (QC) based
  - Will include dynamic SO3 spiking/generation requirement
- New SO_3 manual test method also under development – ASTM WK36509
  - Final validation testing conducted in 2013, early 2014, final ASTM method expected mid to late 2014
  - May be released in late 2013 as an USEPA "Other Test Method" (OTM) in current form
  - Controlled condensation method expected to include many of the method enhancements discussed earlier

© 2013 O' Brien & Gere

Expected ASTM SO3 Manual Sampling Method Details

- Acceptable for use at "clean" test location only(0.07 gr/dscf)
- Can be used downstream of wet FGD units as H2SO4 droplet particle size is relatively small so isokinetic sampling is not needed
- Sample train conditioning run required to be conducted prior to testing
- Sample probe and filter temperature varies with probe length
- Specified condenser coil dimension specifications
- Condenser coil temperature varies with flue gas moisture
- Sulfuric acid mist filter required (same temperature as coil)
- Required conditioned field blank train
- Condenser coil blanks required after each run
- IC analysis/confirmation

© 2013 O' Brien & Gere

O'BRIEN & GERE

QUESTIONS?



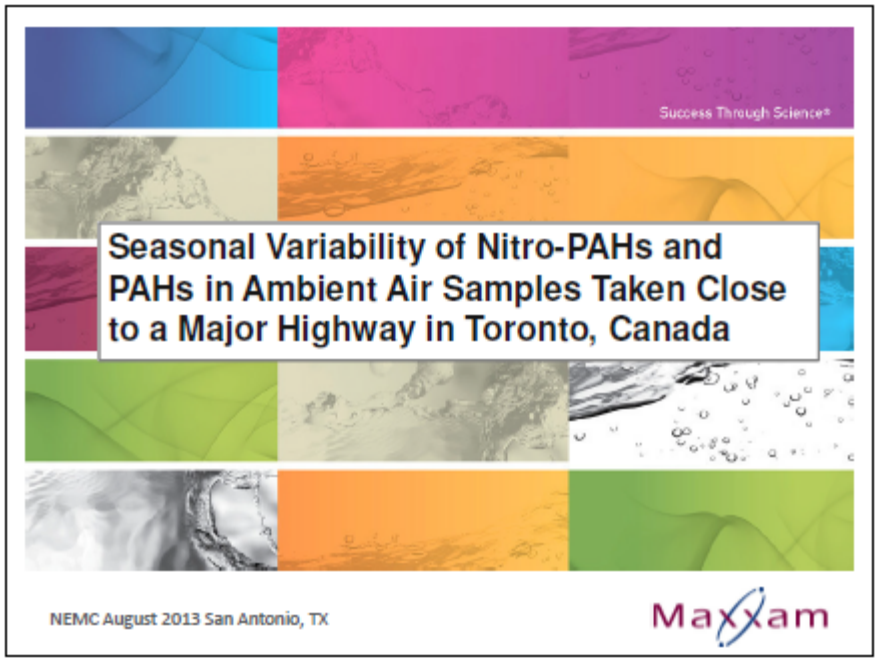
O'BRIEN & GERE

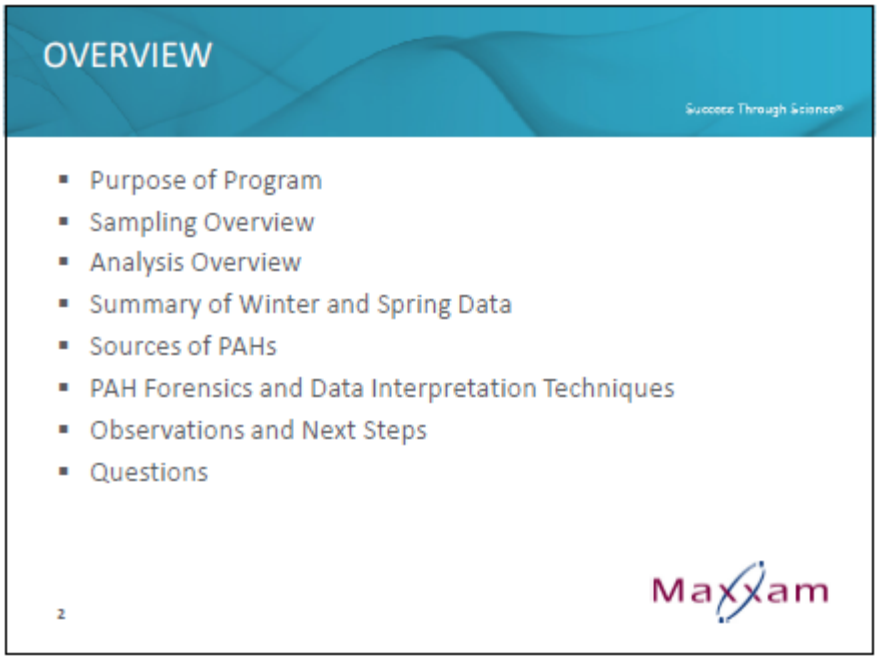
Seasonal Variability of Nitro-PAHs and PAHs in Ambient Air Samples Taken Close to a Major Highway in Toronto, Canada

Shawn Heier
Maxxam

Abstract

A year-long study of airborne nitro-PAH and PAH is planned to determine the seasonal variations at a monitoring site near the busiest highway in Canada and also one of the busiest in North America. Traffic flows along the highway at some points reach over 500,000 vehicles per day including trucks, cars, motorcycles etc. Results from the first two seasonal sampling periods (Winter and Spring, 2013) will be presented. Nitro-PAHs and PAHs associated with airborne particulate and the gas phase are being collected using a Hi-Vol (PS1) sampler equipped with a glass fibre filter and a combination polyurethane foam (PUF) and XAD resin to trap the target compounds. Particulate and gas phase sampling media were extracted separately via a Soxhlet method with dichloromethane and extracts were then cleaned, concentrated and then analyzed by High Resolution Mass Spectroscopy (HRMS). Results will be correlated with traffic volumes as determined from Ministry of Transport data, meteorological parameters (WD and WS particularly) and other air pollutants (PM2.5, O3 and NO2) measured at nearby sites operated by MOE. The results of this preliminary investigation may indicate the need for more intensive monitoring.


Success Through Science®
Seasonal Variability of Nitro-PAHs and PAHs in Ambient Air Samples Taken Close to a Major Highway in Toronto, Canada
NEMC August 2013 San Antonio, TX
Maxxam


OVERVIEW
Success Through Science®
Purpose of Program
Sampling Overview
Analysis Overview
Summary of Winter and Spring Data
Sources of PAHs
PAH Forensics and Data Interpretation Techniques
Observations and Next Steps
Questions
2
Maxxam

Purpose of the Sampling Program

Success Through Science®

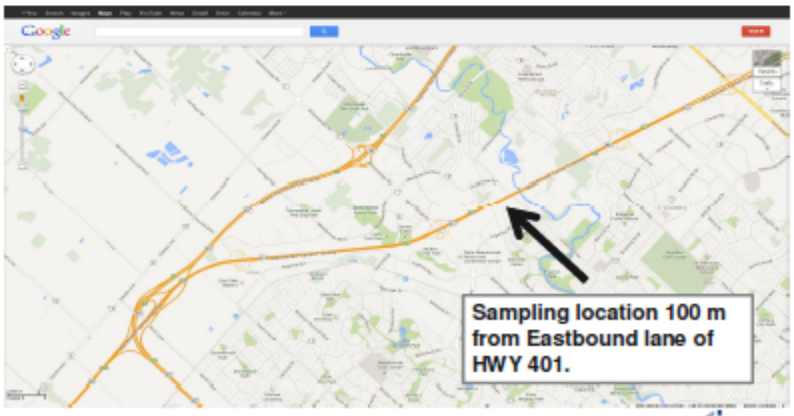
- Determine seasonal variability and correlation to meteorological parameters and other air pollutants ($PM_{2.5}$, O_3 and NO_2)
- Recent PAH Forensics projects have yielded a gap in our database for background nitro-PAHs (NPAH) and PAHs around transportation routes
  - Determine correlation between soil and air data around a major highway
  - Utilize and validate Data Interpretation Techniques based on the source of the PAHs

Maxxam

3

Sampling Location

Success Through Science®



Maxxam

4

Sampling Location

Success Through Science®



- Section of highway is currently under construction
- Average commuter traffic is 160,200 per day
- Waiting on truck volume data

Maxxam

5

US EPA Method TO-13A for PAH & NPAH

Success Through Science®

- High Volume Sampler
- Houses PUF cartridge and round glass fibre pre-filter
- Collects 500 m^3 over 48 hours
- 4 Consecutive days of sampling



← PUF cartridge with XAD-2 resin



Filter and PUF holder →

High Volume Sampler →

Computerized Pump →

Maxxam

6

Modifications to Sampling Protocol

Success Through Science®

- The method requires 300 m^3 to be sampled using a high-volume sampler (0.225 m^3/min for 24 hr). In this study, for lower detection limits, 500 m^3 of air was sampled at 0.176 m^3/min for 48 hr.
- To ensure that the sample volume would not adversely affect the collection efficiency a "breakthrough" study was performed
- d9-1-nitropyrene was spiked onto the front half (FH) PUF and d10-fluorene was spiked onto the back half (BH) PUF.
- No breakthrough (FH to BH) or loss from the BH PUF.

7

Sample Preparation

Success Through Science®

- Samples were divided and extracted as filter (particulate bound), Front Half (FH PUF + XAD-2 resin) and Back Half (BH PUF).
- Samples were then spiked with the following surrogate standards:

1-Nitropyrene-2H9	Acenaphthylene-2H8	Dibenzo(a,h)anthracene-2H14
2,6-Dimethylnaphthalene-2H12	Benz(a)anthracene-2H12	Dibenzo(a,i)pyrene-2H14
2-Methylnaphthalene-2H10	Benzo(a)pyrene-2H12	Fluoranthene-2H10
2-Nitrofluorene-2H9	Benzo(b)fluoranthene-2H12	Indeno(1,2,3-c,d)pyrene-2H12
5-Methylchrysene-2H3	Benzo(g,h,i)perylene-2H12	Naphthalene-2H8
5-Nitroacenaphthene-2H9	Benzo(k)fluoranthene-2H12	Perylene-2H12
6-Nitrochrysene-2H11	Chrysene-2H12	Phenanthrene-2H10

8

Sample Preparation cont.

Success Through Science®

- Spiked samples were soxhlet extracted using dichloromethane for 20 hours and concentrated,
- Concentrated extracts were cleaned using 1% deactivated alumina,
- Cleaned extracts were concentrated and vialed for analysis,
- Prior to analysis the following recovery standards were added for isotope dilution:
  - d10-Acenapthene
  - d10-Pyrene
  - d12-Benzo(e)pyrene

9

Maxxam

Sample Analysis

Success Through Science®

- Sample extracts were analyzed using an Agilent 6890 Plus HRGC coupled with a CTC Analytics A200S auto-sampler and a Micromass Autospec Ultima HRMS
- Data was collected using selected ion monitoring (SIM) and isotope dilution
- Instrument method used was previously developed to achieve lower detection limits vs LRMS and greater specificity. This included column and injector port optimization to ensure all PAH and NPAH were properly recovered and resolved.
- A total of 42 PAH and NPAH compounds were targeted.

10

Maxxam

Why PAHs and NPAHs?

Success Through Science®

- PAHs and their nitrated derivatives or NPAHs are important organic pollutants in the atmosphere,
- The International Agency for Research on Cancer (IARC) has ranked several PAHs and NPAHs as group 2A or 2B
  - This indicates they are probably or possibly carcinogenic to humans
- PAHs and NPAHs typically originate from incomplete combustion of organic matter:
  - Major sources of PAHs in Canada are forest fires, Al smelting, wood burning, agricultural fires and transportation.
- NPAHs can be formed in the atmosphere via reactions of their parent PAHs with radicals of NO_3 or OH

Maxxam

11

Sampling Conditions and Gross Data

Success Through Science®

	Winter	Spring
Sampling Dates	March 13-21	May 30-June 7
Sample Volume (m3)	507	513
Temperature (°C)	-2.9	17.1
General Weather Conditions	Mainly cloudy with Wet Snow & Rain	Mostly Cloudy with some rain
Ozone (ppb)	35	32
PM2.5 (ug/m3)	5	7
NO2 (ppb)	6	8
Particulate (ug/m3)	25.9	26.3
Total PAHs + NPAHs (ng/m3)	66.8	82.3
Total PAHs (ng/m3)	66.7	82.2
Total NPAHs (ng/m3)	0.052	0.098
% Airborne PAHs & NPAHs	98	98

Maxxam

12

Individual PAH and NPAH Summary Data

Success Through Science®

Parameter (ring number)	Average Winter Conc (ng/m3)	Air & Particulate Split %	Average Spring Conc (ng/m3)	Air & Particulate Split %
Naphthalene (2)	28	100/0	28	100/0
2-Methylnaphthalene	15	100/0	16	100/0
1-Methylnaphthalene	9.7	100/0	14	100/0
2,6-Dimethylnaphthalene	4.6	100/0	6.8	99/1
Phenanthrene (3)	2.6	96/4	5.2	98/2
2,3,5-Trimethylnaphthalene	1.5	100/0	2.5	99/1
Fluorene (2)	1.15	99/100	3.2	100/0
Fluoranthene (3)	0.74	78/22	0.97	82/18
Acenaphthene (2)	0.70	100/0	2.8	100/0
Pyrene (4)	0.59	72/28	0.71	77/23
1-Methylphenanthrene	0.18	94/6	0.36	95/5
Benzo(e)pyrene (5)	0.17	0/100	0.047	12/88
Benzo(b/j)fluoranthene	0.16	0/100	0.069	4/96
Chrysene (4)	0.16	4/96	0.094	13/88

Maxxam

13

Individual PAH and NPAH Summary Data

Success Through Science®

Parameter	Average Winter Conc (ng/m3)	Air & Particulate Split %	Average Spring Conc (ng/m3)	Air & Particulate Split %
Benzo(g,h,i)perylene (6)	0.13	3/97	0.061	4/96
Anthracene	0.11	90/10	0.21	93/7
Benzo(b)fluoranthene (4)	0.11	0/100	0.045	0/100
Dibenzothiophene	0.090	97/3	0.29	99/1
Benzo(a)anthracene	0.073	3/97	0.03	8/92
Indeno(1,2,3-cd)pyrene	0.070	0/100	0.027	0/100
Benzo(j)fluoranthene	0.057	0/100	0.024	0/100
Benzo(k)fluoranthene	0.056	0/100	0.019	0/100
Benzo(a)pyrene (5)	0.056	0/100	0.025	0/100
Acenaphthylene	0.049	0/100	0.12	90/10
4-Nitropyrene	0.040	0/100	0.044	23/77
Perylene (5)	0.035	0/100	0.006	0/100
Coronene (7)	0.026	0/100	0.080	2/23

Maxxam

14

Individual PAH and NPAH Summary Data

Success Through Science®

Parameter	Average Winter Conc (ng/m3)	Air & Particulate Split %	Average Spring Conc (ng/m3)	Air & Particulate Split %
7,12-Dimethylbenzo(a)anthracene	0.023	53/47	0.016	43/57
5-Methylchrysene (4)	0.019	71/29	0.046	63/38
1-Nitropyrene	0.011	0/100	0.034	0/100
Dibenz(a,h)anthracene	0.011	0/100	0.004	0/100
Dibenzo(a,e)pyrene	0.001	0/100	0.0052	0/100
2-Nitrofluorene	<0.001	NA	0.012	100/0
5-Nitroacenaphthene	<0.003	NA	0.0074	100/0
6-Nitrochrysene	<0.03	NA	<0.02	NA
Dibenzo(a,h) acridine	<0.01	NA	<0.001	NA
Dibenzo(a,j) acridine	<0.007	NA	<0.001	NA
Dibenzo(a,h)pyrene	<0.005	NA	<0.005	NA
Dibenzo(a,i)pyrene	<0.004	NA	<0.004	NA
3-Methylcholanthrene	<0.002	NA	<0.002	NA
Dibenzo(a,l)pyrene	<0.002	NA	<0.004	NA
7H-Dibenzo(c,g) Carbazole	<0.001	NA	<0.001	NA

15

Maxxam

Initial Comparison of Soil & Air Concentrations

Success Through Science®

Compound	Total Air	Soil
Units	ppb	ppb
Naphthalene	4.66	4.23
2-Methylnaphthalene	3.78	3.43
1-Methylnaphthalene	2.43	2.25
2,6-Dimethylnaphthalene	1.40	1.86
Fluorene	0.24	1.59
Phenanthrene	0.42	15.6
Anthracene	0.024	6.59
5-Nitroacenaphthene	ND	ND
Fluoranthene	0.084	32.4
Pyrene	0.078	36
2-Nitrofluorene	0.001	ND
Benzo(a)anthracene	0.006	16.2
Chrysene	0.011	30.3
4-Nitropyrene	0.002	ND
1-Nitropyrene	0.0004	ND
6-Nitrochrysene	ND	0.64

- Results from soil sample taken 2 years ago
- Sampling will be repeated and will be done at regular distance intervals from the Hi-Vol Sampler

16

Maxxam



SOURCES OF PAHs

Success Through Science®

Source of PAHs	Where Found	Type
Diesel/Fuel Oil	Leaking USTs, surface spills	Petrogenic
Motor Oils	Surface spills, waste oil USTs	Petrogenic
Coal Tar	Asphalt, Tar based sealers, roof shingles	Pyrogenic
Creosote	Wood treatment	Pyrogenic
Forest Fire Residue	Incomplete combustion	Pyrogenic
Perylene	Marine Sediments	Biogenic
Slag	Poor Quality Fill	Pyrogenic

Petrogenic – fossil fuels
Pyrogenic – combustion source
Biogenic – natural biological source

Maxxam

18

PAH SOURCE RATIOS
Literature Values

Success Through Science®

Ratios	Values / Sources	References
Phenanthrene / Anthracene	< 5 = Pyrogenic; > 5 = Petrogenic	Neff et al., 2005
Fluorene / Pyrene	+ 1 = Pyrogenic. < 1 = Petrogenic	Neff et al., 2005
indeno(1,2,3-cd)pyrene / (indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene	> 0.1 = Combustion	Motelay-Massei et al 2007; Yunker et al., 2002
Fluoranthrene/ Pyrene	< 1 = Petrogenic; >1 Pyrogenic	Motelay-Massei et al 2007
LMW / HMW	< 1 = Combustion	Zhang et al 2005;
benzo(a)pyrene / benzo(a)pyrene + chrysene	< 0.2 = Petrogenic; > 0.35 = Combustion	Zhang et al 2005; Zhang et al 2007

Table courtesy of Trium Environmental Solutions Inc.

Maxxam

19

PAH SOURCE RATIOS
HWY 401 Air

Success Through Science®

Ratios	Values / Sources	Winter	Spring	Ratios Suggest
Phenanthrene / Anthracene	< 5 = Pyrogenic; > 5 = Petrogenic	24	25	Petrogenic
Fluorene / Pyrene	+ 1 = Pyrogenic. < 1 = Petrogenic	2.4	5.5	Pyrogenic
indeno(1,2,3-cd)pyrene / (indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene	> 0.1 = Combustion	0.32	0.35	Combustion
Fluoranthrene/ Pyrene	< 1 = Petrogenic; >1 Pyrogenic	1.4	1.5	Pyrogenic
benzo(a)pyrene / benzo(a)pyrene + chrysene	< 0.2 = Petrogenic; > 0.35 = Combustion	0.4	0.41	Combustion

Maxxam

20

Observations and Next Steps

Success Through Science®

- Spring data is higher than the winter data and all data is consistent with combustion of transportation fuels i.e. vapour phase is > particulate phase or LMW > HMW PAHs
- Low concentrations of NPAHs were detected during both sampling events with higher concentrations in the spring
- Further forensic analysis of a more complete data set is required to determine suitable transportation combustion ratios
  - Soil data and air data will be analysed using double ratio plots
  - Soil data closest to the source should have a similar pattern

21

Maxxam

Observations and Next Steps

Success Through Science®

- More complete utilization of local air monitoring information
  - Site used is south of sampling location and could bias data interpretation.
- Obtain and utilize more complete traffic information
  - Data to date has focused on commuter traffic vs truck and car traffic.
- Analyse extracts for hydroxylated PAHs (OH-PAHs)
  - LC-MS/MS method developed for key indicator OH-PAHs
  - Determine if there is there a relationship between PAHs, NPAHs an OH-PAHs

22

Maxxam


Success Through Science®
QUESTIONS
23
Maxxam

Mil-53(Al) as a Sorbent for Large Volume Air-Sampler for Chemical Warfare Agents

Bill Williamson
Southwest Research Institute

Abstract

Mil-53(Al) (Basolite® A100) is a highly porous, metal organic framework (MOF) material that has favorable properties for the collection and preservation of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs), including high capacity and resistance to water-effects. In order to maximize the high capacity potential of this sorbent, it was coated onto Duocel® that is 80 pores per inch (ppi) reticulated vitreous carbon (RVC) with an open, porous structure allowing a high sampling rate. The combination of the high-capacity sorbent and cross-sectional area of the substrate facilitates much more rapid collection and concentration of chemicals over traditional sampling techniques such as XAD and is especially important for trace-level substances which may be forensically valuable. Small RVC coupons were coated with approximately 8.9 mg of Mil-53(Al) and four parameters (temperature, relative humidity, flow rate, collection volume) were systematically varied to evaluate performance under a range of conditions. All testing was conducted using 16 CWA-related compounds: N,N-diethyl aniline (DEA), 2-chloroethyl ethyl sulfide (CEES), diethyl ethyl phosphonate (DEEP), 2-chloroethyl phenyl sulfide (CEPS), 1,4-dithiane (DITH), O,O'-diethyl methylphosphonothioate (DEMPT), diethyl phosphite (DEP), diisopropyl fluorophosphates (DIFP), 1,4-thioxane (THX), dimethyl phosphite (DMHP), triethyl phosphate (TEP), bis(2-chloroethyl) sulfide (HD), O-isopropyl methylphosphonofluoridate (GB), 3,3-dimethylbutan-2-yl methylphosphonofluoridate (GD), diisopropyl methylphosphonate (DIMP) and dimethyl methylphospnonate (DMMP). Small RVC coupon recoveries for the 16 compounds averaged over all conditions were greater than 70% with the exception of GB (53%) and DMHP (35%). Furthermore, RSD over all conditions was less than 20% with the exception of DMHP (46%). This indicates the sorbent-coated RVC is very robust over conditions that are likely to be encountered in a field-setting. In general, the absorption affinity for the sulfur–containing compounds (THX, CEES, DEMPT, DITH) was lower than for the other classes of compounds tested. Preservation of the compounds on the Mil-53(Al)-coated RVC was tested at 0, 1, 3, 7, 14, 28, and 30 days post-collection. Percent loss over the 30-day period was less than 11% for each compound with the exceptions of DMHP (23%), GB (20%), and GD (20%), demonstrating adequate preservation for a minimum of 1 month. Finally, RVC large coupons containing approximately 30 mg of Mil-53(Al) sorbent were tested to demonstrate the potential to scale-up the sorbent/RVC system without sacrificing performance. In most instances, the large coupon performance was superior to that of the smaller coupons and traditional XAD tubes. Performance increase was especially clear for DMHP which improved significantly in both recovery (93%) and variability (6% RSD) over the small RVC coupons and XAD. The overall performance of the Mil-53(Al)/RVC air collection system indicates very efficient concentration of trace TIC and CWA substances is achievable via rapid, large volume sampling.

Southwest Research Institute

Homeland Security
Science and Technology

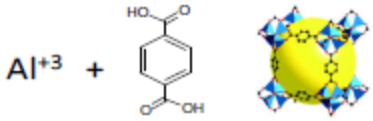
MIl-53(Al) as a Sorbent for Large Volume Air-Sampler for Chemical Warfare Agents

2013 National Environmental Monitoring Conference
San Antonio, TX
Date: August 7, 2013

Bill Williamson
Sr. Research Scientist

Introduction

- Develop a high volume rapid air sample collection system to collect, concentrate, and preserve volatile and semivolatile chemical warfare agents (CWA)
  - First Year: Surveyed 10 porous coordination polymers
    Selected Mil-53(Al)



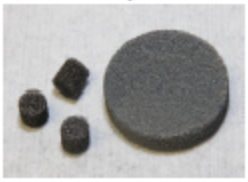
  - Second Year: Developed a sorbent/substrate preconcentrator. Focus of this presentation

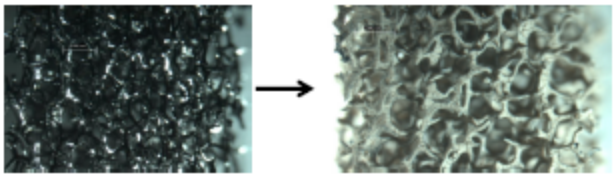
Evaluation Process

- High collection efficiency
  - Determine critical sampling parameters for the coated substrate system (flow rate, sampling time, and relative humidity, etc.)
- Preservation of compounds
  - Determine compound stability on the coated substrate system over a duration of one month prior to extracting the substrate system
- Demonstrate scalability
  - Verify that the substrate can be scaled without loss in performance

Deposition of MIl-53(Al) Onto Substrate

- Substrate selected was reticulated vitreous carbon (RVC) foam from ERG Aerospace
- Electrophetic deposition
  - Small (9 mm dia. x 9 mm)
  - Large (33 mm dia. x 9 mm)
- ESEM (before and after)



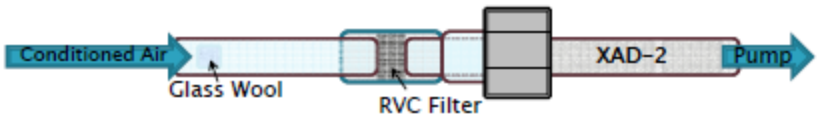


Test Compounds

- CEES: 2-chloroethyl ethyl sulfide
- CEPS: 2-chloroethyl phenyl sulfide
- DEA: N,N-Diethyl aniline
- DEEP: diethyl ethyl phosphonate
- DEMPT: O,O'-diethyl methylphosphonothioate
- DEP: diethyl phosphite
- DIFP: diisopropyl fluorophosphates
- DIMP: diisopropyl methylphosphonate
- DITH: 1,4-dithiane
- DMHP: dimethyl phosphite
- DMMP: dimethyl methylphospnonate
- GB: O-isopropyl methylphosphono-fluoridate
- GD: 3,3-dimethylbutan-2-yl methylphosphono-fluoridate
- HD: bis(2-chloroethyl) sulfide
- TEP: triethyl phosphate
- THX: 1,4-thioxane

5

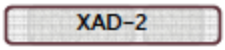
Test Configuration/Procedure



- Test procedure
  - Set temperature and humidity
  - Set flow rate
  - Deposited 10 µL of test compound mix onto glass wool (loading was1000 ng for each compound)
  - Collected air for desired duration

6

Extraction and Analysis

- Each sample yielded 3 extracts
  - Glass wool – verify that compounds were volatilized
    
    Extracted with 2-mL acetone
  - RVC filter – determine whether test compounds were captured
    
    Extract filter & glass with 10-mL acetone
  - XAD-2 – monitor test compound breakthrough
    

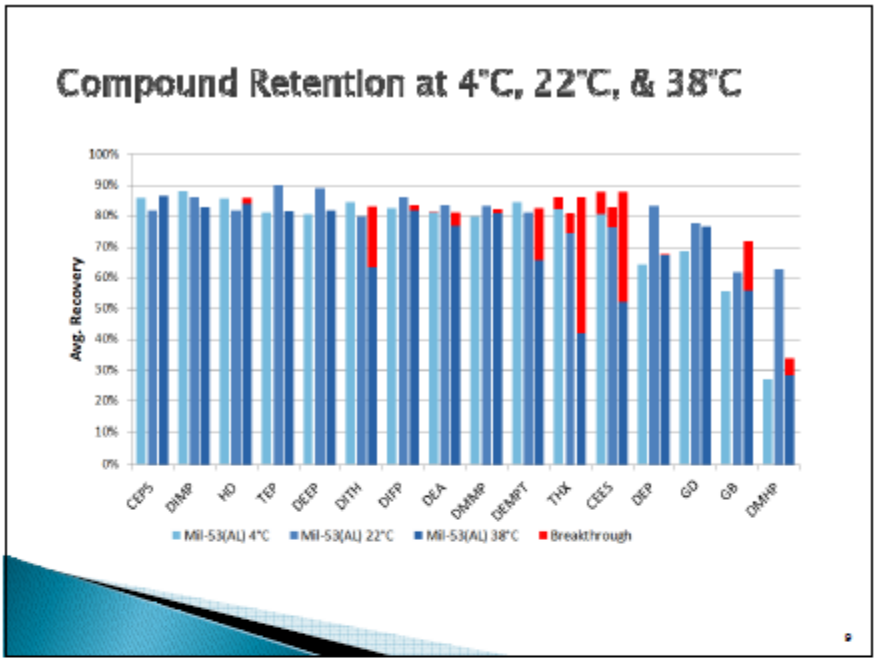
    Extract XAD with 5-mL acetone
- GC/MS analysis (EI, SIM mode)
  - Calibration range 5 – 250pg/µL

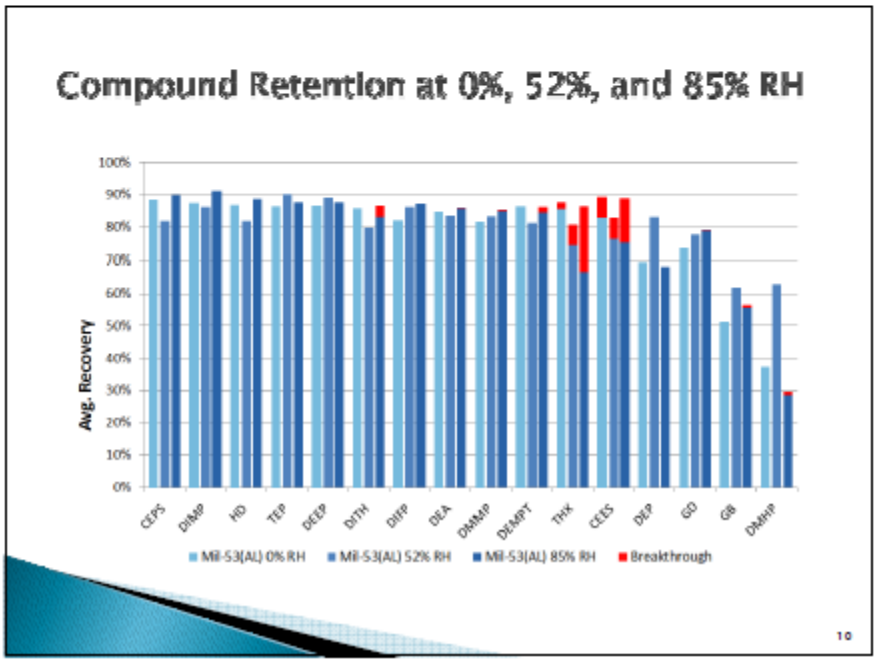
7

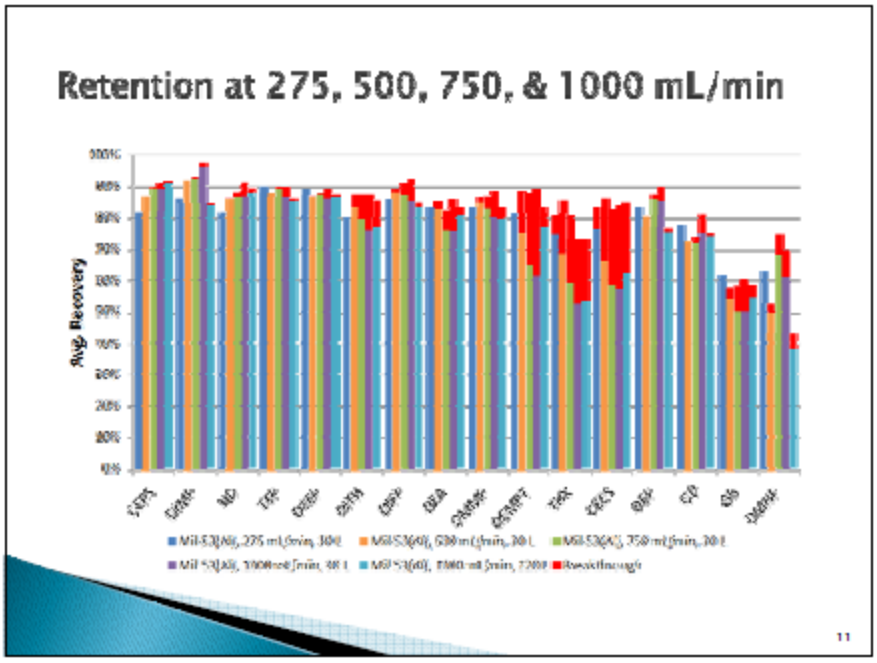
Collection Efficiency Evaluation

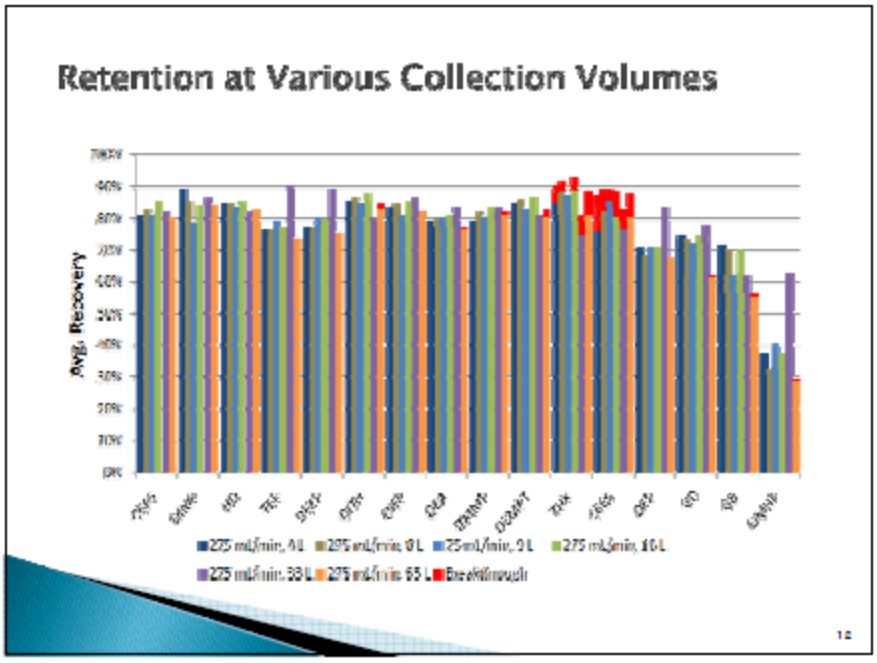
- Base conditions: 22°C, 50% RH, 275mL/min for 2 hr
- Temperature Range: 4 – 38C
- Relative Humidity: 0 – 85%
- Flow rate: 75 – 1000 mL/min
  - Determine critical flow rate
- Collection Volume: 4.1 – 66 L
  - Determine breakthrough volume

8


Compound Retention at 4°C, 22°C, & 38°C
Avg. Recovery
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
CEPS
DIMP
HD
TEP
DEEP
DITH
DIFP
DEA
DMMP
DEMPT
THX
CEES
DEP
GD
GB
DMHP
Mil-53(AL) 4°C
Mil-53(AL) 22°C
Mil-53(AL) 38°C
Breakthrough
9


Compound Retention at 0%, 52%, and 85% RH
Avg. Recovery
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
CEPS
DIMP
HD
TEP
DEEP
DITH
DIFP
DEA
DMMP
DEMPT
THX
CEES
DEP
GD
GB
DMHP
Mil-53(AL) 0% RH
Mil-53(AL) 52% RH
Mil-53(AL) 85% RH
Breakthrough
10


Retention at 275, 500, 750, & 1000 mL/min
Avg. Recovery
11

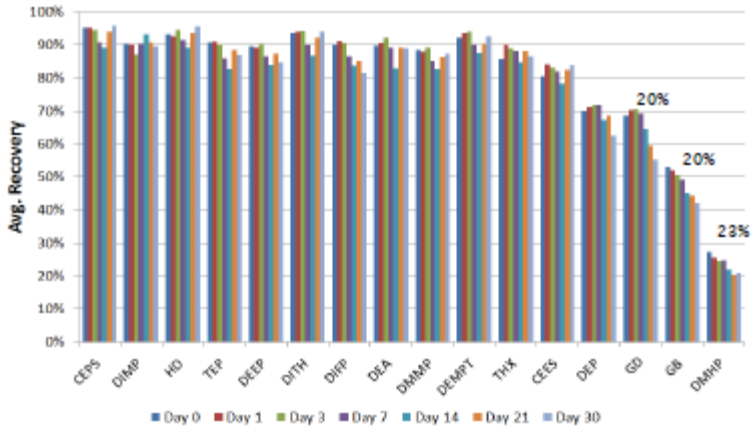

Retention at Various Collection Volumes
Avg. Recovery
12

Compound Preservation Study

- Base conditions: 22°C, 50% RH, 275mL/min for 1 hr.
- Sampled 48 replicates on the same day
  - Extracted all glass wool & XAD tubes on Day 0
  - RVC filters stored in a Freezer (-20°C) until extraction
  - Hold Times: 0, 1, 3, 7, 14, 21, & 30 days

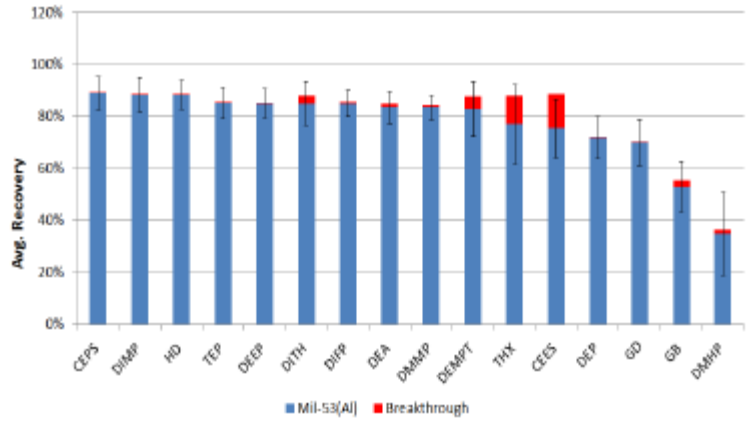
18

Compound Preservation At -20°C



14

Overall Performance of Small Coupons



- Error bars are ± 1sd of mean RVC recovery

15

Overall Performance

- Critical flow rate was between 275 and 500 mL/min for most compounds (face velocity 430 – 790 cm/min)
  - THX and CEES is less than 275 mL/min
- Mil-53(Al) was less selective for sulfur related compounds (CEES, THX, DEMPT, DITH, HD, and CEPS)
- ~9 mg of Mil-53(Al) on the substrate able to sample 65 L of air without significant breakthrough

16

Scaling to Larger Coupons

- Substrate face diameter increased and depth remained the same
- ~30 mg of Mil-53(Al) was deposited on the coupon
- Used a face velocity of 230 cm/min to determine sampling flow rate
  - 150 mL/min for 9mm coupons
  - 2.0 L/min for 33mm coupons
- Evaluated collection efficiency of large coupons

17

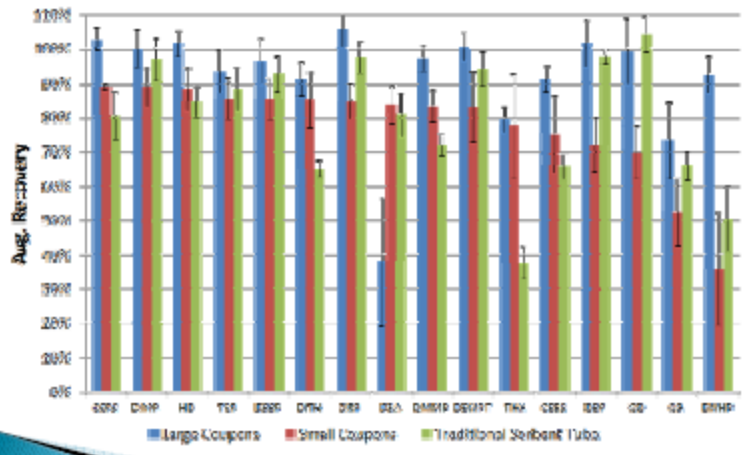
Setup for Testing Large Coupons



- Collected ambient laboratory air
  - 20°C
  - 2.0 L/min for 2 hr
- Loading was 2000 ng for each compound

18

Performance of Large Coupons



- Error bars are ± 1sd of mean RVC recovery

19

Conclusion

- Favorable collection performance over various climatic conditions.
- Easily extractable with low background, high sensitivity, high recovery, and low variability.
- Preserved test compounds for 1 month without significant loss.
- Can be scaled to adapt to various sampling requirements

20

Acknowledgements

- Funding for this project was provided by the DHS Chemical Forensics Program, Threat Attribution and Characterization Branch, Chemical and Biological Defense Division, Science and Technology Directorate, Department of Homeland Security under Contract / Interagency Agreement HSHQDC-10-C-00058

- Southwest Research Institute
  - Kristin Favela, PhD
  - Jeffrey Jones, MD
  - Charles Baker, PhD

21

Evaluation of an Automated Continuous Air Sampling System for Vapor Intrusion

Kyle Hunt
Signature Science

Abstract

Focus will be on an extended five week continuous sampling project conducted at Hill AFB in Utah to monitor VOCs.

Manually collecting SUMMA® canisters or sorbent tubes during vapor intrusion (VI) monitoring typically employs a single device to collect single samples with limited duplicates or distributive pairs. Such labor and equipment intensive sampling provides limits spatial and temporal data while also limiting the capability to record flow rates and sample durations real-time. Signature Science developed LESS™, a fully programmable, constant flow air sampler with an integrated micro-controller and data acquisition system that can collect up to 28 discrete air samples including simultaneous duplicates using a common manifold. Flow rates range from 5-750 mL/min.
To validate this new collection system against traditional technologies, comparison thermal desorption tubes were collected using LESS™ and a manual air sampling pump in a controlled laboratory test against 109 compounds (nC2 – nC12). Individual, duplicate, or distributive volume pair samples were collected to determine recoveries, false-positives, and false-negatives at safe sampling volumes.

Fifty-four (54) of 109 targets were quantified by a third-party NELAC accredited laboratory using EPA's Method TO-17. Remaining analytes were reported as TICs yielding total detections of 103 analytes: the exception being the most volatile hydrocarbons (acetylene, ethylene, ethane, and propane), 1-butanol, and methanol (spiking solvent). False-negatives were observed for 3 compounds at the 1 ppb-v concentration: 2-hexanone (31%), naphthalene (6%), and acetone (3%). Blank samples reported false-positives for acetone, hexachlorobutadiene, 1,2,3- and 1,2,4-trichlorobenzene, with levels at or near the analytical reporting limit.

At all test concentrations and collection volumes, LESS™ recovered the target analytes at similar precision and accuracy as the traditional manual pump. Recoveries for both were between 80% and 180% with correlations at or above 0.90.

In the spring of 2012, LESS™ was employed in a VI study at Hill AFB in Utah. The study was a long-term characterization of VI over diurnal sampling events across a year to estimate the changes in contamination levels over time. Typically, sampling methods for VI collect infrequent samples using SUMMA® canisters over a 24-hour time period. This approach produces limited sample data that may not accurately assess VI occurrence or the magnitude. Using a LESS™ manifold based sampler, continuous collection (at 4-hour intervals) over a five-week period showed the utility of dense sampling and the results demonstrated periods of vapors associated with VI in February and March, with less frequency episodes toward the end of sampling period.
For each collection event described above, this poster will present the data and summarize the findings.

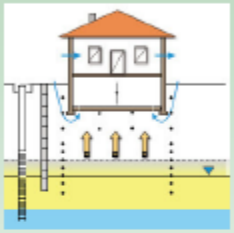


Topics

- Introduction
- Project Overview
- Monitoring Network
- LESS involvement
- Data trends
- Observations and thoughts
- On-going work
- Q and A

Introduction

- Vapor intrusion (VI) is a process by which chemicals in soil or groundwater migrate to indoor air above a contaminated site
- VI is an emerging concept with draft guidance starting in 2002 from the U.S. EPA
- Various guidance documentation from state agencies on the collection and frequency of samples to characterize VI



- signature science

ASU's Research Study

- Emphasis on temporal changes in indoor concentrations for VI
- Differences between indoor and subsurface sources
- Relationship between groundwater concentration and indoor air concentrations
- Factors that affect spatial and temporal variability
- Changes in vapor emissions over time
- Alternative assessments to point-in-time and point-in-space sampling
- Indoor chemical sources



- signature science

Hill AFB Off-Site Plumes

- Hill AFB Situation:
  - About 3000 homes above dissolved CHC plumes (10-100 µg/L, mean ~ 30 µg/L)
  - About half of the home owners have opted for indoor monitoring at least once a month
  - ASU purchased a home in Layton, UT for testing and research



- signature

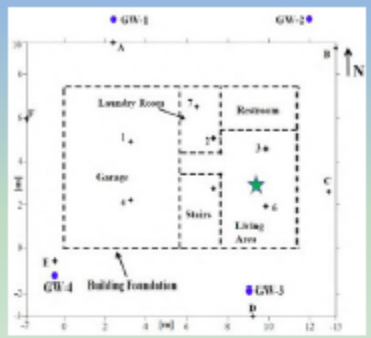
Sun Devil Manor



- signature

Monitoring Network

- Multi-level soil gas and groundwater sampling points
- Indoor air monitoring (VOCs, radon)
- Differential pressures, soil moisture, soil temperature



- Weather (wind, barometric pressure, rainfall, outdoor T)
- HVAC operation, indoor T, exchange rate (SF_6)

signature

Samples Collected: Natural Conditions

- **Indoor air**: About 8000 samples across 30 months at 2h (inst) and 4h (avg'd) intervals
- **Building dynamics**: Every 2 min or 10 min across 24 months
- **Indoor Air Exchange Rate**: About every 30 min over 20 months





signature

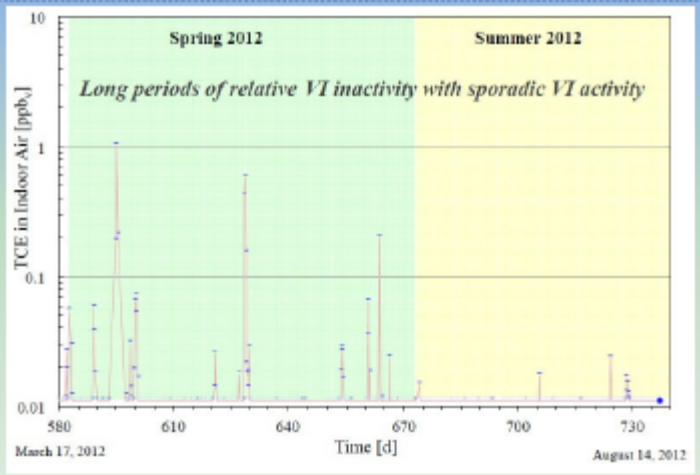
Where do we come in?

- ASU sorbent collections:
  - Using two SRI 10-port gas sampling valves controlled by PeakSimple.
  - Tenax GR/Carboxen 569
  - 40 tubes per "event" using manual process
- LESS sorbent collections:
  - Carbograph TD1/Carboxen 1003
  - Automated process
  - Mimic ASU's sample collection
  - Collections over ~ 2 months



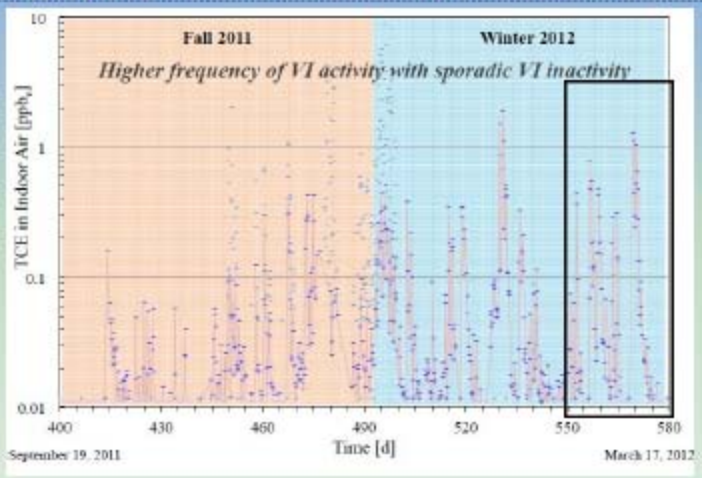
- signature science

Temporal Trends (Part 1)



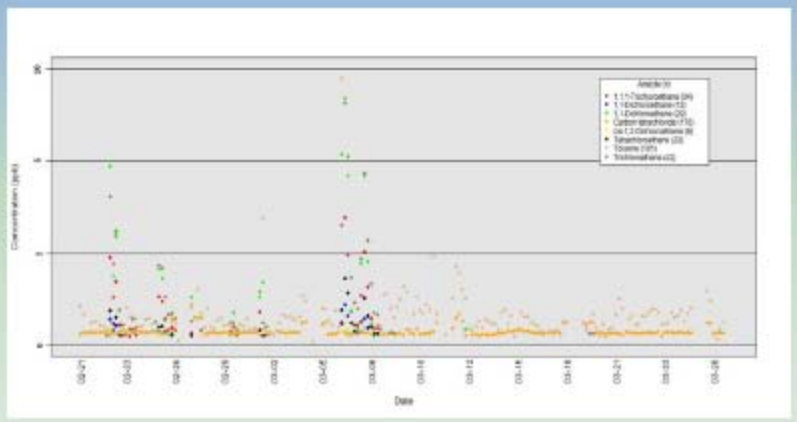
- signature science

Temporal Trends (Part 2)



signature science

LESS Field Data



signature science

Observations and Thoughts



- Temporal concentration behavior appears to be "structured" and not random
- Over some time periods the temporal behavior has a repeatable daily pattern
- Periods of activity and inactivity
- Considerations should be made for sampling plans and frequency, especially if this a new site characterization

Sampler Comparisons

- Both sampling systems show similar trends in VI activity
- Unlike the manual ASU system, LESS can sample 24/7/365; no down time
- LESS can support remote communications
- LESS is portable to allow various sampling collections to characterize the entire site
- Efficient collection of samples with LESS helps researchers minimize labor and analysis costs



Thanks to:

- Chase Holton, Dr. Emma Luo, Yuanming Guo, Dr. Paul Dahlen and with the *Fulton Schools of Engineering at ASU*....Go Sun Devils!



- Kyle Gorder and Erik Dettenmaier at *Hill AFB*.

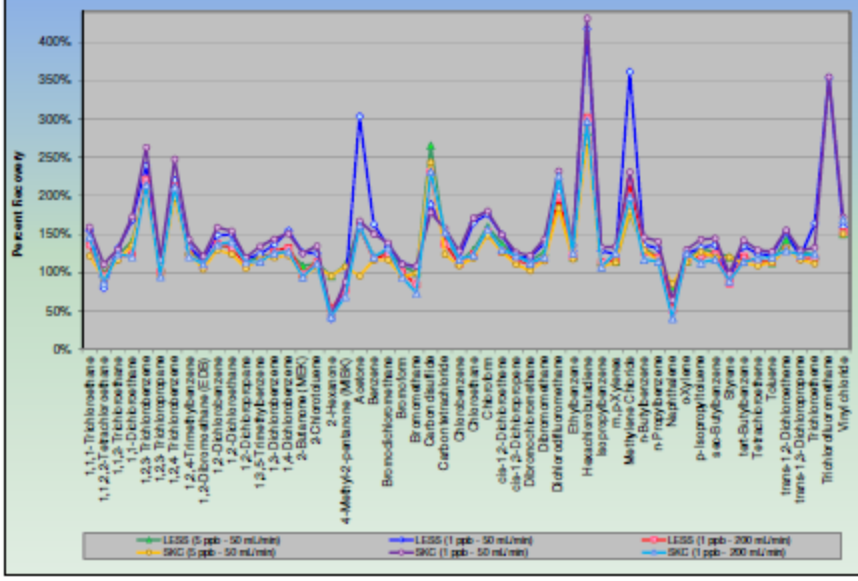
On-going work

- Completed a short collection study with Air Alliance Houston
- Collected diurnal air samples in Pasadena, Texas
- Upcoming project collecting samples outside of Alberta (oil sands region) to investigate odor complaints





I have a Poster!



Questions?

- **Contact:**

Kyle Hunt, CQA
Signature Science, LLC
8329 North MoPac Expressway
Austin, TX 78759
Office: 512.583.2463
Mobile: 512.705.0123
kylehunt@signaturescience.com



- signature science

Mobile Monitoring to Locate and Quantify Open Source Emission Plumes

Chatten Cowherd
MRI Global

Abstract

Open sources are those that emit air pollutants to the atmosphere without passing through a confined flow stream like a stack or a duct. Traditionally inventoried open dust sources include paved and unpaved roadways, surface mining, agriculture and wind erosion. Across the nation, open sources account for the majority of directly emitted PM 10, and for emissions of gasses such as ammonia, biogenic species and other pollutants of regulatory concern. Besides the open sources associated with traditional emission inventory categories, interest has also developed in a range of other source activities associated with oil and gas recovery and with leaks in chemical processing operations. It should be noted that unlike the case for ducted sources, emission test methods for open sources have never been subjected to the extensive standardization required to support emission standards.

This paper explores the use of vehicle-mounted "continuous" pollutant concentration monitors for mapping the plumes crossing roadways downwind of emission release points at "ground level." Analysis of lateral (cross-wind) structure can be used to evaluate plume configuration--clearly distinguishable plumes vs. overlapping plumes of more diffuse characteristics. In addition, knowledge of meteorological conditions during the monitoring period can be used to identify the locations of emission release points and to assess the magnitude of emissions. One of the key advantages of this approach is the ease of implementation in comparison with other monitoring strategies. The proposed approach requires only a light-duty test vehicle (and operator), a continuous pollutant monitor, a GPS unit, and a data logger for accumulating the instantaneous readings. In the case of mixed gas releases, a predominant pollutant such as methane can be used as a tracer. Information derived from this approach can be used to classify the importance of the sources within a study area based on the magnitude of cumulative impacts. This paper also assesses the accuracy of the mobile monitoring method in comparison with alternative test methods that utilize fixed platforms to quantify emissions from open sources.

Mobile Monitoring to Locate and Quantify Open Source Emission Plumes

August 7, 2013

by Chatten Cowherd, Ph.D.

Presentation Outline

- Importance of open sources of air pollutants
- Measurement and modeling challenges
- Deficiencies in current assessment tool kit
- Progressive quantification using low-cost screening methods for tiered application
- Mobile monitoring as an effective tool for locating and quantifying open source emissions
- Conclusions

2

Source Definition

- Open sources releases are by definition unconfined (non-ducted) in nature
- Gaseous emissions that occur as leaks from confined process flows are included
- Open sources also include conglomerations of scattered ducted sources for which individual characterization is not feasible, as in roadway traffic

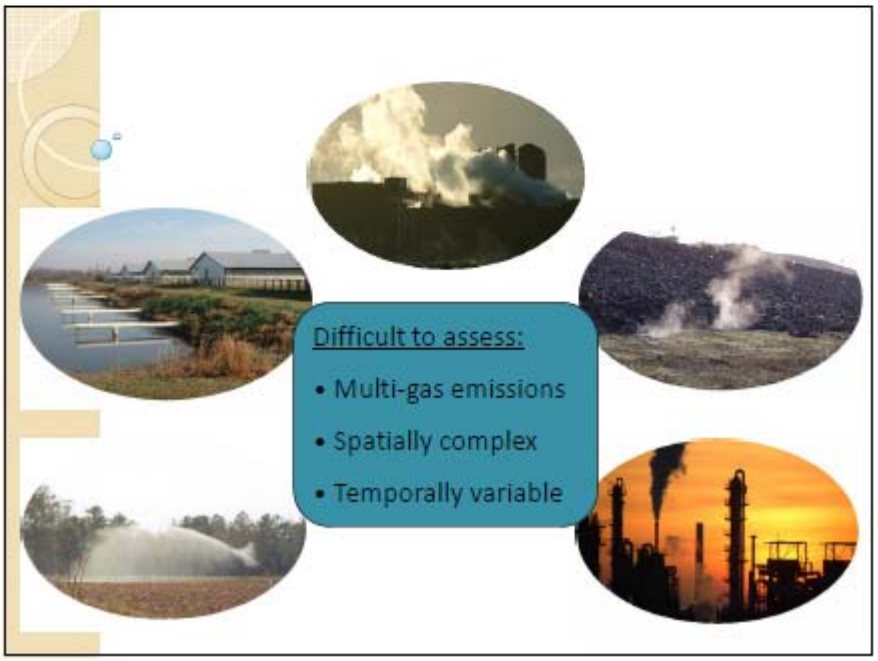
3

Example Open (Non-Ducted) Sources

- Dust releases from soil disturbance (vehicles and wind)
  - Public roads
  - Open pit mines
  - Desert high winds
- Wildfires
- Regulated gas emissions (e.g. GHGs)
  - Area sources
  - Processing leaks

4



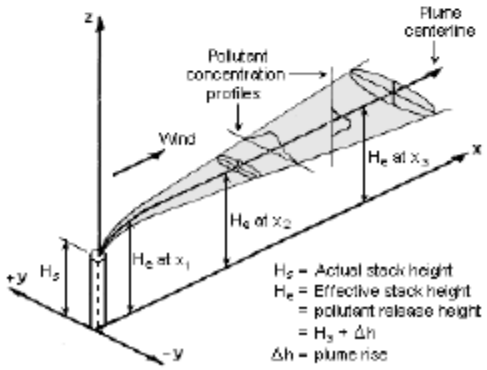

Difficult to assess:
• Multi-gas emissions
• Spatially complex
• Temporally variable

Convention Air Pollution Control

- Designed for applicability to ducted sources
  - Easily identifiable fixed locations
  - Relatively steady emissions
- Well developed assessment tools apply mostly to point and uniform area sources
  - Emission measurement
  - Dispersion modeling
  - Validation protocols supported by USEPA

7

Idealized Dispersion as Basis for Plume Models



8

Source Complexities in Open Pit Mine

Moving point sources of varying intensity



9

Open Source Emission Testing Challenges

- High natural variability (spatial and temporal)
  - Variations in source location
  - Variations in emission rate
- Lack of plume containment
  - Plume development influenced by turbulence and buoyancy
  - Plume transport affected by flow obstacles
- Similar challenges for dispersion modeling and impact assessment

10

Open Source Test Methods

Method Name	Monitor Location	Platform	Monitor Configuration
Plume (flux) profiling	Within plume flux plane downwind of source	Fixed	Samplers at multiple heights (tower)
Inverse modeling			Samplers distributed laterally at one height
Plume transect monitoring		Mobile	Vehicle-mounted at one sampling height
Lateral scanning	From remote position outside plume	Fixed	Standoff detection (path integrating)

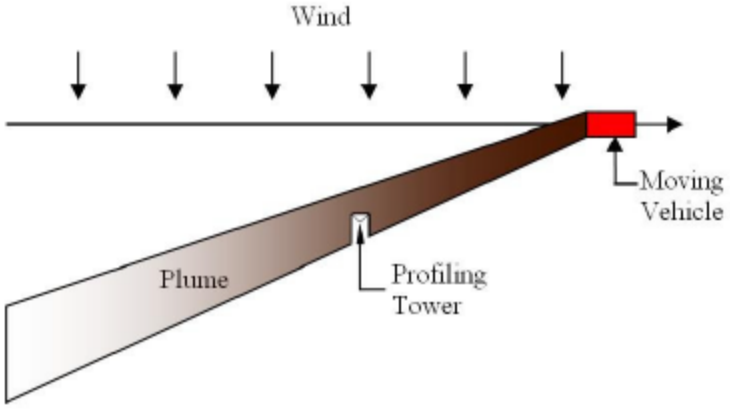
11

Plume (Flux) Profiling: Accepted Reference

- Profiling tower(s) deployed immediately downwind from source edge
- Multipoint plume measurements versus height
  - Mass concentration
  - Wind speed
  - Flux = concentration X wind speed
- Requires stable ambient crosswinds
- Utilizes simple mass balance calculation scheme independent of dispersion modeling

12

Cross-Wind Plume Dynamics
(moving point source)



13

Collocated Plume Profilers



14

Reverse-Impact Dispersion Modeling

- Measure ground-level pollutant concentration across sampling array in ambient impact zone (>50 m downwind)
- Collect applicable meteorological data (wind speed and direction, atmospheric stability)
- Apply dispersion model in reverse
  - What emission rate produces the observed air quality impacts?

15

Progressive Quantification

- An effective strategy for identifying and quantified undocumented open sources,
- Start with survey methods using mobile platforms
- Progress to more direct (and expensive) methods as survey results demonstrate source significance

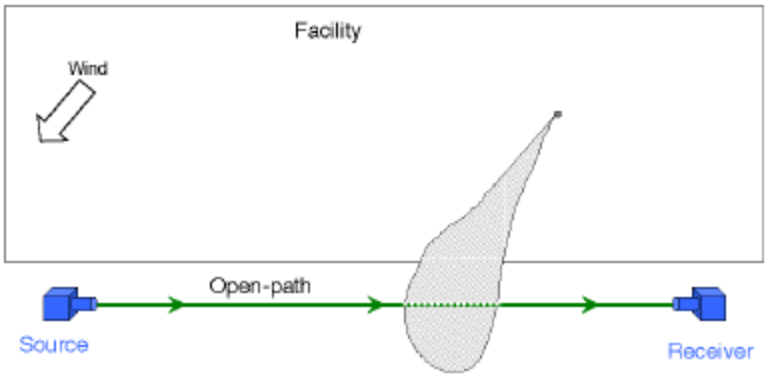
16

New Measurement Technology

- High-tech options involving fixed platforms and stand-off detection, e.g., fence-line monitoring
  - Best for long term application on fixed sources
- Infrared cameras for visualizing emissions from flares
  - Suitable for identifying sources but not emission rates
- Mobile platforms for "drive-by" scans of plume structure
  - Suitable for survey analysis of source components

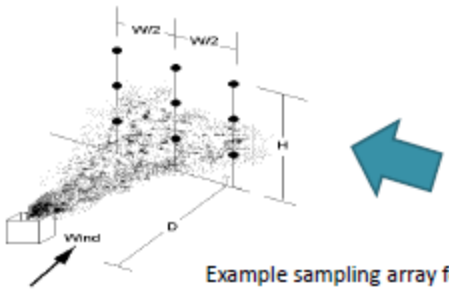
17

Fenceline Monitoring with Lateral Scanning



18

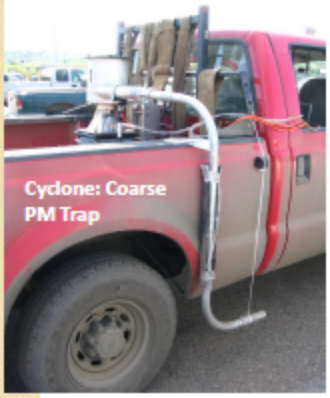
Reference Profiling Array for Validating Lateral Scanning



Example sampling array for cross-referencing against standoff detection method involving lateral scanning

19

Mobile Monitor for Road Dust Emissivity Mapping





20

Mobile Monitoring--Road Survey



21

Elements of Mobile Monitor

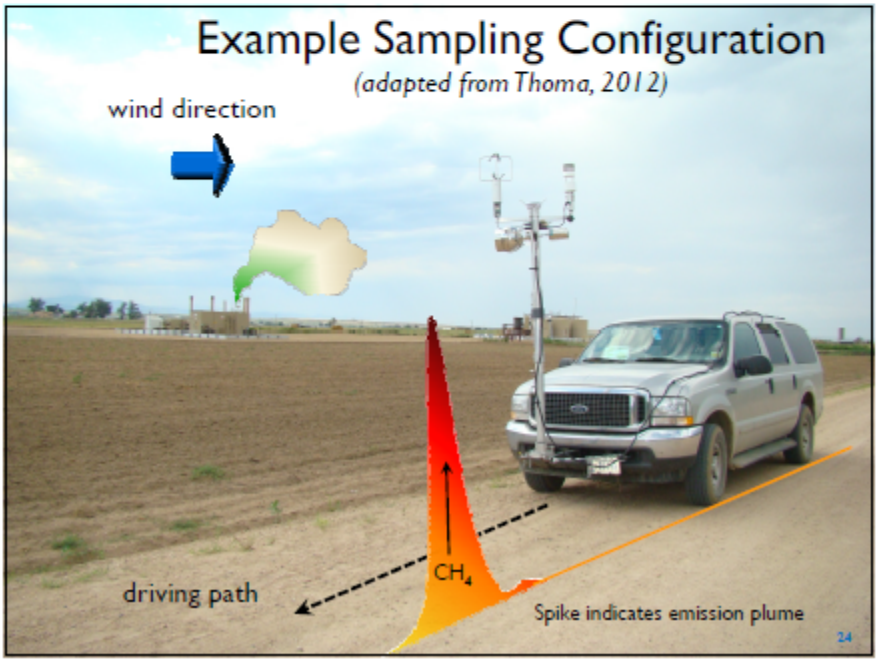
- Light-duty host vehicle
- Continuous concentration monitor
- Sampling line with inlet above vehicle
- GPS unit for locating monitoring points
- Data logger

22

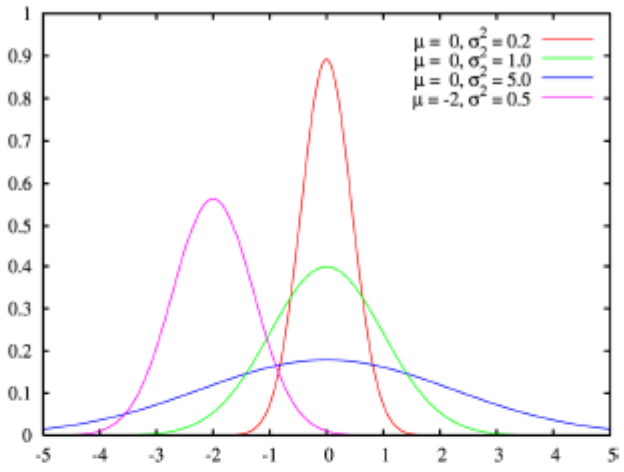
Operation of Mobile Monitor

- Drive when wind conditions are most suitable for consistent plume transport
  - Moderate wind speeds (5 to 12 mph)
  - Consistent wind direction (low meander)
  - Absence of plume lofting (neutral to stable atmospheres)
- Drive at constant speed until locating plume(s)
- Perform multiple scans of identified plumes

23



Idealized Overlapping Plumes



25

Analysis of Plume Scans

- Isolate significant plumes obtained from mobile monitoring
- Repeat monitoring for different wind directions
- Use information to project locations of sources
- Apply inverse dispersion modeling to bracket emission rates
- Refine process to improve quantification

26

Conclusions

- Open sources are receiving increasing attention as contributors to air quality problems
- Traditional assessment tools are not well suited to addressing open sources
- Mobile monitoring is an effective survey method to locate and characterize problematic open sources
- For sources indicated as significant, more refined (and expensive) methods can be applied
- Check out www.openairsource.org for more information

27

On-Site Real-Time Air Monitoring for Chemical Emergencies

Dominic Lortie
Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ)

Abstract

The Centre d'expertise en analyse environnementale du Quebec (CEAEQ) is a government agency within the ministry of Sustainable Development, Environment, Wildlife and Parks of the province of Quebec, Canada, which brings together a wide range of specialists in the fields of biology, chemistry, ecotoxicology and microbiology. The CEAEQ is renowned internationally for its expertise in environmental analysis laboratory certification, quality management systems, the preparation and sale of reference materials, and for international proficiency testing.

With its fleet of mobile labs, the CEAEQ Field Studies team of specialized chemists and technicians can be deployed rapidly on the field. One of the key roles of the Field Studies team is to provide 24/7 assistance to the technical advisers from Urgence-Environnement Québec, giving scientific support directly on the field. The most serious emergencies very often have an impact on ambient air quality while directly threatening populations, first responders and the environment. To respond to this type of event, the Field Studies team frequently put its TAGA (Trace Atmospheric Gas Analyzer) mobile laboratory into action. This mobile lab is equipped with over twenty detectors and scientific instruments, including a tandem atmospheric pressure chemical ionisation mass spectrometer (APCI-MS/MS). These instruments allow for a complete real-time characterisation of ambient air, directly on-site, thus giving the emergency team most valuable information on the emitted contaminants. Concrete examples of environmental emergencies and air quality studies made with the TAGA mobile lab will be presented. The contaminants identified and the concentrations measured during these interventions will be illustrated to highlight the contribution of the TAGA mobile lab and its team to the management of these situations.


Centre d'expertise
en analyse environnementale
du Québec
On-Site Real-Time Air Monitoring
for Chemical Emergencies
Your Text Here
Dominic Lortie, M.Sc. Chemist
Québec


Centre d'expertise
en analyse environnementale
du Québec
CEAEQ – The Organization
Québec

Centre d'expertise
en analyse environnementale
du Québec



CEAEQ – The Organization

- …is an agency within the Ministry of the Environment of the Province of Québec…
  - Laboratory analyses (chemistry, biology, microbiology)
  - Accreditation and proficency testing
  - Ecotoxicological studies
  - Field studies (emergencies)

Québec

Centre d'expertise
en analyse environnementale
du Québec



Field Studies – Emergency Team

- 5 Chemists + 2 technicians
- Services supported by mobile laboratories
  - Analytical and scientific support
  - In-situ sampling and analysis (water, air, soil, etc.)
  - Real-time air and water monitoring
  - Emission source identification and localization
  - Surveillance of decontamination activities
  - Calibration and maintenance of field instruments
  - Training of emergency responders

Québec

Centre d'expertise en analyse environnementale du Québec

TAGA Mobile Laboratory

TAGA : « Trace Atmospheric Gas Analyzer »

Real-time in-situ analysis of vapors, gases and particulate matters using a tandem mass spectrometer (MS/MS) and other instruments



Québec

Centre d'expertise en analyse environnementale du Québec

MS/MS

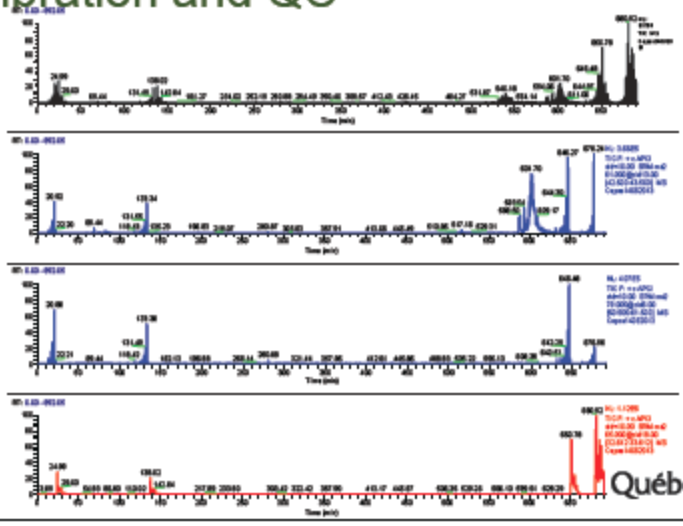
- Thermo Quantum Discovery MAX
- Customized source housing
- APCI source
- APPI capabilities
- Syringe system for standard injection
- Spring and air cushion table



Québec

Centre d'expertise
en analyse environnementale
du Québec

Calibration and QC



Québec

Centre d'expertise
en analyse environnementale
du Québec

10 Other Fixed Instruments

- Total Polyaromatic Hydrocarbons
  - *Ecochem PAS 1000i*



- Nitrogen Oxides
  - *Thermo 42i*



- Particles
  - *GRIMM 180*



Québec

Centre d'expertise en analyse environnementale du Québec

10 Other Fixed Instruments

- Sulfur Dioxide
  - *API 100E*



- Total Reduced Sulfurs
  - *CDN-101 thermal oxidizer*



- Sulfur Compounds
  - *Chromatotec Chroma-S*



- BTEX and VOCs
  - *Chromatotec AirmoBTX*



Québec

Centre d'expertise en analyse environnementale du Québec

10 Other Fixed Instruments

- Mercury
  - *Tekran 2537B*





- Metals
  - *Pall XACT 625*

- $\delta^{13}C$ signature for CO_2 and CH_4
  - *Piccaro G2201-i CRDS isotopic carbon analyzer*



Centre d'expertise en analyse environnementale du Québec

Portable Spectrometers

- GC-MS
  - *Inficon Hapsite E/R*



- FTIR
  - *Gasmet DX-4040*



- UV
  - *Cerex UV Hound*



Québec

Centre d'expertise en analyse environnementale du Québec

Other Portables



O_2, LEL, CO, H_2S, Cl_2, NH_3





O_2, CO_2, CH_4



4 gases + PID (MAH, NH_3, etc)



VOC, NH_3, aldehydes, etc.

FID / PID





VOC



Particulate matters



CH_4



Combustibles

Québec

Centre d'expertise
en analyse environnementale
du Québec

Remote Monitors







Québec

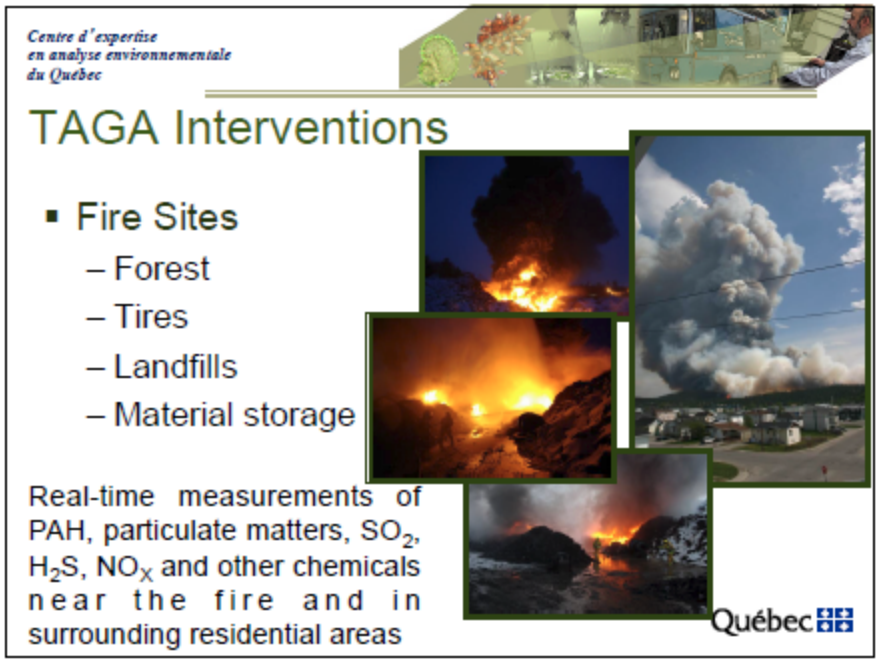
Centre d'expertise
en analyse environnementale
du Québec

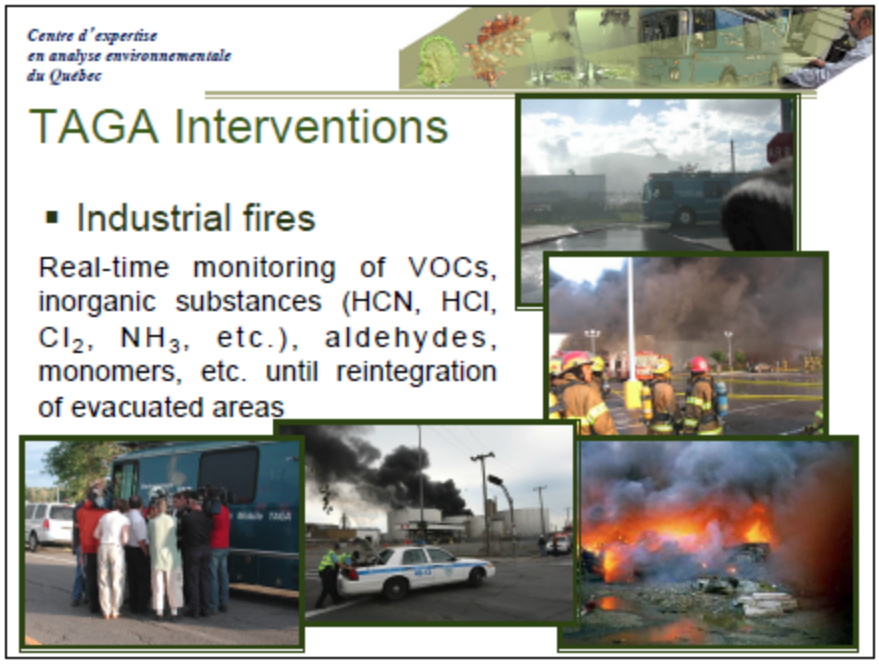
Local Weather Conditions





Québec


Centre d'expertise
en analyse environnementale
du Québec
TAGA Interventions
Fire Sites
– Forest
– Tires
– Landfills
– Material storage
Real-time measurements of PAH, particulate matters, SO_2, H_2S, NO_X and other chemicals near the fire and in surrounding residential areas
Québec


Centre d'expertise
en analyse environnementale
du Québec
TAGA Interventions
Industrial fires
Real-time monitoring of VOCs, inorganic substances (HCN, HCl, Cl_2, NH_3, etc.), aldehydes, monomers, etc. until reintegration of evacuated areas

Centre d'expertise en analyse environnementale du Québec

TAGA Interventions

- Chemical spills

  Real-time monitoring of chemical substances released in ambient air



October 2005
Sodium hydrosulfite
(H_2S, SO_X)



April 2007
Sichem Aneline
(Benzene)

Québec

Centre d'expertise en analyse environnementale du Québec

Recent Emergency Interventions – 2013

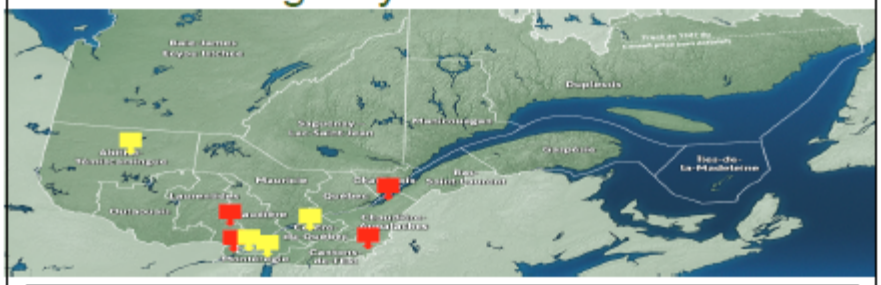


July	Train accident and explosion	BTEX
June	Fireworks warehouse explosion	SO_2
April	Home evacuation	CO_2
March	Tire warehouse fire	SO_2

Québec

Centre d'expertise en analyse environnementale du Québec

Recent Emergency Interventions – 2012

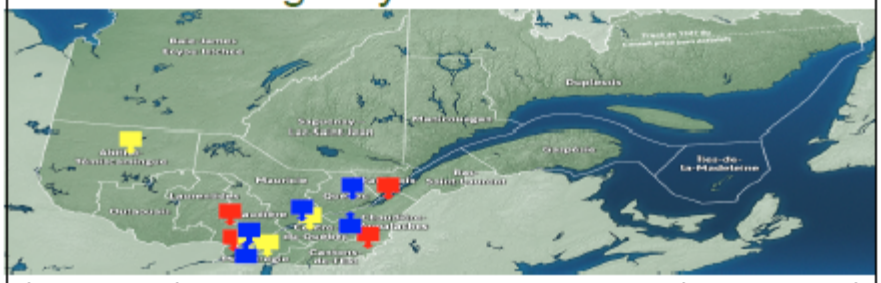


October	Massive mining blast	NO_2
May	Dry material landfill fire	CO, $PM_{2.5}$
May	Hydrogen cyanide release	HCN
May	Food-processing plant fire	HCN, NH_3

Québec

Centre d'expertise en analyse environnementale du Québec

Recent Emergency Interventions – 2011



October	Car salvage yard fire	Hg, SO_2
July	Artificial plants fire	HCl, Cl_2
June	Magnesium industry fire	NH_3, BTEX
April	Home evacuations	CO
March	Abandoned plant fire	BTEX

Centre d'expertise en analyse environnementale du Québec



Results

- Case 1
  - Petroleum train derailment and explosion
- Case 2
  - Emission of toxic fumes from an industrial processing plant
- Case 3
  - Unknown substance odour coming from sewer

Québec

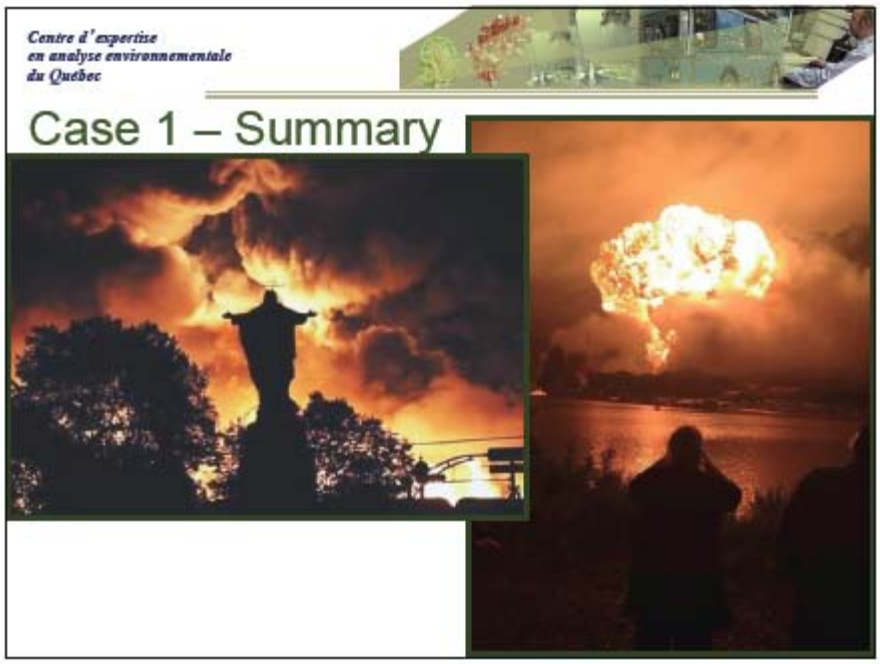
Centre d'expertise en analyse environnementale du Québec

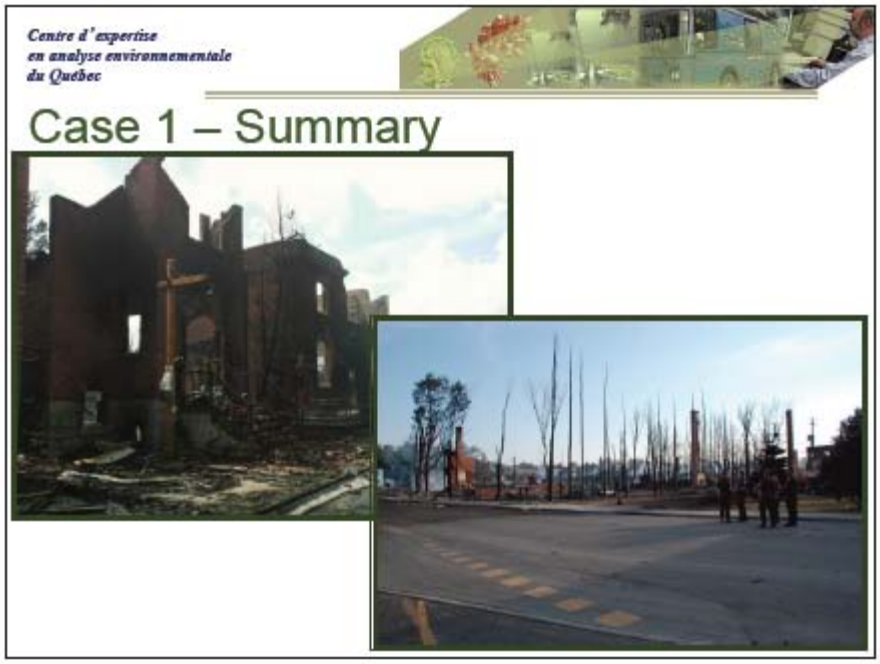


Case 1 – Summary

- July 6th 2013
  - A stopped train of 72 cars filled with petroleum starts moving, no-one on board, at around 1:00AM. The train, going downhill, speeds up rapidly to miss a curve and derails in downtown Lac-Mégantic at 1:14 AM. Massive explosions followed by a huge petroleum fire occur. It will take 36 hours to extinguish the fire.

Québec


Centre d'expertise
en analyse environnementale
du Québec
Case 1 – Summary


Centre d'expertise
en analyse environnementale
du Québec
Case 1 – Summary


Centre d'expertise
en analyse environnementale
du Québec
Case 1 – Summary


Centre d'expertise
en analyse environnementale
du Québec
Case 1 – Summary

Centre d'expertise en analyse environnementale du Québec

Case 1 – Summary

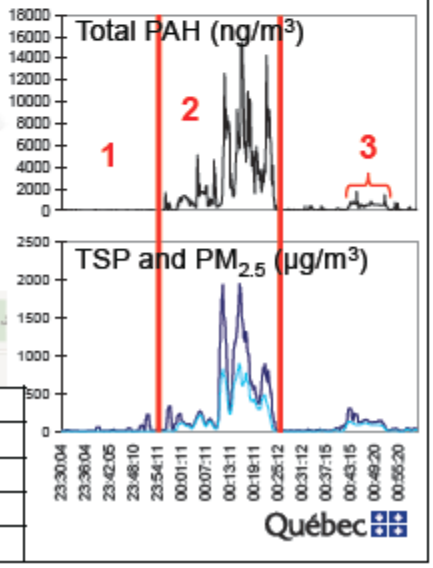
- TAGA team is reached and starts doing real-time ambient air analysis a few hours later
  - PAH
  - BTEX
  - Particulate matters
  - NO_X
  - SO_2
  - CO
- Results from the TAGA are very useful to the first responders, identifying another complete residential area that needs to be evacuated. Around 1000 more people are evacuated based on these results

Québec

Centre d'expertise en analyse environnementale du Québec

Case 1 – Results





	Concentration (µg/m³)			
	B	T	E	X
1	1	1	<1	<1
2	290	120	27	91
3	34	26	11	60

Québec

Centre d'expertise en analyse environnementale du Québec

Case 2 – Summary

- July 21st 2011
  - Saint-Félix-de-Valois' Fire Department is contacted by a citizen not feeling good because of bad air quality. Firefighters find toxic fumes coming from a chick hatchery which uses a mix of formol and potassium permenganate to sterilize the hatchers. The citizen's house is less than 3 meters away from the hatchery

Québec

Centre d'expertise en analyse environnementale du Québec

Case 2 – Summary



Centre d'expertise en analyse environnementale du Québec

Case 2 – Summary

- TAGA team is contacted to identify and quantify ambient air contaminants in this area
  - Methanol
  - Formaldehyde
  - Dimethoxymethane
  - Formic acid



Québec

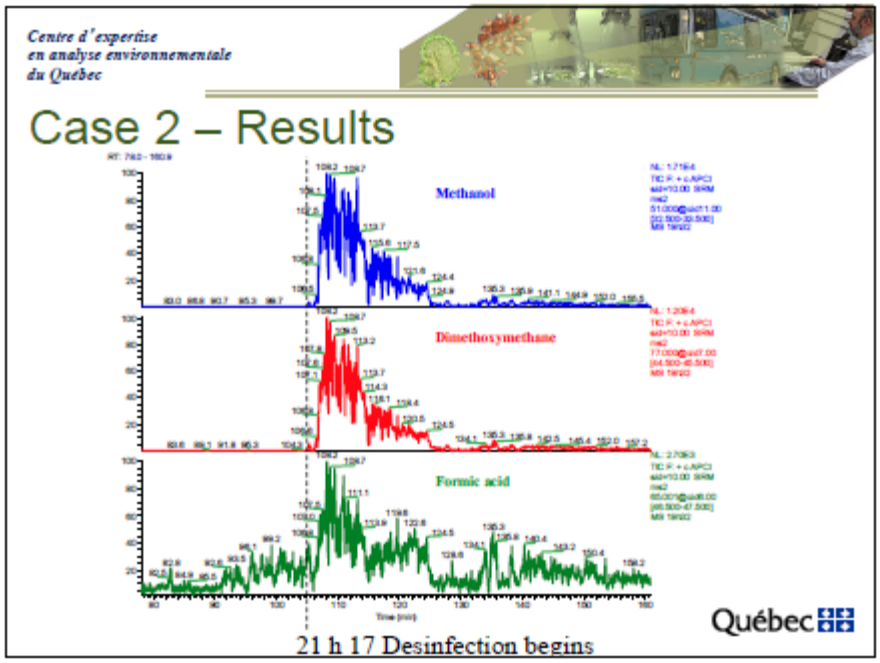
Centre d'expertise en analyse environnementale du Québec

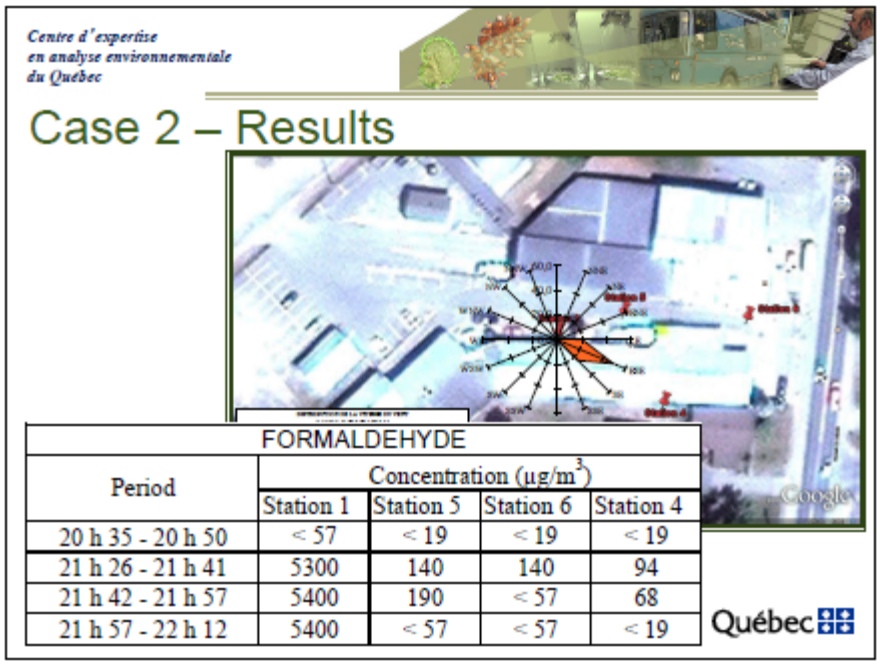
Case 2 – Results

- Concentrations are followed in real-time with the mass spectrometer
- Formaldehyde measurements based on TO-11A method from US EPA

Period	Concentration (µg/m³)						
	Formaldehyde	Methanol		Dimethoxymethane		Formic acid	
	Average	Average	Maximum	Average	Maximum	Average	Maximum
20 h 35 - 20 h 50	< 19	< 10	< 10	< 10	< 10	< 83	< 83
21 h 26 - 21 h 41	140	96	2530	75	2600	< 83	190
21 h 42 - 21 h 57	190	45	340	50	470	< 83	130
21 h 57 - 22 h 12	< 57	< 10	87	< 10	55	< 83	91

Québec





FORMALDEHYDE				
Period	Concentration (µg/m^3)			
	Station 1	Station 5	Station 6	Station 4
20 h 35 - 20 h 50	< 57	< 19	< 19	< 19
21 h 26 - 21 h 41	5300	140	140	94
21 h 42 - 21 h 57	5400	190	< 57	68
21 h 57 - 22 h 12	5400	< 57	< 57	< 19

Centre d'expertise
en analyse environnementale
du Québec

Case 3 – Summary

- September 15th 2009
  - The odour of an unknown substance is detected in the sewer of Sherbrooke City. The smell forces the evacuation of a few houses. Odour reaches a long-term care centre, for which evacuation is very risky given the health status of patients



Québec

Centre d'expertise
en analyse environnementale
du Québec

Case 3 – Summary









Centre d'expertise en analyse environnementale du Québec

Case 3 – Summary

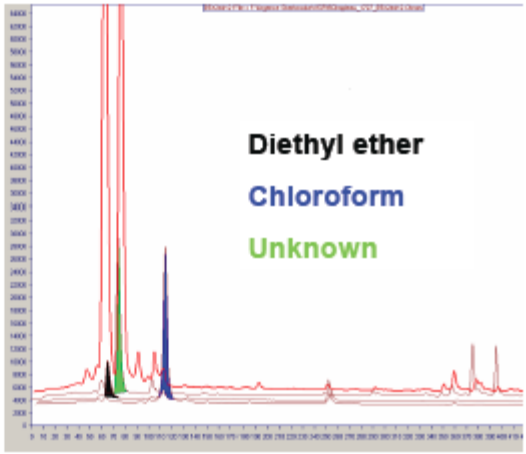
- Local authorities ask the TAGA and its team to determine the product that causes this smell. Concentrations have to be determined in the sewer, in evacuated houses and in the long-term health care centre

Québec

Centre d'expertise en analyse environnementale du Québec

Case 3 – Results

- First analyses in the sewer reveal 3 compounds with higher concentrations



Centre d'expertise en analyse environnementale du Québec

Case 3 – Summary

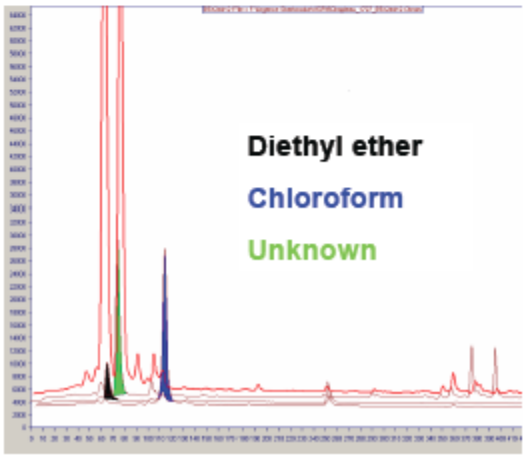
- Local authorities ask the TAGA and its team to determine the product that causes this smell. Concentrations have to be determined in the sewer, in evacuated houses and in the long-term health care centre

Québec

Centre d'expertise en analyse environnementale du Québec

Case 3 – Results

- First analyses in the sewer reveal 3 compounds with higher concentrations

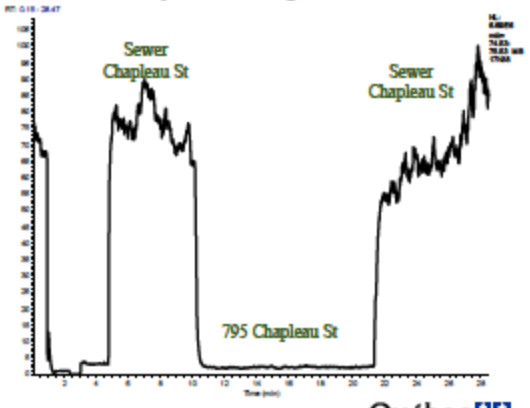


Centre d'expertise en analyse environnementale du Québec

Case 3 – Results

- Chloroform and diethyl ether are now added to the MS method to follow their concentrations in real-time

MS Diethyl ether signal



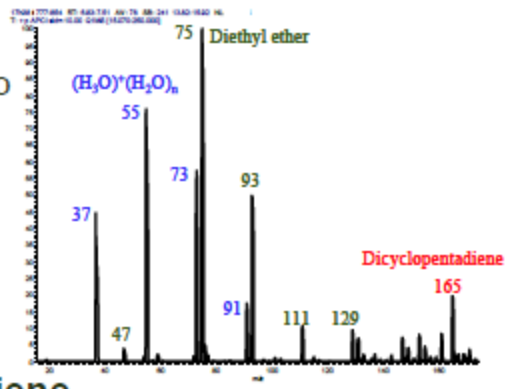
Québec

Centre d'expertise en analyse environnementale du Québec

Case 3 – Results

- Investigation, calculations and deductions lead to the identification of the third product:

Sewer Chapleau St

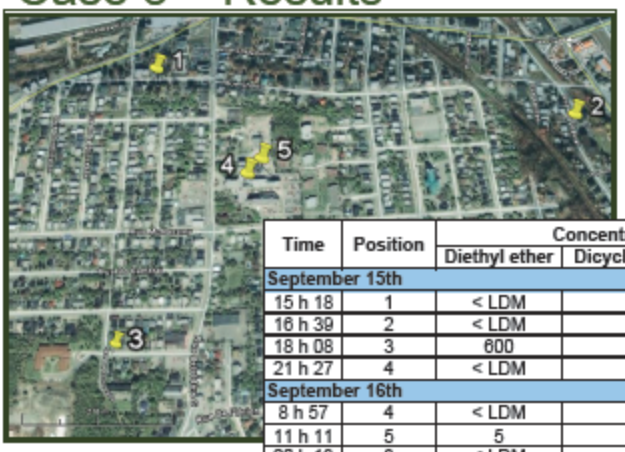


Dicyclopentadiene

Québec

Centre d'expertise en analyse environnementale du Québec

Case 3 – Results



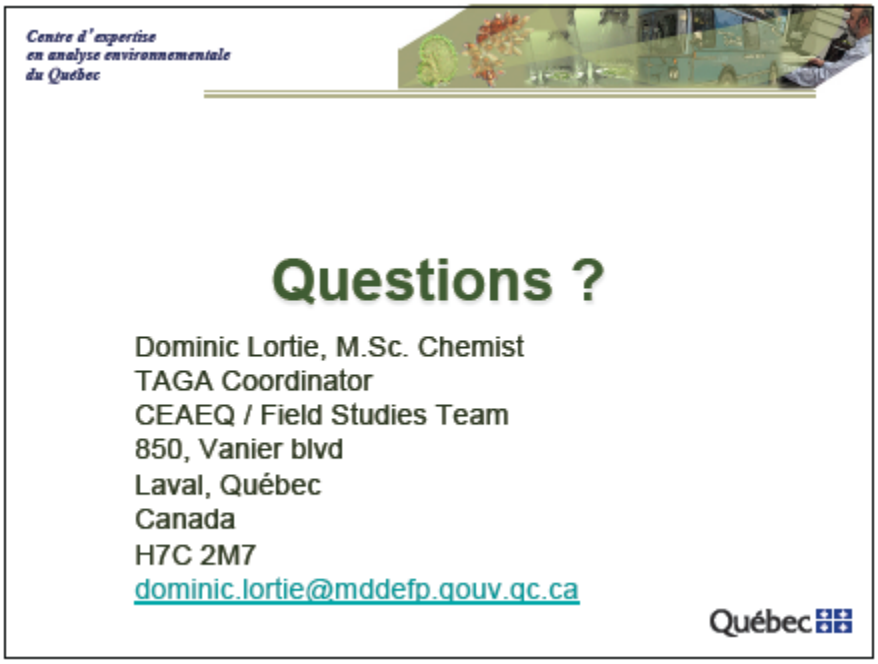
Time	Position	Concentration (µg/m³)		
		Diethyl ether	Dicyclopentadiene	Chloroform
September 15th				
15 h 18	1	< LDM	60	< LDM
16 h 39	2	< LDM	< LDM	< LDM
18 h 08	3	600	1600	470
21 h 27	4	< LDM	70	< LDM
September 16th				
8 h 57	4	< LDM	32	< LDM
11 h 11	5	5	10 000	310
20 h 13	3	< LDM	480	320
September 17th				
12 h 06	4	< LDM	< LDM	< LDM

Centre d'expertise en analyse environnementale du Québec

Future



Québec


Centre d'expertise
en analyse environnementale
du Québec
Questions ?
Dominic Lortie, M.Sc. Chemist
TAGA Coordinator
CEAEQ / Field Studies Team
850, Vanier blvd
Laval, Québec
Canada
H7C 2M7
dominic.lortie@mddefp.gouv.qc.ca
Québec

SECTION 14

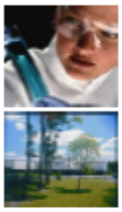
FORENSIC CHEMISTRY

Fingerprinting of Crude Oil Spill Sources

Kesavalu Bagawandoss
Accutest Laboratories

Abstract

Environmental characterization of oil spills requires fingerprinting analysis. All oil spill characterization efforts require sound sampling techniques to obtain representative samples and these samples must be processed by strictly following approved laboratory protocol. This technique is routinely used in NAPL identifications in Groundwater plumes. Further, liability allocation based on the source contributions could be assessed. Fingerprinting analysis provides essential information required to identify the source of an oil spill and facilitate the evaluation of Environmental Risks, Natural Resources Damage Assessments (NRDA), and Litigation. Fingerprinting is complex in nature. Standard materials are not available for all the constituents of concern in the source, therefore parent versus alkyl response factors have to be developed to quantify the constituents present. Several analytes and methods are employed to identify and compare two sources to each other to determine if they are related or unrelated. This presentation will outline the laboratory methods involved in fingerprinting natural and anthropogenic sources. Complex Gas Chromatographic and Mass Spectrometric Single Ion Monitoring techniques are employed to determine if the sources are petrogenic, pyrogenic, diagenic, or biogenic in nature. The data generated will be compared to sources or a library of patterns to determine the source of contamination or migration. Key indicators and diagnostics will be outlined for each of the processes. Diagnostic ratios, histograms, and ion chromatographic patterns for the various hydrocarbons, isoprenoids, parent polycyclic aromatic hydrocarbons (PAHs), alkyl substituted polycyclic aromatic hydrocarbons (alkyl PAHs), and biomarkers (hopanes, steranes, sesquiterpanes and terpanes) for the identifications will be presented. Comparisons will be presented for each of the classifications and groups.



NEMC 2013

Fingerprinting of Crude Oil Spill Sources

Kesavalu M. Bagawandoss, Ph.D., J.D.
August 7, 2013

Total Performance You Can Count On

Presentation Format

- Introduction
- Methods
- Analytical Parameters
- Data Presentation & Techniques
- Factors affecting Fingerprinting
- Processes and Patterns
- PAH, Biomarker, and Metal classifications
- Comparative Analyses
- Histograms
- Data Interpretation
- Summary
- References

2

Introduction

- Crude Oil spill analyses
- Finger Printing and comparisons to source oils
- Hydrocarbon GW Plume Source determinations
- Age Dating of sources
- Tiered approach to characterization

3

Methods

- GC & GC/MS using a combination of methods
- Methods include SW846 – 8015M, ASTM-D7363-07, D5739-00/SW846- 8270 D & 8272/USEPA CLP SOMO2.1/SINTEF/Nordtest
- Prep Methods- Liquid/Liquid, SPE and Soxhlet extractions
- Complex SIM GC/MS & GC/FID analysis
- Statistical Tools for plotting data – PCA (Principal Component Analysis) analysis and Cluster Plots

4

Analytical Parameters

- Alkyl PAH's, Parent PAH's
- Saturated Hydrocarbons (weathering and retention time markers, pristane - phytane indices)
- PIANO Analysis (environmental) (Paraffins, Iso-paraffins, Aromatics, Naphthenes, Olefins)
- Biomarkers (hopanes, steranes, terpanes, sesqui terpanes, cholestanes and triaromatic steroids)
- Indicator Compounds for Process determination

5

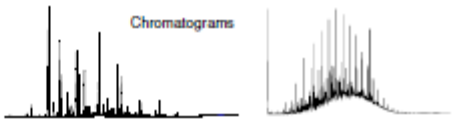
Data Presentation

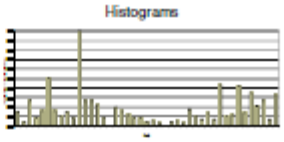
- Typical quantitation reports
- GC/FID traces and comparisons
- SIM patterns for PAH's, Hydrocarbons and Biomarkers (Total Ion Chromatograms)
- Weathering patterns
- PAH / Biomarker Diagnostic ratios
- Scatter Plots
- Histograms for individual samples for each fraction
- Histogram comparisons of source vs. samples
- Determination of processes (Petrogenic, Pyrogenic, Biogenic etc…)
- Principal Component Analysis (PCA) using statistics
- Data Interpretation Report

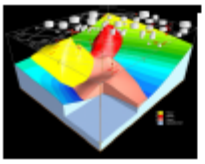
6

Techniques

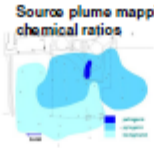
- Fingerprints
- Diagnostic Ratios
- Models, statistics, chemometrics
- Mapping and visualization

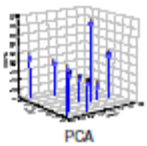






3-D Plume mapping

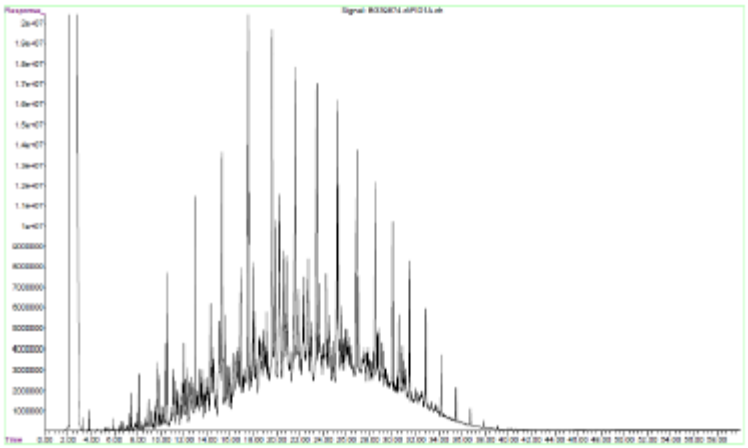




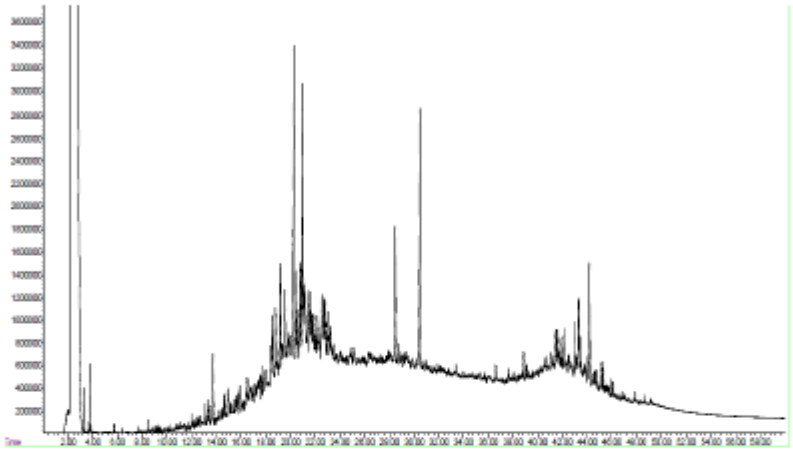
PCA

Example GC-FID pattern

Diesel Fuel – GC/FID Chromatogram



GC - FID - UCM



Example of Unresolved Complex Mixtures

9

Factors Affecting Fingerprinting

- Weathering
- Crude Oil Genesis
- Petroleum Refining
- Mixing in the environment

Background Sources: Naturally occurring and Anthropogenic

10

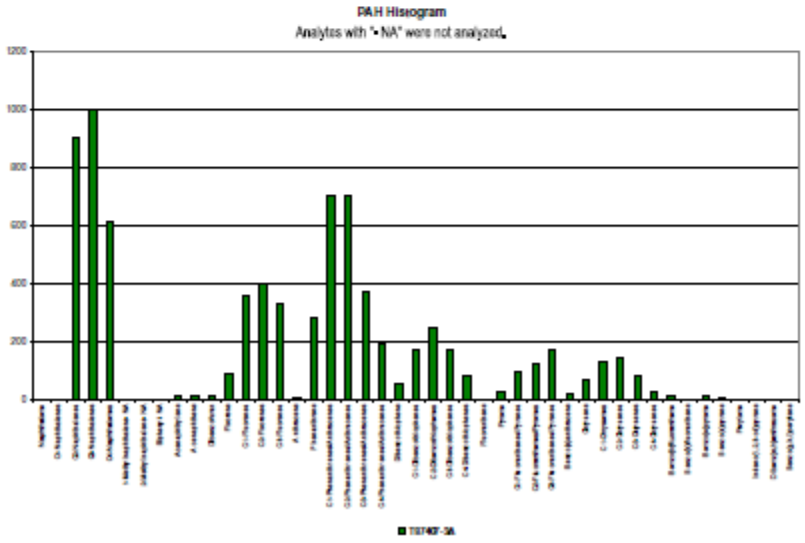
Processes and Patterns

- **Diagenic Process**
- **Biologically degraded (Biogenic)(presence of Perylene)**
- **Natural**
- **Bacterial modifications yield perylene**

- **Petrogenic Process (typically alkyl > parent PAHs)**
- **Petrogenesis (crude)(presence of 2-4 ring PAH)**
- **Refining**
- **The relative abundances of the alkyl homologues can diagnose different petroleum sources**
- **Dominated by alkyl PAH's**

11

Sample - Alkyl PAH Distribution - Petrogenic



Processes and Patterns

- Pyrogenic Process (typically alkyl < parent PAHs)
- Combustion (PAH distribution dominated by 4-6 ring PAH)
- Dominated by parent PAH's
- Pyrolysis
- Unique pattern compared to the Petrogenic process

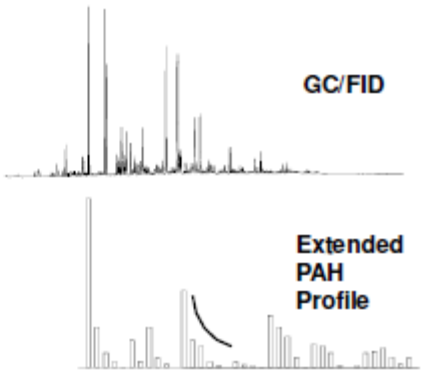
Characteristic compounds will be formed to identify process

Diagnostic ratios will also provide information to identify process

13

Pyrogenic Sources

- Produced at high temperatures
  - incomplete combustion
  - destructive distillation
  - pyrolysis
  - cracking, reforming
- Primarily aromatic
- Includes coat tar, tar products, creosote, exhaust, fire residual



PAH - Classifications

- Naphthalenes (2 rings)
- Acenaphthenes (2.5 rings)(due to two hex and 1 penta)
- Fluorenes (2.5 rings)
- Phenanthrenes, Anthracenes, Acridines (3 rings)
- Fluoranthenes, Pyrenes (4 rings)
- Benz (a) anthracene, Chrysene (4 rings)
- Benzo (b)/(k) Fluoranthenes, Benzo(a) Pyrene (5 rings)
- Dibenz(a,h)anthracene, Indeno(1,2,3-cd)pyrene (5 rings)
- Cornene (6 rings)
- Ovalene (10 rings)

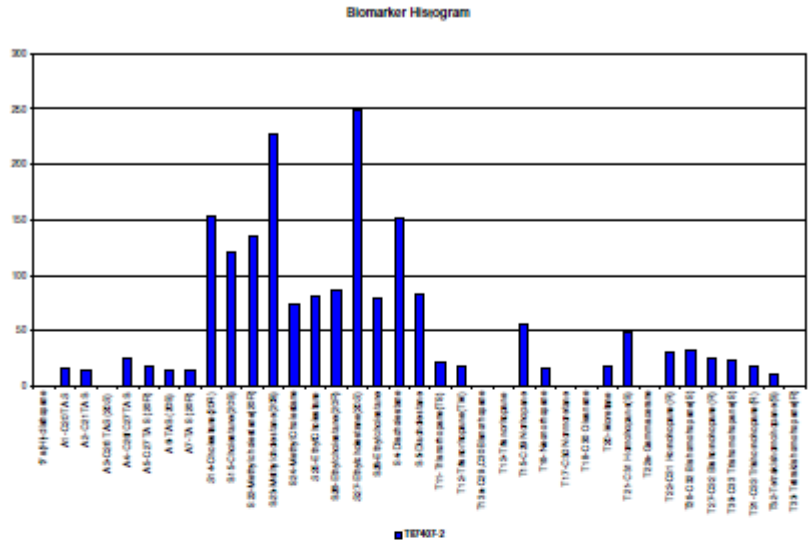
15

Biomarker Classifications

- Biomarkers are naturally occurring and stable hydrocarbons present in crude oils and most petroleum products (complex molecular fossils)
- Terpanes
- Hopanes
- Sesquiterpanes
- Cholestanes
- Triaromatic Steroids
- Other biomarkers
- The ratios of the biomarkers provide information on sources and age
- Biomarker ratios are used in dating by geochemists

16

Sample - Biomarkers



Metals

- Mettalo - Porphyrins are formed in crude oil
- Mettalo Porphyrin biomarkers are derived from terrapyrroles which is a component of chlorophyll
- Nickel and Vanadium form the Porphyrins
- Ni/V ratios are calculated to determine source rock depositions

18

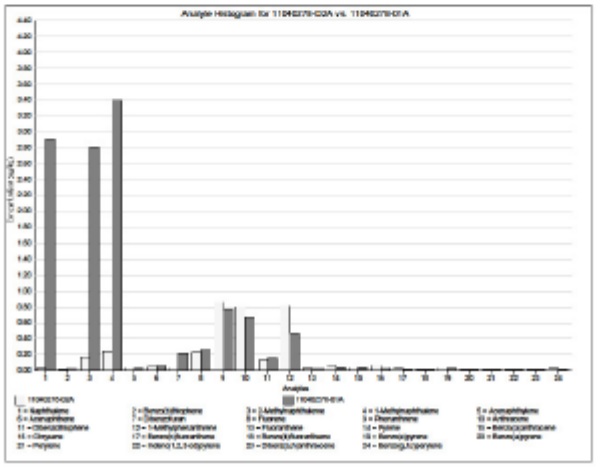
Comparative Analysis

Comparisons consist of:

- Visual comparison of chromatograms
- Chromatographic overlays
- Check for characteristic compounds
- Weathering checks of hydrocarbons and PAH's
- Ion chromatographic comparisons
- Diagnostic ratio calculations for the hydrocarbons, PAH's and biomarkers
- Double Ratio Plots
- Histogram development for comparisons

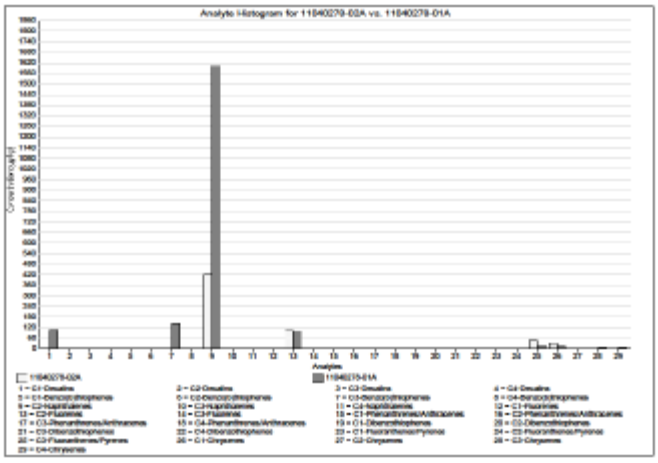
19

Comparison of Parent PAHs



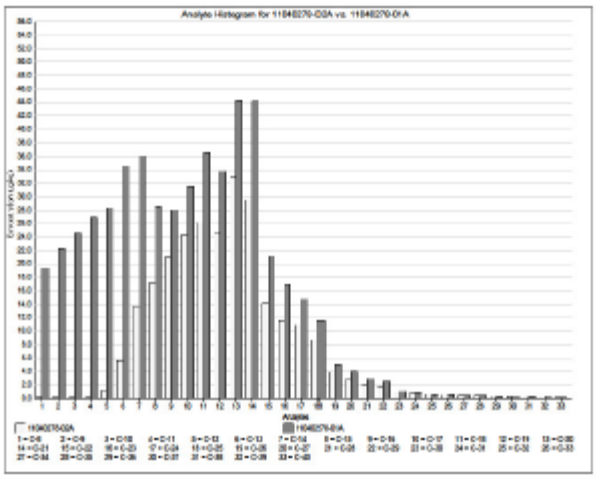
20

Comparison of Alkyl PAH's



21

Comparison of Oil Standard – C chains



22

Data Interpretation

Typical PAH Diagnostic Ratios

- C2-dbt/c2-phe (%) = 100*[c2-dibenzothiophene/c2-dbt+c2-phenanthrene]
- C3-dbt/c3-phe (%) = 100*[c3-dibenzothiophene/c3-dbt+c3-phenanthrene]
- C3-dbt/c3-chr (%) = 100*[c3-dibenzothiophene/c3-dbt+c3-chrysene]
- 2mp/1mp (%) = 100*[2-methyl phenanthrene/2-mp+1-methyl phenanthrene]
- 4md/1md (%) = 100*[4-methyl dibenzothiophene/4-md+1-methyl dibenzothiophene]

23

Data Interpretation

Typical Hydrocarbon Diagnostic ratios

- n-C17/pristane = [n-C17/n-C17+pristane]
- n-C18/phytane = [n-C18/n-C18+phytane]
- pristane/phytane = [pristane/phytane]
- n-C17/n-C18 = [n-C17/n-C18]

24

Data Interpretation

- The following slides provide examples for a spill oil comparison and biomarker ratio calculations

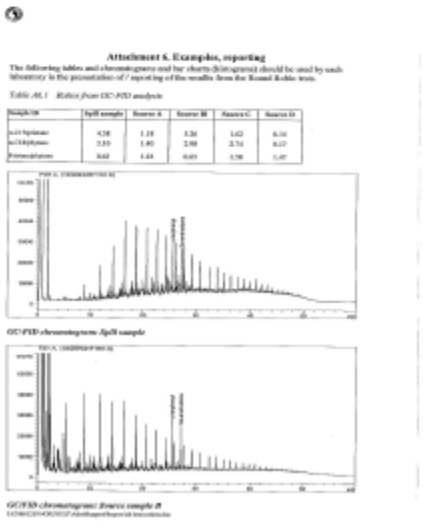
25

Example

Source: SINTEF Method

Spill

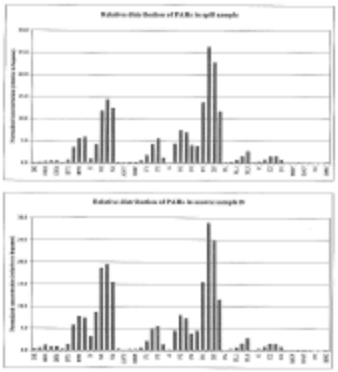
Source B



GC/FID Pattern

26

Example



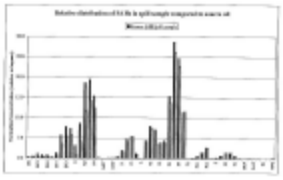
Spill

Source B

Histogram of PAH's

27

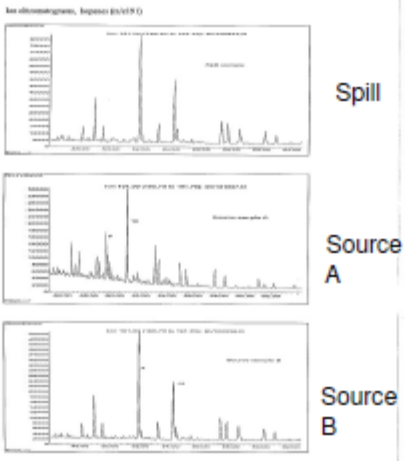
Example



PAH Plot of Spill and Source B

28

Example



Hopane – Spill, Source A & Source B

29

Data Interpretation

Final results expressed as:

- **Positive match / Perfect match**
- **Possible match / Probable match**
- **No match**
- **Interpretation Report on possibilities and pathways**

30

Summary

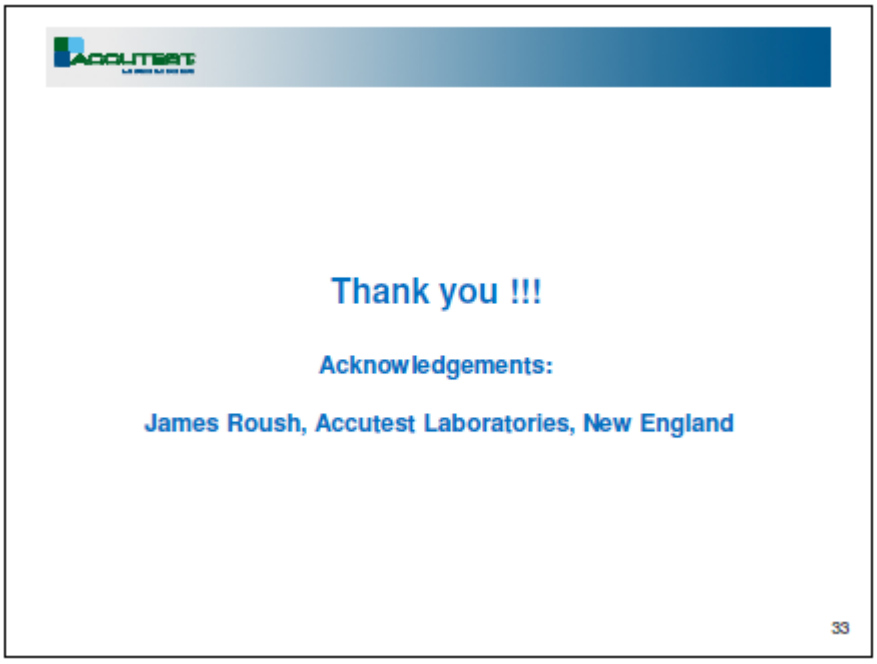
- No specific methodology – combination of methods
- Complex SIM analysis
- Source & Library necessary for interpretation
- Precision of the source is important
- Multiple paths of data interpretation
- The more data one accumulates the better the interpretation would be
- Interpretation consists of visual and quantitative techniques
- Overall it is a complex process

31

References

- ASTM - D7363-07
- ASTM - D5739-00
- SW846 - 8270 D; SW846 – 8015M
- SW846 – 8272 Draft method
- USEPA CLP SOMO2.1
- SINTEF/Nordtest Methodology for Oil Spill Indentification, Faksness, Weiss and Daling, 2002
- Environmental Forensics Principles and Applications by Robert D. Morrison, 2000
- Oil Spill Environmental Forensics – Fingerprinting and Source Identification by Zhendi Wang and Scott A. Stout, 2007

32


Thank you !!!
Acknowledgements:
James Roush, Accutest Laboratories, New England
33

The Added Value of Utilizing Stable Isotopes in Environmental Forensics

Paul Philp, Tomasz Kuder and Jon Allen
University of Oklahoma School of Geology and Geophysics

Abstract

Environmental forensics is primarily directed towards determining who was responsible for the release of contaminants into some area of the environment. The contaminated environment may be air, water or soil but all of the investigations will have a common goal. There are many analytical techniques in the tool box of the environmental forensic scientist. However this talk will focus on one tool in particular that continues to increase in terms of applicability, namely stable isotopes. This does not imply stable isotopes can be thought of as a stand-alone tool but for this talk they will be the focus. The purpose of this presentation will be to illustrate with various examples how the carbon, hydrogen and chlorine stable isotope compositions of various compound classes are being used as tools to determine the source of contaminants and also evaluate whether specific compounds are undergoing degradation through natural attenuation. Specific examples to be discussed with include contamination of water samples with ethylene dibromide, thought to have been originated from its use as a lead scavenger in leaded gasoline; a groundwater case where the groundwater was contaminated with chlorinated solvents; and a vapor intrusion study to illustrate how a multiple isotope approach can be used to evaluate possible sources of specific VOCs in indoor air samples; and finally a example of water well contamination related to hydrofracturing. In addition to illustrating the applications to the specific case studies, time will be devoted to explaining some of the shortcomings of the approach and potential pitfalls in the interpretation. Finally if time permits, potential applications for future forensic studies incorporating stable isotopes will be discussed.

The Added Value of Stable Isotopes in Environmental Forensic Investigations.

R. Paul Philp, Tomasz Kuder and Jon Allen, School of Geology and Geophysics, University of Oklahoma, Norman, OK. 73019.

Introduction and Overview

- Introduction
- Environmental Forensics
- Stable Isotopes
- Vapor Intrusion
- Fate and transport modeling
- Summary

Environmental Forensics

- The basic questions:
  - What is it?
  - Where did it come from-point of release?
  - When was it released?
  - Is it degrading and/or how quickly is it degrading?

Environmental Forensics

- Two basic schools of thought:
  - EPA methods. However these methods are for the most part useless in terms of forensic investigations.
  - For environmental forensic investigations a far more detailed and comprehensive approach is necessary than simply determining concentrations of target compounds. The approach involves using a variety of techniques and very detailed fingerprinting of compounds or compound classes, many of which are not even on the list of EPA target compounds.

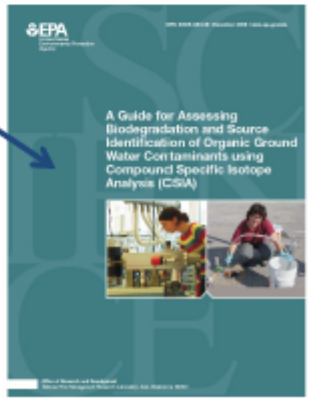
Environmental Forensics

- **Important analytical techniques for organics:**
  - Gas chromatography (GC)
  - Gas chromatography-Mass Spectrometry (GCMS)
  - GCGCTOFMS;GCMSMS;
  - Gas chromatography-isotope ratio mass spectrometry (GCIRMS-C;H;Cl;N;S).

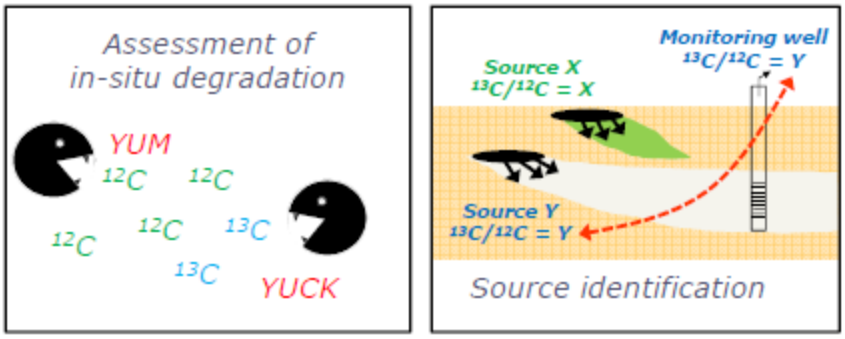
CSIA in Ground WaterContaminant Studies

CSIA is established in ground water contaminant work, with large number of peer-reviewed publications and industry applications.

CSIA applications fairly novel in vadose zone and vapor phase contaminant studies: several peer-reviewed papers to date

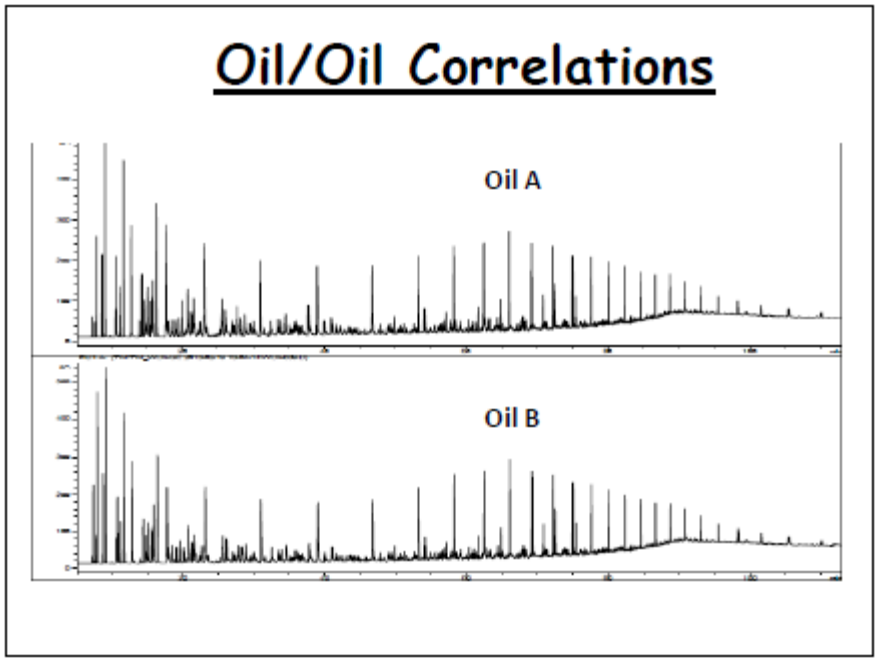


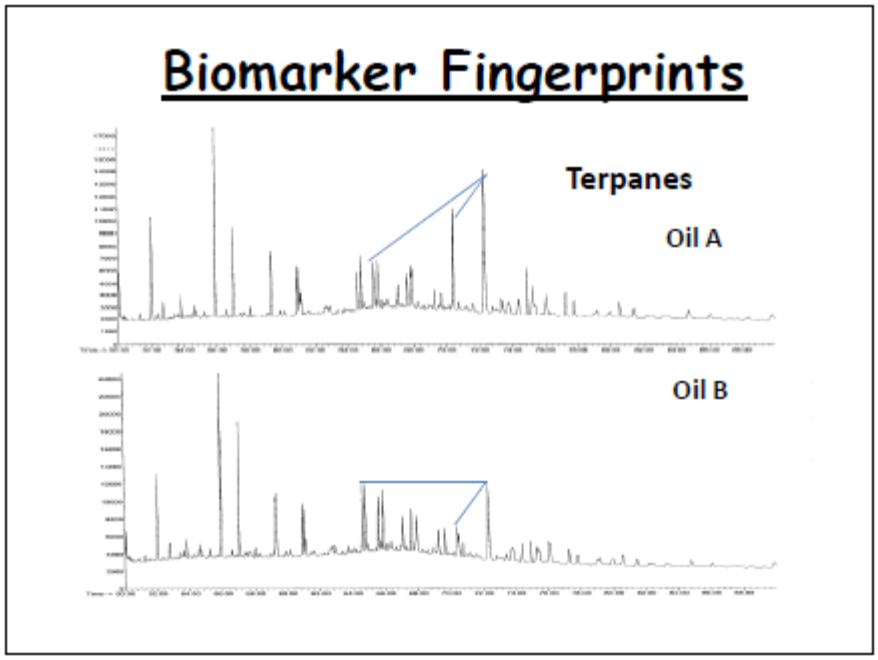
Stable Isotopes-Major Applications

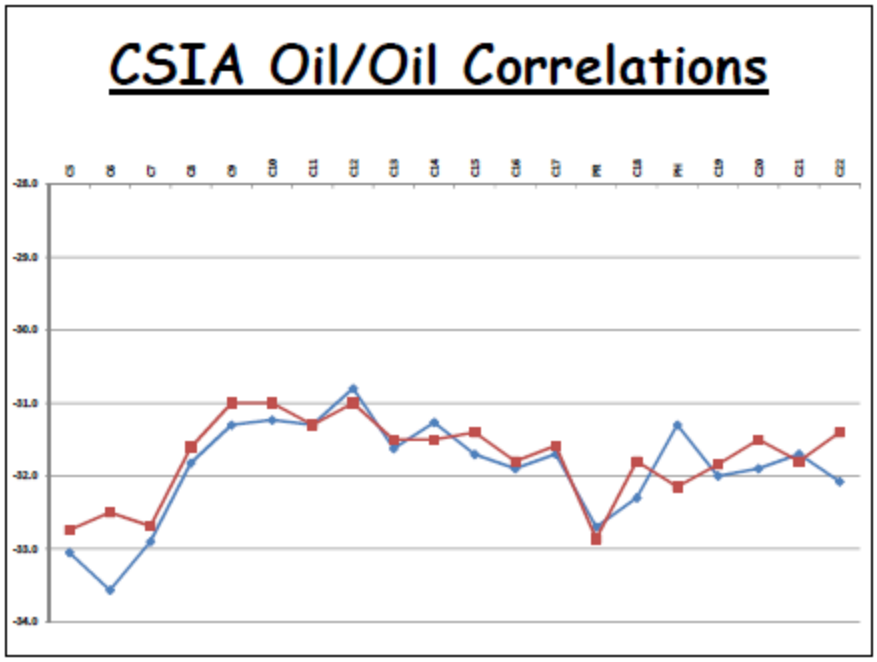


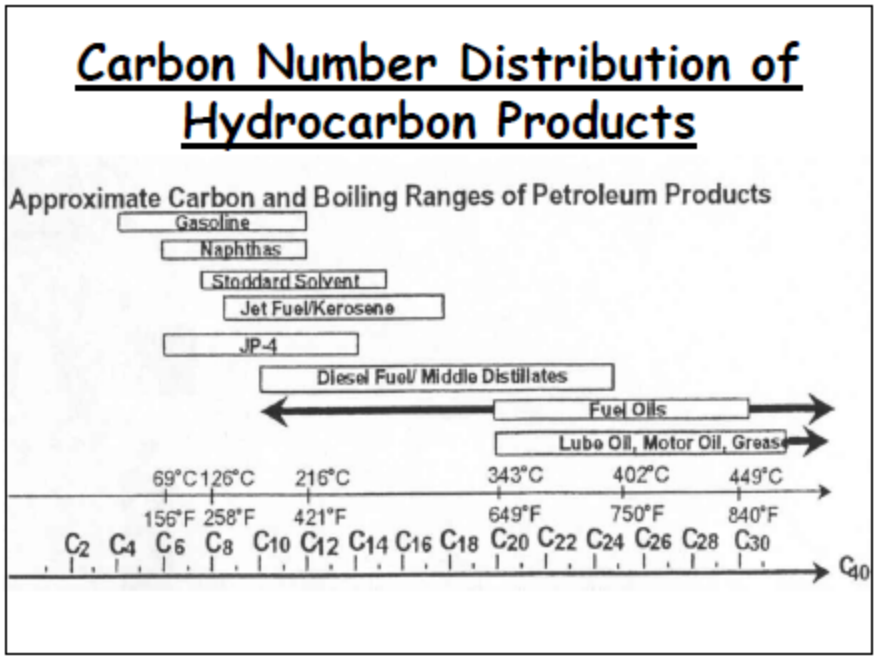
Environmental Forensics

- **Biomarkers**-a detailed understand of these compounds can provide significant information that may not be obvious to the in-experienced investigator.
- Many people have heard enough about steranes, terpanes and isoprenoids to be dangerous.
- Not possible to routinely determine stable isotope values of individual biomarkers.

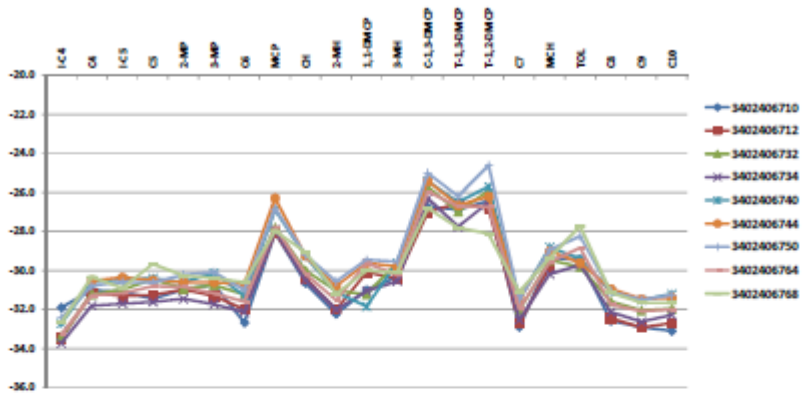

Oil/Oil Correlations
Oil A
Oil B


Biomarker Fingerprints
Terpanes
Oil A
Oil B


CSIA Oil/Oil Correlations


Carbon Number Distribution of Hydrocarbon Products
Approximate Carbon and Boiling Ranges of Petroleum Products
Gasoline
Naphthas
Stoddard Solvent
Jet Fuel/Kerosene
JP-4
Diesel Fuel/ Middle Distillates
Fuel Oils
Lube Oil, Motor Oil, Grease
69°C 126°C 216°C 343°C 402°C 449°C
156°F 258°F 421°F 649°F 750°F 840°F
C2 C4 C6 C8 C10 C12 C14 C16 C18 C20 C22 C24 C26 C28 C30
C40

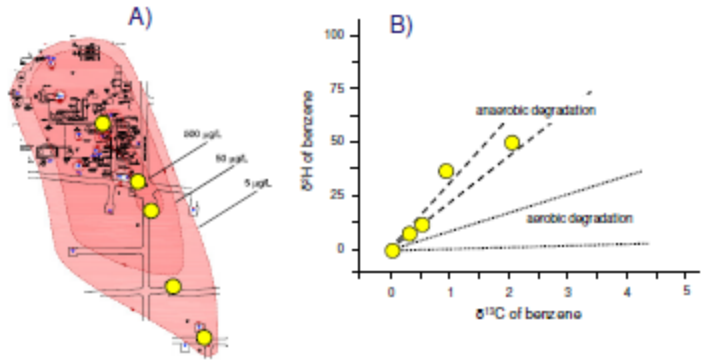
Correlations using C_7 Components



Stable Isotopes

- **Where they will not work at this time:**
  - If you cannot see the compound on the GC trace cannot get an isotope number.
  - Age dating.
  - Identifying manufacturers of spilled products.
  - Spilled product and source may be isotopically similar but that does not necessarily prove they are related. If isotopically different, and not biodegraded, then probably not related.
  - Isotopically light TCE not necessarily produced in environment by reductive dechlorination

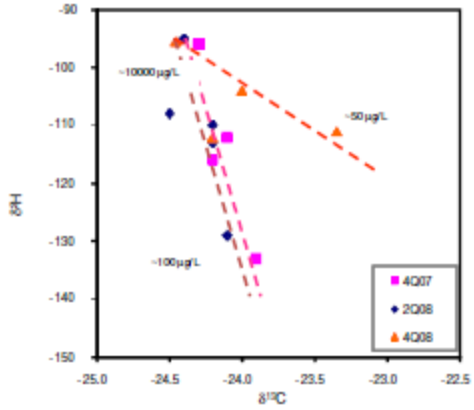
2D-CSIA Discrimination of Benzene Degradation Pathways



Application of CSIA at an industrial site. A) Locations of monitoring wells within a benzene plume; B) 2D-CSIA of benzene from the five monitoring wells. Note that net fractionation is larger for hydrogen than for carbon by a factor of ~20. This is consistent with anaerobic degradation in the core of the plume, but not consistent with aerobic degradation. At this site, the extent of isotope fractionation accounts for 50-60% of benzene mass removal in the distal monitoring well.

15

2D-CSIA Discrimination of Benzene Degradation Pathways

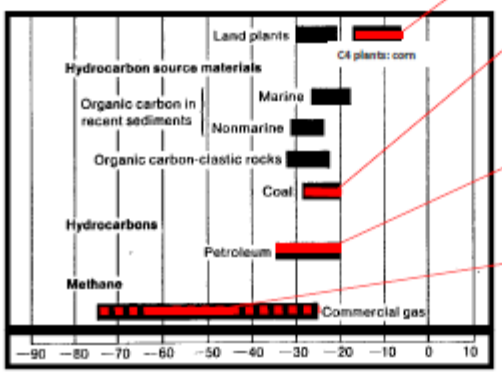


2D-CSIA plot of data from a benzene site in California. Three quarterly sample sets are shown. Note the inverse H fractionation, similar to the trends observed for volatilization of MTBE from NAPL phase. The difference between 4Q08 vs. the two other sets may represent relatively less prominent volatilization in 4Q08.

16

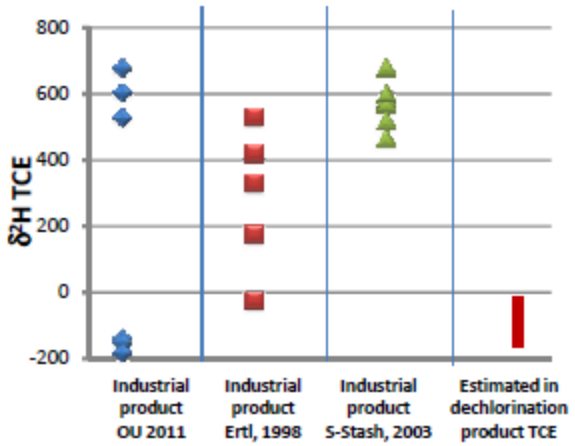
Vapor Intrusion

The Isotopes in Manufactured Chemicals are Inherited from Synthetic Feedstocks

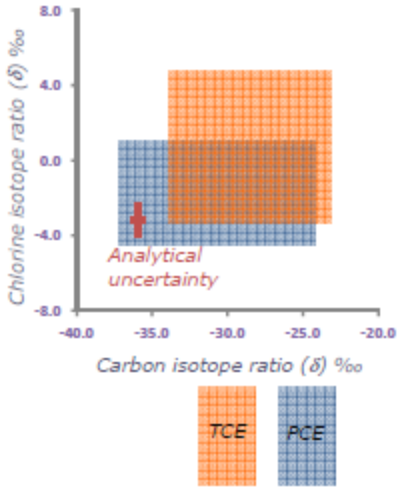


H Isotope Ratios of Manufactured TCE

(Source or PCE Degradation)



Indoor Sources: Narrow Range of Isotope Ratios



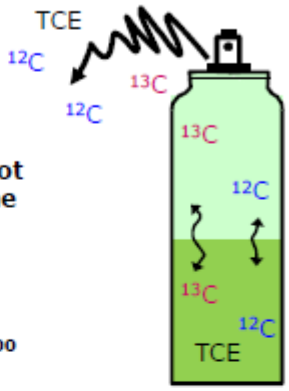
Isotope ratios of undegraded VOCs tend fall within a relatively narrow range of values.

Isotope ratios of vapor emanating from an indoor source are near-identical to those of the source (± phase change effects).



VOCs Isotope Ratios in Vapor Emitted from Consumer Products: Minor Depletion of ^{13}C, Moderate depletion of ^{37}Cl

- Molecules with different isotope substitution differ in their partitioning and diffusion coefficients
- Vapor escaping from a closed product can will be similar but not identical to the product inside the can.
- Expect that vapor evolving from an indoor source will show a < 1‰ depletion of $\delta^{13}C$ and 1-2 ‰ depletion of $\delta^{37}C$

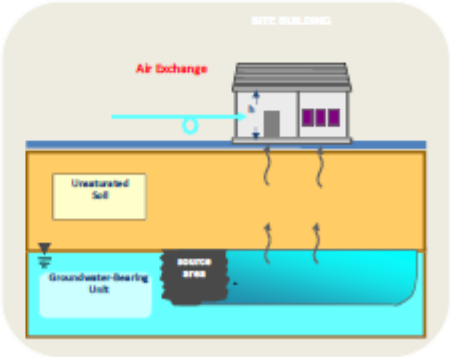


Problem Statement

In vapor intrusion (VI) management, VOCs of interest may also originate from household products (solvents, glues etc.)

VI assessment is complicated by the indoor sources of VOCs

Can we use stable isotopes to distinguish the indoor and subsurface sources?



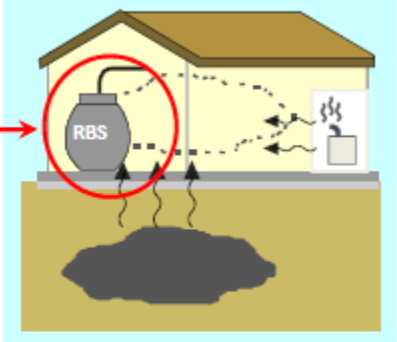
Technical Challenge of CSIA Application to VI Sites

Need >75 ng of TCE or PCE to get accurate C stable isotope ratio measurement.

Need 75 L sample at 1 µg/m³ conc.

Really Big Summa

Sampling challenge met by application of active sorbent samplers.

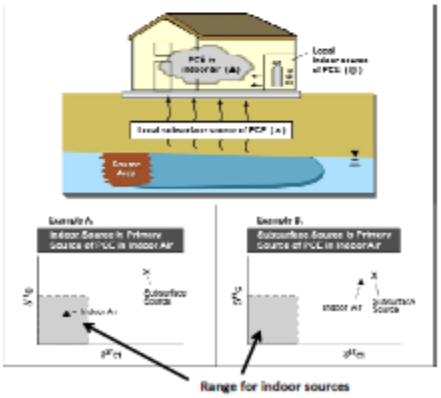


The Rationale of Using Isotope Ratios of VOCs in VI Source Discrimination

CSIA permits determination of isotope ratios (C, Cl, H) in target VOCs

Isotope ratios compared between indoor and subsurface sources and indoor air.

Predominant VOCs sources identified by their difference/similarity to the indoor air VOCs.



Isotope Ratio Analysis: Detection Limits

(Based on recent OU methodology for adsorbent tube samples)

Carbon and/or Chlorine CSIA

TCE, PCE ~75 ng
Benzene ~15 ng

Hydrogen CSIA

TCE ~ 2.5 µg
Benzene ~ 1 µg

★ *CSIA detection limits require preconcentration of the target VOCs from relatively large volume of air (esp. indoor or ambient air)*

CSIA of Chlorinated Ethenes: Detection Limits for High-Precision CSIA

(based on recent OU methodology for aqueous samples)

Carbon and Chlorine CSIA

VC 1 ug/L

DCE, TCE, PCE 1 ug/L*

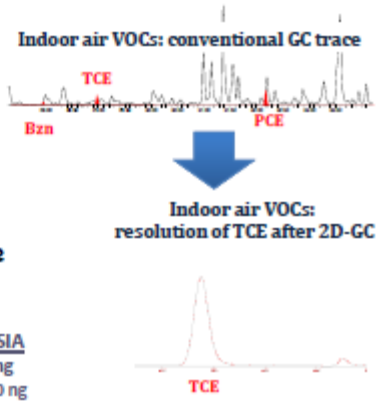
Hydrogen CSIA

VC, DCE	10 ug/L
TCE	30 ug/L

* 0.5 ug/L if larger volume of sample is available

Technical Challenges of CSIA Application to VI Sites

- Very complex mixtures: 2D-GC is required (C CSIA)
- Vapor samples have to meet the method detection limits. VOCs have to be recovered from large air volume (logistics!)



C and/or Cl CSIA	Hydrogen CSIA
TCE, PCE ~ 50 ng	TCE ~ 2500 ng
Benzene ~ 20 ng	Benzene ~ 500 ng

(based on recent OU methodology)

Technical Challenge: The Need for Validation of Adsorbent Performance for CSIA

Adsorbent tubes for thermal desorption can be used to extract VOCs from air. Relatively easy to implement in routine sampling.

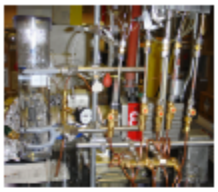


If target analyte breaks through in sampling or is not completely desorbed, there is a possibility of isotope fractionation.

Total sample volume; Pump flow rate; Adsorbent tube storage; Humidity; Non-target VOCs can affect target retention and recovery.

Adsorbent Testing Approach: Simulate Worst-Case Sampling Scenarios

Performance Objectives



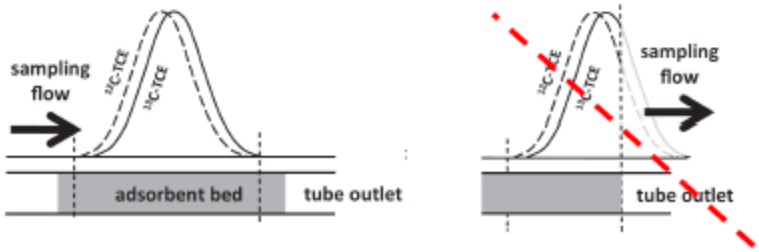
Fractionation-free recovery of TCE, PCE and benzene from up to 100 L of air.

Good performance for "difficult" sampling conditions, including maximum air volume and competitive adsorption. All analyte added at T=0 and subject to maximum air volume flushing.

Good performance for different combinations of air volume/water vapor/non-target VOCs/target VOCs loading.

Conceptual Model of Fractionation in Adsorbent Sampling: Analyte Breakthrough

★ ^{12}C-TCE appears to have greater affinity to carbonaceous adsorbent. ^{13}C-TCE breaks through preferentially. Caused by Dispersion Force?



Complete retention = no fractionation

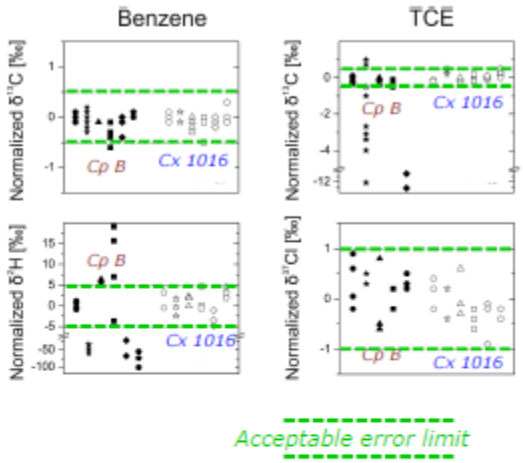
Partial breakthrough = ^{13}C-TCE lost preferentially; Analyte fractionation.

Validation of Active Adsorbent Samplers

★ *CARBOXEN 1016 and CARBOPACK B selected for full evaluation*

★ *Tested at 6 different air volume/humidity/VOCs loadings combinations*

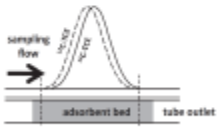
★ *Performance for Cx 1016 good in all treatments. Recommended max sample volume 100 L*



Interim Conclusions: Adsorbent Samplers Validation

CX 1016 offers good performance for all tested treatments and analytes.

CX 1016 is a recommended choice for sampling TCE, PCE or benzene from air, up to 100 L.

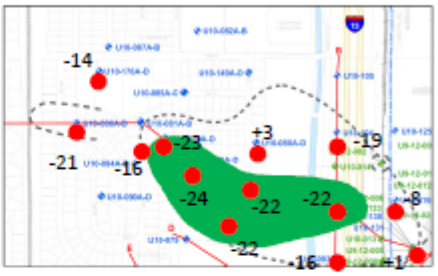


These results should not be extrapolated to different analytes, isotope ratios, or adsorbents. Actual performance validation is required.

These results should not be extrapolated to more challenging sampling conditions (larger air volume etc.) Actual performance validation is required.

Effects of Biodegradation in Subsurface Sources

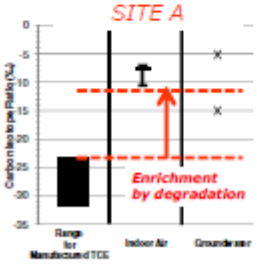
- *Preferential biodegradation of ^{12}C-TCE causes ^{13}C-TCE enrichments in undegraded residue. Robust evidence of subsurface origin of the analyte.*
- *In part of the plume (green), TCE values are near the "heavy" end of the -23/-33 range of indoor sources*
- *Isotope ratios are "heavier" than the range of indoor sources in the remainder of the plume footprint*



Example: Carbon isotope data from a TCE plume in UT

Examples: Predominant Subsurface Sources of TCE in Residential Air (True VI): Hill AFB Study

SITE A

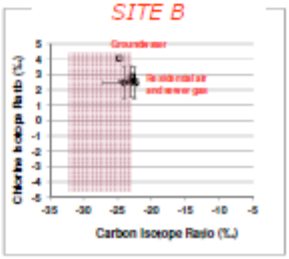


Indoor air TCE shows strong ^{13}C enrichment indicative of a biodegraded subsurface source

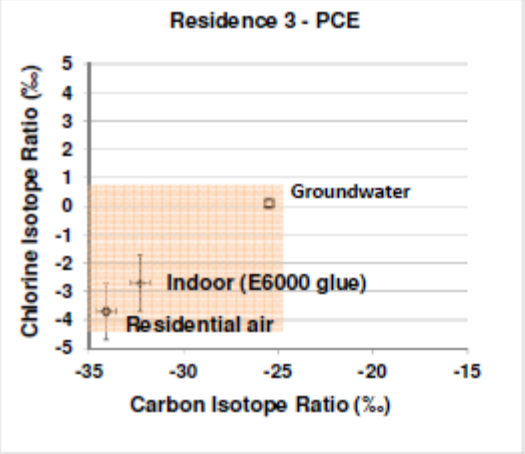
Clear case of subsurface source of TCE, evident by C CSIA data alone.

Good match of TCE isotope ratios between residential air and sewer gas supports existing conceptual model for this residence.

SITE B



Predominant Indoor Source; Hill AFB Study



Close match of C and Cl in indoor air PCE and a PCE-containing product identified on site (a tube of glue found on-site).

Clear case of indoor source of PCE.

Modeling Studies-Background

- Compound-Specific Isotope Analysis (CSIA) provides direct evidence of mass destruction of chlorinated ethenes, however, *quantitative interpretation of results is often problematic due to complex hydrogeology and/or competing reaction pathways.*
- Integration of CSIA with Reactive Transport Modeling (RTM) offers a means of accounting for the site-specific complexity.
- RTM with high-quality field data will confirm whether integration of CSIA with RTM offers a benefit versus the traditional approaches (RTM with contaminant concentrations only; interpretation of CSIA data based on Rayleigh Model).

36

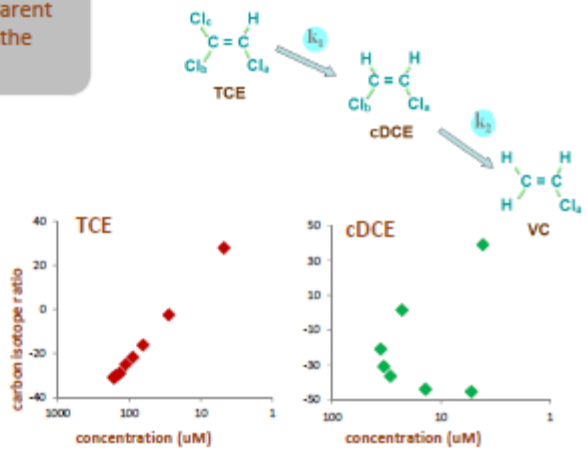
Why is Reactive Transport Modeling (RTM) needed for CSIA data?

- The analytical Rayleigh equation can only calculate the extent of mass destruction for a *parent* compound (e.g., PCE/TCE). This equation *underestimates* the true extent of degradation due to hydrodynamic disperion attenuating the isotope signals.
- To quantitatively assess the fate of reaction products, e.g. lower chlorinated ethenes (DCE, VC) and the supposed stable ethene, a RTM approach is required.
- Furthermore, full complexity can be accounted for with RTM: hydrodynamic dispersion, effects of isotopologue-dependent diffusion and sorption, advanced degradation kinetics, etc
- RTM can be simple like any other model: a 1-D model with user adjustable parameter values (rate constants, fractionation factors, dispersivities, etc) without the need to understand the working of the "engine".

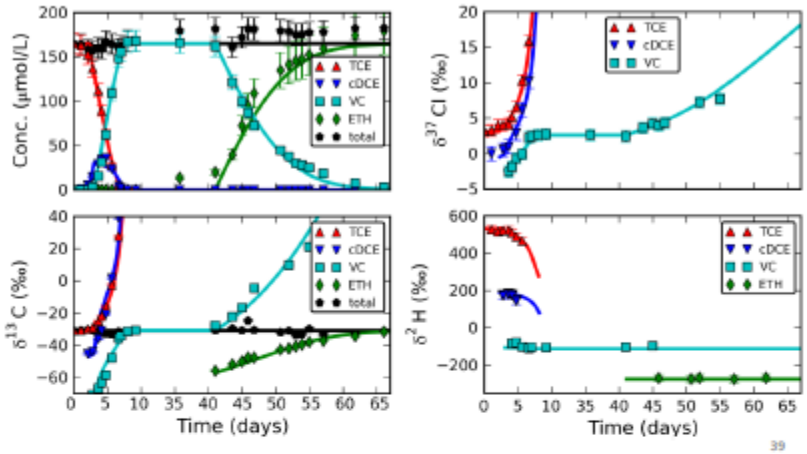
37

CSIA for Degradation Intermediates

- Isotope effects in the parent compound conform to the Rayleigh model.
- Isotope effects in the intermediates reflect their production and degradation.

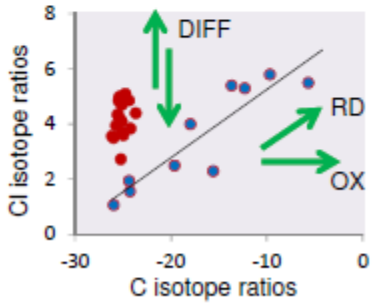


Model Calibration with the Microcosm Data

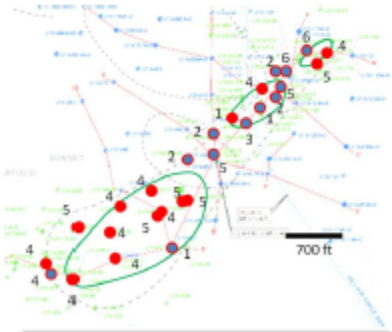


39

2D-CSIA Data: Consider Different Scenarios



A C-Cl trend consistent with reductive dechlorination apparent for a group of samples



Bimodal distribution of data can be rationalized by several alternative scenarios, to be tested by RTM.

40

Summary

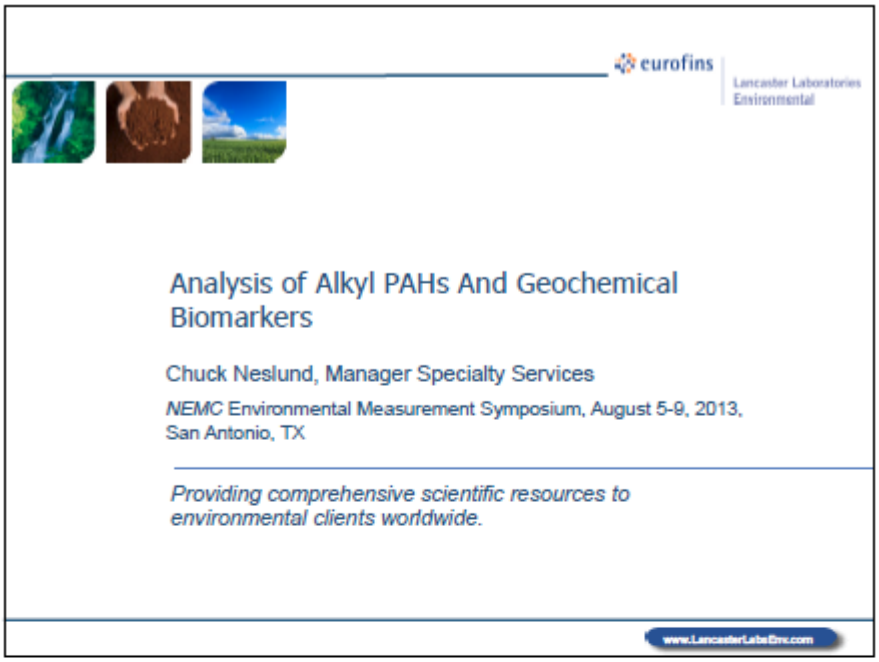
- Environmental forensics utilizes a wide range of techniques and approaches which are far more flexible than the standard EPA methods.
- ^{14}C isotopes has a role to play in certain environmental applications
- Stable isotopes continue to evolve and play a role in a number of environmental forensic studies.
- Vapor intrusion studies and RTM studies are emerging applications.
- Don't rediscover the wheel!

Analysis of Alkyl PAHs, Geochemical Biomarkers for Fingerprinting Petroleum Products

Charles Neslund
Eurofins Lancaster Laboratories

Abstract

The analysis of PAHs and alkyl substituted PAHs at sub ug/l concentrations is a challenging but more thorough approach to the assessment of petroleum contamination and exposure. By including the analysis of saturated hydrocarbons (alkanes) and biomarkers additional information is provided that can be useful in the determination of sample weathering, sample source and extent of biodegradation on the sample. The analytical challenges associated with this type of analysis, it's use as a forensic tool and the use of additional quality assurance practices to enhance data reliability will also be discussed.


eurofins
Lancaster Laboratories
Environmental
Analysis of Alkyl PAHs And Geochemical Biomarkers
Chuck Neslund, Manager Specialty Services
NEMC Environmental Measurement Symposium, August 5-9, 2013, San Antonio, TX
Providing comprehensive scientific resources to environmental clients worldwide.
www.LancasterLabsEnv.com


PAHs and Alkyl PAHs
Most important target analytes in damage assessment from petroleum products
Known to originate from 2 sources
- Petrogenic
- Pyrogenic
eurofins
Lancaster Laboratories
Environmental

PAHs and Alkyl PAHs



- Can be used in forensic analysis to qualitatively fingerprint petroleum sample
- Crude oils contain primarily alkyl PAHs and relatively smaller concentrations of unsubstituted PAHs

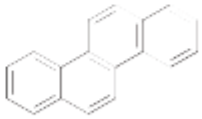
eurofins | Lancaster Laboratories Environmental

What are Alkyl PAHs?



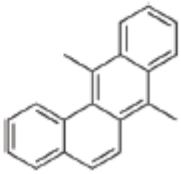
- Parent PAHs are 2 or more fused conjugated rings

  naphthalene chrysene



- Alkylated PAHs are the parent PAH with various alkyl groups attached

  2,3,5-trimethylnaphthalene
  7,12-dimethylchrysene



eurofins | Lancaster Laboratories Environmental

What are Alkyl PAHs?



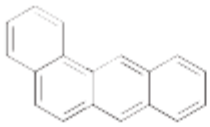
- Categorized by the total number of alkyl carbon atoms present
- A homolog group includes all of the isomers with the same number of carbon atoms
- C3 includes propyl, isopropyl, trimethyl and ethylmethyl

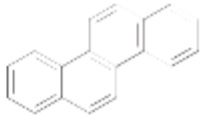
eurofins | Lancaster Laboratories Environmental

What are Alkyl PAHs?



- Parent PAHs that are isomers of other parent PAHs are combined for reporting purposes
  - phenanthrene/anthracene
  - fluoranthene/pyrene
  - benz(a)anthracene/chrysene





eurofins | Lancaster Laboratories Environmental

Why do we care?



- Traditional methods focused on the 16 Priority Pollutant PAHs identified by EPA
- There are hundreds if not thousands of alkylated forms that are unaccounted for in traditional methods

eurofins | Lancaster Laboratories Environmental

Why do we care?



- Less toxicity data available for alkyl PAHs than their parent compounds
- Alkyl PAHs are more abundant and persist longer than their parent compounds
- Analysis of alkyl PAHs in combination with the parent compounds is a better estimation of total exposure to toxic effects of PAHs

eurofins | Lancaster Laboratories Environmental

Method Summary



- Extraction methods are relatively standard for those used for soil and water
  - SW-846 3510 for waters
  - SW-846 3546 for soils
- Alumina column clean-up used as needed

eurofins | Lancaster Laboratories Environmental

Method Summary



- Tuning and calibration similar to 8270 SIM
- Alkyl PAHs calculated from a multipoint calibration
- A representative target compound is used to represent a homolog series for quantification
- Results generated for alkyl PAHs should be treated as semiquantitative

eurofins | Lancaster Laboratories Environmental

PAHS Reported



- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(e)pyrene
- Benzo(g,h,i)perylene
- Benzo(k)fluoranthene
- Benzothiophene
- Biphenyl
- Chrysene
- cis/trans-Decalin
- Dibenz(a,h)anthracene
- Dibenzofuran
- Dibenzothiophene
- Fluoranthene
- Fluorene
- Indeno(1,2,3-cd)pyrene
- Naphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- 2,6-Dimethylnaphthalene
- 2,3,5-Trimethylnaphthalene
- Naphthobenzothiophene
- Perylene
- Phenanthrene
- 1-Methylphenanthrene
- Pyrene
- Retene
- Total Aromatics (Includes alkylated)

eurofins | Lancaster Laboratories Environmental

Alkyl PAHS Reported



- C1-Naphthalenes
- C2-Naphthalenes
- C3-Naphthalenes
- C4-Naphthalenes
- C1-Fluorenes
- C2-Fluorenes
- C3-Fluorenes
- C1-Phenanthrenes/Anthracenes
- C2-Phenanthrenes/Anthracenes
- C3-Phenanthrenes/Anthracenes
- C4-Phenanthrenes/Anthracenes
- C1-Benzo(b)thiophene
- C2-Benzo(b)thiophene
- C3-Benzo(b)thiophene
- C4-Benzo(b)thiophene
- C1-Naphthobenzothiophenes
- C2-Naphthobenzothiophenes
- C3-Naphthobenzothiophenes
- C1-Decalin
- C2-Decalin
- C3-Decalin
- C4-Decalin
- C1-Dibenzothiophenes
- C2-Dibenzothiophenes
- C3-Dibenzothiophenes
- C4-Dibenzothiophenes
- C1-Fluoranthenes/pyrenes
- C2-Fluoranthenes/pyrenes
- C3-Fluoranthenes/pyrenes
- C4-Fluoranthenes/pyrenes
- C1-Benzanthrene/chrysenes
- C2-Benzanthrene/chrysenes
- C3-Benzanthrene/chrysenes
- C4-Benzanthrene/chrysenes

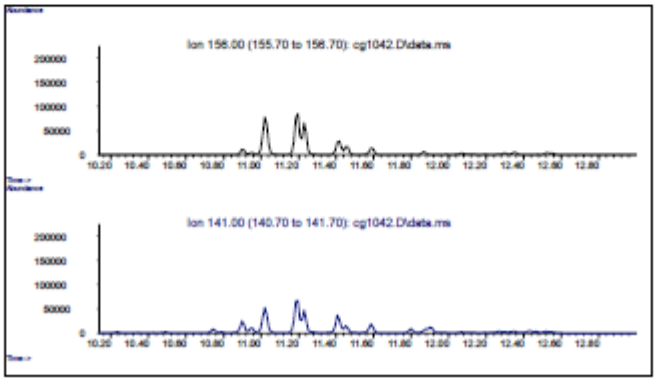
eurofins | Lancaster Laboratories Environmental

Method Summary

- To create SIM method large investment in establishing correct windows
- Analysis of reference oils to determine alkyl PAH windows
- Requires analysis of windowing standard at start of each tune
- Alkanes added to the calibration and analysis mix

eurofins | Lancaster Laboratories Environmental

C2-Naphthalenes
Mass 156, 141 amu; 10.2 to 12.8 min



eurofins | Lancaster Laboratories Environmental

Alkanes Reported



n-Decane
n-Undecane
n-Dodecane
n-Tridecane
n-Tetradecane
n-Pentadecane
n-Hexadecane
n-Heptadecane
n-Octadecane
n-Nonadecane

n-Eicosane
n-Henicosane
n-Docosane
n-Tricosane
n-Tetracosane
n-Pentacosane
n-Hexacosane
n-Heptacosane
n-Octacosane

n-Nonacosane
n-Triacontane
n-Hentriacontane
n-Dotriacontane
n-Tritriacontane
n-Tetratriacontane
n-Pentatriacontane
Pristane
Phytane
Total Alkanes

eurofins | Lancaster Laboratories Environmental

What are Geochemical Biomarkers?



- Complex organic compounds that are found in petroleum and show little to no change in structure from their parent molecules found in living organisms.
- Categorized into different classes, terpanes, steranes and triaromatic steroids

eurofins | Lancaster Laboratories Environmental

What are Geochemical Biomarkers?



- Several reference biomarker compounds are in calibration mixes
- Biomarkers grouped according to reference used for quantification
- Analysis of reference oils key to biomarker identification

eurofins | Lancaster Laboratories Environmental

Biomarkers reported



A1-C20-TAS
A2-C21-TAS
A3-C26 TAS(20S)
A4-C26/C27-TAS
A5-C27-TAS(20R)
A6-TAS(20S)
A7-TAS(20R)
T1-C20Diterpane
T2-C21Diterpane
T3-C22Diterpane
T4-C23Diterpane
T5-C24Diterpane
T6-C25Diterpane
T6a-C24TetracyclicTerpane
T6b-C26Tricyclic[S]
T6c-C26Tricyclic[R]
T7-C28Tricyclictriterpane[S]
T8-C28Tricyclictriterpane[R]
T9-C29Tricyclictriterpane(S)
T10-C29Tricyclictriterpane(R)
T11-Trisnorhopane(TS)
T12-Trisnorhopane(TM)
T13-Trisnorhopane
T13a-29,30-Bisnorhopane
T14-Bisnorhopane
T14a-C28,C30Bisnorhopane
T14b-C29,C25Norhopane
T15-C29-Norhopane
T16-Norneohopane
17a(H)-diahopane
T17-C30-Normoretane
T18-C30-Oleanane
T19-C30-Hopane
T20-Moretane
T21-C31-Homohopane(S)
17b(H),21b(H)-Hopane
T22-C31-Homohopane(R)
T22a-Gammacerane
T23-Homohopane
T24-Homomoretane
T25-Diploptene
T26-C32-Bishomohopane(S)
T27-C32-Bishomohopane(R)
T28-Bishomomoretane
T29-Homohopane
T30-C33-Trishomohopane(S)
T31-C33-Trishomohopane(R)
T32-Tetrakishomohopane(S)
T33-Tetrakishomohopane(R)
T34-Pentakishomohopane(S)
T35-Pentakishomohopane(R)
S4-Diacholestane
S5-Diacholestane
5a-cholestane
S6-Diacholestane
S7-Diacholestane
S8-Methyldiacholestane
S10-Methyldiacholestane
S11-Methyldiacholestane
S12-Cholestane
S14-Cholestane(20R)
S15-Cholestane(20S)
S18-Ethyldiacholestane
S19-Ethyldiacholestane
S20-Methyldiacholestane
S22-Methylcholestane(20R)
S23-Methylcholestane(20S)
S24-MethylCholestane
S25-EthylCholestane
S26-Ethylcholestane(20R)
S27-Ethylcholestane(20S)
S28-Ethylcholestane

eurofins | Lancaster Laboratories Environmental

Why do we care?



- Very useful in forensic petroleum analysis when alkane pattern is weathered
- Complements and enhances conventional GC/FID fingerprinting capabilities
- Can be analyzed simultaneously with the Alkyl PAHs.

eurofins | Lancaster Laboratories Environmental

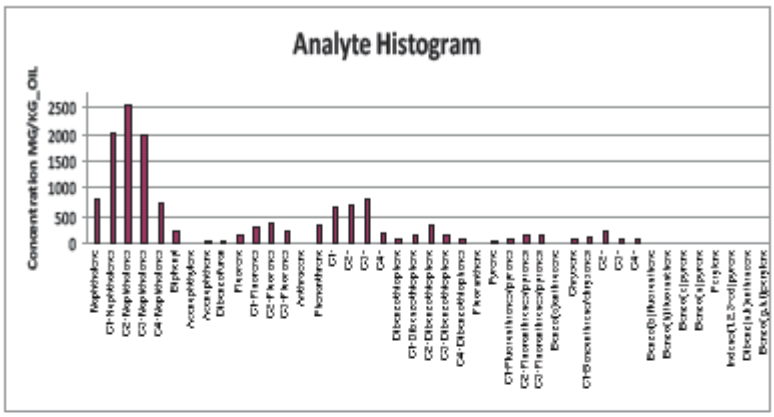
Results



- Specialized report format and electronic spreadsheet
- Histograms for qualitative analysis of PAHs/Alkyl PAHs
- Extracted ion current profiles provided for biomarkers

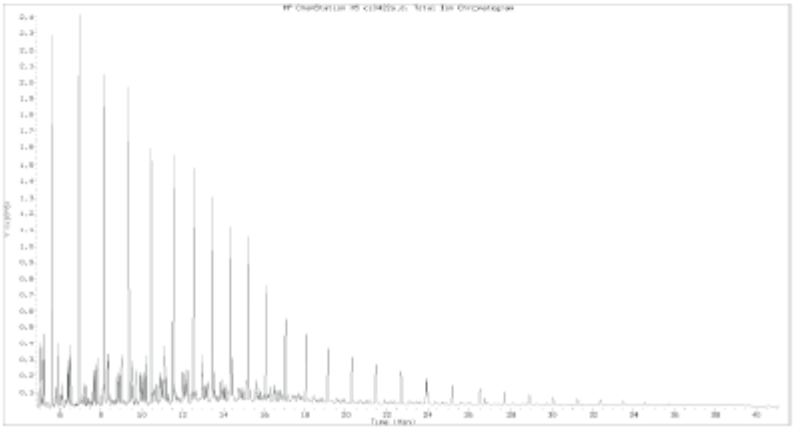
eurofins | Lancaster Laboratories Environmental

PAH/Alkyl PAH Histogram



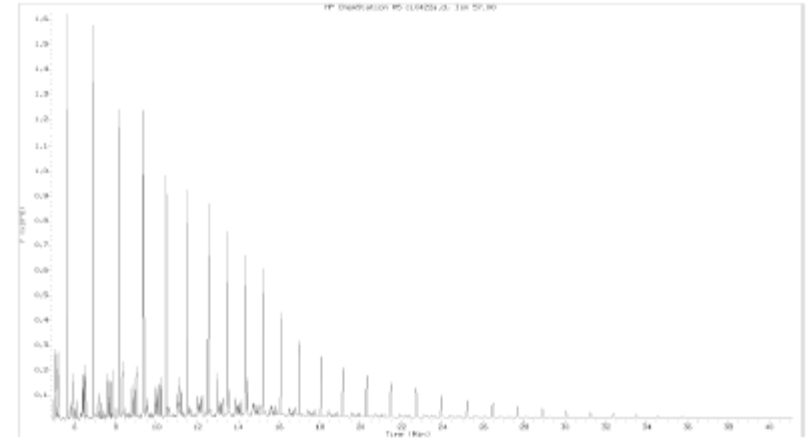
eurofins | Lancaster Laboratories Environmental

Arabian Light –Total Ion Chromatogram



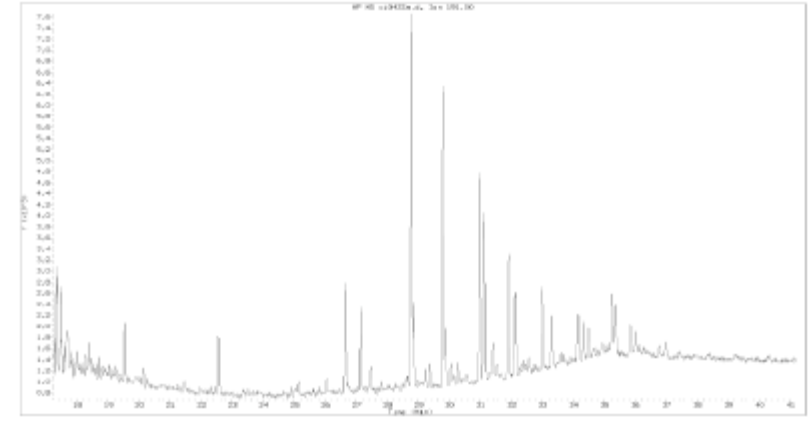
eurofins | Lancaster Laboratories Environmental

Arabian Light – Mass 57 amu EICP

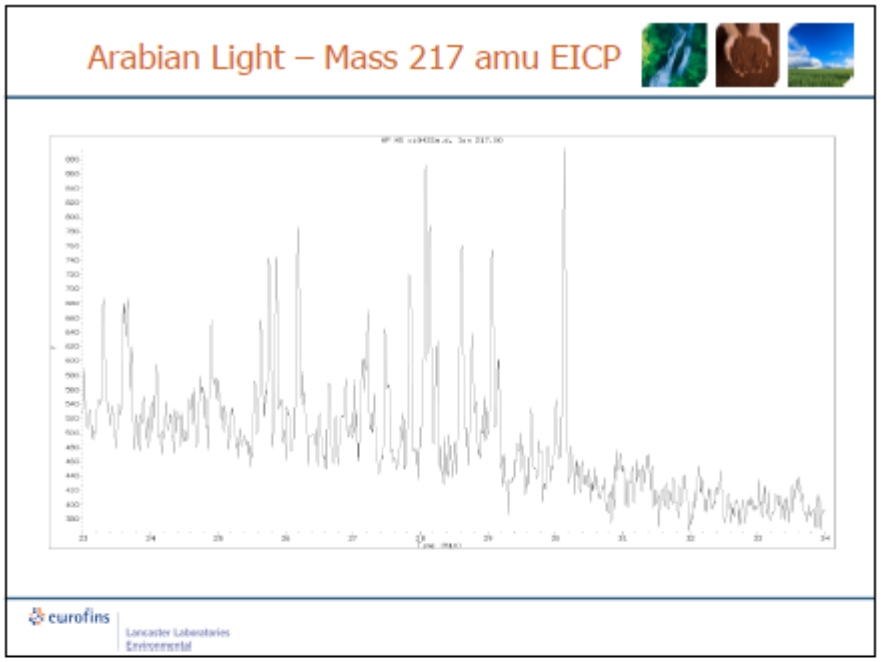


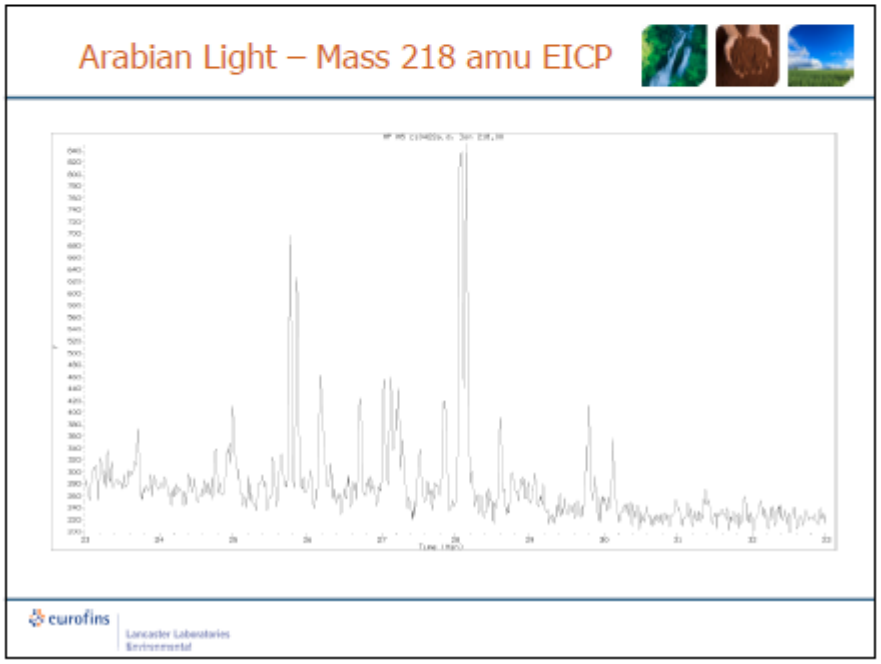
eurofins | Lancaster Laboratories Environmental

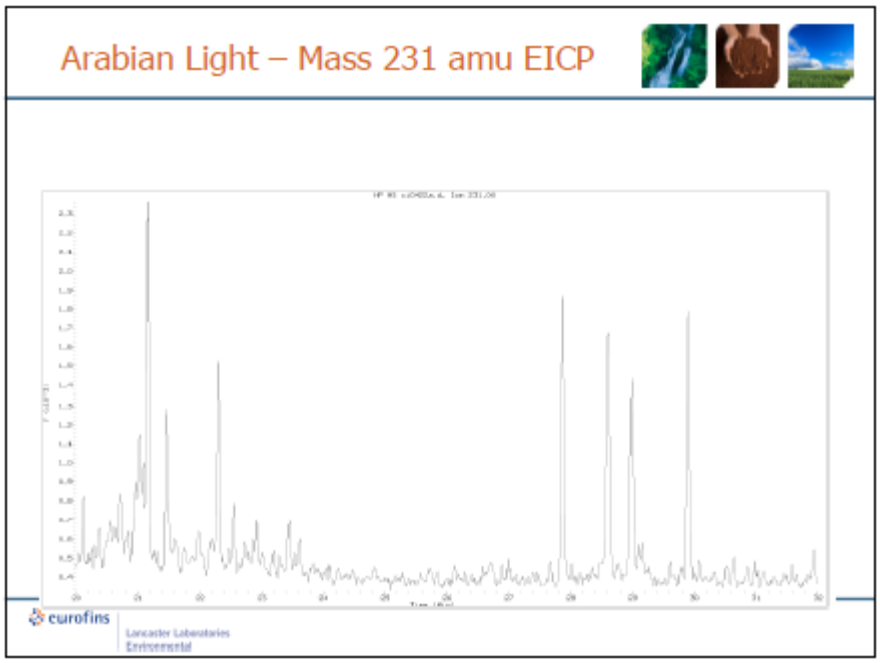
Arabian Light – Mass 191 amu EICP

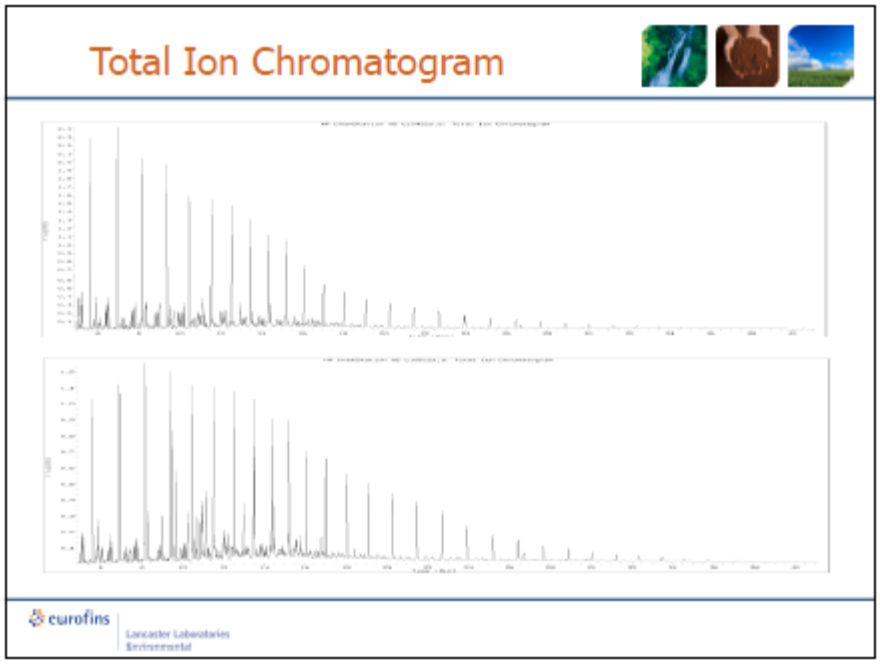


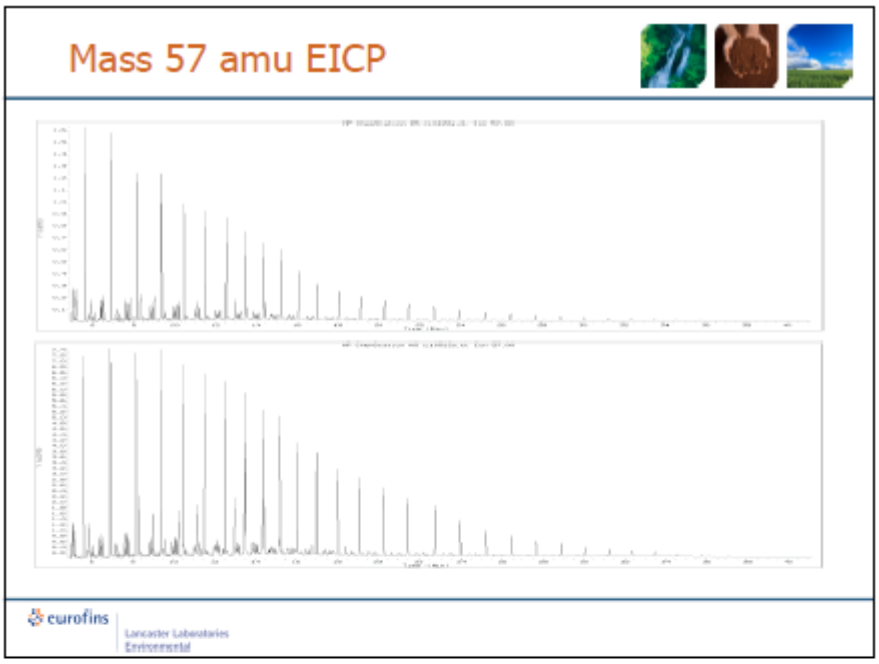
eurofins | Lancaster Laboratories Environmental

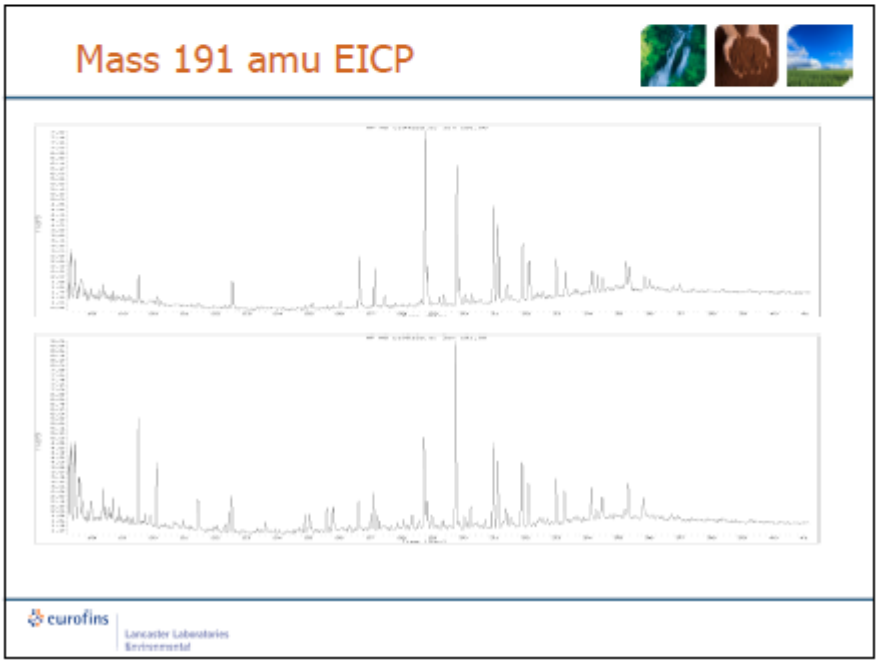

Arabian Light – Mass 217 amu EICP
eurofins
Lancaster Laboratories
Environmental

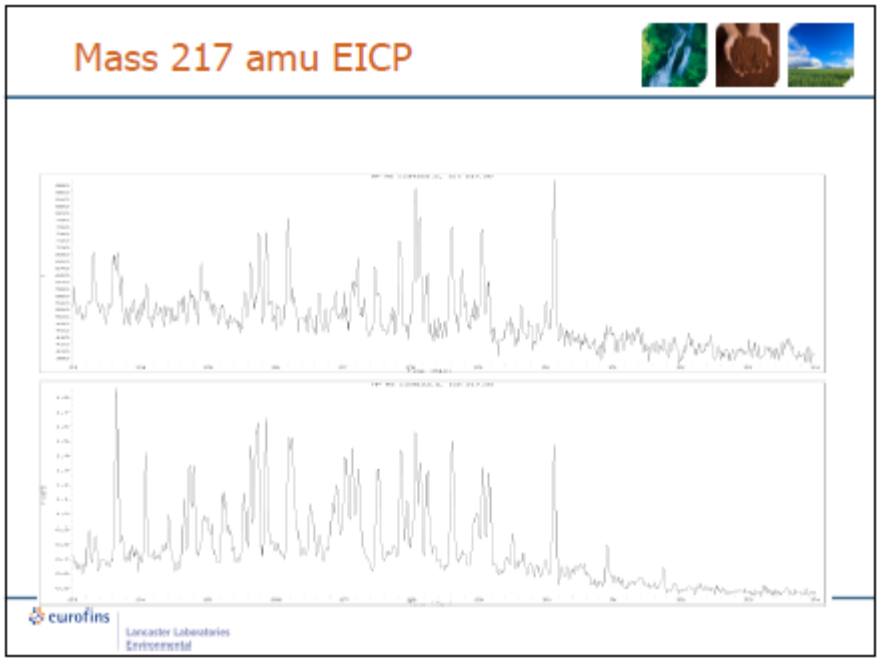

Arabian Light – Mass 218 amu EICP
eurofins
Lancaster Laboratories
Environmental

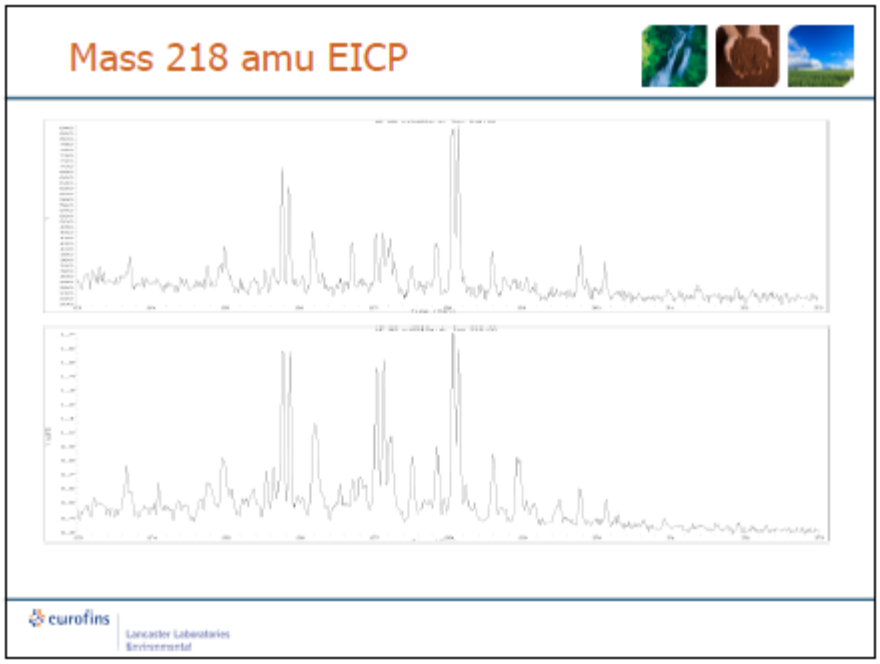

Arabian Light – Mass 231 amu EICP
eurofins
Lancaster Laboratories
Environmental


Total Ion Chromatogram
eurofins
Lancaster Laboratories
Environmental

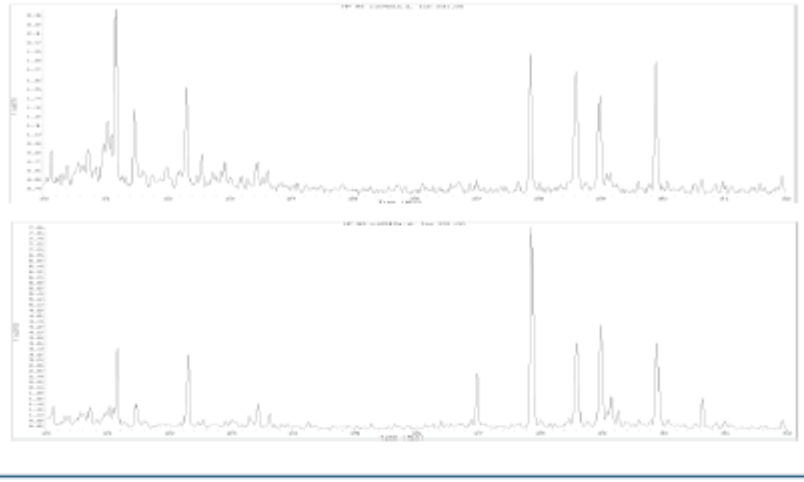

Mass 57 amu EICP
eurofins
Lancaster Laboratories
Environmental


Mass 191 amu EICP
eurofins
Lancaster Laboratories
Environmental


Mass 217 amu EICP
eurofins
Lancaster Laboratories
Environmental


Mass 218 amu EICP
eurofins
Lancaster Laboratories
Environmental

Mass 231 amu EICP



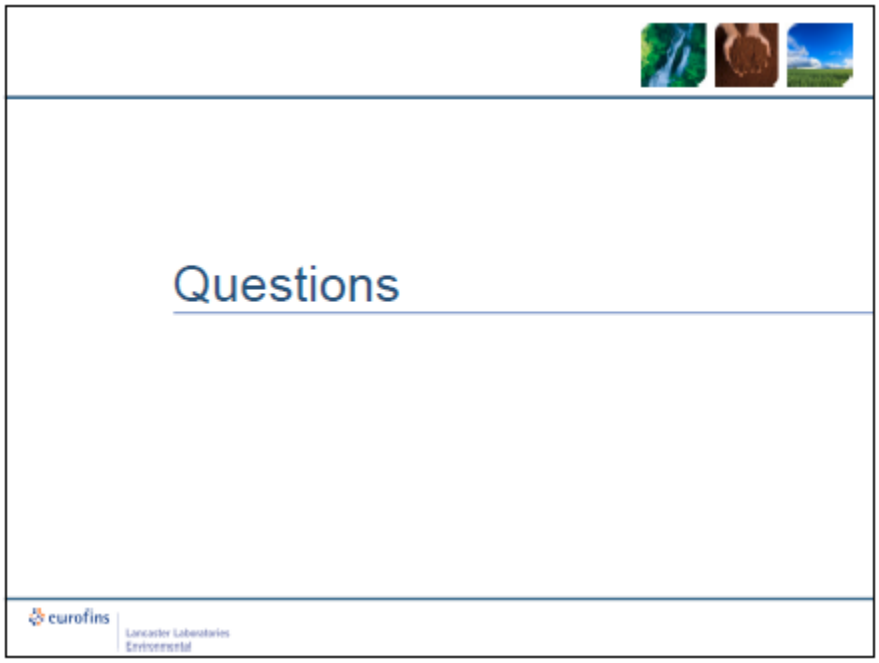
eurofins | Lancaster Laboratories Environmental

Acknowledgement

Richard Karam, Manager, Semivolatiles, Eurofins Lancaster Laboratories Environmental

Tim Trees, Principal Chemist, Eurofins Lancaster Laboratories Environmental

eurofins | Lancaster Laboratories Environmental


Questions
eurofins
Lancaster Laboratories
Environmental

Dominguez Channel: A Petroleum Spill in Pipeline Alley

Alan Jeffrey
DPRA/Zymax Forensics

Abstract

In 2011, an oil slick appeared in the Dominguez Channel, a channeled river in Los Angeles. Potential sources were abundant: crude oil and petroleum product pipelines under the Channel; a multitude of pipelines along the sides of the Channel currently and historically carrying a variety of petroleum products; neighboring gas stations and businesses storing petroleum products; and, to top it off, potential oil seeps from underlying Los Angeles Basin oil reservoirs.

This discussion will show how attempts to identify the source were complicated by the sampling methodology, and how refinements in the sampling and wider collection of samples helped to better identify the spilled product. Further complications arose because of changes in the formulation of petroleum products like gasoline over time, which can make the identity of gasoline-range hydrocarbons ambiguous.

The discussion will show how forensics chemical analysis of the oil slick and the subsurface light non-aqueous phase liquid (LNAPL) feeding the oil slick helped to eliminate some potential sources and narrow the search for the most likely source(s).

Dominguez Channel: a Petroleum Spill in Pipeline Alley



Alan Jeffrey, Ph.D.
National Environmental Monitoring Conference
August, 2013



DPRA

ZymaX forensics

Common Environmental Forensic Questions

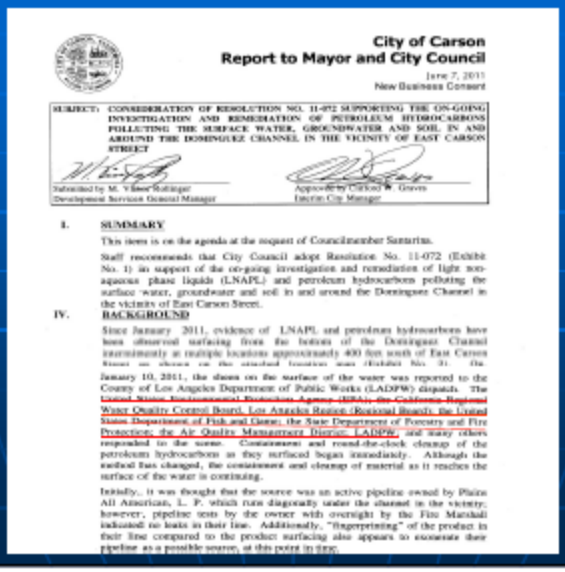
- What is the chemical pollutant?
- What is the source?
- Who is responsible? [Liability]
- What is my cost? [Apportionment]



Dominguez Channel



Dominguez Channel Oil Slick



City of Carson
Report to Mayor and City Council

June 7, 2011
New Business Consent

SUBJECT: CONSIDERATION OF RESOLUTION NO. 11-072 SUPPORTING THE ON-GOING INVESTIGATION AND REMEDIATION OF PETROLEUM HYDROCARBONS POLLUTING THE SURFACE WATER, GROUNDWATER AND SOIL IN AND AROUND THE DOMINGUEZ CHANNEL IN THE VICINITY OF EAST CARSON STREET

Submitted by M. Ylber Bollinger
Development Services General Manager

Approved by Clifford W. Graves
Interim City Manager

I. **SUMMARY**

This item is on the agenda at the request of Councilmember Santarina.

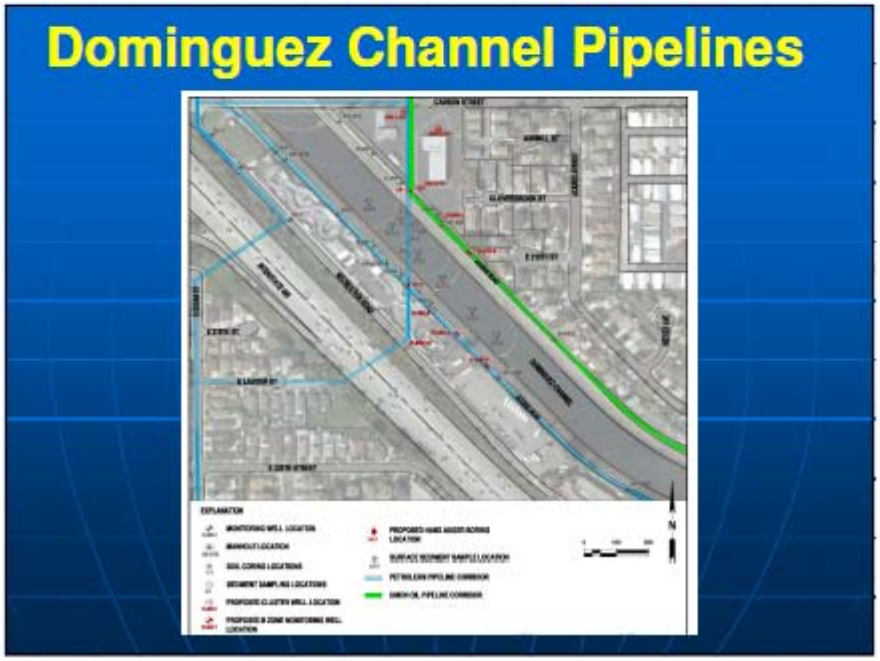
Staff recommends that City Council adopt Resolution No. 11-072 (Exhibit No. 1) in support of the on-going investigation and remediation of light non-aqueous phase liquids (LNAPL) and petroleum hydrocarbons polluting the surface water, groundwater and soil in and around the Dominguez Channel in the vicinity of East Carson Street.

IV. **BACKGROUND**

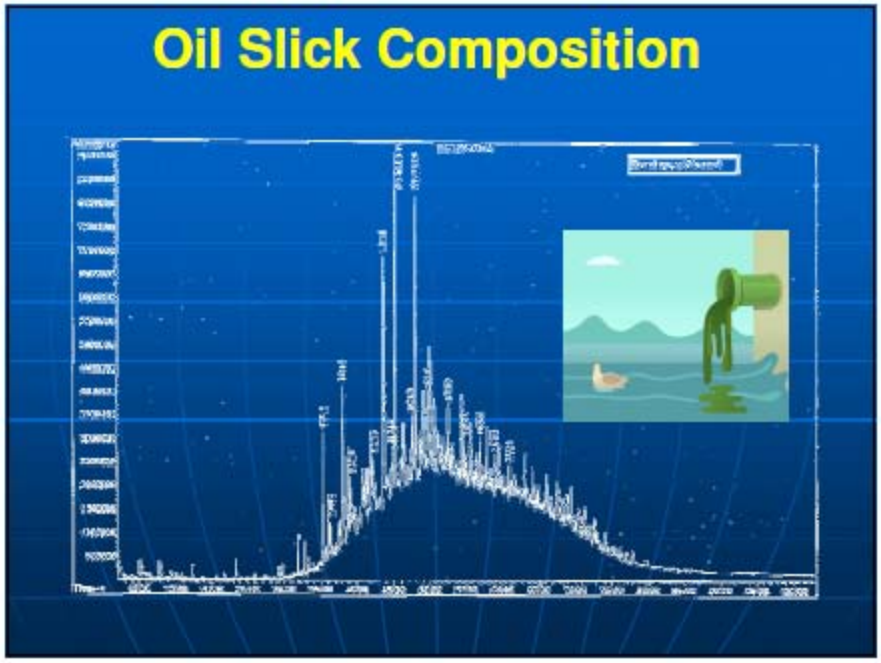
Since January 2011, evidence of LNAPL and petroleum hydrocarbons have been observed surfacing from the bottom of the Dominguez Channel intermittently at multiple locations approximately 400 feet south of East Carson Street as shown on the attached location map (Exhibit No. 3). On January 10, 2011, the sheen on the surface of the water was reported to the County of Los Angeles Department of Public Works (LADPW) dispatch. The United States Environmental Protection Agency (EPA), the California Regional Water Quality Control Board, Los Angeles Region (Regional Board), the United States Department of Fish and Game, the State Department of Forestry and Fire Protection, the Air Quality Management District, LADPW, and many others responded to the scene. Containment and round-the-clock cleanup of the petroleum hydrocarbons as they surfaced began immediately. Although the surface has changed, the containment and cleanup of material as it reaches the surface of the water is continuing.

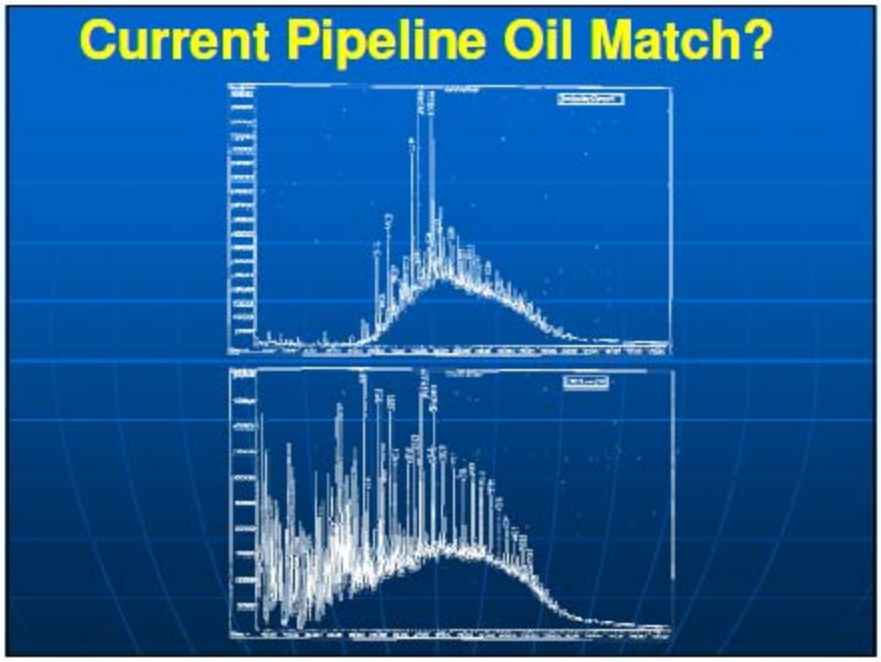
Initially, it was thought that the source was an active pipeline owned by Plains All American, L. P. which runs diagonally under the channel in the vicinity; however, pipeline tests by the owner with oversight by the Fire Marshall indicated no leaks in their line. Additionally, "fingerprinting" of the product in their line compared to the product surfacing also appears to exonerate their pipeline as a possible source, at this point in time.

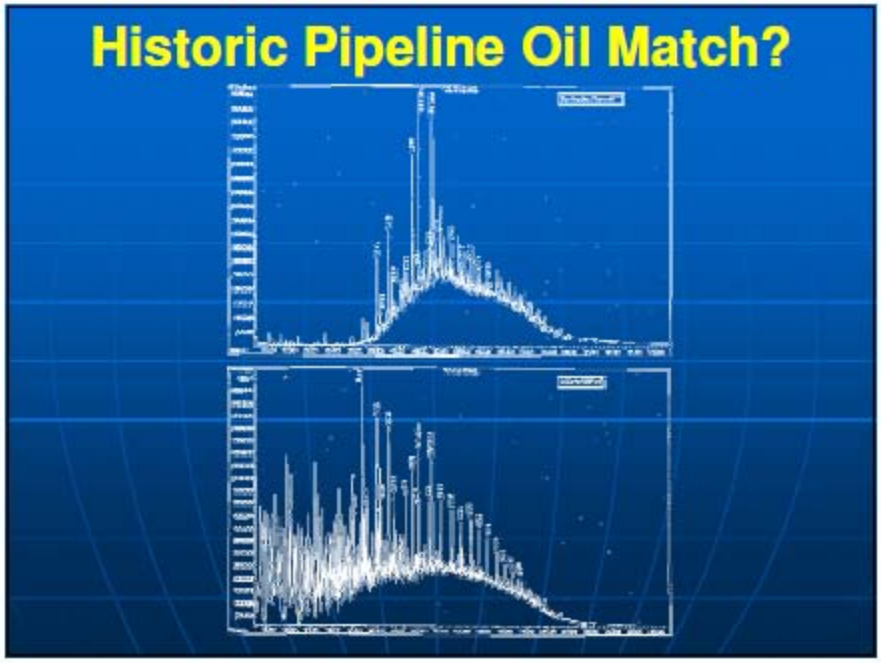

Petroleum Sources
CARSON AIR HARBOR (CAR)
21611 South Perry Street
FORMER TEXACO
1209 East Carson Street
FORMER ACTIVE RV
1202 East Carson Street
76 STATION
1025 East Carson Street

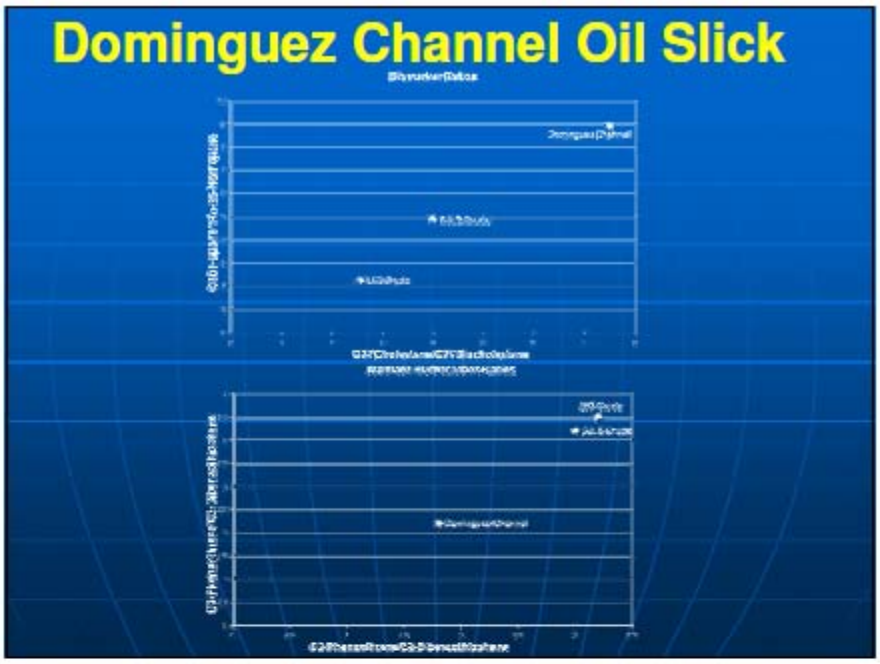

Dominguez Channel Pipelines

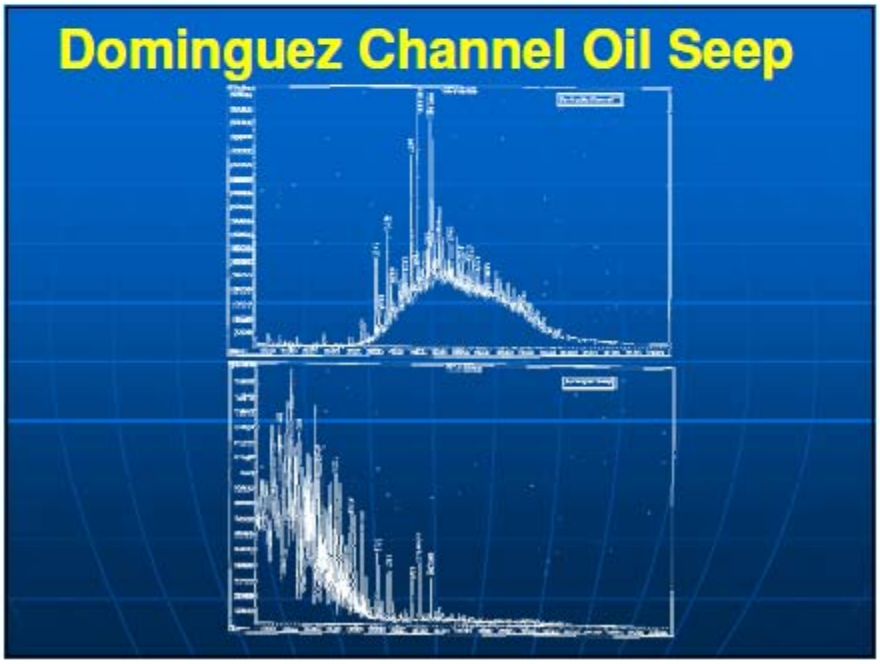

Dominguez Channel Oil Slick

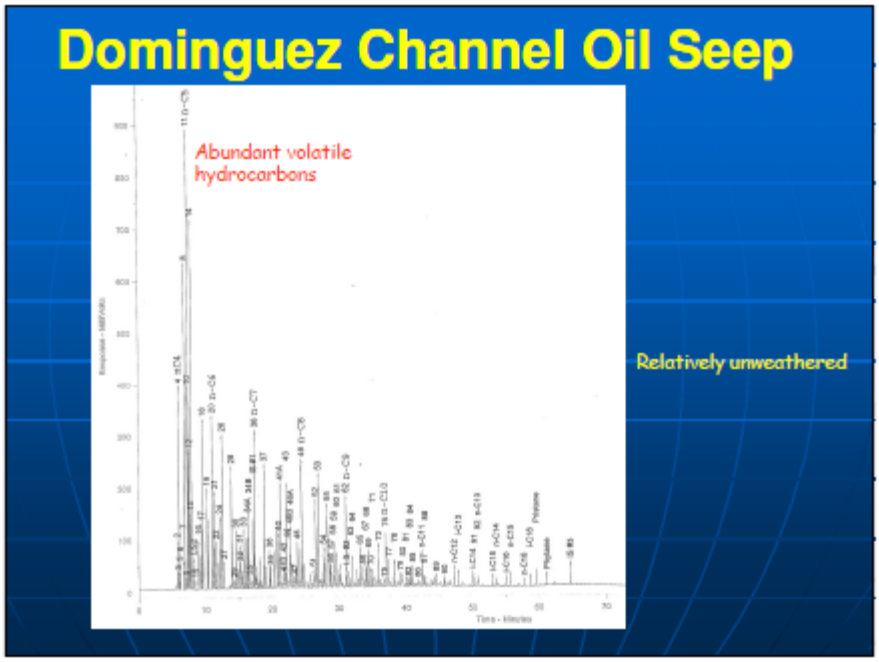

Oil Slick Composition

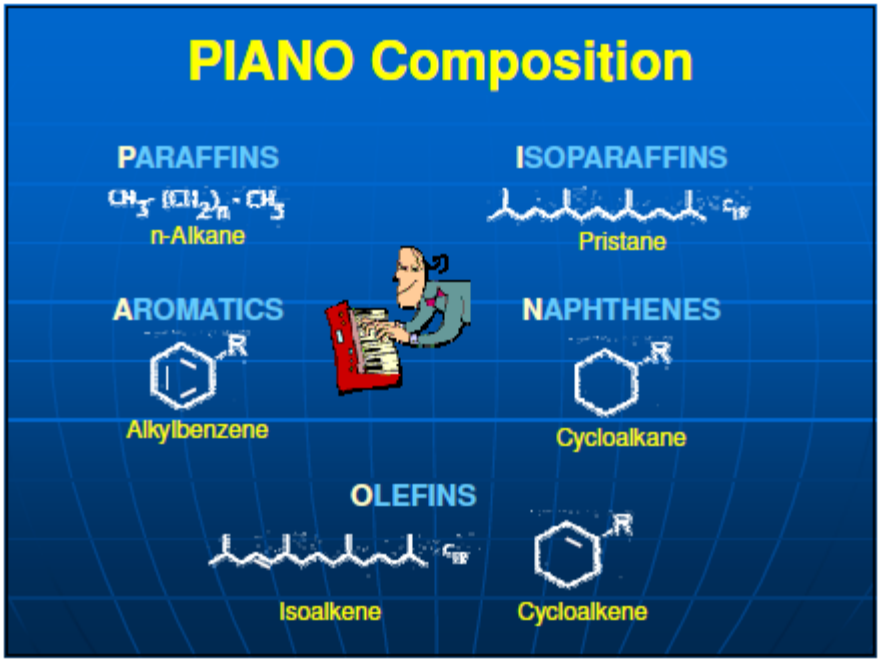

Current Pipeline Oil Match?

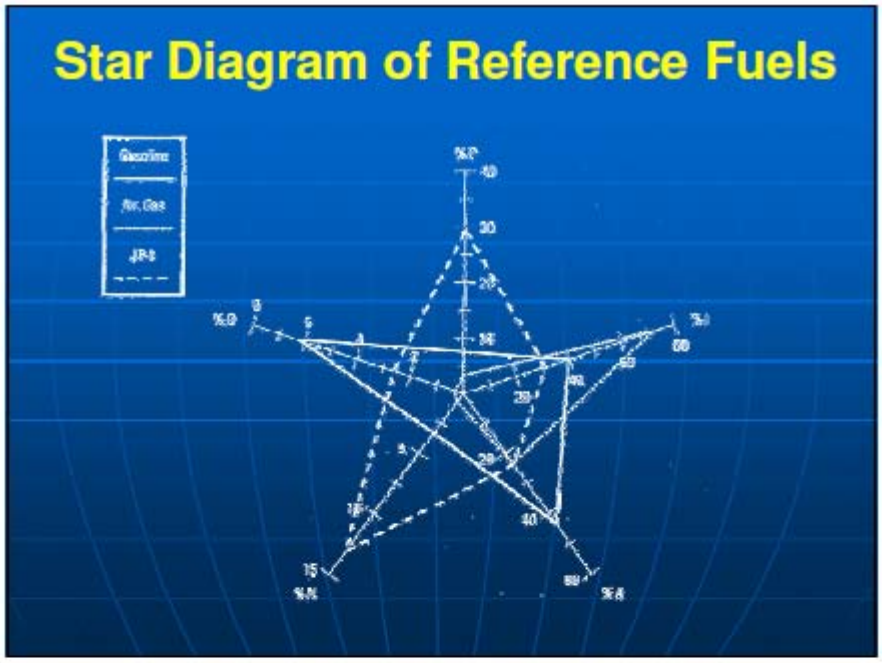

Historic Pipeline Oil Match?

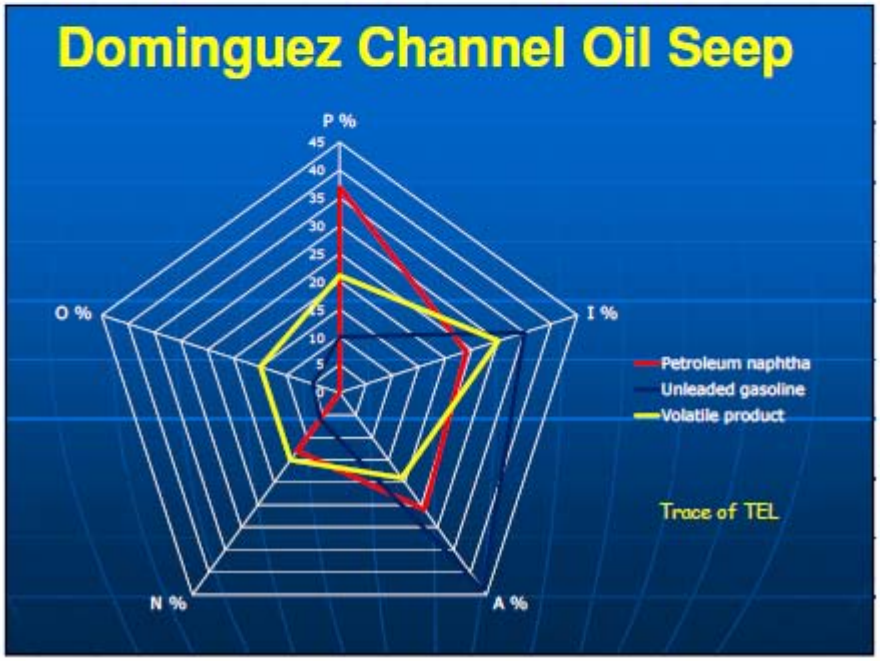

Dominguez Channel Oil Slick


Dominguez Channel Oil Seep


Dominguez Channel Oil Seep
Abundant volatile hydrocarbons
Relatively unweathered


PIANO Composition
PARAFFINS
n-Alkane
ISOPARAFFINS
Pristane
AROMATICS
Alkylbenzene
NAPHTHENES
Cycloalkane
OLEFINS
Isoalkene
Cycloalkene

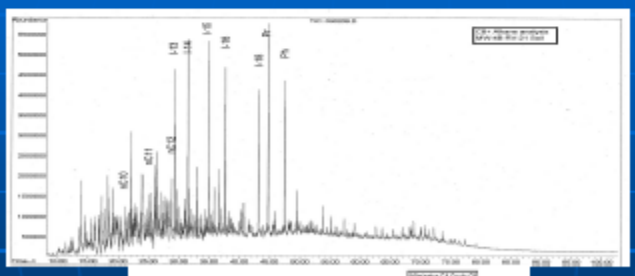

Star Diagram of Reference Fuels


Dominguez Channel Oil Seep
P %
I %
A %
N %
O %
45
40
35
30
25
20
15
10
5
0
Petroleum naphtha
Unleaded gasoline
Volatile product
Trace of TEL

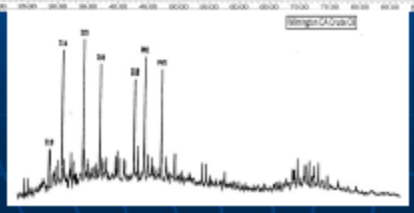
What is the Chemical Pollutant?
Volatile product

- High paraffin content like naphtha (first distillation product of crude oil) – but contains olefins like gasoline
- Higher paraffin and olefin content than unleaded gasoline
- High paraffin content like historic leaded gasoline (high naphtha content) – but only a trace of lead
- Cracked naphtha – refinery intermediate

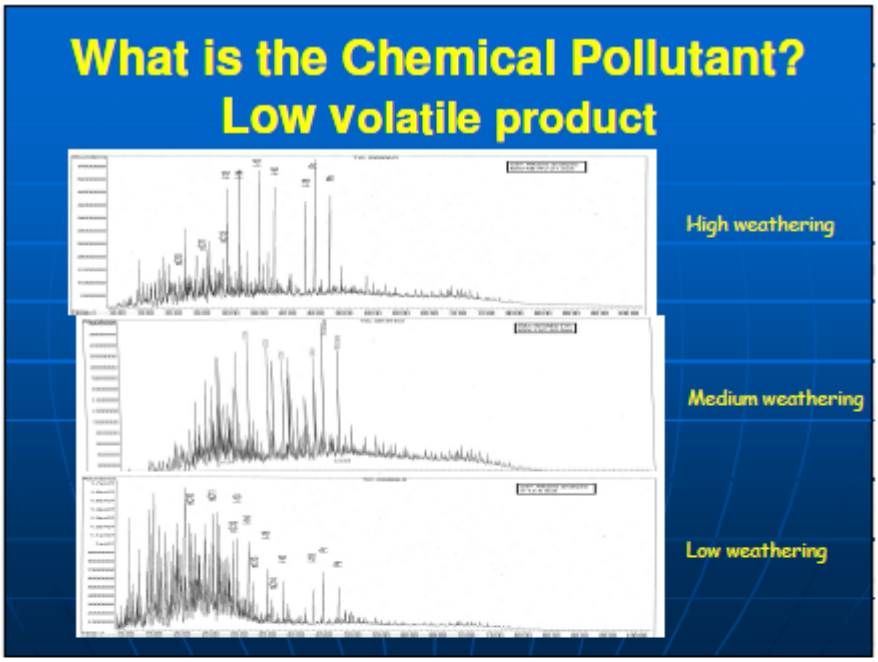
What is the Chemical Pollutant?
Low volatile product

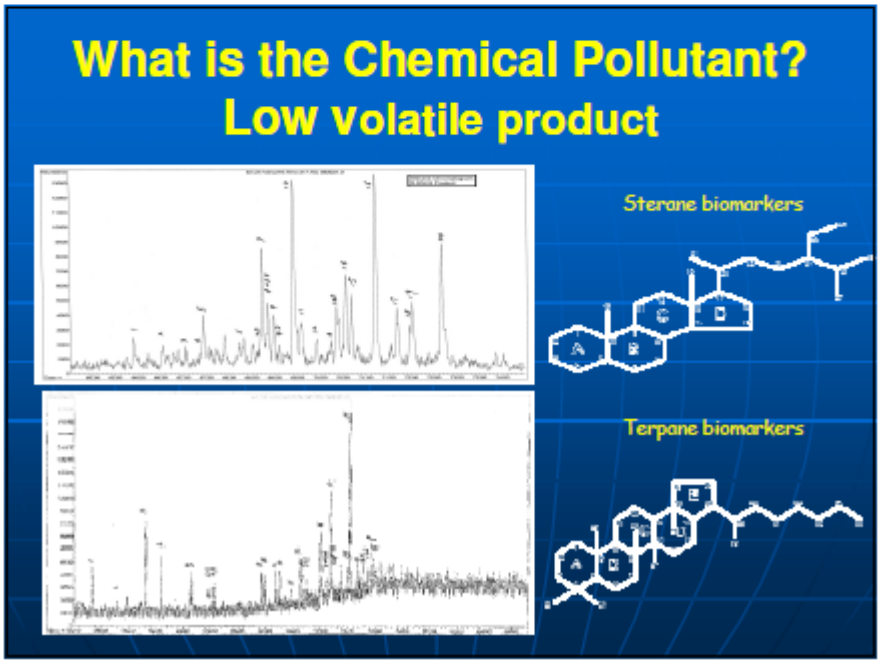


Weathered seep in soil



Wilmington, CA crude oil


What is the Chemical Pollutant?
Low volatile product
High weathering
Medium weathering
Low weathering


What is the Chemical Pollutant?
Low volatile product
Sterane biomarkers
Terpane biomarkers

What is the Source?

- Pipeline currently or historically carrying cracked naphtha
- Pipeline carrying Wilmington or similar S. California crude oil

Who is Responsible?

- Naphtha: X Co.

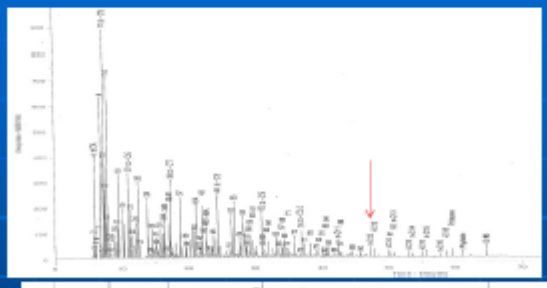
and

- Crude oil: Y Co.

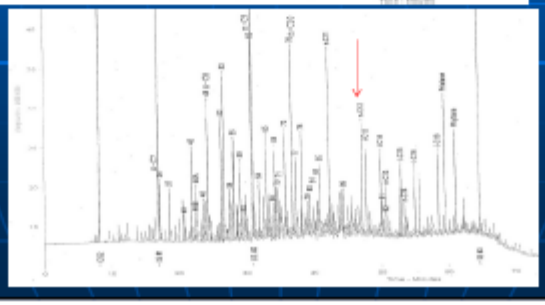
Apportionment?

- Complicated by:
- Overlap of carbon range of products – crude oil hydrocarbons in naphtha range
- Weathering – loss of naphtha component

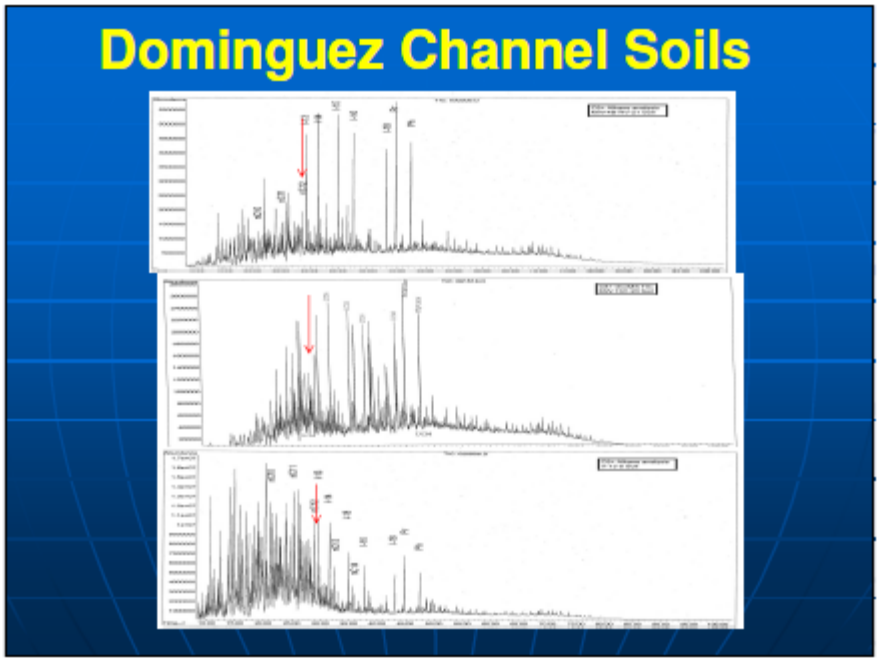
Dominguez Channel LNAPLs

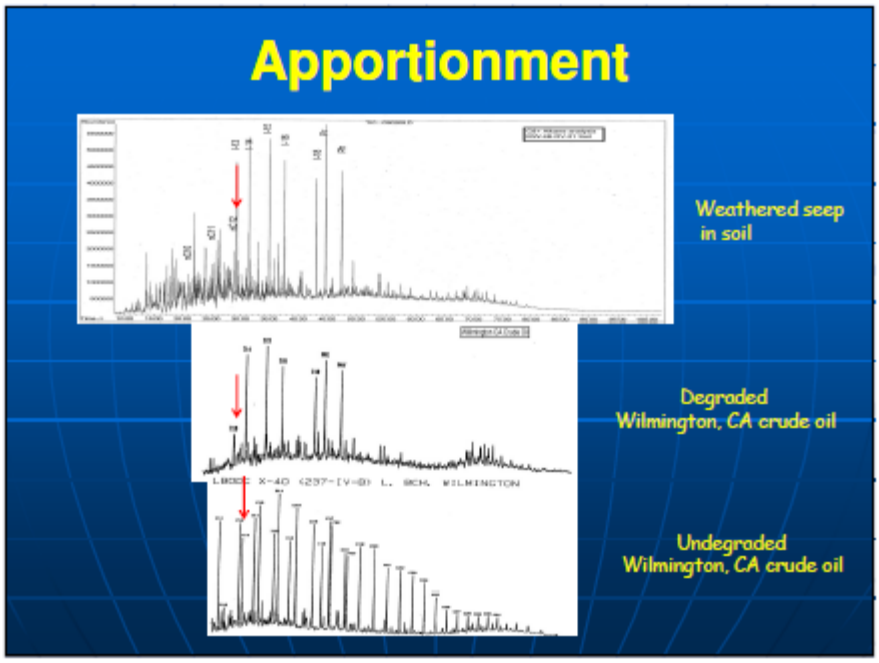


Unweathered



Weathered


Dominguez Channel Soils


Apportionment
Weathered seep in soil
Degraded Wilmington, CA crude oil
Undegraded Wilmington, CA crude oil

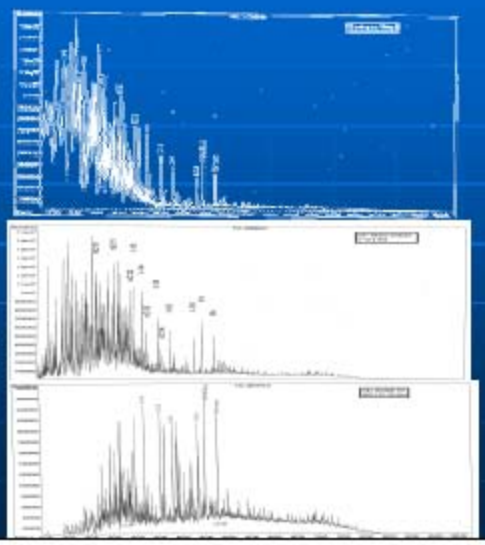
Apportionment

- Naphtha: TPH (C4-C12) – portion of the TPH (C4-C12) assigned to crude oil
- Crude oil: TPH (C12-C40) + portion of the TPH (C4-C12) assigned to crude oil
- No example of pure crude oil
- Percentage of hydrocarbons in pipeline grade S. California oils in the in C4-C12 range calculated (Y%)

Apportionment

- Naphtha: TPH (C4-C12) – TPH (C12-C40) x Y/100-Y
- Crude oil: TPH (C12-C40) + TPH (C12-C40) x Y/100-Y
- Site divided into zones
- Extensive TPH analysis in each zone
- Average naphtha and crude oil percentage calculated for each zone

Apportionment



Conclusions

In a complicated area with multiple potential sources, hydrocarbon forensic analysis helped:

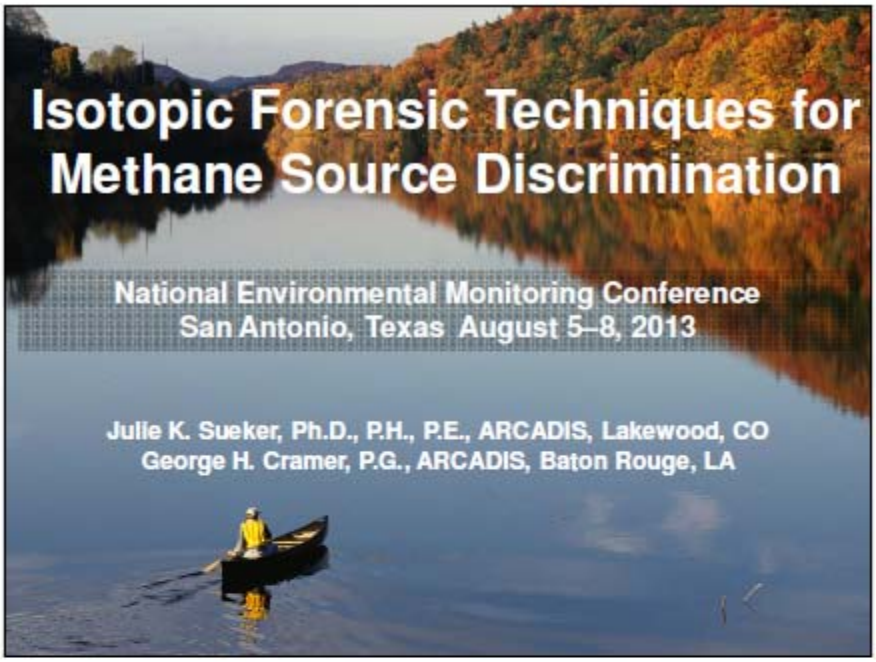
- Identify constituents of seep
- Eliminate similar but unrelated source
- Identify most likely sources
- Apportion responsibility for seep based on relative amounts of constituents in seep

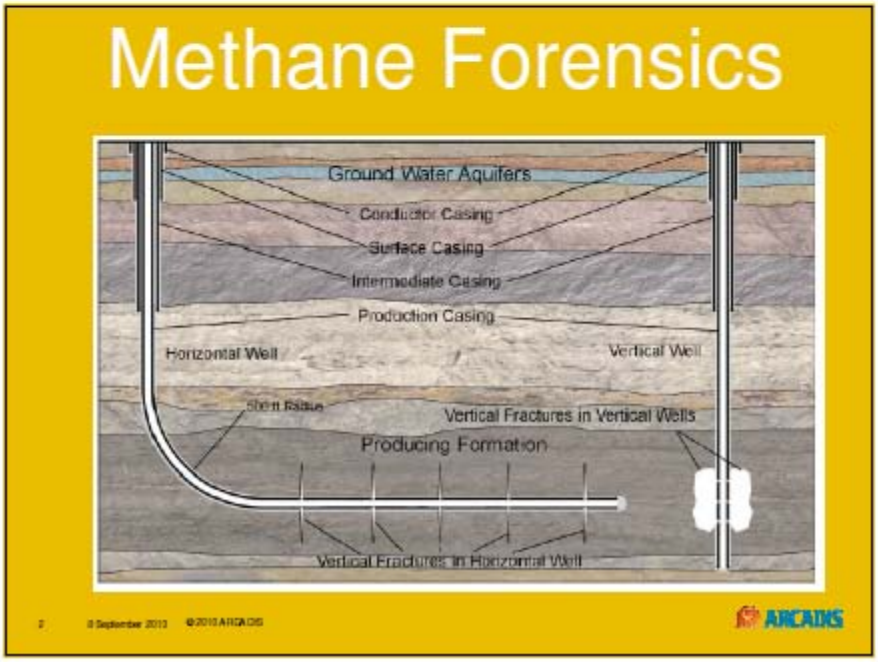
Isotopic Forensic Techniques for Methane Source Descrimination

Julie K. Sueker, George H. Cramer
ARCADIS

Abstract

Combustible gases, such as methane, in soil and shallow groundwater present a safety concern due to potential offgassing and accumulation in water well and plumbing systems that could lead to an explosion. Elevated concentrations of methane in enclosed spaces also pose an asphyxiation hazard. Methane observed in shallow subsurface environments can be derived from many potential sources including swamps, landfills, coal beds, and natural gas production and storage operations. Understanding methane provenance may be important for sites where methane hazards are present and multiple unrelated methane sources exist. Generation of methane and other light hydrocarbon gas occurs via three principal mechanisms; 1) biogenesis – microbial decomposition of organic matter (e.g., carbon dioxide reduction and acetate fermentation); 2) thermogenesis – thermal decomposition of deeply buried organic matter (associated with coal, oil, and gas formation); and 3) abiogenesis – formation of methane within Earth's mantle. These different methane generation mechanisms result in differing compositions of light hydrocarbon gases as well as in differing stable carbon and hydrogen isotope ratios which can be used to assess methane provenance. Carbon-14 (14C) age dating can further discriminate methane sources, as thermogenic gases are "fossil" carbon sources and do not contain measureable quantities of 14C, whereas biogenic gases are typically "modern" and contain measurable quantities of 14C. Methane forensic techniques were utilized to distinguish a single source of natural gas released from a Gulf Coast region salt dome cavern storage facility from other sources of methane known to occur naturally in the region. The natural gas release was caused by a breach of a storage well casing at an elevation above the storage cavern. Natural gas escaped through the well casing breach into overlying formations and migrated to the surface. Application of methane forensic techniques resulted in delineation of a significantly smaller affected footprint than originally interpreted.


Isotopic Forensic Techniques for Methane Source Discrimination
National Environmental Monitoring Conference
San Antonio, Texas August 5–8, 2013
Julie K. Sueker, Ph.D., P.H., P.E., ARCADIS, Lakewood, CO
George H. Cramer, P.G., ARCADIS, Baton Rouge, LA


Methane Forensics
Ground Water Aquifers
Conductor Casing
Surface Casing
Intermediate Casing
Production Casing
Horizontal Well
Vertical Well
Vertical Fractures in Vertical Wells
Producing Formation
Vertical Fractures in Horizontal Well
ARCADIS

Overview

- Why use stable isotope forensics for stray gas assessments?
- Methane generation mechanisms
- Stray gas forensic techniques
  - Geochemistry
  - Isotopes
  - Structural Geology
  - Geophysics
  - Well integrity
- Case study
  - Salt dome storage cavern gas release



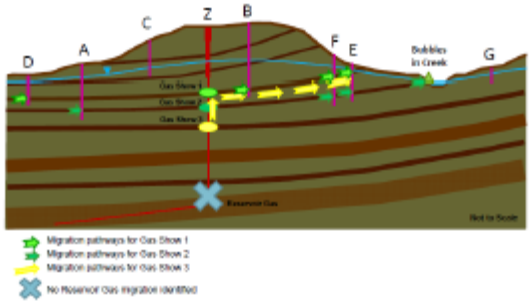
Methane bubbles in swamp

 ©2010 ARCADIS

ARCADIS

Stray Gas Forensics

- Methane derived from numerous sources (biogenic, thermogenic)
- Potential methane release site may have multiple unrelated methane sources including thermogenic sources
- Methane forensic techniques used in various settings to differentiate methane sources

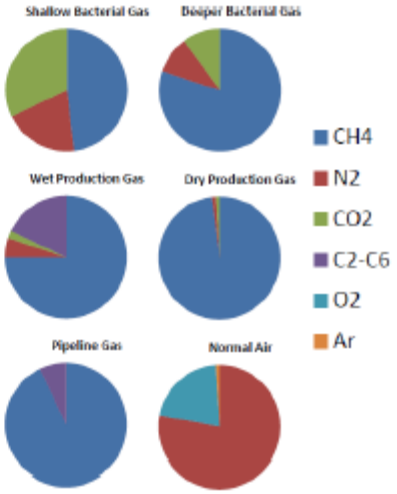


Imagine the result

ARCADIS

Methane Generation Mechanisms

- Thermogenic
  - Coal bed and oil & gas formations
- Biogenic
  - Methanogenesis – "drift gas"
  - Acetate fermentation – "swamp gas" and "landfill gas"
- Abiogenic
  - Mantel gas

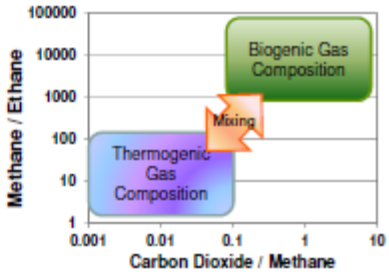


 ©2013 ARCADIS

ARCADIS

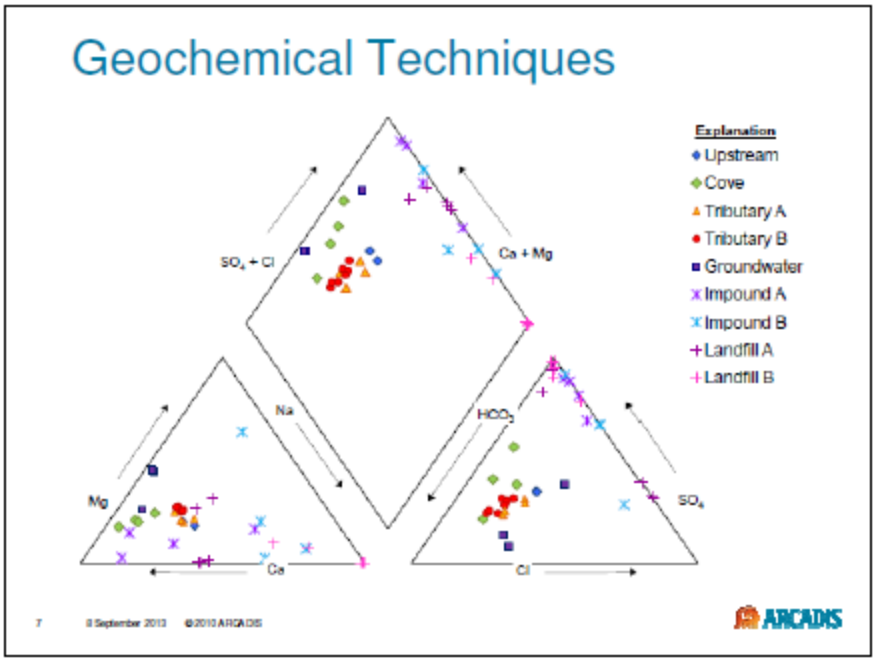
Geochemical Techniques

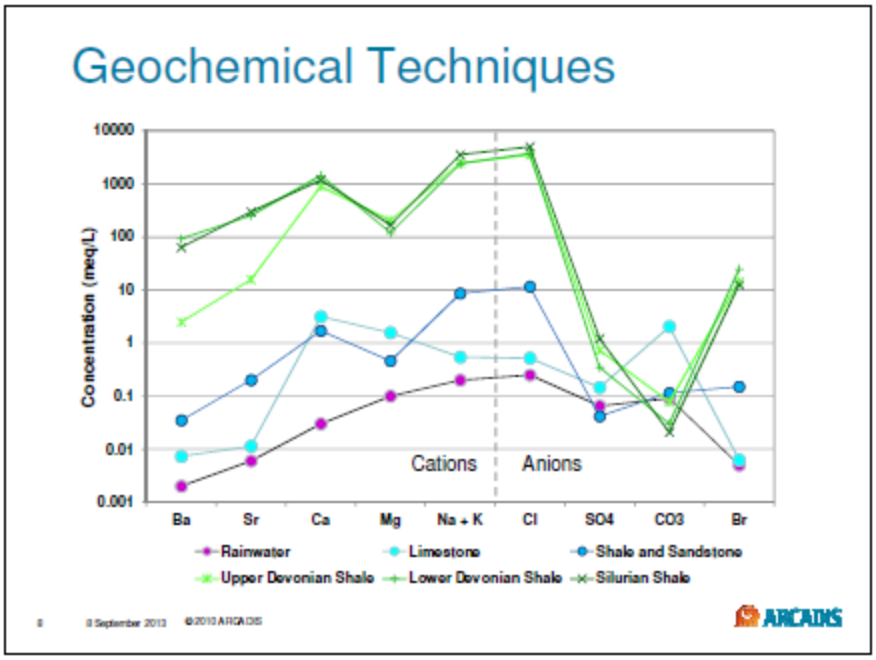
- Light hydrocarbon gas composition
  - Thermogenic versus biogenic
- Composition of other gases (CO_2, O_2, H_2, Ar, He, etc.)
  - Gas source, migration pathway
- Groundwater geochemistry
  - Differentiate water "types"
  - Trace CH_4 generation pathway
  - Identify formation/produced water

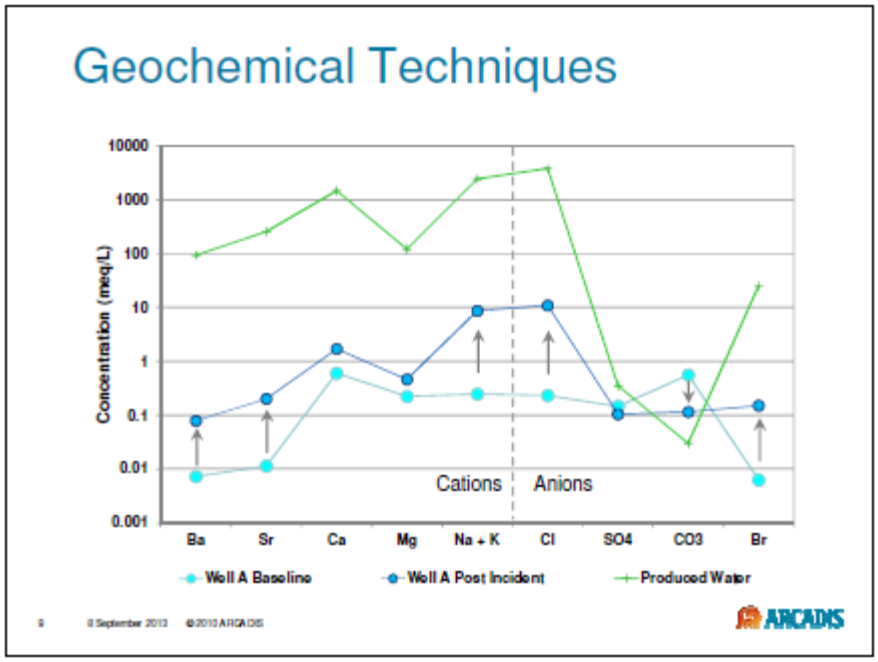


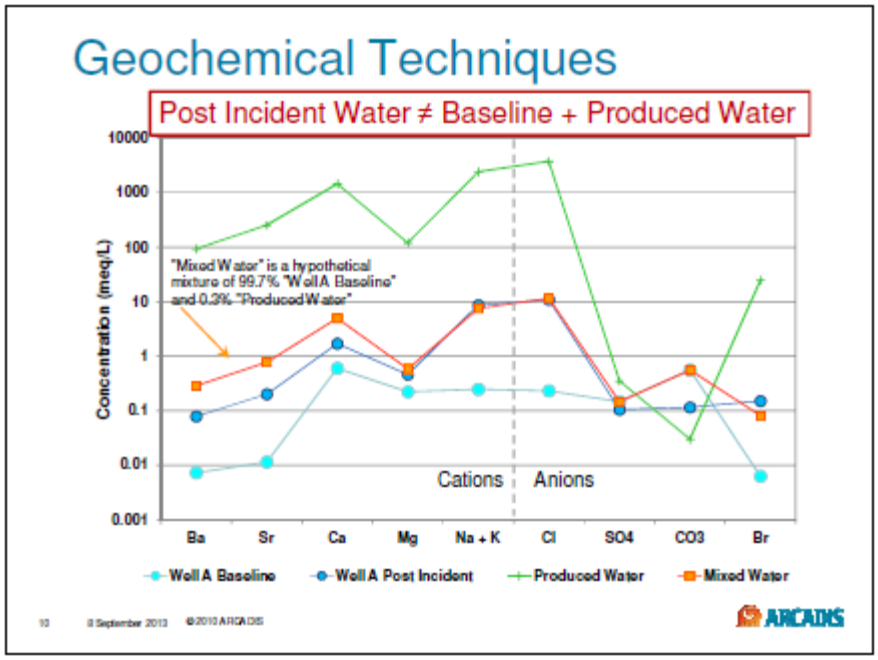
 ©2013 ARCADIS

ARCADIS


Geochemical Techniques
Explanation
Upstream
Cove
Tributary A
Tributary B
Groundwater
Impound A
Impound B
Landfill A
Landfill B
SO4 + Cl
Ca + Mg
Na
HCO3
Mg
Ca
Cl
SO4
7
8 September 2013
©2013 ARCADIS
ARCADIS

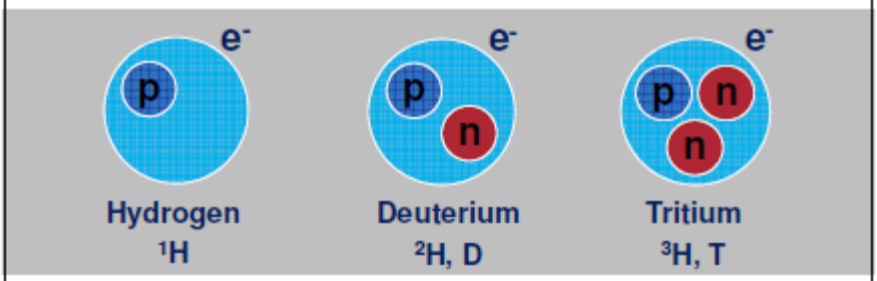

Geochemical Techniques
Concentration (meq/L)
10000
1000
100
10
1
0.1
0.01
0.001
Cations
Anions
Ba
Sr
Ca
Mg
Na + K
Cl
SO4
CO3
Br
Rainwater
Limestone
Shale and Sandstone
Upper Devonian Shale
Lower Devonian Shale
Silurian Shale
8
8 September 2013
©2013 ARCADIS
ARCADIS


Geochemical Techniques
10000
1000
100
10
1
0.1
0.01
0.001
Concentration (meq/L)
Cations
Anions
Ba
Sr
Ca
Mg
Na + K
Cl
SO4
CO3
Br
Well A Baseline
Well A Post Incident
Produced Water
8 September 2013
©2013 ARCADIS
ARCADIS


Geochemical Techniques
Post Incident Water ≠ Baseline + Produced Water
10000
1000
100
10
1
0.1
0.01
0.001
Concentration (meq/L)
"Mixed Water" is a hypothetical mixture of 99.7% "Well A Baseline" and 0.3% "Produced Water"
Cations
Anions
Ba
Sr
Ca
Mg
Na + K
Cl
SO4
CO3
Br
Well A Baseline
Well A Post Incident
Produced Water
Mixed Water
10
8 September 2013
©2013 ARCADIS
ARCADIS

What are Isotopes?

- Atoms of same element with differing masses
  - same # of protons, different # of neutrons



Lighter → *Heavier*

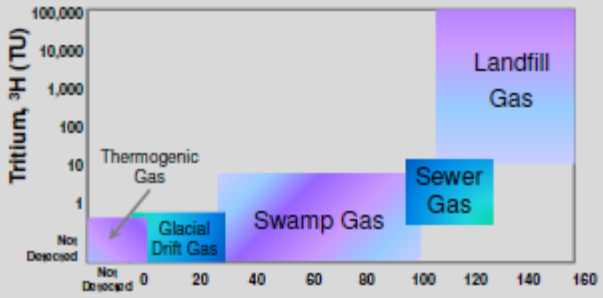
Sum of protons and neutrons is the atomic mass

Imagine the result
11

ARCADIS

Isotope Techniques

- Stable carbon and hydrogen isotopes of methane
- Carbon-14 (^{14}C) and ^{3}H of methane
- Other isotopic tracers, $^{87}Sr/^{86}Sr$, noble gases, water H & O

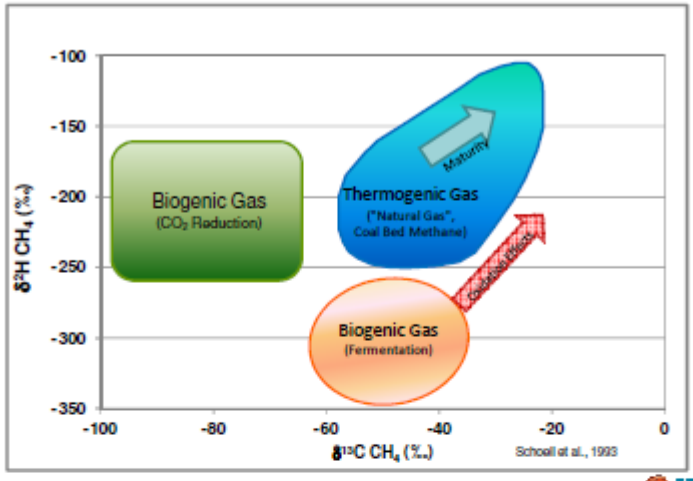


Coleman et al., 1993

12 8 September 2013 ©2010 ARCADIS

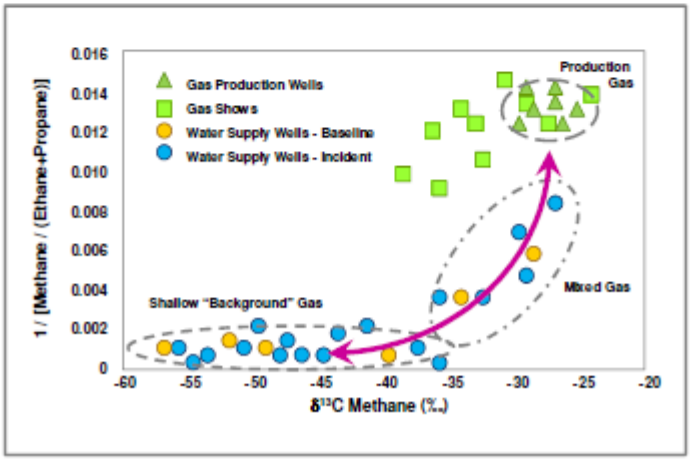
ARCADIS

Stable Isotope Signatures



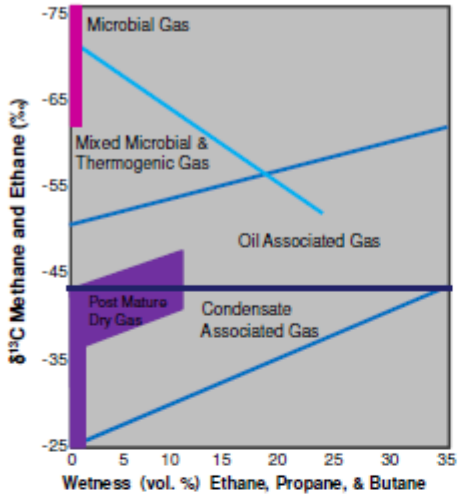
13 8 September 2013 ©2010 ARCADIS

Molecular and Isotopic Data



14 8 September 2013 ©2010 ARCADIS

Thermogenic Gases

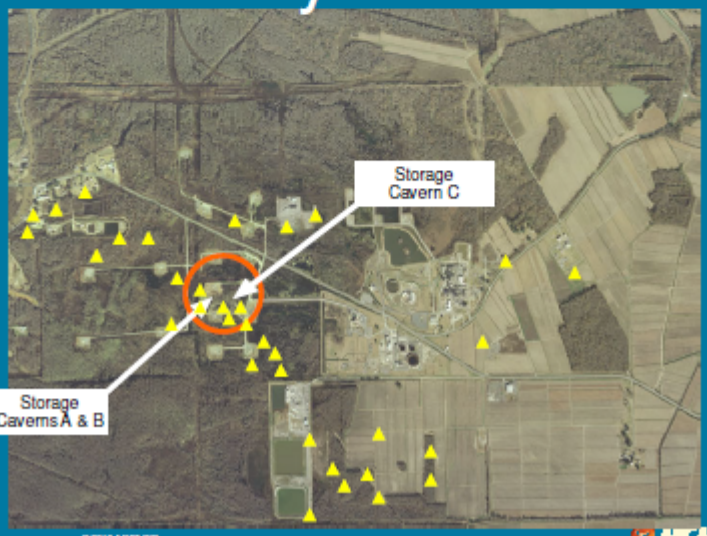


- Thermogenic gas molecular and isotopic composition related to thermal maturity
- Oil associated gas
  - dry to wet
  - lighter $\delta^{13}C$ values
- Condensate associated gas
  - dry to wet
  - heavier $\delta^{13}C$ values
- Post mature dry gas
  - dry
  - heavier $\delta^{13}C$ values
- May have thermogenic gas correlated with depth

15 8 September 2013 ©2013 ARCADIS

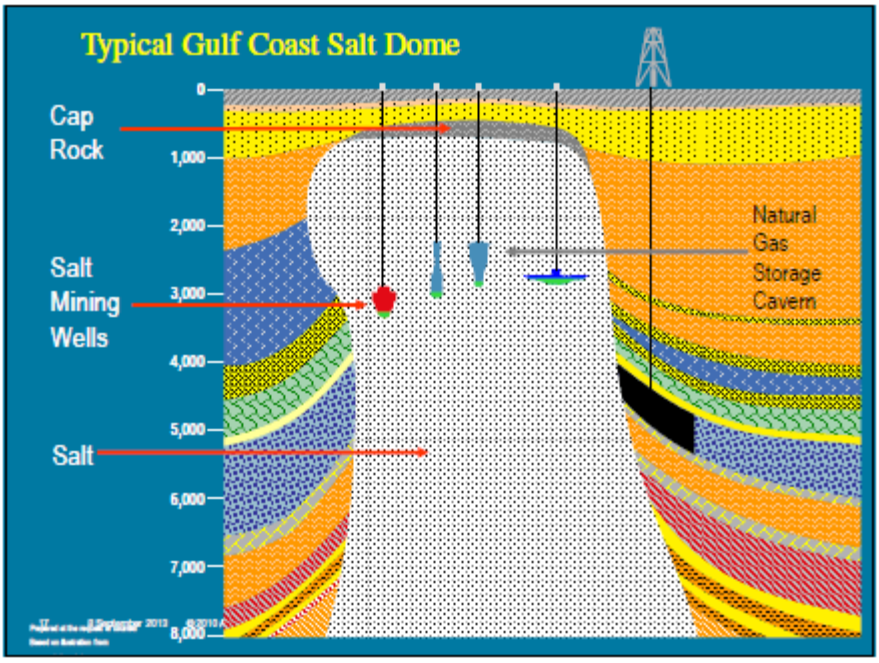
ARCADIS

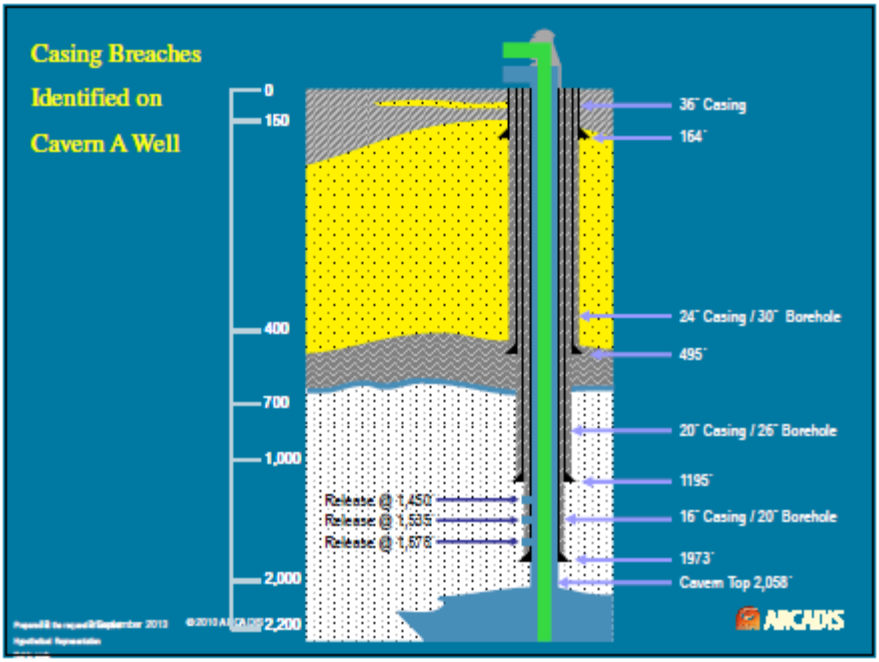
Case Study

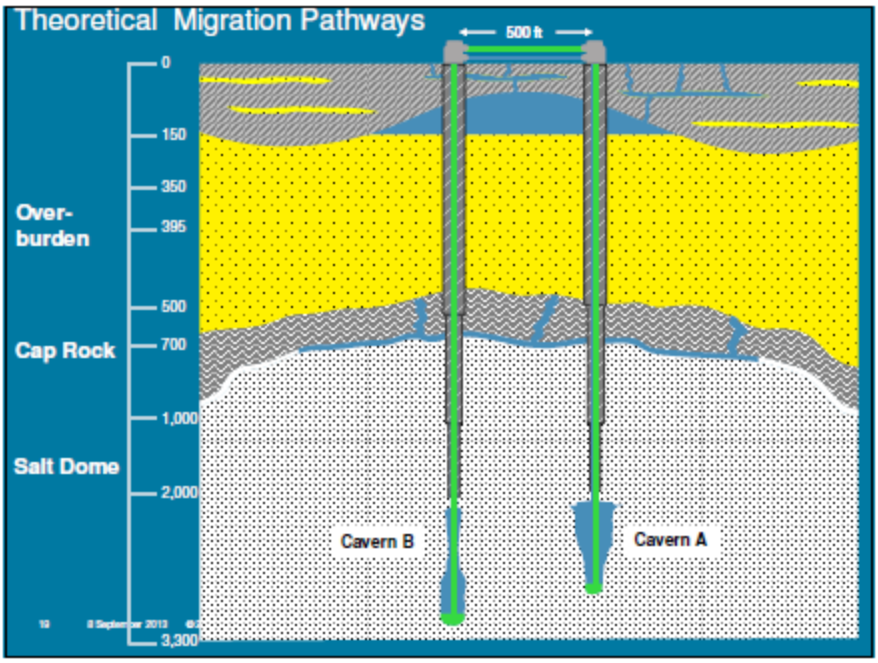


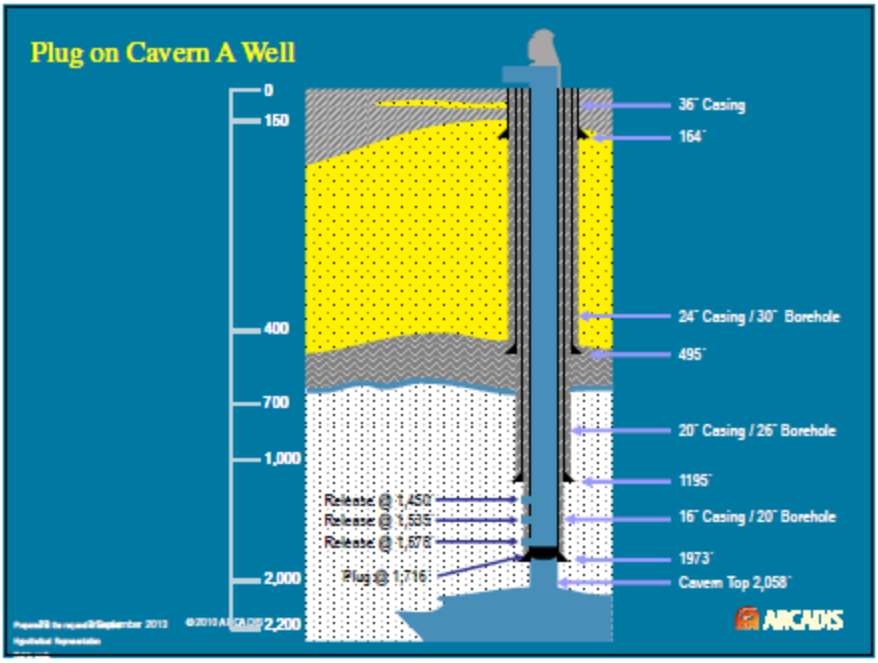
16 8 September 2013 ©2013 ARCADIS

ARCADIS


Typical Gulf Coast Salt Dome
Cap Rock
Salt Mining Wells
Salt
Natural Gas Storage Cavern
0
1,000
2,000
3,000
4,000
5,000
6,000
7,000
8,000


Casing Breaches Identified on Cavern A Well
0
150
400
700
1,000
2,000
2,200
36" Casing
164'
24" Casing / 30" Borehole
495'
20" Casing / 26" Borehole
1195'
16" Casing / 20" Borehole
1973'
Cavern Top 2,058'
Release @ 1,450'
Release @ 1,535'
Release @ 1,578'
ARCADIS


Theoretical Migration Pathways
500 ft
0
150
350
395
500
700
1,000
2,000
3,300
Over-
burden
Cap Rock
Salt Dome
Cavern B
Cavern A


Plug on Cavern A Well
0
150
400
700
1,000
2,000
2,200
36" Casing
164'
24" Casing / 30" Borehole
495'
20" Casing / 26" Borehole
1195'
16" Casing / 20" Borehole
1973'
Cavern Top 2,058'
Release @ 1,450
Release @ 1,535
Release @ 1,578
Plug @ 1,715
ARCADIS

Preparing Cavern A Well for Snubbing Operations



 ©2013 ARCADIS

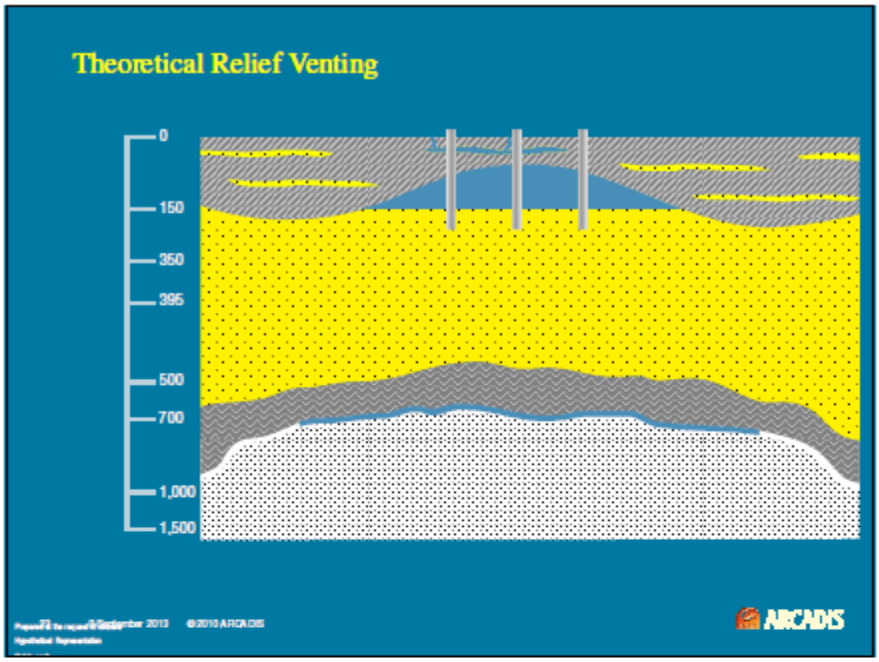
ARCADIS

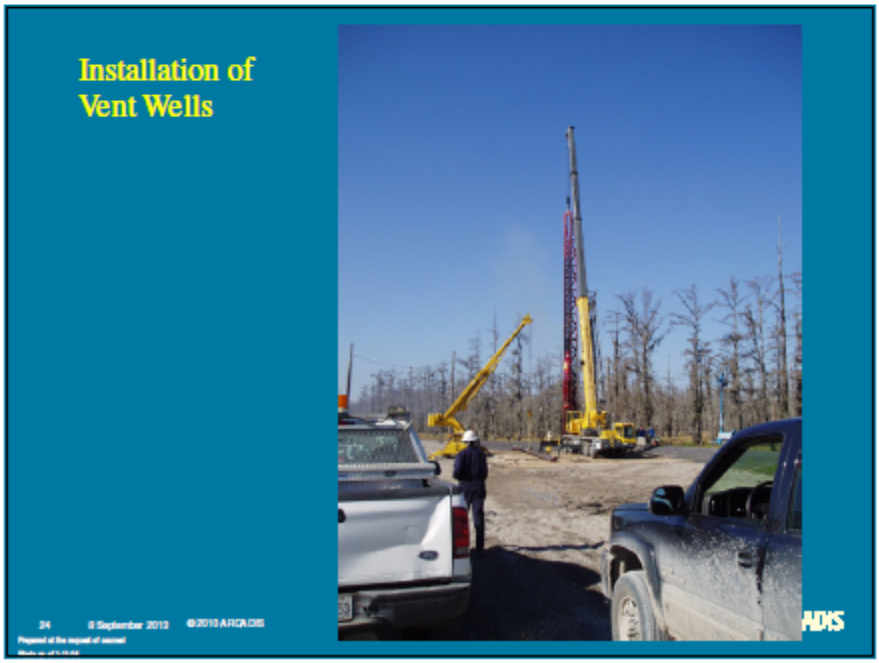
Snubbing Operations on Cavern A Well

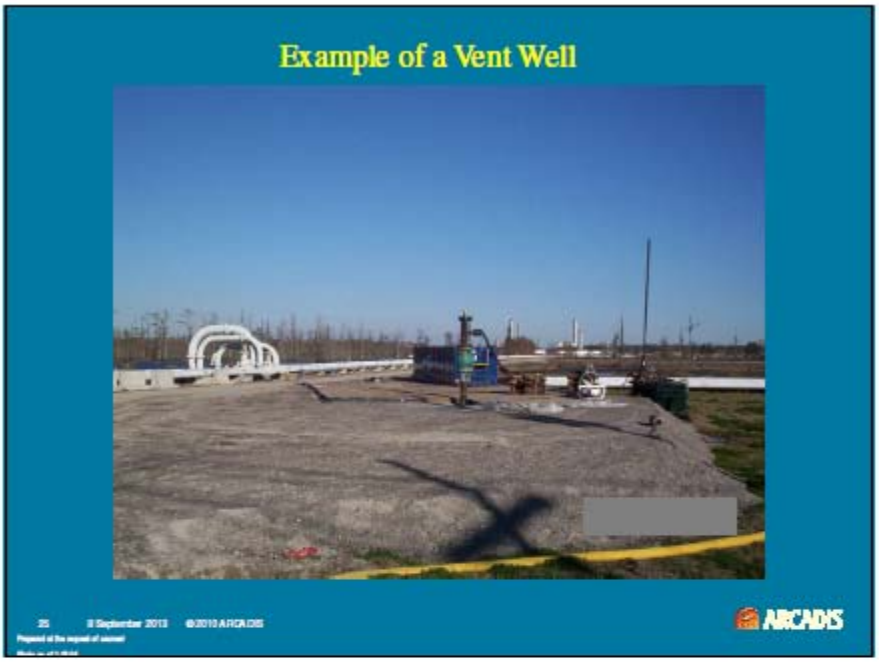


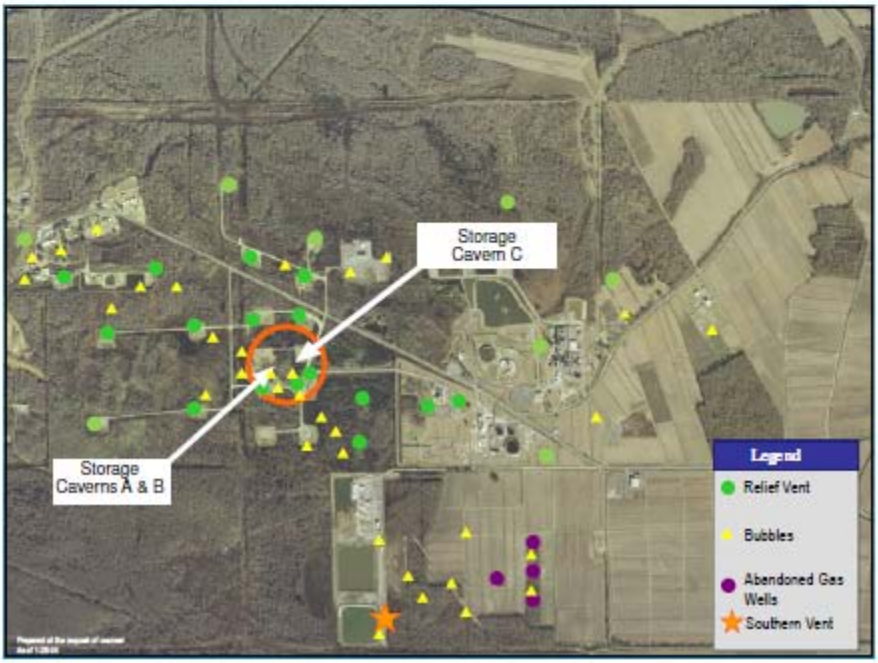
 ©2013 ARCADIS

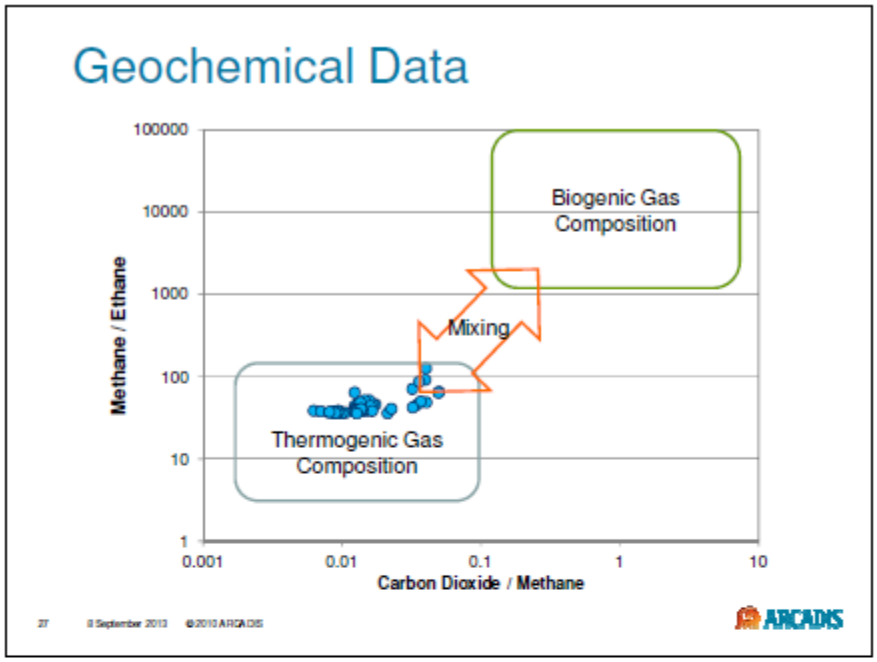
ARCADIS

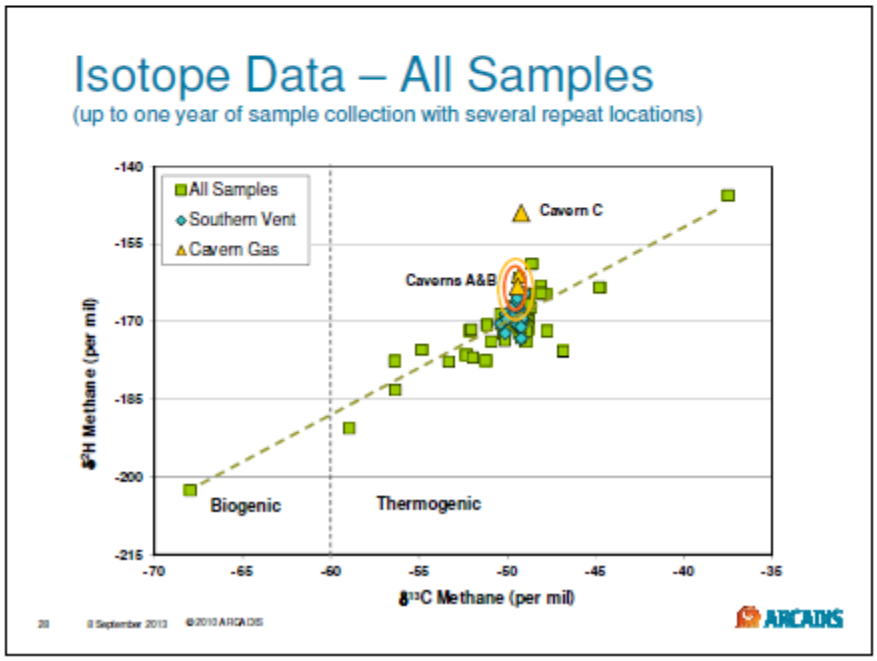

Theoretical Relief Venting
0
150
350
395
500
700
1,000
1,500
ARCADIS

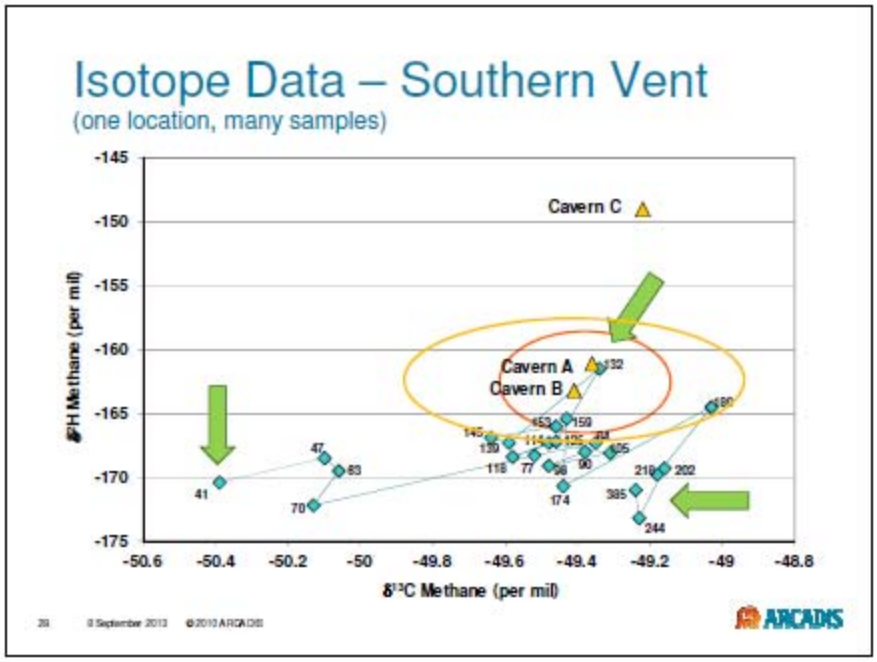

Installation of
Vent Wells
ADIS

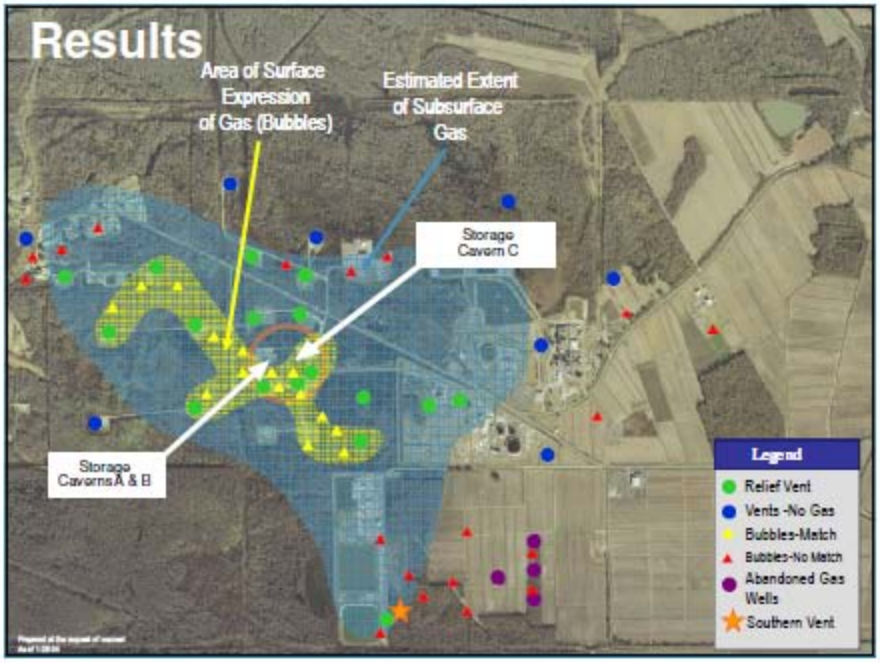

Example of a Vent Well
ARCADIS


Storage Cavern C
Storage Caverns A & B
Legend
Relief Vent
Bubbles
Abandoned Gas Wells
Southern Vent

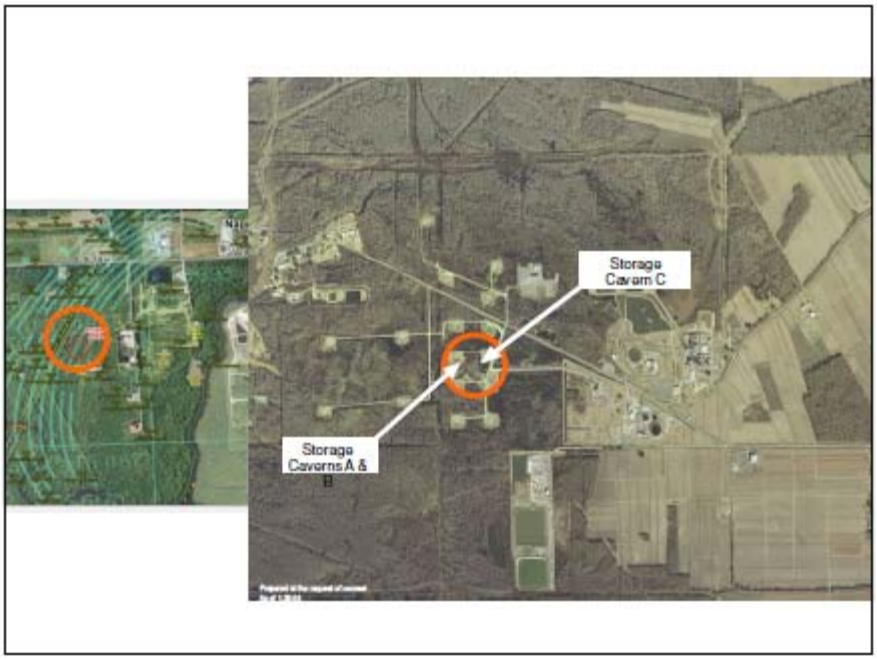

Geochemical Data
100000
10000
1000
100
10
1
Methane / Ethane
Biogenic Gas Composition
Mixing
Thermogenic Gas Composition
0.001
0.01
0.1
1
10
Carbon Dioxide / Methane
27
8 September 2013
©2013 ARCADIS
ARCADIS

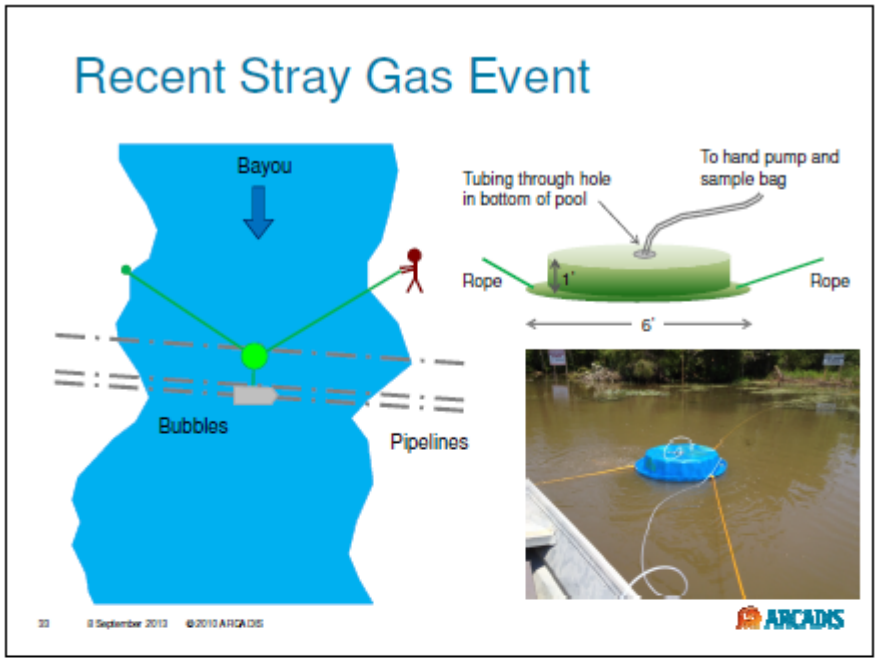

Isotope Data – All Samples
(up to one year of sample collection with several repeat locations)
All Samples
Southern Vent
Cavern Gas
Cavern C
Caverns A&B
Biogenic
Thermogenic
δ2H Methane (per mil)
δ13C Methane (per mil)
-140
-155
-170
-185
-200
-215
-70
-65
-60
-55
-50
-45
-40
-35
20
8 September 2013
©2013 ARCADIS
ARCADIS

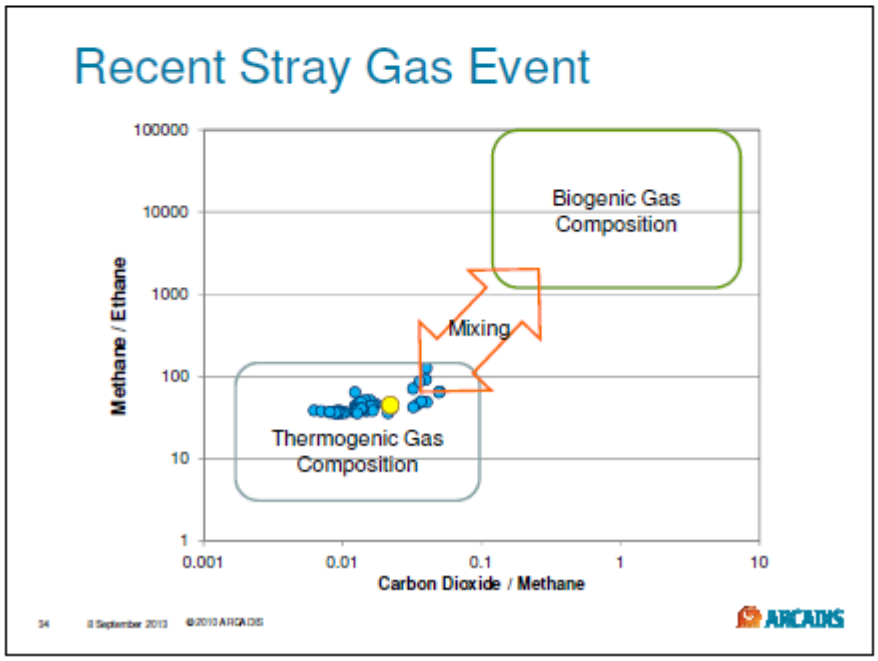

Isotope Data – Southern Vent
(one location, many samples)
Cavern C
Cavern A
Cavern B
δ²H Methane (per mil)
δ¹³C Methane (per mil)
-145
-150
-155
-160
-165
-170
-175
-50.6
-50.4
-50.2
-50
-49.8
-49.6
-49.4
-49.2
-49
-48.8
ARCADIS


Results
Area of Surface Expression of Gas (Bubbles)
Estimated Extent of Subsurface Gas
Storage Cavern C
Storage Caverns A & B
Legend
Relief Vent
Vents -No Gas
Bubbles-Match
Bubbles-No Match
Abandoned Gas Wells
Southern Vent

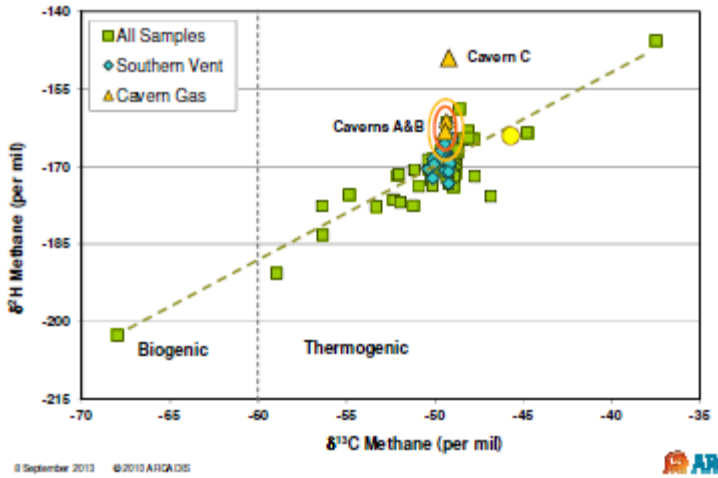

New Event
ARCADIS


Storage Cavern C
Storage Caverns A &


Recent Stray Gas Event
Bayou
Bubbles
Pipelines
Tubing through hole in bottom of pool
To hand pump and sample bag
Rope
Rope
1'
6'
33
8 September 2013
©2010 ARCADIS
ARCADIS


Recent Stray Gas Event
100000
10000
1000
100
10
1
Methane / Ethane
Biogenic Gas Composition
Mixing
Thermogenic Gas Composition
0.001
0.01
0.1
1
10
Carbon Dioxide / Methane
34
8 September 2013
©2010 ARCADIS
ARCADIS

Recent Stray Gas Event



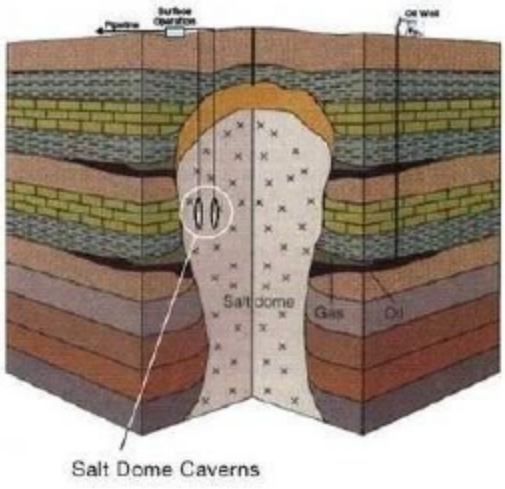
 ©2010 ARCADIS

Recent Stray Gas Event



 ©2010 ARCADIS

Recent Stray Gas Event



Salt Dome Caverns

37 8 September 2013 ©2013 ARCADIS

ARCADIS



Methane Forensic Techniques

- Cost effective and definitive investigation tool
- Highest standard of environmental forensics practice
- Establish baseline conditions
- Evaluate extent of gas migration

ARCADIS

Questions?



Mother Goose and Grimm ©2001 Grimmy, Inc.
Dist. By Tribune Media Services. All rights reserved.

ARCADIS



Extraction of Contaminant Source Information from Site Investigation Data

Jun Lu
AECom

Abstract

During site investigations, large amounts of chemical data are collected from various types of media including soil, water and air. The data are typically used for delineation of contaminants or to assess other environmental concerns (i.e., health and safety, toxicity, vapor intrusion, etc.). At sites where the financial responsibility is not an issue, effort made to understand the source(s) of contaminants is typically minimal. Unfortunately, sources of contaminants cannot be neglected in site investigations, especially for large and complicated sites. As the source is the starting point of the contaminant migration pathways, which governs the distribution of contaminants of concern, erroneous interpretation of the source(s) results in a flawed conceptual site model (CSM). A flawed CSM can then result in an inappropriate approach and design basis for a remediation system.

Source issues are typically resolved using environmental forensics. However, at sites under investigation, “real” forensic data are often not collected. This paper presents various methods to maximize the use of typical site investigation data to better understand contaminant source(s). Case studies will be presented to demonstrate how the laboratory data obtained using EPA Methods 8015, EPA 8260, EPA 8070 and other analyses are employed for source identification of and age dating contaminants such as petroleum hydrocarbons, chlorinated solvents, and PAHs. The processing and analysis of site investigation data for source related information may be sufficient to resolve source issues. When the aforementioned analysis does not meet the project objectives, the initial findings can be used as the basis to conduct additional laboratory analyses to address data gaps including any specific forensic analyses.

AECOM

Extraction Of Contaminant Source Information From Site Investigation Data



National Conference of Environmental Monitoring

August 7, 2013

San Antonio, Texas

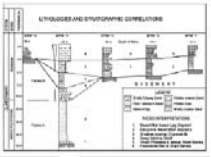
Jun Lu, PhD

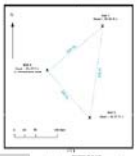
Copyright© 2012, AECOM. All rights reserved.

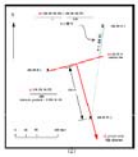
Site Investigation Data

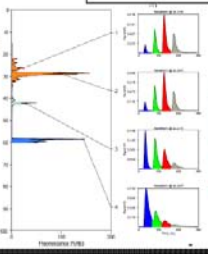
- Site history
- Geological/hydrogeological data
  - Borehole lithology correlation and cross sections
  - Groundwater flow
    - Fluid level gauging
    - Effective porosity
    - Hydraulic conductivity
- High resolution site characterization data
  - Membrane interface probe (MIP)
  - Laser induced fluorescence (LIF)
- **Laboratory analytical data**













AECOM

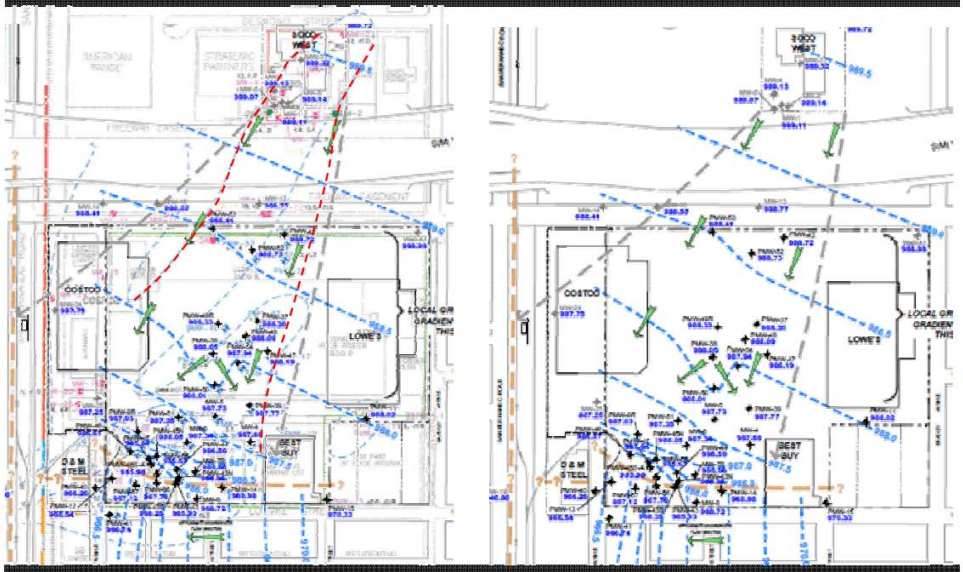
Laboratory Analytical Data

- Contaminant Concentration Data
  - Spatial patterns
  - Temporal trends
  - Diagnostic ratios and correlations
  - Phase equilibrium
  - Mass flux and discharge
- Geochemical parameters
- Compound specific isotope analysis (CSIA)



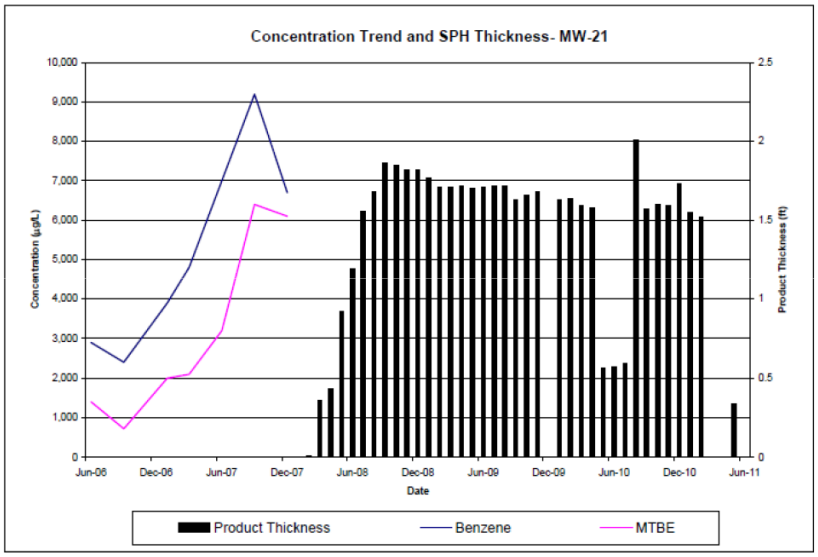
AECOM

Spatial Pattern



AECOM

Temporal Trend



AECOM

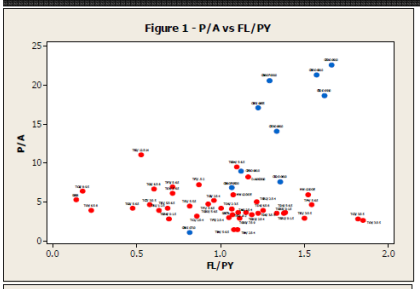
Diagnostic Ratios and Correlations

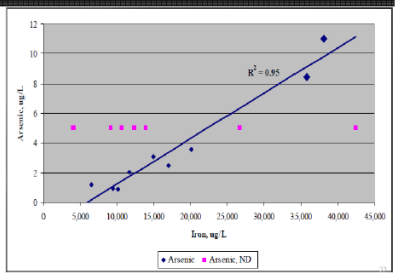
- BTEX
- Oxygenates
  - MTBE and TBA
- PAHs
  - P/A; FL/PY; BaP/BeP; BbF/BkF; BaA/C; Per/BaP
- Chlorinated solvents
  - TCA and 1,1-DCE
- Metals/semi-metals

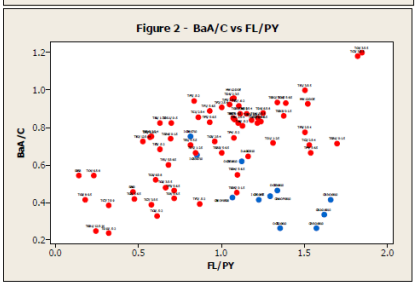


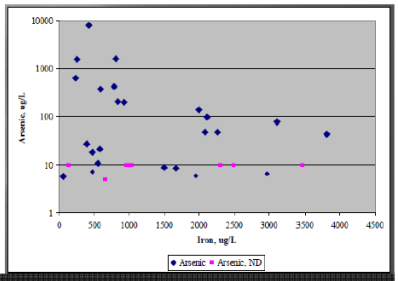
AECOM

Diagnostic Ratios and Correlations - Examples









Page 7

AECOM

Phase Equilibrium

- **Total Soil Chemical Concentration**

$$C_t = (M_s + M_w + M_a) / \rho_b$$

$$M_s = C_s * \rho_b$$

$$M_w = C_w * \theta_w$$

$$M_a = C_a * \theta_a * \rho_b$$

- **Distribution between phases in the sample**

$$C_t = (C_s * \rho_b + C_w * \theta_w + C_a * \theta_a) / \rho_b$$

$$Kd = C_s / C_w \qquad C_s = K_d * C_w$$

$$Hc = C_a / C_w \qquad C_w = H_c * C_a$$

$$C_t = (K_d * C_w * \rho_b + C_w * \theta_w + C_w * H_c * \theta_a) / \rho_b$$

- **Chemical concentration in pore water**

$$C_w = C_t * \rho_b / (K_d * \rho_b + \theta_w + H_c * \theta_a)$$

- **Effective solubility**

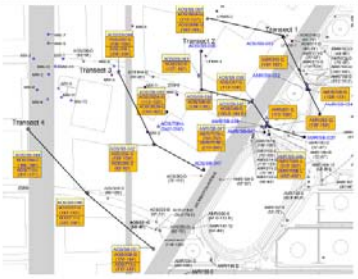
M_s: Mass of chemical sorbed on soil solids (ug)
M_w: Mass of chemical in pore water (ug)
M_a: Mass of chemical in soil gas (ug)
θ_w: Water-filled porosity (volume fraction)
θ_a: Air-filled porosity (volume fraction)
P_b: Dry bulk density of the soil sample (g/cm3)
K_d: Partition coefficient between pore water and soil solids (cm3/g)
H_c: Dimensionless Henry's Law Constant
C_t: Total soil chemical concentration (ug/g, dry weight)
C_s: Chemical concentration sorbed on the soil solids (ug/g, dry weight)
C_w: Chemical concentration in the pore water (mg/L)
C_a: Chemical concentration in the soil gas (mg/L)

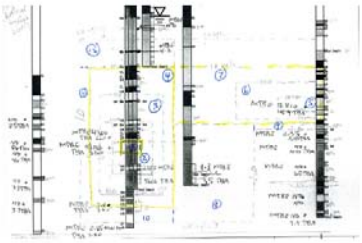
Page 8

AECOM

Mass Flux and Discharge

- Four transect lines
- Data input
  - Cross sectional areas (A)
  - Hydraulic conductivity and gradient (k and i)
  - Concentration of MTBE and TBA (C)
- Mass fluxes for each transect
  - K*i*A*C (gram/day)

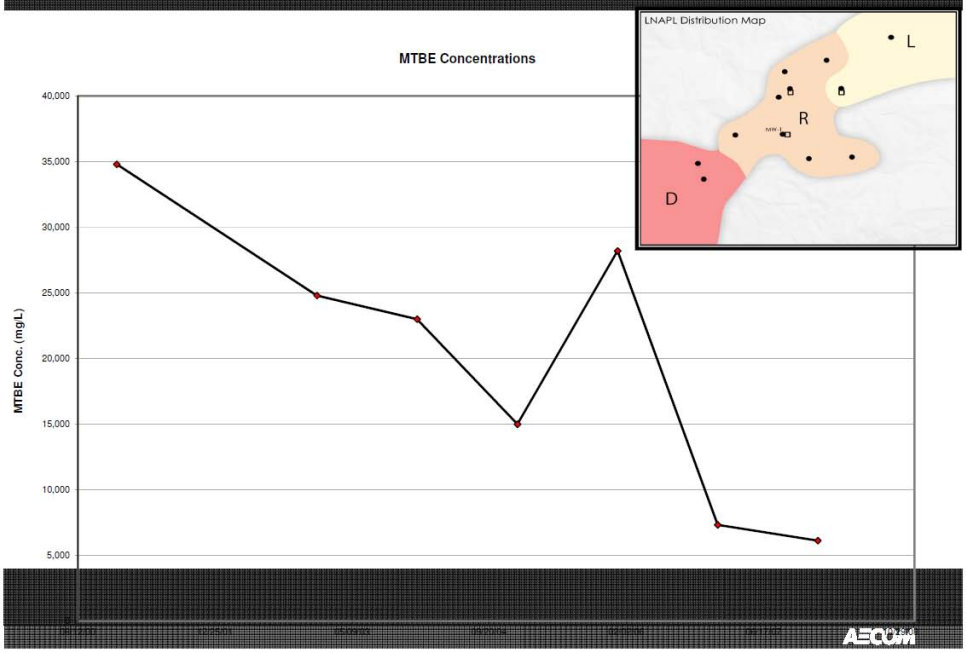




Transects	1	2	3	4
MTBE, ug/L	82	49	48	35

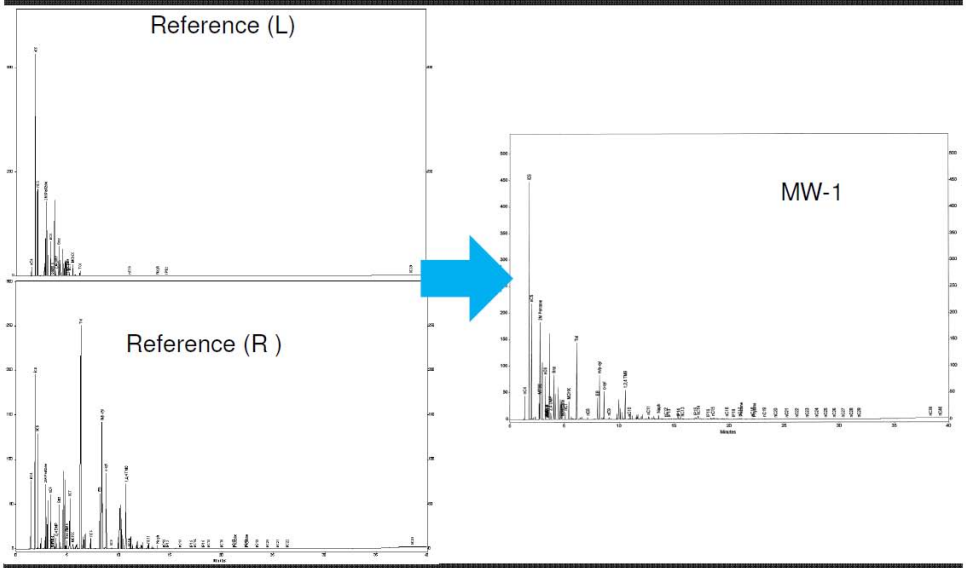
AECOM

MTBE in LNAPL



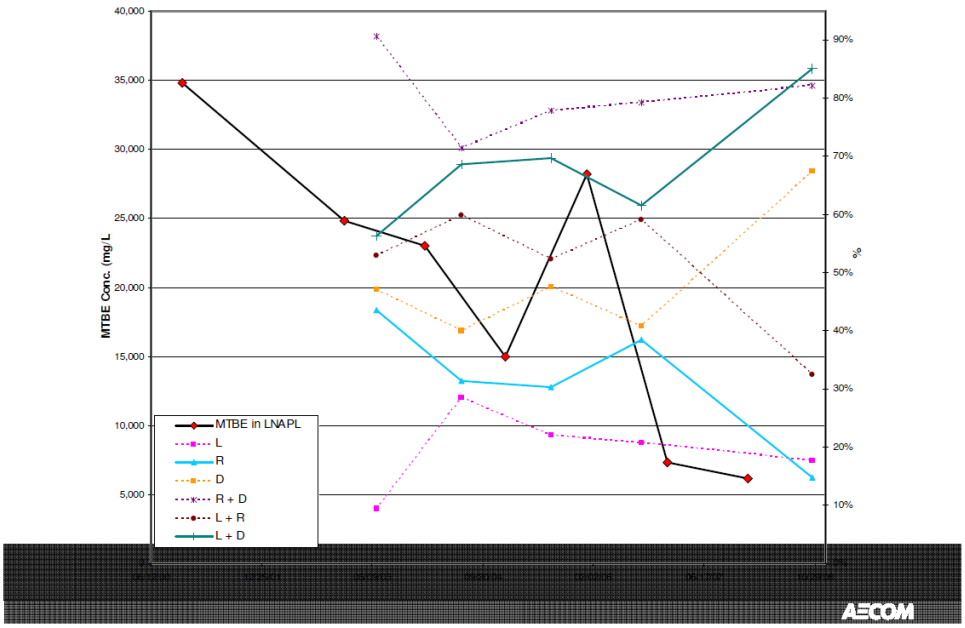
AECOM

GC/FID Chromatograms



AECOM

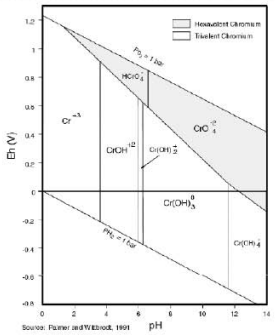
Correlation of MTBE and Types of LNAPL

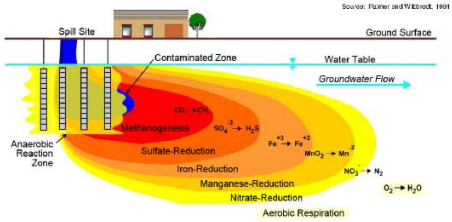


AECOM

Geochemical Parameters

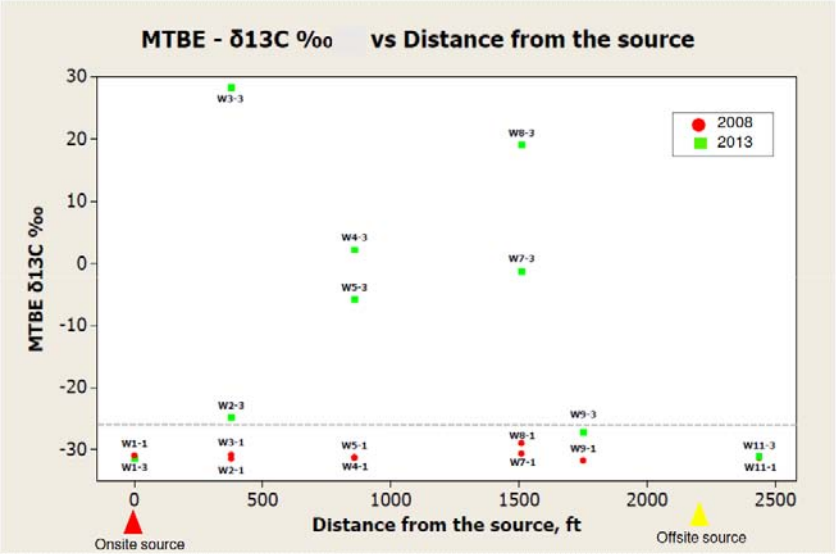
- Field Parameters
  - DO
  - ORP
  - pH
  - Conductivity
- Geochemical parameters
  - Nitrate,
  - Manganese (II),
  - Fe(II)
  - Sulfate
  - Methane
  - Chloride
  - Alkalinity





AECOM

CSIA – MTBE Degradation and Potential Offsite Source



AECOM

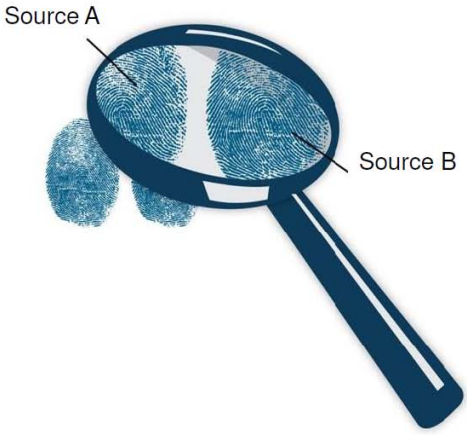
Summary

- Contaminant source information may be extracted from various types of site investigation data
- Laboratory analyses are one of the most important datasets for source evaluation
- Concentration data may be used alone or with concentrations of other chemicals or aquifer parameters to resolve source issues
- Data gaps identified from existing data can be used to plan a more focused source investigation using environmental forensics



Questions?

Jun Lu, Ph.D.
AECOM Environment
Long Beach, CA
(562) 213-4120
Jun.Lu@aecom.com



SECTION 15

OPERATIONAL AND ADVOCACY ISSUES IMPACTING THE ENVIRONMENTAL LABORATORY INDUSTRY

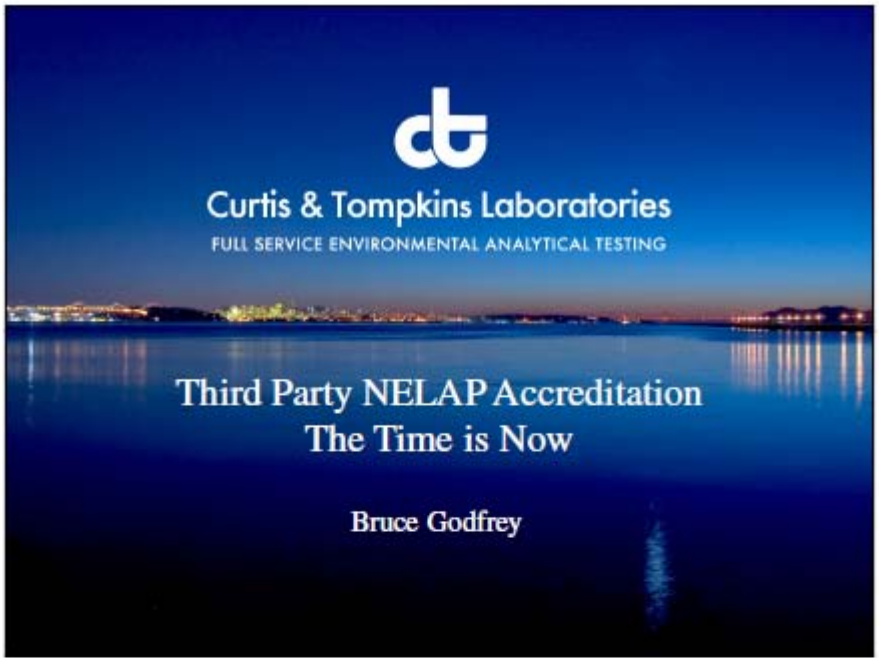
Third Party NELAP Accreditation -- The Time Has Arrived

Bruce Godfrey
Curtis & Tompkins Laboratories

Abstract

Conformity assessment (i.e., inspection and certification) carried out by third-party private sector organizations is well established and recognized by several federal agencies. Allowing third party private accrediting bodies (AB's) to provide National Environmental Laboratory Accreditation Program (NELAP) accreditation services in support, or in place of state AB's appears critical to the maintenance, if not the survival of NELAP. Long-standing government policy supports the use of private sector accreditation infrastructure for many professions. The infrastructure in the form of the multilateral mutual recognition arrangements of the International Laboratory Accreditation Cooperation (ILAC)(www.ilac.org) and the International Accreditation Forum (IAF) (www.iaf.nu) and The NELAC Institute (www.nelac-institute.org) are already in place for recognizing private AB's performing NELAP assessments. ACIL, the trade association for commercial laboratories (www.acil.org) takes the position that there is little, if any, need for federal or state agencies to administer their own programs or systems for NELAP laboratory accreditation, either for themselves or for recognition of AB's.

Washington's experience with NELAP Third Party Accreditation (TPA) and the impending implementation of TPA NELAP accreditations for laboratories in NJ and FL will be discussed along with the advantages of implementing TPA to improve CA's troubled public environmental laboratory accreditation authority. TPA allows private accrediting bodies, (e.g. A2LA, Perry Johnson, LAB, etc..) to perform onsite NELAP laboratory assessments while preserving the state's authority through their issuance of a laboratory license. Significant cost savings and conformity assessment program performance improvements are experienced by public agencies implementing TPA.



The oldest Testing Lab in the US

In 1878… Curtis & Tompkins began as a laboratory analyzing wine samples for export…





Curtis & Tompkins Laboratories
FULL SERVICE ENVIRONMENTAL ANALYTICAL TESTING

We need to talk…

- NELAP's future
- Non-Government accreditation
  - Why it's best for commercial labs
  - Why we should act now



Accreditation Goals

- Ensure conformance to program requirements & standards
- Detect and correct substandard practices
- Ensure protections for end users of measurement data



Trends

- User perception of decreasing quality of government AB capabilities & results
- Increasingly successful and capable NonGovernment AB programs
- Shrinking federal & state budgets
- User perception of lack of AB control and program accountability at TNI



NELAP Today

- Efficient means to access state markets
- Inadequate for federal agency buyers
- Uneven state participation and commitment
- Gov ABs providing poor service at high cost
- Insufficient program accountability for ABs



Authority, Recognition, Reciprocity

Accrediting Authority-States

- Retain authority through licensing

Accrediting Body (AB)

- Provide standard(s) based accreditation services to laboratories

AB Recognition Authorities

- ILAC, NACLA, TNI

Standards Generation & Maintenance Organization

- ISO, TNI



State ABs

- Many perform very well, some present serious issues
- Resource constraints significantly affect audits, oversight of audits, and follow up on issues discovered in audits
- NELAP creates Two Tier accreditation system
- Inconsistent standards at state tier
- Majority of customers are small municipal/utility labs
- None are ISO 17011 compliant/ILAC recognized



State NELAP Audits

- Biannual, typically 2 auditors for 2-3 days
- Delays in audit scheduling
- Quality of audits no better than 5 years ago, some are noticeably worse
- Weak quality systems assessments
- Significant delays in closing audits
- Least likely to detect serious lab problems
- Increasingly more expensive



Success Story: DoD Audits

- Timely: Scheduled in advance, 3 days two assessors, reports issued at exit debrief, most assessments completed on-time
- Professional: Quality of assessors is generally excellent
- Impartial – no potential for conflicts of interest
- Thorough – Standards based, focused on QA systems & method conformance
- Cost Effective – Not inexpensive, but efficient & effective. Add value, reduce user costs by increasing labs in program
- No Surprises – ISO 17011 compliant AB process. Issues discussed & resolved during audit. Daily debriefs, effective systems for resolving disputes



"The Big Idea"

Bring private ISO17011 ILAC Recognized ABs into NELAP as primary accreditors of laboratories

Why?

•One organization to address conformity assessment needs

What' s in it for TNI-NELAP?

Government agency signatories, ISO/ILAC recognition

Legitimacy, Relevance, Recognition



The ACIL Approach

- Separate licensing and accreditation services at states
- Choice: either primary state AB or an ISO 17011/ILAC recognized non-Government AB
- Fees charged are appropriate to the level of effort
- Accommodate unique state requirements
- Loss of accreditation means loss of license(s)



Benefits

- Improve assessment consistency & standard interpretation
- Likely to reduce state's staffing costs
- Probably reduce costs for commercial labs
- National and international NELAP relevance/recognition
- Probably save commercial lab users & taxpayers $
- Improved lab access to NELAP
- Accommodation of unique state requirements
- Likely to increase states participating in NELAP



Concerns

- Shift state AB costs to smaller municipal/utility labs
- Reduced state regulatory "control"
- Outsourcing state government function
- Minutiae of implementation
- Loss of state expertise/capability



Design Considerations

- States recognize ISO 17011 compliant NACLA and/or ILAC and/or TNI recognized ABs
- Level of effort based fees imposed by states
- Labs are free to choose from among several AB's
- Sustainable mechanism (TNI) to ensure development and improvement of the NELAP standard



Non Government accreditation is working today!

- Washington
- New Mexico

Other states moving this way….

•New Jersey, Florida, Minnesota and Texas



Action Items

- TNI recognition of private ABs by 2014
  - **ISO 17011 compliant and ILAC/NACLA recognized**
- States separate licensing and accreditation functions



Conclusion

- Commercial labs need NELAP
- NELAP needs nonGovernment ABs



Acknowledgements

- ACIL Environmental Sciences Section colleagues for their insights and information on state and regional variance

Public/Private Partnerships to Improve Environmental Monitoring and Compliance

JoAnn Slavin
H2M Labs

Abstract

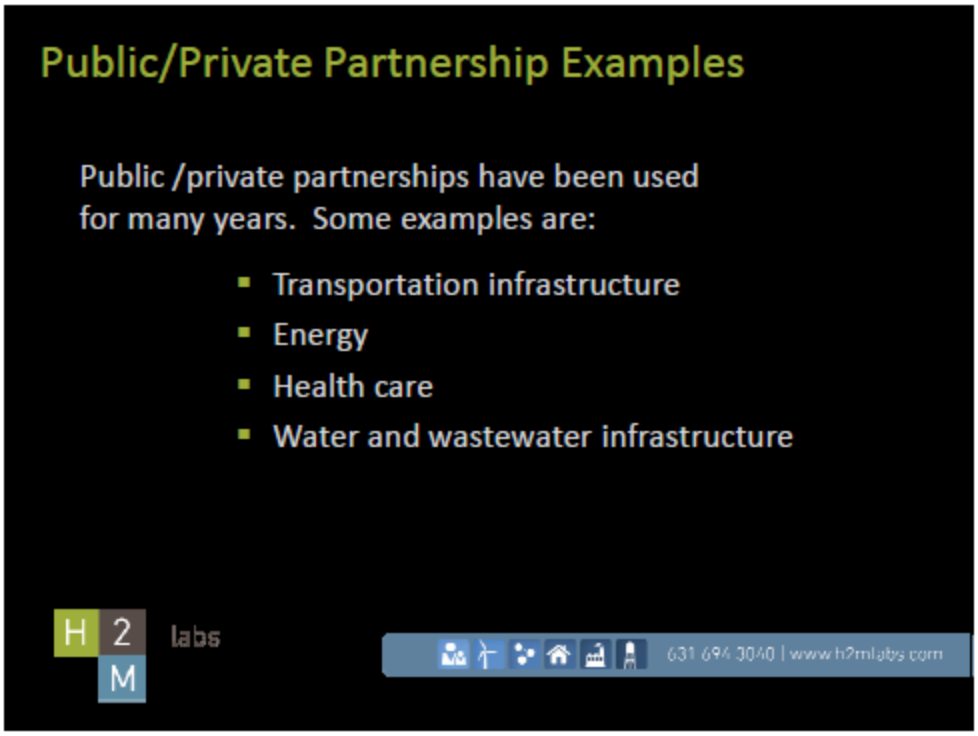
The need for synergism with public agencies and the private sector with respect to advances and improvements in the environmental testing industry is critical to implementing needed change. As part of its goal of improving environmental monitoring and advancing monitoring technology, the Independent Laboratory Institute (ILI) has implemented a forum to address a number of issues of importance to EPA and the monitoring support community. The Independent Laboratories Institute (ILI) is a non-profit, 501(c)(3), scientific educational organization established in 1992 that is multi-disciplined and member-driven. Its goal is to provide quality training for the laboratory community.

ILI is sponsored by individual and corporate/institutional sponsors. The American Council of Independent Laboratories (ACIL) is one of its principle supporters.

Beginning in 2012 and ongoing, members of the laboratory, technology innovation, and measurement science communities are meeting with the EPA to discuss ways to improve existing methods and other innovative technologies in order to address concerns in the industry.

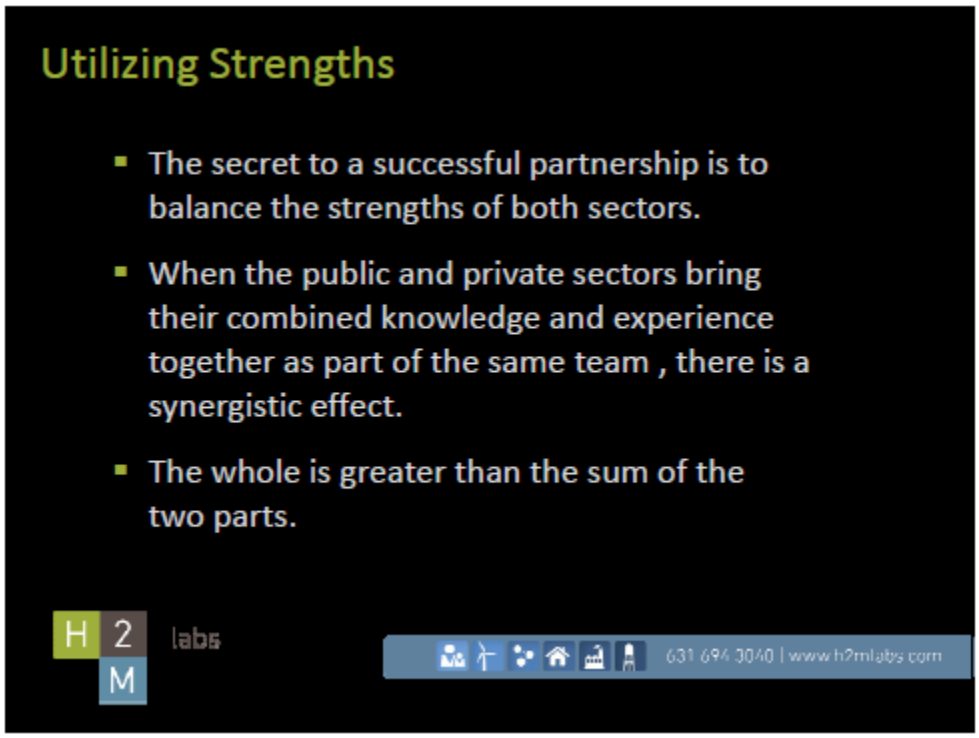

Public/Private Partnerships to Improve Environmental Monitoring and Compliance
Presented by
Joann M. Slavin
Senior Vice President
H 2 M labs
631 694 3040 | www.h2mlabs.com

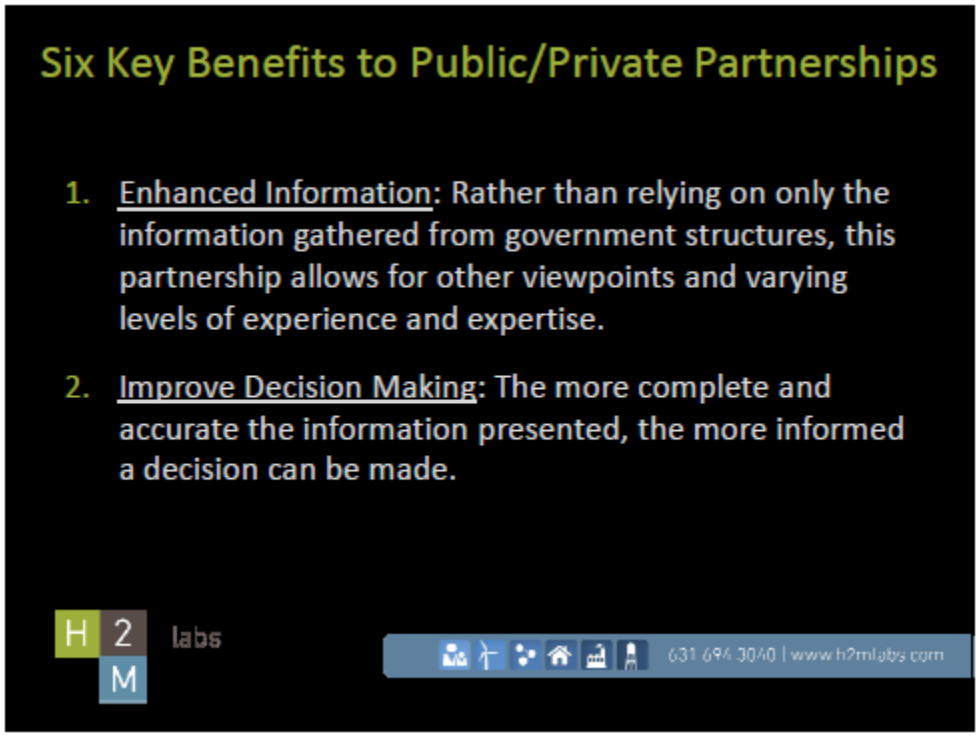

What is a Public/Private Partnership?
A public-private partnership (PPP or P3) is a contractual agreement between a public agency and a private sector entity. Through this agreement, the skills and assets of each sector are shared in delivering a service or facility for the use of the general public. In addition to the sharing of resources, each party shares in the risks and rewards potential in the delivery of the service and/or facility
Source: www.ncppp.org
H 2 M labs
631 694 3040 | www.h2mlabs.com


Public/Private Partnership Examples
Public /private partnerships have been used for many years. Some examples are:
Transportation infrastructure
Energy
Health care
Water and wastewater infrastructure
H 2 M labs
631 694 3040 | www.h2mlabs.com

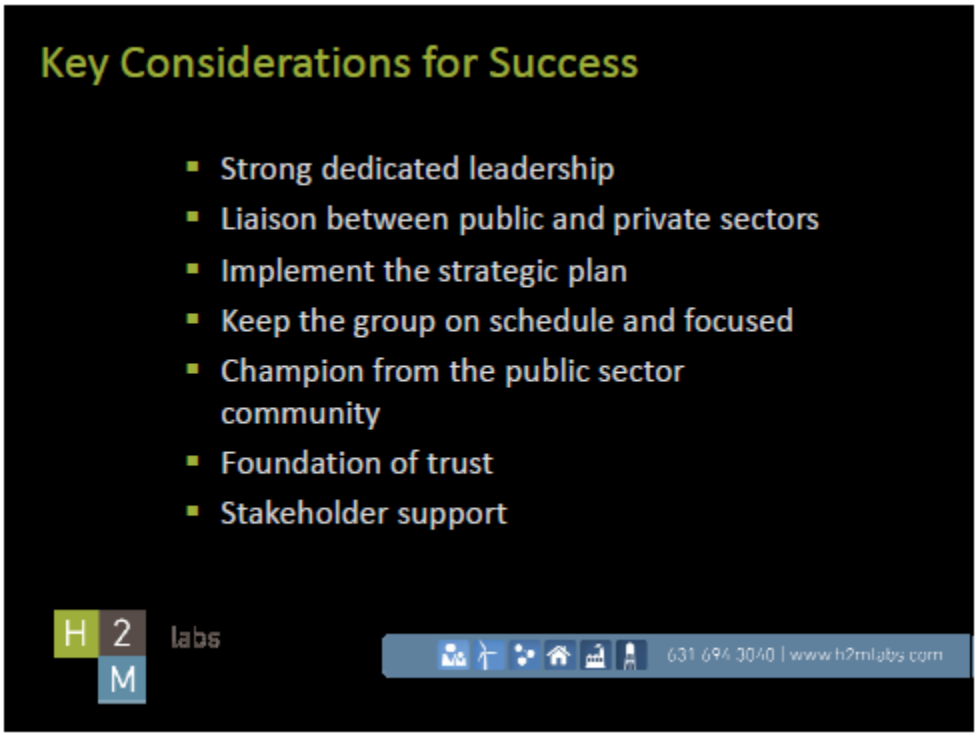

Types of Public/Private Partnership
Public/private partnerships can take various forms and include collaborative or contractual.
Collaborative partnership is a non-legal working relationship that occurs between the public and private sectors to meet a common goal.
These partnerships are often used to provide knowledge exchange or collective leveraging resources to achieve a common goal.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Challenging Times! Let's Meet the Challenge!
Deficits at all levels of government in the United States and around the world.
Requirements for a balanced budget.
Doing more with less.
Public/private partnerships may be the answer and provides a valuable tool.
This is a growing trend at all levels of government which is often born out of necessity.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Utilizing Strengths
The secret to a successful partnership is to balance the strengths of both sectors.
When the public and private sectors bring their combined knowledge and experience together as part of the same team , there is a synergistic effect.
The whole is greater than the sum of the two parts.
H 2 M labs
631 694 3040 | www.h2mlabs.com

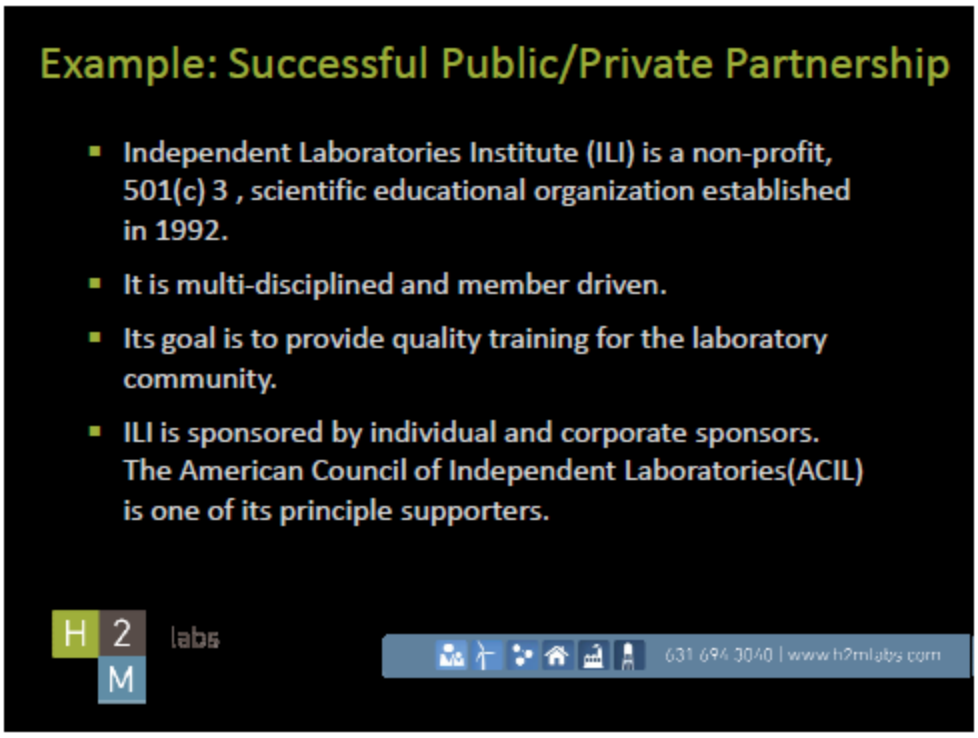

Six Key Benefits to Public/Private Partnerships
1. Enhanced Information: Rather than relying on only the information gathered from government structures, this partnership allows for other viewpoints and varying levels of experience and expertise.
2. Improve Decision Making: The more complete and accurate the information presented, the more informed a decision can be made.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Six Key Benefits to Public/Private Partnerships
3. Access More Resources: Working together , there are more resources working on a combined solution.
4. Improved Timeliness
5. Increased Effectiveness: Improved understanding of the varying aspects of all parties involved.
6. Build Strong Relationships: The value of a good working relationship between the public and private sector is built from working face to face.
H 2 M labs
631 694 3040 | www.h2mlabs.com

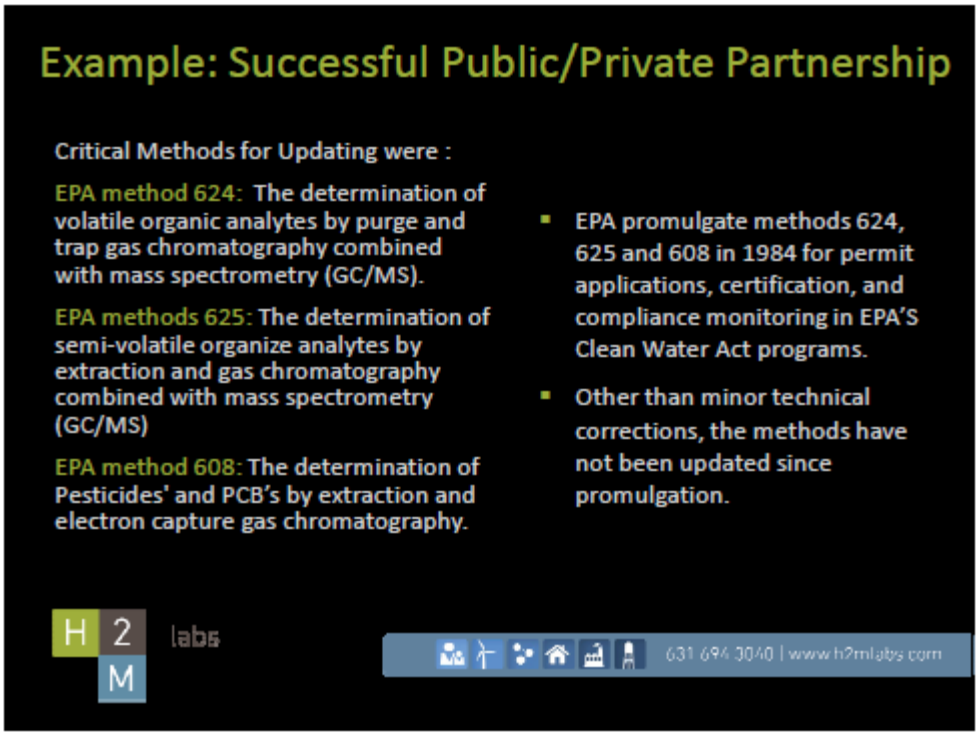

Key Considerations for Success
Strong dedicated leadership
Liaison between public and private sectors
Implement the strategic plan
Keep the group on schedule and focused
Champion from the public sector community
Foundation of trust
Stakeholder support
H 2 M labs
631 694 3040 | www.h2mlabs.com

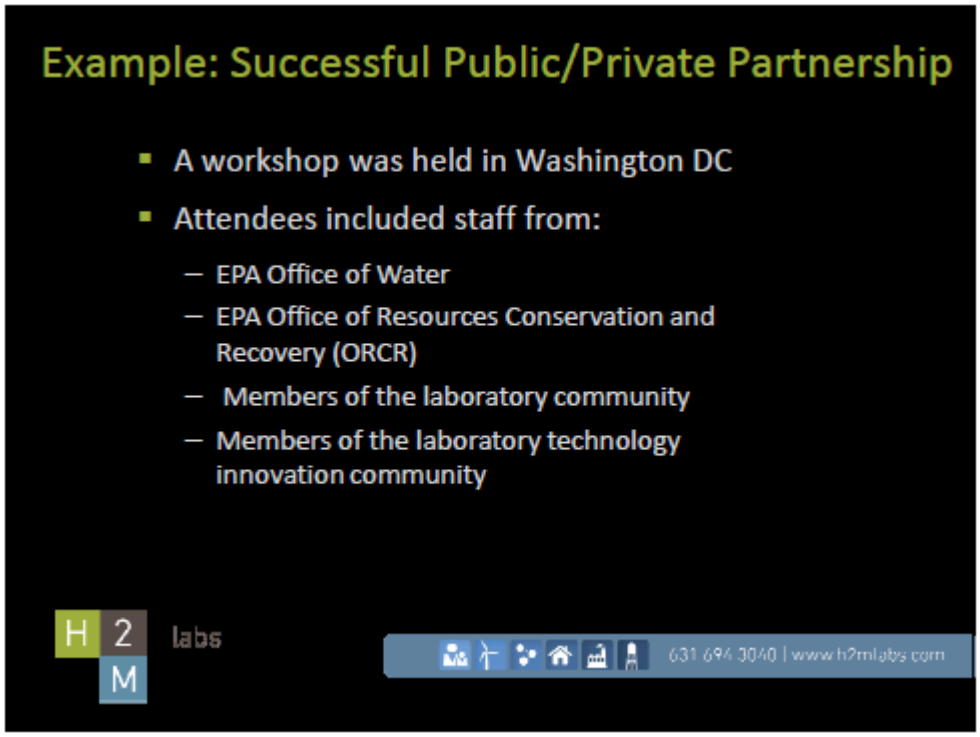

Key Considerations for Success
Resources
Tools needed
Facilities to meet
Funding
Support efforts
The right opportunity
The right partner
H 2 M labs
631 694 3040 | www.h2mlabs.com

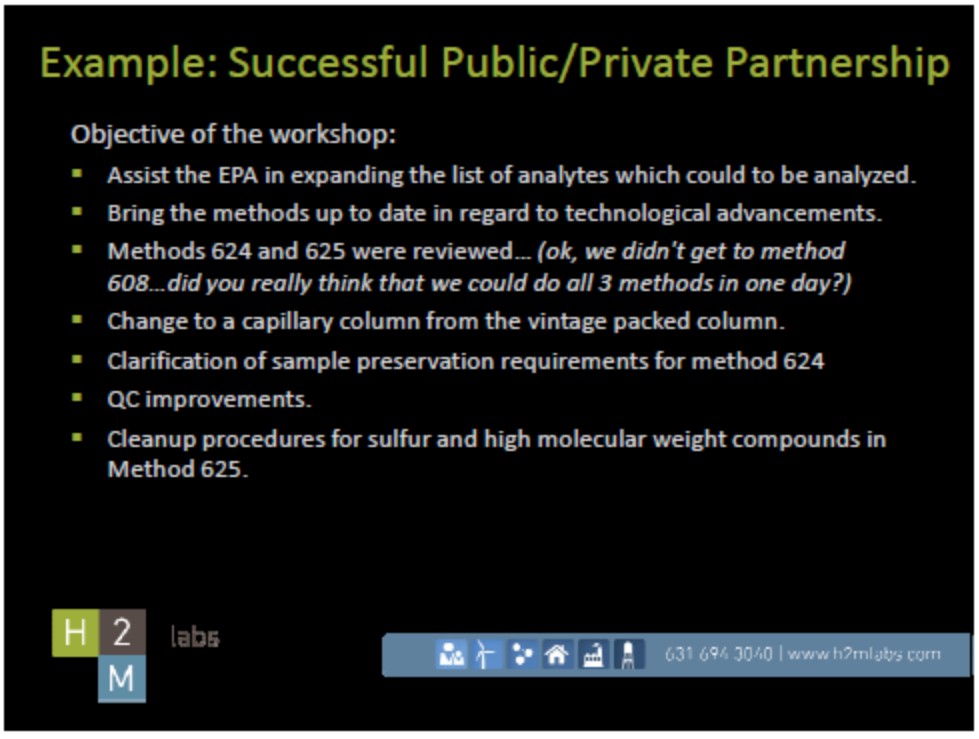

Key Considerations for Success
Engagement
Active support and participation
Two way communication
Face to face meetings with interactive sessions
Good working relationship
Open forum for idea exchange
Follow-up
Goals and objectives
Sustainable for long term viability
Strategic plans
H 2 M labs
631 694 3040 | www.h2mlabs.com


Example: Successful Public/Private Partnership
Independent Laboratories Institute (ILI) is a non-profit, 501(c) 3 , scientific educational organization established in 1992.
It is multi-disciplined and member driven.
Its goal is to provide quality training for the laboratory community.
ILI is sponsored by individual and corporate sponsors. The American Council of Independent Laboratories(ACIL) is one of its principle supporters.
H 2 M labs
631 694 3040 | www.h2mlabs.com

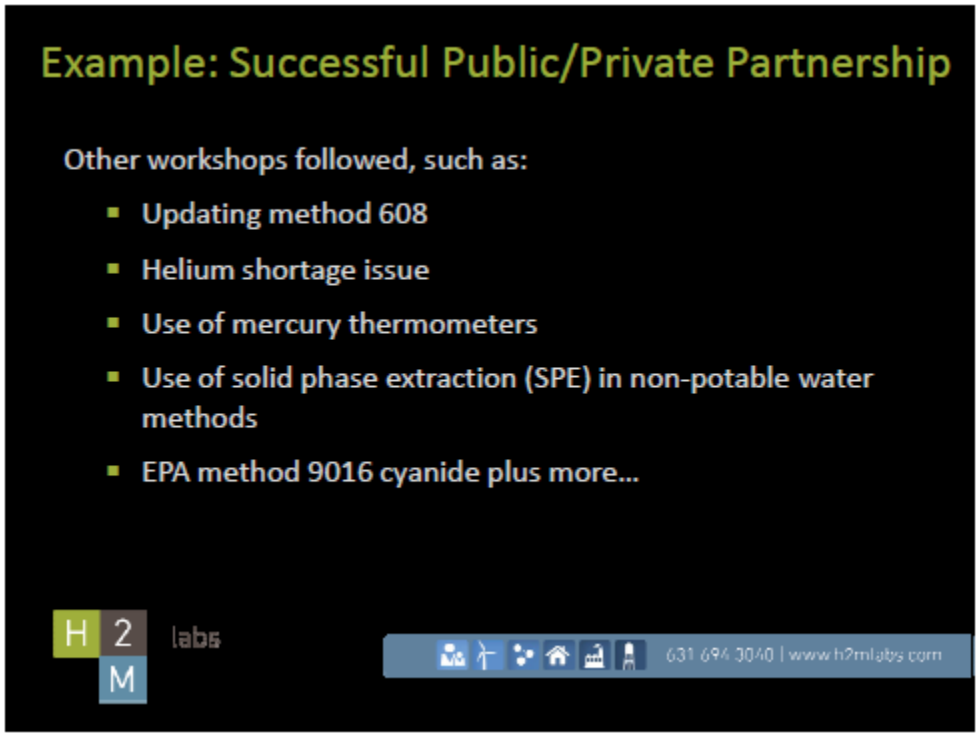

Example: Successful Public/Private Partnership
Under the direction of the ILI workshop chairman David Freidman, ILI initiated a partnership with the EPA .
Goal of the workshop is improving environmental monitoring and advancing monitoring technology for issues that are of importance to the EPA and the monitoring support community.
EPA wanted to update the 600 series methods.
The testing community was able to prioritize the list of methods based upon the most used. This saved time by not having to rework methods that were not used by the majority of the laboratories.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Example: Successful Public/Private Partnership
Critical Methods for Updating were :
EPA method 624: The determination of volatile organic analytes by purge and trap gas chromatography combined with mass spectrometry (GC/MS).
EPA methods 625: The determination of semi-volatile organize analytes by extraction and gas chromatography combined with mass spectrometry (GC/MS)
EPA method 608: The determination of Pesticides' and PCB's by extraction and electron capture gas chromatography.
EPA promulgate methods 624, 625 and 608 in 1984 for permit applications, certification, and compliance monitoring in EPA'S Clean Water Act programs.
Other than minor technical corrections, the methods have not been updated since promulgation.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Example: Successful Public/Private Partnership
A workshop was held in Washington DC
Attendees included staff from:
EPA Office of Water
EPA Office of Resources Conservation and Recovery (ORCR)
Members of the laboratory community
Members of the laboratory technology innovation community
H 2 M labs
631 694 3040 | www.h2mlabs.com

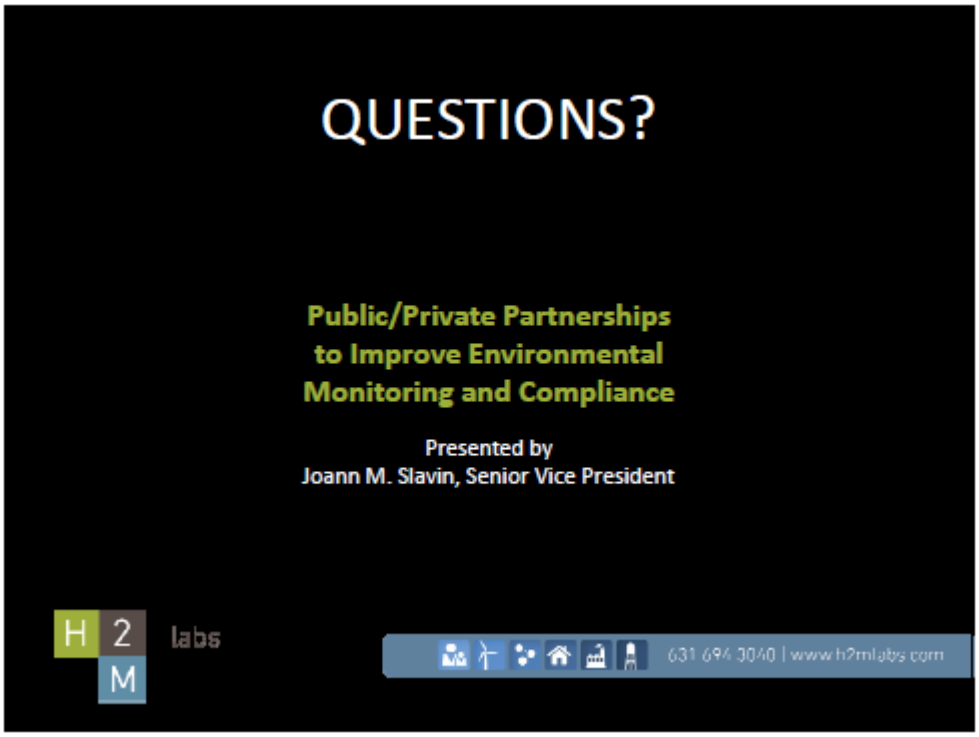

Example: Successful Public/Private Partnership
Objective of the workshop:
Assist the EPA in expanding the list of analytes which could to be analyzed.
Bring the methods up to date in regard to technological advancements.
Methods 624 and 625 were reviewed… (ok, we didn't get to method 608…did you really think that we could do all 3 methods in one day?)
Change to a capillary column from the vintage packed column.
Clarification of sample preservation requirements for method 624
QC improvements.
Cleanup procedures for sulfur and high molecular weight compounds in Method 625.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Example: Successful Public/Private Partnership
List of suggestions was developed and changes were presented to EPA.
Changes were reviewed internally by EPA and nearly all of the changes were incorporated into revised versions of the method.
With this great success under our belt… A small group representing ILI, the lab community, and the technology innovation community met with representatives from the Office of Water and a meeting with the ORCR to discuss our willingness to work together with EPA.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Example: Successful Public/Private Partnership
Other workshops followed, such as:
Updating method 608
Helium shortage issue
Use of mercury thermometers
Use of solid phase extraction (SPE) in non-potable water methods
EPA method 9016 cyanide plus more…
H 2 M labs
631 694 3040 | www.h2mlabs.com


Why this Partnership was a Success!
Strong leadership in the workshop chairman, David Friedman.
Champion from the public sector, Lem Walker, and others.
Resources , time commitment from EPA staff, lab community and technology innovation community.
Right people in the workshop - engaged and dedicated.
Working towards the same goal.
H 2 M labs
631 694 3040 | www.h2mlabs.com


Why this Partnership was a Success!
Main ingredient in the success:
Working through the challenges together!
We need to capture this new way of working in order to maximize the strengths of both the public and private sector.
H 2 M labs
631 694 3040 | www.h2mlabs.com


QUESTIONS?
Public/Private Partnerships
to Improve Environmental
Monitoring and Compliance
Presented by
Joann M. Slavin, Senior Vice President
H 2 M
labs
631 694 3040 | www.h2mlabs.com

Tools for Managing an Environmental Laboratory Program

John Phillips, Ford Motor Company
Jim Tomalia, Enovis, Inc.

Abstract

Accurate, defensible, timely and cost effective analytical data is critical for environmental programs associated with any sized corporation. The authors will present a number of the tools in the Enovis tool box, which were designed with corporate environmental programs in mind and have been used by Ford Motor Company over the past ten years. The Ford environmental laboratory program will be used as an example of how these tools can be utilized to ensure accurate, defensible, timely and cost effective analytical data for environmental compliance needs. Some of the tools to be discussed in detail include; the Enovis Collaborative Laboratory Management System (CLMS), initial laboratory qualification, laboratory selection, performance monitoring metrics, double blind PT evaluations, on-site audit assessments, security related issues, electronic data management, data validation and reporting tools. The authors will show how these tools can be used to dramatically reduce the cost and time requirements of managing an environmental laboratory program. Examples will also be provided which demonstrate continuous improvement in data quality and laboratory performance. The presentation will provide practical solutions for managing complex environmental programs, including local compliance with CWA, SDWA and RCRA programs as well as property management for site investigation, remediation and Superfund activities.

Tools for Managing an Environmental Laboratory Program

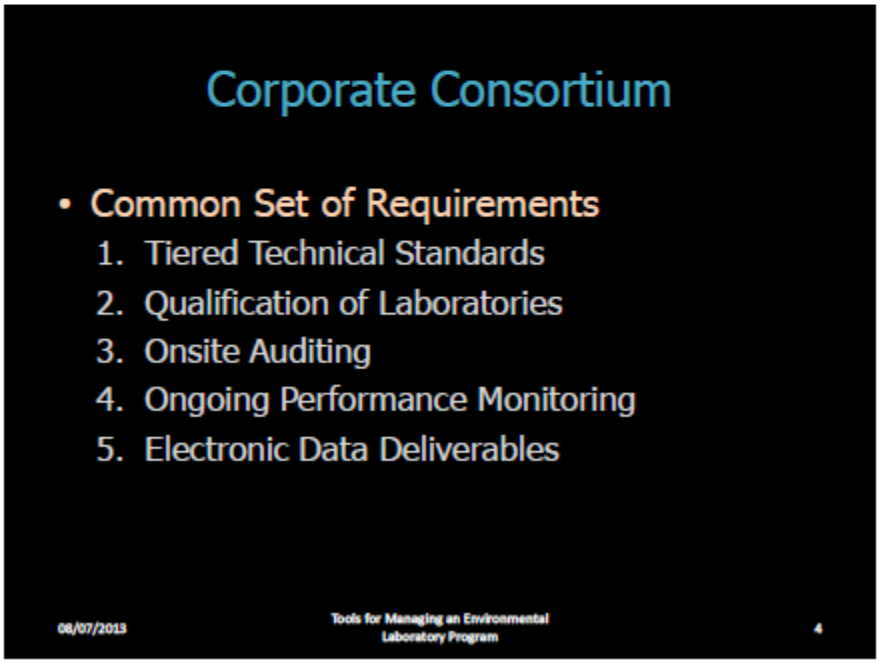
John Phillips – Ford Motor Company

Jim Tomalia – Enovis, Inc.

Corporate Environmental Data Needs

- Environmental Data Must Be;
  1. Accurate
  2. Defensible
  3. Timely
  4. Cost Effective
- Corporate Consortium (2000 – 2004)
  - Ford Motor Company
  - Environmental Standards, Inc.


Corporate Consortium
3M
BASF
CSX
Chevron
ConocoPhillips
DUPONT
ExxonMobil
Ford
GM
Honeywell
IBM
LTV
MERCK
Be well
TEXACO
UNION PACIFIC
USS
VEOLIA
ENVIRONMENTAL
Visteon
WM
WASTE MANAGEMENT


Corporate Consortium
• Common Set of Requirements
1. Tiered Technical Standards
2. Qualification of Laboratories
3. Onsite Auditing
4. Ongoing Performance Monitoring
5. Electronic Data Deliverables
08/07/2013
Tools for Managing an Environmental Laboratory Program
4



Services Offered by enovis

- Onsite Auditing
  - Initial Qualification Audits
  - Ongoing Monitoring Audits
- Performance Test Sample Data
  - Single Blind PT Database
    - Performance statistics by
    - Lab – Parameter – Method - Matrix
  - Double Blind PT Program
    - From bottle order to final report

08/07/2013 Tools for Managing an Environmental Laboratory Program 6

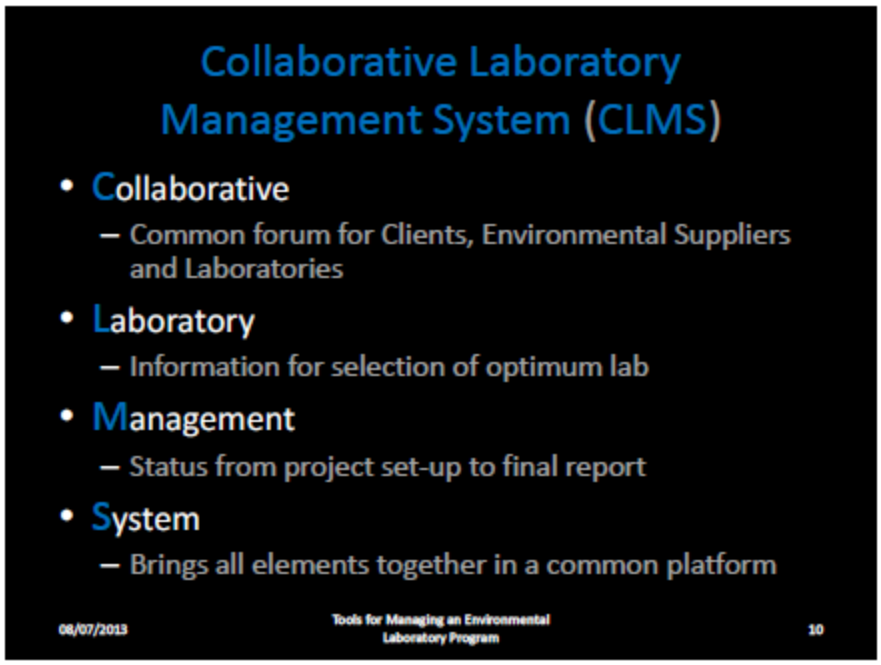
Services Offered by enovis

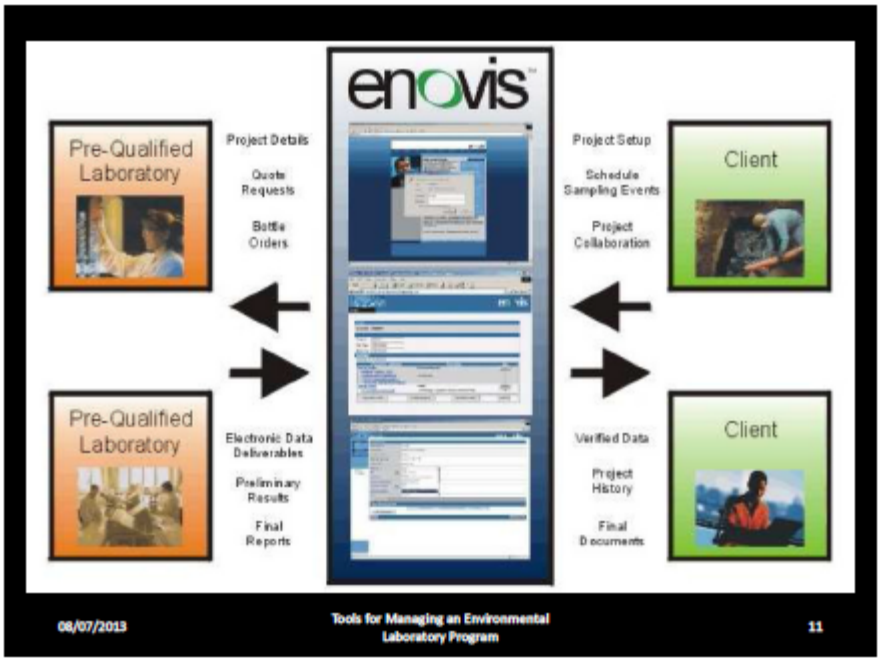
- Collaborative Laboratory Management System (CLMS) – Web Based
- Data Validation
  - Automated Level II Data Verification
  - Level IV Data Validation
- Data Management
  - Data Storage and Database Management
  - Data Querying Capabilities

Services Offered by enovis

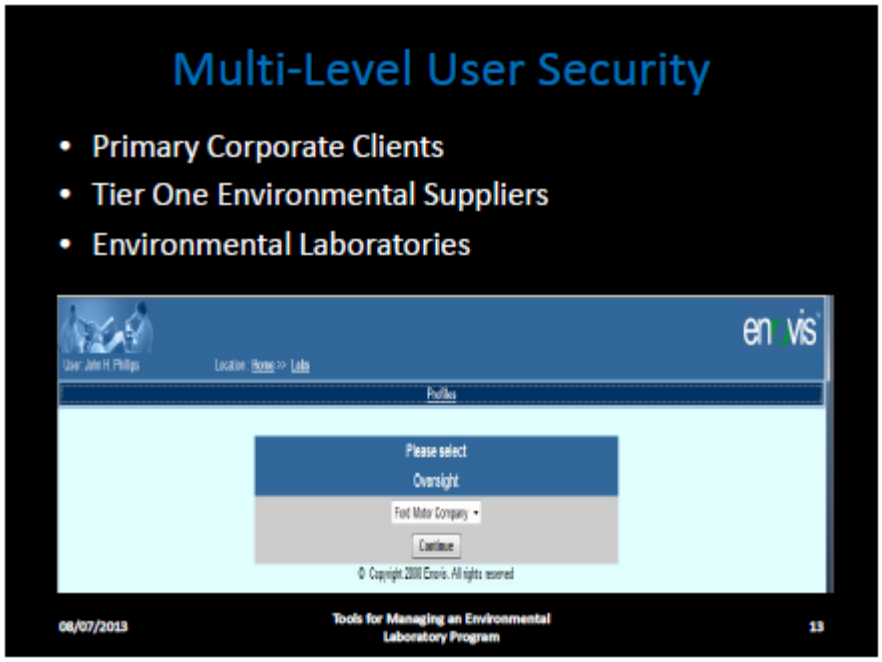
- Data Reporting
  - Standard reports derived from EDD
    - Data Verification Report
    - Analytical Results Summary (ARS)
    - Qualified Analytical Report (QAR)
  - Custom reports from EDD
    - Criteria Reports
    - User Defined – (RCRA Reporting Tool)
- Laboratory Performance Reports

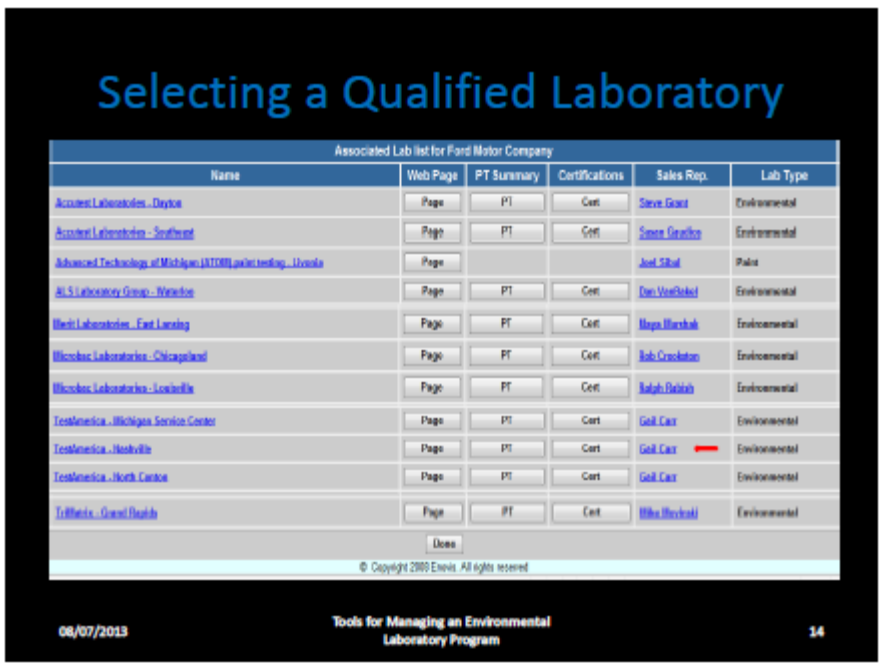

Services Offered by enovis
• Program Management
– Project set-up
– Project monitoring
– Project summaries
• Centralized Billing and Accounting
– Laboratory quotations
– Invoicing
– Spending breakdowns
08/07/2013
Tools for Managing an Environmental Laboratory Program
9


Collaborative Laboratory Management System (CLMS)
• Collaborative
– Common forum for Clients, Environmental Suppliers and Laboratories
• Laboratory
– Information for selection of optimum lab
• Management
– Status from project set-up to final report
• System
– Brings all elements together in a common platform
08/07/2013
Tools for Managing an Environmental Laboratory Program
10

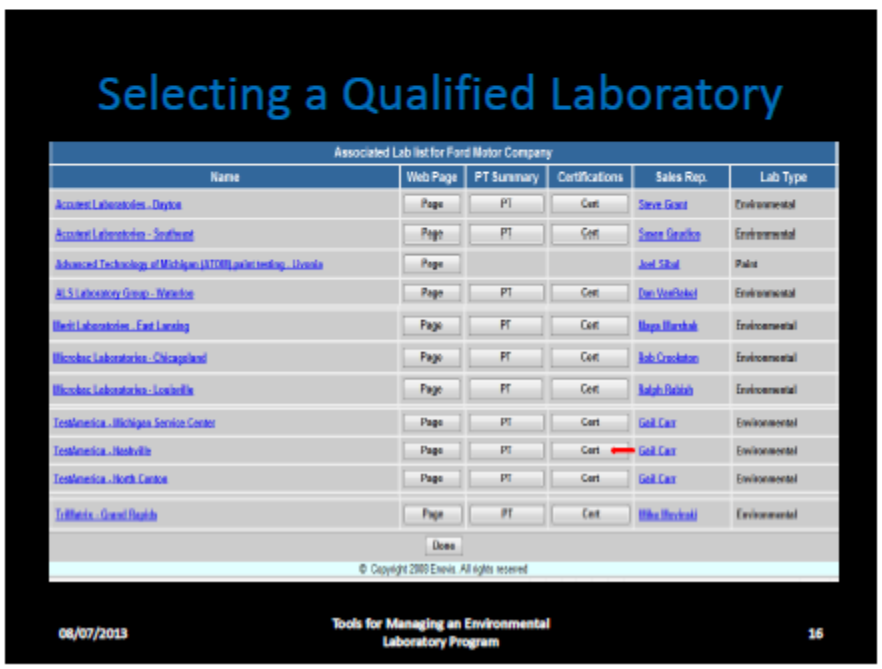

enovis
Pre-Qualified Laboratory
Project Details
Quote Requests
Battle Orders
Project Setup
Schedule Sampling Events
Project Collaboration
Client
Pre-Qualified Laboratory
Electronic Data Deliverables
Preliminary Results
Final Reports
Verified Data
Project History
Final Documents
Client
08/07/2013
Tools for Managing an Environmental Laboratory Program
11


www.enovis-inc.com
enovis
HOME
ABOUT
FAQ
SERVICES
DEMOS
CONTACT
LINKS
MEMBERS
Welcome to Enovis
Creating the Global Laboratory Management Marketplace, Enovis is the world's premier laboratory management exchange, harnessing the power of Internet technology to bring scientists, engineers, laboratories and corporations together - revolutionizing the way industry does business.
Enovis is the first comprehensive analytical testing exchange, offering clients access to a network of pre-qualified analytical laboratories through a web-based, intelligent interface. Enovis provides the tools and services necessary for engineers, scientists, geologists and others who generate environmental samples for laboratory analysis to streamline the interaction with analytical laboratories.
Enovis is Laboratory Management made Simple.™
ANNOUNCEMENTS
April 2008: Enovis adds additional functionality to the Collaborative Laboratory Management System. Users may now download data from the Project page in several electronic formats. Enhanced Lab page now allows users to access laboratory webpages without leaving the CLMS. A Library of program and client related documents has been added.
The system allows Clients, Contractors, participating Laboratories and Enovis project scientists to effectively manage and collaborate on projects.
Click here to download the Enovis Training Manual.
Click here to launch the CLMS.
08/07/2013
Tools for Managing an Environmental Laboratory Program
12


Multi-Level User Security
• Primary Corporate Clients
• Tier One Environmental Suppliers
• Environmental Laboratories
envis
User: John H. Phillips
Location: Home >> Labs
Profiles
Please select
Oversight
Ford Motor Company
Continue
© Copyright 2000 Envis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
13


Selecting a Qualified Laboratory
Associated Lab list for Ford Motor Company
Name
Web Page
PT Summary
Certifications
Sales Rep.
Lab Type
Accutest Laboratories - Dayton
Accutest Laboratories - Southwest
Advanced Technology of Michigan (ATOM) paint testing - Livonia
AL5 Laboratory Group - Waterloo
Merit Laboratories - East Lansing
Microbac Laboratories - Chicagoland
Microbac Laboratories - Louisville
TestAmerica - Michigan Service Center
TestAmerica - Nashville
TestAmerica - North Canton
Trifilletrix - Grand Rapids
Page
PT
Cert
Steve Grant
Simon Gravlice
Joel Sibal
Dan VanBakel
Maya Marshak
Bob Crookston
Ralph Rabish
Gail Carr
Mike Movinski
Environmental
Paint
Done
© Copyright 2000 Envis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
14


Contact Information
Person Contact Information
Name: Gail Carr
Org: TestAmerica
Phone: 810-229-2763
Alt Phone: 734-276-7655
Fax: 734-205-2533
E-Mail: gail.carr@testamericainc.com
Address: 10448 Citation Drive Suite 200
City: Brighton
State: MI
Zip Code: 48116
Country: US
Done
08/07/2013
Tools for Managing an Environmental Laboratory Program
15


Selecting a Qualified Laboratory
Associated Lab list for Ford Motor Company
Name
Web Page
PT Summary
Certifications
Sales Rep.
Lab Type
Accutest Laboratories - Dayton
Accutest Laboratories - Southwest
Advanced Technology of Michigan (ATOM) paint testing - Livonia
ALS Laboratory Group - Waterloo
Merit Laboratories - East Lansing
Microbac Laboratories - Chicagoland
Microbac Laboratories - Louisville
TestAmerica - Michigan Service Center
TestAmerica - Nashville
TestAmerica - North Canton
Trillfatrix - Grand Rapids
Page
PT
Cert
Steve Grant
Simon Gourlice
Joel Sibal
Dan VanRekel
Mayo Marshak
Bob Crookston
Ralph Rabish
Gail Carr
Gail Carr
Gail Carr
Mike Wovinski
Environmental
Paint
Done
© Copyright 2008 Enovis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
16

Lab Certification

Lab: TestAmerica Office: Nashville

Current Certifications

Cert. Body	Program	Issued	expiration	Number	Notes
		02-14-2008	01-26-2009		
A2LA	Environmental Testing	11-20-2012	12-31-2013	0453.07	Wyoming LUST, RCRA Methods
	Nashville A2LA123113rev112612.pdf				
Alaska	UST Contaminated Sites	07-24-2012	07-24-2013	UST-087	
	Nashville AKcert_scope072413.pdf				
Arizona	DW, WW, SHW, Air	05-06-2013	05-05-2014	AZ0473	
	Nashville AZcert_scope050214.pdf				
Arkansas	CWA, RCRA	04-25-2013	04-25-2014	88-0737	
	Nashville Arkansas cert_scope042514.pdf				
California	SDWA, CWA, RCRA	11-05-2012	10-31-2013	01168CA	
	Nashville CAcert_scope103113rev030113.pdf				
Connecticut	SDWA, CWA, RCRA	02-17-2012	12-31-2013	PH-0220	
	Nashville CTcert_scope123113rev021712.pdf				
Florida	SDWA, CWA, RCRA	02-15-2013	06-30-2013	E87358	
	Nashville FLcert_scope063013rev021513.pdf				
Illinois	SDWA, CWA, RCRA	12-05-2012	12-09-2013	200060	
	Nashville ILcert_scope120913.pdf				
Iowa	UST Soil & Water, CWA, RCRA	05-01-2012	05-01-2014	131	
	Iowa certification exp 20140501.pdf				
Kansas	SDWA, CWA, RCRA	11-01-2012	10-31-2013	E-10229	

nelap

NELAP RECOGNIZED

CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM BRANCH

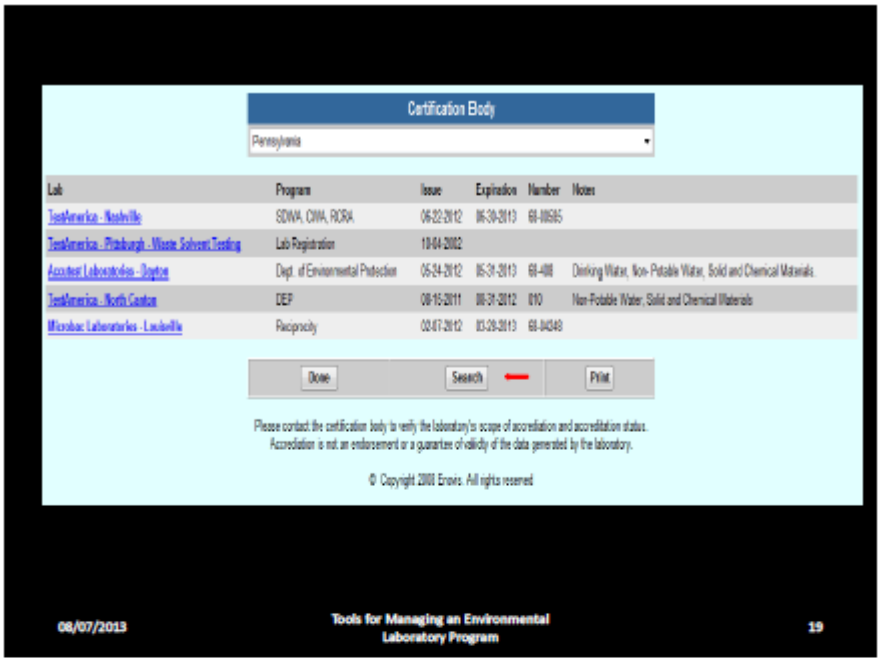
NELAP Fields of Accreditation

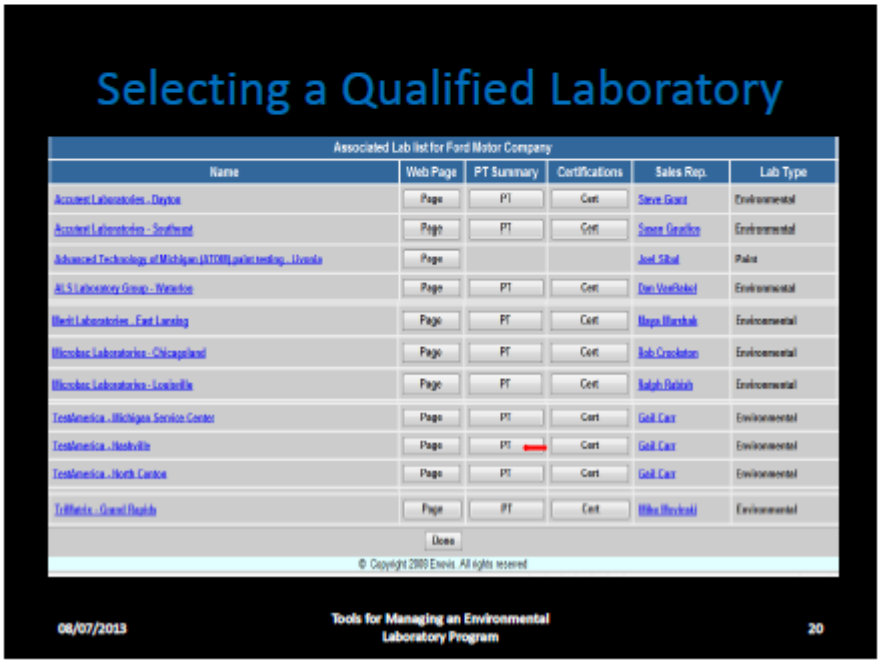
Testamerica Laboratories, Inc.
Nashville Division
2960 Foster Creighton Drive
Nashville, TN 37204
Phone: (615) 726-0177

Primary AA: FL E87358

Certificate No. 01168CA
Renew Date: 10/31/2013

102 - Inorganic Chemistry of Drinking Water			
102.030	003	EPA 300.0	Chloride
102.030	005	EPA 300.0	Fluoride
102.030	006	EPA 300.0	Nitrate
102.030	007	EPA 300.0	Nitrite
102.030	010	EPA 300.0	Sulfate
102.050	001	EPA 335.4	Cyanide
102.060	001	EPA 353.2	Nitrate-nitr.
102.061	001	EPA 353.2	Nitrite
102.140	001	SM2540C	Total Dissolved Solids
102.150	002	SM4110B	Fluoride
102.150	003	SM4110B	Nitrate
102.150	004	SM4110B	Nitrite
102.150	005	SM4110B	Sulfate
102.520	001	EPA 200.7	Calcium
102.520	002	EPA 200.7	Magnesium
102.520	003	EPA 200.7	Sodium


Certification Body
Pennsylvania
Lab
Program
Issue
Expiration
Number
Notes
TestAmerica - Nashville
SDWA, CWA, RCRA
06-22-2012
06-30-2013
68-00585
TestAmerica - Pittsburgh - Waste Solvent Testing
Lab Registration
10-04-2002
Accutest Laboratories - Dayton
Dept. of Environmental Protection
05-24-2012
05-31-2013
68-498
Drinking Water, Non-Potable Water, Solid and Chemical Materials
TestAmerica - North Canton
DEP
08-16-2011
06-31-2012
010
Non-Potable Water, Solid and Chemical Materials
Microbac Laboratories - Louisville
Reciprocity
02-07-2012
03-28-2013
68-04048
Done
Search
Print
Please contact the certification body to verify the laboratory's scope of accreditation and accreditation status.
Accreditation is not an endorsement or a guarantee of validity of the data generated by the laboratory.
© Copyright 2008 Enovis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
19


Selecting a Qualified Laboratory
Associated Lab list for Ford Motor Company
Name
Web Page
PT Summary
Certifications
Sales Rep.
Lab Type
Accutest Laboratories - Dayton
Page
PT
Cert
Steve Grant
Environmental
Accutest Laboratories - Southeast
Page
PT
Cert
Simon Geoffrey
Environmental
Advanced Technology of Michigan (ATOM) paint testing - Livonia
Page
Joel Sibal
Paint
ALS Laboratory Group - Waterloo
Page
PT
Cert
Dan VanRobaid
Environmental
Merit Laboratories - East Lansing
Page
PT
Cert
Mega Marshak
Environmental
Microbac Laboratories - Chicagoland
Page
PT
Cert
Bob Crockston
Environmental
Microbac Laboratories - Louisville
Page
PT
Cert
Ralph Rabish
Environmental
TestAmerica - Michigan Service Center
Page
PT
Cert
Gail Carr
Environmental
TestAmerica - Nashville
Page
PT
Cert
Gail Carr
Environmental
TestAmerica - North Canton
Page
PT
Cert
Gail Carr
Environmental
Tri Metrix - Grand Rapids
Page
PT
Cert
Mike Wavinski
Environmental
Done
© Copyright 2009 Enovis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
20

Laboratory Name: **TestAmerica - Nashville**

PT Type	PT Source	PT Date	N	C	W	O	% Error	Comment
WS-186	ERA	01/09/2012	288	8	0	0	2.99	Not Acceptables - Nitrate+Nitrite as N, Nitrate as N, Tert-Butyl Alcohol
WP-204	ERA	01/16/2012	1645	20	0	0	1.22	Not Acceptables -Nitrite as N, Tin, Surfactants (MBAS), Acidity as CaCO3, 2,4,5-T, Total Organic Halides (TOX).
Soil-77	ERA	01/23/2012	1177	17	0	0	1.44	Not Acceptables - Zinc, Corrosivity (pH), Benzene, tert-Butyl methyl ether (MTBE), Ethylbenzene, Toluene.
Soil-77	ERA	01/23/2012	1176	18	0	0	1.53	Not Acceptables: Zinc, Corrosivity (pH), Benzene, tert-Butyl methyl ether (MTBE), Ethylbenzene, Toluene, bis(2-Chloroethyl)ether.
WS-189	ERA	04/09/2012	8	0	0	0	0.00	
WP-207	ERA	04/16/2012	22	0	0	0	0.00	
Soil-78	ERA	04/23/2012	16	0	0	0	0.00	
WS-192	ERA	07/09/2012	269	12	0	0	4.46	Not Acceptables-Conductivity at 25 C, Aluminum, Molybdenum, Tert-Butyl Alcohol, and Bromochloromethane.
WP-210	ERA	07/16/2012	1684	35	0	0	2.08	Not Acceptables-Aroclor 1016, Aroclor 1242, C9-C12 Aliphatics (MA VPH), C19-C36 Aliphatics (MA EPH), Fluorene in EPH, Non-Filterabl Residue (TSS), Chlorobenzene, Ethylbenzene, Xylenes, total, Benzo(a)anthracene.
		Total	10720	230	0	23	2.57	

%Error = [(C+W+O)/N]*100

N = Total number of parameters

C = Number of parameters outside of control limit

W = 0.5 x number of parameters between the warning and control limit

O = Number of parameters more than an order of magnitude from the true or expected value

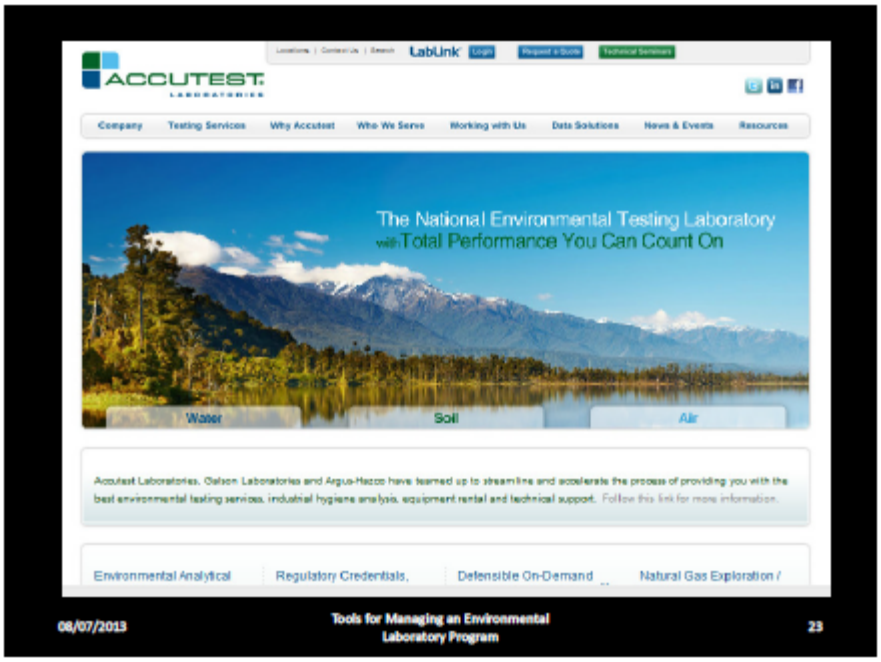
Selecting a Qualified Laboratory

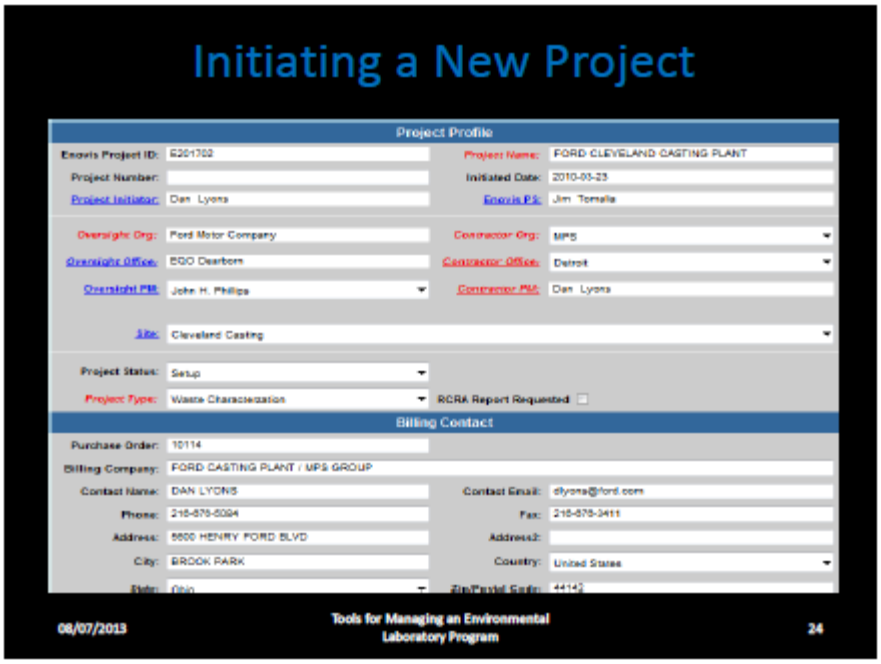
Associated Lab list for Ford Motor Company

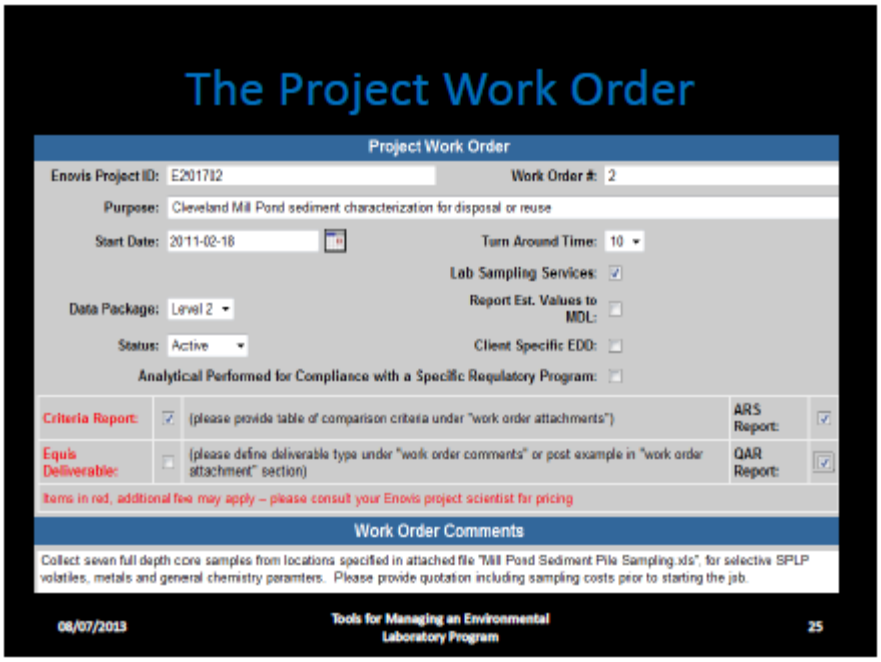
Name	Web Page	PT Summary	Certifications	Sales Rep.	Lab Type
Accutest Laboratories - Dayton	Page	PT	Cert	Steve Grant	Environmental
Accutest Laboratories - Southwest	Page	PT	Cert	Susan Gaudice	Environmental
Advanced Technology of Michigan (ATOM) paint testing - Livonia	Page			Joel Sibal	Paint
ALS Laboratory Group - Waterloo	Page	PT	Cert	Dan VanRakel	Environmental
Merit Laboratories - East Lansing	Page	PT	Cert	Maya Marshak	Environmental
Microbac Laboratories - Chicagoland	Page	PT	Cert	Bob Crookston	Environmental
Microbac Laboratories - Louisville	Page	PT	Cert	Ralph Rabish	Environmental
TestAmerica - Michigan Service Center	Page	PT	Cert	Gail Carr	Environmental
TestAmerica - Nashville	Page	PT	Cert	Gail Carr	Environmental
TestAmerica - North Canton	Page	PT	Cert	Gail Carr	Environmental
TriMatrix - Grand Rapids	Page	PT	Cert	Mike Mavinski	Environmental

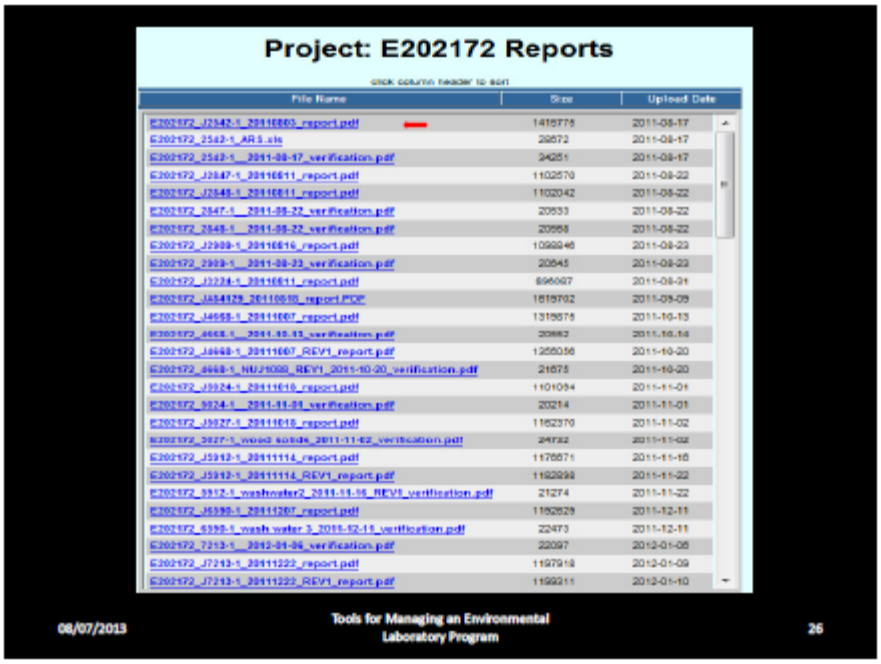
Done

© Copyright 2009 Enovis. All rights reserved


ACCUTEST
LABORATORIES
LabLink
Company
Testing Services
Why Accutest
Who We Serve
Working with Us
Data Solutions
News & Events
Resources
The National Environmental Testing Laboratory
with Total Performance You Can Count On
Water
Soil
Air
Accutest Laboratories, Gelson Laboratories and Argus-Hazco have teamed up to streamline and accelerate the process of providing you with the best environmental testing services, industrial hygiene analysis, equipment rental and technical support. Follow this link for more information.
Environmental Analytical
Regulatory Credentials,
Defensible On-Demand
Natural Gas Exploration /
08/07/2013
Tools for Managing an Environmental Laboratory Program
23

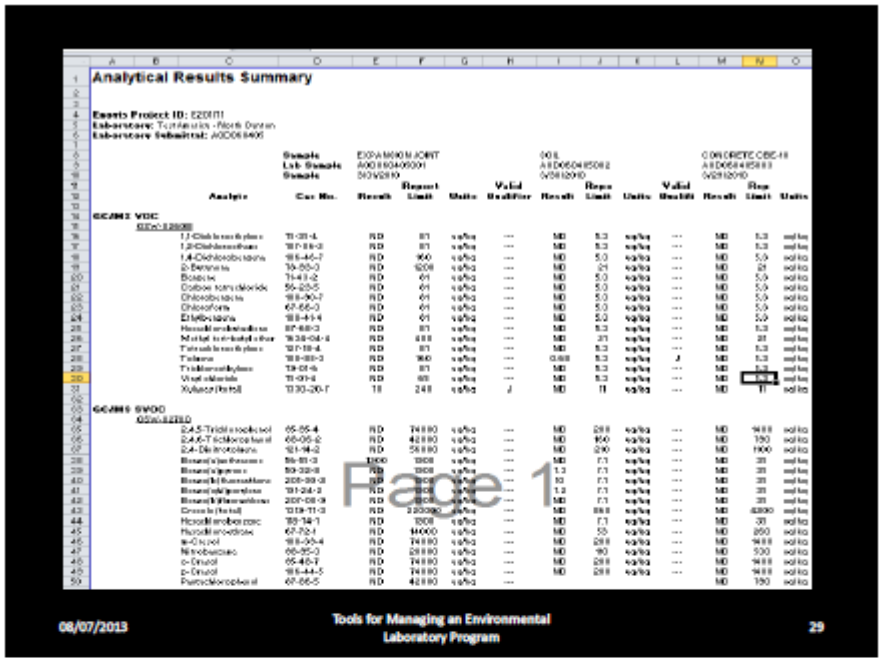

Initiating a New Project
Project Profile
Enovis Project ID: E201702
Project Name: FORD CLEVELAND CASTING PLANT
Project Number:
Initiated Date: 2010-03-23
Project Initiator: Dan Lyons
Enovis PS: Jim Tomalia
Oversight Org: Ford Motor Company
Contractor Org: MPS
Oversight Office: EGO Dearborn
Contractor Office: Detroit
Oversight PM: John H. Phillips
Contractor PM: Dan Lyons
Site: Cleveland Casting
Project Status: Setup
Project Type: Waste Characterization
RCRA Report Requested
Billing Contact
Purchase Order: 10114
Billing Company: FORD CASTING PLANT / MPS GROUP
Contact Name: DAN LYONS
Contact Email: dlyons@ford.com
Phone: 216-676-5094
Fax: 216-676-3411
Address: 5600 HENRY FORD BLVD
Address2:
City: BROOK PARK
Country: United States
State: Ohio
Zip/Postal Code: 44142
08/07/2013
Tools for Managing an Environmental Laboratory Program
24


The Project Work Order
Project Work Order
Enovis Project ID: E201712
Work Order #: 2
Purpose: Cleveland Mill Pond sediment characterization for disposal or reuse
Start Date: 2011-02-18
Turn Around Time: 10
Lab Sampling Services:
Data Package: Level 2
Report Est. Values to MDL:
Status: Active
Client Specific EDD:
Analytical Performed for Compliance with a Specific Regulatory Program:
Criteria Report:
(please provide table of comparison criteria under "work order attachments")
ARS Report:
Equis Deliverable:
(please define deliverable type under "work order comments" or post example in "work order attachment" section)
QAR Report:
Items in red, additional fee may apply – please consult your Enovis project scientist for pricing
Work Order Comments
Collect seven full depth core samples from locations specified in attached file "Mill Pond Sediment Pile Sampling.xls", for selective SPLP volatiles, metals and general chemistry paramters. Please provide quotation including sampling costs prior to starting the job.
08/07/2013
Tools for Managing an Environmental Laboratory Program
25


Project: E202172 Reports
File Name
Size
Upload Date
08/07/2013
Tools for Managing an Environmental Laboratory Program
26


TestAmerica
ANALYTICAL REPORT
08/07/2013
Tools for Managing an Environmental Laboratory Program
27


enovis
08/07/2013
Tools for Managing an Environmental Laboratory Program
28

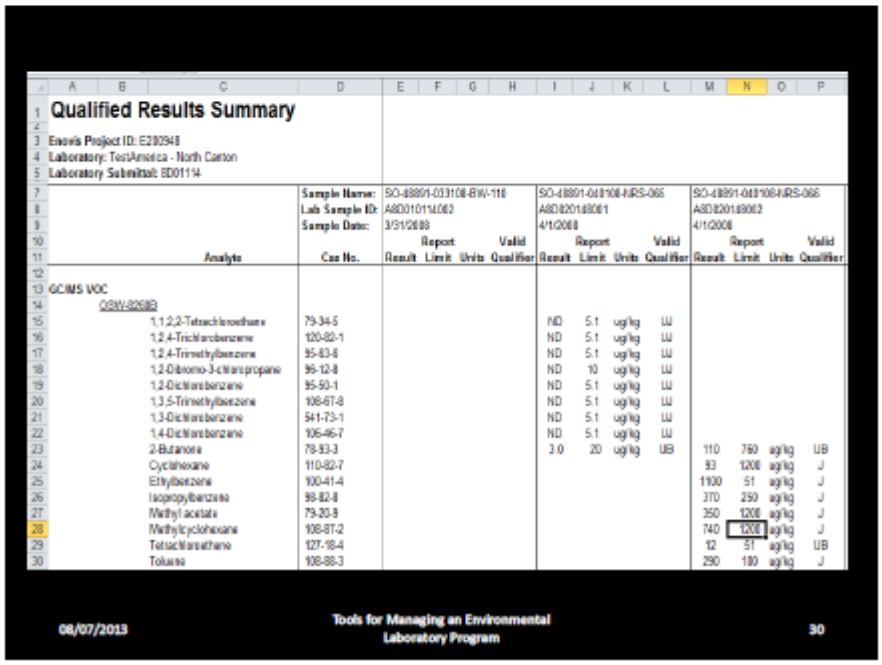


Analytical Results Summary

Enovis Project ID: E20011
Laboratory: TestAmerica - North Canton
Laboratory Submittal: ADD61400

Analyte	Cas No.	Sample Lab Sample Sample	Result	Report Limit	Units	Valid Qualifier	Lab Sample	Result	Report Limit	Units	Valid Qualifier	Lab Sample	Result	Report Limit	Units
GC/MS VOC															
1,1-Dichloroethane	75-34-3		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
1,2-Dichloroethane	107-06-2		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
1,4-Dichlorobutane	106-46-7		ND	300	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
2-Butanone	78-93-3		ND	1200	ug/kg	---		ND	21	ug/kg	---		ND	21	ug/kg
Benzene	71-43-2		ND	61	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
Carbon tetrachloride	56-23-5		ND	61	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
Chlorobenzene	108-90-7		ND	61	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
Chloroform	67-66-3		ND	61	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
Ethylbenzene	100-41-4		ND	61	ug/kg	---		ND	5.0	ug/kg	---		ND	5.0	ug/kg
Hexachlorobutadiene	87-68-3		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
Methyl tert-butyl ether	1634-04-4		ND	610	ug/kg	---		ND	31	ug/kg	---		ND	31	ug/kg
Tetrachloroethene	127-18-4		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
Toluene	108-88-3		ND	300	ug/kg	---		0.68	5.3	ug/kg	J		ND	5.3	ug/kg
Trichloroethylene	79-01-6		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
Vinyl chloride	75-01-4		ND	61	ug/kg	---		ND	5.3	ug/kg	---		ND	5.3	ug/kg
Xylenes (total)	1330-20-7		18	240	ug/kg	J		ND	11	ug/kg	---		ND	11	ug/kg
GC/MS SVOC															
2,4,5-Trichlorophenol	95-95-4		ND	74000	ug/kg	---		ND	280	ug/kg	---		ND	1400	ug/kg
2,4,6-Trichlorophenol	88-06-2		ND	42000	ug/kg	---		ND	190	ug/kg	---		ND	780	ug/kg
2,4-Dichlorophenol	120-83-2		ND	58000	ug/kg	---		ND	210	ug/kg	---		ND	1000	ug/kg
Benzo(a)anthracene	56-55-3		ND	1800	ug/kg	---		ND	7.1	ug/kg	---		ND	35	ug/kg
Benzo(a)pyrene	50-32-8		ND	1800	ug/kg	---		1.3	7.1	ug/kg	---		ND	35	ug/kg
Benzo(b)fluoranthene	205-99-2		ND	1800	ug/kg	---		10	7.1	ug/kg	---		ND	35	ug/kg
Benzo(k)fluoranthene	207-08-9		ND	1800	ug/kg	---		1.2	7.1	ug/kg	---		ND	35	ug/kg
Bis(2-ethylhexyl)phthalate	117-81-7		ND	1800	ug/kg	---		ND	7.1	ug/kg	---		ND	35	ug/kg
Chrysene	218-01-9		ND	1800	ug/kg	---		ND	7.1	ug/kg	---		ND	35	ug/kg
Dibenz(a,h)anthracene	53-70-3		ND	2300	ug/kg	---		ND	9.6	ug/kg	---		ND	4600	ug/kg
Hexachlorobenzene	118-74-1		ND	1800	ug/kg	---		ND	7.1	ug/kg	---		ND	35	ug/kg
Hexachloroethane	67-72-1		ND	14000	ug/kg	---		ND	55	ug/kg	---		ND	260	ug/kg
m-Cresol	108-39-4		ND	74000	ug/kg	---		ND	280	ug/kg	---		ND	1400	ug/kg
Nitrobenzene	98-95-3		ND	28000	ug/kg	---		ND	110	ug/kg	---		ND	530	ug/kg
o-Cresol	95-48-7		ND	74000	ug/kg	---		ND	280	ug/kg	---		ND	1400	ug/kg
p-Cresol	106-44-5		ND	74000	ug/kg	---		ND	280	ug/kg	---		ND	1400	ug/kg
Pentachlorophenol	87-86-5		ND	42000	ug/kg	---							ND	190	ug/kg

Page 1



Qualified Results Summary

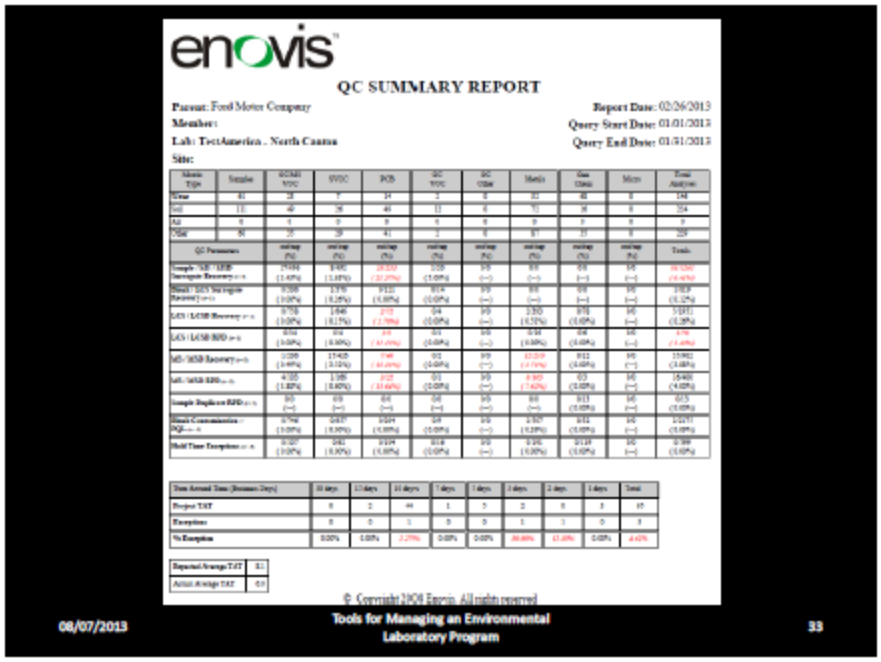
Enovis Project ID: E20948
Laboratory: TestAmerica - North Canton
Laboratory Submittal: ED0114

Analyte	Cas No.	Sample Name:	Result	Report Limit	Units	Valid Qualifier	Sample Name:	Result	Report Limit	Units	Valid Qualifier	Sample Name:	Result	Report Limit	Units	Valid Qualifier
		Lab Sample ID:					Lab Sample ID:					Lab Sample ID:				
		Sample Date:					Sample Date:					Sample Date:				
GC/MS VOC																
OSW-8260B																
1,1,2,2-Tetrachloroethane	79-34-5							ND	5.1	ug/kg	UJ					
1,2,4-Trichlorobenzene	120-82-1							ND	5.1	ug/kg	UJ					
1,2,4-Trimethylbenzene	95-63-6							ND	5.1	ug/kg	UJ					
1,2-Dibromo-3-chloropropane	96-12-8							ND	10	ug/kg	UJ					
1,2-Dichlorobenzene	95-50-1							ND	5.1	ug/kg	UJ					
1,3,5-Trimethylbenzene	108-67-8							ND	5.1	ug/kg	UJ					
1,3-Dichlorobenzene	541-73-1							ND	5.1	ug/kg	UJ					
1,4-Dichlorobenzene	106-46-7							ND	5.1	ug/kg	UJ					
2-Butanone	78-93-3							3.0	20	ug/kg	UB		110	760	ug/kg	UB
Cyclohexane	110-82-7												93	1200	ug/kg	J
Ethylbenzene	100-41-4												1100	51	ug/kg	J
Isopropylbenzene	98-82-8												370	250	ug/kg	J
Methyl acetate	79-20-9												350	1200	ug/kg	J
Methylcyclohexane	108-87-2												740	1200	ug/kg	J
Tetrachloroethene	127-18-4												12	51	ug/kg	UB
Toluene	108-88-3												290	180	ug/kg	J

	A	B	C	D	E	F	G	H
7		MDEQ Criteria				Sample Location / Lab Sample ID / Sample Name		
8		MDEQ Part 201 Generic Cleanup Criteria for Residential Drinking Water Protection	MDEQ Part 201 Generic Cleanup Criteria for Industrial Drinking Water Protection	MDEQ Part 201 Generic Cleanup Criteria for Groundwater/ Surface Water Interface	MDEQ Part 201 Generic Cleanup Criteria for Direct Contact	Dup100-111108-AS S39015.07 Dup100-111108-AS	PRBB2-111108-AS S39015.01 PRBB2-111108-AS	PRBB3-111108-AS S39015.02 PRBB3-111108-AS
15	Parameter							
16	GC/MS VOC (ug/L)							
17	1,1,1,2-Tetrachloroethane	77	320	ID (X)	30,000	<1	1000	335
18	1,1,1-Trichloroethane	200 (A)	200 (A)	200	1.3E+6 (S)	<1	<10	<1
19	1,1,2,2-Tetrachloroethane	8.5	35	78 (S)	4,700	<1	<10	<1
20	1,1,2-Trichloroethane	5.0 (A)	5.0 (A)	330 (X)	21,000	<1	<10	<1
21	1,1-Dichloroethane	880	2,500	740	2.4E+06	<1	<10	<1
22	1,1-Dichloroethene	7.0 (A)	7.0 (A)	65 (S)	11,000	<1	<10	<1
23	1,2,3-Trichlorobenzene	NA	NA	NA	NA	<5	<50	<5
24	1,2,3-Trichloropropane	42	120	NA	84,000	<1	<10	<1
25	1,2,3-Trimethylbenzene	NA	NA	NA	NA	<1	<10	<1
26	1,2,4-Trichlorobenzene	70 (A)	70 (A)	30	19,000	<5	90	2
27	1,2,4-Trimethylbenzene	63 (E)	63 (E)	17	56,000 (S)	<1	<10	<1
28	1,2-Dibromo-3-chloropropane	0.2 (A)	0.2 (A)	NA	390	<5	<50	<5
29	1,2-Dibromoethane	0.05 (A)	0.05 (A)	0.2 (X)	25	<1	<10	<1
30	1,2-Dichlorobenzene	600 (A)	600 (A)	16	1.6E+5 (S)	<1	<10	<1
31	1,2-Dichloroethane	5.0 (A)	5.0 (A)	360 (X)	19,000	<1	<10	<1
32	1,2-Dichloropropane	5.0 (A)	5.0 (A)	290 (X)	16,000	<1	<10	<1
33	1,3,5-Trimethylbenzene	72 (E)	72 (E)	45	61,000 (S)	<1	<10	<1
34	1,3-Dichlorobenzene	6.6	19	38	2,000	<1	<10	<1
35	1,4-Dichlorobenzene	75 (A)	75 (A)	13	6,400	<1	<10	<1
36	2-Butanone (MEK)	13,000	38,000	2,200	2.4E+6 (S)	<30	<300	<30

Laboratory Quality Control Reports

- The number of samples analyzed by matrix
- Number of analyses by test type
- Number reports issued
- Batch Quality Control Statistics
- A detailed description for each QC failure
- Turn-Around-Time (TAT) statistics
- TAT details



enovis

QC SUMMARY REPORT

Parent: Ford Motor Company
Member:
Lab: TestAmerica - North Canton
Site:

Report Date: 02/26/2013
Query Start Date: 01/01/2013
Query End Date: 01/31/2013

Matrix Type	Samples	GC/MS VOC	SVOC	PCB	GC VOC	GC Other	Metals	Gen Chem	Micro	Total Analyses
Water	81	28	7	14	3	0	32	46	0	130
Soil	131	49	36	46	11	0	71	38	0	254
Air	0	0	0	0	0	0	0	0	0	0
Other	26	25	29	41	1	0	107	19	0	229

QC Parameter	out/tot (%)	out/tot (%)	out/tot (%)	out/tot (%)	out/tot (%)	out/tot (%)	out/tot (%)	out/tot (%)	Total
Surrogate Recovery (SUR)	17/488 (3.48%)	8/280 (2.86%)	28/328 (8.23%)	3/328 (0.91%)	0/0 (---)	0/0 (---)	0/0 (---)	0/0 (---)	56/1424 (3.93%)
Blank / LCS Out Legal Review	9/288 (3.13%)	1/176 (0.57%)	9/123 (7.32%)	0/14 (0.00%)	0/0 (---)	0/0 (---)	0/0 (---)	0/0 (---)	19/619 (3.07%)
LCS / LCSD Recovery	0/78 (0.00%)	1/46 (2.17%)	2/33 (6.06%)	0/4 (0.00%)	0/0 (---)	2/30 (6.67%)	0/0 (0.00%)	0/0 (---)	5/191 (2.62%)
LCS / LCSD RPD	0/52 (0.00%)	0/31 (0.00%)	1/21 (4.76%)	0/3 (0.00%)	0/0 (---)	0/20 (0.00%)	0/0 (0.00%)	0/0 (---)	1/170 (0.59%)
MS / MSD Recovery	0/209 (0.00%)	17/425 (4.00%)	7/46 (15.22%)	0/2 (0.00%)	0/0 (---)	12/219 (5.48%)	0/12 (0.00%)	0/0 (---)	36/913 (3.94%)
MS / MSD RPD	4/105 (3.81%)	1/95 (1.05%)	2/23 (8.70%)	0/1 (0.00%)	0/0 (---)	8/165 (4.85%)	0/3 (0.00%)	0/0 (---)	15/400 (3.75%)
Sample Duplicate RPD	0/0 (---)	0/0 (---)	0/0 (---)	0/0 (---)	0/0 (---)	0/0 (---)	0/13 (0.00%)	0/0 (---)	0/13 (0.00%)
Method Contamination (> RL)	0/78 (0.00%)	0/47 (0.00%)	0/29 (0.00%)	0/9 (0.00%)	0/0 (---)	2/167 (1.20%)	0/32 (0.00%)	0/0 (---)	2/371 (0.54%)
Hold Time Exceptions	0/107 (0.00%)	0/82 (0.00%)	0/39 (0.00%)	0/18 (0.00%)	0/0 (---)	0/191 (0.00%)	0/149 (0.00%)	0/0 (---)	0/586 (0.00%)

Turn Around Time (Business Days)	10 days	15 days	20 days	5 days	3 days	4 days	2 days	1 days	Total
Project TAT	0	2	44	1	5	2	0	3	57
Exceptions	0	0	1	0	0	1	1	0	3
% Exception	0.00%	0.00%	2.27%	0.00%	0.00%	50.00%	100.00%	0.00%	5.26%

Reported Average TAT	11
Actual Average TAT	9.9

© Copyright 2008 Enovis. All rights reserved.

08/07/2013 Tools for Managing an Environmental Laboratory Program 33

Laboratory Performance Reports

- **Batch QC data by test type** [Out/Total]
  - Surrogate recovery by matrix
  - Laboratory Control Sample (LCS) recovery
  - LCS/LCSD Relative Percent Difference (RPD)
  - Matrix Spike (MS) recovery
  - MS/MSD Relative Percent Difference (RPD)
  - Sample duplicate RPD
  - Method blanks greater than RL
  - Number of analyses
  - Number of hold time exceptions

08/07/2013 Tools for Managing an Environmental Laboratory Program 34

Matrix Type	Samples	GC/MS VOC	SVOC	PCB
Water	61	23	7	14
Soil	111	49	26	49
Air	0	0	0	0
Other	60	35	29	41
QC Parameters		out/rep (%)	out/rep (%)	out/rep (%)
Sample / MS / MSD Surrogate Recovery (r= 8)		17/496 (3.43%)	8/492 (1.63%)	*55/255 (21.57%)*
Blank / LCS Surrogate Recovery (r= 1)		0/306 (0.00%)	1/378 (0.26%)	0/121 (0.00%)
LCS / LCSD Recovery (r= 1)		0/758 (0.00%)	1/646 (0.15%)	*2/72 (2.78%)*
LCS / LCSD RPD (r= 1)		0/34 (0.00%)	0/4 (0.00%)	*1/9 (11.11%)*

08/07/2013 Tools for Managing an Environmental Laboratory Program 35

QC Summary Detail Report

Parent: Ford Motor Company
Laboratory: ALS Laboratory Group - Waterloo
Date Range: 01/01/2013 - 01/31/2013

Issue: GC/MS VOC - LCS/LCSD Recovery: 4/143

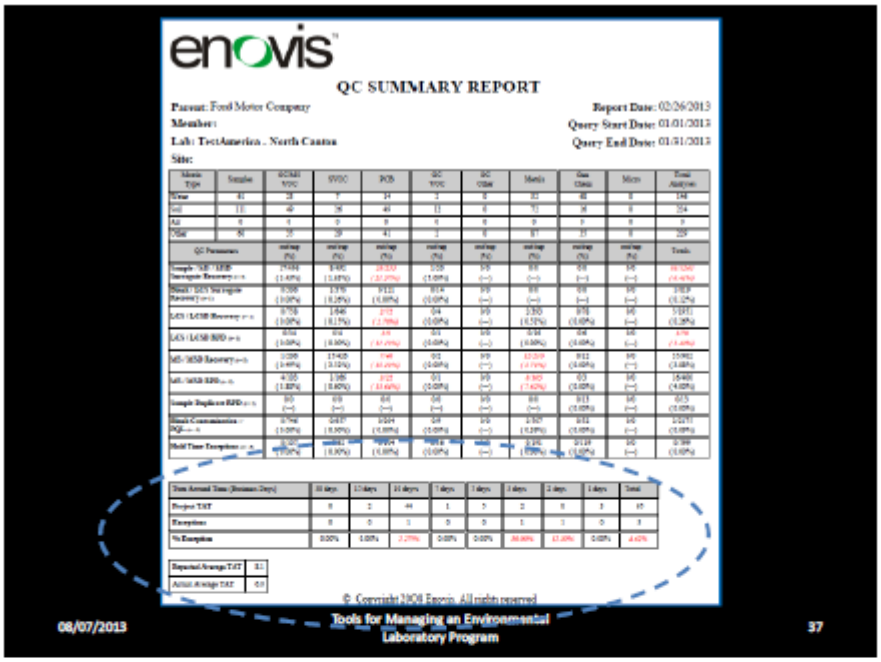
Enovis Project ID: E202062
Client: CRA
Site: St. Thomas Assembly
Project: Ford St. Thomas Assembly Plant - Phase II ESA
Lab Submittal: L1256764

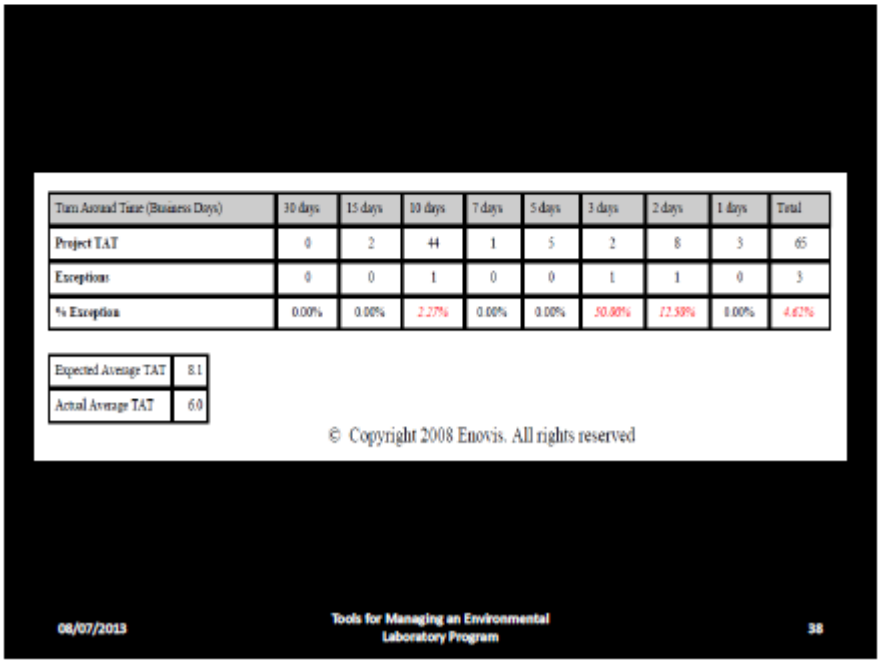
GCMS VOC CVS recovery was an outlier biased low for dichlorodifluoromethane. Client sample result for this analyte should be considered to be estimated and qualified with a UJ flag.

Enovis Project ID: E202062
Client: CRA
Site: St. Thomas Assembly
Project: Ford St. Thomas Assembly Plant - Phase II ESA
Lab Submittal: L1257203

GCMS VOC CVS recoveries were outliers biased low for dichlorodifluoromethane. Client samples L-73149-011113-SM-091, L-73149-011113-SM-092 and L-73149-011113-SM-093 dichlorodifluoromethane results should be considered to be estimated and qualified with UJ flags.

08/07/2013 Tools for Managing an Environmental Laboratory Program 36


enovis
QC SUMMARY REPORT
Parent: Ford Motor Company
Member:
Lab: TestAmerica - North Canton
Site:
Report Date: 02/26/2013
Query Start Date: 01/01/2013
Query End Date: 01/31/2013
Turn Around Time (Business Days)
Project TAT
Exceptions
% Exception
Expected Average TAT
Actual Average TAT
© Copyright 2008 Enovis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
37


Turn Around Time (Business Days) | 30 days | 15 days | 10 days | 7 days | 5 days | 3 days | 2 days | 1 days | Total
Project TAT | 0 | 2 | 44 | 1 | 5 | 2 | 8 | 3 | 65
Exceptions | 0 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 3
% Exception | 0.00% | 0.00% | 2.27% | 0.00% | 0.00% | 50.00% | 12.50% | 0.00% | 4.62%
Expected Average TAT | 8.1
Actual Average TAT | 6.0
© Copyright 2008 Enovis. All rights reserved
08/07/2013
Tools for Managing an Environmental Laboratory Program
38

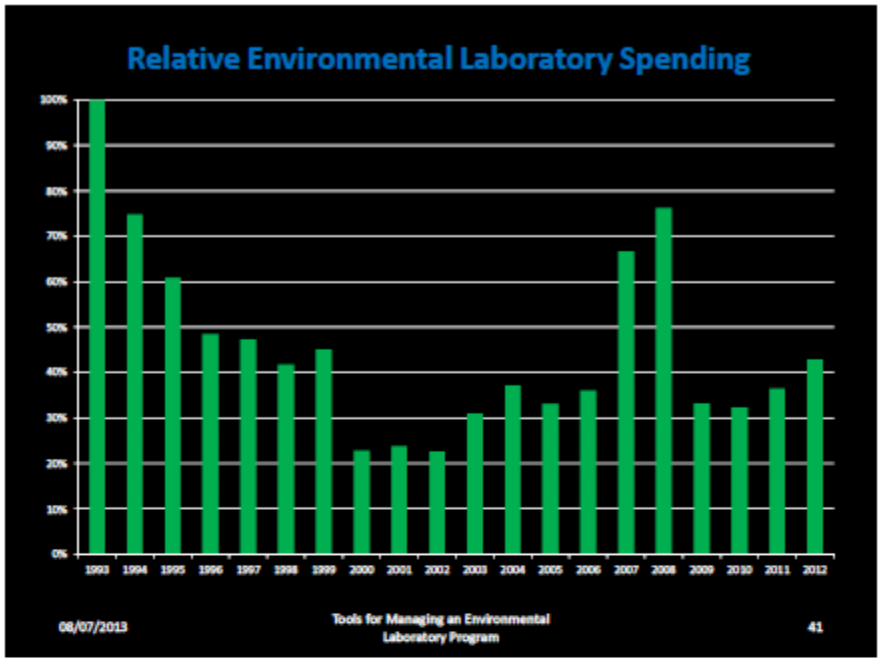
QC Turn Around Exceptions

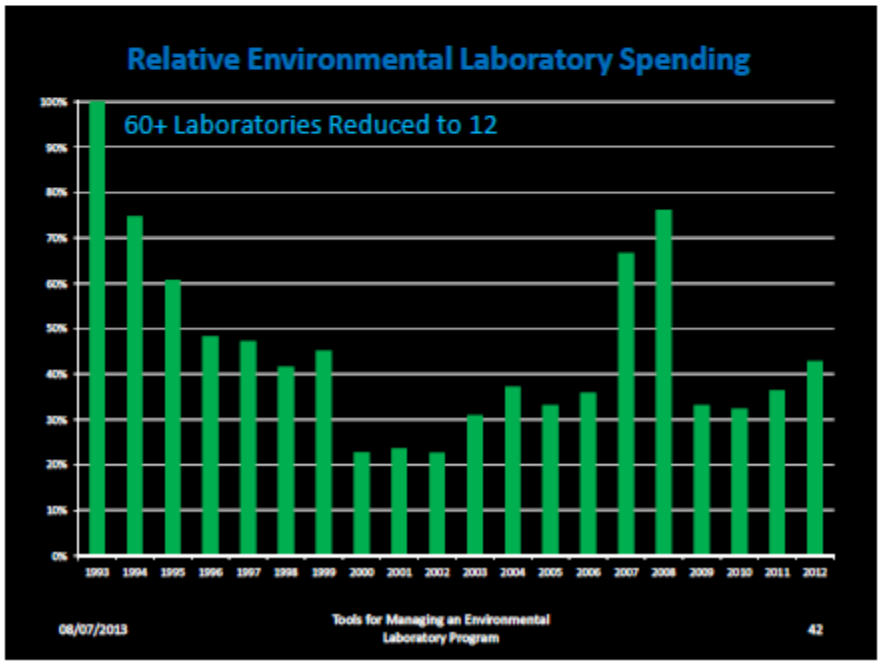
Parent: Ford Motor Company
Member: CRA
Lab: TestAmerica-North Canton
Site: Wixom Assembly
Project: E200948
Lab Submittal: 20087-1
Expected TAT: 10
Actual TAT: 11

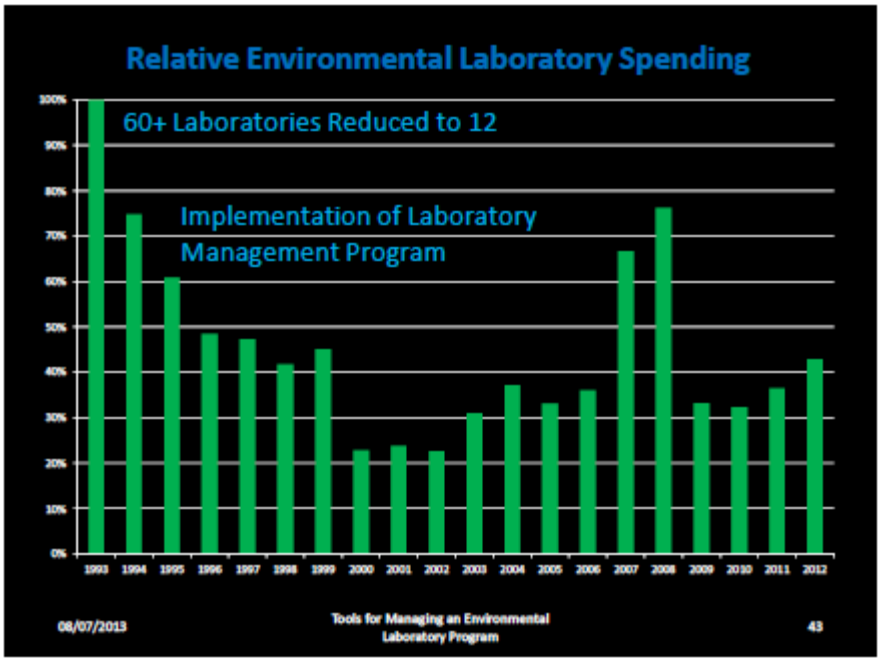
Parent: Ford Motor Company
Member: ERM
Lab: TestAmerica-North Canton
Site: Nashville - NGP
Project: E202269
Lab Submittal: 20497-1
Expected TAT: 2
Actual TAT: 3

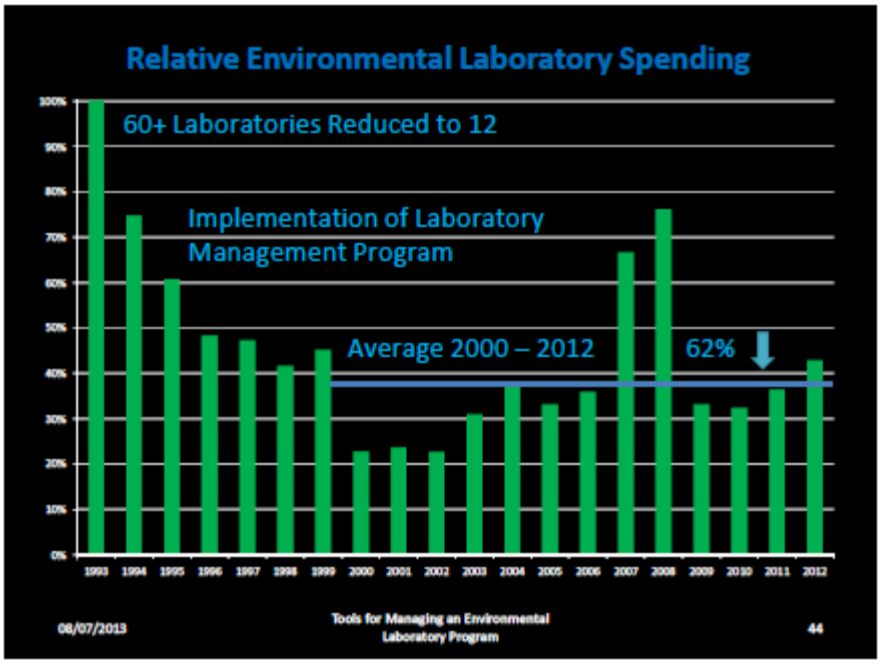
Benefits of a Laboratory Management Program

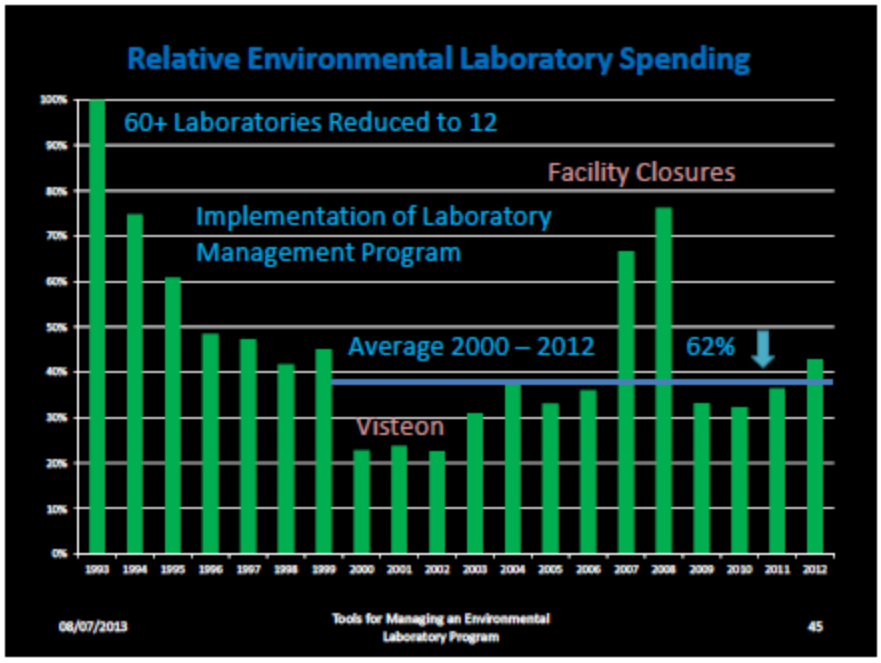


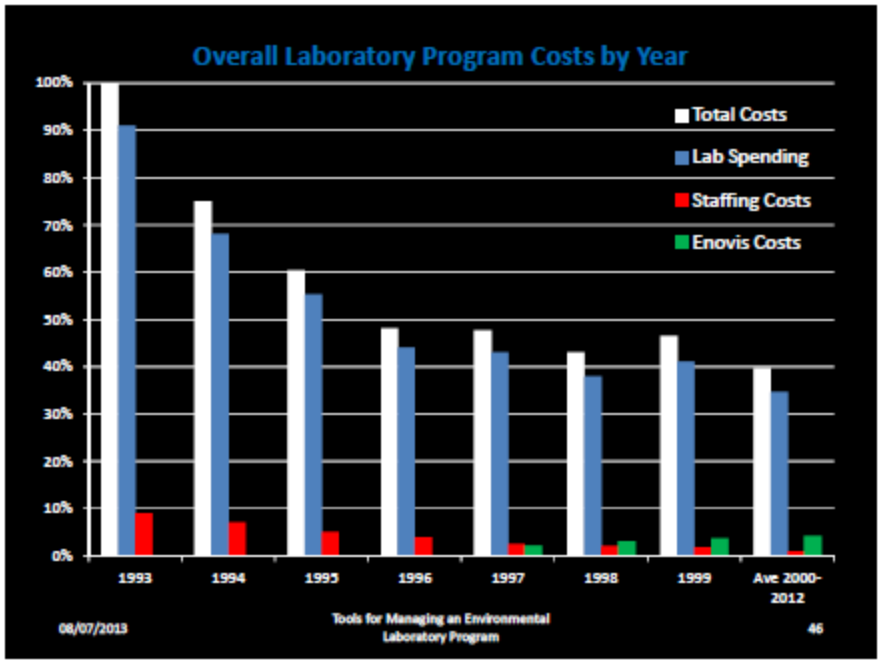

Relative Environmental Laboratory Spending
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
41


Relative Environmental Laboratory Spending
60+ Laboratories Reduced to 12
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
42


Relative Environmental Laboratory Spending
60+ Laboratories Reduced to 12
Implementation of Laboratory Management Program
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
43


Relative Environmental Laboratory Spending
60+ Laboratories Reduced to 12
Implementation of Laboratory Management Program
Average 2000 – 2012
62%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
44


Relative Environmental Laboratory Spending
60+ Laboratories Reduced to 12
Facility Closures
Implementation of Laboratory Management Program
Average 2000 – 2012
62%
Visteon
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
45


Overall Laboratory Program Costs by Year
Total Costs
Lab Spending
Staffing Costs
Enovis Costs
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1993
1994
1995
1996
1997
1998
1999
Ave 2000-2012
08/07/2013
Tools for Managing an Environmental Laboratory Program
46

Reasons for Reduces Staff Time

- Automated data collection and review
- Quality control data summaries & metrics
- Improved project management & control
- Onsite auditing of labs performed by Enovis
- Annual double blind PT study by Enovis
- Searchable environmental database

Overall Benefits to Ford from Enovis

1. Reduced overall program costs
2. Less staff time required to manage program
3. Improved communication
   Ford staff - Tier one suppliers - Laboratories
4. Laboratory performance more closely monitored
   Continuous improvement in data quality & service
5. Level II validation on 100% of analytical data
6. Improved efficiency in managing data


For more information please contact the authors:
John Phillips – Ford Motor Company
(313) 845-1648 "jphill12@ford.com"
Jim Tomalia – Enovis, Inc.
(517) 819-0356 "jtomalia@enovis-inc.com"
08/07/2013
NEMC 2013
49

The Effect of Method Flexibility on Efficiency Improvements, Waste Reduction, and Supplies Conservation

J.D Gentry
ESC Lab Sciences

Abstract

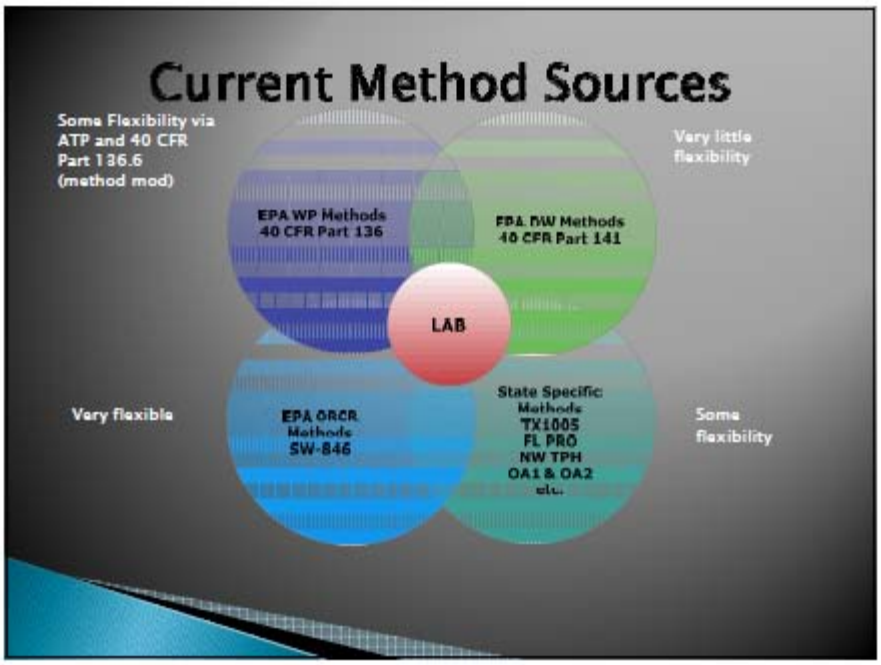
Performance Based Measurement Systems have been a topic of discussion in the laboratory community for quite some time. Historically, method modification has been a difficult process where EPA approved methods are of concern. The Office of Resource Conservation and Recovery has always allowed for some flexibility as their methods are not promulgated. The Office of Water, until recently, has required the use of the Alternate Testing Protocol procedure to modify existing methods. Technology moves at a faster pace than the method approval process, therefore the EPA has changed and clarified their process to allow the incorporation of new techniques into existing methods on a more timely basis.

The recent Methods Update Rule in May 2012 provided much needed clarification to the use of methods for compliance with the Clean Water Act. The Methods Innovation Rule in June 2005 stated the allowance for method flexibility and removal of some requirements where RCRA related sample and analysis is affected. These changes have given laboratories the ability to improve method efficiency and reduce waste from the process, which equates to an overall reduction in consumables. There are many other benefits when one looks at the entire process from sample collection to disposal. This session will focus on the options and allowances under both rules and identify those methods where ATP is no longer required. In addition, method examples will be addressed to represent newer technologies that have emerged recently.

The Effect of Method Flexibility on Efficiency Improvements, Waste Reduction, and Supplies Conservation

By J.D. Gentry
ESC Lab Sciences
Mt. Juliet, TN

Current Method Sources



SW-846 Methods

- ✓ Promulgation of the Methods Innovation Rule (MIR) (70 FR 34547, June 14, 2005, allows for the use of any appropriate method for RCRA applications
- ✓ This includes new methods
- ✓ "These new SW-846 methods are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. Therefore these methods can be used for any RCRA applications for which their performance can be demonstrated to be appropriate, i.e. applications for which they can be demonstrated to work."

Trends in Method Revisions

- Many method revisions are moving towards a prove it and you can use it "Performance Based" approach.
- Examples 624, 625, 608, etc.
- Allowance for alternate sample size, run time, extraction, carrier gas and in some cases instrumentation.
- Requires proper method validation

What does more flexibility bring

- The opportunity for labs to improve processes with new equipment and fresh approaches. Technology is rapidly changing but methods change at a much slower pace.
- The chance for savings in runtimes, shipping, waste reduction and supplies.





Examples of the impact of method flexibility and new technology

- 3510 reduced volume extraction approach
- 3511 extraction method
- Purge and Traps, faster temperature ramping, faster GC cooling, etc.
- GC-MS systems with much higher sensitivity
- Solid Phase Micro extraction (SPME)
- Micro/Midi Distillation
- Differential Analyzers
- Microwave Prep

What is Reduced Volume 3510 Extraction

- With the use of a large volume injectors you
  - ✓Eliminate or reduce the amount of toxic solvents or reagents in current methods by 90% or more.
  - ✓Allow traditional methods to be scaled down to much smaller sample volumes.
  - ✓Reduce usage and exposure to harmful solvents

Reduces the overall carbon footprint for:

- ★ Sample Collection
- ★ Analysis
- ★ Transportation
- ★ Handling
- ★ Disposal



SW846 Method 3510C (Traditional)

- 3510C is found in SW846 and was first published in Rev.0 in 1986
- Separatory Funnel Liquid–Liquid extraction
- Uses 1000mL sample
- Requires **180mL** of solvent
- Used for methods 8270, 8081, 8082, etc.

3510C – Reduced Volume 100mL

"A Greener Version"

- Same as the 1000mL method
- Method is scaled to a 100mL sample
- Solvent is reduced to 18mL which is **90% less** than the original method
- Method is executed exactly as written, therefore it is **not considered** to be a **modification**
- **Instrumentation involves Large Volume Injection (LVI)– Same as 3511**

Method 3511

Currently classified as a "New Method"

An Innovative approach to traditional sample extraction processes

- "The micro-scale approach minimizes sample size and solvent usage, thereby reducing the supply costs, health and safety issues, and waste generated."
  (from Method 3511 scope & application)

What is method 3511

- Similar extraction to 8011 for EDB/DBCP
- 40mL VOA vial sampling
- 2mL of methylene chloride
- 5 minute shake
- Uses Large Volume Injection



Why 3511? – Container Size Matters

Traditional Sampling/Handling	3511 Sampling/Handling
1000mL Amber Glass Bottle	40mL VOA vial

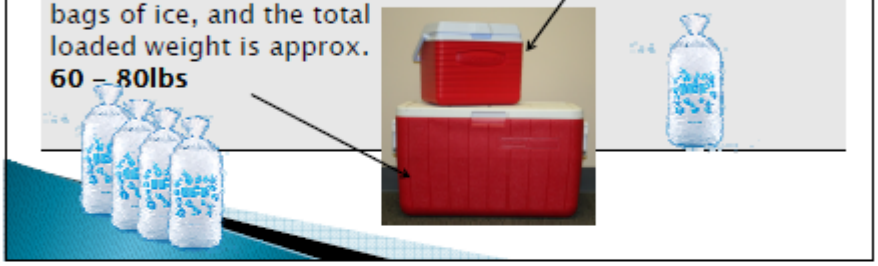






Why 3511? – Weight

Traditional Sampling/Handling	3511 Sampling/Handling
Typically **4 Sample Sets** (8 total sample bottles) fit into the largest cooler, which is 48qt, weighs 10 lbs, takes 4 bags of ice, and the total loaded weight is approx. **60 – 80lbs**	**8 Sample Sets** (16 Vials) will fit in a 10qt cooler. Total weight **<15lbs**



Why 3511? – Volume Matters

Traditional Sampling/Handling	3511 Sampling/Handling
Low purge well may not produce enough volume	Much easier to produce the 40mL volume needed Allows for easy collection of duplicate samples





3511 Regulatory Acceptance

- ✓ 3511 Accreditation via A2LA (ISO 17025), Dept. of Defense (DOD), NELAP since 2010
- ✓ Multiple states have granted accreditation/ certification – Formal written approval has been received from **25+ states**, since early 2010.
- ✓ Multiple data user divisions have granted approval – Some are states where no formal cert/accred program exists
- ✓ Well received by on-site Assessors. Assessors have been impressed at the execution, process and results from 3511.
- ✓ **.....Momentum to migrate to 3511 has increased**

MDL Comparison for PAH's by 8270SIM

Analyte	8270 RDL ppb	3510 MDL ppb	3511 MDL ppb	3511 RDL/MDL Ratio
1-Methylnaphthalene	0.25	0.0189	0.00821	30.5
2-Chloronaphthalene	0.25	0.0165	0.0059	42.4
2-Methylnaphthalene	0.25	0.0155	0.0068	36.8
Acenaphthene	0.05	0.00823	0.00739	6.8
Acenaphthylene	0.05	0.0109	0.00588	8.5
Anthracene	0.05	0.0131	0.00601	8.3
Benzo(a)anthracene	0.05	0.0124	0.00895	5.6
Benzo(a)pyrene	0.05	0.0123	0.0116	4.3
Benzo(b)fluoranthene	0.05	0.0192	0.0138	3.6
Benzo(g,h,i)perylene	0.05	0.0194	0.0114	4.4
Benzo(k)fluoranthene	0.05	0.013	0.0136	3.7
Chrysene	0.05	0.0144	0.00923	5.4
Dibenz(a,h)anthracene	0.05	0.00454	0.00385	13.0
Fluoranthene	0.05	0.0165	0.012	4.2
Fluorene	0.05	0.00898	0.0085	5.9
Indeno(1,2,3-cd)pyrene	0.05	0.00739	0.0148	3.4
Naphthalene	0.25	0.0123	0.0198	12.6
Phenanthrene	0.05	0.0184	0.00807	6.2
Pyrene	0.05	0.013	0.0102	4.9

- Reporting limits remain the **same** regardless of prep method
- RDL/MDL ratio well within acceptance (should be 3X or greater)
- Average recovery across MDL study 101 – 130% at 0.05ppb

LCS Recovery & Limits Comparison

Compound Name	3510C 1000mL with 8270C SIM			3511 with 8270C SIM		
	Average %Rec	LCL	UCL	Average %Rec	LCL	UCL
1-METHYLNAPHTHALENE	87	48	126	90	52	128
2-CHLORONAPHTHALENE	88	47	129	90	70	109
2-METHYLNAPHTHALENE	84	43	126	91	69	113
ACENAPHTHENE	86	51	121	91	72	111
ACENAPHTHYLENE	88	50	125	97	66	127
ANTHRACENE	97	61	133	100	68	133
BENZO(A)ANTHRACENE	91	58	123	108	71	145
BENZO(A)PYRENE	95	58	132	105	80	130
BENZO(B)FLUORANTHENE	92	53	131	95	70	119
BENZO(G,H,I)PERYLENE	96	54	139	89	62	116
BENZO(K)FLUORANTHENE	96	55	137	89	63	115
CHRYSENE	95	58	132	92	71	114
DIBENZ(A,H)ANTHRACENE	94	57	131	94	67	121
FLUORANTHENE	95	57	134	100	69	131
FLUORENE	89	52	125	92	70	114
INDENO(1,2,3-CD)PYRENE	95	56	133	95	70	120
NAPHTHALENE	82	41	122	89	73	105
PHENANTHRENE	90	54	127	91	73	110
PYRENE	95	55	135	99	74	125

Using method flexibility to Reduce Your Carbon Footprint

3511 provides significant Environmental benefits!!

- Lighter coolers for reduced shipping fuel usage
- Smaller sample containers to dispose
- Smaller sample volumes to dispose
- 2mL's of Methylene Chloride used compared to 180 for traditional extraction. Where does the180mL in the concentration step go?



The Challenges of RV 3510, 3511 and large volume injection

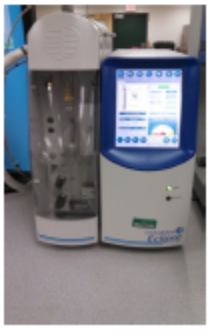
- Initial investment of equipment
- Development time
- Longer runtimes
- Dealing with larger solvent volumes in the inlet
- Solving the complex extraction riddle? (BNA)



The Effect of new Technology

- Technology is constantly improving. Instruments are faster and more sensitive than ever.





Combining Multiple Technologies to Increase Efficiency

- New Technology often means shorter run times and/or lower detection limits
- Combining new technology can create a stacking effect that can give faster run times, more sensitivity and a fast cycle time in between samples.
- For DRO analysis this can mean using 3511 extraction to save the client field time, the lab shipping/container costs, reduced waste volume and employee solvent exposure. Adding an aftermarket GC temperature accelerator can when properly developed cut run times in half. Adding an aftermarket GC oven cooling vent can cut cycle times in half.

ESC LAB SCIENCES

7890 GC-FID with large volume injector and temperature enhancements



OI Eclipse and CDS 7400



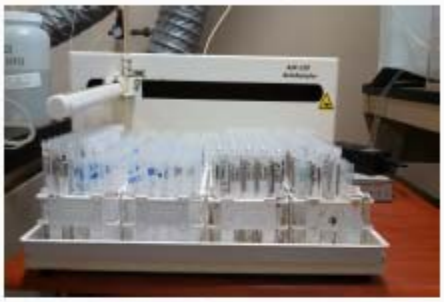
Microwave Sample Prep

- Better recoveries
- Reduced solvent usage
- Reduced usage of sodium sulfate
- Less glassware
- Faster and more efficient!!!!



Specialized Auto Samplers for Metals Analysis

- Faster sample loading
- Higher capacity
- Better reproducibility

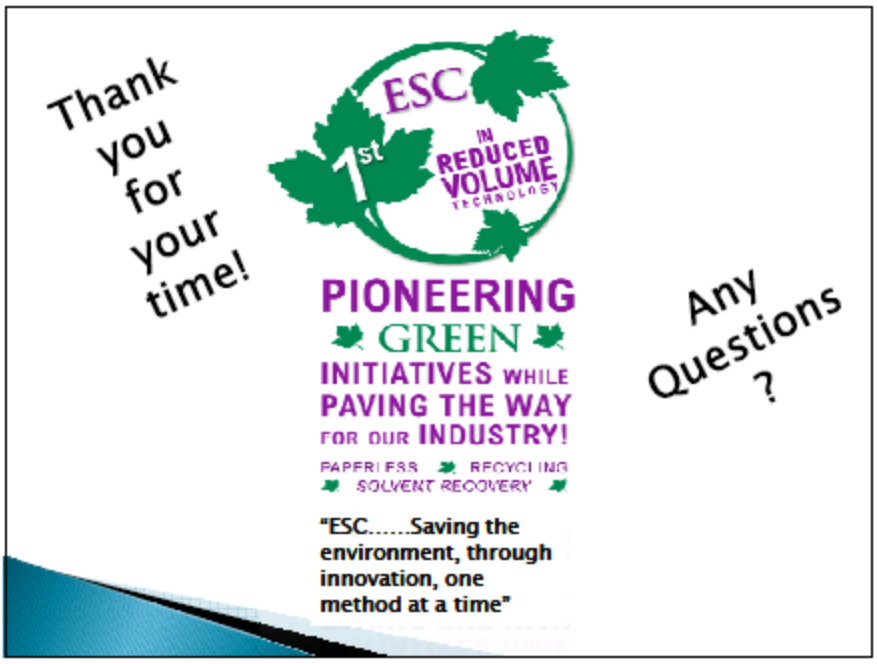


ASX-520 Auto Sampler

Conclusion

Innovation, flexibility, and availability of methods has allowed development of techniques that benefit:

- ✓The sampling process
- ✓The analytical process
- ✓The environment


Thank you for your time!
ESC
1st
IN REDUCED VOLUME TECHNOLOGY
PIONEERING
GREEN
INITIATIVES WHILE PAVING THE WAY FOR OUR INDUSTRY!
PAPERLESS
RECYCLING
SOLVENT RECOVERY
"ESC……Saving the environment, through innovation, one method at a time"
Any Questions ?

A New GC/MS System Designed for Helium Carrier Gas Conservation

Dale Walker
Agilent Technologies

Abstract

This presentation will highlight the Eco Friendly features of a new GC/MS system introduced by Agilent Technologies. With the recent global shortage of helium and increased pricing, many labs are looking to alternate carrier gases such as hydrogen. Unfortunately revalidating helium methods converted to hydrogen carrier gas consumes labor resources, increased operating costs, and disrupts workflow. The software and hardware of this new GC/MS system makes it easier to set-up and routinely use new energy and helium carrier gas conservation features such as gas saver and sleep/wake modes.

US EPA Method 8270 is used to determine the concentration of semi volatile organic compounds in extracts prepared from several different types of solid and waste matrices, soil, air sampling, and water samples. This presentation will provide details for meeting the performance criteria set forth in the USEPA method 8270. The performance demonstrated is designed to be at or below the levels typically seen in laboratories today. The new gas conservation features will allow a lab to lower operation costs without compromising performance for this demanding method.

These new gas conservation features can extend the life of helium tanks up to thirty times longer thus reducing the frequency of replacement.

A New GC/MS System Designed for Helium Carrier Gas Conservation



Approaches for the Smarter Use of Helium

Dale R. Walker
GCMS Applications Specialist
August, 7, 2013

Helium Facts

- How it's produced
- Where did it all go?
- What can you do conserve?
- Is there an alternative gas?

Helium Facts

A brief history of Helium

Created by radioactive decay of heavy radioactive elements

- Primarily Thorium and Uranium
- Produces Alpha particles which form He nuclei
- Trapped in Natural Gas Fields – mainly in American Great Plains
- Up to 7% by volume
- Separated from natural gas by low temperature fractional distillation

Helium Facts continued.

National Helium Reserve - Amarillo, Texas (Dept. of Interior)

- Fed by 425 mile pipeline from Kansas to Texas
- Five Helium plants feed the pipeline

1996 Congress decided to phase out the Helium Reserve

- Helium Reserve was $1.4 Billion in debt in 1996
- Plan is to empty the reserve to recover the funds
- Expected to be empty by 2018
- As of 2012 the Reserve supplied 30% of the worlds Helium

Helium Facts cont.

For many years the U.S. supplied 90% of the world's Helium

- New plant in Algeria can supply all of Europe's demand
- Other plants are now on line in Canada and Poland

U.S. maintains reserves in Kansas, Oklahoma, and Texas

- New plants coming on line – Wyoming, Qatar, and Russia
- New plants are not expected to ease the shortage

Helium Facts cont.

Most Helium is used for cryogenics (MRI's) and welding

- Also controlled atmospheres such as wind tunnels
- Gas Chromatography is a minor consumer

Prices are expected to continue to rise

- From 2002 to 2007 world prices doubled
- From 2007 to 2013 world prices have more than doubled again

Helium Facts continued

What can you do?

There are only two realistic choices:

Option 1: Implement Helium conservation measures. This approach extends the lifetime of existing Helium supplies, reduces operating costs, and ensures business continuity.

Option 2: Switch to a different carrier gas such as Hydrogen.

Option 1: Helium Conservation

Environmental Protection Agency, Region 6 – Houston, Texas

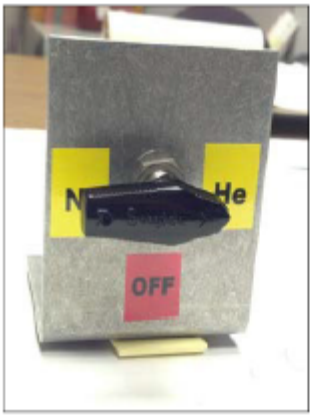
The Environmental Protection Agency (EPA) Region 6 Laboratory is working with manufacturers to find solutions to the ongoing Helium shortage that is affecting many laboratories.

Option 1: Helium Conservation

Approach 1: Manual switching valve

A manual switching valve is connected to both a Nitrogen and Helium cylinder and is manually switched at the end of each day, this requires someone to be physically present to switch the valve.

Option 1: Helium Conservation
An example installation





The EPA tested manual valve switching and found it suitable

Option 1: Helium Conservation

This simple cost saving alternative to switching carrier gases can be implemented immediately, with no time needed for method development, and without any noticeable effects on hardware or performance.

Depending on the total number of instruments and the time between sequences, this procedure has the potential to save laboratories thousands of dollars per year by conserving Helium.

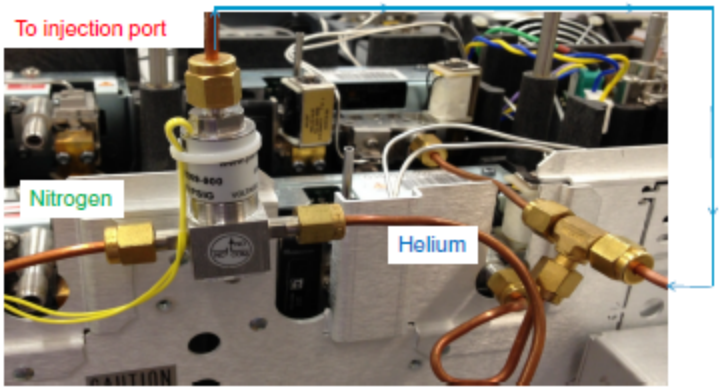
Option 1: Helium Conservation

Approach 2: Automated valve

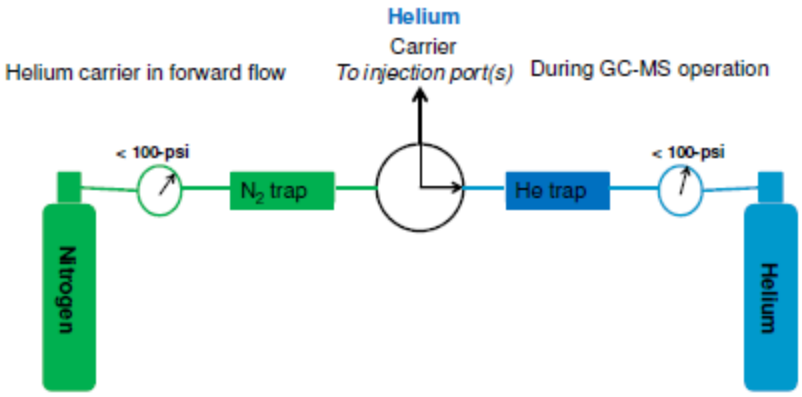
A better approach is to use an automated switching device that delivers Helium or Nitrogen to the GC flow control modules.

This type of automatic valve switching is preferred to the manual valve because it does not require user interaction. This switch may be programed to engage or disengage at the beginning or the end of your analytical run or sequence.

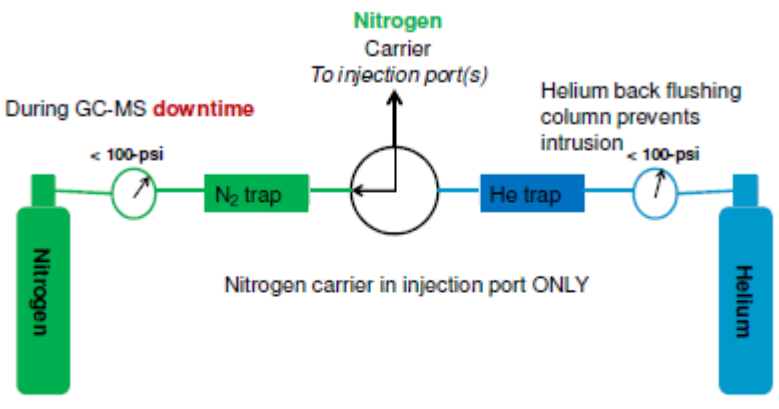
Option 1: Helium Conservation
Automated switching valve: SW controlled



Option 1: Helium Conservation
Switching the Carrier with the *Carrier Saver switch*



Option 1: Helium Conservation
Switching the Carrier with the *Carrier Saver switch*



15 Agilent Technologies August 7, 2013

Option 1: Helium Conservation
Switching the Carrier with the *Carrier Saver switch*

Approach 3: Automated Helium conservation

Seamless integrated system includes GC hardware and software control which allows laboratories to integrate programmable Helium conservation into the daily operation of the GC or GC/MS system.

16 Agilent Technologies August 7, 2013

Option 1: Helium Conservation
Introducing the Programmable Helium Conservation Module

Combines with 7890B Sleep-Wake feature

Automatically switches carrier gas supply to N_2 during GC idle time

TWO Critical Components

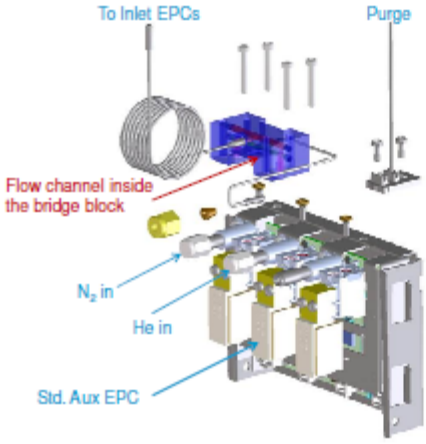
- **Carrier gas switching EPC module**
- **7890B Sleep/Wake Feature**

Plus ...

- **Chromatographic grade N_2 gas**

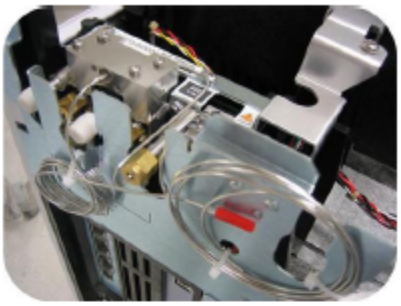


Carrier Gas Switch EPC Module
Ensures Business Continuity



- Built on 5th generation EPC
- Fully integrated and controlled by OpenLAB CDS
- Purge channel prevents cross contamination of gases
- Precise pressure control between tank and GC
- In AWAKE mode, switches between gases within 15-30 min for most detectors including MSD

Option 1: Helium Conservation
Introducing the Programmable Helium Conservation Module



Option 1: Helium Conservation
Introducing the Programmable Helium Conservation Module

Greater reliability

Based on proven 5th generation AUX EPC

Provides Nitrogen substitution when the GC is idle

It also provides additional warnings if set points are not reached.

This safety feature is very important when using Hydrogen. If a leak is detected an auto shutdown occurs and it remains in that state until reset by the user.

Option 1: Helium Conservation

Introducing the Programmable Helium Conservation Module

Greater performance

Purge channel prevents cross contamination of gases and acts as an intermediate pressure regulator from the tank to inlet EPC to ensure greater analytical precision.

Because there are no changes during the analytical sequence this eliminates the need for method revalidation.

Option 1: Helium Conservation

Introducing the Programmable Helium Conservation Module

Seamless integration

Fully integrated within the 7890B GC
(Open LAB, Chem Station, Mass Hunter)

Method identifies both gases and uses the appropriate flows for each gas.

Switching between each gas is easily implemented using new OpenLAB Sleep/Awake functions.

Option 1: Helium Conservation

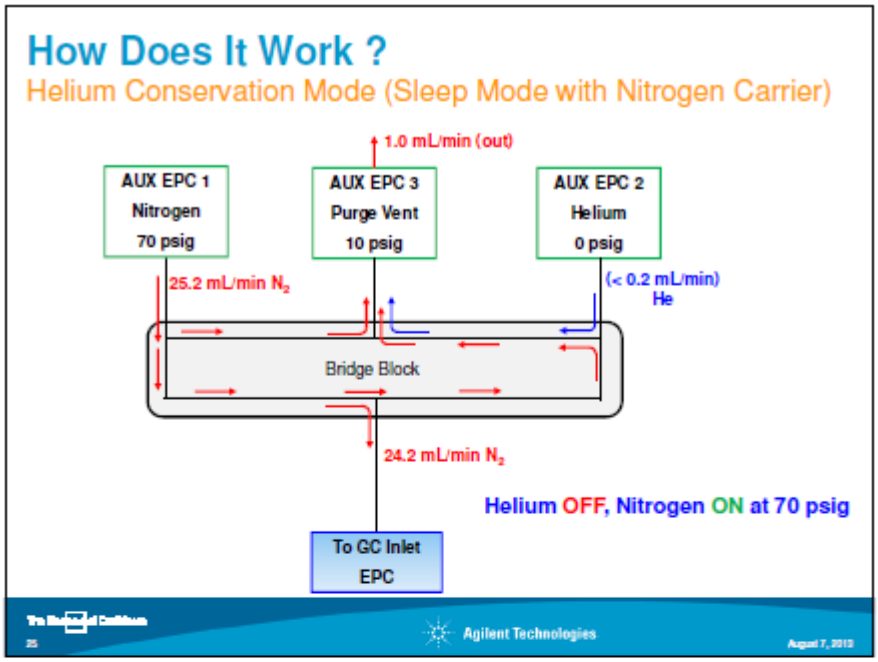
Introducing the Programmable Helium Conservation Module

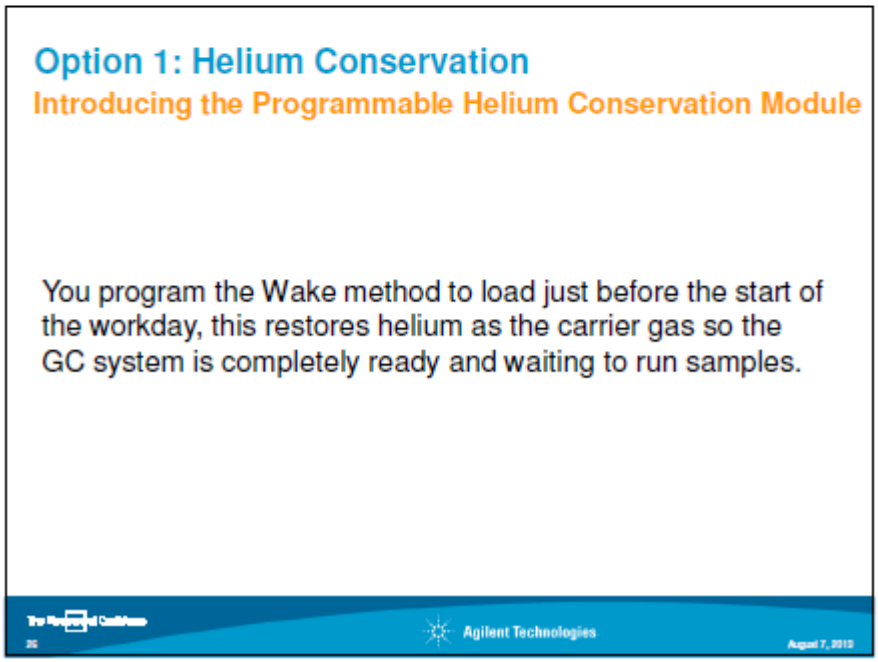
The new Agilent Open Lab CDS software provides many possible Sleep/Wake program configurations and operates much like a programmable home heating system.

Option 1: Helium Conservation

Introducing the Programmable Helium Conservation Module

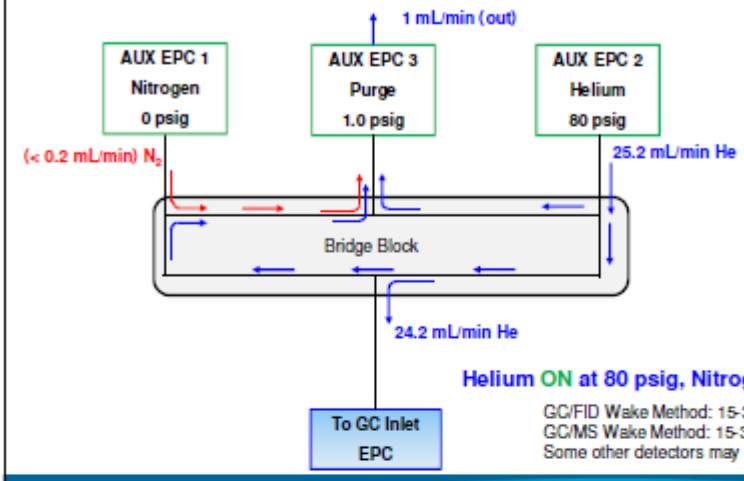
You program the 7890B GC to load the Sleep method when not in operation, this eliminates the use of Helium by using Nitrogen as a carrier gas.


How Does It Work ?
Helium Conservation Mode (Sleep Mode with Nitrogen Carrier)
1.0 mL/min (out)
AUX EPC 1
Nitrogen
70 psig
AUX EPC 3
Purge Vent
10 psig
AUX EPC 2
Helium
0 psig
25.2 mL/min N2
(< 0.2 mL/min)
He
Bridge Block
24.2 mL/min N2
Helium OFF, Nitrogen ON at 70 psig
To GC Inlet
EPC
Agilent Technologies


Option 1: Helium Conservation
Introducing the Programmable Helium Conservation Module
You program the Wake method to load just before the start of the workday, this restores helium as the carrier gas so the GC system is completely ready and waiting to run samples.
Agilent Technologies

How Does It Works ?

Normal Operation Mode (Wake Mode with Helium Carrier)



Helium ON at 80 psig, Nitrogen OFF

GC/FID Wake Method: 15-30 Min
GC/MS Wake Method: 15-30 Min
Some other detectors may need longer

Option 1: Helium Conservation

Introducing the Programmable Helium Conservation Module

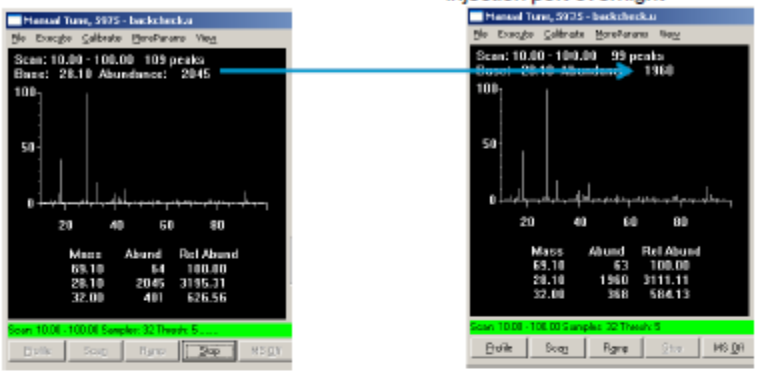
For GC and GC/MS systems, it only takes 15 minutes to completely remove all of the Nitrogen from the internal GC flow paths. The GCMS will pass the Nitrogen background test and be available to start the analytical sequence within 20 minutes of loading the wake method.

Programmable Helium Conservation Module

Perfomrance Testing: Switching from Helium to Nitrogen

Running Helium only

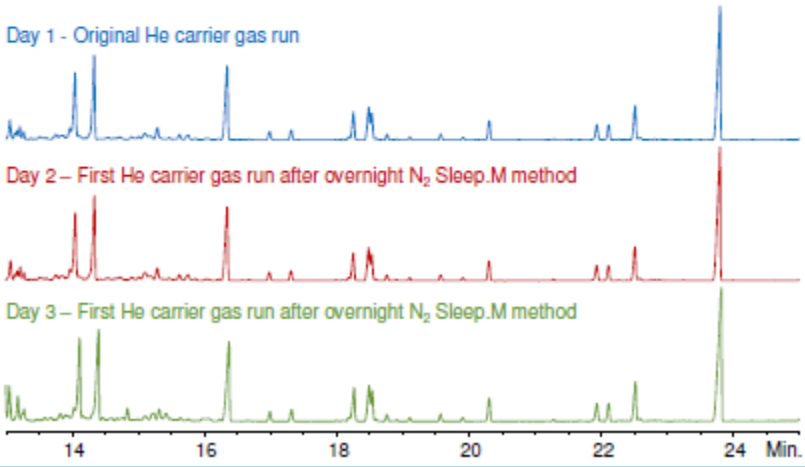
Running Nitrogen in the injection port overnight



Running over a weekend with Nitrogen purge in the inlet shows no back-diffusion of Nitrogen into the MS

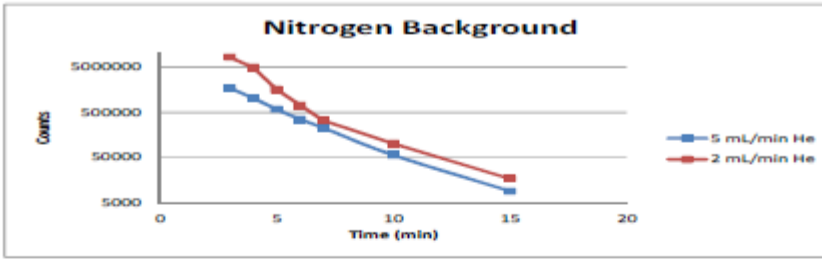
Agilent Technologies

Performance: No Change in Chromatography After N_2 Carrier Sleep Method (GC/FID)



Agilent Technologies

Performance: Pass MS Tune Within 15min After Switching From N_2 to He as Carrier (GC/MSD)



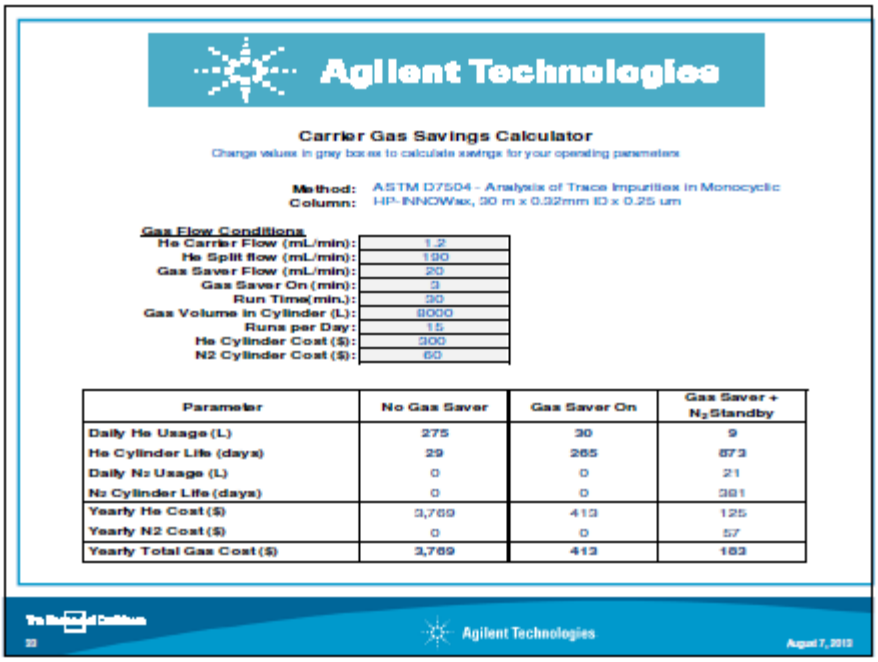
		Counts of Nitrogen Ion		
Time (min)	5 mL/min He	Relative to Saturation	2 mL/min He	Relative to Saturation
3	1735168	20.69%	8388096	100.00%
4	1033280	12.32%	4959232	59.12%
5	590080	7.03%	1618944	19.30%
6	354112	4.22%	722944	8.62%
7	228480	2.72%	333696	3.98%
10	56984	0.68%	102576	1.22%
15	9052	0.11%	17080	0.20%

Carrier Gas Savings Calculator

Save Helium by > 90% compared to a typical use

Helium supplies last **MUCH** longer

- ✓ Gas saver mode: 9 times longer
- ✓ N_2 standby: another 3.3 times more
- ✓ Total save: last **30 times** longer



Agilent Technologies

Carrier Gas Savings Calculator

Change values in grey boxes to calculate savings for your operating parameters

Method: ASTM D7504 - Analysis of Trace Impurities in Monocyclic
Column: HP-INNOWax, 30 m x 0.32mm ID x 0.25 um

Gas Flow Conditions

He Carrier Flow (mL/min):	1.2
He Split flow (mL/min):	100
Gas Saver Flow (mL/min):	20
Gas Saver On (min):	3
Run Time(min.):	30
Gas Volume in Cylinder (L):	8000
Runs per Day:	15
He Cylinder Cost ($):	300
N2 Cylinder Cost ($):	60

Parameter	No Gas Saver	Gas Saver On	Gas Saver + N_2 Standby
Daily He Usage (L)	275	30	9
He Cylinder Life (days)	29	265	873
Daily N2 Usage (L)	0	0	21
N2 Cylinder Life (days)	0	0	381
Yearly He Cost ($)	3,769	413	125
Yearly N2 Cost ($)	0	0	57
Yearly Total Gas Cost ($)	3,769	413	183

Option 2: Hydrogen Carrier

Hydrogen is great for many GC methods such as ECD and FID.

Many people have been successful switching their GCMS methods to Hydrogen carrier gas as well

- Vince Marti at Region 8 lab for 8270 and 8260
  - Vince uses cylinder Hydrogen
- Lisa Wool at Region 6 for Pesticide's, PCB's, TPH
  - Lisa uses a Hydrogen generator

Option 2: Hydrogen Carrier

However, Hydrogen is not the best gas for GCMS methods. Depending on the method requirements

- The main issue with Hydrogen carrier is that it is not inert
- There is some reactivity with specific compounds
- Reactivity with Dichloromethane forms HCL in the GC inlet

(Vince Marti in Region 8 discovered cooler inlet temps avoid this problem)

- BFB tuning anomalies can occur (ion 96)
- DFTPP tuning seems to be less effected

Pertinent Application Notes

Reducing Helium Costs more than 10-fold with the PCT Gas Saver mode

Agilent Technologies, Inc., April 1, 2010

5990-5444EN

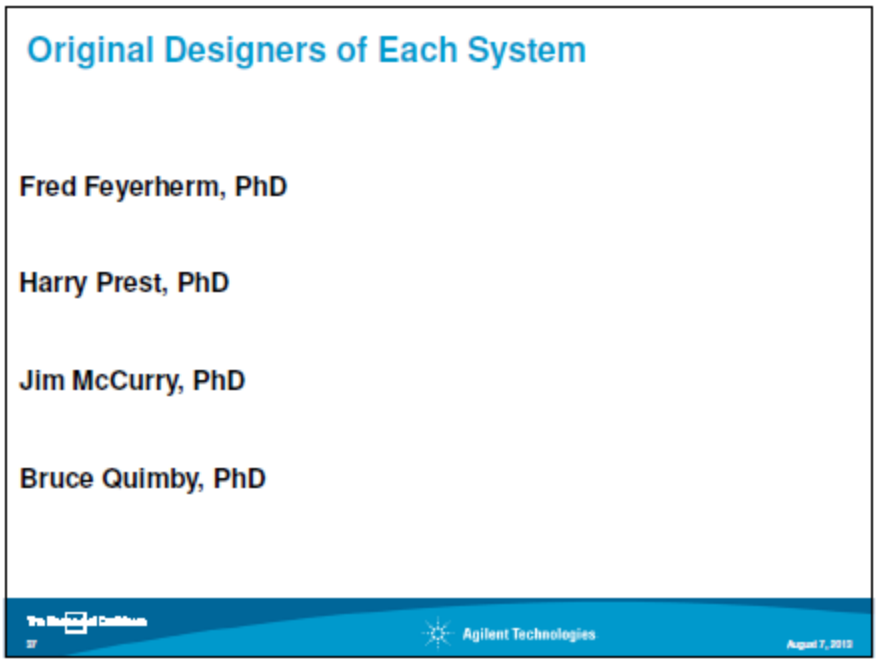
Prevent Business Disruptions by Managing your Helium Usage

Agilent Technologies, Inc., April 30, 2013

5991-2256EN

Successfully converting from Helium to alternate gases when analyzing VOC's following EPA 524.2 methodology

Agilent Technologies, Inc., August 2013


Original Designers of Each System
Fred Feyerherm, PhD
Harry Prest, PhD
Jim McCurry, PhD
Bruce Quimby, PhD
Agilent Technologies

Acrolein, Acrylontrile, Styrene, and Vinyl Chloride; Acid Reactive Compounds or Not?

Stephen Zeiner
Environmental Standards

Abstract

The Environmental Protection Agency (EPA) has indicated that vinyl chloride and styrene should not be preserved to pH less than 2 [SW-846 Chapter 2 Table 2-40(A) and Chapter 4 Table 4-1]. The EPA also indicates that acrolein and acrylonitrile need to be preserved to a pH between 4 and 5 [SW-846 Chapter 2 Table 2-40(A) and Chapter 4 Table 4-1 and Federal Register Volume 77, Number 97 (EPA-HQ-OW-2010-0192)]. The EPA indicates that these analytes should be analyzed within 7 days of collection; 3 days for acrolein and acrylonitrile if not pH preserved.

It is difficult and burdensome to preserve samples in the field to a narrow pH range. In addition, it is costly to collect and analyze separate sample aliquots for acrolein, acrylontrile, styrene, and vinyl chloride. The analysis cost is also impacted by the 7 or 3 day holding time from collection to analysis.

A limited study was designed and executed to investigate if the acrolein and acrylonitrile pH preservation is necessary, if styrene and vinyl chloride are impacted by acid preservation, and if the 7 or 3 day holding time is accurate. The study included deionized water and groundwater samples that were spiked with acrolein, acrylontrile, styrene, and vinyl chloride. To evaluate the chemical preservation, half of the samples were only temperature preserved (?6?C) and half of the samples were preserved to pH<2 with hydrochloric acid. Three preserved and three unpreserved samples were analyzed every other day for 16 days.

This presentation will provide the details of the study design, findings, and conclusions as to the stability of acrolein, acrylontrile, styrene, and vinyl chloride in an acidic environment (pH<2) and just how long these compounds appear to be stable in water.

Acrolein, Acrylonitrile, Styrene, and Vinyl Chloride; Acid Reactive Compounds or Not?

National Environmental Monitoring Conference
San Antonio, TX
August 2013

Stephen T. Zeiner, CEAC
Environmental Standards, Inc.

Co-authors:
David R. Blye, CEAC – Environmental Standards, Inc.
Lance Holman – URS Corporation
Kelly Rinehimer – URS Corporation

ENVIRONMENTAL STANDARDS

Discussion Topics

- ✓ EPA Preservation Requirements
- ✓ Logistical Issues
- ✓ Study Objectives
- ✓ Study Design
- ✓ Study Results
- ✓ Study Summary
- ✓ Conclusions



2

ENVIRONMENTAL STANDARDS

Current Aqueous Sample EPA Preservation Requirements

- Vinyl Chloride and Styrene:
  - No chemical preservation; temperature < 6°C
  - Analyze within 7 days
- Acrolein and Acrylonitrile:
  - Chemical preservation to pH 4 to 5; temperature < 6°C
  - Analyze within 14 days
  - Analyze within 3 days if not chemical preserved
- 2-Chloroethyl Vinyl Ether
  - No chemical preservation; temperature < 6°C
  - Analyze within 7 days
- Preservation for Majority of Volatile Organic Compounds (VOCs)
  - Chemical preservation to pH< 2 w/HCl; temperature < 6°C
  - Analyze within 14 days

3

ENVIRONMENTAL STANDARDS

Logistical Issues

- These five compounds are generally included in a longer list of VOC target analytes resulting in:
  - Potentially up to 3 analyses for volatile lists
  - Additional costs for shipping
  - Higher costs for expedited analysis
  - Difficulty in field preservation of samples to pH 4 to 5

4

ENVIRONMENTAL STANDARDS

Study Objectives

- Does preservation to pH< 2 degrade compounds?
- Is unpreserved holding time of 7 days for 2-Chloroethyl Vinyl Ether, Styrene, and Vinyl Chloride valid?
- Is unpreserved holding time of 3 days for Acrolein and Acrylonitrile valid?
- Study conducted on behalf of DuPont; study design by URS, analyses conducted by Lancaster Laboratories, Inc. (now Eurofins Lancaster Laboratories Environmental, LLC)

5

ENVIRONMENTAL STANDARDS

Study Design

- Matrices:
  - Deionized (DI) water and authentic site groundwater (GW)
- Sample Types:
  - Unpreserved - temperature < 6°C; no chemical preservation
  - Preserved - temperature < 6°C and pH< 2 using HCl
- Each aliquot spiked with 100 µg/L of analyte.
- Analyzed 3 aliquots of each sample type every other day for 16 days.

6

ENVIRONMENTAL STANDARDS

Study Design

- Samples were stored in a monitored refrigerator at < 6°C, but not frozen
- SW-846 Method 5030B was used for the purge and trap step
- SW-846 Method 8260B was used for the analytical determination
  - Instrument calibrated over a range of concentrations
  - Periodic instrument tune and calibration verifications
  - Surrogate recoveries monitored
  - Internal standard areas monitored

7

ENVIRONMENTAL STANDARDS

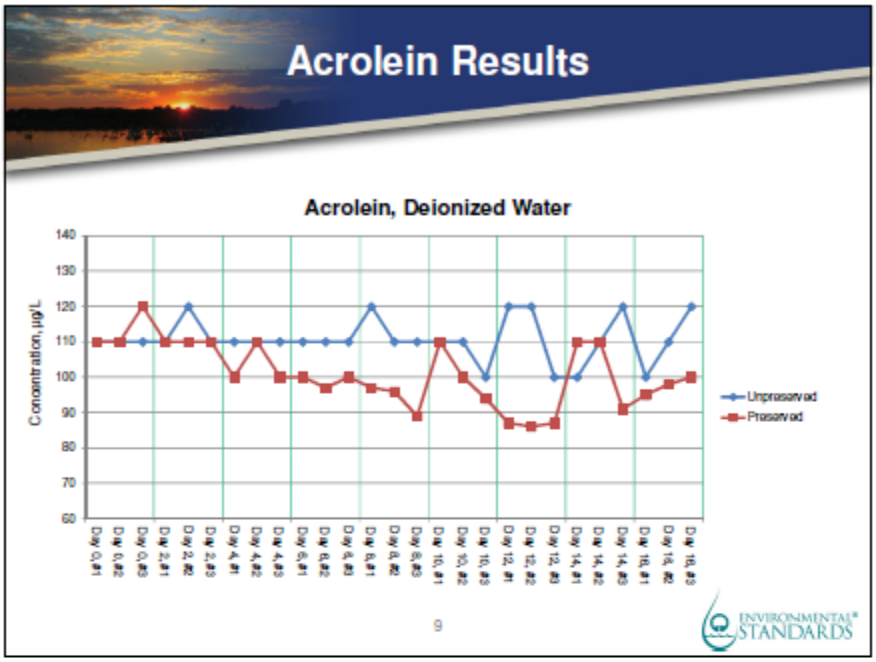
Study Evaluation

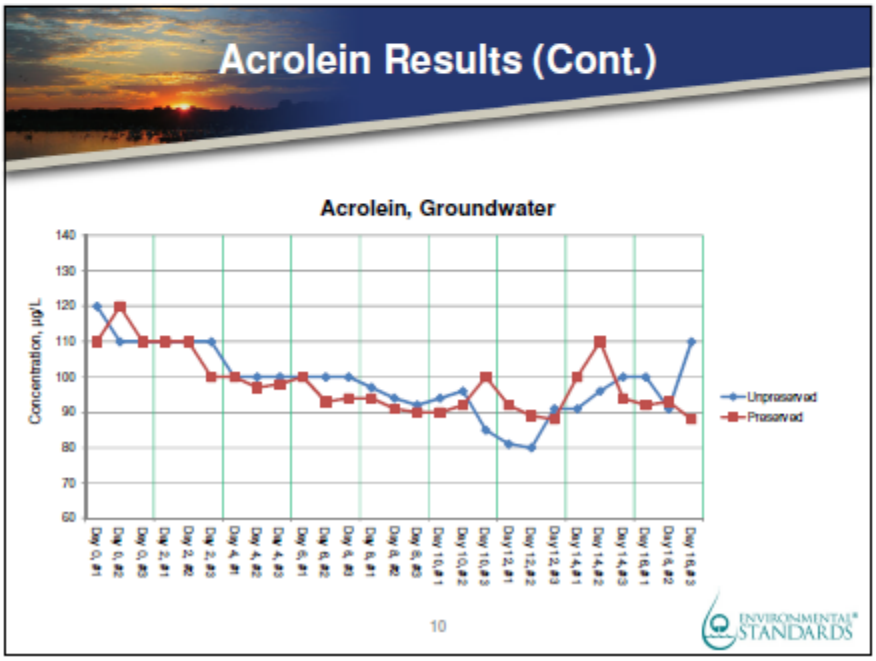
- Sample results between 70 and 130 µg/L.
- Relative standard deviation < 20%.
- Any trends in results over study time.



8

ENVIRONMENTAL STANDARDS


Acrolein Results
Acrolein, Deionized Water
Concentration, µg/L
140
130
120
110
100
90
80
70
60
Unpreserved
Preserved
9
ENVIRONMENTAL STANDARDS


Acrolein Results (Cont.)
Acrolein, Groundwater
Concentration, µg/L
140
130
120
110
100
90
80
70
60
Unpreserved
Preserved
10
ENVIRONMENTAL STANDARDS

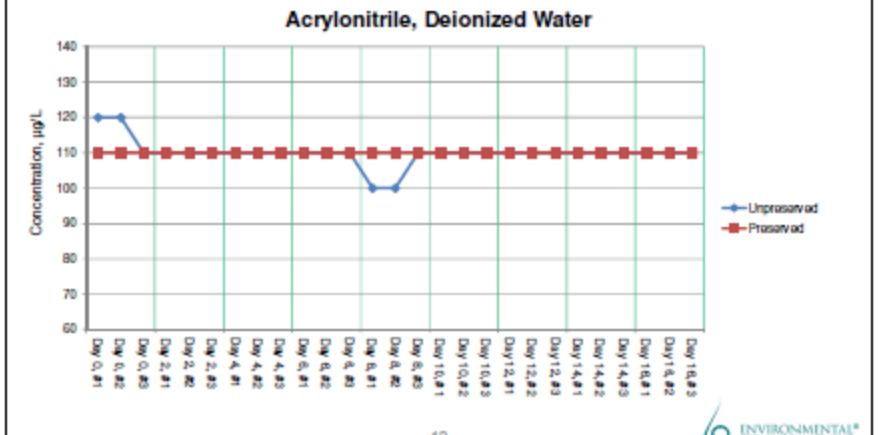
Acrolein Results (Cont.)

	Average Result (µg/L)	Minimum Result (µg/L)	Maximum Result (µg/L)	%RSD
DI, Unpreserved	111	100	120	5
DI, Preserved	101	86	120	9
GW, Unpreserved	99	80	120	10
GW, Preserved	98	88	120	9

11

ENVIRONMENTAL STANDARDS

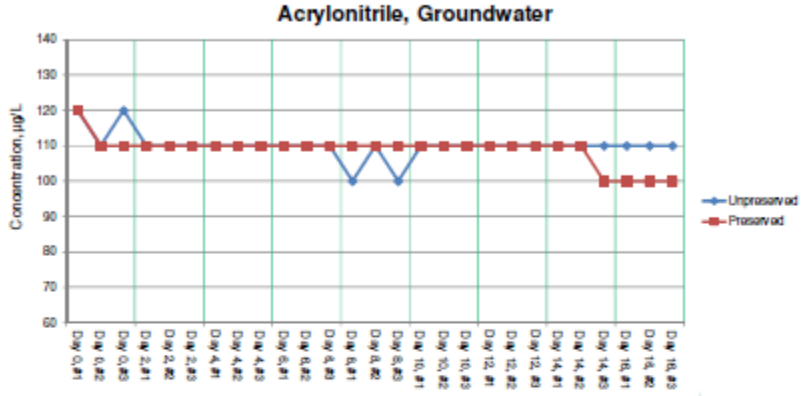
Acrylonitrile Results



12

ENVIRONMENTAL STANDARDS

Acrylonitrile Results (Cont.)



13

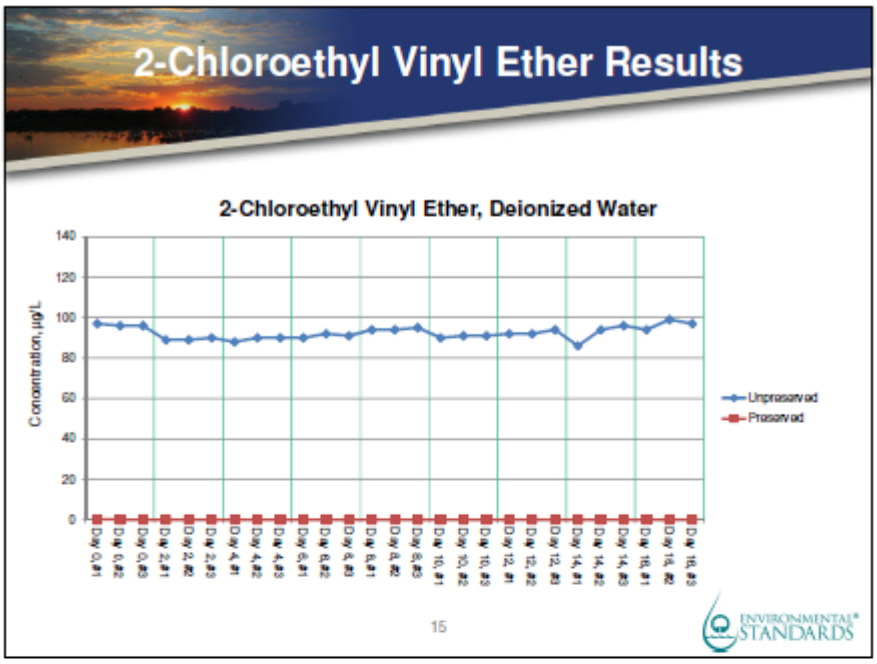
ENVIRONMENTAL STANDARDS

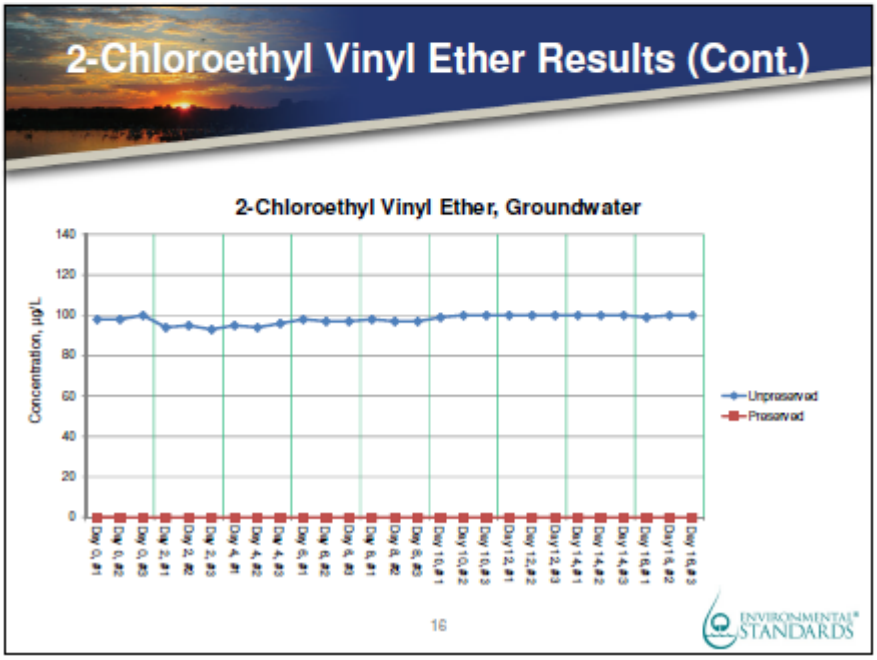
Acrylonitrile Results (Cont.)

	Average Result (µg/L)	Minimum Result (µg/L)	Maximum Result (µg/L)	%RSD
DI, Unpreserved	110	100	120	4
DI, Preserved	110	110	110	0
GW, Unpreserved	110	100	120	4
GW, Preserved	109	100	120	4

14

ENVIRONMENTAL STANDARDS


2-Chloroethyl Vinyl Ether Results
2-Chloroethyl Vinyl Ether, Deionized Water
Concentration, µg/L
140
120
100
80
60
40
20
0
Unpreserved
Preserved
15
ENVIRONMENTAL STANDARDS


2-Chloroethyl Vinyl Ether Results (Cont.)
2-Chloroethyl Vinyl Ether, Groundwater
Concentration, µg/L
140
120
100
80
60
40
20
0
Unpreserved
Preserved
16
ENVIRONMENTAL STANDARDS

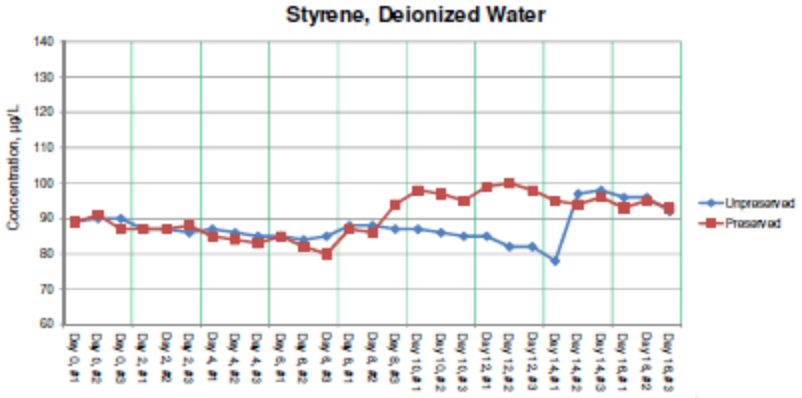
2-Chloroethyl Vinyl Ether Results (Cont.)

	Average Result (µg/L)	Minimum Result (µg/L)	Maximum Result (µg/L)	%RSD
DI, Unpreserved	92	86	99	3
DI, Preserved	0	0	0	0
GW, Unpreserved	98	93	100	2
GW, Preserved	0	0	0	0

17

ENVIRONMENTAL STANDARDS

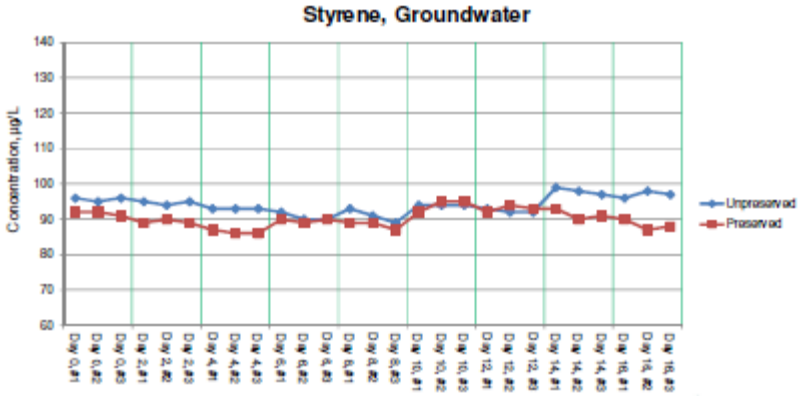
Styrene Results



18

ENVIRONMENTAL STANDARDS

Styrene Results (Cont.)



19

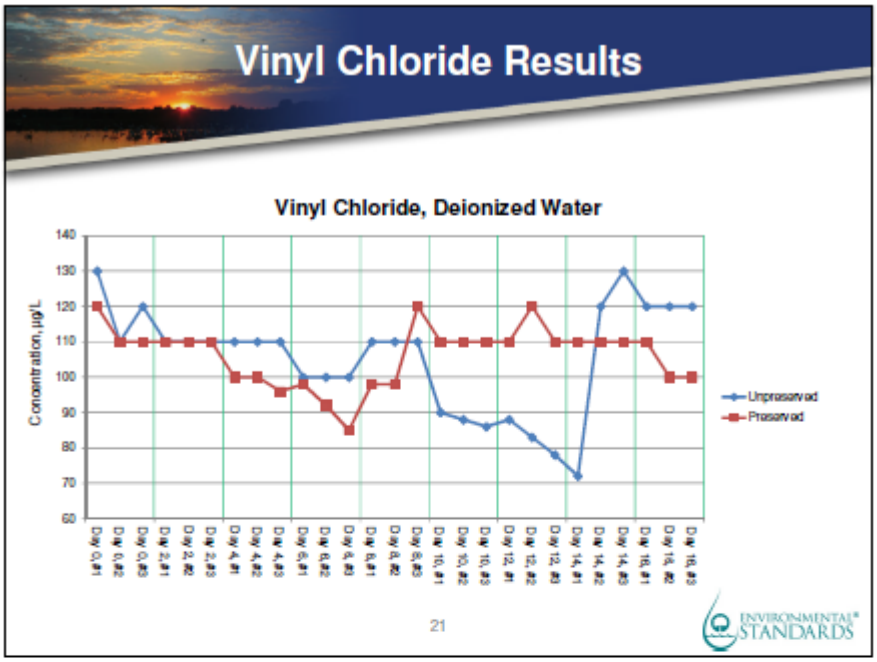
ENVIRONMENTAL STANDARDS

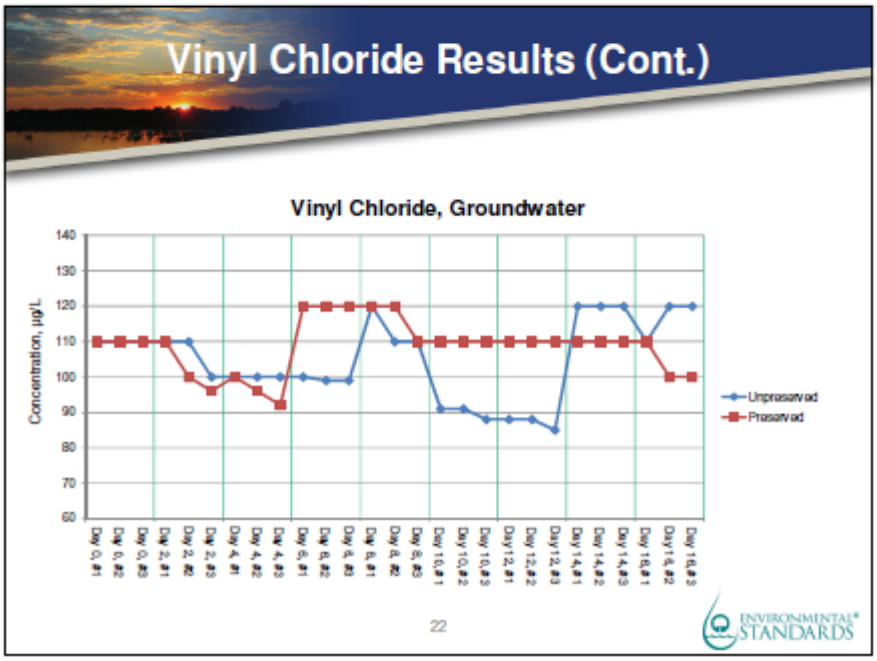
Styrene Results (Cont.)

	Average Result (µg/L)	Minimum Result (µg/L)	Maximum Result (µg/L)	%RSD
DI, Unpreserved	88	78	98	6
DI, Preserved	91	80	100	7
GW, Unpreserved	94	89	99	3
GW, Preserved	90	86	95	3

20

ENVIRONMENTAL STANDARDS


Vinyl Chloride Results
Vinyl Chloride, Deionized Water
Concentration, µg/L
140
130
120
110
100
90
80
70
60
Unpreserved
Preserved
21
ENVIRONMENTAL STANDARDS


Vinyl Chloride Results (Cont.)
Vinyl Chloride, Groundwater
Concentration, µg/L
140
130
120
110
100
90
80
70
60
Unpreserved
Preserved
22
ENVIRONMENTAL STANDARDS

Vinyl Chloride Results (Cont.)

	Average Result (µg/L)	Minimum Result (µg/L)	Maximum Result (µg/L)	%RSD
DI, Unpreserved	105	72	130	14
DI, Preserved	106	85	120	8
GW, Unpreserved	105	85	120	10
GW, Preserved	109	92	120	7

23

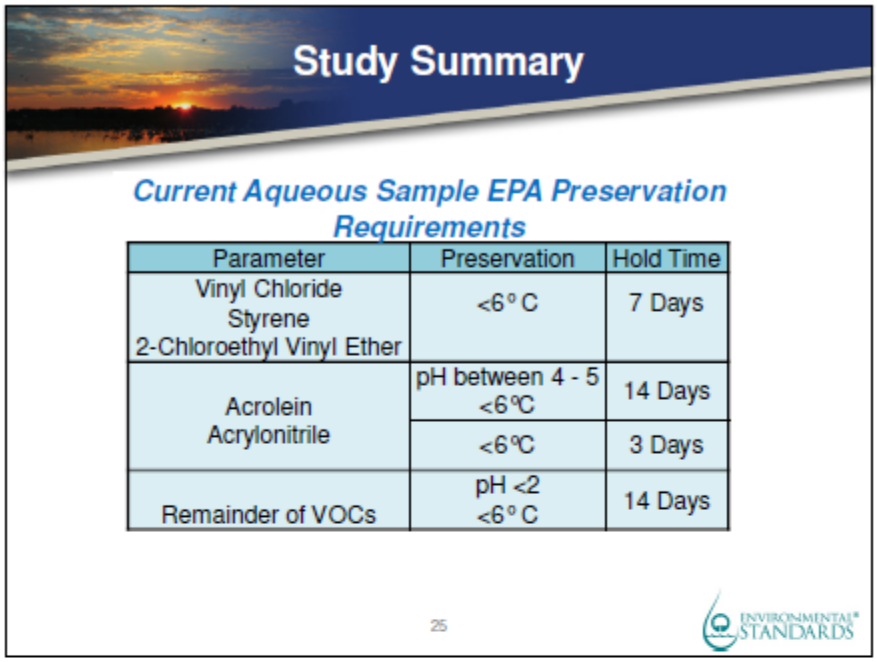
ENVIRONMENTAL STANDARDS

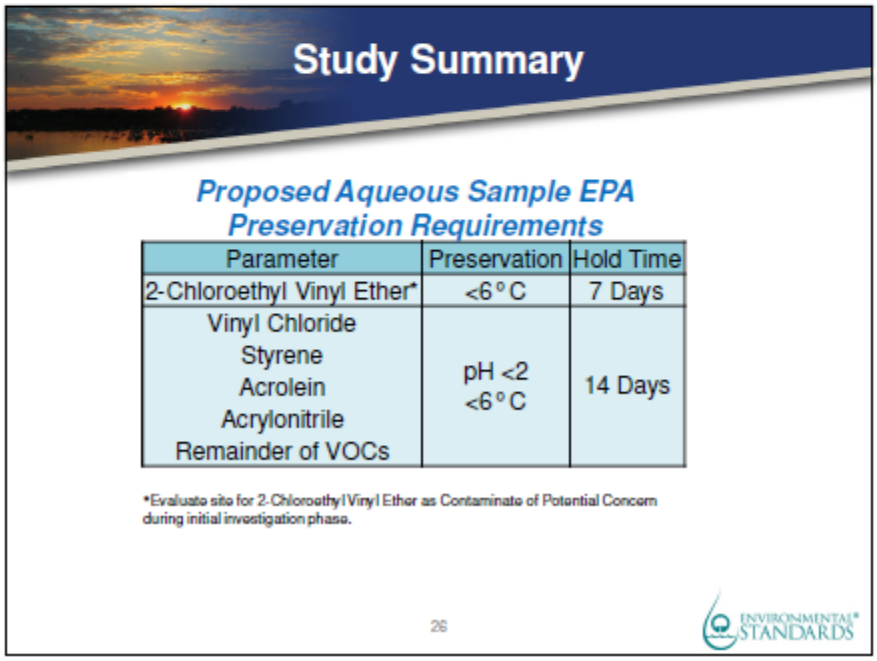
Study Summary

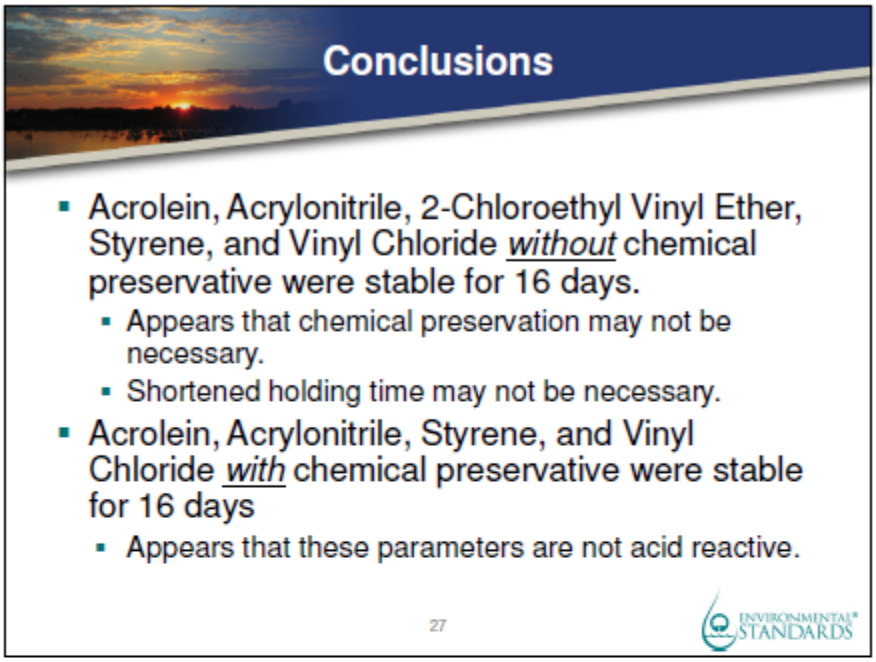
- 2-Chloroethyl Vinyl Ether recoveries for the chemical preserved samples were 0%.
- Recoveries for deionized water were within 70-130 µg/L for all except 2-Chloroethyl Vinyl Ether.
- %RSDs were below 20%.
- No trends in recovery were observed.

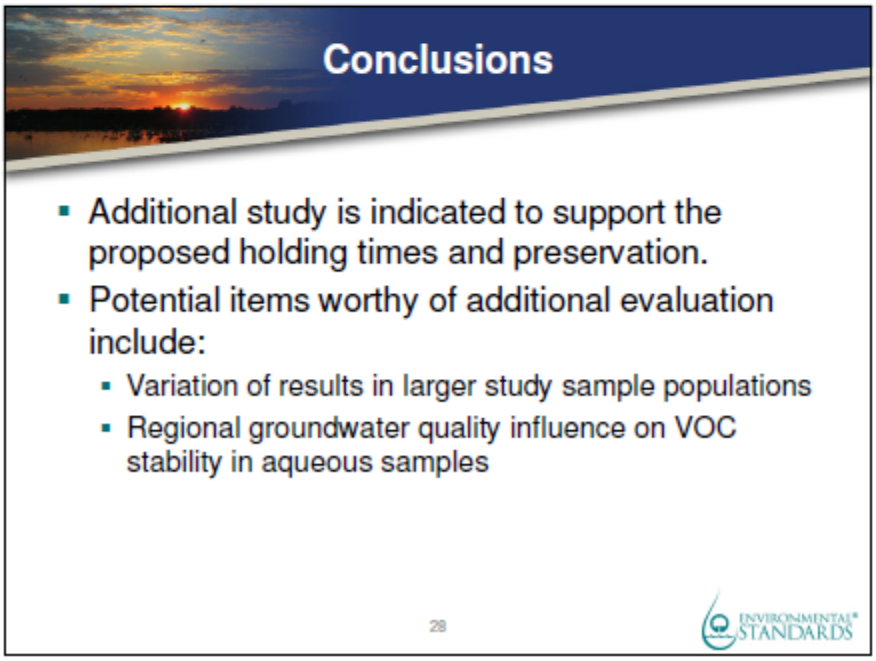
24

ENVIRONMENTAL STANDARDS

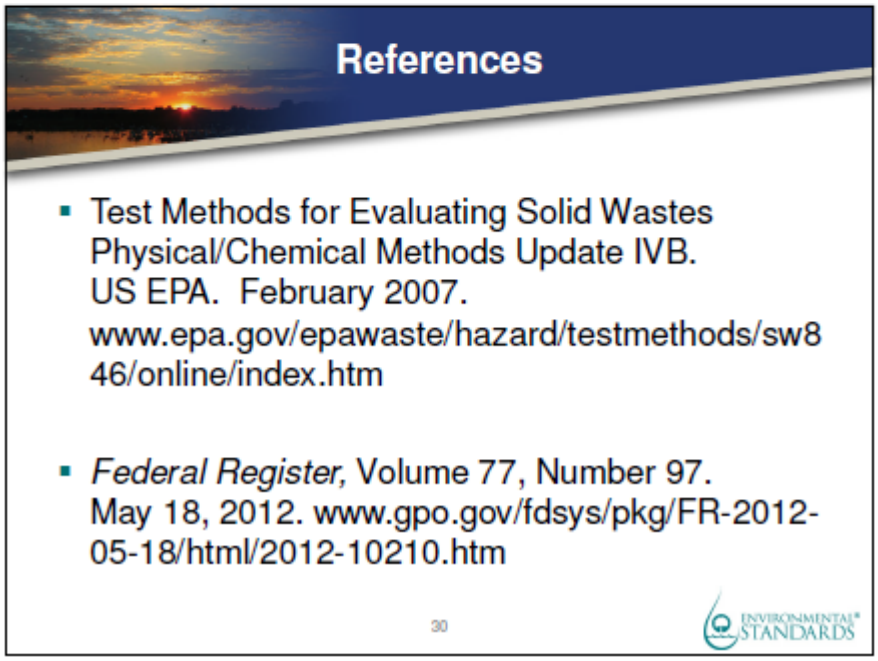

Study Summary
Current Aqueous Sample EPA Preservation Requirements
Parameter
Preservation
Hold Time
Vinyl Chloride
Styrene
2-Chloroethyl Vinyl Ether
<6° C
7 Days
Acrolein
Acrylonitrile
pH between 4 - 5
<6°C
14 Days
<6°C
3 Days
Remainder of VOCs
pH <2
<6° C
14 Days
25
ENVIRONMENTAL STANDARDS


Study Summary
Proposed Aqueous Sample EPA Preservation Requirements
Parameter
Preservation
Hold Time
2-Chloroethyl Vinyl Ether*
<6° C
7 Days
Vinyl Chloride
Styrene
Acrolein
Acrylonitrile
Remainder of VOCs
pH <2
<6° C
14 Days
*Evaluate site for 2-Chloroethyl Vinyl Ether as Contaminate of Potential Concern during initial investigation phase.
26
ENVIRONMENTAL STANDARDS


Conclusions
Acrolein, Acrylonitrile, 2-Chloroethyl Vinyl Ether, Styrene, and Vinyl Chloride without chemical preservative were stable for 16 days.
Appears that chemical preservation may not be necessary.
Shortened holding time may not be necessary.
Acrolein, Acrylonitrile, Styrene, and Vinyl Chloride with chemical preservative were stable for 16 days
Appears that these parameters are not acid reactive.
27
ENVIRONMENTAL STANDARDS


Conclusions
Additional study is indicated to support the proposed holding times and preservation.
Potential items worthy of additional evaluation include:
Variation of results in larger study sample populations
Regional groundwater quality influence on VOC stability in aqueous samples
28
ENVIRONMENTAL STANDARDS


Thank You
David R. Blye – Environmental Standards, Inc.
Lance Holman – URS Corporation
Kelly Rinehimer – URS Corporation
Eurofins Lancaster Laboratories Environmental, LLC
29
ENVIRONMENTAL STANDARDS


References
Test Methods for Evaluating Solid Wastes Physical/Chemical Methods Update IVB. US EPA. February 2007. www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm
Federal Register, Volume 77, Number 97. May 18, 2012. www.gpo.gov/fdsys/pkg/FR-2012-05-18/html/2012-10210.htm
30
ENVIRONMENTAL STANDARDS


Contact
ENVIRONMENTAL®
STANDARDS
www.envstd.com
Environmental Standards, Inc.
"Setting the Standards for Innovative Environmental Solutions"
Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577
Virginia 1208 East Market Street | Charlottesville, VA 22902 | 434.293.4039
Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590
Texas 11200 Richmond Avenue, Suite 350 | Houston, TX 77082 | 281.752.9782
Web www.envstd.com | E-mail solutions@envstd.com
31

Document Control and Document Archival Procedures

Catherine Katsikis
Laboratory Data Consultants FL, Inc.

Abstract

Document Control and Document Archival Procedures (2 or 4 hr)

The impact of document control and archival in any organization becomes apparent during audits, legal cases and simply, when internal and external interested parties need to use or reference records, procedures and/or documents. In this class we will present the importance of Document Control and Document Archival for administrative, field, laboratory and support organizations (such as consultants and field organizations).

Record archival, retrieval and documentation of these tasks, are extremely important to any organization and the methodologies on how to achieve these functions will also be presented. Several external standards exist on Document Control and Archival such as ISO, EPA, NELAC, etc.

Examples and exercises of how to control paper and electronic documentation will be discussed and several States specific requirements will be given as references to the attendees.

Document Control and Document Archival Procedures



Presented by:
Catherine Katsikis, LDCFL, Inc.
561-512-9956, ckatsikis@ldcfl.com

NEMC August 5-9 2013 San Antonio, Texas

Agenda

- Purpose
- Definitions
- Common problems
- Document Control Implementation
- Examples
- Document Archival/ Retrieval Implementation
- Summary
- References

Why Document control?

- Ancient Egyptians wrote their history on walls, because they were smart enough to know that, if they put it in the files, it would be lost forever.

(from a cartoon)
http://walrus.wr.usgs.gov



Purpose

- An organization must manage documents associated with the EMS in a manner that ensures they are easily identifiable; regularly reviewed and revised as necessary; available in current versions at all locations where they are needed; and promptly removed from service when obsolete.
- Similarly, records relevant to the EMS must be controlled in a manner that ensures they are properly collected, identified, indexed, filed, stored, and maintained.
- Records must also be retained in accordance with applicable laws, regulations, and/or other requirements to which the organization subscribes.

EMS: Environmental Management System
http://www.epa.gov/region07/ems/document_control.htm

Purpose

- Multiple references in NELAC/TNI 2009
  - 4.2.8.4 Quality Assurance Plan
  - 4.3 Document Control *(ISO/IEC 17025:2005(E), Clause 4.3)*
  - 4.13 Control of Records
  - 5.4.7 *Control of Data*





Goals

- Data of known and documented quality, to protect you and your organization.
- Prevention of incorrect documentation use.
- Easy document retrieval.

Definitions

- **Document Control – The process of managing, distributing, and controlling documents.**
- **The act** of ensuring that documents and revisions to the documents are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity is performed (ASQC, 1996).

ASQC= American Society for Quality



Common Problems

- Revision(s) time management, distribution, training.
- Document control of External documentation
- Too many documents, difficult to maintain.
- Inconsistent use of other documents (forms, templates, memos, maps, etc.).
- Electronic distribution.



Implementation

- Discuss your organization's needs.
- Create or adapt a Document control Standard Operating Procedure (SOP), or policy.
- Train employees.
- Ensure understanding of SOP/policy.
- Follow through and test the procedure.
- Periodic review of SOP/policy (usually an annual review).

Example Implementation EPA Module 11

Define the mechanism for controlling documents. Ensure that that personnel requiring access to your organization's documents have the most up-to-date versions and are aware of the document control process.

Activities Affected: All areas and departments
References: ISO 14001

http://www.epa.gov/sectors/sectorinfo/sectorprofiles/shipbuilding/module_11.pdf

Common Controlled Documents

- Quality Systems related documents (Quality Manuals, SOPs, reports, research documents, field notes, forms, logbooks, audits, COC, etc.).
- Technical related documents (monitoring plans, methods manuals, policies, other written instructions or directives etc.
- External documents (if distributed as a new procedure, rule, directive, etc.).

Implementation steps

- Create a record log (paper or electronic)
  Record:
  - Document Control ID (unique)
  - Name of document
  - Creator
  - Date created
  - Approval date
  - Revision or version
  - Retired date
  - etc.



- Don't forget to give a document control ID to the record log

Definition

- Controlled Copy – **A hard copy of a document that is uniquely identified such that the** organization can maintain control over the use and fate of the copy.
- The location of a controlled copy or identity of an individual receiving a controlled copy is recorded such that the document can be recalled as needed.



Implementation steps

- Create a traffic control log (paper or electronic)
  Record:
  - Document Control ID (unique)
  - Name of document
  - Revision or version
  - Control copy number
  - Received By
  - Date of Receipt
  - Date of Withdrawal
  - Withdrawal By
  - Destroyed By
  - etc.
- Don't forget to give a document control ID to the traffic control log

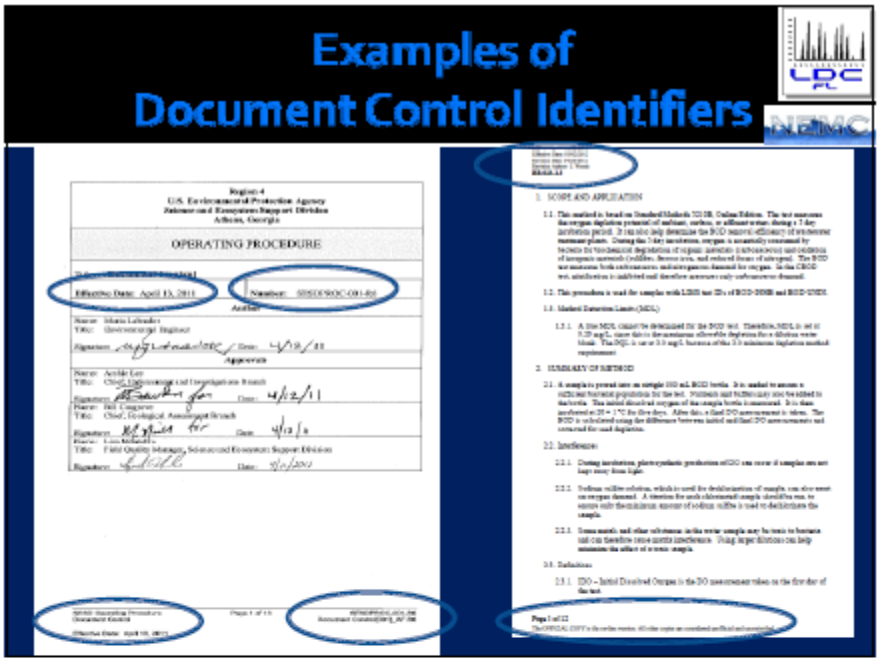


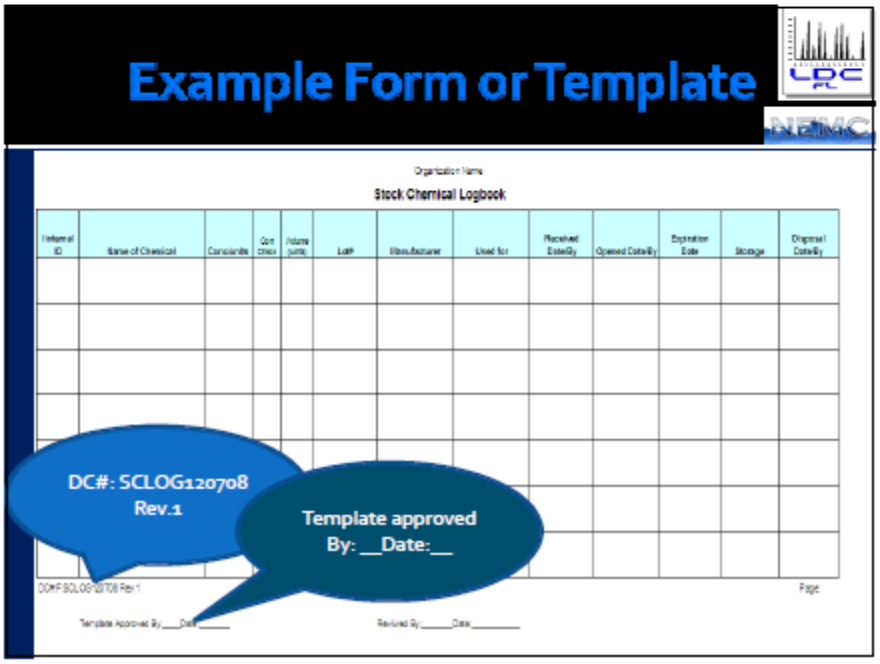
Electronic Distribution

- Challenging to control.
- Keep distribution list.
- At minimum , ask for "READ" follow up (if email is used).
- Add clause.
- Document procedure in SOP/policy/QMP.

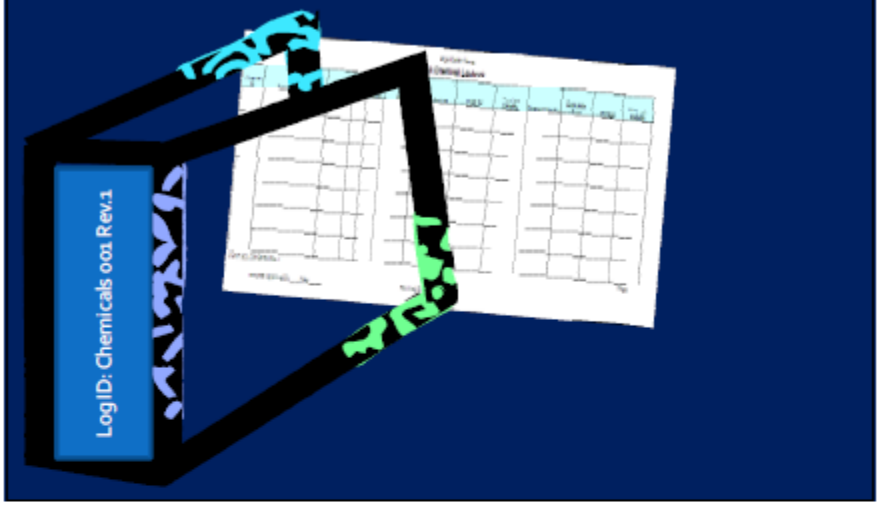
Electronic Distribution

- If you are converting to a virtual system, be sure to carefully document how the original document will be stored, if at all.
- Have a backup solution. If changing to an automated system, use a pilot roll out strategy.
- After full conversion, wait a few months before destroying or filing paper documents.


Examples of
Document Control Identifiers
NEMC
OPERATING PROCEDURE


Example Form or Template
NEMC
Stock Chemical Logbook
DC#: SCLOG120708
Rev.1
Template approved
By: __Date:__

Example Logbook/Binder



Document the Relationship

Master Form (s) Log - Table of contents (TOC)

#:	:vs	Description	Assigned	Form(s) in Notebook
N01	1	Reagent Log Book (Chemical Receipt)	N01:10.27.04:1	Bound Notebook
N02	2	Chain of Custody (COC)	N02:2009:3	F01:2

Master Form (s) Log - Table of contents (TOC)

#:	:vs	Description	Assigned	Notebook for form
F01	2	Chain Of Custody (COC)	F01:10.26.02:1	N02:3
F02	2	Sample Log In Sheet	F02:10.26.02:2	N03:2

Example Bound Notebook



Log ID: Maintenance log GCA-001
Name:_____
From:_____to:_____
Department:_____
Control copy:_____????

Definitions

- Archived Document – **A document or version of a document that is outdated and no longer** authorized for use in a designated area (electronic or physical) and is placed in a document archive for historical preservation and reference.

Storage/Archival

- Paper (Documents, Maps, logbooks, Memos, QMPs, etc.)
- Electronic (Saving in the right format, keep device that can read archived documents, when scanning use the proper pixel resolution.)
- Documents staying on site, or outside storage.
- Appoint approved personnel for external record retrieval.
- Storage facility should be air conditioned, protected against fire, theft, loss, environmental deterioration, vermin and, in the case of electronic records, electronic or magnetic sources.
  - Records are food for thought, not for mice!



Internal Storage/Archival

- Create storage/archival log(s) (paper or electronic)
  Record:
  - ID of Storage vehicle (box, cabinet, ...)
  - In house Location (room, shelve #, file cabinet #, etc.)
  - Document Control ID (unique)
  - Name of document
  - Section
  - Date stored
  - By whom
  - Duration ??
- Don't forget to give a document control ID to the record log.



External Storage/Archival

- Create storage/archival log (paper or electronic)
  Record:
  - ID of box
  - Document Control ID ?
  - Name of document ?
  - Date of move to outside storage
  - Facility
  - Facility's box ID label (barcode, pre-printed IDs....)
  - Contact info
  - Date of move
  - Storage duration
- Don't forget to give a document control ID to the archiving log.

Exercise
Record Retrieval

TNI V1M2:
4.13.3 e) Access to archived information shall be documented with an access log.

- Internal Access /Retrieval Log

Record:

_____
_____
_____
_____
_____
_____
_____
_____



- Don't forget to ?_____



Record Retrieval

- External Access/Retrieval Log

Record:

- Box ID
- Document ID
- Requested Date/By
- Arrival Date
- Section
- Purpose
- Contact phone or email
- Return date/By
- Etc.

Archival Duration

- **The time of archival will depend on the organization/project/type and their applicable requirements as defined by the End User, State Administrative Code, state DEP/DEQ, EPA, etc. Examples:**
  - TNI: five (5) years from generation of the last entry in the records.
  - Currently: FDEP 5 years after project completion (i.e. permit)
- **Periodic check on regulations for changes**
  - Example: Upcoming: FDEP 5 years after the date of generation or completion of the records
- **Identify the different types of retention period requirements. Examples:**
  - Fiscal year ?
  - Calendar year?
  - Anniversary year?
  - Months? Days?
  - Triggering event?



Summary

- Protect revised or retired documents from unintentional use.
- Segregate or destroy obsolete documents.
  - Remember to always keep and identify the main document (paper/electronic) for historical reference.
- Keep records of documents' location.
- Personal Papers

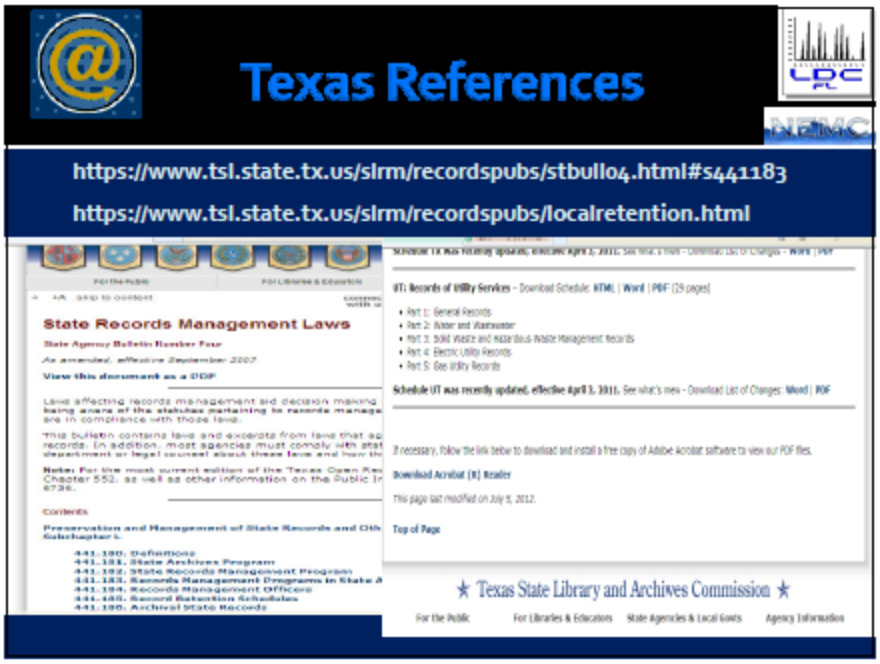
  http://www.epa.gov/records/faqs/personal.htm

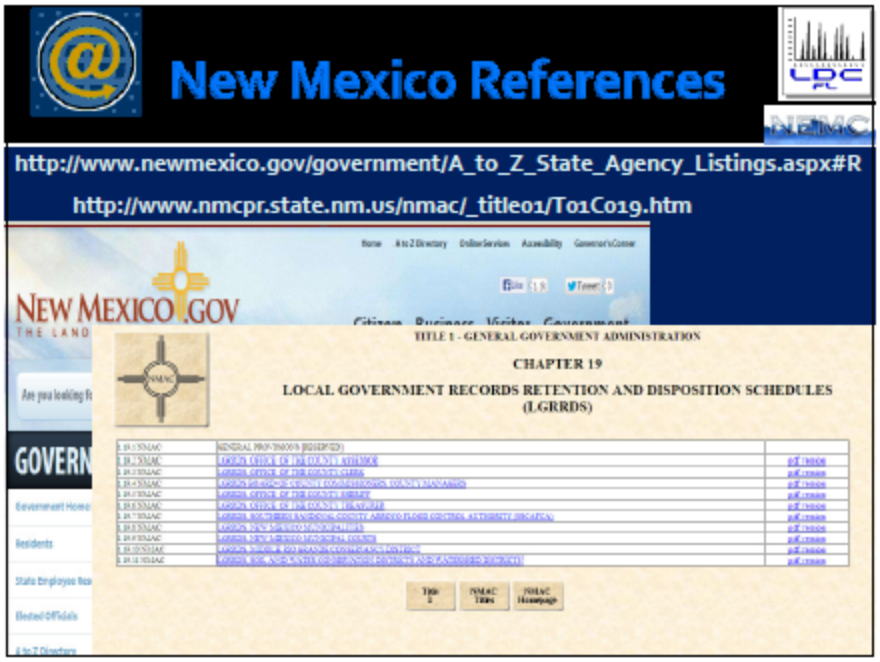


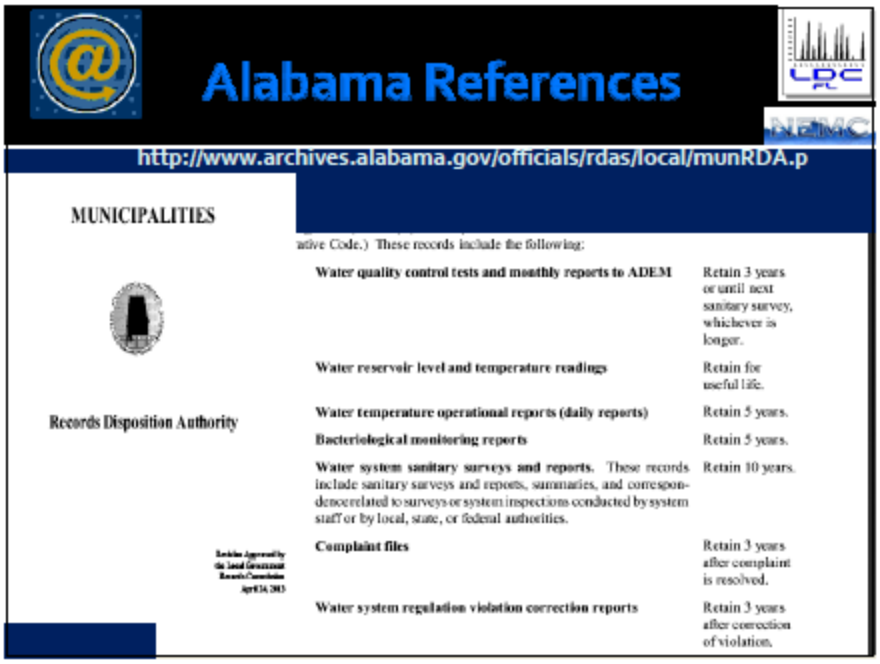
Summary

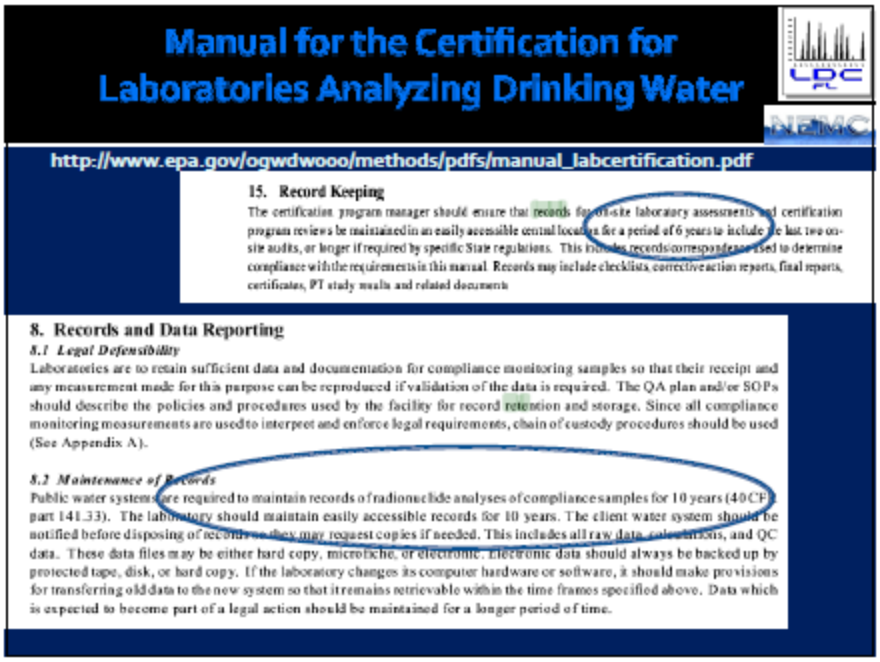
- Document control is probably one the most important part of the quality system in an organization since nearly every action is driven by it.
- Document Control will be successful if it is made simple and understandable.
- The minimum document control elements should be consistently placed on each page of the document, normally in the header and/or footer.
- Keep record lists to track and access the documentation.

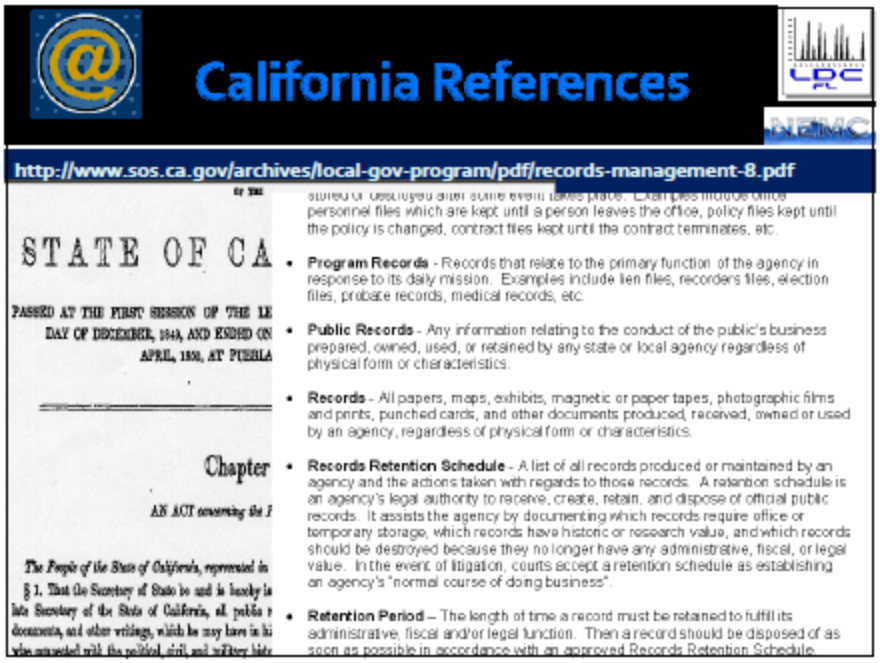

Florida References
http://dlis.dos.state.fl.us/index_RecordsManagers.cfm
Florida Department of State
Division of Library & Information Services
Citizens
State Employees
Libraries
Archivists
Records Managers
Search this web site
Search
Services for Records Managers
About Records Management
Florida's records management program promotes the efficient, effective, and economical management of public records.
Proper records management ensures that information is available when and where it is needed, in an organized and efficient manner, and in an appropriate environment.
Records management is more than retention, storage, and disposition of records; it entails all record-keeping requirements and practices that allow an organization to establish and maintain control over information flow and administrative operations. Florida's records management program is authorized by section 257.36, Florida Statutes and applies to public records as defined in 119.011(12), F.S.
Records management seeks to control and manage records throughout their life cycle, from their creation through active use, inactive storage, and final disposition.
Among the many benefits of records management are:
Space savings
Reduced expenses for filing equipment
Increased efficiency of information retrieval
Compliance with records retention requirements
Services for Records Managers
About Records Management / Home
General Records Schedules
Records Retention Scheduling & Disposition
Records Management Liaison Officers
Publications & Forms
Statutes & Rules
Training
Records Storage Center
Total Recall Web Module
Disaster Recovery
Frequently Asked Questions
Related Links
Quick Access
Features
Get the current General Records Schedule (GS1-SL)
Electronic Recordkeeping Strategic Plan 2010-2012
Customer Satisfaction Survey
Disaster Recovery and Relief
Total Recall User Training


Texas References
https://www.tsl.state.tx.us/slrm/recordspubs/stbull04.html#s441183
https://www.tsl.state.tx.us/slrm/recordspubs/localretention.html
State Records Management Laws
State Agency Bulletin Number Four
View this document as a PDF
Contents
441.180. Definitions
441.181. State Archives Program
441.182. State Records Management Program
441.183. Records Management Programs in State A
441.184. Records Management Officers
441.185. Record Retention Schedules
441.186. Archival State Records
IT: Records of Utility Services - Download Schedule: HTML | Word | PDF (29 pages)
Part 1: General Records
Part 2: Water and Wastewater
Part 3: Solid Waste and Hazardous Waste Management Records
Part 4: Electric Utility Records
Part 5: Gas Utility Records
Schedule UT was recently updated, effective April 1, 2011. See what's new - Download List of Changes: Word | PDF
If necessary, follow the link below to download and install a free copy of Adobe Acrobat software to view our PDF files.
Download Acrobat (R) Reader
This page last modified on July 9, 2012.
Top of Page
★ Texas State Library and Archives Commission ★
For the Public
For Libraries & Educators
State Agencies & Local Govts
Agency Information


New Mexico References
http://www.newmexico.gov/government/A_to_Z_State_Agency_Listings.aspx#R
http://www.nmcpr.state.nm.us/nmac/_title01/T01C019.htm
NEW MEXICO.GOV
TITLE 1 - GENERAL GOVERNMENT ADMINISTRATION
CHAPTER 19
LOCAL GOVERNMENT RECORDS RETENTION AND DISPOSITION SCHEDULES (LGRRDS)


Alabama References
http://www.archives.alabama.gov/officials/rdas/local/munRDA.p
MUNICIPALITIES
Records Disposition Authority
Water quality control tests and monthly reports to ADEM
Retain 3 years or until next sanitary survey, whichever is longer.
Water reservoir level and temperature readings
Retain for useful life.
Water temperature operational reports (daily reports)
Retain 5 years.
Bacteriological monitoring reports
Retain 5 years.
Water system sanitary surveys and reports. These records include sanitary surveys and reports, summaries, and correspondence related to surveys or system inspections conducted by system staff or by local, state, or federal authorities.
Retain 10 years.
Complaint files
Retain 3 years after complaint is resolved.
Water system regulation violation correction reports
Retain 3 years after correction of violation.


Manual for the Certification for Laboratories Analyzing Drinking Water
http://www.epa.gov/ogwdwooo/methods/pdfs/manual_labcertification.pdf
15. Record Keeping
The certification program manager should ensure that records for on-site laboratory assessments and certification program reviews be maintained in an easily accessible central location for a period of 6 years to include the last two on-site audits, or longer if required by specific State regulations. This includes records/correspondence used to determine compliance with the requirements in this manual. Records may include checklists, corrective action reports, final reports, certificates, PT study results and related documents
8. Records and Data Reporting
8.1 Legal Defensibility
Laboratories are to retain sufficient data and documentation for compliance monitoring samples so that their receipt and any measurement made for this purpose can be reproduced if validation of the data is required. The QA plan and/or SOPs should describe the policies and procedures used by the facility for record retention and storage. Since all compliance monitoring measurements are used to interpret and enforce legal requirements, chain of custody procedures should be used (See Appendix A).
8.2 Maintenance of Records
Public water systems are required to maintain records of radionuclide analyses of compliance samples for 10 years (40 CFR part 141.33). The laboratory should maintain easily accessible records for 10 years. The client water system should be notified before disposing of records so they may request copies if needed. This includes all raw data, calculations, and QC data. These data files may be either hard copy, microfiche, or electronic. Electronic data should always be backed up by protected tape, disk, or hard copy. If the laboratory changes its computer hardware or software, it should make provisions for transferring old data to the new system so that it remains retrievable within the time frames specified above. Data which is expected to become part of a legal action should be maintained for a longer period of time.


California References
http://www.sos.ca.gov/archives/local-gov-program/pdf/records-management-8.pdf
STATE OF CA
PASSED AT THE FIRST SESSION OF THE LE
DAY OF DECEMBER, 1849, AND ENDED ON
APRIL, 1850, AT PUEBLA
Chapter
AN ACT concerning the
The People of the State of California, represented in
§ 1. That the Secretary of State be and is hereby la
late Secretary of the State of California, all public r
documents, and other writings, which he may have in hi
personnel files which are kept until a person leaves the office, policy files kept until the policy is changed, contract files kept until the contract terminates, etc.
Program Records - Records that relate to the primary function of the agency in response to its daily mission. Examples include lien files, recorders files, election files, probate records, medical records, etc.
Public Records - Any information relating to the conduct of the public's business prepared, owned, used, or retained by any state or local agency regardless of physical form or characteristics.
Records - All papers, maps, exhibits, magnetic or paper tapes, photographic films and prints, punched cards, and other documents produced, received, owned or used by an agency, regardless of physical form or characteristics.
Records Retention Schedule - A list of all records produced or maintained by an agency and the actions taken with regards to those records. A retention schedule is an agency's legal authority to receive, create, retain, and dispose of official public records. It assists the agency by documenting which records require office or temporary storage, which records have historic or research value, and which records should be destroyed because they no longer have any administrative, fiscal, or legal value. In the event of litigation, courts accept a retention schedule as establishing an agency's "normal course of doing business".
Retention Period – The length of time a record must be retained to fulfill its administrative, fiscal and/or legal function. Then a record should be disposed of as soon as possible in accordance with an approved Records Retention Schedule.

Take away messages

- "Information which is not communicated is valueless. Information which cannot be found is worthless. The value of Information is directly related to its accessibility."
- "If only we knew what we already know."

USGS science for a changing world



References

- ISO 9001
- ISO 17025
- ISO 14000
- www.9000world.com
- FDEP F.A.C. 62-160, QA Rule
- FDEP SOPs FD1000 Documentation Procedures
- TNI 2009/NELAC
- www.slideshare.net
- www.qualitydigest.com
- www.epa.gov/region07/ems/document_control.htm
- www.epa.gov/ogwdw000/methods/pdfs/manual_labcertification.pdf
- Document Control Procedures | eHow.com
- TX: www.tsl.state.tx.us/slrm/recordspubs/stbull04.html#s441183
- CA: www.sos.ca.gov/archives/local-gov-program/pdf/records-management-8.pdf
- AL: www.archives.alabama.gov/officials/rdas/local/munRDA.pdf
- State of Florida *General Records Schedule GS14 For Public Utilities*
- Florida Statutes and Administrative Code Rules Relating to Archives and Records Manag. http://dlis.dos.state.fl.us/recordsmgmt/statutes.cfm
- NM:www.newmexico.gov/government/A_to_Z_State_Agency_Listings.aspx#R
- walrus.wr.usgs.gov/infobank/programs/html/training/recordsmanagement/rmhumor.html

Contacts

LDCFL, Inc.
Catherine Katsikis
Senior Scientist/QA Manager
561-512-9956
ckatsikis@ldcfl.com



SECTION 16

ADVANCES IN SAMPLE PREPARATION AND CLEAN-UP

Productivity Enhancements in Microwave Assisted Extractions (EPA Method 3546) of Semi Volatile Organic Compounds (SVOCs) from Environmental Samples

Sumedh Phatak
Milestone Inc.

Abstract

Microwave Assisted Extraction offers significant benefits over conventional techniques like soxhlet and sonication for the extraction of SVOCs from environmental samples. These benefits include higher throughput, cost savings, reduced solvent usage, safer work environment and most importantly reduced run times while yielding accurate and reproducible data. Microwave Assisted Extractions reduce run times to an average of 20 minutes as opposed to a several hours with the conventional techniques. Even with reduced extraction times, several steps are still necessary to complete the back-end clean-up of the samples run. Environmental laboratories have fundamentally embraced the technology switch but are still experiencing hesitation from the additional preparation steps and time- consuming cleaning that goes along with first generation techniques. This presentation will show the differences in sample preparation, clean-up and data between conventional microwave extractions and the key changes necessary in the following areas for:

- Reduced sample prep time
- Reduced number of preparation steps
- Elimination of run to run sample contamination
- Seamless move to array of testable organic compounds

Productivity Enhancements in Microwave Assisted Extractions (EPA Method 3546) Of Semi Volatile Organic Compounds From Environmental Samples

Sumedh Phatak
Milestone Inc



Agenda

- Introduction to EPA 3546
- Conventional Extraction Methods
- Microwave Assisted Extraction
- Data Comparison
- Improvements To Increase Throughput
- Summary
- Q&A

What is EPA Method 3546?

- Method for extracting water insoluble or slightly soluble organic compounds from soils, clays, sediments, sludge and solid wastes.
- Employs closed vessel microwaves to achieve the extraction of analytes at high temperatures and pressures
- Recovery equivalent to Soxhlet extraction (EPA method 3540) with – less solvent, shorter time and better precision in most cases

EPA Method 3546



Typical Parameters – EPA 3546

Application: Soils, Clays, Sediments, Sludge, Solid Wastes
Sample Size: 2 – 20 g
Solvent Volume: 25 ml
Temperature: 100 – 115 ^{0}C
Pressure: 50 – 150 psi

EPA Method 3546



The need for EPA 3546…

- Extraction demands
- Data quality
- Representative sampling
- Productivity enhancement
- Cost effectiveness

Conventional Techniques

Soxhlet:

- Regarded as the standard method
- Inexpensive equipment
- Able to process large amounts of sample
- Separate filtration is unnecessary



Conventional Techniques

Limitations of Soxhlet Extractions:

- Long operation times - ~4 – 48 hours
- Large solvent consumption – 200 – 500 ml
- Large operation cost
- Only extraction capabilities
- High exposure to toxic materials

Conventional Techniques

Sonication:

- Fast method – 30 – 60 min
- Inexpensive equipment
- Able to process large amounts of sample
- Matrix Independent



Conventional Techniques

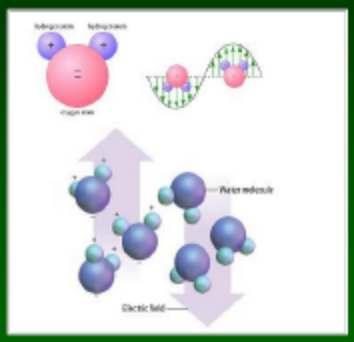
Limitations of Sonication Extractions:

- Large solvent consumption – 200 – 500 ml
- Labor intensive
- Filtration required
- High exposure to toxic materials

Microwave Theory

How Microwaves Work:

- Polar molecules rapidly oscillate with the oscillating electromagnetic field.
- Rotating molecules push, pull, collide other molecules and generate heat



Microwave Extraction

- Specially designed microwaves
- Rotors with multiple vessels
- Samples + mixture of solvents added
- Closed vessels ensure no loss of volatiles
- Concentration
- Analysis



Advantages of Microwave Assisted Extraction

- High throughput
- Reduction of operation time
- Minimum consumption of solvents
- Save of space
- Reduction of operation cost
- No expensive glassware
- Broad range of sample sizes
- Flexible platform (multiple chemistries)
- Conforms with EPA's pollution prevention goals



Milestone's Ethos EX

- Chassis
- Safety features
- Color touch-screen controller
- PID Control



Improvements to Enhance Productivity – Rotors & Vessels

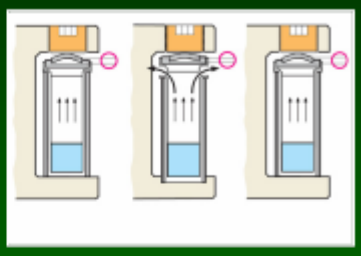
Milestone Ethos EX Rotors - Specifications



SK-10	SK-12	Q-20	PRO-16/24	LVR	MUP-41
Max. temp & pressure Max. Press. 100 bar Max. Temp. 300°C	Max. temp & pressure Max. Press. 35 bar Max. Temp. 300°C	Max. temp & pressure Max. Press. 60 bar Max. Temp. 250°C	Max. temp & pressure Max. Press. 30 bar Max. Temp. 260°C	Max. temp & pressure Max. Press. 10 bar Max. Temp. 200°C	Max. temp & pressure Max. Press. 30 bar Max. Temp. 260°C
Number of Samples 10	Number of Samples 12	Number of Samples 20	Number of Samples 24	Number of Samples 6	Number of Samples 41
Vessel Volume 100 mL	Vessel Volume 100 mL	Vessel Volume 45 mL	Vessel Volume 75 mL	Vessel Volume 270 mL	Vessel Volume 70 mL
Minimum vol. 10 mL	Minimum vol. 10 mL	Minimum vol. 3 ml	Minimum vol. 10 mL	Minimum vol. 10 mL	Minimum vol. 10 mL
Max. sample wt. Up to 20 g	Max. sample wt. Up to 15 g	Max. sample wt. Up to 2 g	Max. sample wt. Up to 15 g	Max. sample wt. Up to 30 g	Max. sample wt. 10 g
Vessel Material TFM	Vessel Material TFM	Vessel Material TFM	Vessel Material TFM	Vessel Material TFM	Vessel Material TFM or PFA
Vessel Technology Vent-and-Reseal	Vessel Technology Vent-and-Reseal	Vessel Technology Vent-and-Reseal	Vessel Technology Vent-and-Reseal	Vessel Technology Vent-and-Reseal	Vessel Technology Self-regulating

Productivity Enhancement – High Sample Size & Solvent Volume

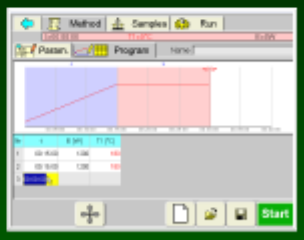
- Patented by Milestone
- Cap is held in place by a PEEK spring which deforms as pressure pushes the cap upwards
- Overpressure is gently and controllably released
- Pressure is maintained in the vessel even while venting
- No ejection of contents or loss of volatiles

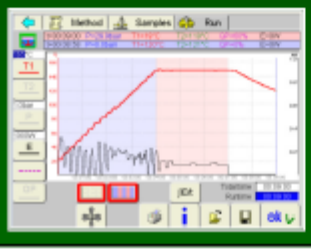


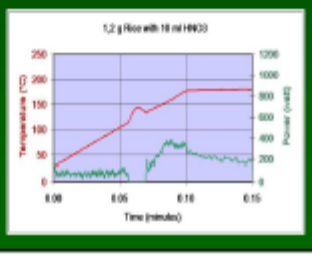
Vent and Reseal Technology

Productivity Enhancement – Temperature Control

- Fiber Optic Probe
- Direct temperature measurement
- PID Control







Technology Comparison

Soxhlet vs Microwaves

	Method 3540C		Microwave Extraction	
	12 Samples	1000 Samples	12 Samples	1000 Samples
Labor Cost	$140	$11,666	$41	$3,383
Solvent Cost	$108	$9,000	$8.40	$400
Total Cost	$248	$20,666	$49	$3,783
Total Time Required	316 hours	13,167 hours	3.08 hours	257 hours
Total Solvent Consumed	5.4 L	450 L	420 ml	15.96 L

Data Analysis

- Instrument setup
- 15g of Ottawa Sand
- Disposable Glass inserts were used

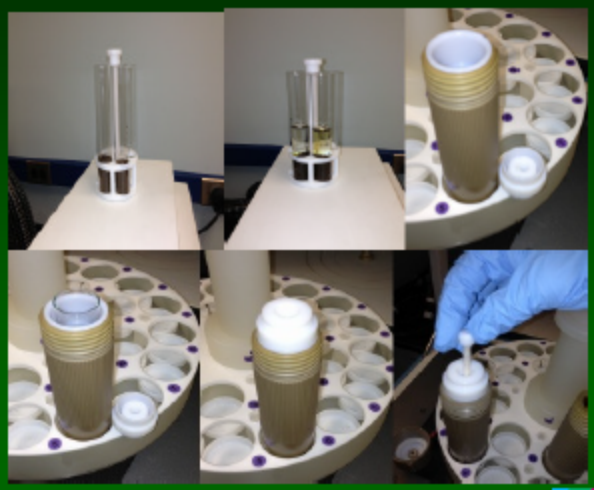
Run 1:

- 25ml of 1:1 hexane acetone
- 10 min to 100 ^{0}C + 20 min at 100 ^{0}C

Run 2:

- 25 ml of 1:1 DCM acetone
- 10 min to 100 ^{0}C + 20 min at 100 ^{0}C

Further Enhancement – Disposable Glass Vials



Data Run - 1

- Sample: 15 g soil
- Solvent: 15 ml Hexane + 15 ml Acetone
- Dilution Factor: 1
- Final Volume: 1 ml
- Spikes analyzed in duplicates: Aniline, Phenol, 2-Chlorophenol, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-methylphenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloroanile, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 4-nitrophenol, azobenzene, pentachlorophenol, anthracene, fluoroanthene
- Average % Recovery: 78.98%
- Surrogates analyzed: 2-fluorophenol, phenol d-6, nitrobenzene d-5, 2,4,6-tribromophenol, 4-terphenyl – d14
- Average % Recovery: 85.93%

Data Run - 2

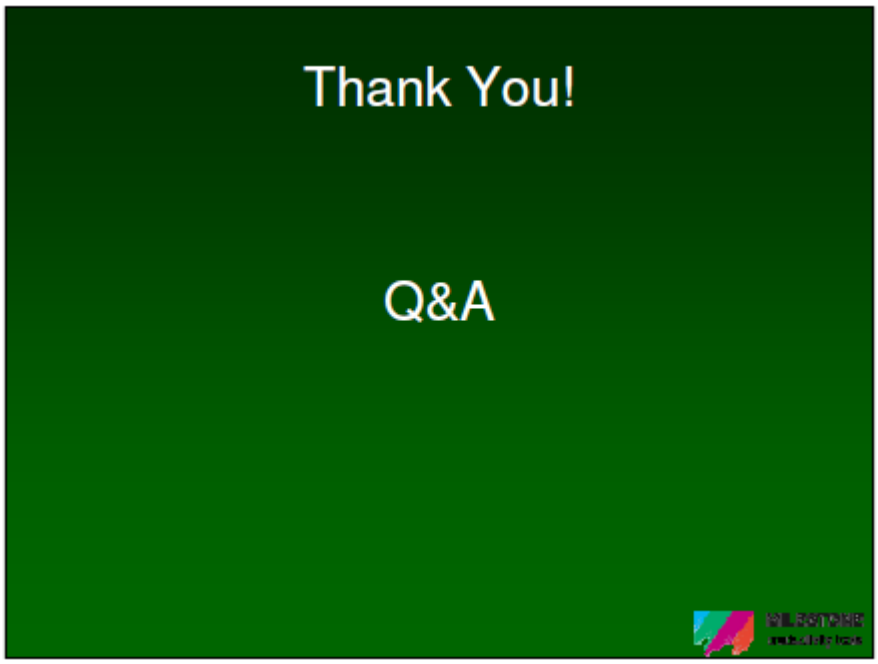
- Sample: 15 g soil
- Solvent: 15 ml Hexane + 15 ml Acetone
- Dilution Factor: 1
- Final Volume: 1 ml
- Spikes analyzed in duplicates: Phenol, 2-Chlorophenol, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-methylphenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloroanile, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 4-nitrophenol, anthracene, fluoroanthene
- Average % Recovery: 75.45%
- Surrogates analyzed: 2-fluorophenol, phenol d-6, nitrobenzene d-5, 2,4,6-tribromophenol, 4-terphenyl – d14
- Average % Recovery: 75.15%

Advantages of Disposable Glass Vials

- No cleaning step required post extraction
- No need to purchase additional rotors
- Clean environment – low blanks
- Comparable or better recoveries
- Inexpensive

Summary

- Microwave extraction offers significant benefits over traditional extraction techniques.
- Modifications and upgrades are made to enhance productivity – Rotor design, safety features, temperature measurement, software
- The use of disposable glass vials further increase the productivity of a lab – no downtime, no cleaning, great results


Thank You!
Q&A

Simultaneous Extraction of PAHs and PCBs from Tissue and Soil Samples Using a New Accelerated Solvent Extraction (ASE) Procedure

Richard Jack
Thermo Fisher Scientific

Abstract

Laboratories that are involved in food safety or environmental analysis are often dealing with many types of matrices and broad ranges of compounds. In some cases, certain solvents are used for specific analyte types, and more than one extraction of the same sample may be required to obtain the levels of all of the contaminants present. For example, a dichloromethane/acetone mixture is often used for PAHs while hexane/acetone mixtures are often used for PCBs. In many cases, it would be advantageous to have a single extraction procedure for both of these compound classes.

ASE is accepted under USEPA Method 3545A for the extraction of a broad spectrum of compound classes. ASE uses elevated pressures and temperatures to effect rapid extractions with small solvent volumes. We will present the results of our work to develop a single extraction procedure for the determination of PAHs and PCBs in soil and animal tissue samples. Analysis of the PAHs was done by GC-MS, and GC with electron capture was used for the PCBs. In-cell clean-up procedures were used to provide interference free extracts of the animal tissue samples. We will demonstrate the impact of adsorbent and extraction temperature on analyte recovery and amount of coextractables present in the final extract.

ThermoFisher SCIENTIFIC

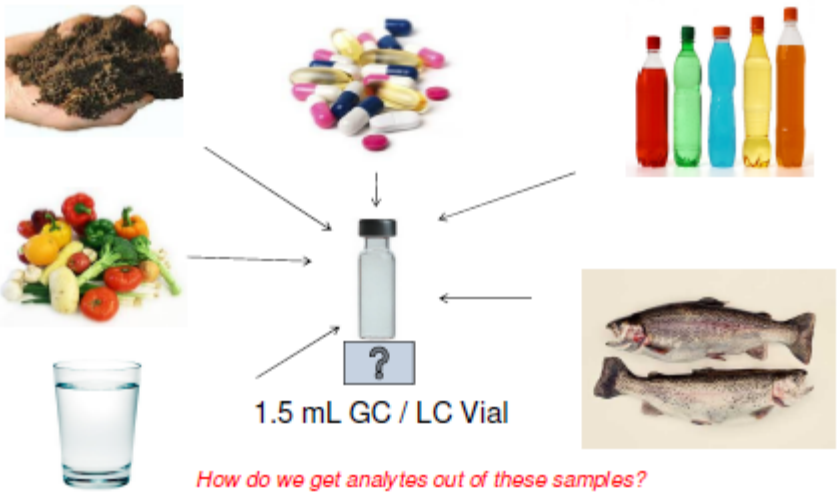
Simultaneous Extraction of PAHs and PCBs from Tissue and Soil Samples Using a New Accelerated Solvent Extraction (ASE) Procedure

Richard Jack, Ph.D., Brett Murphy, Selvan Lingam, David Knowles, Bruce Richter and Richard Carlson

Thermo Fisher Scientific

The world leader in serving science

The Challenge for Analysis



How do we get analytes out of these samples?

2

ThermoFisher SCIENTIFIC

The Answer is Sample Preparation

- Extraction
  - Removes analytes from the sample
  - Eliminates compounds that interfere with the analysis (Clean Up)
- Evaporation
  - Concentrates extracted analytes for analysis
  - Evaporates extracted samples for re-constitution
- Most time consuming part of analytical procedure (>60%)*
- Single largest source of errors in the workflow (>30%)*

*Majors, R.E. *LC-GC*, **1995**, *13*, 742-749, and **Majors, R.E. *LC-GC*, **1999**, *17*, S8 - S13

3

ThermoFisher SCIENTIFIC

Importance of Sample Preparation

"Eighty Percent of the Variance in an Assay Usually Arises from the Sample Prep."

R. Stevenson, "Pittcon® '98: Part 3 Sample Prep: The Place to Make a Difference" American Laboratory, Vol. 30, No. 14 p.21, 1998

4

ThermoFisher SCIENTIFIC

Analysis Techniques!



5

ThermoFisher SCIENTIFIC

Sample Preparation…



8

ThermoFisher SCIENTIFIC

The Important Parameters for Sample Prep

- Solvent Use
  - Amount of solvent consumed for the extraction
  - Solvents are expensive; reducing use reduces costs
- Extraction Time
  - Amount of time required for each extraction to occur
  - Reducing extraction time increases lab throughput
- % Recovery
  - Amount of analyte recovered following the extraction
  - Low % recovery yields poor analytical results
- % Relative Standard Deviation (RSD)
  - Measure of reproducibility between extractions
  - Extraction results have greater reproducibility with lower %RSDs

These Parameters Evaluate SP Techniques

7

ThermoFisher SCIENTIFIC

Thermo Scientific Dionex Sample Prep Product Line



Thermo Scientific™ Dionex ™ASE™ 150 and 350 Accelerated Solvent Extractor



Thermo Scientific Dionex AutoTrace™ 280 Solid-Phase Extraction (SPE) Instrument



Thermo Scientific Dionex SolEx™ SPE Cartridges



Genevac Rocket™ Evaporator

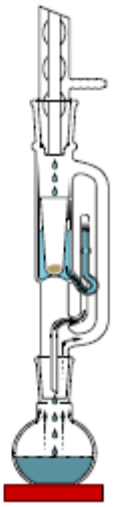
Novel & Innovative Solutions

8

ThermoFisher SCIENTIFIC

In the Beginning, There Was Soxhlet . . .

- 1879 Franz von Soxhlet
- *de facto* standard for solvent extraction
- Slow, high solvent usage



9

ThermoFisher SCIENTIFIC

Key Parameters for Liquid-Solid Extraction

- Temperature
  - Increases analyte solubility
  - Increases diffusion rate
  - Decreases solvent viscosity
- Solubility
  - Increases as temperature increases
  - E.g. Anthracene solubility increases 13 fold in DCM (50°C to 150°C)
- Viscosity
  - Decreases as temperature increases
  - Allows solvents to migrate through the matrix easier
- Surface Tension
  - Increased temperature decreases solvent surface tension
  - Lower surface tension allows the solvent to better cover the matrix

10

ThermoFisher SCIENTIFIC

Now . . . Accelerated Solvent Extraction

- Automates sample preparation for solid and semisolid samples using solvents at elevated temperatures and pressure.
- Operates above the boiling point of extraction solvents by using sealed extraction cells.
- Pressure is used to keep solvents liquid during extraction (1500 psi).
- Well established and proven technique that is superior to Soxhlet and approved for U.S. EPA Method 3545A.



Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor system

10

ThermoFisher SCIENTIFIC

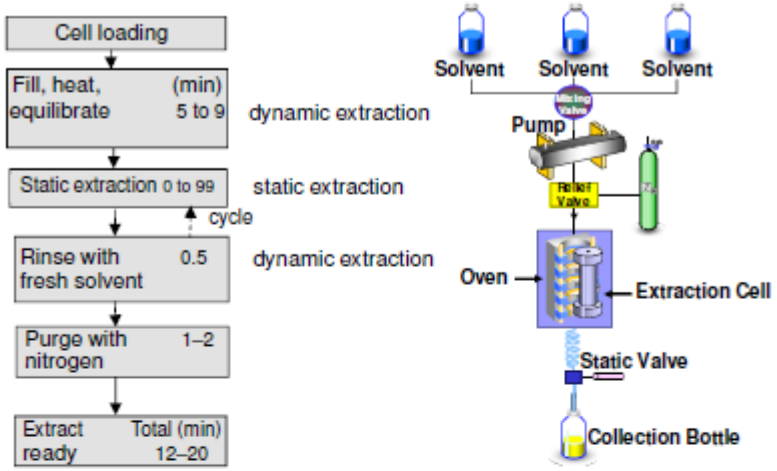
ASE® Technology

- Patented flow-through design allows:
  - In-line filtration
  - In-cell cleanup
  - Fractionation or selectivity
- Control of temperature and pressure for each individual sample:
  - Requires small quantities of solvent and short periods of time
  - 50 mL vs. hundreds of mL
  - 15 min vs. several hours
- Multiple cell sizes support a wide range of sample sizes (1–100 g).
- Ability to extract up to 24 samples in a single batch.

12

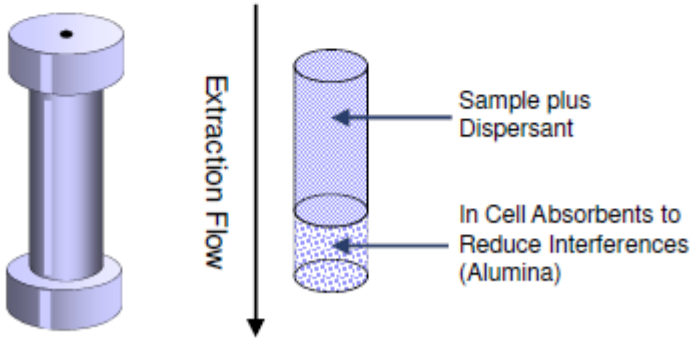
ThermoFisher SCIENTIFIC

How Does Accelerated Solvent Extraction Work?



ThermoFisher SCIENTIFIC

Schematic of Selective Extraction Using ASE®



ThermoFisher SCIENTIFIC

Simultaneous PAH and PCB Extraction with ASE

- The ability to perform a simultaneous extraction of PAHs and PCBs in a single method was evaluated using Accelerated Solvent Extraction.
- Extractions were performed on both spiked mussel and spiked soil samples to evaluate the % recovery and %RSD for PAHs and PCBs.
- Analytical determinations were made using GC-MS for the PAHs and GC-ECD for the PCBs.

15 ThermoFisher SCIENTIFIC

Accelerated Solvent Extraction Conditions

Table 1. Accelerated solvent extraction conditions.

	Method 1	Method 2
System Pressure	10 MPa (1500 psi)	10 MPa (1500 psi)
Oven Temperature	125 °C	100 °C
Sample Size	5 g	5 g
Oven Heatup Time	6 min	5 min
Static Time	6 min	4 min
Static Cycles	4	5
Rinse Volume	40 mLs (60% of extraction cell volume)	40 mLs (60% of extraction cell volume)
Solvent	Dichloromethane	Dichloromethane
Nitrogen Purge	300 s	300 s
Extraction Time	30 min	25 min
Cell Size	66 mLs	66 mLs

18 ThermoFisher SCIENTIFIC

Sample Preparation

- Both commercially purchased mussel and contaminated soil were spiked with PAH, Base/Neutral, PCB, and Arochlor surrogates.
  - PAH & Base/Neutral Surrogates = 5.0 µg/g
  - PCB = 30 ng/g
  - Arochlor = 2 mg/g
- Both samples were mixed with 10 g of DE dispersant, homogenized, and added to a 66 mL extraction cell.
- 20 g of acidic alumina were added to each cell prior to sample introduction.

17

ThermoFisher SCIENTIFIC

GC-ECD / GC-MS Conditions

GC-MS Conditions	
Column:	5% Diphenyl Capillary Column 30 m × 0.25 mm i.d., d_f = 0.5 µm
Injection Port Temperature:	280 °C
Injection Mode:	Splitless
Column Flow Rate:	1.4 (mL/min) constant flow
Oven Temp.:	50 °C (hold for 1 min) to 320 °C at 6 °C/min (hold for 10 mins)

GC-ECD Conditions	
Column:	Capillary Column 40 m × 0.18 mm i.d., d_f = 0.18 µm
Injection Port Temperature:	250 °C
Injection Mode:	Splitless
Purge Time:	1.00 min
Makeup Gas:	Nitrogen
Column Flow Rate:	1.5 (mL/min) constant flow
Oven Temp.:	100 °C (hold 1 for min) to 200 °C at 30 °C/min to 320 °C at 2 °C/min (hold 2 min)

18

ThermoFisher SCIENTIFIC

Extraction Method 1 – Mussel & Soil

Table 2. Data for mussel and soil samples extracted by Method 1.

PAH Recoveries – Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
Nitrobenzene-d5**	83.3	0.54	13.05
2-Fluorobiphenyl**	95.1	0.43	9.13
p-Terphenyl-d4**	91.4	0.27	5.92
Naphthalene	89.1	0.28	6.33
Acenaphthylene	101.2	0.30	5.91
Acenaphthene	98.3	0.28	5.65
Fluorene	107.5	0.46	8.65
Phenanthrene	104.6	0.30	5.70
Anthracene	100.1	0.29	5.77
Fluoranthene	97.1	0.30	6.24
Pyrene	88.9	0.24	5.31
Benzo(a)anthracene	85.4	0.21	4.85
Chrysene	95.5	0.27	5.66
Benzo(b)fluoranthene	91.7	0.31	6.72
Benzo(k)fluoranthene	88.3	0.20	4.43
Benzo(a)pyrene	89.9	0.28	6.29
Benzo(ghi)perylene	94.1	0.31	6.60
Dibenzo(a,h)anthracene	92.3	0.28	6.06
Indeno(1,2,3-cd) pyrene	91.1	0.31	6.72
PCB Recoveries – Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
2,4,5,6-tetrachloro-m-xylene**	93.1	0.48	5.21
Aroclor 1254	95.9	0.06	3.26

PAH Recoveries – Soil (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
Nitrobenzene-d5**	94.6	0.81	17.20
2-Fluorobiphenyl**	101.2	0.25	4.87
p-Terphenyl-d4**	102.1	0.10	1.94
Naphthalene	79.0	0.47	6.29
Acenaphthylene	76.3	0.21	5.44
Acenaphthene	102.9	0.33	6.40
Fluorene	80.3	0.21	5.31
Phenanthrene	114.8	0.37	6.39
Anthracene	91.4	0.51	11.19
Fluoranthene	103.6	0.12	2.23
Pyrene	97.4	0.14	2.90
Benzo(a)anthracene	99.0	0.17	3.35
Chrysene	91.2	0.09	1.90
Benzo(b)fluoranthene	96.3	0.14	2.82
Benzo(k)fluoranthene	92.8	0.13	2.70
Benzo(a)pyrene	83.0	0.23	5.52
Benzo(ghi)perylene	82.4	0.13	3.22
Dibenzo(a,h)anthracene	78.9	0.15	3.68
Indeno(1,2,3-cd) pyrene	84.6	0.11	2.65
PCB Recoveries – Soil (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
2,4,5,6-tetrachloro-m-xylene**	86.7	1.2	4.72
Aroclor 1254	101.6	0.19	3.15

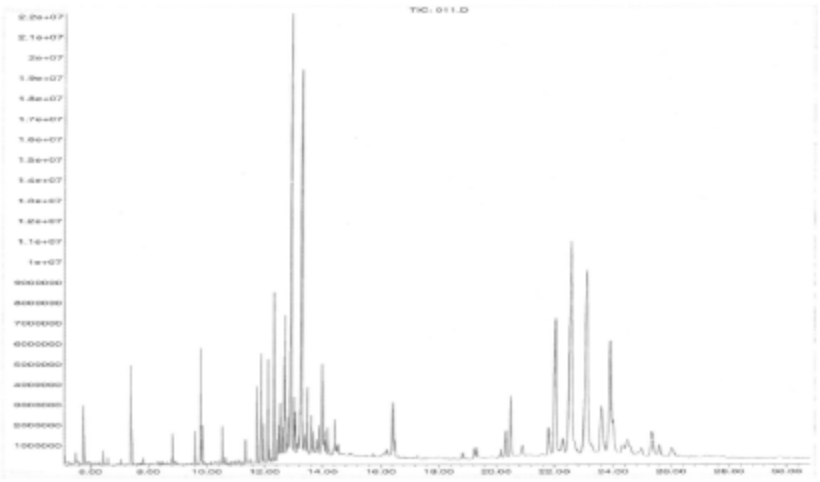
**Surrogate Spike

Recovery Ranges from 83 – 107 %

19

ThermoFisher SCIENTIFIC

Extraction Method 1 – Mussel Tissue



20

Interference due to Co-Extractable Compounds

ThermoFisher SCIENTIFIC

Extraction Method 2 - Mussel Tissue

Table 3. Data for mussel samples extracted by Method 2.

PAH Recoveries - Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
Nitrobenzene-d5**	84.8	0.11	12.46
2-Fluorobiphenyl**	112.3	0.06	5.12
p-Terphenyl-d14**	105.8	0.10	9.09
Naphthalene	72.5	0.08	10.85
Acenaphthylene	82.3	0.09	10.50
Acenaphthene	81.2	0.07	9.20
Fluorene	79.5	0.06	7.41
Phenanthrene	95.3	0.06	6.49
Anthracene	85.2	0.07	8.01
Fluoranthene	90.8	0.08	8.43
Pyrene	86.2	0.07	7.62
Benzo(a)anthracene	84.7	0.09	10.48
Chrysene	114.0	0.11	9.99
Benzo(b)fluoranthene	89.2	0.07	7.97
Benzo(k)fluoranthene	84.7	0.05	5.33
Benzo(a)pyrene	77.7	0.08	10.39
Benzo(ghi)perylene	87.5	0.14	16.46
Dibenzo(a,h)anthracene	77.7	0.08	10.85
Indeno(1,2,3-cd) pyrene	83.5	0.07	7.97
PCB Recoveries – Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
2,4,5,6-tetrachloro-m-xylene**	94.67	3.75	3.96
Aroclor 1254	85.68	1.87	2.18

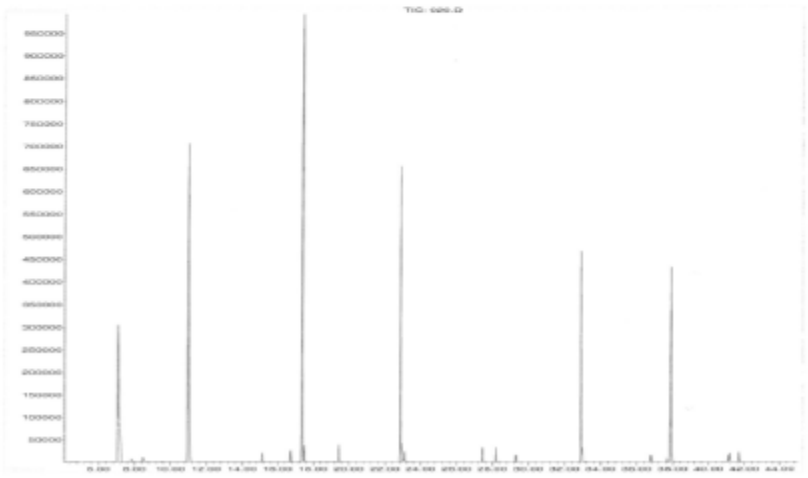
**Surrogate Spike

Recovery Ranges from 83 – 114%

21

ThermoFisher SCIENTIFIC

Extraction Method 2 – Mussel Tissue

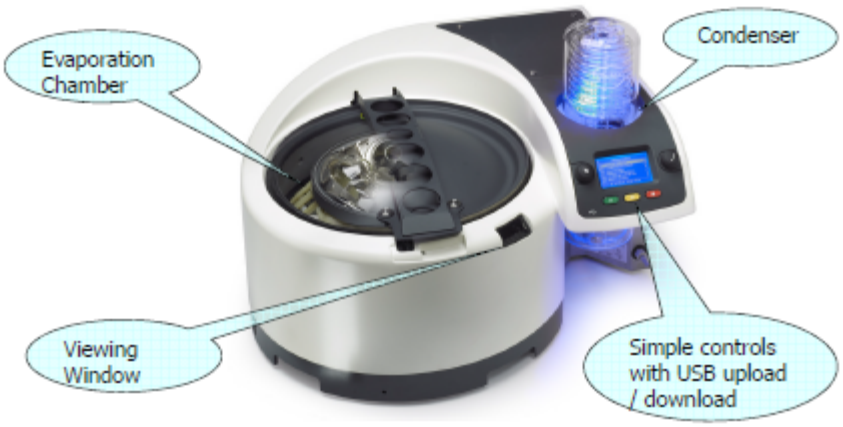


22

No Interferences from Co-Extracting Compounds

ThermoFisher SCIENTIFIC

System Overview



23

ThermoFisher SCIENTIFIC

Working principle

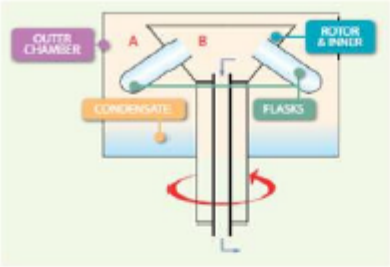


- Developed to handle larger numbers or higher volume samples
- Dries or concentrate up to 6 x 450 mL flasks or 18 x 60 mL ASE tubes
- Sample Genie Flasks that evaporate or concentrate into multiple vial sizes
- **Why spend time on evaporation when it can be used for science?**

24

ThermoFisher SCIENTIFIC

Working Principle



- Samples are loaded into the rotor and placed under vacuum (B);
- Low pressure steam is used to heat the samples (A);
- The steam condenses on the flasks/tubes, which are cold due to the solvent(s) boiling inside them (A);
- Condensate is thrown off the spinning flask and recycled (A).

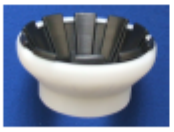
25

ThermoFisher SCIENTIFIC

Sample Genie For Evaporating or Concentrating



- Dries sample directly into storage vial
- Works with vials from 12 – 28 mm diameter & up 70 mm height





- Concentrates sample into GC autosampler vials
- Vial is insulated so that only solvent in flask evaporates



28

ThermoFisher SCIENTIFIC

60 mL ASE Vials for Direct Transfer

- Pucks accept 60 mL ASE vials
- Each puck accepts 3 vials
  - Total capacity per system is 18 vials
- Working volume is 55 mL each



27

ThermoFisher SCIENTIFIC

60 mL ASE Vial Flip Flop



- GC Vial is inserted into the flip flop funnel
- GC vial is insulted to prevent boiling of solvent
- ASE vial is inserted directly into the Rotor
- GC vial is placed directly into autosampler once complete

28

ThermoFisher SCIENTIFIC

How Fast Does it Go?

	100 mL	250 mL	450 mL
DCM (dichloromethane)	10 min	20 min	35 min
Methanol	20 min	45 min	1.5 h
DMF	30 min	1 h	2 h
Water	35 min	1.5 h	2 h
Water/ACN (1:1)	1 h	1.5 h	3 h

Times are given for complete dryness for 6 flasks simultaneously evaporated

29

ThermoFisher SCIENTIFIC

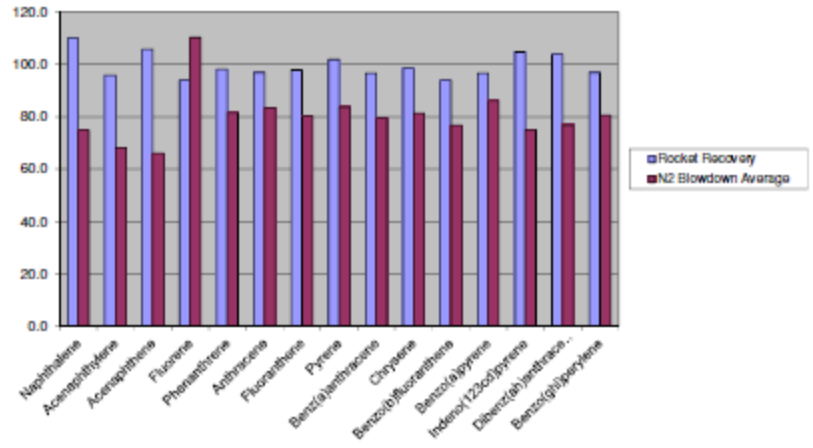
What About Solvent Recovery?

Solvent	Recovery
DCM	80%
DMF	99%
Ethanol	99%
Methanol	98%
Water	99%
Water/acetonitrile	98%

30

ThermoFisher SCIENTIFIC

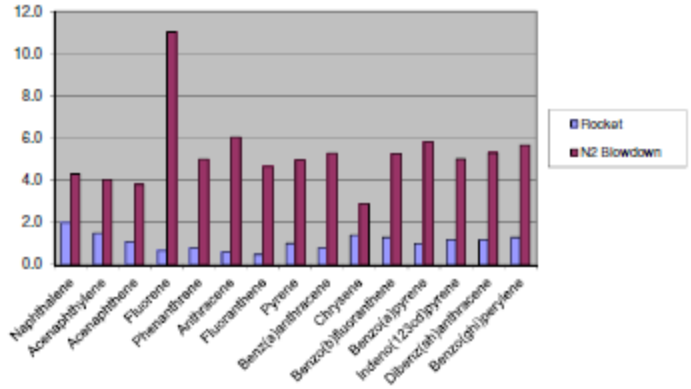
PAH Recoveries: Rocket v. Nitrogen Blow down



31

ThermoFisher SCIENTIFIC

PAH Recoveries: Standard Deviations



32

ThermoFisher SCIENTIFIC

Conclusions

- The use of Accelerated Solvent Extraction increases extraction efficiency of PAHs and PCBs from two different environmental matrices.
- Both classes of compounds can be extracted under a single set of conditions within the same run in less than 45 min.
- The ASE Method is optimized to remove co-extracting compounds that cause interferences in the analysis.
- The use of alumina for in-cell clean up eliminates the need to GPC clean up prior to analysis.

33

ThermoFisher SCIENTIFIC

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) Extraction Approach and Comprehensive Two - Dimensional Gas Chromatography of Persistent Organic Pollutants in Human Breast Milk (Advances in Sample Preparation and Clean-up)

Christopher Rattray
Restek

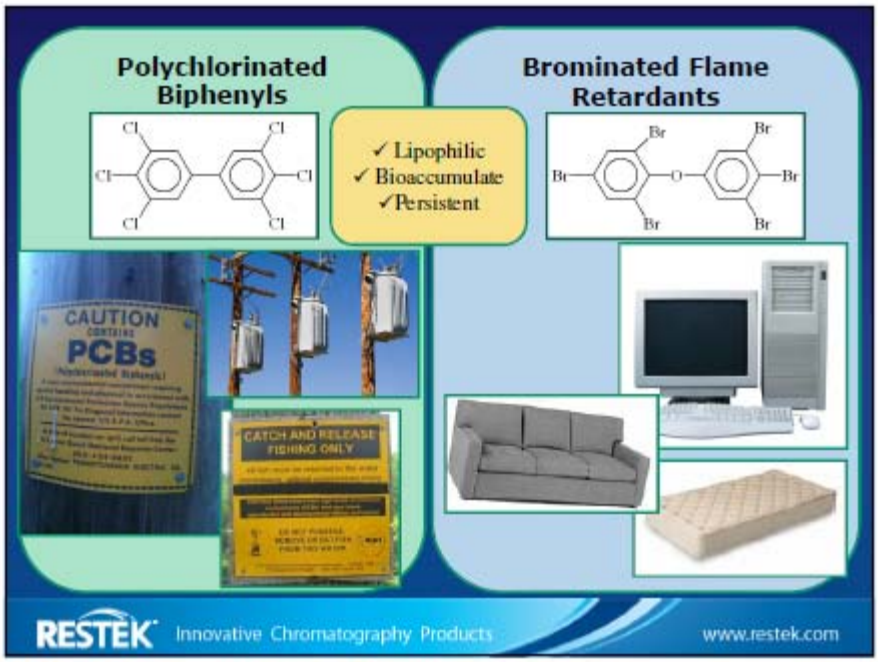
Abstract

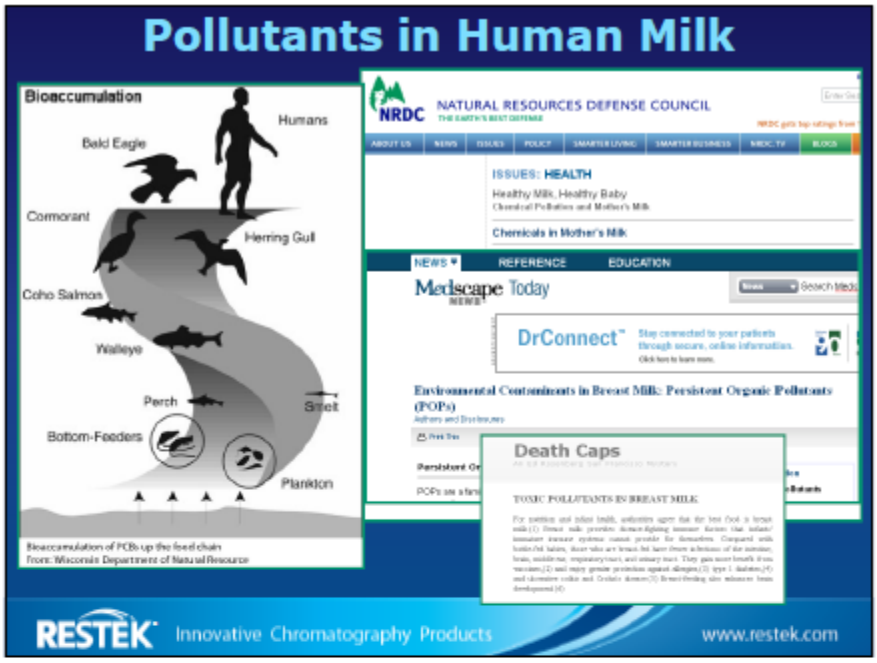
Persistent organic pollutants (POPs) are a group of chemicals that include brominated flame retardants (BFRs) and polychlorinated biphenyls (PCBs). These chemicals can be distributed throughout the environment through soil, water, and air contamination and once in the environment do not readily break down. Due to the lipophilic nature of these components they accumulate in the fatty tissue of animals and bioaccumulate up the food chain. According to the World Health Organization human breast milk is an ideal matrix to monitor the levels of POPs in not only the mother and infant, but also as a key indicator of the levels of these chemicals in the local environment.

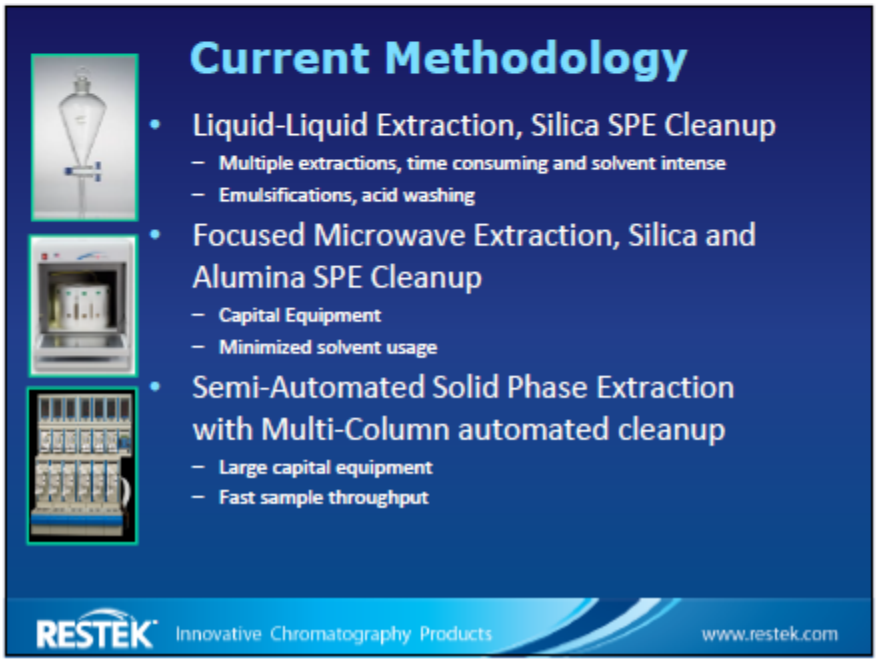
Current sample preparation for the analysis of POPs typically involves liquid-liquid or pressurized fluid extraction with extensive clean-up. These methods often include expensive equipment and/or large amounts of solvent usage. The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) methodology was developed for the determination of multi-residue pesticides in fruits and vegetables. The low solvent consumption and multi-residue approach of QuEChERS may be an attractive sample preparation alternative for biomonitoring efforts for halogenated POPs in human breast milk.

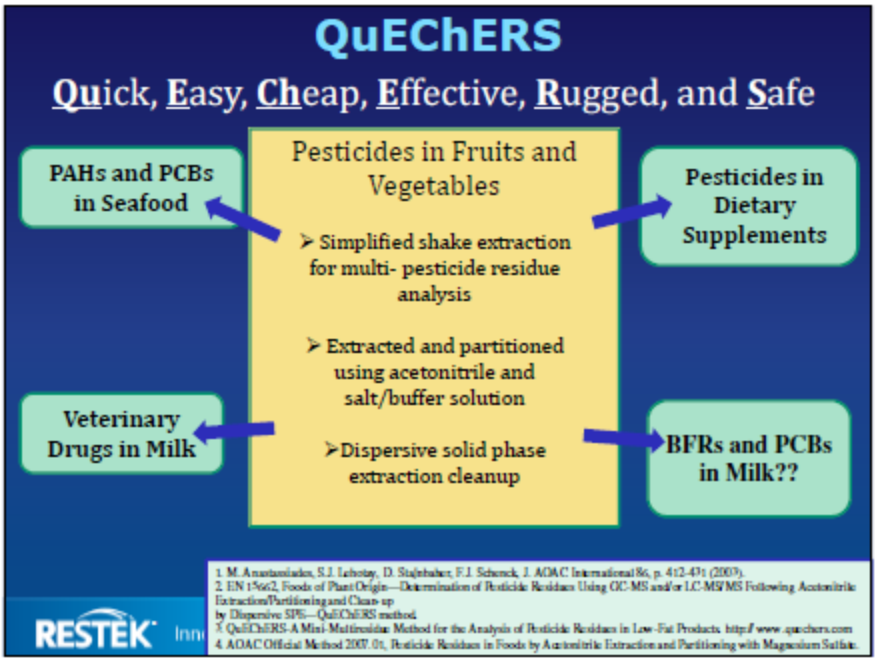
Comprehensive two-dimensional gas chromatography (GCxGC) with an electron capture detector (ECD) may offer a more cost-effective alternative than high resolution mass spectrometry (HRMS), due to the sensitivity of the ECD, coupled with the selectivity afforded by a multidimensional separation. Alternatively, GCxGC with a time of flight mass spectrometer (TOFMS) utilizes full mass acquisition for non-target analysis. Method performance was evaluated by analyzing a NIST standard reference material of human milk.

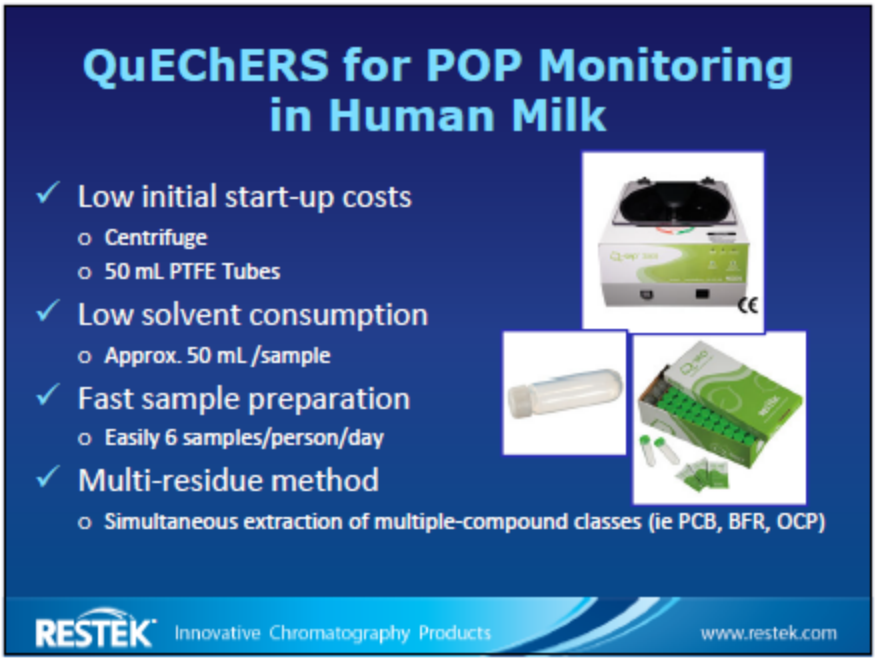

The QuEChERS Extraction Approach and Comprehensive Two-Dimensional Gas Chromatography of Persistent Organic Pollutants in Human Breast Milk
Chris Rattray, Michelle Misselwitz, Jack Cochran and Julie Kowalski
RESTEK
Innovative Chromatography Products
www.restek.com

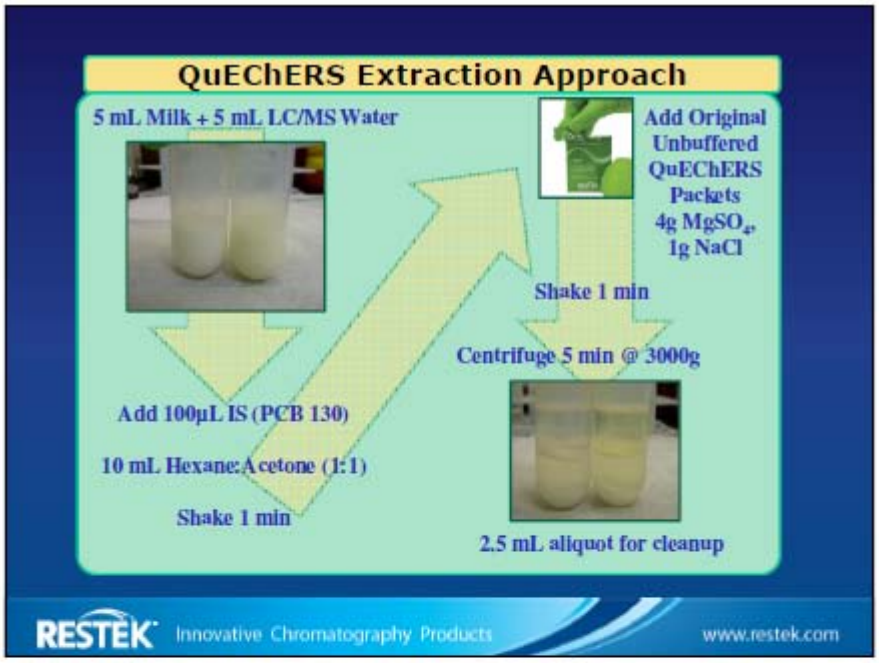

Polychlorinated Biphenyls
Brominated Flame Retardants
✓ Lipophilic
✓ Bioaccumulate
✓Persistent
CAUTION
PCBs
CATCH AND RELEASE
FISHING ONLY
RESTEK
Innovative Chromatography Products
www.restek.com

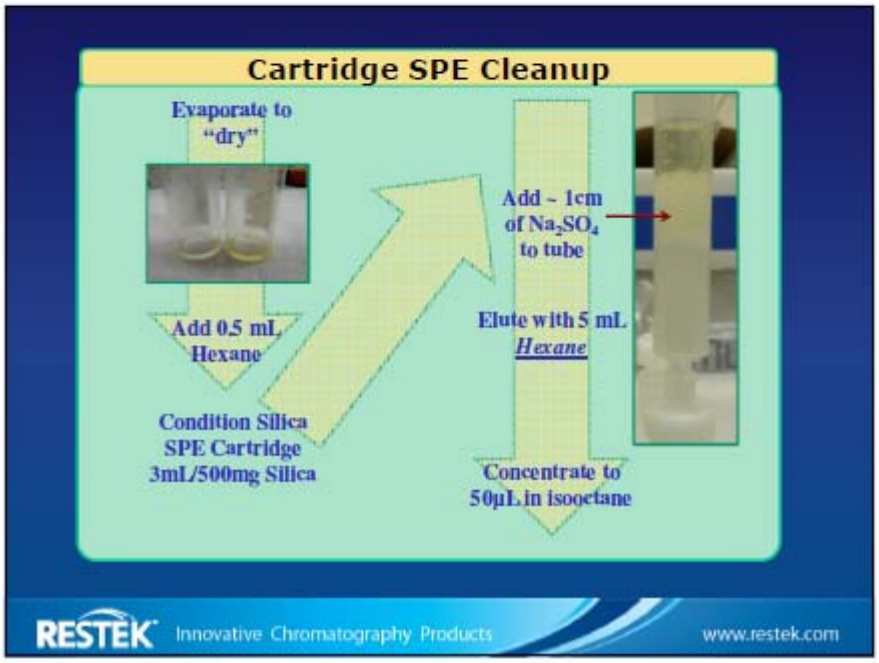

Pollutants in Human Milk
Bioaccumulation
Humans
Bald Eagle
Cormorant
Herring Gull
Coho Salmon
Walleye
Perch
Smelt
Bottom-Feeders
Plankton
Bioaccumulation of PCBs up the food chain
From: Wisconsin Department of Natural Resource
NRDC
NATURAL RESOURCES DEFENSE COUNCIL
ISSUES: HEALTH
Healthy Milk, Healthy Baby
Chemicals in Mother's Milk
NEWS
REFERENCE
EDUCATION
Medscape Today
DrConnect™
Environmental Contaminants in Breast Milk: Persistent Organic Pollutants (POPs)
Death Caps
TOXIC POLLUTANTS IN BREAST MILK
RESTEK
Innovative Chromatography Products
www.restek.com


Current Methodology
• Liquid-Liquid Extraction, Silica SPE Cleanup
– Multiple extractions, time consuming and solvent intense
– Emulsifications, acid washing
• Focused Microwave Extraction, Silica and Alumina SPE Cleanup
– Capital Equipment
– Minimized solvent usage
• Semi-Automated Solid Phase Extraction with Multi-Column automated cleanup
– Large capital equipment
– Fast sample throughput
RESTEK
Innovative Chromatography Products
www.restek.com


QuEChERS
Quick, Easy, Cheap, Effective, Rugged, and Safe
PAHs and PCBs in Seafood
Pesticides in Fruits and Vegetables
➢ Simplified shake extraction for multi- pesticide residue analysis
➢ Extracted and partitioned using acetonitrile and salt/buffer solution
➢ Dispersive solid phase extraction cleanup
Pesticides in Dietary Supplements
Veterinary Drugs in Milk
BFRs and PCBs in Milk??
RESTEK
1. M. Anastasiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenck, J. AOAC International 86, p. 412-431 (2003).
2. EN 15662, Foods of Plant Origin—Determination of Pesticide Residues Using GC-MS and/or LC-MS/MS Following Acetonitrile Extraction/Partitioning and Clean-up by Dispersive SPE—QuEChERS method.
3. QuEChERS-A Mini-Multiresidue Method for the Analysis of Pesticide Residues in Low-Fat Products. http://www.quechers.com
4. AOAC Official Method 2007.01, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate.


QuEChERS for POP Monitoring in Human Milk
✓ Low initial start-up costs
o Centrifuge
o 50 mL PTFE Tubes
✓ Low solvent consumption
o Approx. 50 mL /sample
✓ Fast sample preparation
o Easily 6 samples/person/day
✓ Multi-residue method
o Simultaneous extraction of multiple-compound classes (ie PCB, BFR, OCP)
RESTEK Innovative Chromatography Products www.restek.com


QuEChERS Extraction Approach
5 mL Milk + 5 mL LC/MS Water
Add Original Unbuffered QuEChERS Packets 4g $MgSO_4$, 1g NaCl
Shake 1 min
Centrifuge 5 min @ 3000g
Add 100µL IS (PCB 130)
10 mL Hexane:Acetone (1:1)
Shake 1 min
2.5 mL aliquot for cleanup
RESTEK Innovative Chromatography Products www.restek.com


Cartridge SPE Cleanup
Evaporate to "dry"
Add ~ 1cm of Na_2SO_4 to tube
Add 0.5 mL Hexane
Elute with 5 mL Hexane
Condition Silica SPE Cartridge 3mL/500mg Silica
Concentrate to 50µL in isooctane
RESTEK Innovative Chromatography Products www.restek.com

Instrument Conditions

GC X GC Conditions

Injection

Temp: 250°C
Injection: 1 µL fast, splitless (1.0 min)
Liner: Sky Single Taper w/ wool

Column

Rxi-XLB 30m x 0.25mmID x 0.25µm
Rxi-17Sil MS 1.0m x 0.25mm x 0.25µm

Conditions

Oven: 80°C (1 min) to 120°C @ 10°C/min to 300°C @ 3°C/min
Secondary Oven Offset: 5°C
Carrier: He, constant flow 1.4 mL/min
Modulator Temperature Offset: 20°C
Modulation Time: 3 sec

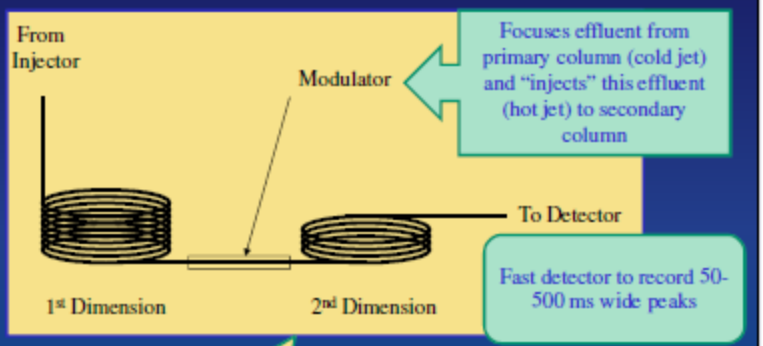
LECO Pegasus® TOFMS Conditions

Transfer Line Temperature: 300°C
Source Temperature: 225°C
Electron Ionization: 70 eV
Stored Mass Range: 45 to 750 u
Acquisition Rate: 50 spectra/sec

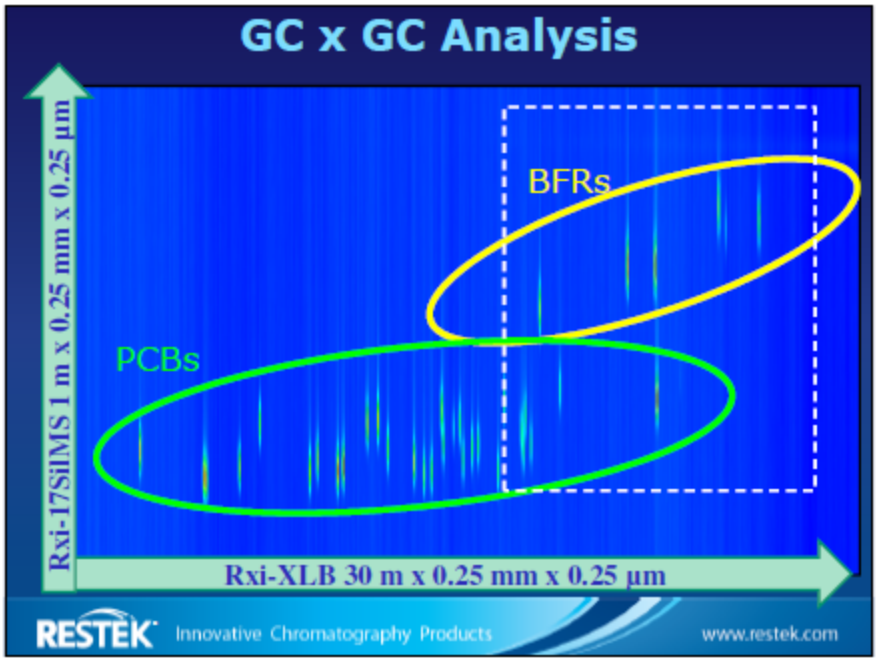


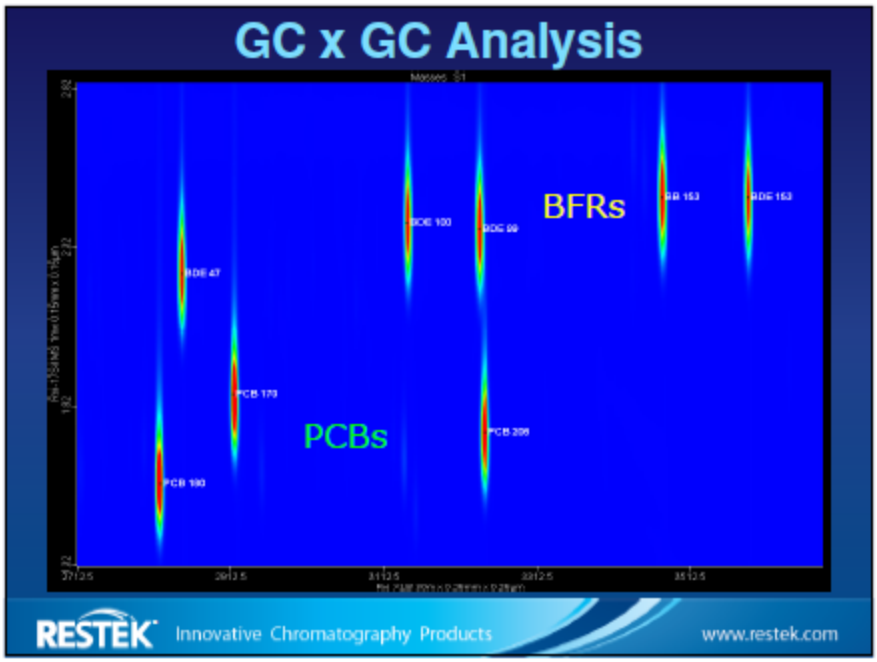
RESTEK Innovative Chromatography Products www.restek.com

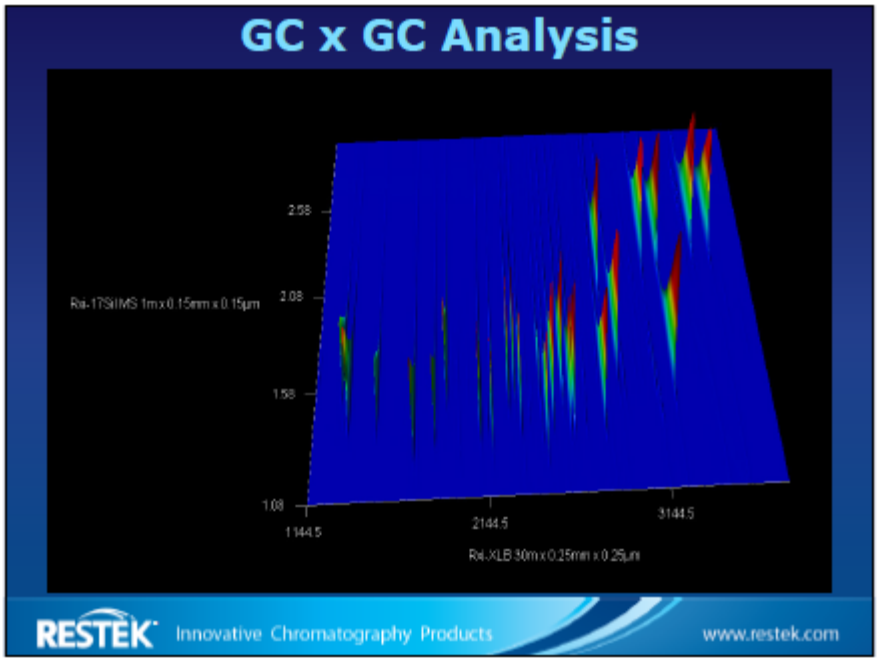
Basics of GCxGC

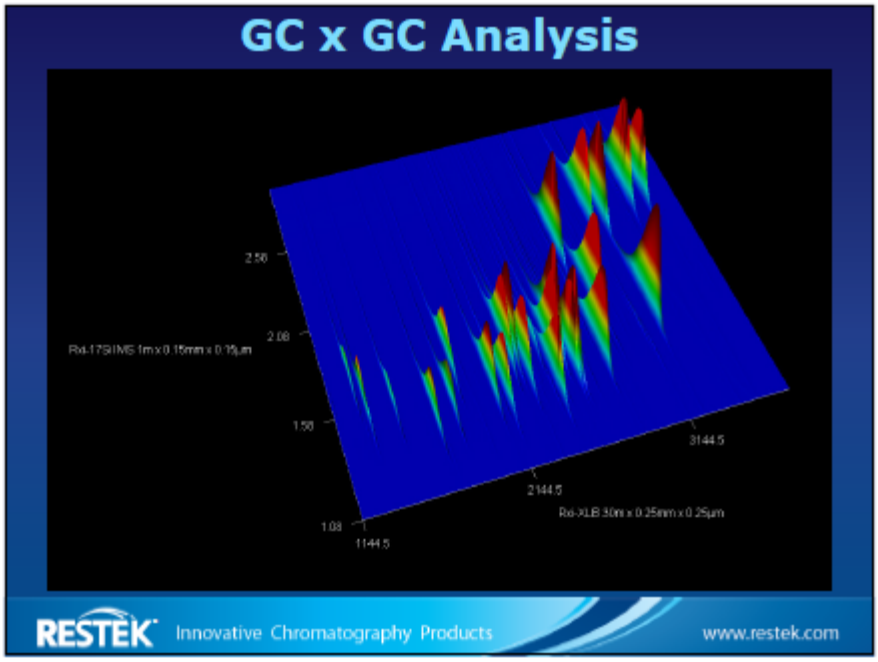


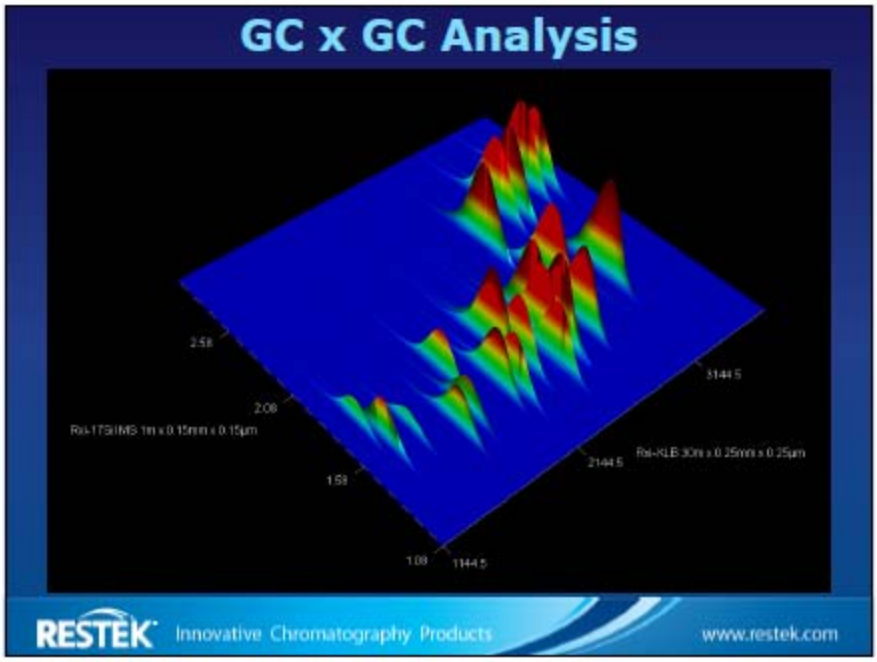
RESTEK Innovative Chromatography Products www.restek.com

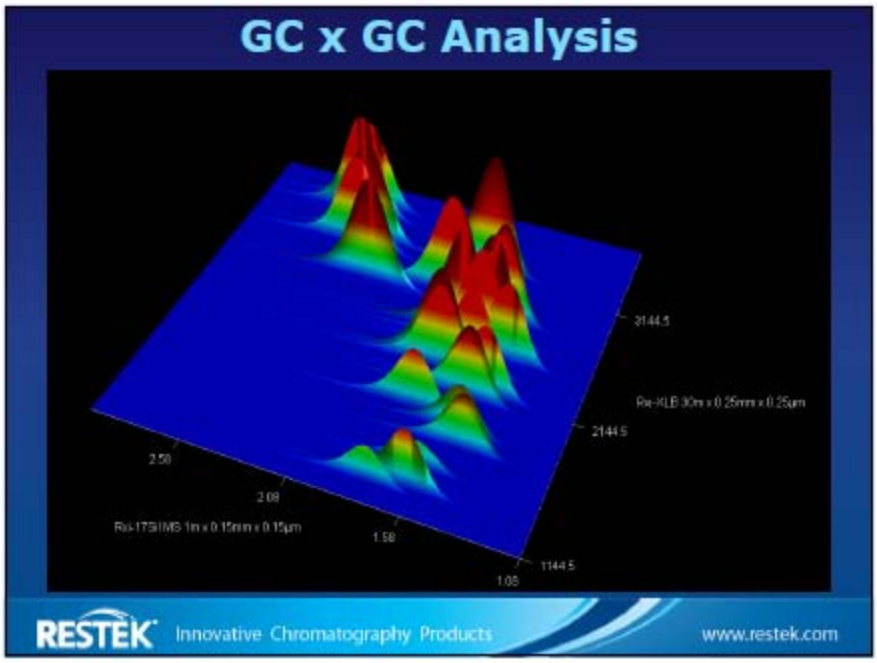

GC x GC Analysis
Rxi-17SilMS 1 m x 0.25 mm x 0.25 µm
BFRs
PCBs
Rxi-XLB 30 m x 0.25 mm x 0.25 µm
RESTEK
Innovative Chromatography Products
www.restek.com

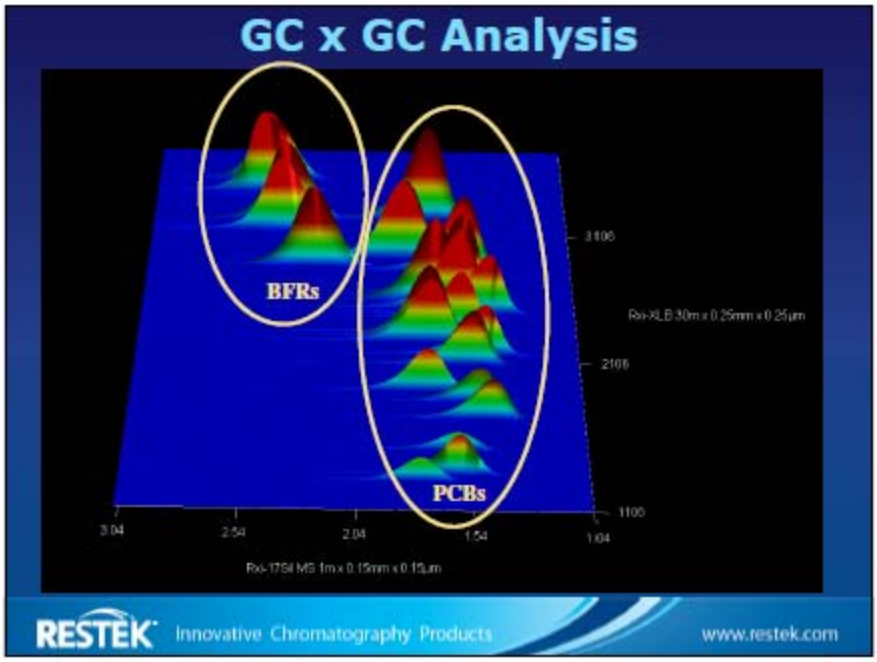

GC x GC Analysis
BFRs
PCBs
RESTEK
Innovative Chromatography Products
www.restek.com

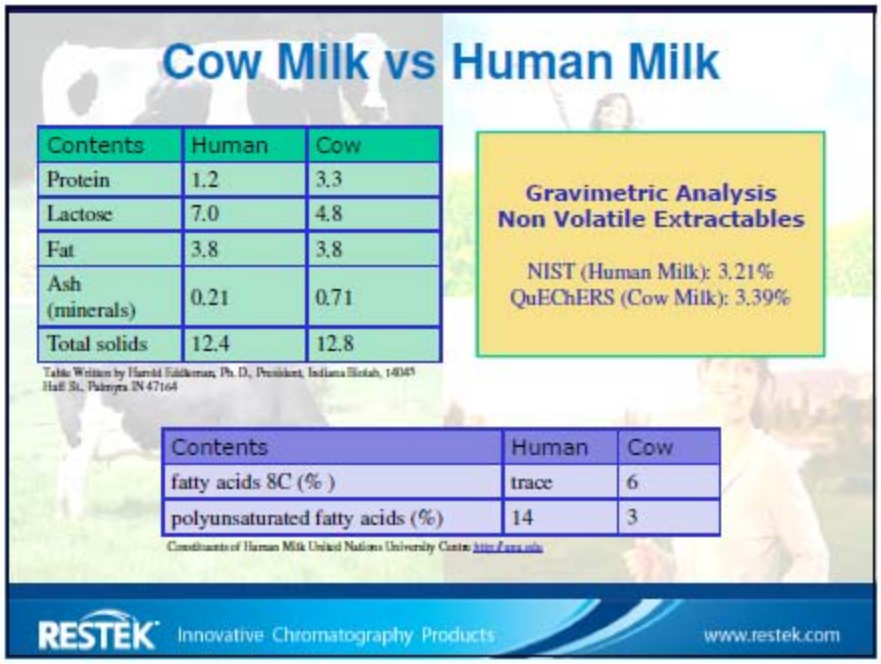

GC x GC Analysis
2.58
2.08
1.58
1.08
Rxi-17SilMS 1m x 0.15mm x 0.15µm
1144.5
2144.5
3144.5
Rxi-XLB 30m x 0.25mm x 0.25µm
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC Analysis
2.58
2.08
1.58
1.08
Rxi-17SilMS 1m x 0.15mm x 0.15µm
1144.5
2144.5
3144.5
Rxi-XLB 30m x 0.25mm x 0.25µm
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC Analysis
2.58
2.08
1.58
1.08
1144.5
2144.5
3144.5
Rxi-17SilMS 1m x 0.15mm x 0.15µm
Rxi-XLB 30m x 0.25mm x 0.25µm
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC Analysis
3144.5
Rxi-XLB 30m x 0.25mm x 0.25µm
2144.5
2.58
2.08
Rxi-17SilMS 1m x 0.15mm x 0.15µm
1.58
1144.5
1.08
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC Analysis
BFRs
PCBs
3.04
2.54
2.04
1.54
1.04
3100
2100
1100
RESTEK
Innovative Chromatography Products
www.restek.com


Cow Milk vs Human Milk
Contents | Human | Cow
Protein | 1.2 | 3.3
Lactose | 7.0 | 4.8
Fat | 3.8 | 3.8
Ash (minerals) | 0.21 | 0.71
Total solids | 12.4 | 12.8
Gravimetric Analysis
Non Volatile Extractables
NIST (Human Milk): 3.21%
QuEChERS (Cow Milk): 3.39%
Contents | Human | Cow
fatty acids 8C (%) | trace | 6
polyunsaturated fatty acids (%) | 14 | 3
RESTEK
Innovative Chromatography Products
www.restek.com

Cow Milk - Percent Recoveries (n=3)

	0.1 ppb	0.5 ppb	1 ppb	10 ppb
PCB 18	138	103	152	90
PCB 52	131	122	163	97
PCB 44	111	107	157	98
PCB 66	108	112	165	99
PCB 101	114	111	162	101
PCB 110	110	112	167	102
PCB 151	109	111	161	103
PCB 153	114	116	154	104
PCB 138	149	118	155	106
PCB 187	118	116	155	106
PCB 183	110	118	154	106
PCB 180	111	124	144	107
BDE 47	186	140	83	98
PCB 170	114	125	138	107
BDE 100	131	167	63	96
BDE 99	130	154	53	94
PCB 206	114	136	101	104
PBB 153	107	175	38	86
BDE 153	119	180	32	82
Average	**122**	**129**	**126**	**99**
%RSD	**16**	**18**	**38**	**7**

RESTEK Innovative Chromatography Products www.restek.com

Blanks

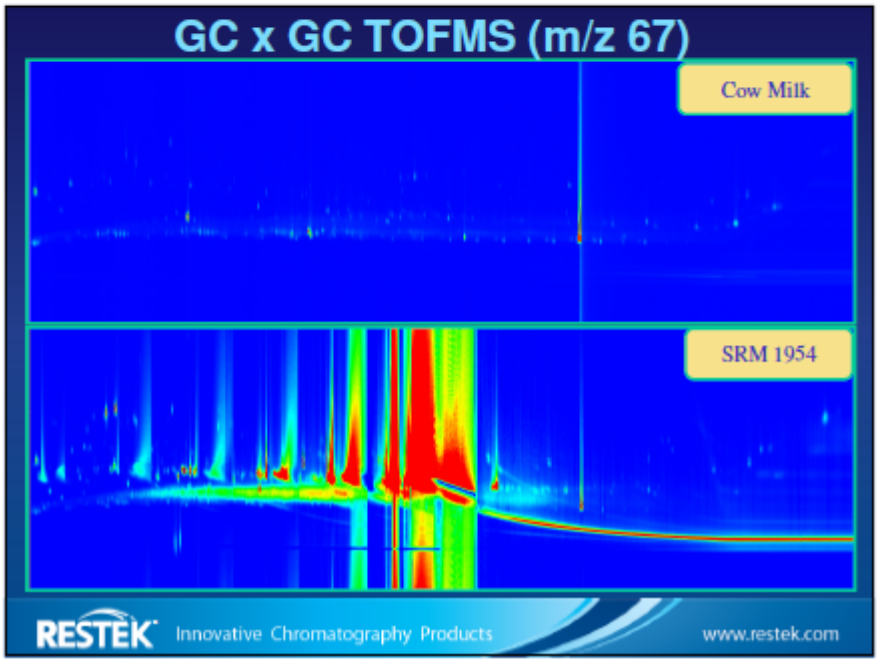
	LC/MS Water	
	ng/kg	pg on-column
PCB 52	3.88	0.97
PCB 99	3.28	0.82
PCB 110	5.2	1.3
PCB 118	4.5 CR1	1.13
PCB 153	2.32	0.58
PCB 105	1.48	0.37
BDE 47	67.4	16.9
BDE 100	4.48	1.12
BDE 99	29.4	7.34

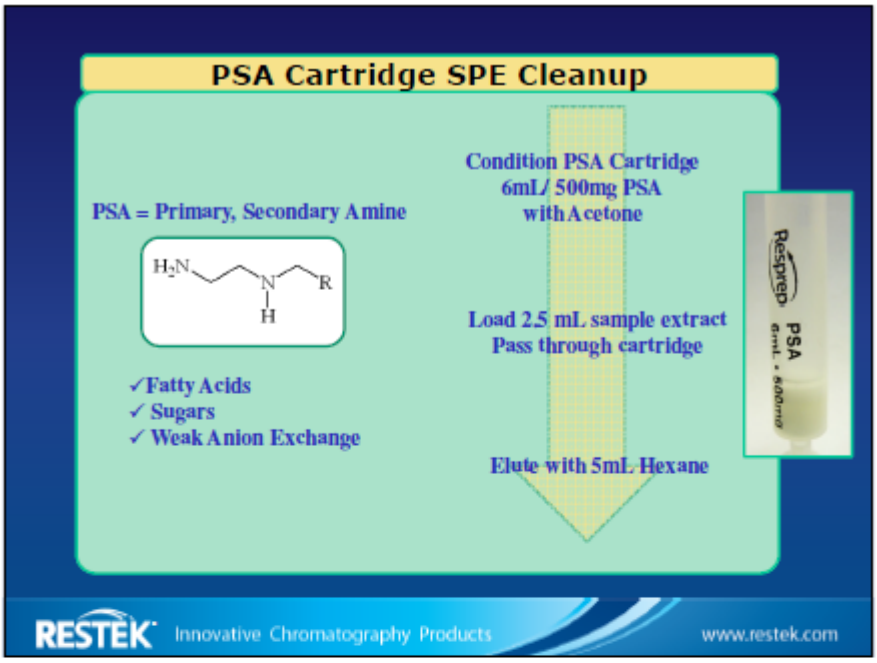
RESTEK Innovative Chromatography Products www.restek.com

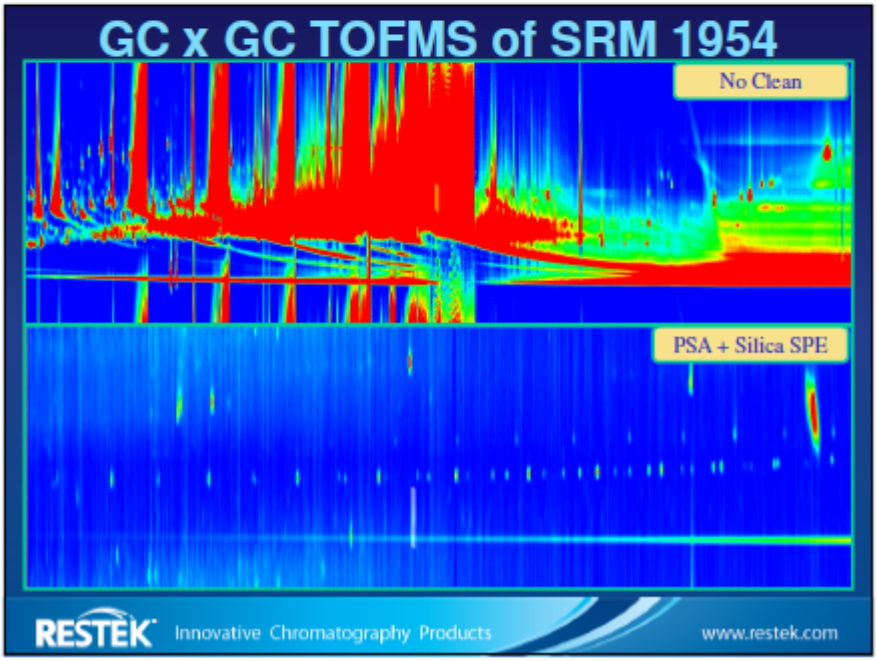
Slide 20

CR1 sig figs 2.0
Chris Rattray, 8/1/2013


Fortified Human Milk – SRM 1954
National Institute of Standards & Technology
Certificate of Analysis
Standard Reference Material® 1954
Organic Contaminants in Fortified Human Milk
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC TOFMS (m/z 67)
Cow Milk
SRM 1954
RESTEK
Innovative Chromatography Products
www.restek.com


PSA Cartridge SPE Cleanup
PSA = Primary, Secondary Amine
H_2N
N
H
R
✓Fatty Acids
✓ Sugars
✓ Weak Anion Exchange
Condition PSA Cartridge
6mL/ 500mg PSA
with Acetone
Load 2.5 mL sample extract
Pass through cartridge
Elute with 5mL Hexane
Resprep
PSA
RESTEK
Innovative Chromatography Products
www.restek.com


GC x GC TOFMS of SRM 1954
No Clean
PSA + Silica SPE
RESTEK
Innovative Chromatography Products
www.restek.com

	QuEChERS (n=3) (ng/kg)	NIST Certified (ng/kg)	Percent Error
PCB 28	562	519	8
PCB 74	643	563	14
PCB 66	**384**	**428**	**10**
PCB 99	655	558	17
PCB 110	**399**	**458**	**13**
PCB 118	530	597	11
PCB 146	503	492	2
PCB 153	**1080**	**977**	**11**
PCB 105	360	482	25
PCB 138	**982**	**639**	**54**
PCB 178	514	449	14
PCB 167	478	467	2
PCB 177	470	447	5
PCB 156	516	511	1
PCB 172	578	443	31
PCB 157	450	467	4
PCB 180	**896**	**696**	**29**
BDE 47	**2970**	**2570**	**16**
BDE 100	**1220**	**1280**	**5**
BDE 99	**637**	**739**	**14**
BDE 154	414	464	11
PBB 153	**297**	**474**	**37**
BDE 153	**1340**	**1440**	**7**

RESTEK Innovative Chromatography Products www.restek.com

National Institute of Standards & Technology

Certificate of Analysis

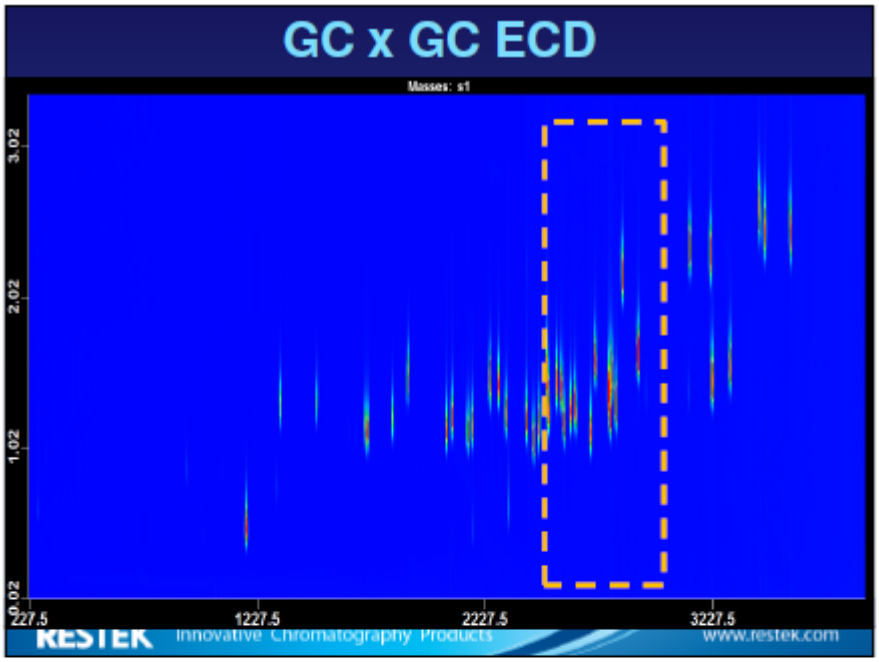
Standard Reference Material® 1953

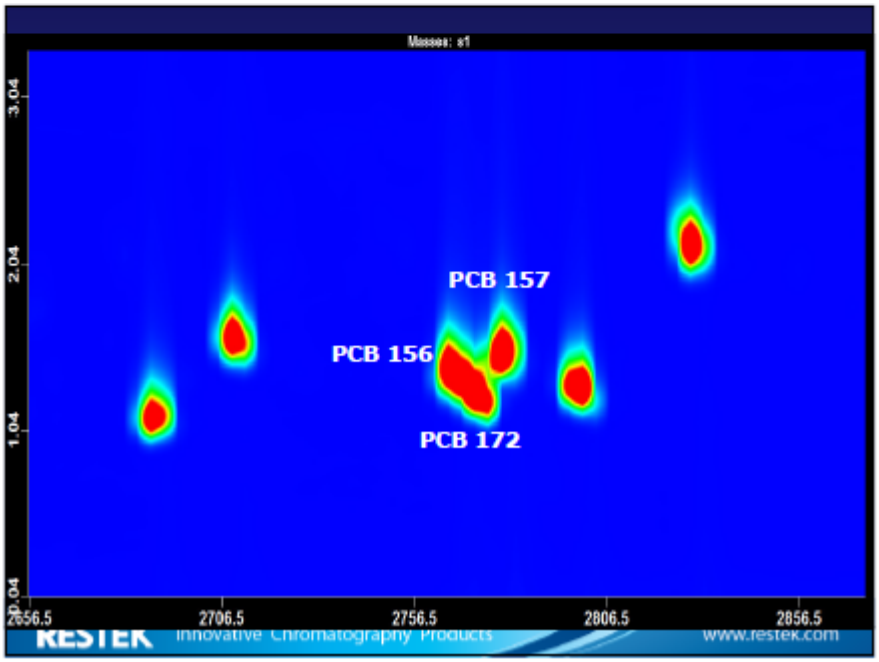
Organic Contaminants in Non-Fortified Human Milk

SRM 1953

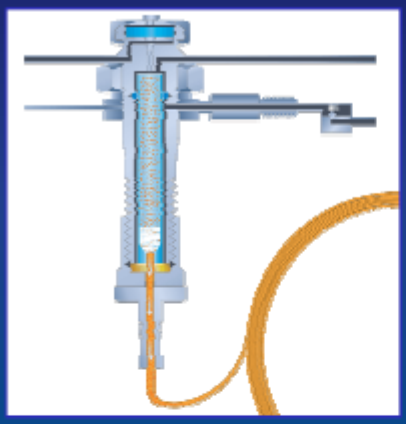
- ✓Non-fortified milk
- ✓Target concentration 10x less than fortified sample
  - Final concentration in low pg/µL amt

RESTEK Innovative Chromatography Products www.restek.com


GC x GC ECD
Masses: s1
3.02
2.02
1.02
0.02
227.5
1227.5
2227.5
3227.5
RESTEK
Innovative Chromatography Products
www.restek.com


Masses: s1
3.04
2.04
1.04
0.04
PCB 157
PCB 156
PCB 172
2656.5
2706.5
2756.5
2806.5
2856.5
RESTEK
Innovative Chromatography Products
www.restek.com

Concurrent Solvent Recondensation Large Volume Splitless Injection



No modifications necessary to inject up to 30 µL on Agilent split/splitless injection port

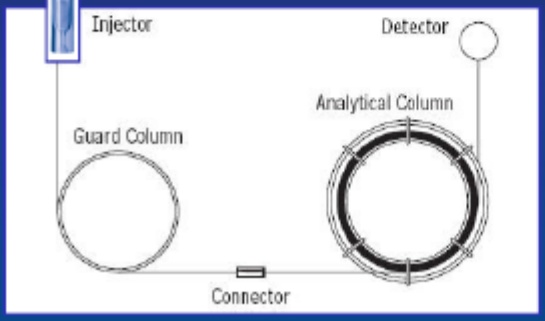
P. Magni, T. Porzano, Concurrent Solvent Recondensation Large Sample Volume Splitless Injection, J. Sep. Sci. 26 (2003) 1491.

Patent No: US 6,955,709 B2.

RESTEK Innovative Chromatography Products www.restek.com

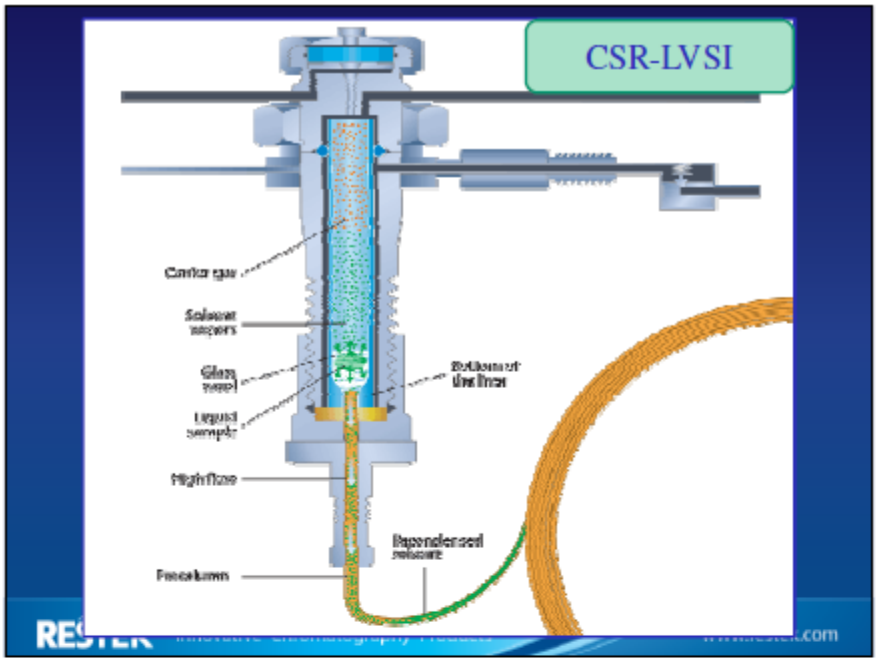


- ✓ Fast autosampler injection
- ✓ Single taper/gooseneck inlet liner with wool
- ✓ 5 meter guard column / retention gap
- ✓ Initial oven temperature below boiling point of solvent





RESTEK Innovative Chromatography Products www.restek.com



Instrument Conditions

GC X GC Conditions

Injection

Temp: 250°C
Injection: 10 µL fast, splitless (1.0 min)
Liner: Sky Single Taper w/ wool

Column

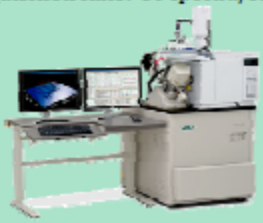
IP Deact Guard 5m x 0.53mmID
Rxi-XLB 30m x 0.25mmID x 0.25µm
Rxi-17Sil MS 1.0m x 0.25mm x 0.25µm

Conditions

Oven: 80°C (1 min) to 120°C @ 10°C/min to 300°C @ 3°C/min
Secondary Oven Offset: 5°C
Carrier: He, constant flow 1.4 mL/min
Modulator Temperature Offset: 20°C
Modulation Time: 3 sec

LECO Pegasus® TOFMS Conditions

Transfer Line Temperature: 300°C
Source Temperature: 225°C
Electron Ionization: 70 eV
Stored Mass Range: 45 to 750 u
Acquisition Rate: 50 spectra/sec



RESTEK Innovative Chromatography Products www.restek.com

	QuEChERS (n=3) (ng/kg)	NIST Certified (ng/kg)	Percent Error
PCB 28	46.7	63.1	26
PCB 74	117	149	21
PCB 66	31.6	32.8	4
PCB 99	109	138	21
PCB 110	19.9	12.4	61
PCB 118	**198**	**213**	**7**
PCB 146	42.4	55.6	24
PCB 153	459	480	4
PCB 105	**47.8**	**45.7**	**5**
PCB 138	412	317	30
PCB 178	18.5	22.2	16
PCB 167	**15.4**	**15.8**	**3**
PCB 177	18.1	24.5	26
PCB 156	**51.9**	**59.7**	**13**
PCB 172	11.3	14.8	24
PCB 157	**14.5**	**14.6**	**0**
PCB 180	251	236	7
BDE 47	2700	2200	23
BDE 100	985	839	17
BDE 99	392	342	15
BDE 154	40.6	42.8	5
PBB 153	30.9	36.6	16
BDE 153	968	984	2

RESTEK Innovative Chromatography Products www.restek.com

QuEChERS Extraction with PSA and Silica SPE Cleanup

- **Overview**
  - 5 mL Milk + 5 mL Water
  - 10 mL Hexane:Acetone (1:1)
  - Unbuffered QuEChERS Extraction
  - PSA cSPE pass through
  - Silica cSPE cleanup
  - GC x GC TOFMS analysis

Summary

- ✓ Good agreement with SRM certified values
  - Avg Error = 15%
- ✓ Low solvent usage
  - ~ 50 mL total
- ✓ Cost Effective

RESTEK Innovative Chromatography Products www.restek.com

Conclusion

- The QuEChERS extraction approach using Hexane:Acetone is a viable approach for multi-analyte screening in human milk
- Using a combination of PSA then Silica cSPE provides the needed removal of fatty acid interferences in human milk
- Using GC x GC allows simultaneous determination of PCBs and BFRs
- Concurrent solvent recondensation – large volume splitless injection can greatly increase detectability without the need for a specialized injection port. However extract cleanup efficiency may need to be revisited to increase system robustness.

RESTEK Innovative Chromatography Products www.restek.com

Thank You!



RESTEK Innovative Chromatography Products www.restek.com

How Solid Phase Chemistries Are Enabling Broader Adoption of SPE in Environmental Applications

Kory Kelly
Phenomenex

Abstract

Recent separation technology advancements, particularly those delivering more sophisticated analytical instrumentation, have opened new possibilities for environmental monitoring. As analytical technologies improve, laboratories will have the ability to detect harmful toxins and contaminants that had previously gone undetected. However, new methods may fall short of unlocking the full potential of these new LC/MS/MS and GC/MS technologies if they do not also adopt advanced sample preparation technologies in parallel.
New pollutants continue to emerge, elevating demands for versatile sample preparation methods using a single SPE sorbent chemistry able to encompass the extraction of a wide spectrum of analytes. As new Solid Phase Extraction (SPE) sorbent chemistries and unique analyte extraction mechanisms are discovered, the broader adoption of SPE in environmental applications grows.

This presentation will examine how sample preparation techniques have evolved to complement various environmental analyses. Comparisons will be drawn between traditional sample preparation techniques (i.e. LLE, soxhlet, etc) and various formats of SPE (i.e. tubes, disks, and dispersive). Further comparisons will be drawn between the original SPE “sorbent flavor” and the recent developments of specialty sorbents such as those designed to overcome challenges of specific environmental applications like removing humic acid interferences from PAH samples and separating aliphatic hydrocarbons from aromatic hydrocarbons. By adopting fully optimized procedures from sample extraction through analysis, laboratories can more effectively improve their entire analyses as opposed to advancing a single aspect. Chemistry is still king in the field of separation science and stands as the pivotal source for application improvements.

Broader Adoption of SPE in Environmental Applications Enabled by Selective SPE Chemistries



Kory Kelly and Allen Misa

Environmental Monitoring
Still evolving

- New emerging harmful pollutants
- New sources of pollutants
- Greater need for:
  - More versatile sample preparation for wider range of analytes
  - More targeted extraction of analytes
- More demanding regulatory requirements:
  - Improved LOQ and LOD
  - Higher throughput ability



Will require innovative solutions and support

Separation Technology Advancements

- Use of more sophisticated instruments
- Open new possibilities for environmental monitoring
- Greater ability to detect previously undetectable harmful toxins and pollutants
- Separation advancement not limited to instruments
  - Use of unique SPE chemistries allow improved analytical capability



Sample Preparation

- Clean up and removal of interferences
- Concentration of target analytes
- Solvent switching capabilities
- Specifically extract targeted compound
- Improve system and instrumentation lifetime
- Improve analytical results



Sample Preparation Technique

Liquid-Liquid Extraction

- Benefits
  - Non-specific technique, could be useful when analyzing a wide range of compounds
  - **Easy procedure**
- Challenges
  - Low recoveries (emulsions)
  - Contamination
    - Signal to noise
    - Instrument maintenance
  - Labor intensive
  - Large solvent usage/disposal (hazardous)



Application challenge drives us to move beyond traditional approaches to increase productivity



Sample Preparation Techniques


Supercritical Fluid Extraction


Microwave Assisted Extraction


Soxhlet


ASE

Challenges

- High cost – instrumentation + cost per sample
- Poor selectivity
- Extensive glassware and vessels to wash

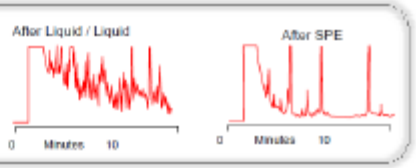
Sample Preparation Techniques

Selectivity

"Chemistry is still KING"
In the field of separation science



Solid Phase Extraction Benefits
- Superior cleanup due to selective sorbent chemistry
- Higher recoveries of key analytes
- Greater reproducibility
- Concentration of key analytes



Solid Phase Extraction (SPE) Chemistry

Historic uses in EPA and environmental samples

- Silica Based Stationary Phases
  - C18, C8, Phenyl, Si, NH_2, IEX, Florisil®
- Narrow range of particle and sorbent mass/volume selection
- Benefits were not compelling enough to justify the change
  - Throughput
  - Limited versatility
  - Limited selectivities

Advancements in SPE Chemistries

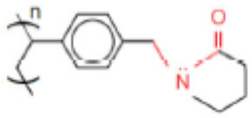
- Versatile SPE Sorbents
  - Wide range capabilities
  - Greater ability for stronger wash steps for cleaner extracts
- Targeted Selectivities
  - Ability for specific targeted extractions
  - Higher recoveries

Versatile SPE sorbents

Wide range capabilities

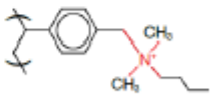
Strata™-XL

Large particle, wide pore reversed phase functionalized polymeric sorbent that provides strong retention of neutral, acidic, or basic compounds under aggressive, high organic wash conditions. Ideal use for High volume high flow samples.

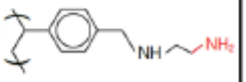


Strata-XL

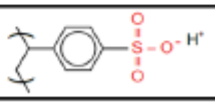
Strata-XL-A



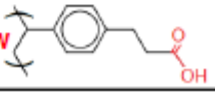
Strata-XL-AW



Strata-XL-C



Strata-XL-CW

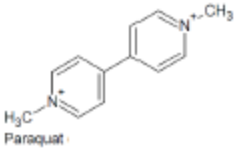


Diquat/Paraquat extraction from water

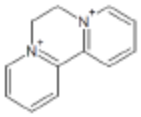
Previous Challenges

Widely used Herbicide

- EPA 549.2 calls for a C8 SPE phase using an ion-pairing agent.
- Ion-pairing methods tend to be irreproducible, leading to variable and inaccurate results
- Silica SPE phase is not dry resistant- requires more attention during loading
- Loading can be a slow, long process
- Overall, method is unreliable



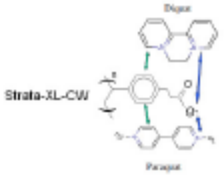
Paraquat


Diquat

Diquat/Paraquat extraction from water

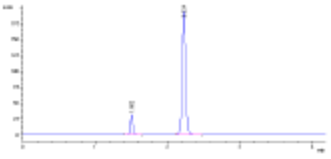
Strata™-XL-CW Advantages

- With new method, predominant interaction is ion-exchange
- Also have retention mechanism by RP from the polymeric SDVB backbone
- Sorbent tested to demonstrate required ionic capacity for ion exchange- extremely consistent from batch-to-batch
- Polymeric sorbents are dry resistant- no need to monitor loading
- Large particle sorbent for much faster flow & loading
- Overall, a much more robust & reproducible method



Green Arrow = Hydrophobic and Aromatic Interaction

Blue Arrow = Ionic Interaction

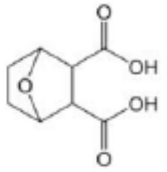


Endothall extraction from water

Previous Challenges

Widely used Herbicide

- Per EPA 548.1, bulk anion exchange resin is hand-packed by user
- Labor & time intensive
- Hand packing introduces variability
  - Inconsistency packing from user-to-user
- Ion exchange that was recommended was not ideal
  - Works for DI water with no ions
  - Presence of other ions requires EDTA treatment
- Poor recoveries, inaccurate & irreproducible results (high RSD%)



Endothall

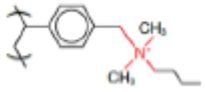
Matrix	Recovery(%)
De-ionized Water	75
Tap Water	20-50
Tap with Ca + Sulfate	<10

Endothall extraction from water

Strata™-XL-A Advantages

- Pre-packed SPE tubes with Strata-XL-A sorbent
  - time savings
  - Reliable tube & packing consistency
- ISO-certified QC process to ensure quality & process conformity
- Optimized material for higher extraction efficiencies, flow, and reproducibility
  - Consistent high recoveries
  - No need for EDTA
- Establish more robust method

Strata-XL-A



Matrix	Suggested Material *	Strata-XL-A
De-ionized Water	75	68.1
Tap Water	9-43	68.2
Tap with Ca + Sulfate	<10	58.5

* Data taken from method validation data provided with method 548.1

Targeted Selectivites in SPE

Unique Sorbent Chemistries



Extractable Petroleum Hydrocarbons

Tests for the presence of gasoline or fuel oil in drinking water. These tests provide information needed to determine if drinking water supplies near petroleum spills are contaminated with petroleum above health-based guidelines.



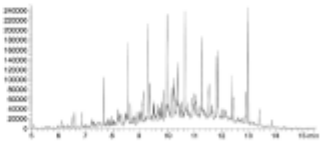
Polycyclic Aromatic Hydrocarbon

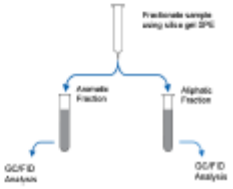
Polycyclic aromatic hydrocarbon compounds (PAHs) resultant from fire and fuel burning are effectively extracted from water samples while humic acids, which often interfere with chromatographic separation, are removed from the sample

Application Challenge

Extractable Petroleum Hydrocarbons

- Total Petroleum Hydrocarbon (TPH or EPA 8015)
- Application Goal
  - Reproducible fractionation of aliphatic and aromatic hydrocarbons
- General Purpose Solution
  - Silica-Gel SPE Tubes
- Challenges to Overcome- Productivity Thieves
  - Irreproducible fractionation
  - Time-consuming
  - Phthalate contamination

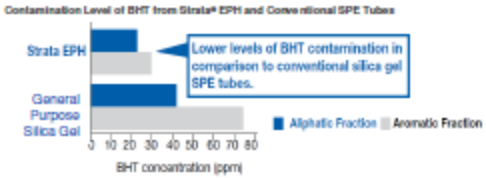




Application-Specific Solution
Extractable Petroleum Hydrocarbons-
Overcoming Challenges

General Purpose Challenges	Application-Specific Solution
Irreproducible Fractionation	• **Refined SPE material**
Time-Consuming	• **Increased flow rate**
Phthalate Contamination	• **PTFE coating**

Contamination Level of BHT from Strata® EPH and Conventional SPE Tubes



Application-Specific Advantage
Extractable Petroleum Hydrocarbons

Strata® EPH SPE Tubes:

- Decreased plasticizer contamination such as BHT
- Provide fast, consistent flow rates
- Maintains consistent recovery and efficient fractionation
- Reduces processing time from 50 min to only 26 min.
- Translates to 100 % increase in productivity

+2x more samples to be processed each hour over a general purpose alternative



Application Challenge

Polycyclic Aromatic Hydrocarbons (PAHs)

- Application Goal
  - Deliver consistent recoveries of PAH compounds when extracted from water
- General Purpose Solution
  - C18 SPE Sorbent
- Challenges – Productivity Thieves
  - Humic acid interference
  - Poor recoveries

Application challenge drives us to move beyond general purpose technologies to increase productivity

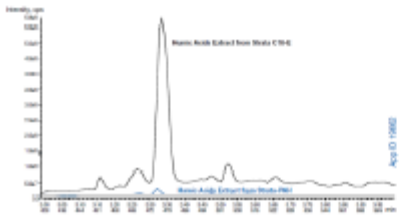


Application-Specific Solution

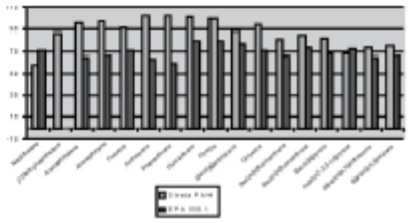
Polycyclic Aromatic Hydrocarbons (PAHs)- *Overcoming Challenges*

General Purpose Challenges	Application-Specific Solution
Humic acid interferences	• **Isolate with targeted selectively**
Poor recoveries	• **Optimized sorbent chemistry**

Effective Removal of Humic Acids



PAH Percent Recoveries from Tap Water



Application-Specific Advantage

Polycyclic Aromatic Hydrocarbons (PAHs)

Strata® PAH SPE Tubes

•SPE sorbent that targets PAHs and simultaneously removes humic acids from the sample

•PAHs can then be eluted while humic acids remain bound in the sorbent

Delivers cleaner extracts and also higher recoveries of PAHs as compared to the EPA 550.1 method general purpose approach



Selective SPE chemistries

- Unlocks GC/MS and LC/MS Advancements
- Innovative Sorbent Advancements
  - Increased possibility of detection of previously undetected harmful toxins and Pollutants
  - Higher sensitivity
  - Flexibility for greater screening and targeted analysis
- Improved Productivity
  - Quality results (Specific extraction)
  - Reduce sample preparation method development and troubleshooting
  - Increases instrumentation lifetime


phenomenex
Application Specific Support
www.phenomenex.com/Environmental
On-Site Lab Demos
Environmental Testing Web Page
Environmental Edge Newsletter
EDGE
Technical Notes
SPE Method Development Tool
Digital Learning Tutorials
Search Thousands of Application Notes
Search
Thank You!
For Questions email:
Allenm@phenomenex.com

Recent Advances in Solid Phase Extraction for the Determination of a Full Range of Organic Compounds from Challenging Samples

David Gallagher
Horizon Technology

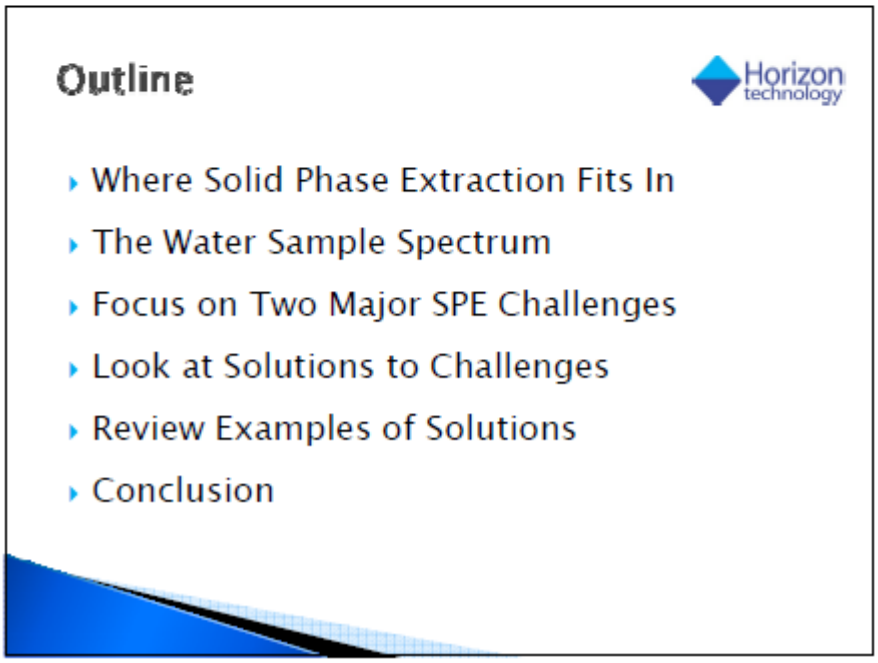
Abstract

Solid Phase Extraction (SPE) is a well know and useful technique for the extraction of organic compounds from aqueous samples. And while many EPA methods exist which allow, or demand the use of SPE, there are still two major challenges that SPE must overcome – the ability to successfully capture all of the target analytes from the water sample without breakthrough, and the ability to process samples with a high particulate loading, without plugging the SPE bed.

This paper will address both the chemical and physical issues, and present data which shows that with proper use, that SPE can successfully be used to process typical environmental samples, such as EPA methods 8270 and 625, effectively, efficiently, and provide comparable, or better data than achieved now with conventional liquid/liquid extraction techniques.

Additionally, these SPE techniques can be completely automated, which significantly reduces costs further, by allowing labor to be re-purposed.

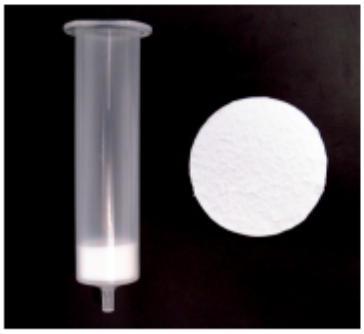

Horizon technology
Recent Advances in Solid Phase Extraction for the Determination of a Full Range of Organic Compounds from Challenging Samples
David Gallagher
Horizon Technology, Inc., Salem, NH, USA


Outline
Horizon technology
Where Solid Phase Extraction Fits In
The Water Sample Spectrum
Focus on Two Major SPE Challenges
Look at Solutions to Challenges
Review Examples of Solutions
Conclusion

Where SPE Fits In

- SPE resolves many problems associated with LLE, such as
  - Incomplete phase separations
  - Less than quantitative recoveries
  - Use of expensive / breakable glassware
  - If CLLE, cooling water and electricity requirements
  - Both LLE and CLLE use great volumes of solvent
  - Must evaporate great volumes of solvent – up the hood, or recycle?
- In Comparison, SPE is
  - More efficient (x50) than LLE and CLLE
  - Many SPE phases to choose from
  - Yields quantitative extractions that are easy to work with – no emulsions
  - Is typically faster
  - Solvent use and labor time are significantly reduced
  - Can be automated

SPE Cartridges and Disks

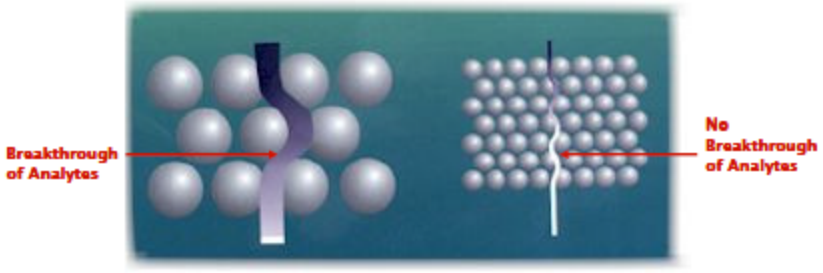


- Cartridges are good for
  - Clean samples
  - Sample sizes (≤ 250 mL)
- Disks are good for
  - Dirty samples
  - Sample sizes (≥ 250 mL)

Key Point – cartridges require a slow and controlled flow rate to work properly. This could impact sample through-put and/or economic benefits.

Size Does Matter!

Horizon technology

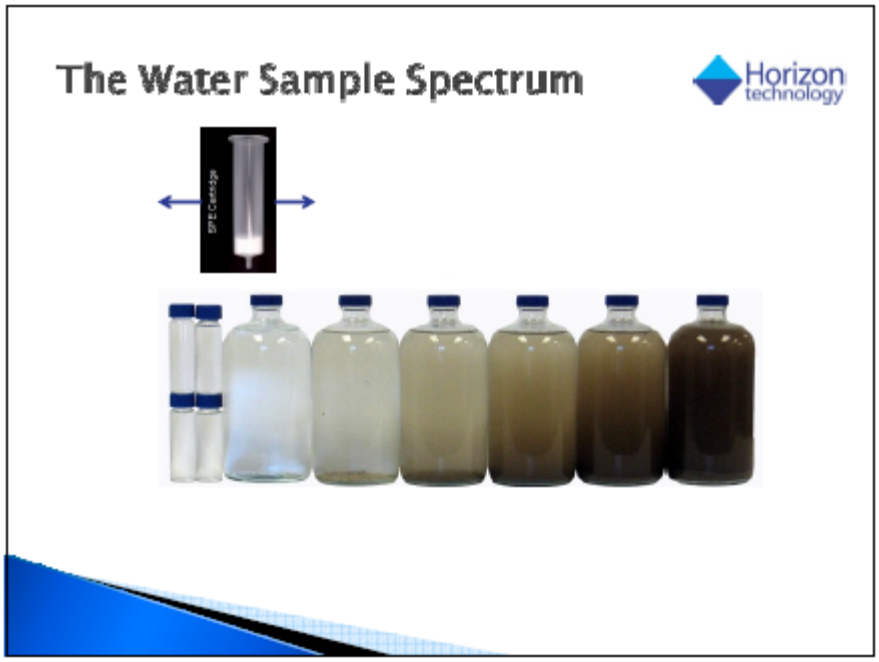


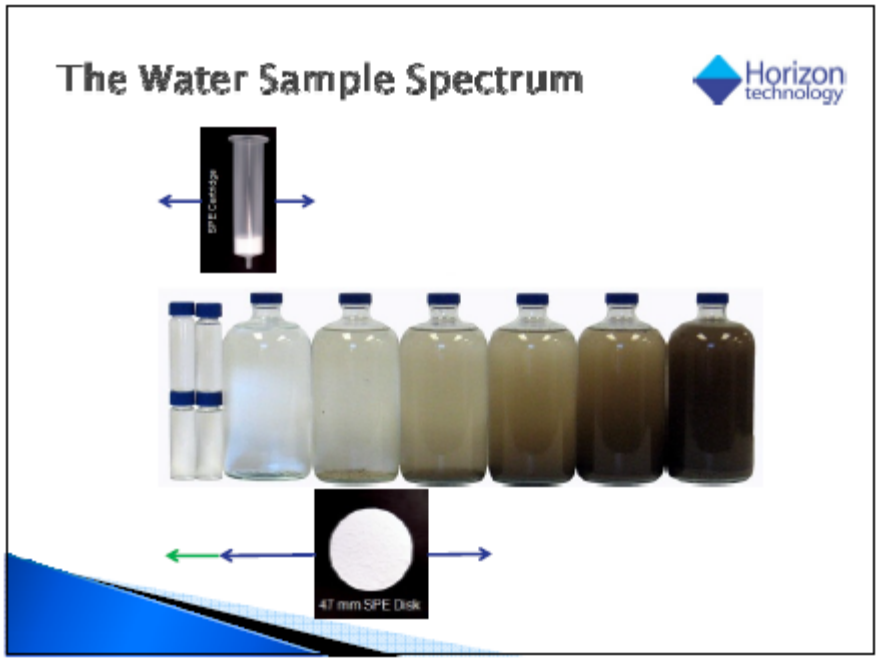
- Cartridges; requires slow flow rates to prevent breakthrough (~ 10 mL/min)
- Disks; fast flow rates are possible (~ 150 – 200 mL/min)

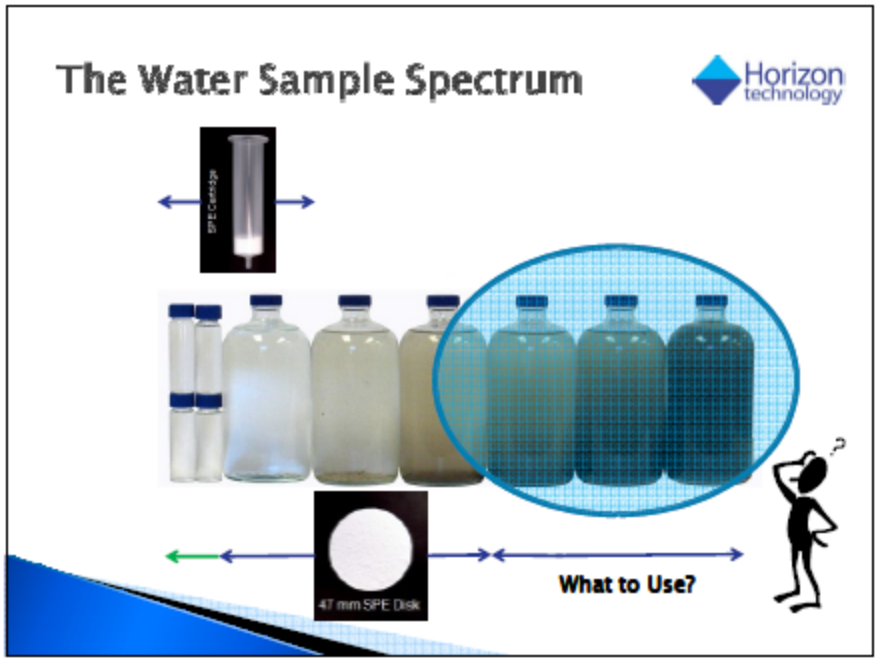
The Water Sample Spectrum

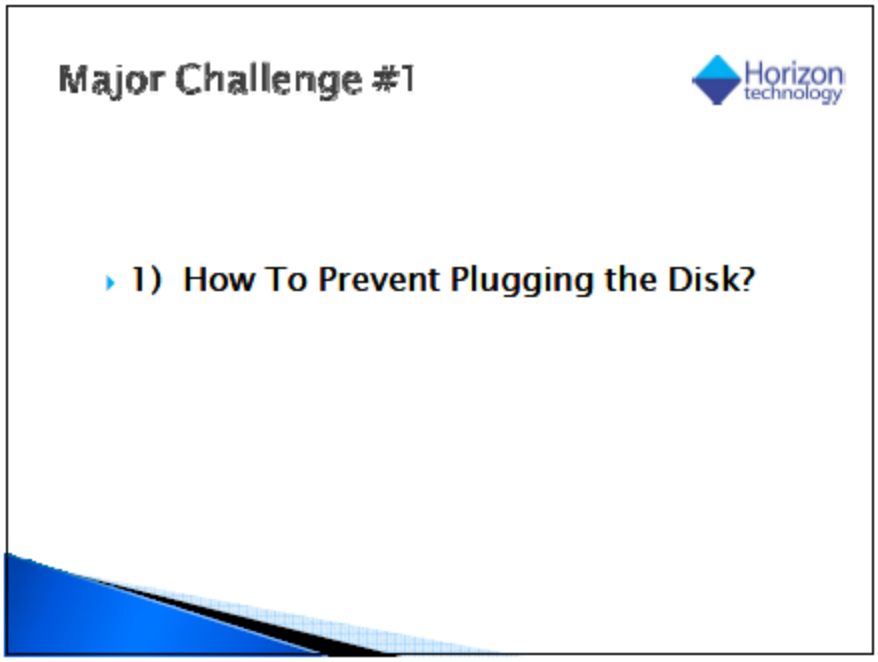
Horizon technology




The Water Sample Spectrum
Horizon technology


The Water Sample Spectrum
Horizon technology
47 mm SPE Disk


The Water Sample Spectrum
Horizon technology
47 mm SPE Disk
What to Use?

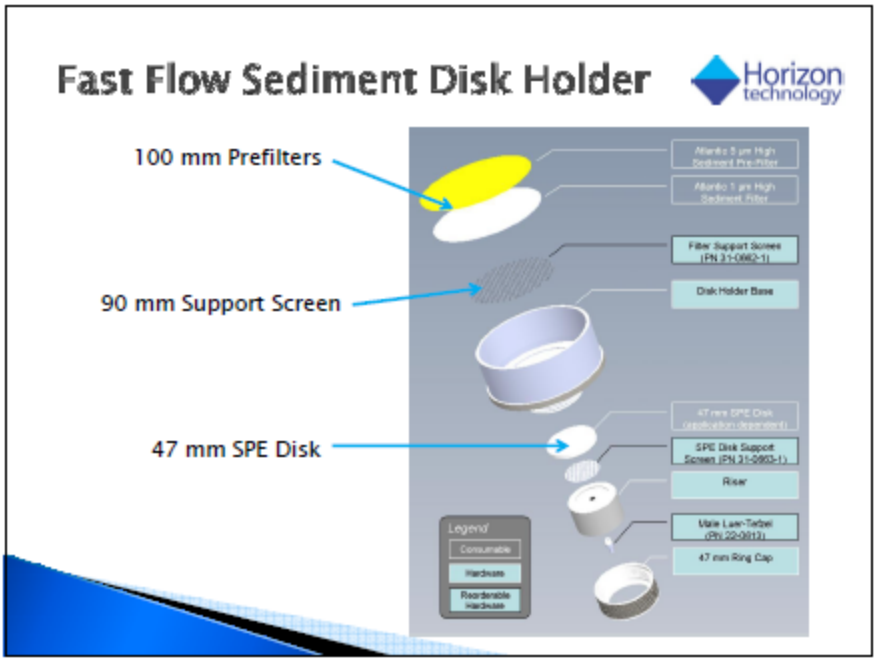

Major Challenge #1
Horizon technology
1) How To Prevent Plugging the Disk?

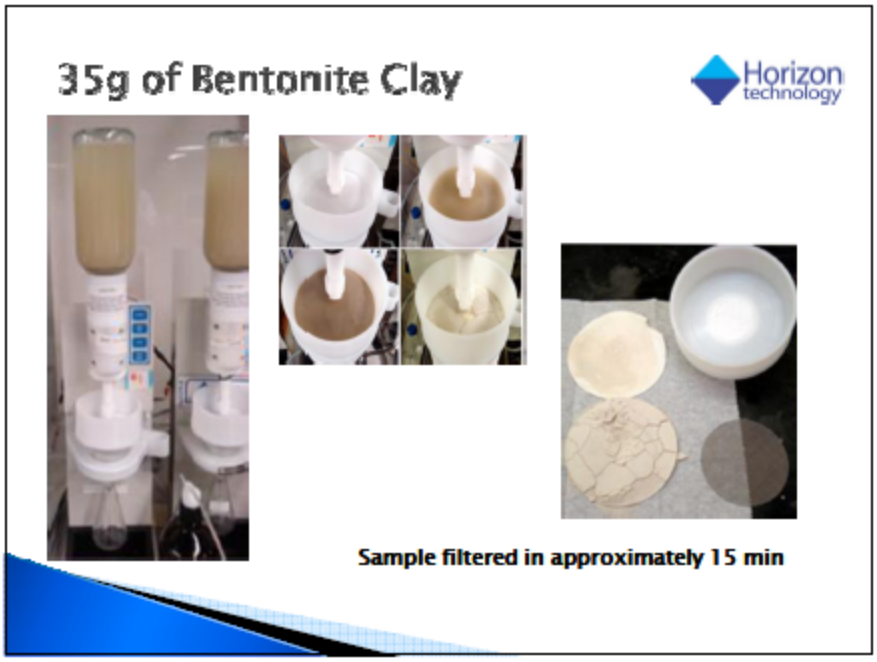
Challenge #1: How to Prevent Plugging?

- The conventional logic was that if a small 47mm SPE disk was good for clean samples, than a larger (i.e.) 90mm SPE disk had to be better for the dirty samples
- While a greater surface area is indeed beneficial, the added cost of a larger disk eliminates all economic justifications (4 to 5 X the packing material)
- Bottom line: Larger SPE disks are typically not used for organic analysis

Challenge #1: What's the Solution?

- A standard 47 mm SPE disk has the loading capacity to retain the compounds of interest, at the concentration levels currently found in environmental samples.
- Goal – Protect the surface of the analytical SPE disk, from the particulate matter.
- Use a larger prefilters (100 mm) on top of the 47 mm SPE disk.


Fast Flow Sediment Disk Holder
Horizon technology
100 mm Prefilters
90 mm Support Screen
47 mm SPE Disk
Disk Holder Base
Riser
47 mm Ring Cap
Legend
Consumable
Hardware
Reorderable Hardware


35g of Bentonite Clay
Horizon technology
Sample filtered in approximately 15 min

8270 Analysis on Waste Water

Horizon technology

This is 500 mL of an actual customer wastewater sample!!!

Run using FFSDH with 1 Atlantic Fine Prefilter and 2 Atlantic Coarse Prefilters.





Base

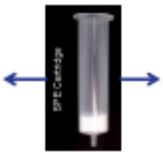


Process Time: 22 min

Process Time (w/ Carbon): 25 min

The Water Sample Spectrum

Horizon technology











Major Challenge #2

- 2) How To Retain a Full Range of Compounds on the SPE Media?

Challenge #2: How to Retain Compounds?

- First, need to know the class, or functionality of compounds.
- Select the proper SPE packing material, to retain the compounds of interest. (reverse phase, ion exchange, etc)
- Understand the retention mechanism in order to effectively remove the retained analytes from the packing material.
- Key Point – start at the back end of the analytical process and work forward. Understand the impacts of the evaporation, drying, and extraction steps.

Solutions to the Challenges

- Examine EPA Method 8270
- Examine how to extract 5 OPP's in a single SPE extraction

EPA Method 8270

PAHs
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
2-Methylnaphthalene
Anthracene
Fluoranthene
Pyrene
Benz[a]anthracene
Chrysene
Benzo[b,k]fluoranthene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Dibenz[a,h]anthracene
Benzo[g,h,i]perylene

Phenols
Phenol
2-Chlorophenol
2-Methyl phenol
3 & 4-methyl phenol
2-Nitrophenol
2,4-Dimethyl phenol
2,4-Dichlorophenol
2,6-Dichlorophenol
4-Chloro-3-methyl phenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Pentachlorophenol

Phthalates
Dimethyl phthalate
Diethyl phthalate
Di-n-butylphthalate
Butyl benzyl phthalate
Bis(2-ethylhexyl)phthalate
Di-n-butyl phthalate

OP Pesticides
Dimethoate
Malathion
Ethion
Azinphos-methyl
Disulfoton

Chlorinated Hydrocarbons
2-Chloronaphthalene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
Hexachlorobenzene
1,2,4-Trichlorobenzene
Hexachloroethane
Hexachlorocyclopentadiene

Amines, Nitroaromatics & Nitrosamines
Benzidine
2,4-Dinitrotoluene
Nitrobenzene
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine
Aniline
4-Chloroaniline
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline

OC Pesticides
Aldrin
alpha-BHC
beta-BHC
gamma-BHC
delta-BHC
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
a-Endosulphan
b-Endosulphan
Endosulphan sulphate
Endrin
Heptachlor
Heptachlor epoxide

Ethers
4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether
Bis(2-chloroethyl) ether
Bis(2-chloroethoxy)methane

Others
3,3-Dichlorobenzidine
Benzoic Acid
Isophorone
Dibenzofuran
Surrogate (Nitrobenzene-d5)
Surrogate (Terphenyl-d14)

Development Efforts

Horizon technology

CHRONOLOGY

Technology & Chemistry	2006	2007	2008	2009	2010	2011	2012	2012
DVB Disk	✓							
HLB Disk		✓	✓	✓	✓			
Dual pH Kit			✓	✓	✓			
Carbon Cartridge & Kit				✓	✓	✓	✓	
FFSDH					✓	✓	✓	
8270 One Pass Disk						✓	✓	
MeAc/MeFm							✓	✓
8270 One Pass L Disk/ Carbon Cartridge Light								✓
8270 ANALYTES & PERFORMANCE								
Lipophilic Compounds (Neutrals & Acids)	✓	✓	✓	✓	✓	✓	✓	✓
Hydrophilic Compounds (Phenols)		✓	✓	✓	✓	✓	✓	✓
Organic Bases (Anilines)			✓	✓	✓	✓	✓	✓
Light End Organics (NDMA, methyl methane sulfonate)				✓	✓	✓	✓	✓
High Sediment Samples					✓	✓	✓	✓
M 625 Performance Requirements							✓	
1/10th sample volume lower cost disk, lower solvent consumption								✓

SPE Disk Evolution

Horizon technology

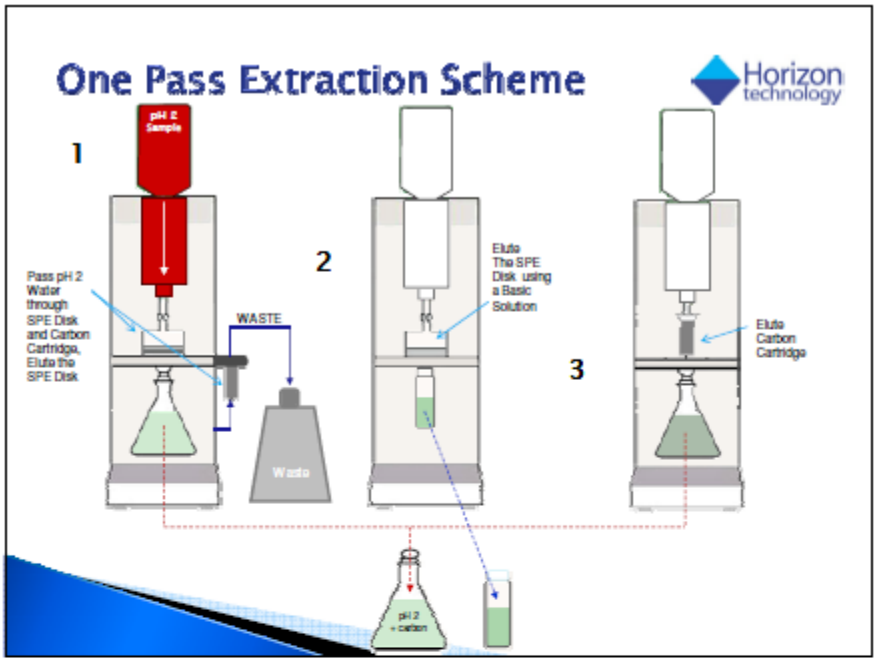
SPE Chronology 2008 2009 2010 2011

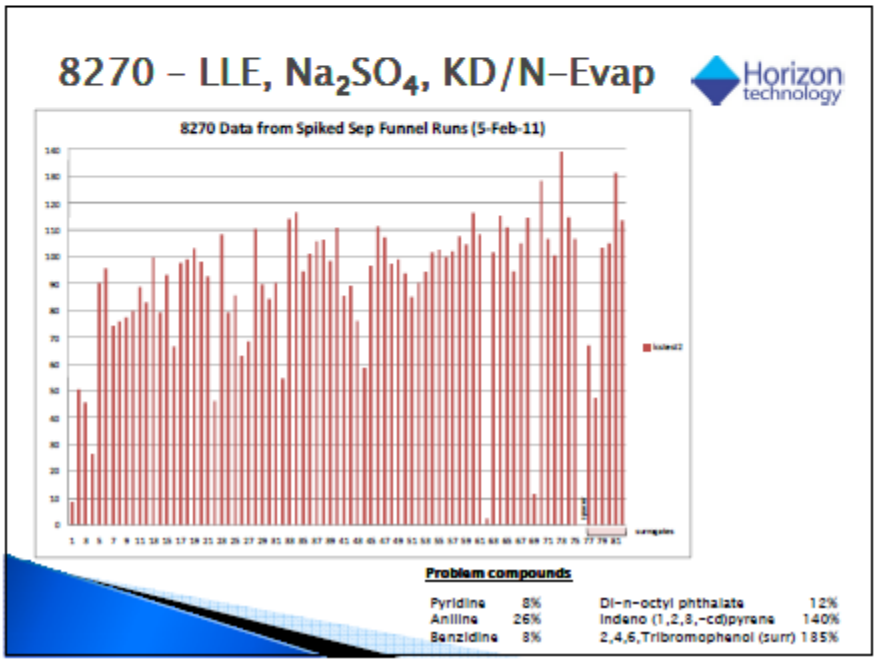
Introduce a SPE Disk with Three Mechanisms for Analyte Retention.



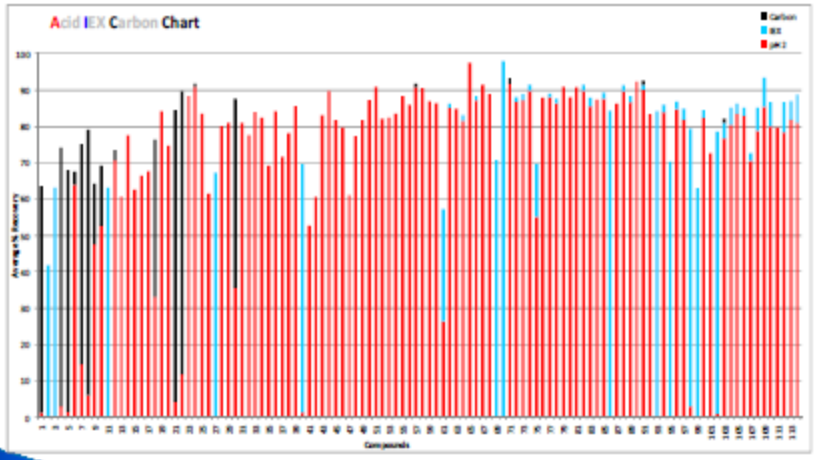
Atlantic™ "One Pass" Disk

- Incorporate Ion Exchange with Hydrophilic and Lipophilic character to the disk.
- Formulated to handle high levels of inorganic cations, hard water, brackish and near sea water levels of sodium.


One Pass Extraction Scheme
Horizon technology
1
pH 2 Sample
Pass pH 2 Water through SPE Disk and Carbon Cartridge, Elute the SPE Disk
WASTE
Waste
2
Elute The SPE Disk using a Basic Solution
3
Elute Carbon Cartridge
pH 2 + carbon


8270 – LLE, Na_2SO_4, KD/N-Evap
Horizon technology
8270 Data from Spiked Sep Funnel Runs (5-Feb-11)
Problem compounds
Pyridine 8%
Aniline 26%
Benzidine 8%
Di-n-octyl phthalate 12%
Indeno (1,2,3,-cd)pyrene 140%
2,4,6,Tribromophenol (surr) 185%

Recoveries on One Pass SPE Disk



OPP's in Single Extraction

- This work was done at the request of the Taiwan government, to develop a method to demonstrate the extraction of five organophosphate compounds using a single SPE disk:
  - Monocrotophos
  - Diazinon
  - Malathion
  - EPN
  - Methamidaphos
- Methamidaphos is problematic to extract in traditional SPE and LLE methodologies due to its extreme hydrophilic nature making exchange into a non-polar solvent or absorption onto a solid phase sorbent very difficult, resulting in extremely low recoveries of this compound.

Start at the Back

- When developing a new analytical method, start at the back end, and understand the impact of each step of the analytical process
- Evaporation/concentration step
- Residual Water removal step
- Extraction step
- With these three steps, you can identify a potential problem(s) with the method

Drying and Evaporation

- DryVap Drying and Evaporation/Concentration System

Parameter	Setting
Dry Volume	20 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	20 psi
Vacuum	-7 in. Hg

DryDisk Membrane

- Hydrophobic membrane which retains water, but allows organic solvents to pass through
- No Contamination – 100% PTFE
- Physical separation, not chemical adsorption like sodium sulfate
- **Retained water can be re-extracted – very key benefit**
- Better recoveries than with sodium sulfate – no adsorption of compounds



Results for Concentration

- To isolate where the analytes may be lost, a recovery study without water was performed using the drying and evaporation step. 30 µg of each compound were spiked into 25 mL of a 20/80 acetone/MeCl mix and reduced to 1 mL. Recoveries were excellent, and resulted in an average recovery range with a low of 89% to a high of 106% for all solvent spikes. This data also demonstrates excellent reproducibility with the RSD's lying between 6.2% and 8.5% for all fractions. These results indicate that the extreme hydrophilic nature of Methamidaphos may prevent absorption onto the SPE disk during initial extraction and also repartition into residual water during the drying step may be an additional problem.

Compound	% Rec	%Rec	%Rec	Ave %Rec	%RSD
Methamidaphos	97	106	114	106	8.10
Monocrotophos	97	105	115	106	8.55
Diazinon	82	92	94	89	7.32
Malathion	84	93	96	91	6.85
EPN	88	94	99	94	6.21

Method Summary

- Install the 8270 One Pass Hardware Kit
- Adjust a 1 L aqueous sample to pH 2 with HCl, and add 100 grams of NaCl
- Load the sample bottle into the SPE-DEX 4790 Extractor and start the extraction process
- Move the carbon cartridge and elute with the SPE-DEX 4790 system
- Use the DryVap concentrator to evaporate the solvent and concentrate the combined extract sample to 1mL

Results

- Recovery data from clean aqueous samples (spiked at 10 µg/L) using 47 mm HLB-H disks

Compound	%Rec	%Rec	%Rec	%Rec	%Rec	Ave %Rec	STDev	%RSD
Methamidaphos	4	5	4	5	5	5	0.24	5.28
Monocrotophos	83	88	89	94	101	91	7.10	7.81
Diazinon	69	74	74	71	77	73	3.09	4.24
Malathion	79	81	88	86	93	85	5.58	6.53
EPN	80	80	92	85	92	86	5.87	6.85

- Extraction results for HLB Disks showed very good recoveries for Monocrotophos, Diazinon, Malathion, and EPN with a low of 73% and a high of 91% and poor recovery of 5% for Methamidaphos.

Results

Horizon technology

- Recovery data from clean aqueous samples (spiked at 10 µg/L) for the Carbon cartridge after the HLB disk

Compound	%Rec	%Rec	%Rec	%Rec	%Rec	Ave %Rec	STDev	%RSD
Methamidaphos	53	53	55	50	44	52	5.26	10.13
Monocrotophos	7	8	7	8	7	8	0.40	5.27
Diazinon	0	0	0	0	0	0	0.00	0.00
Malathion	0	0	0	0	0	0	0.00	0.00
EPN	6	6	6	6	6	6	0.11	1.33

- The data show the results of the carbon cartridge fractions and average recoveries of Methamidaphos were 52% indicating that Methamidaphos is being retained on the carbon cartridge.

Results

Horizon technology

- Recovery data from clean aqueous samples (spiked at 10 µg/L) for the HLB disk + Carbon Cartridge after the disk

Compound	%Rec	%Rec	%Rec	%Rec	%Rec	Ave %Rec	STDev	%RSD
Methamidaphos	57	63	59	54	49	56	5.16	9.13
Monocrotophos	90	96	96	101	109	98	6.99	7.10
Diazinon	69	74	74	71	77	73	3.09	4.24
Malathion	79	81	88	86	93	85	5.58	6.53
EPN	87	86	98	91	98	92	5.86	6.36

- The data for HLB and Carbon Cartridge combined shows a low of 56% for Methamidaphos and a high of 98% for Monocrotophos. This data also demonstrates excellent reproducibility with the RSD's lying between 4.2% and 9.1% for all fractions.

Results

- Due to the extreme hydrophilic properties of Methamidaphos, it has a tendency to repartition back into the residual water and not transfer with the solvent when extracts are dried using the DryDisk. If higher recoveries of Methamidaphos are desired, an additional extraction of this residual water fraction is required. Recovery data from clean aqueous samples, total HLB-H Carbon Cartridge and LLE of residual water is shown here.

Compound	HLB -H	Carbon	LLE	Total	HLB -H	Carbon	LLE	Total	HLB -H	Carbon	LLE	Total
Methamidaphos	5	61	35	101	5	56	15	77	7	55	30	93
Monocrotophos	96	0	0	96	104	0	0	104	109	0	0	109
Diazinon	83	0	0	83	82	0	0	82	85	0	0	85
Malathion	94	0	0	94	96	0	0	96	101	0	0	101
EPN	91	0	0	91	93	0	0	93	97	0	0	97

- Excellent recoveries for all five compounds being studied with a low of 83% for Diazinon and a high of 103% for Monocrotophos.

Results

- Recovery data from clean aqueous samples (spiked at 10 µg/L) for the HLB disk + Carbon Cartridge after the disk+ LLE of residual water

Compound	%Rec	%Rec	%Rec	%Rec	STDev	%RSD
Methamidaphos	101	77	93	90	12.45	13.83
Monocrotophos	96	104	109	103	6.72	6.50
Diazinon	83	82	85	83	1.67	2.00
Malathion	94	96	101	97	3.52	3.65
EPN	91	93	97	94	3.12	3.33

- Recoveries were excellent for Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos with very good reproducibility ranging between 2.0% and 13.8% for all compounds.

Conclusions

- Recent developments SPE sorbents and accessories have extended the range of environmental samples that can be processed via SPE disks.
- Therefore, "dirty" samples can now be handled more efficiently and cost effectively.
- Full compound suite methods like 8270 and 625 can be processed.
- By knowing the chemical characteristics of the target compounds, effective SPE methods can be developed.

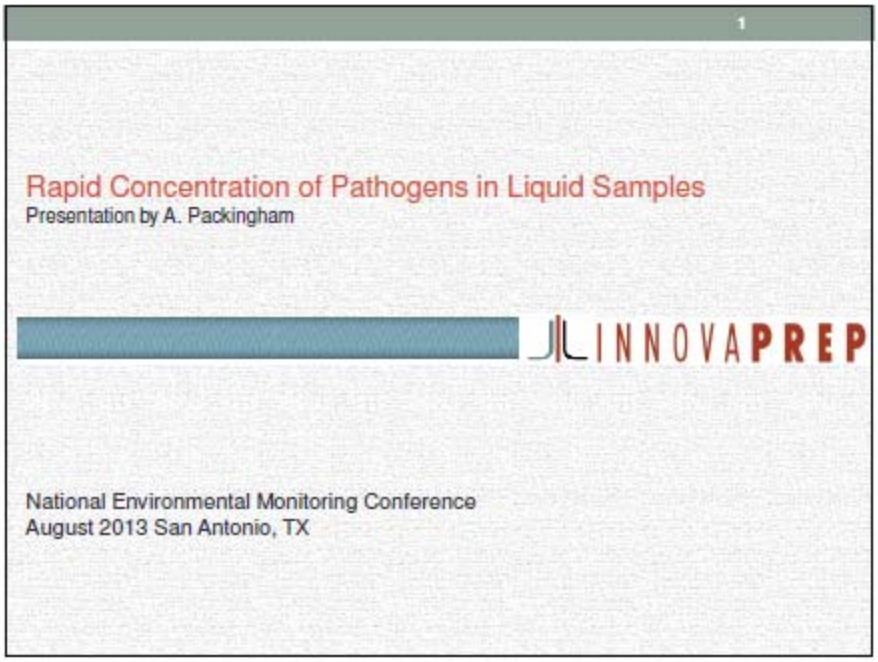
Thank You

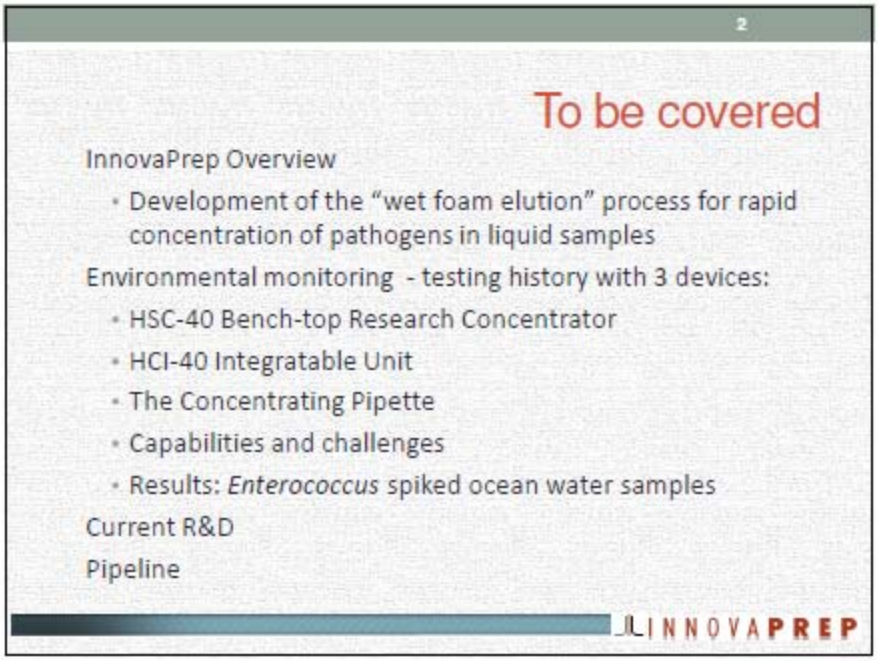
Rapid Concentration of Pathogens in Liquid Samples

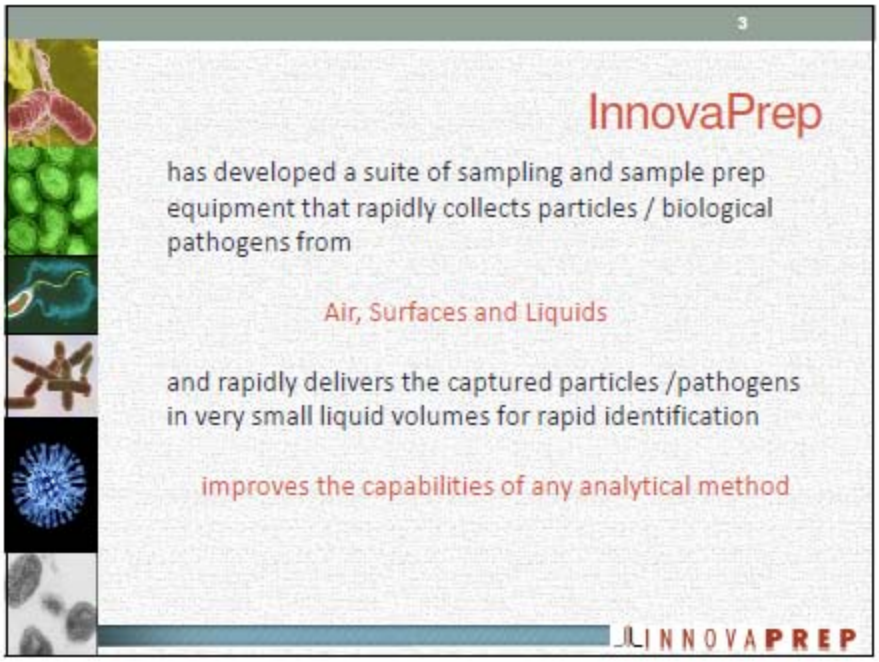
Ann Packingham
InnovaPrep

Abstract

Rapid evaluation of threats in environmental and drinking water requires concentration of the samples for near real-time identification of pathogens. Novel approaches to address this scenario will be discussed, including traditional methods and new alternatives being developed. Alternatives to enrichment and centrifugation include concentration using two different approaches; online 24/7 monitoring and sample-to-sample individual analysis. For field and portable laboratory use, rapid microbiological methods are becoming the norm. The combination of rapid concentration with rapid assays allows faster identification of threats than has been previously possible. Concerns include potential for false positives and false negative results, which can be reduced through advanced sample preparation techniques.

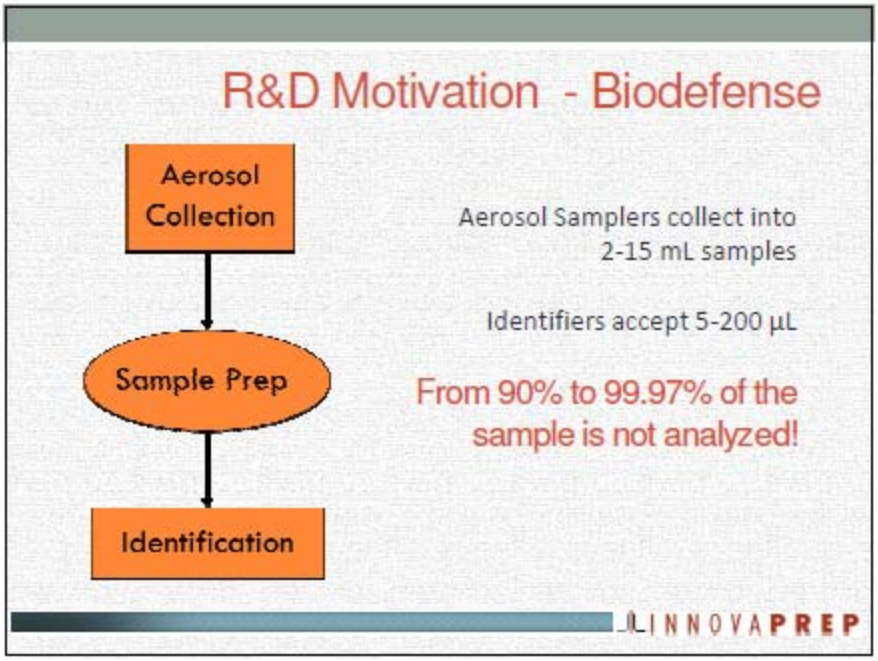

1
Rapid Concentration of Pathogens in Liquid Samples
Presentation by A. Packingham
INNOVAPREP
National Environmental Monitoring Conference
August 2013 San Antonio, TX


2
To be covered
InnovaPrep Overview
• Development of the "wet foam elution" process for rapid concentration of pathogens in liquid samples
Environmental monitoring - testing history with 3 devices:
• HSC-40 Bench-top Research Concentrator
• HCI-40 Integratable Unit
• The Concentrating Pipette
• Capabilities and challenges
• Results: Enterococcus spiked ocean water samples
Current R&D
Pipeline
INNOVAPREP


3
InnovaPrep
has developed a suite of sampling and sample prep equipment that rapidly collects particles / biological pathogens from
Air, Surfaces and Liquids
and rapidly delivers the captured particles /pathogens in very small liquid volumes for rapid identification
improves the capabilities of any analytical method
INNOVAPREP


Aerosol Research –
Midwest Research Institute to AlburtyLab Inc.
Dave Alburty
CEO
Andy Page
President & CTO
Pam Murrowchick
Director of Laboratory Operations
INNOVAPREP


AlburtyLab, Inc. Aerosol Research & Testing
Aerosol Wind Tunnel Engineering & Research Laboratory
Custom Aerosol Generators
Microbiology Lab & BSL-2 Field Station
Computational Fluid Dynamics /Flow modeling


R&D Motivation - Biodefense
Aerosol Collection
Sample Prep
Identification
Aerosol Samplers collect into 2-15 mL samples
Identifiers accept 5-200 µL
From 90% to 99.97% of the sample is not analyzed!
INNOVAPREP

7

Rapid identification requires rapid sample prep!







Problem

- Very small unconcentrated biological sample volumes = likely false negative results. The entire sample needs to be analyzed
- Concentration via centrifugation or enrichment + incubation are too slow and tedious
- Affinity capture only works for a target organism
- Filtration works but particle recovery from filters is difficult

INNOVAPREP

8

R&D - recovering particles from filters

Membrane



Hollow Fiber





Depth filters



INNOVAPREP

4

Core Technology: Wet Foam Elution
For rapid sample recovery

Volume Expansion

Elution fluid expands to 6X its liquid volume

Increased Viscosity

The higher viscosity of foam prevents channeling and creates a more uniform flow across the filter surface.



Bubble Dynamics

The microbubbles in the foam behave as deformable solids. As they travel across the surface of the filter they move as a ridged body with a narrow lubricating layer; effectively squeegeeing the particles off of the surface.

Exfoliating Action

The turbulence and energy produced helps to lift particles that are adhering to the membrane.

INNOVAPREP

10

InnovaPrep Concentration Instruments



2009
HSC-40
Bench-top
Research
Unit



2010
HCI-40
Integratable



2012
Concentrating
Pipette

INNOVAPREP

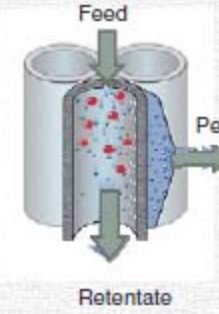
11

HSC-40



Hollow fiber dead-end filtration wet foam elution





INNOVAPREP

12

HCI-40 Integratable



The HCI-40 serves as a macro to micro interface between large sample volumes collected and the tiny volume needed for analysis

INNOVAPREP

13

Autonomous BioAerosol Monitoring



Air deposited into ~10 mL liquid Concentration Rapid ID (qPCR)

Biowatch Gen 3 Department of Homeland Security project

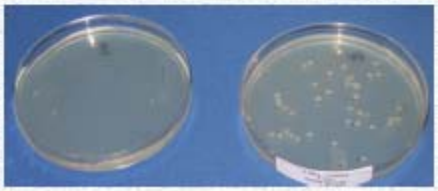
- System runs autonomously for up to 30 days
- Detects bacteria, viruses, and toxins
- Provides results in as little as two hours
- Results reported via a secure wireless network in real time

INNOVAPREP

14

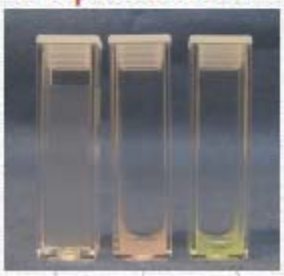
Biological Concentration and Separation

Plated sample of bacteria before and after 73x concentration with the HSC-40



Feed
6 CFU/mL

Concentrate
440 CFU/mL



Particle Mixture Bacterial Sized Particles Viral Sized Particles

INNOVAPREP

15

Air to liquid concentration – validation testing





Outdoor air samples collected at a rate of 60 CFM for periods of 48 to 72 hours.

Particulate recovered from the filters by rinses with 0.05% Triton X-100/TBS.

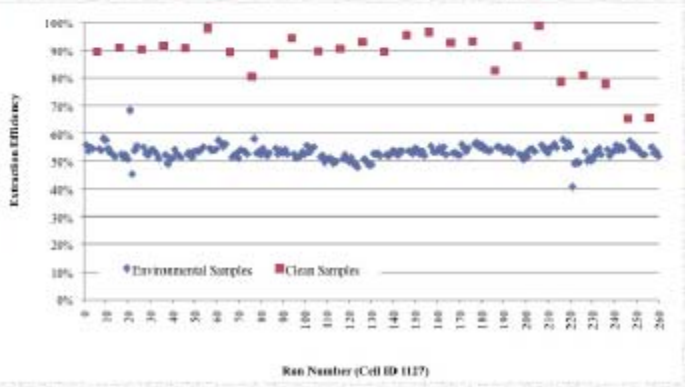
The total air to liquid volume ratio was the same as that of the biodefense system. (2 hours at 400 Lpm concentrated into 10 mL

INNOVAPREP

16

Hollow fiber concentration cell longevity testing





INNOVAPREP

17

Concentrating Pipette

- Sample is contained within the disposable tip
- No cross contamination between samples
- No decontamination between samples needed
- Simplified user interface
- Canned elution fluid



INNOVAPREP

18



Single-Use Tips

- **Particle Size Capabilities:** Tip specific – current tips are 0.1 µm and 0.4 µm for bacteria, parasites, mold, spores and whole cells
- **Speed:** up to 100+ mL /min*
- **Intake Volume:** >1 Liter *
- **Final Volume:** user selectable from 200-1000µL

*dependent on matrix & tip type

INNOVAPREP

19

Canned Elution Fluid

- Provides up to 50 elutions
- Does not inhibit detection
- Organisms remain viable
- 2 fluid types offered
  - PBS recommended for classical analytical methods
  - Tris recommended for rapid analytical methods
- Canned maintenance fluids for system decontamination



INNOVAPREP

20

Concentrating Pipette



INNOVAPREP

21

Representative Results

Relatively clean matrices such as drinking water

Concentration and Recovery of Microorganisms with the 0.1 µm PES filter tip

Species	Concentration factor
Escherichia coli	345X
Staphylococcus aureus	274X
Pseudomonas aeruginosa	201X
Bacillus subtilis	253X
Aspergillus niger	344X
Candida albicans	277X

100 mL spiked PBS samples concentrated down to 250 µL average run time 2 minutes.

INNOVAPREP

22

Concentrating difficult matrices

Matrix	Pretreatment required	Vol.	time
Honey - pollen	5 mL diluted to 100 mL / no prefilter	100 mL*	~ 2 min.
Vegetable oil	No pretreatment/ no prefilter	56 mL	~30 min.
Hydrofracturing flow-back (frack fluid)	Prefilter (330 µm mesh filter sleeve)	100mL	~ 3 min.
Blood	Pretreatment - enzymes	5 mL	~ 3 min.
Urine (UTI)	3 mL diluted to 10 mL Prefilterd	10 mL*	1:30 min.
Apple juice	No pretreatment/ no prefilter	100 mL	19:15 min.
Milk/dairy	Pretreatment – enzymes	Ongoing method development	
Pulverized spinach	Prefilter required		
Environmental samples - high humic content	Pretreatment, specially coated membranes		

INNOVAPREP

23

Pipette tip prefilters



330 µm mesh filter sleeve



Common syringe filter with Luer connector

INNOVAPREP

24

Ocean water samples

Ocean Beach and Mission Bay samples - San Diego, CA



INNOVAPREP

25

Testing method

Sample type	Mission Bay	Ocean Beach
Starting volume	100 mL each	
Enterococcus faecalis BioBall™ spike	0.9 CFU/mL	1.05 CFU/mL
Pretreatment	Autoclave 20 min	none
Pipette tip pre-filter	none	10 µm syringe filter
Filter tip type	0.4 Polycarbonate Track Etch (PCTE)	
Control	PBS spike 1.2 CFU/mL	
# runs	3 each	
Analysis by plating, incubation, and enumeration		

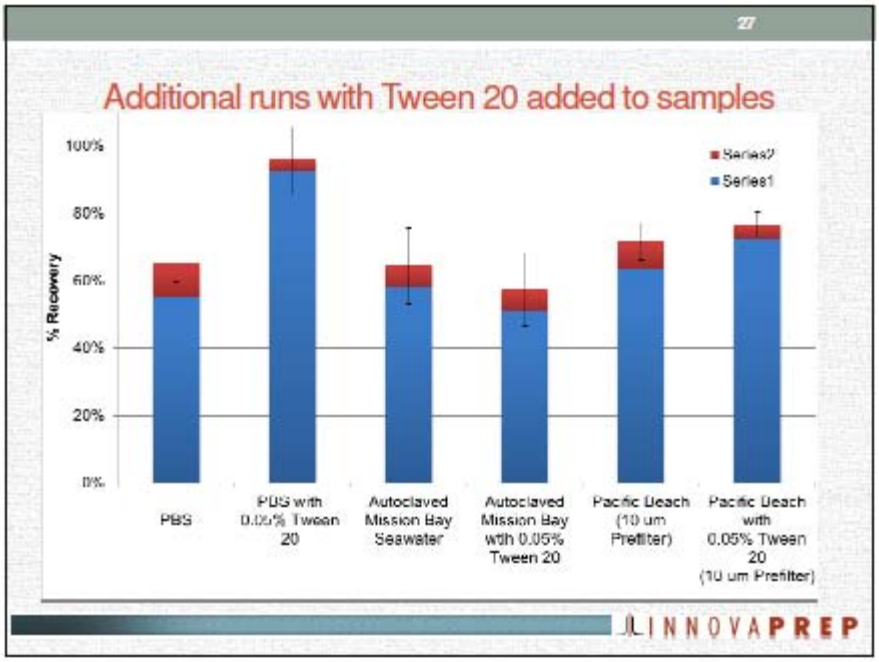
INNOVAPREP

26

Results

	Mission Bay	Ocean Beach	PBS
Time	1:11	1:10	1:04
Average final concentrate volume	295 µL	282 µL	189 µL
Average % Efficiency	58.1%	63.8%	54.9%
Concentration factor	203X	221X	287X
Extract #2			
Average % Efficiency	6.3%	7.9%	10%
Average total efficiency Extract 1&2	64.4%	71.7%	65%

INNOVAPREP


27
Additional runs with Tween 20 added to samples
% Recovery
100%
80%
60%
40%
20%
0%
Series2
Series1
PBS
PBS with 0.05% Tween 20
Autoclaved Mission Bay Seawater
Autoclaved Mission Bay with 0.05% Tween 20
Pacific Beach (10 um Prefilter)
Pacific Beach with 0.05% Tween 20 (10 um Prefilter)
INNOVAPREP


28
Current R&D
Single-use Hollow fiber packed Concentrating Pipette tips
~10X increased surface area to process larger volumes and more difficult sample matrices
INNOVAPREP

29

Current R&D
Sample Fractionation Cartridge
(under phase 2 DHS funding)

Remove environmental debris (including humics)

- Separates up to ~ 20 mL Sample into 5 fractions
  1. Whole bacteria
  2. DNA from bacteria
  3. Proteins from bacteria
  4. Free DNA and Viruses
  5. Free Proteins
- Concentrates all fractions at once into separate
  100 µL samples
- In less than 15 minutes



INNOVAPREP

30

Pipeline



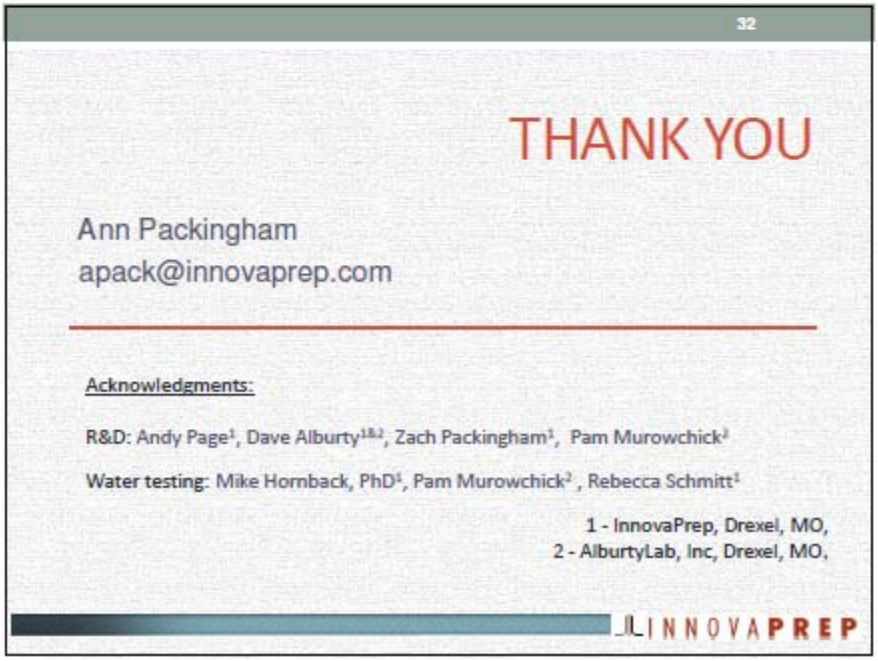
AutoElutor -
for rapid concentration of *cryptosporidium* & *giardia* from large water volumes

Disposable zero-power handheld concentrator
for use in austere environments



INNOVAPREP


31
Funding Agencies
U.S. DEPARTMENT OF HOMELAND SECURITY
FDA
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
UNITED STATES AIR FORCE MEDICAL SERVICE
U.S.ARMY
LWI
Leonard Wood Institute


32
THANK YOU
Ann Packingham
apack@innovaprep.com
Acknowledgments:
R&D: Andy Page[1], Dave Alburty[1&2], Zach Packingham[1], Pam Murowchick[2]
Water testing: Mike Hornback, PhD[1], Pam Murowchick[2], Rebecca Schmitt[1]
1 - InnovaPrep, Drexel, MO,
2 - AlburtyLab, Inc, Drexel, MO,
INNOVAPREP

SECTION 17

ANALYSIS OF METALLIC SPECIES AND ORGANOMETALLICS

Evaluation of Preservation and Holding Time Requirements for Hexavalent Chromium to Meet Data Quality Objectives for a Logistically Challenged Site

Ruth Forman
Environmental Standards, Inc.

Abstract

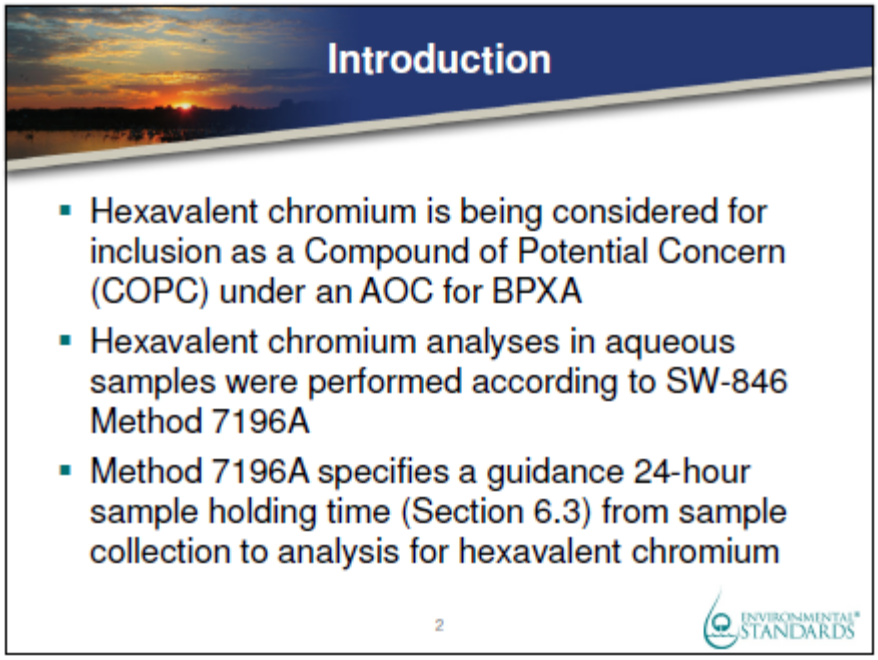
Hexavalent chromium is being considered for inclusion as a Compound of Potential Concern (COPC) under the Administrative Order for Corrective Action for BPXA's Prudhoe Bay Facility. Previously, the analysis for hexavalent chromium in aqueous samples was performed according to US EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846 Method 7196A. Method 7196A specifies a guidance 24-hour sample holding time (Section 6.3) from sample collection to analysis for hexavalent chromium.

Transportation and timing logistics from North Slope Project sites to the project laboratory precludes meeting the holding time guidance in Method 7196A as specified in the QAPP.

On Monday, March 12, 2007, the US EPA issued "40 CFR Part 122, 136, et al. – The "Method Update Rule (MUR)" extended the hexavalent chromium holding time to 28 days from the 24 hours stipulated in Section 8.3 of US EPA Method 218.6, Revision 3.3 if samples are preserved using ammonium sulfate buffer as indicated in the associated footnote. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

In accordance with the US EPA-recommended action relative to applying the ammonium sulfate buffer specified in Method 218.6 and extending the holding time to 28 days when using Method 218.6, the authors conducted a hexavalent chromium preservation and holding time study. The purpose of the holding time study was to evaluate and compare the long-term effects of collecting both unpreserved and buffer preserved samples when analyzing by US EPA Method 218.6. Results of the holding time study and the implications of the findings will be presented.


Evaluation of Preservation and Holding Time Requirements for Hexavalent Chromium To Meet Data Quality Objectives for a Logistically Challenged Site
National Environmental Monitoring Conference
San Antonio, Texas
August 8, 2013
Ruth L. Forman, CEAC - Environmental Standards, Inc.
Rock J. Vitale, CEAC - Environmental Standards, Inc.
Lester J. Dupes, CEAC - Environmental Standards, Inc.
Alyssa M. Kress - Environmental Standards, Inc.
Mike Mc Anulty - BP Exploration (Alaska) Inc.
ENVIRONMENTAL STANDARDS


Introduction
Hexavalent chromium is being considered for inclusion as a Compound of Potential Concern (COPC) under an AOC for BPXA
Hexavalent chromium analyses in aqueous samples were performed according to SW-846 Method 7196A
Method 7196A specifies a guidance 24-hour sample holding time (Section 6.3) from sample collection to analysis for hexavalent chromium
2
ENVIRONMENTAL STANDARDS

Logistically Challenged Site Problem



- Transportation/timing logistics from North Slope Project sites to the project laboratory precludes meeting the holding time guidance in Method 7196A
- Typically requires a minimum of 2-3 days after collection to deliver to the contract laboratory
  - Field collection locations require significant travel time
  - No local laboratories present on North Slope with capability for hexavalent chromium analysis
  - Limited flight schedules – weather or mechanical delays
- Estimation or rejection of hexavalent chromium results due to holding time during data validation

3

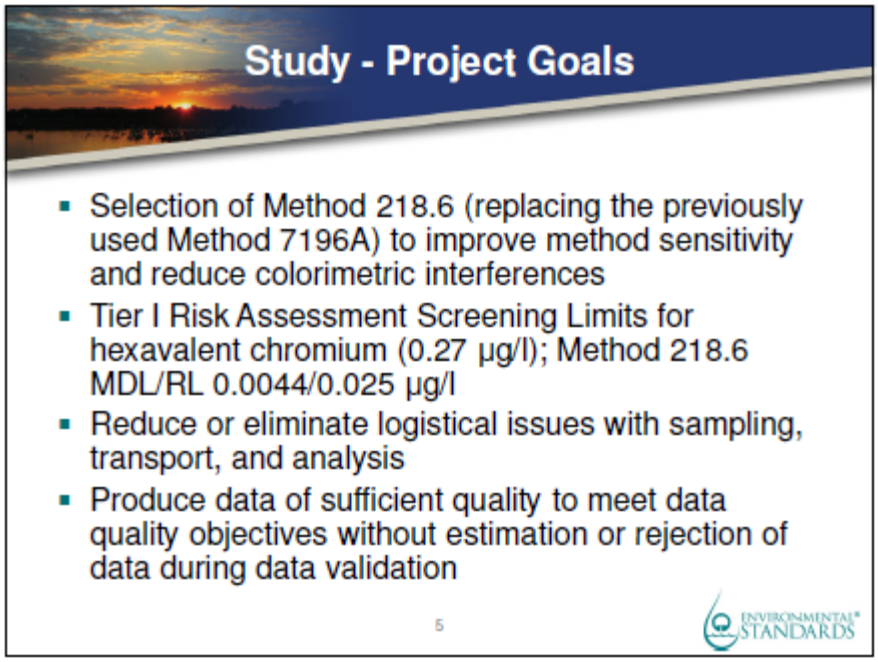
ENVIRONMENTAL STANDARDS

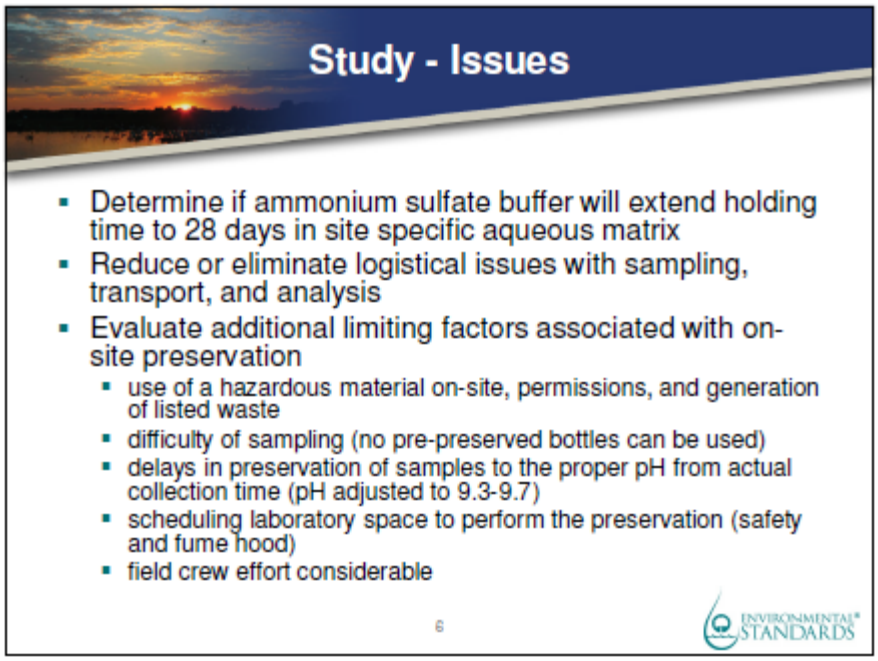
March 12, 2007, Method Update Rule (MUR)

- Extends hexavalent chromium holding time to 28 days from the 24 hours as stipulated in Section 8.3 of US EPA Method 218.6, Revision 3.3…
- …if samples are preserved using ammonium sulfate buffer as indicated in the associated footnote
- Footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed

4

ENVIRONMENTAL STANDARDS


Study - Project Goals
Selection of Method 218.6 (replacing the previously used Method 7196A) to improve method sensitivity and reduce colorimetric interferences
Tier I Risk Assessment Screening Limits for hexavalent chromium (0.27 µg/l); Method 218.6 MDL/RL 0.0044/0.025 µg/l
Reduce or eliminate logistical issues with sampling, transport, and analysis
Produce data of sufficient quality to meet data quality objectives without estimation or rejection of data during data validation
5
ENVIRONMENTAL STANDARDS


Study - Issues
Determine if ammonium sulfate buffer will extend holding time to 28 days in site specific aqueous matrix
Reduce or eliminate logistical issues with sampling, transport, and analysis
Evaluate additional limiting factors associated with on-site preservation
use of a hazardous material on-site, permissions, and generation of listed waste
difficulty of sampling (no pre-preserved bottles can be used)
delays in preservation of samples to the proper pH from actual collection time (pH adjusted to 9.3-9.7)
scheduling laboratory space to perform the preservation (safety and fume hood)
field crew effort considerable
6
ENVIRONMENTAL STANDARDS

Study – Additional Issues Investigated

- Investigate if differences between filtered and unfiltered samples and preserved and unpreserved samples existed
- Determine if samples collected unfiltered and unpreserved to support a 28-day holding time would meet data quality objectives
  - eliminate use of a hazardous material on-site
  - ease of sampling – no preservation
  - field crew effort reduced

7

ENVIRONMENTAL STANDARDS

Study Parameters – Collected Samples

- Collected eight aqueous samples for study in four types
  - Samples collected by Method 218.6; requires 0.45-µm field filtration prior to preservation to prevent interconversion of the two chromium species of interest
  - Samples collected unfiltered in order to determine the effects of filtration on the recovery of hexavalent chromium
  - Samples also collected unpreserved (without addition of ammonium sulfate buffer)
  - Samples also collected preserved (ammonium sulfate buffered) to determine the effects of sample preservation on the recovery of Cr^{+6} over time

8

ENVIRONMENTAL STANDARDS

Collected Sample Summary

- Collected in 1-liter polyethylene bottles for analysis in four separate aliquots of the eight samples were collected in the following manner:
  - Unpreserved/unfiltered
  - Preserved/unfiltered
  - Unpreserved/filtered
  - Preserved/filtered
- The samples were maintained at a temperature of ≤ 6°C upon sample collection through packaging and shipment to the laboratory

9

ENVIRONMENTAL STANDARDS

Laboratory Analysis – Sample Aliquots

- Preserved, unpreserved, filtered, and unfiltered sample bottles were homogenized by shaking and then subsampled
- Each of the eight unpreserved/unfiltered; preserved/unfiltered; unpreserved/ filtered, and preserved/filtered sample sets (32 total samples) was homogenized and split into individual sample aliquots (64 total)

10

ENVIRONMENTAL STANDARDS

QC and Sample Spiking

- A method blank was prepared and analyzed with each sample analysis group
- An unpreserved LCS and preserved LCS were prepared and analyzed with each sample analysis group
- Unspiked samples were analyzed prior to the study to determine background concentrations of Cr^{+6} prior to the preserved, unpreserved, filtered, and unfiltered spiking trials
- The sample spiking was performed by a single analyst, all at the same time
- The spiked aliquots were placed in a refrigerator at ≤ 6 °C in dark conditions during the study period and only removed prior to analysis

11

ENVIRONMENTAL STANDARDS

QC and Sample Spiking (Cont.)

- Each of the eight unpreserved/unfiltered; preserved/unfiltered; unpreserved/ filtered, and preserved/filtered sample sets (32 total samples) was homogenized and split into 64 sample aliquots.
- Thirty-two homogenized aliquots of the preserved, unpreserved, filtered, and unfiltered samples sample aliquots were quantitatively spiked at 0.050-µg/L Cr^{+6} (2× the RL) volume to and analyzed for Cr^{+6} at 7-, 14-, 21-, and 28-day intervals.
- Thirty-two homogenized aliquots of the preserved, unpreserved, filtered, and unfiltered samples; sample aliquots were quantitatively spiked at 0.075-µg/L Cr^{+6} spike (LCS level concentration) volume to and analyzed for Cr^{+6} at 7-, 14-, 21-, and 28-day intervals.

12

ENVIRONMENTAL STANDARDS

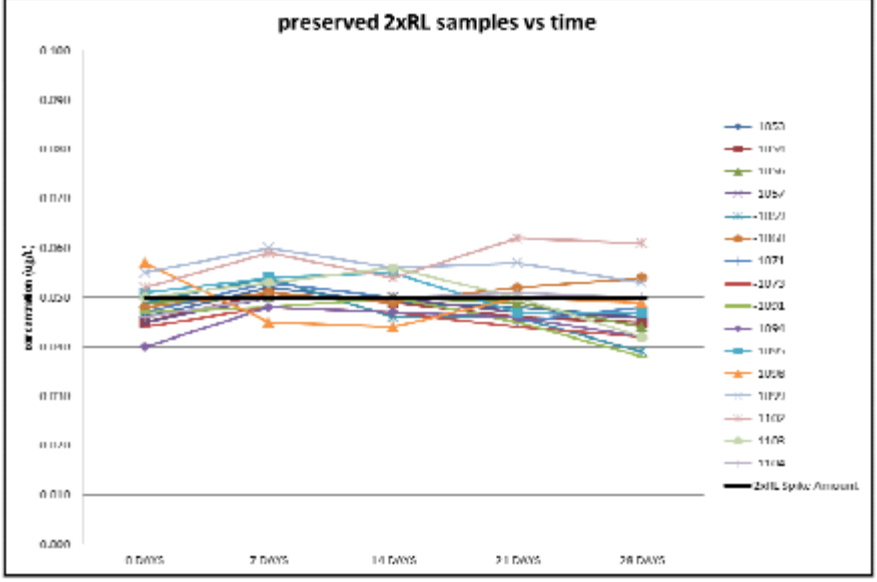
Summary of Analytical Results – Preserved Filtered and Unfiltered

- Individual recoveries for Cr^{+6} in the preserved samples, regardless if filtered or unfiltered, ranged from 89% to 115%
- These data provide good correlation for support of the ammonium sulfate preservation and holding time requirements stipulated in Method 218.6 for site samples

13

ENVIRONMENTAL STANDARDS

Preserved – Filtered and Unfiltered



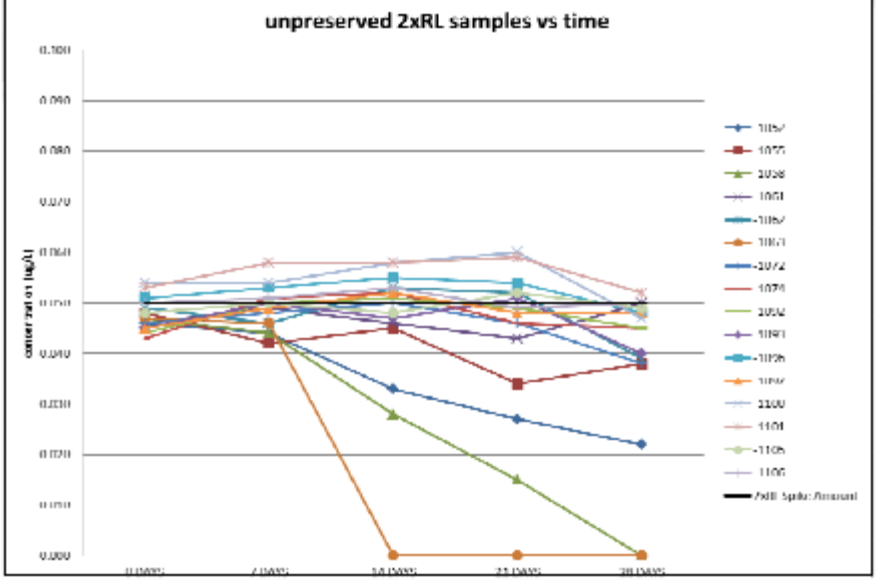
Summary of Analytical Results – Unpreserved Filtered and Unfiltered

- Individual recoveries for Cr^{+6} in the unpreserved samples, regardless if collected filtered or unfiltered, ranged from 68% to 112%, with the exception of four samples
- Regarding the recoveries of those four samples, three maintained recoveries of 92%, 88%, and 88% through 7 days of analysis, while the fourth maintained a recovery of 96% through 14 days of analysis
- The low or zero recoveries in samples for the unpreserved/unfiltered sample aliquots exhibited an apparent reduction of Cr^{+6} to Cr^{+3} after 7 days
- All remaining unpreserved sample aliquots exhibited similar Cr^{+6} recoveries to preserved samples through the 28-day analysis period

15

ENVIRONMENTAL STANDARDS

Unpreserved – Filtered and Unfiltered



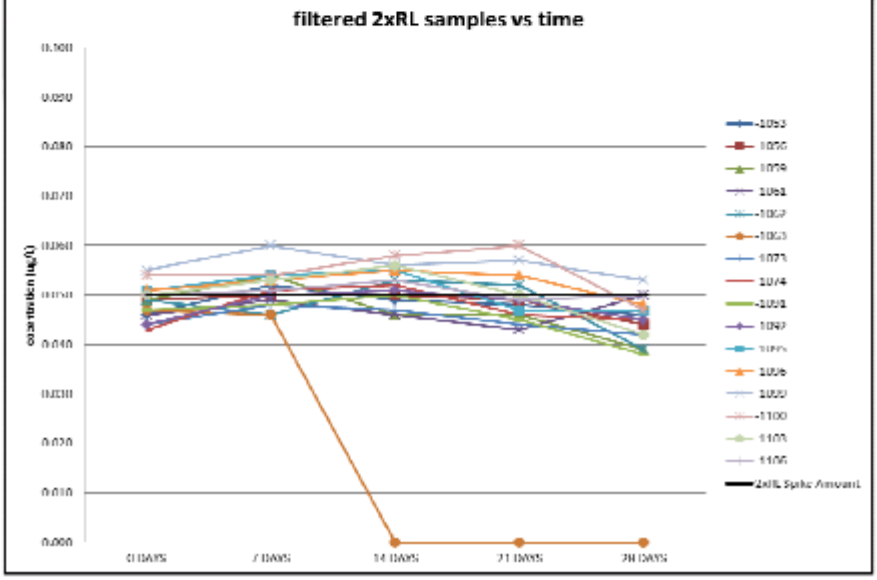
Summary of Analytical Results – Filtered Preserved and Unpreserved

- Individual recoveries for Cr^{+6} in the filtered samples, regardless if collected preserved or unpreserved, ranged from 90% to 112%
- Exception of two samples that had recoveries of 40% and 44%
- Regarding the outlier recoveries of 40% and 44%, the samples recovered 92% and 88%, respectively, 7 days beyond the spike date; these recoveries suggest a possible spiking error for the two sample aliquots analyzed at the 7-day point

17

ENVIRONMENTAL STANDARDS

Filtered – Preserved and Unpreserved



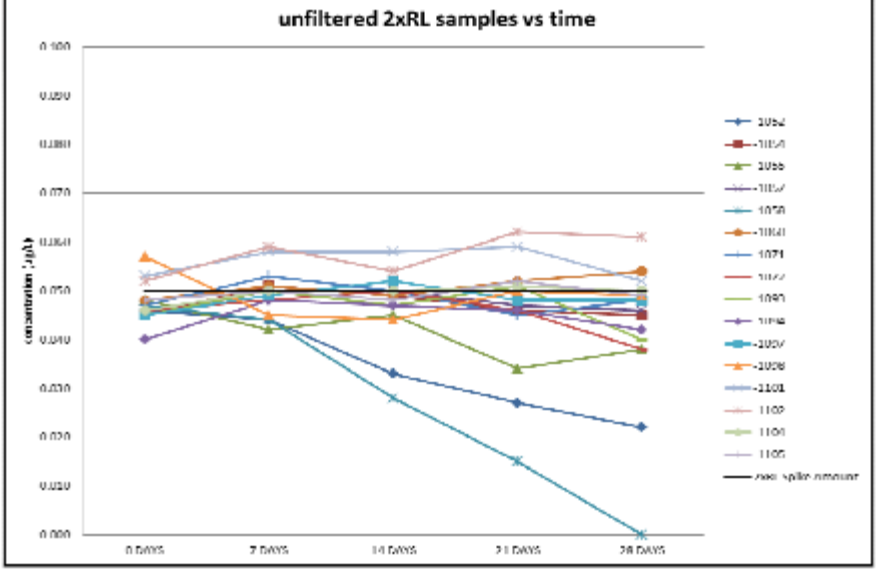
Summary of Analytical Results – Unfiltered Preserved and Unpreserved

- Individual recoveries for Cr^{+6} in the unfiltered samples, regardless of preservation, ranged from 68% to 115%, with the exception of two samples
- Regarding those two samples, one maintained a recovery of 88% through 7 days of analysis while the other maintained a recovery of 96% through 14 days of analysis

19

ENVIRONMENTAL STANDARDS

Unfiltered – Preserved and Unpreserved

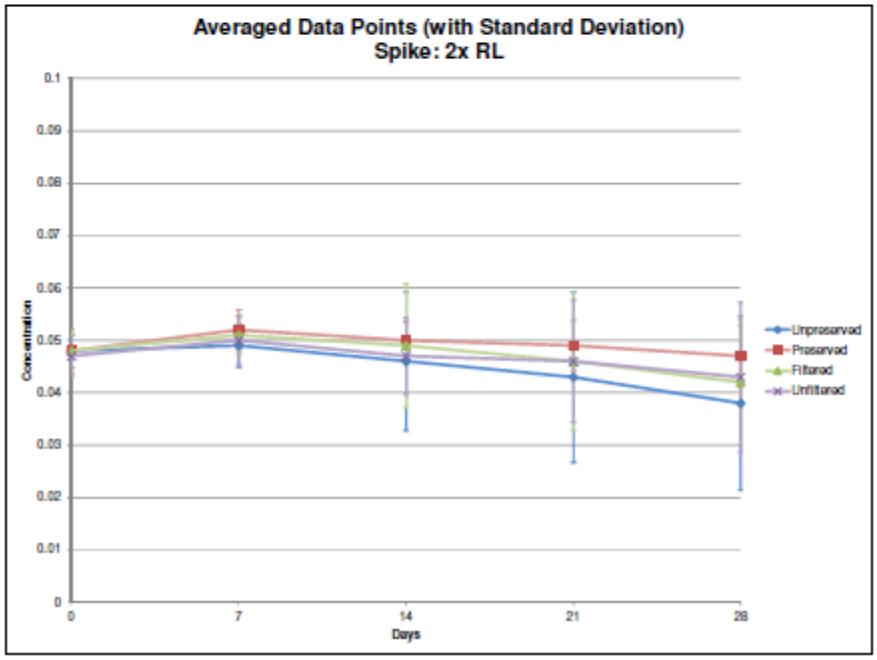


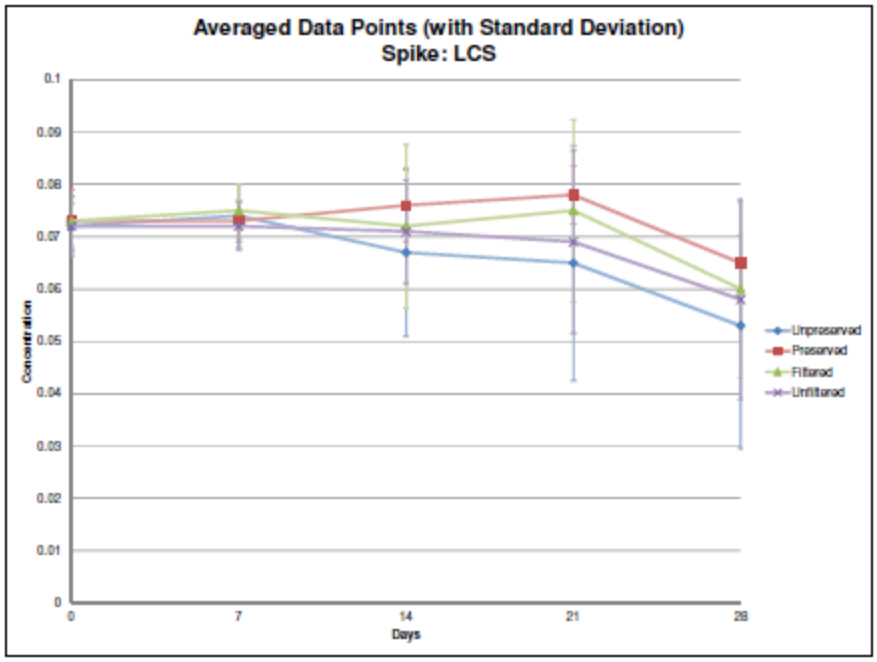
Summary Table of Results

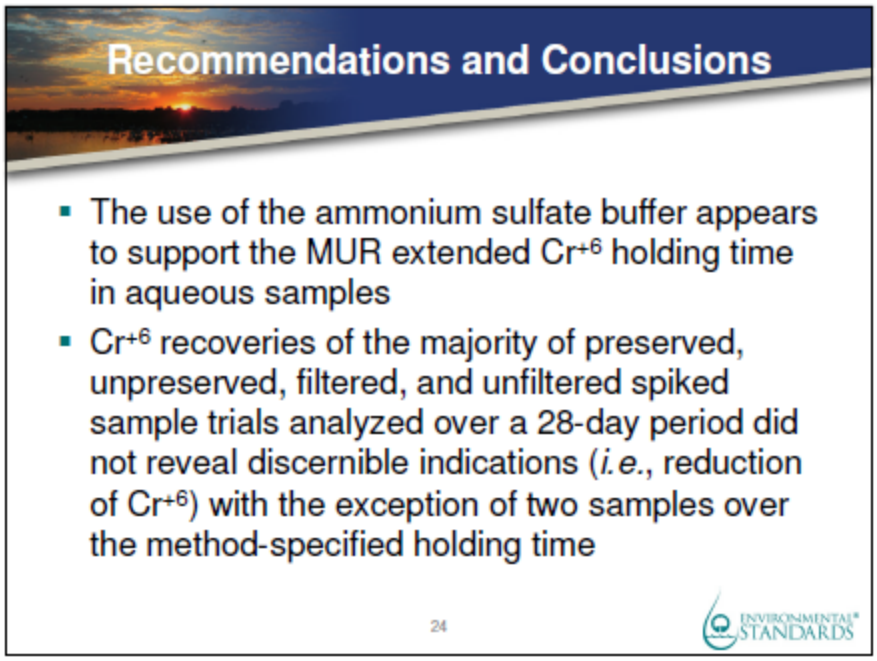
Sample Identification	Total Average Recovery	%Recovery Range	Removal of Outliers*	Day 7 Average Recovery	Day 7 %Recovery Range	Day 28 Average Recovery	Day 28 %Recovery Range*
Unfiltered/Unpreserved							
2× RL Spike (0.05 µg/L)	0.044	53-112%	83-112%	0.048	84-116%	0.036	76-104%
LCS Spike (0.075 µg/L)	0.064	49-104%	82-104%	0.072	85-108%	0.050	64-95%
Unfiltered/Preserved							
2× RL Spike (0.05 µg/L)	0.049	89-115%	n/a	0.051	90-118%	0.049	84-122%
LCS Spike (0.075 µg/L)	0.072	93-104%	n/a	0.072	88-101%	0.065	78-97%
Filtered/Preserved							
2× RL Spike (0.05 µg/L)	0.049	90-112%	n/a	0.052	96-120%	0.044	76-106%
LCS Spike (0.075 µg/L)	0.073	93-106%	n/a	0.074	94-107%	0.065	77-104%
Filtered/Unpreserved							
2× RL Spike (0.05 µg/L)	0.046	40-109%	93-109%	0.050	92-108%	0.041	78-100%
LCS Spike (0.075 µg/L)	0.069	44-105%	94-105%	0.076	88-133%	0.056	77-93%

21

ENVIRONMENTAL STANDARDS




Averaged Data Points (with Standard Deviation)
Spike: LCS
Concentration
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
7
14
21
28
Days
Unpreserved
Preserved
Filtered
Unfiltered


Recommendations and Conclusions
The use of the ammonium sulfate buffer appears to support the MUR extended Cr+6 holding time in aqueous samples
Cr+6 recoveries of the majority of preserved, unpreserved, filtered, and unfiltered spiked sample trials analyzed over a 28-day period did not reveal discernible indications (i.e., reduction of Cr+6) with the exception of two samples over the method-specified holding time
24
ENVIRONMENTAL STANDARDS

Recommendations and Conclusions

- Proposed a modification to the sample preservation requirement to permit ammonium sulfate preservation to be added to site samples within 7 days of sample collection by the laboratory with an overall Cr+6 holding time of 14 days after collection
- Based on US EPA Region X review, the data appears to support the position that Cr^{+6} is stable in unpreserved/unfiltered site samples up to 7 days after collection
- Modification approved by EPA Region X
- Eliminated field sample collection and data quality objective issues

25

ENVIRONMENTAL® STANDARDS

Contact

ENVIRONMENTAL® STANDARDS
www.envstd.com

Environmental Standards, Inc.
"Setting the Standards for Innovative Environmental Solutions"

Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577
Virginia 1208 East Market Street | Charlottesville, VA 22902 | 434.293.4039
Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590
Texas 11200 Richmond Avenue, Suite 350 | Houston, TX 77082 | 281.752.9782
Web www.envstd.com | E-mail solutions@envstd.com

26

Cr(VI) EXTRACTION METHOD FOR COPR-CONTAMINATED SOILS

√Stuart J. Nagourney, Research Scientist
√NJ Department of Environmental Protection
√Office of Quality Assurance
√RETIRED

DISCLAIMER

The content of this presentation reflects my views and not those of any other organization or individual

SPECIATION & ENVIRONMENTAL REGULATIONS IN THE US

- Nearly all environmental regulations in the US are based upon the measurement of the total element/compound/ion, not specific species
- Most regulators and legislators have a limited understanding of speciation and its impact on environmental and biological assessments
- Until recently, there were a limited number of specie-based analytical methods for speciation found in government methods compendiums/regulatory guidance documents; now, more are available.
- Greater commercial laboratory capability, combined w/certification of speciation methods by State/NELAC lab. programs, is needed
- **SRMs to appropriately QA speciation measurements must be developed to support all of the above**

ANALYSIS OF Cr(VI) IN SOILS

- Two steps needed:
  - Extraction
  - Determination







Cr(VI) IN SOIL: ANALYTICAL CHRONOLOGY

- SW846 includes Method 3060 (hot alkaline digestion) and colorimetric determination (Method 7196A)
- 1992: Many problems (mostly low spike recoveries) cause EPA to withdraw Method 3060; **a 1st and only!!**
- Some states, including NJ, come up with their own alkaline extraction methods
- 1994: EPA approves Method 7199 (IC)
- 1995: Industry-sponsored research provides data for an alternate alkaline extraction method, brought to EPA
- 1996: EPA approves as 3060A, **but with additional QA**
- 1998: EPA approves Method 6800 (SIDMS)
- 2008: NIST SRM 2701 Available

SUMMARY OF METHOD 3060A

- 2.5 g soil sample in 50 mL of basic extraction sol.
  - 0.28 M Na_2CO_3/0.5 M NaOH
- Cover, stir, and heat at 90-95 ° C for 60 min.
- Filter solution through 0.45 mm membrane filter
- Neutralize the extract by slowly adding HNO_3
- Adjust to pH of 7.5
- Transfer and dilute to 100 mL

METHOD 3060A QC

- Use of Mg^{+2} to suppress oxidation
- Prep. blank < 10% of Cr(VI) action level
- LCS: 80 - 120 % Recovery
- Duplicate sample 1 per batch
- Pre-Digestion Spikes
  - Soluble and Insoluble: 75 - 125%
  - If < 75% or > 125%, re-digest
  - If still outside, measure pH, ORP/Eh, Fe^{+2}, S^{-2}
- Post-Digestion Spike: 85-115% Recovery

Cr SPECIATION MEASUREMENT CONCERNS

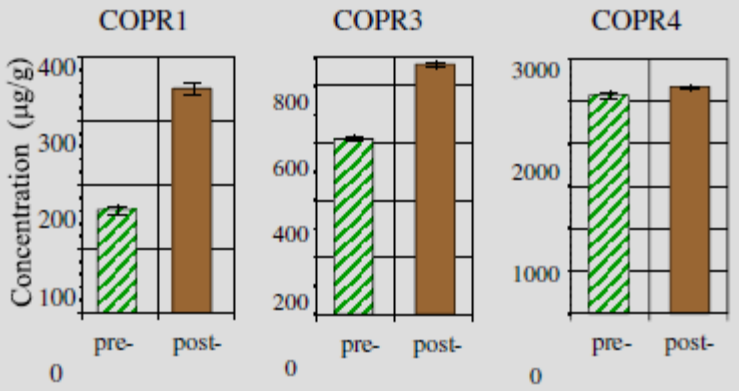
- Extraction must be quantitative and selective, without causing:
  - Oxidation of Cr(III) to Cr(VI) and/or
  - Reduction of Cr(VI) to Cr(III)
- Known problems include:
  - During extraction, some metals promote oxidation (Mn); others can cause reduction (Fe)
  - Organics, sulfides and others promote reduction
  - What about the methods of detection?

EFFECT of Fe on Cr(VI) USING METHOD 3060A

	Concentration of Chemicals	Concentration of Cr(VI) (ppm)	Recovery (%)
Fe(II)	0.4 ppm	0.251	93.9
		0.506	93.3
		0.755	97.4
		1.00	97.7
	1.6 ppm	0.251	81.7
		0.506	85.9
		0.755	85.6
		1.00	83.2
Fe(III)	2.0 ppm	0.251	91.6
		0.506	94.9
		0.755	93.2
		1.00	92.8
	8.0 ppm	0.251	66.7
		0.506	66.8
		0.755	66.7
		1.00	67.5

15

OXIDATION of Cr(III) DURING ALKALINE EXTRACTION



SOME ISSUES w/METHOD 3060A

- Oxidation of soluble Cr(III)
- Re-precipitation of Cr(VI) by Pb, Ba and/or Fe
- Reduction of Cr(VI) by soil matrix components
- Different types of soils cause differing problems
- ~2/3 of NJ soils fail method QC
- We need a material of known Cr(VI) and matrix composition to evaluate these issues

NIST SRM 2701

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2701

Hexavalent Chromium in Contaminated Soil (High Level)

Table 1. Certified Values for SRM 2701

Hexavalent Cr	551.2	mg/kg	±	34.5	mg/kg
Total Cr (mass fraction)	4.26	%	±	0.12	%
Fe (mass fraction)	23.73	%	±	0.19	%

The material was collected by S.H. Long of the NIST Analytical Chemistry Division and H.S. MacDonald of the NIST Measurement Services Division in collaboration with S.J. Nagourney of the New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA).

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

NIST SRM 2701

Appendix A

Multi-laboratory Testing Using Approved U.S. EPA Analytical Methods: Method 3060A, 7196A, Method 7199 (Hexavalent Chromium), Method 3050 (Leachable Chromium) and Method 3052 (Total Chromium)

	Method 7196A Cr(VI) mg/kg	Method 7199 Cr(VI) mg/kg	Method 3050 Leachable Cr % mass fraction	Method 3052 Total Cr % mass fraction
Mean	**384.3**	**388.7**	**0.411**	**1.025**

XANES

- Electrons are accelerated in a ring, in which each curvature of their trajectory will produce the so-called "synchrotron light"



ESRF, Grenoble, FRANCE

In-situ method not requiring Cr(VI) solubilization



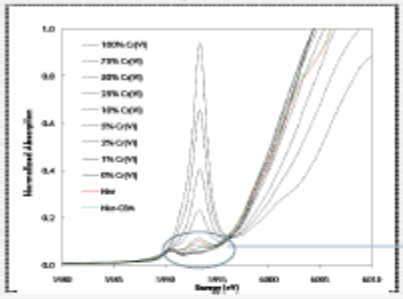
- The X Rays produced will probe the matter.
- Information on the sample will be retrieved through absorption, photoelectron energies or fluorescence.

XANES ANALYSIS of NIST SRM 2701

Malherbe, J. et. al., ES&T, 2011, 45, 10492-10500

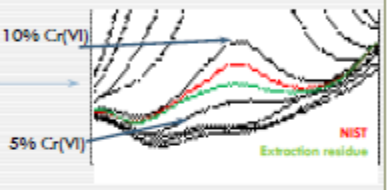
- **Certified values using EPA 3060A and 6800:** Cr(VI)= 551.2 ppm; Cr tot= 4.26%, hence Cr(VI) represents 1.3% of the total chromium

XANES quantification



- SRM 2701 clearly appears to have a Cr(VI) content is around 9% of Cr tot. Hence Cr(VI) should be around 3700 ppm

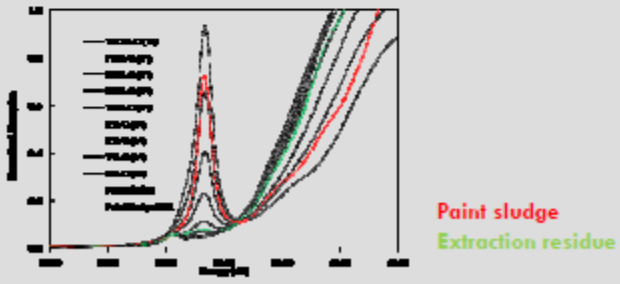
Only ~15% of the Cr(VI) in NIST SRM is removed by Method 3060A



NIST

PAINT SLUDGE

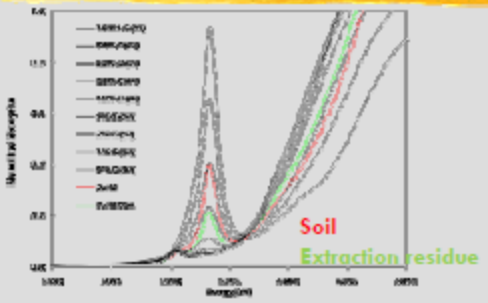
Description: Wet chemistry interlaboratory trials [4]; Cr(VI) 11360ppm Cr_{tot} 14800 ppm matrix, Cr(VI) represents 77% of Cr_{tot}.



- The quantification gives Cr(VI)= 80% of Cr_{tot}
- In this case, EPA3060A is almost quantitative
- In the residue, 6% of the chromium is in the hexavalent form Cr_{tot} is being analysed…

LOAMY SOIL

Description: Wet chemistry interlaboratory trials [4]; Cr(VI) 2007ppm, Cr_{tot} 8700 ppm matrix, Cr(VI) represents 23% of Cr_{tot}.



- XANES quantification gives Cr(VI)=43% of Cr_{tot}
- In the extraction residue, CrVI represent 22% of Cr_{tot}. In this case, EPA 3060A is not complete; underestimation of Cr(VI)/ Cr_{tot} is being analysed…

COMPARISON OF SOILS



- The major forms of chromium are different in each of these soils
- The extraction efficiency differences observed among these soils might be explained by their different matrices and their different chromium species

WORK IN PROGRESS AT USGS

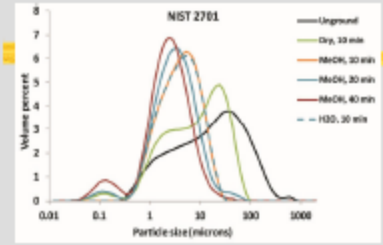
- Improve extraction of Cr(VI) from solid materials
  - Grinding of samples to breakdown mineral phases prior to extraction
  - Modifications of 3060A
    - ☒0.5 g sample + 200 mL (0.28M Na_2EDTA/0.5 M NaOH), 90° C, 2 Hrs
    - ☒No $MgCl_2$ and no K_2PO_4/$KHPO_4$ buffer
    - ☒Adjust pH with conc. HNO_3, final volume 250 mL
  - Alternative extraction solutions (e.g. EDTA)
- Analyze pre- and post-extraction materials by SEM-EDX, XRD, XANES
  - XANES performed July 15-19 – data being processed
- Analyze extracts by HPLC-ICP-MS and Method 7196A

Disclaimer: all USGS data presented is preliminary in nature and does not represent any official USGS finding.

TEST PLAN

	2701						COPR 2B				
		Methanol			Water	Dry			Methanol	Water	Dry
Samples for XANES	no treatment	10 min	20 min	40 min	10 min	10 min	no treatment	shatter-boxed	10 min	10 min	10 min
Not Extracted	x	x	x	x	x	x	x	x	x	x	x
Modified 3060 A - 2 hours	x	x	x	x	x	x	x	x	x	x	x
Modified 3060 A - 24 hours		x									
Modified 3060 A - 48 hours		x									
Modified 3060 A - 72+ hours		x									
EDTA - 2 hours		x									
EDTA - 24 hours		x									
EDTA – 48+ hours		x									

X indicates sample for X



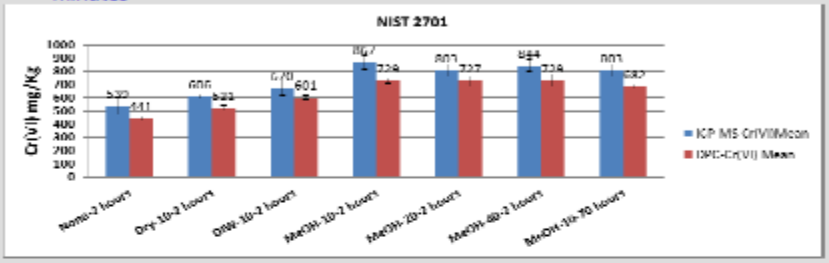
Dry/wet grind NIST 2701 and un-ground COPR soil 2B

Soil 2B has not been previously ground

Test extraction efficiency differences with different particle size distributions at different extraction times

TREATMENT RESULTS - NIST 2701

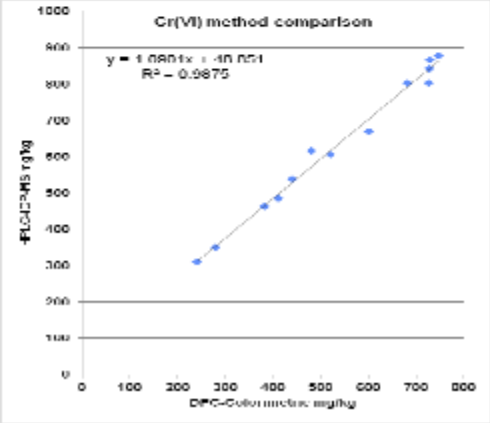
- Grinding of NIST 2701 increased Cr(VI) recovery by 60% over untreated NIST 2701
  - 867 mg/kg compared to ~3000 mg/kg estimated by XANES (Malherbe, et al, Environ. Sci. Technol. 2011, 45, 10492–10500)
- Recovery after grinding in methanol higher than DIW
- No real difference with increasing grinding time in methanol beyond 10 minutes



EXTRACT COMPARISON

All extracts measured by HPLC-ICP-MS method and DPC-colorimetric method (7196A)

- Untreated NIST 2701 results by HPLC-ICP-MS close to certified value
  - 539 ± 61 (n=4) vs 551.2 ± 34.5 (certified)
    - 98% recovery
  - Note: Isotope dilution was NOT used
- HPLC-ICP-MS method consistently higher for all treatments
  - Bias appears to be highly reproducible and systematic as shown by the plot
  - Each point in plot is mean of n=4 samples



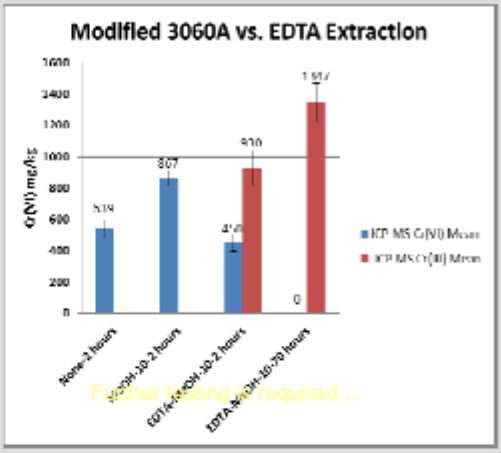
Further work plan to investigate source of bias

EDTA EXTRACTION – NIST 2701

- 0.5 g sample
- 80 mM EDTA
- Adjust to pH 10.0 with NH_4OH
- Final volume 250 mL

Preliminary Conclusions:

- Extracts more total Cr than Method 3060A
- Cr(VI) appears to convert to Cr(III) during extraction and/or storage
- 2 hr. extraction time shows mix of Cr(VI) and Cr(III)
- After 70 hr. extraction time all Cr is present as Cr(III)
- 7106A Method doesn't appear to work with EDTA extracts



COPR SOIL 2B

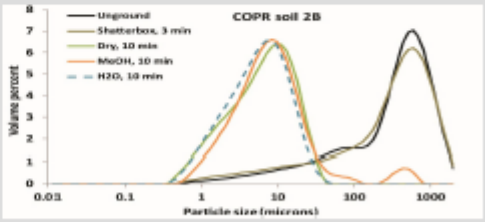
Second COPR contaminated soil

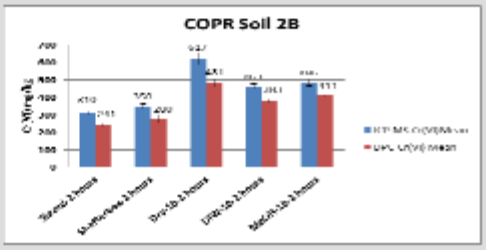
- Never ground as was 2701
- Material was sieved and shatterboxed
- Particle size analysis of unground (sieved) and shatterboxed samples similar
- Shatterboxed sample was ground in micronizer under wet and dry treatments for 10 minutes
  - Particle sizes similar

Modified 3060A Extraction

- Dry ground sample had highest extracted Cr(VI)

Results may indicate potential differences in results for NIST SRM vs "real" samples





NEXT STEPS

- Compare extraction results to XANES data
- Examine method bias causes between 7196A and HPLC-ICP-MS determination methods
  - Analysis of same aqueous standards by both techniques
- Stabilty study on EDTA extracts
- XRD and SEM-EDX analysis of extract residues to see if mineralogy changes occur during extraction
- Preparation for next round of XANES
- **Can we come up with a more ruggedized extraction method to propose to the USEPA as a replacement for 3060A?**

Application of Selenium Speciation Analysis to Elucidate Limitations with Accepted Total Selenium Methods

Russell Gerads
Applied Speciation and Consulting

Abstract

Current accepted methods for total selenium quantification are known to produce bias results depending on the selenium species and other compounds present in solution. The issues with the current methodologies are holistic including: selection of sample vessels, preservation techniques, applied digestion procedures, and analytical methods. Certain selenium species are known to form insoluble precipitates and colloidal elemental selenium in the presence of nitric acid which either adsorb onto the walls of the container or deposit to the container floor. With the remaining selenium species present in solution most analytical methods exacerbate the bias with chemical and spectral interferences. Selenium speciation analytical methods, using various ion chromatography method coupled to inductively coupled plasma collision reaction cell mass spectrometry (IC-ICP-CRC-MS), was applied to quantify and track which selenium species are not supported by existing preparatory and analytical approaches.

The most prevalent selenium species in industrial and natural aquatic systems are selenite, selenate, selenocyanate, and methyl seleninic acid. Scientific publications have confirmed that naturally occurring microbes (Pseudomonas fluorescens) were identified to generate selenocyanate as a metabolic byproduct confirming that selenocyanate is a naturally occurring selenium species. Selenocyanate has been proven to convert to elemental selenium in the presence of 1% nitric acid, which is recommended by all current EPA methods for total recoverable metals analysis of surface and groundwater matrices. Selenite, which has been accepted to be stable in solution, has also been documented to become destabilized in complex matrices resulting in precipitation from solution upon preservation following EPA protocols. As much as a 47% loss of selenium was reported when EPA methods were applied to specific matrices.

The situation is further complicated by the biases associated with the accepted analytical platforms specified in EPA Methods 6020, 200.8, and 1638. Although most of the limitations and interferences associated with the suggested analytical platforms are known they cannot be accounted for on an absolute basis.

Comparison between various hyphenated techniques for selenium speciation analyses will be presented alongside the corresponding total selenium results which have been analyzed in conformance to EPA protocols.

Application of Selenium Speciation Analysis to Elucidate Limitations with Accepted Total Selenium Methods

Russell Gerads
(russ@appliedspeciation.com)

2013 National Environmental Monitoring Conference



APPLIED SPECIATION
AND CONSULTING, LLC

info@appliedspeciation.com
www.appliedspeciation.com

Total Selenium

- Total Selenium – Quantification of all forms of selenium present in the sample, regardless of speciation and phase

- Total Filtered Selenium – Quantification of all forms of selenium present in a sample which pass through a 0.45µm filter, regardless of speciation and phase

Very simple concept…until now.



APPLIED SPECIATION
AND CONSULTING, LLC

Current Promulgated Methods Associated with Selenium Analysis of Aqueous Matrices

EPA Approved Analytical Methods	EPA Approved Digestion Methods	Standard Methods
6020	3005	3114
200.8	3010	3113
200.9	3015	3120
270.2	3020	3125
6010	7740	3500-Se
270.3	7741A	3030
1638	7742	
200.7	200	
	200.2	



APPLIED SPECIATION AND CONSULTING, LLC

Identification of Problem

- Filtered selenium concentrations greater than unfiltered selenium concentration
- Discrepancy of speciation results by IC-ICP-MS when compared to total selenium
- Interlaboratory comparisons identify different total selenium results between laboratories
- Temporally variable selenium concentrations



APPLIED SPECIATION AND CONSULTING, LLC

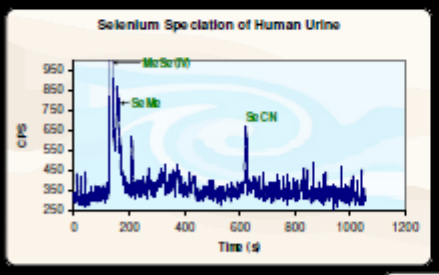
Identification of Problem

Results From Industrial Wastewater

Sample ID	Se(IV)	Se(VI)	SeCN	MSe(IV)	Total Se (1% HNO_3)
Sample 1	19.6	4.4	1.82	2.3	49.5
Sample 2	12.0	5.1	ND (<0.44)	2.0	33.3
Sample 3	47.3	25.6	ND (<0.44)	2.6	140
Sample 4	46.1	21.5	ND (<0.44)	2.7	137
Sample 5	40.5	17.4	ND (<0.44)	1.9	101
Sample 6	31.1	10.5	ND (<0.44)	2.3	85.1
Sample 7	84.4	ND (4.3)	1629	ND (0.44)	23.1
Sample 8	3.41	ND (4.3)	6.84	ND (0.44)	10.6
Sample 9	75.9	8.2	ND (<0.44)	1.1	128
Sample 10	10.1	8.5	ND (<0.44)	1.6	50.8

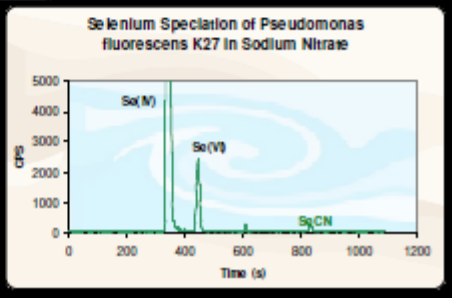
APPLIED SPECIATION AND CONSULTING, LLC

Occurrence of SeCN



- Municipal wastewater treatment plants

- Naturally occurring selenium reducing bacteria (river sediment)
- Industrial wastewater treatment plants incorporating biological treatment



APPLIED SPECIATION AND CONSULTING, LLC

Fate of SeCN

SeCN reaction with 1% HNO_3 in glass

1ppm SeCN Solution



1ppm SeCN Solution
2 min after HNO_3 addition



APPLIED SPECIATION
AND CONSULTING, LLC

Fate of Elemental Selenium

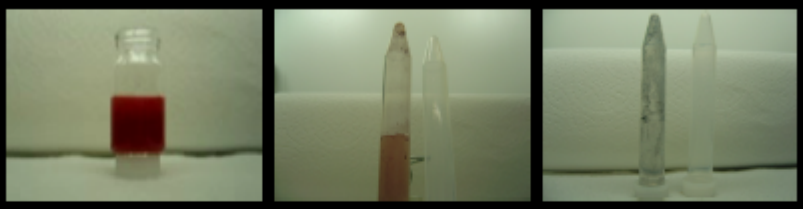
Vessel	Preservation	Ovened?	Mass of Se^0	% Recovery
125mL Amber HDPE	1% HNO3	yes	10mg	0.04
125mL Amber HDPE	10% HNO3	yes	10mg	1.4
125mL Amber HDPE	1% HNO3	no	10mg	0.02
125mL Amber HDPE	10% HNO3	no	10mg	0.02
60mL Clear HDPE	1% HNO3	yes	10mg	0.05
60mL Clear HDPE	10% HNO3	yes	10mg	4.0
60mL Clear HDPE	1% HNO3	no	10mg	0.01
60mL Clear HDPE	10% HNO3	no	10mg	0.01
50mL Polypropylene	1% HNO3	yes	10mg	0.2
50mL Polypropylene	10% HNO3	yes	10mg	79
50mL Polypropylene	1% HNO3	no	10mg	0.04
50mL Polypropylene	10% HNO3	no	10mg	0.05
40mL Amber Glass	1% HNO3	yes	10mg	1.6
40mL Amber Glass	10% HNO3	yes	10mg	96.0
40mL Amber Glass	1% HNO3	no	10mg	0.18
40mL Amber Glass	10% HNO3	no	10mg	0.30

APPLIED SPECIATION
AND CONSULTING, LLC

Fate of Elemental Selenium

Comparison of different containers

Red Se(0) in glass | Red Se(0) in polyethylene | Black Se(0) in polyethylene



APPLIED SPECIATION AND CONSULTING, LLC

Elemental Selenium

- Elemental selenium occurs in two forms
  - Amorphous red elemental selenium – Insoluble in water but can be suspended in solution as a colloid or particulate
  - Crystalline black elemental selenium – Insoluble in water but depending on the size of the crystals it may float on water due to surface tension
- Depending on the conditions of the sample matrix (salts, pH, ORP, etc.) interconversion between forms may occur resulting in further loss and an increased energy demand for digestion

APPLIED SPECIATION AND CONSULTING, LLC

Elemental Selenium

- Why is element selenium important if it is insoluble?
  - Chemical and biological (microbial) processes convert Se(0) to SeO_3 and SeO_4
  - Up to 10% of red, amorphous, elemental selenium was found to be converted to SeO_3 after 125days[1]
  - Se(0) found to have similar induction into glutothione peroxidase, phospholipid hydroperoxide glutathione peroxidase (PHGPx), thioredoxin reductase-1, and protein integration

[1]Losi, M, Frankenberger, W. 1998. *Microbial Oxidation and Solubilization of Precipitated Elemental Selenium in Soil*. Journal of Environmental Quality. 27: 836-843.



APPLIED SPECIATION AND CONSULTING, LLC

Current issues with accepted methodologies

- SeCN is known to convert to elemental selenium when 1% HNO_3 (w/v) preservation is applied
- Elemental selenium is known to adsorb onto plastic bottle walls
- Oxidation of elemental selenium is an endothermic reaction which is facilitated by heating and is not efficiently converted with 1% HNO_3
- Some EPA methods require an aliquot of sample be transferred from the original sample collection vessel prior to digestion, regardless of material (plastic or glass)



APPLIED SPECIATION AND CONSULTING, LLC

Possible Corrections

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Target the sample digestion scheme to focus on elemental selenium and other suspended particulate forms of selenium (SeS_2?)
- Solubilization and stabilization of selenium species (especially colloidal elemental selenium) requires the sample to be digested. What are the options and issues associated with external and in-bottle digestion?



APPLIED SPECIATION
AND CONSULTING, LLC

Sample Preservation

- Do not preserve sample with HNO_3
  - Will result in low recoveries for other metals (Pb, Zn, Cu, etc.) due to adsorption onto bottle walls
  - Inconsequential if colloidal elemental selenium is present in sample
  - Field preservation increases the possible sources of contamination; therefore, there is no advantage of field preservation if preserved in the laboratory

Samples should not be preserved prior to digestion



APPLIED SPECIATION
AND CONSULTING, LLC

Sampling Vessels

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
  - Lowest adsorption capacity of all tested sample vessel materials for elemental selenium
  - Colloidal elemental selenium may aggregate and precipitate out of solution necessitating vigorous shaking prior to subsampling

Sampling Vessels should be limited to borosilicate glass to minimize adsorption of elemental selenium.

APPLIED SPECIATION AND CONSULTING, LLC

Sample Digestion

- Target the sample digestion scheme to focus on elemental selenium and other suspended particulate forms of selenium (SeS_2?)
  - The oxidation potential of the sample must be increased
  - The volume of chemical(s) used for in-bottle digestions must not alter the final volume of the sample which may result in an increased variability due to unknown dilution. Addition of solid chemical is optimal. Sodium sulfite has been applied extensively in academia to quantitate elemental selenium in soil and sediment matrices – does it show promise for aqueous matrices as well?
  - Current data shows external digestion of elemental selenium (red and black) with 10% concentrated HNO_3 (v/v) yields acceptable recoveries.

APPLIED SPECIATION AND CONSULTING, LLC

Sample Digestion

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Target the sample digestion scheme to focus on elemental selenium and other suspended particulate forms of selenium (SeS_2?)
  - Sodium sulfite has been applied extensively in academia to quantitate elemental selenium in soil and sediment matrices – does it show promise for aqueous matrices as well?
  - While the $SeSO_3^{2-}$ complex can be stabilized the performance is operationally defined by the sample matrix (sulfite consumption)



APPLIED SPECIATION
AND CONSULTING, LLC

Sample Digestion

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Target the sample digestion scheme to focus on elemental selenium and other suspended particulate forms of selenium (SeS_2?)
  - Sodium sulfite has been applied extensively in academia to quantitate elemental selenium in soil and sediment matrices – does it show promise for aqueous matrices as well?
  - While the $SeSO_3^{2-}$ complex can be stabilized the performance is operationally defined by the sample matrix (sulfite consumption)

Currently concentrated HNO_3 shows the most promise for conversion of elemental selenium to selenite in some of the most difficult matrices.



APPLIED SPECIATION
AND CONSULTING, LLC

Sample Digestion

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Concentrated HNO3 should be applied for conversion of elemental selenium to selenite
- Solubilization and stabilization of selenium species (especially colloidal elemental selenium) requires the sample to be digested. What are the options and issues associated with external and in-bottle digestion?
  - A minimum of 10% HNO_3 (v/v) was required to recover 96% of 10mg Se^0 in a highly complex industrial waste influent sample. Application of an in-bottle digestion necessitates a known volume of sample which is typically not available.

External Digestion is required for total selenium quantification on a reproducible basis.

APPLIED SPECIATION AND CONSULTING, LLC

Sample Digestion

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Concentrated HNO_3 should be applied for conversion of elemental selenium to selenite
- Pipette 4mL concentrated HNO_3 into a 40mL I-Chem vial. Shake the borosilicate glass sample vial vigorously then bring the 40mL vial up to volume. Cap the 40ml vial and heat at 90°C for a minimum of 4 hours. Let the sample equilibrate to room temperature and analyze.
- The final volumes can change according to the available glass digestion vessels; however, the ratio and procedure should remain the same.
- The sample should NEVER be pipetted from the original sample bottle.

APPLIED SPECIATION AND CONSULTING, LLC

Sample Digestion

- Do not preserve sample with HNO_3
- Limit sample collection to borosilicate glass bottles
- Concentrated HNO_3 should be applied for conversion of elemental selenium to selenite
- Pipette 4mL concentrated HNO_3 into a 40mL I-Chem vial. Shake the borosilicate glass sample vial vigorously then bring the 40mL vial up to volume. Cap the 40ml vial and heat at 90°C for a minimum of 4 hours. Let the sample equilibrate to room temperature and analyze.
- The final volumes can change according to the available glass digestion vessels; however, the ratio and procedure should remain the same.
- The sample should NEVER be pipetted from the original sample bottle.

Now how do we analyze the digest?

APPLIED SPECIATION AND CONSULTING, LLC

Analytical Techniques

- Reactionary Based Analyses
  - Hydride generation atomic absorption spectrophotometry (HG-AAS)
- Direct Analysis (Plasma)
  - Inductively coupled plasma atomic emission spectroscopy (ICP-AES)
  - Inductively coupled plasma mass spectrometry (ICP-MS)

APPLIED SPECIATION AND CONSULTING, LLC

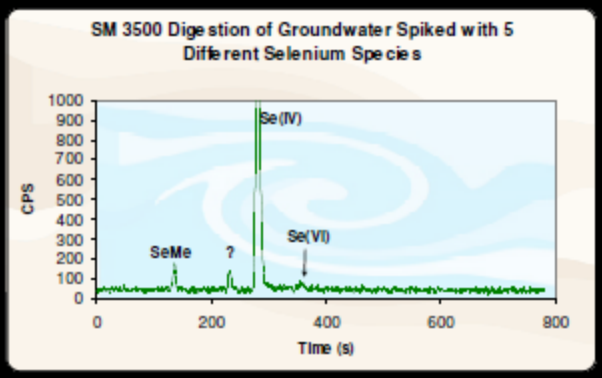
Hydride Generation

- Only Se(IV) can form the volatile hydrides for detection
- Analytical method requires conversion of all selenium species to Se(IV) prior to analysis
  - Multiple sample digestion techniques have been promulgated for analysis via hydride generation (7741A and 7742)
  - Current promulgated digestion techniques do not require incorporation of different selenium species to monitor digestion efficiency
  - Some laboratories have generated their own digestion techniques similar to Standard Method 3500 using persulfate and hydrochloric acid

APPLIED SPECIATION AND CONSULTING, LLC

Performance of Standard Method 3500-Se

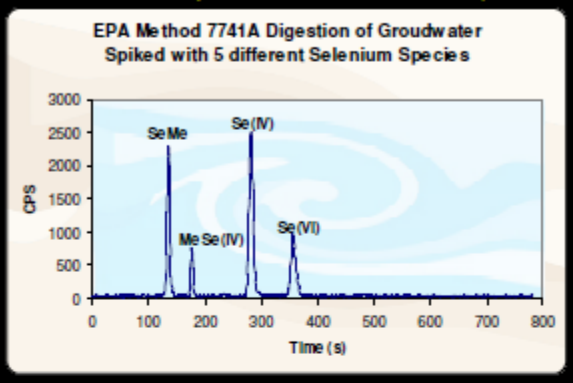
- Digestion facilitates reactions with HCl, $K_2S_2O_8$, and heat (specifics of digestion method can be acquired from Standard Methods)



APPLIED SPECIATION AND CONSULTING, LLC

Performance of EPA Method 7741A

- Digestion facilitates reactions with HNO_3, H_2SO_4, and heat (specifics of digestion method can be acquired from Standard Methods)



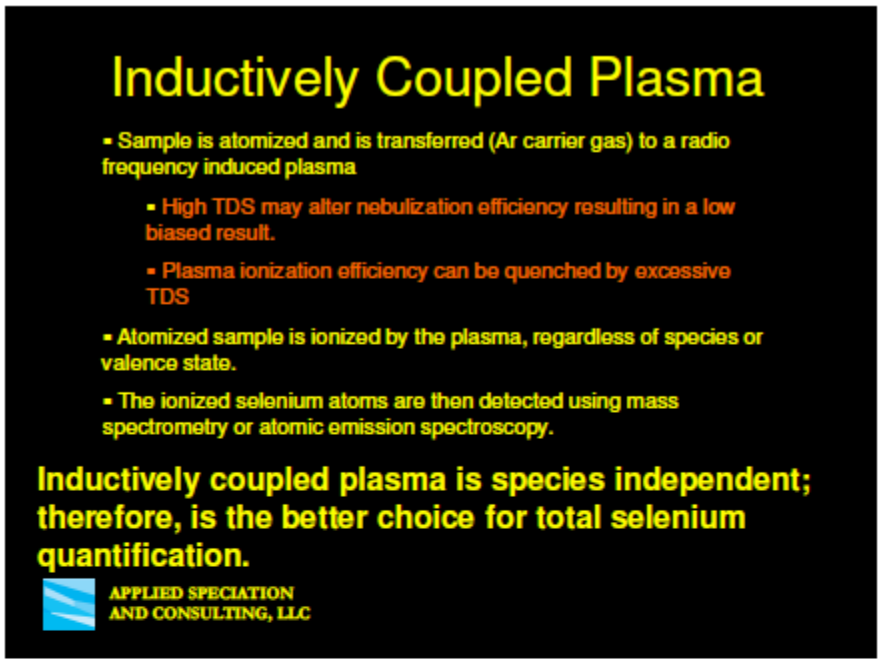
APPLIED SPECIATION AND CONSULTING, LLC

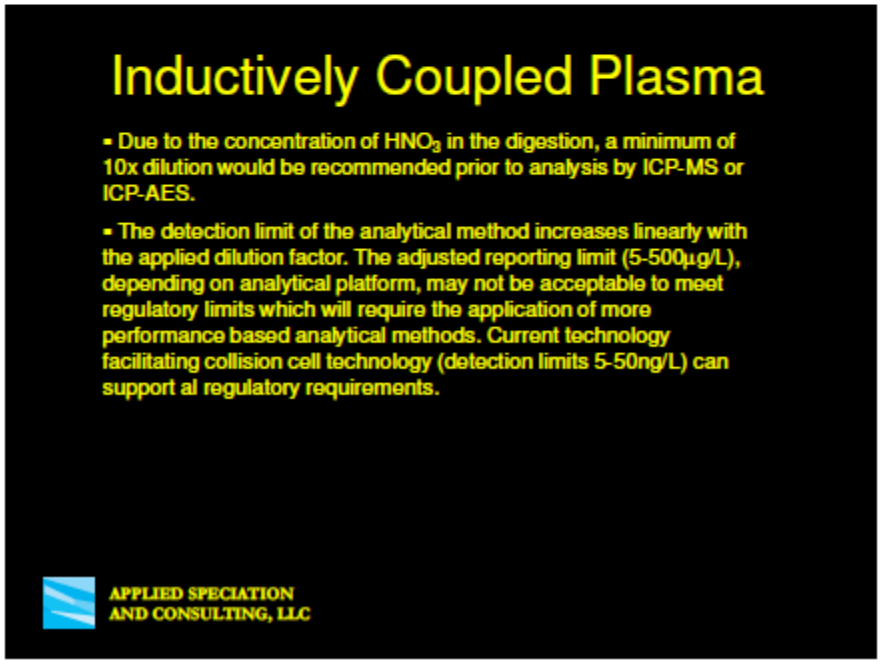
Hydride Generation

- Confirmation that not all selenium species are converted to Se(IV) during digestion which can result in low biased results for all sample matrices

Hydride generation, with any detection scheme, for total selenium quantification is not recommended due to its propensity to produce low biased results for any sample matrix

APPLIED SPECIATION AND CONSULTING, LLC


Inductively Coupled Plasma
▪ Sample is atomized and is transferred (Ar carrier gas) to a radio frequency induced plasma
▪ High TDS may alter nebulization efficiency resulting in a low biased result.
▪ Plasma ionization efficiency can be quenched by excessive TDS
▪ Atomized sample is ionized by the plasma, regardless of species or valence state.
▪ The ionized selenium atoms are then detected using mass spectrometry or atomic emission spectroscopy.
Inductively coupled plasma is species independent; therefore, is the better choice for total selenium quantification.
APPLIED SPECIATION AND CONSULTING, LLC


Inductively Coupled Plasma
▪ Due to the concentration of HNO_3 in the digestion, a minimum of 10x dilution would be recommended prior to analysis by ICP-MS or ICP-AES.
▪ The detection limit of the analytical method increases linearly with the applied dilution factor. The adjusted reporting limit (5-500µg/L), depending on analytical platform, may not be acceptable to meet regulatory limits which will require the application of more performance based analytical methods. Current technology facilitating collision cell technology (detection limits 5-50ng/L) can support al regulatory requirements.
APPLIED SPECIATION AND CONSULTING, LLC

Overview of Method for Total Selenium Quantification in Aqueous Matrices

1) Do not preserve sample with HNO_3
2) Limit sample collection to borosilicate glass bottles
3) Pipette 4mL concentrated HNO_3 into a 40mL I-Chem vial. Shake the borosilicate glass sample vial vigorously then bring the 40mL vial up to volume with sample. Cap the 40ml vial and heat at 90°C for a minimum of 4 hours. Let the sample equilibrate to room temperature and analyzed by ICP-AES or ICP-MS.
4) The final volumes can change according to the available glass digestion vessels; however, the ratio and procedure should remain the same.
5) The sample should NEVER be pipetted from the original sample bottle for quantitation purposes.



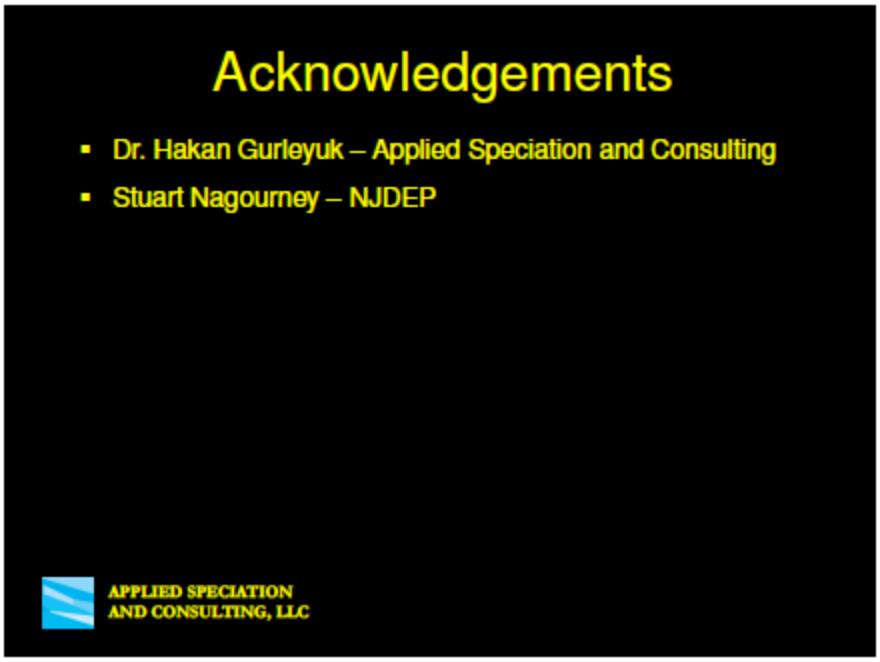
APPLIED SPECIATION
AND CONSULTING, LLC

Final Thoughts

- Elemental selenium is currently being discharged into US rivers and lakes from indutrial treatment facilities.
- Current research has identified a known issue with accepted methodologies for sample collection and digestion prior to analysis.
- Current research has identified that hydride generation may produce unrepresentative results without the performance of method development on each sample type and each selenium species of interest. All selenium species of interest MUST be applied in matrix spikes to generate a true representation of the method' s performance.



APPLIED SPECIATION
AND CONSULTING, LLC


Acknowledgements
Dr. Hakan Gurleyuk – Applied Speciation and Consulting
Stuart Nagourney – NJDEP
APPLIED SPECIATION
AND CONSULTING, LLC

Elemental Speciation as Essential Part of Formulating Exposure Assessments that Support Risk Estimates

Jack Creed
USEPA, Office of Research and Development

Abstract

The chemical form specific toxicity of arsenic has caused scientists to move toward species specific assessments with an emphasis on biological relevance of an exposure. For example, numerous studies on the occurrence of arsenic in rice have documented the exposure potential from this commonly consumed crop, but few have addressed the bioaccessibility question essential to converting occurrence into risk. The first part of this presentation will discuss the use of a speciation based gastrointestinal based assay to estimate the bioaccessibility of arsenicals in rice. Utilizing these estimates within a modeling framework allows for population based exposure (µg/kg of body weight/day) assessment. The approach will be discussed with an emphasis on risk predictive advantages / limitations and how this information can inform decision making.

The second part of this presentation will discuss the need to incorporate gastrointestinal biotransformation of arsenic oxides in order to accurately estimate the pre-systemic species specific distribution available for uptake in the intestine. The methylation and thiolation of the parent arsenic oxide will be estimated using an in vitro anaerobic incubation of the arsenical in the cecum content of a mouse. The analytical techniques used to confirm the identity of these arsenicals will be discussed along with the need to incorporate the microbiological aspects of the intestine within any in vitro assay that intends to predict species specific exposures.

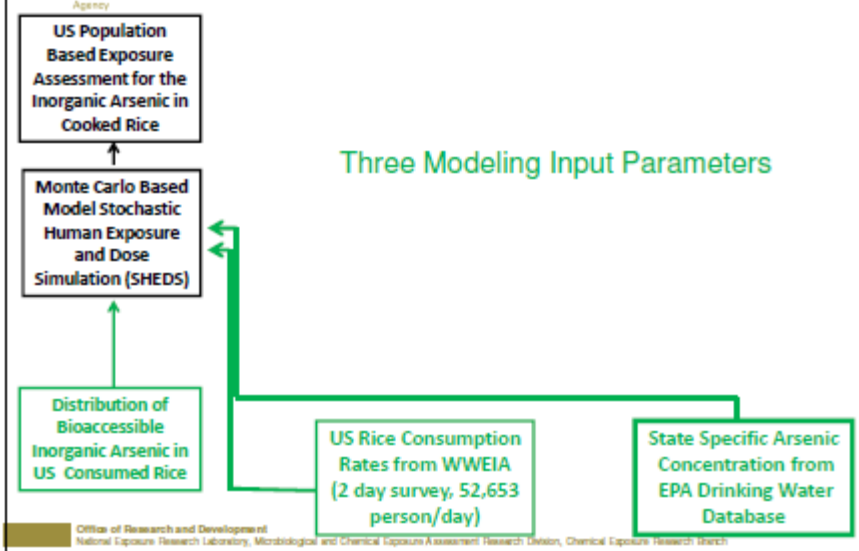
Elemental Speciation as an Essential Part of Formulating Exposure Assessments that Support Risk Estimates

John T. Creed[1], Patricia A. Creed[1], Tatyana Pinyayev[1], Madhavi Mantha[2], John Trent[3], Edward Yeary[3], Jianping Xue[4], Michael Kohan[5], Karen Herbin-Davis[5], David Thomas[5], Kevin Kubachka[6], Traci Hanley[6], Nohora Shockey[6], Douglas Heitkemper[6], Joseph Caruso[7]

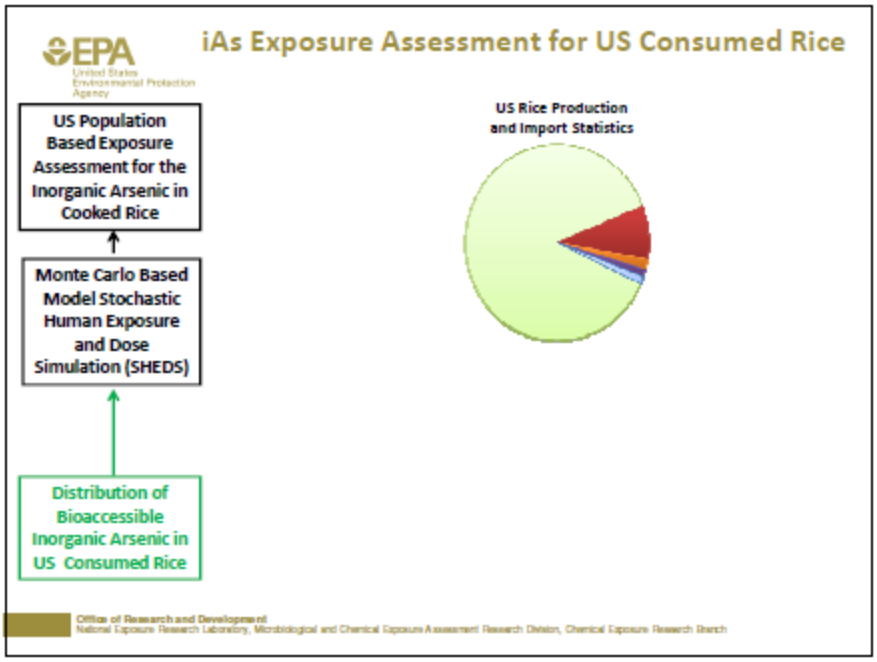
[1]U.S. EPA, NERL, MCEARD, Cincinnati, OH
[2]Oak Ridge Institute for Science and Education Scholar, U.S. EPA, NERL, Cincinnati, OH
[3]Student Services Contractor, NERL, MCEARD, Cincinnati, OH
[4]U.S. EPA, NERL, HEASD, Research Triangle Park, NC
[5]U.S. EPA, NHEERL, ISTD, Research Triangle Park, NC
[6]Food and Drug Administration (FDA), Forensic Chemistry Center, Cincinnati, OH
[7]University of Cincinnati, Department of Chemistry, Cincinnati, OH

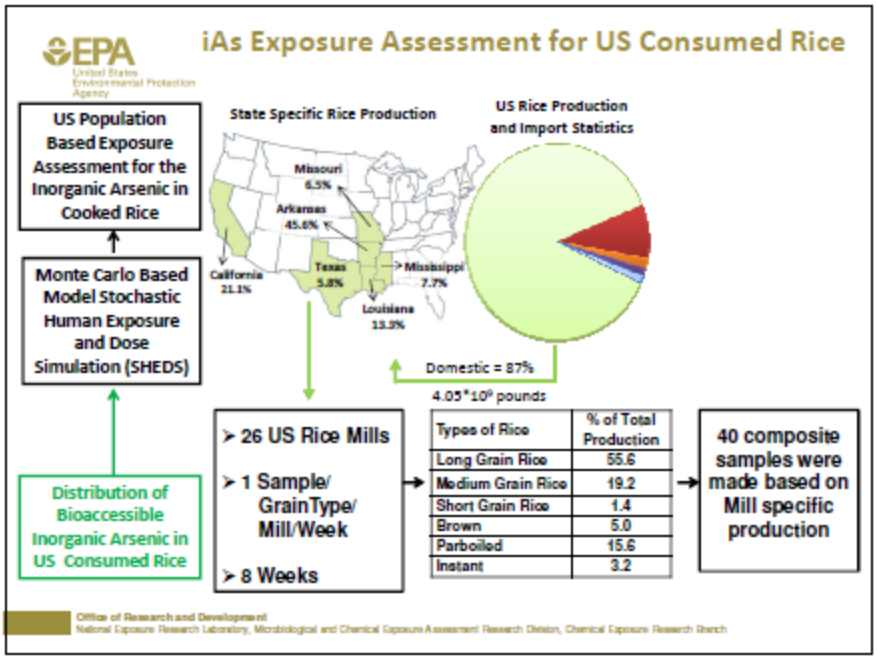
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

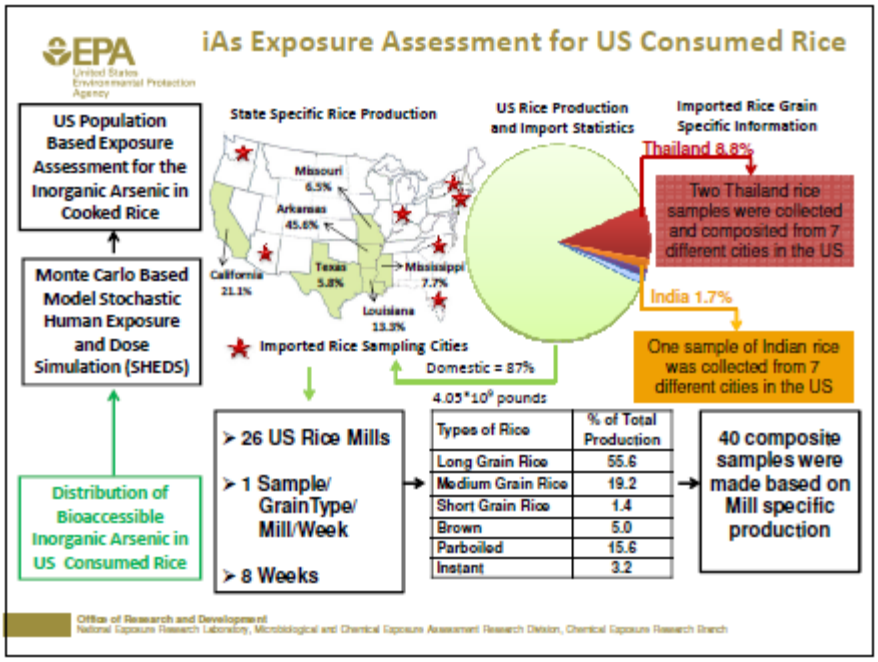
iAs Exposure Assessment for US Consumed Rice

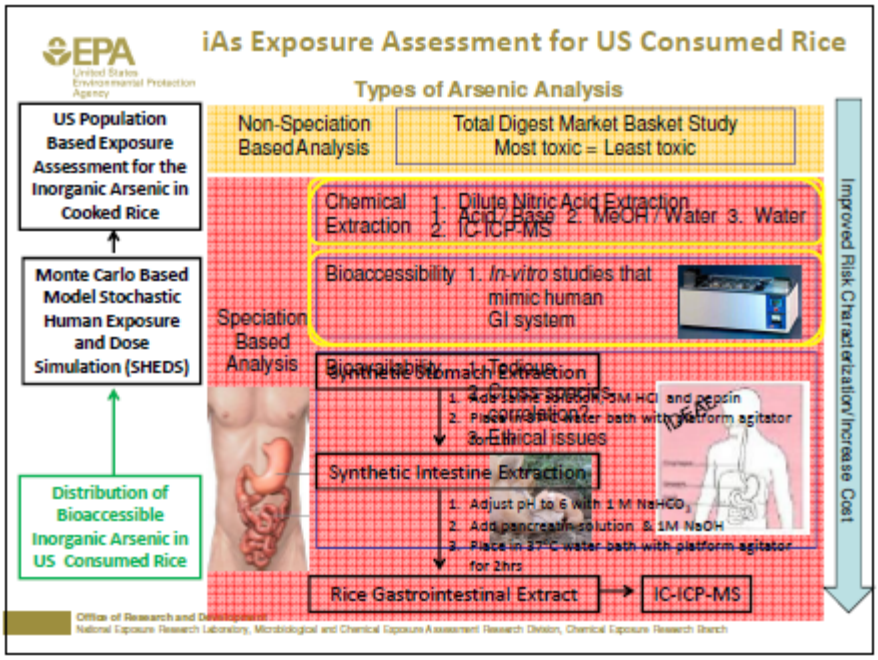


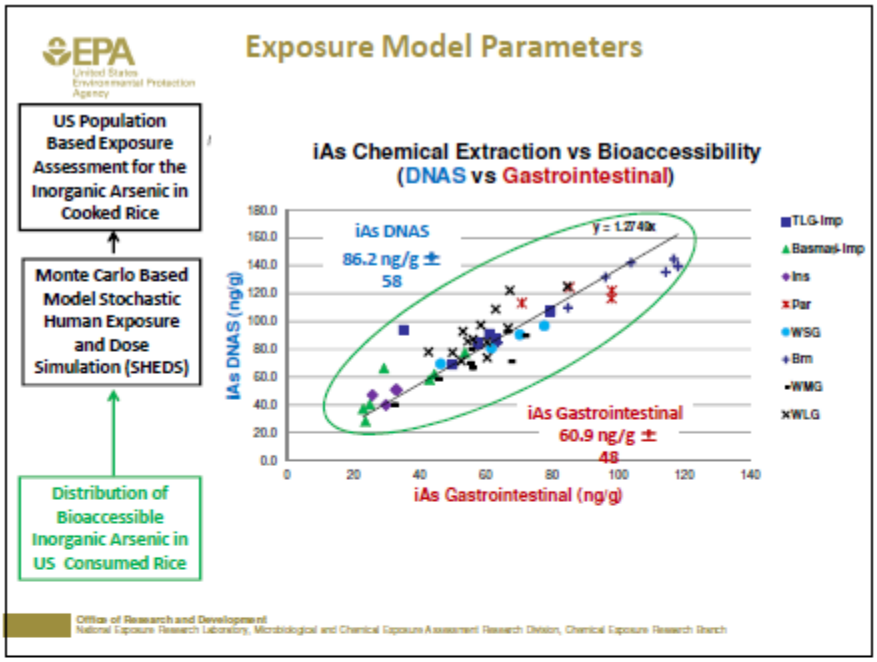
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

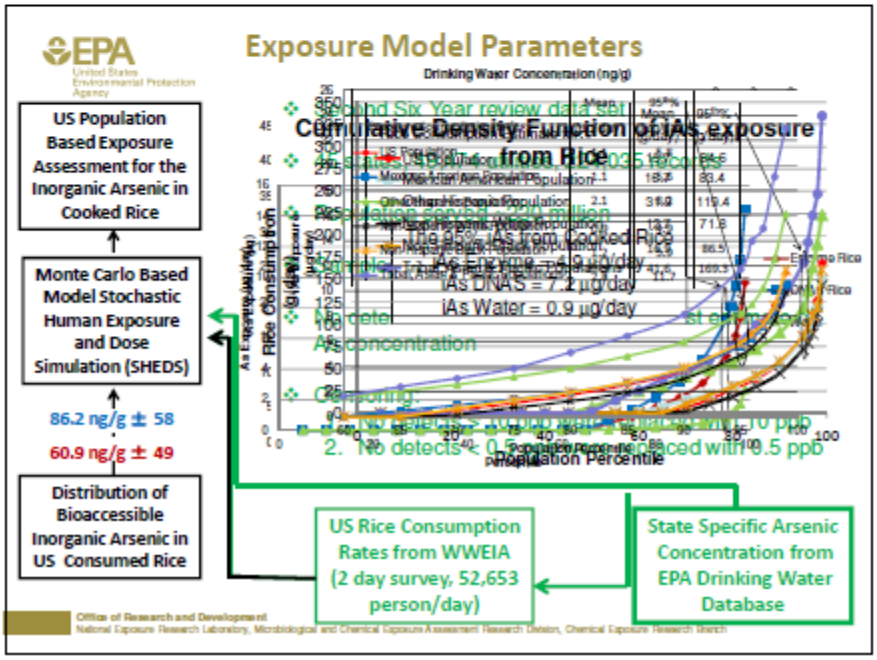

iAs Exposure Assessment for US Consumed Rice
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
US Rice Production and Import Statistics
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

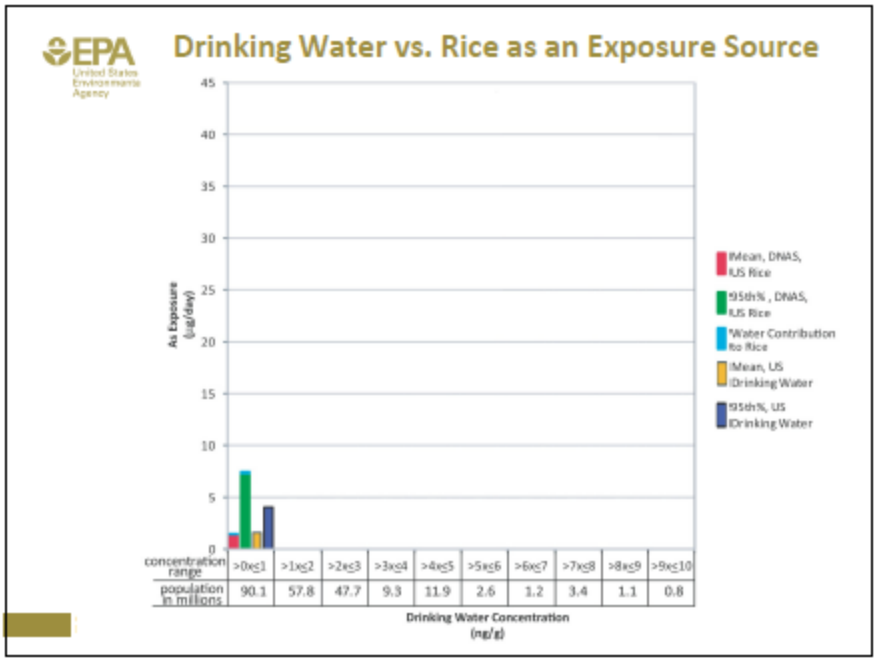

iAs Exposure Assessment for US Consumed Rice
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
State Specific Rice Production
US Rice Production and Import Statistics
Missouri 6.5%
Arkansas 45.6%
California 21.1%
Texas 5.8%
Mississippi 7.7%
Louisiana 13.3%
Domestic = 87%
4.05*10⁹ pounds
➢ 26 US Rice Mills
➢ 1 Sample/ GrainType/ Mill/Week
➢ 8 Weeks
Types of Rice | % of Total Production
Long Grain Rice | 55.6
Medium Grain Rice | 19.2
Short Grain Rice | 1.4
Brown | 5.0
Parboiled | 15.6
Instant | 3.2
40 composite samples were made based on Mill specific production
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

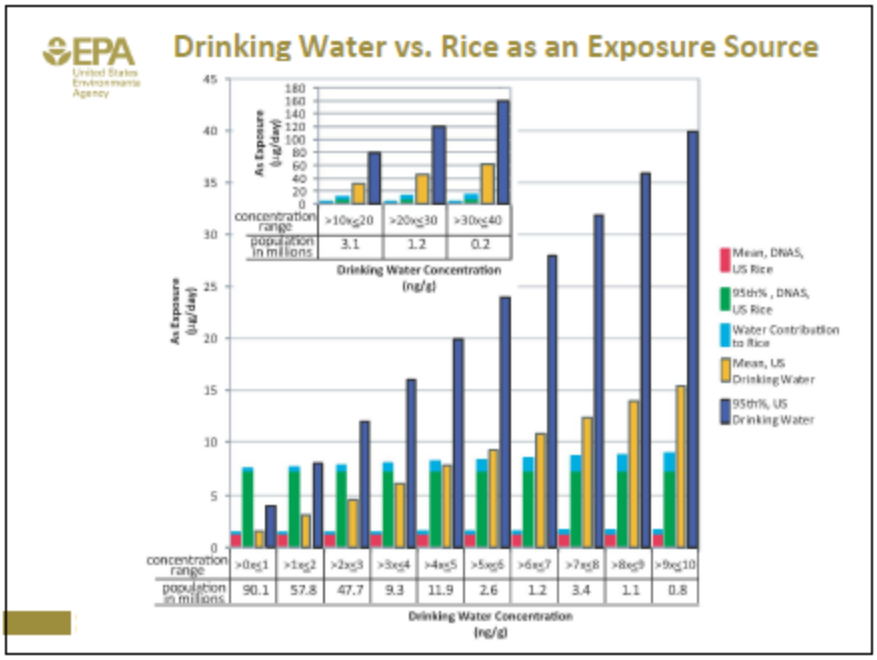

iAs Exposure Assessment for US Consumed Rice
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
State Specific Rice Production
Missouri 6.5%
Arkansas 45.6%
California 21.1%
Texas 5.8%
Mississippi 7.7%
Louisiana 13.3%
Imported Rice Sampling Cities
US Rice Production and Import Statistics
Domestic = 87%
4.05*10^9 pounds
Imported Rice Grain Specific Information
Thailand 8.8%
Two Thailand rice samples were collected and composited from 7 different cities in the US
India 1.7%
One sample of Indian rice was collected from 7 different cities in the US
26 US Rice Mills
1 Sample/ GrainType/ Mill/Week
8 Weeks
Types of Rice | % of Total Production
Long Grain Rice | 55.6
Medium Grain Rice | 19.2
Short Grain Rice | 1.4
Brown | 5.0
Parboiled | 15.6
Instant | 3.2
40 composite samples were made based on Mill specific production

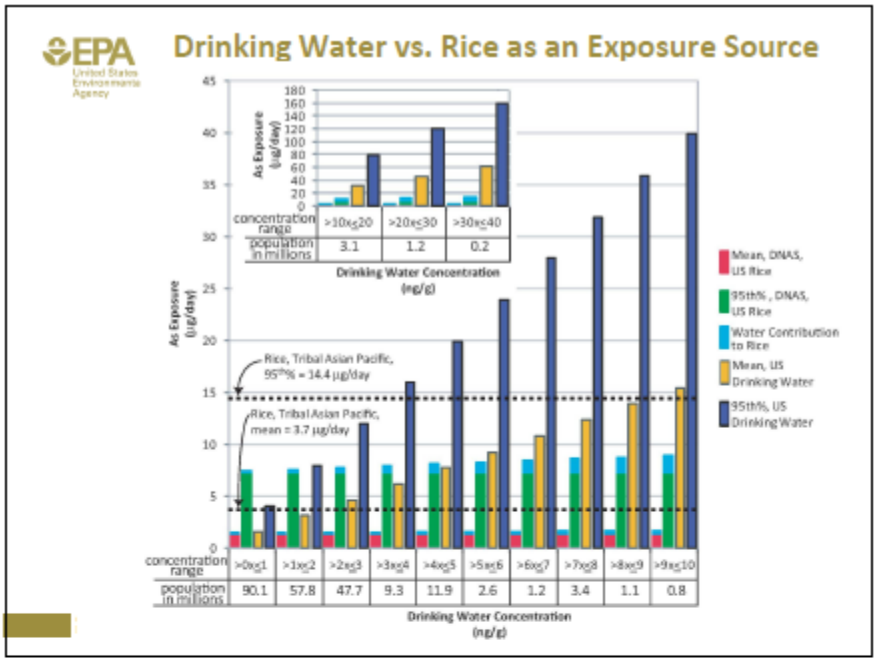

iAs Exposure Assessment for US Consumed Rice
Types of Arsenic Analysis
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
Non-Speciation Based Analysis
Total Digest Market Basket Study
Most toxic = Least toxic
Speciation Based Analysis
Chemical Extraction 1. Dilute Nitric Acid Extraction 2. Acid / Base 2. MeOH / Water 3. Water 2. IC-ICP-MS
Bioaccessibility 1. In-vitro studies that mimic human GI system
Bioavailability 1. Tedious 2. Cost issues 3. Ethical issues
Synthetic Stomach Extraction
Synthetic Intestine Extraction
1. Adjust pH to 6 with 1 M NaHCO3
2. Add pancreatin solution & 1M NaOH
3. Place in 37°C water bath with platform agitator for 2hrs
Rice Gastrointestinal Extract
IC-ICP-MS
Improved Risk Characterization/Increase Cost

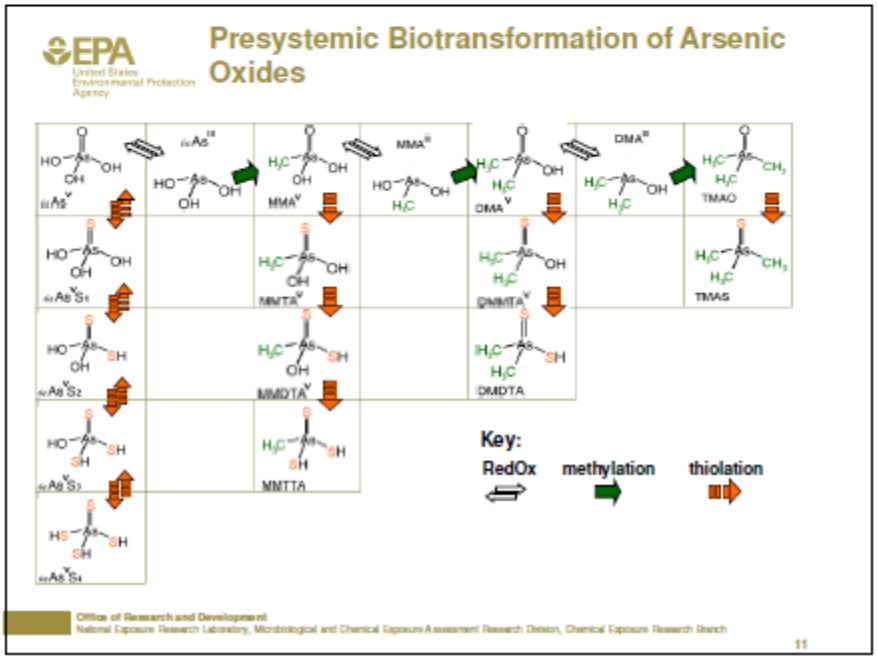

EPA
United States Environmental Protection Agency
Exposure Model Parameters
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
iAs Chemical Extraction vs Bioaccessibility
(DNAS vs Gastrointestinal)
iAs DNAS
86.2 ng/g ± 58
y = 1.2749x
iAs Gastrointestinal
60.9 ng/g ± 48
iAs DNAS (ng/g)
iAs Gastrointestinal (ng/g)
TLG-Imp
Basmati-Imp
Ins
Par
WSG
Brn
WMG
WLG
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

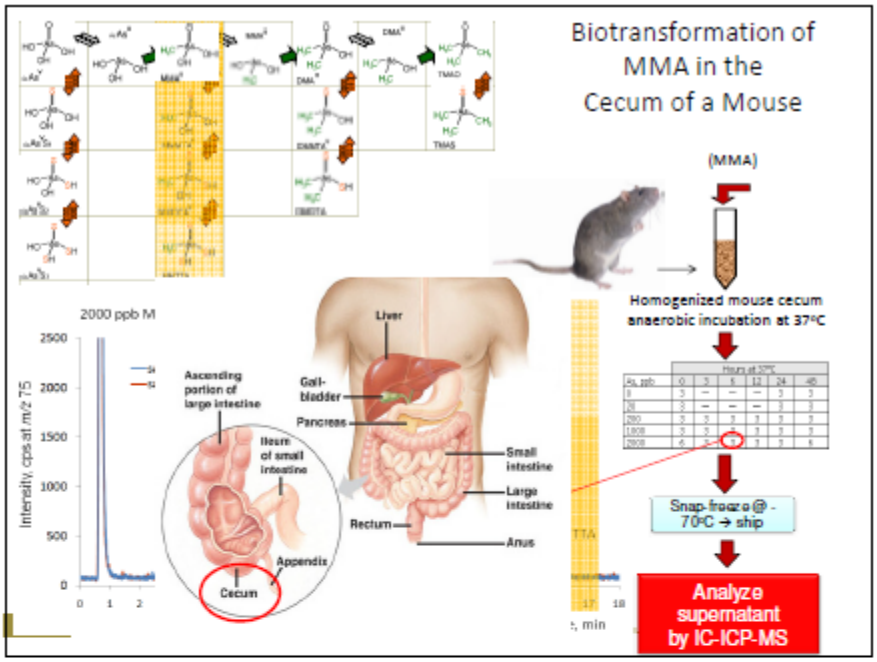

EPA
United States Environmental Protection Agency
Exposure Model Parameters
US Population Based Exposure Assessment for the Inorganic Arsenic in Cooked Rice
Monte Carlo Based Model Stochastic Human Exposure and Dose Simulation (SHEDS)
86.2 ng/g ± 58
60.9 ng/g ± 49
Distribution of Bioaccessible Inorganic Arsenic in US Consumed Rice
Cumulative Density Function of iAs exposure from Rice
Drinking Water Concentration (ng/g)
Rice Consumption (g/day)
Population Percentile
iAs DNAS = 7.2 µg/day
iAs Water = 0.9 µg/day
US Rice Consumption Rates from WWEIA (2 day survey, 52,653 person/day)
State Specific Arsenic Concentration from EPA Drinking Water Database
Office of Research and Development
National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch

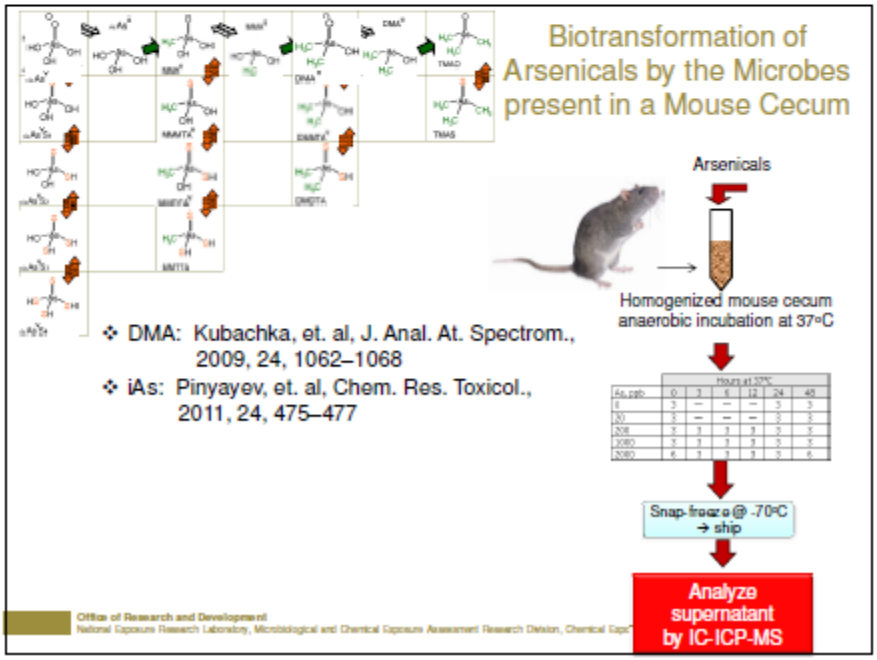

Drinking Water vs. Rice as an Exposure Source
EPA
United States Environmental Agency
As Exposure (ug/day)
45
40
35
30
25
20
15
10
5
0
Mean, DNAS, US Rice
95th% , DNAS, US Rice
Water Contribution to Rice
Mean, US Drinking Water
95th%, US Drinking Water
concentration range
>0≤1
>1≤2
>2≤3
>3≤4
>4≤5
>5≤6
>6≤7
>7≤8
>8≤9
>9≤10
population in millions
90.1
57.8
47.7
9.3
11.9
2.6
1.2
3.4
1.1
0.8
Drinking Water Concentration (ng/g)


Drinking Water vs. Rice as an Exposure Source
EPA
United States Environmental Agency
As Exposure (ug/day)
45
40
35
30
25
20
15
10
5
0
180
160
140
120
100
80
60
40
20
0
Mean, DNAS, US Rice
95th% , DNAS, US Rice
Water Contribution to Rice
Mean, US Drinking Water
95th%, US Drinking Water
concentration range
>10≤20
>20≤30
>30≤40
population in millions
3.1
1.2
0.2
Drinking Water Concentration (ng/g)
concentration range
>0≤1
>1≤2
>2≤3
>3≤4
>4≤5
>5≤6
>6≤7
>7≤8
>8≤9
>9≤10
population in millions
90.1
57.8
47.7
9.3
11.9
2.6
1.2
3.4
1.1
0.8
Drinking Water Concentration (ng/g)

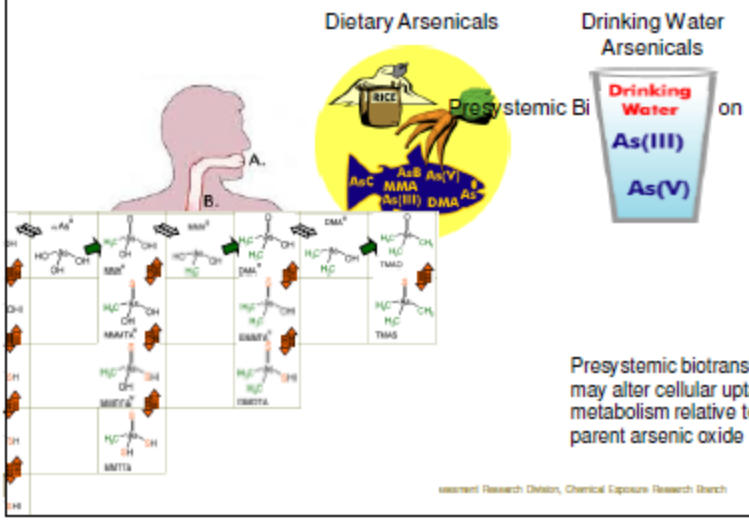

Drinking Water vs. Rice as an Exposure Source
As Exposure (µg/day)
Drinking Water Concentration (ng/g)
concentration range
population in millions
>10x≤20
>20x≤30
>30x≤40
3.1
1.2
0.2
Rice, Tribal Asian Pacific, 95th% = 14.4 µg/day
Rice, Tribal Asian Pacific, mean = 3.7 µg/day
Mean, DNAS, US Rice
95th% , DNAS, US Rice
Water Contribution to Rice
Mean, US Drinking Water
95th%, US Drinking Water
>0x≤1
>1x≤2
>2x≤3
>3x≤4
>4x≤5
>5x≤6
>6x≤7
>7x≤8
>8x≤9
>9x≤10
90.1
57.8
47.7
9.3
11.9
2.6
1.2
3.4
1.1
0.8


Presystemic Biotransformation of Arsenic Oxides
Key:
RedOx
methylation
thiolation
Office of Research and Development
11


Biotransformation of MMA in the Cecum of a Mouse
(MMA)
Homogenized mouse cecum anaerobic incubation at 37°C
Snap-freeze @ -70°C → ship
Analyze supernatant by IC-ICP-MS
2000 ppb M
Intensity, cps at m/z 75
Liver
Gall-bladder
Pancreas
Small intestine
Large intestine
Rectum
Anus
Ascending portion of large intestine
Ileum of small intestine
Appendix
Cecum
TTA


Biotransformation of Arsenicals by the Microbes present in a Mouse Cecum
Arsenicals
Homogenized mouse cecum anaerobic incubation at 37°C
Snap-freeze @ -70°C → ship
Analyze supernatant by IC-ICP-MS
❖ DMA: Kubachka, et. al, J. Anal. At. Spectrom., 2009, 24, 1062–1068
❖ iAs: Pinyayev, et. al, Chem. Res. Toxicol., 2011, 24, 475–477
Office of Research and Development

Arsenicals present in food undergo changes prior to absorption in your intestine



Presystemic biotransformation may alter cellular uptake and metabolism relative to the parent arsenic oxide

Acknowledgement

We would like to thank Steve Hensley and the Rice Federation for providing samples.

Multifaceted Approach to Arsenic Speciation Analysis of Plant and Animal Tissue

Russell Gerads
Applied Speciation and Consulting

Abstract

Mr. Gerads is currently the CEO/President of Applied Speciation and Consulting. Mr. Gerads' responsibilities encompass all business and scientific aspects associated with Applied Speciation and Consulting, LLC. Mr. Gerads is the primary liaison for all internal and external scientific investigations assisting in their formulation, management, and execution. Mr. Gerads holds a Bachelor's degree in Chemistry from the University of Washington and has managed thousands of research projects associated with trace element and trace element speciation analyses associated with environmental, pharmaceutical, nutraceutical, government, forensics, clinical, and chemical manufacturing markets for nearly all matrices.

By invitation, Mr. Gerads has presented to the New Jersey Department of Environmental Protection, National Environmental Monitoring Conference, the Society of Forensic Toxicologists, and the International Water Conference. Mr. Gerads has published a number of scientific articles and also provides workshops and presentations at various scientific conferences throughout the year associated with trace element and trace element speciation analyses.

Multi-faceted Approach to Arsenic Speciation Analysis of Plant and Animal Tissue

Russell Gerads
(russ@appliedspeciation.com)

2013 National Environmental Monitoring Conference



APPLIED SPECIATION AND CONSULTING, LLC

info@appliedspeciation.com
www.appliedspeciation.com

Importance of Arsenic Speciation

inorganic As species are much more toxic than organic species
(LC_{50} = 10 mg/kg vs. 700 mg/kg)
As(III) and As(V) are equally toxic,
since As(V) is quickly reduced inside organisms
but: As(III) and As(V) have different uptake rates and pathways,
so they may not have the same effects

symptoms:
"heavy metal poisoning": deactivation of enzyme systems with –SH groups
decoupling of cellular energy cycle; cell necrosis
deactivation of glutathione



APPLIED SPECIATION AND CONSULTING, LLC

Natural Sources of Arsenic

Volcanic – Minimal atmospheric emissions, mobility limited to runoff

Soil/Sediment – The concentration of arsenic in soil and sediment is highly dependent on the parent material (rock and decomposed organic matter). Typically soils/sediment rich in series 4 transition metals contain elevated concentrations of As. The mobility of As in soil/sediment depends on the complexation of As, pH, redox, soluble cations and anions, temperature, and presence of microbial organisms.

Rock – The concentration and molecular form of As in rock and other minerals is highly dependent on the variables associated with the formation of the solid. Volcanic rock typically contains lower concentrations of As due to the relatively fast formation from homogenous magma. Sedimentary rock can contain significant higher concentration of As due to the slow formation over centuries allowing for aggregation of Fe, Mn, Al, and other elements which have greater capacities for As retention.

Conclusions: The molecular form, concentration, and fate and transport of arsenic in solid substrates cannot be assumed. **Arsenic concentrations in the lithosphere is quite heterogeneous resulting in different forms and concentrations in raw food materials**



APPLIED SPECIATION
AND CONSULTING, LLC

Natural Sources of Arsenic

Oceans – Due to the massive volume and continual mixing of oceans the concentration of As is very homogenous. Elevated concentrations of arsenic are localized to geologically active formations (subsurface volcanic activity) and terrestrial outfalls (rivers). Mean oceanic As concentration = 1-1.8ppb.

River Water – Arsenic concentrations in river water are highly dependent on the source of the water (snow melt or rainfall), runoff, and effluents from industrial complexes. Natural runoff from rocks and soil are heavily impacted by the pH of the rainfall, arsenic concentration in the solid substrate, molecular form of As, and capacity of the substrate to retain As.

Groundwater: The fate and transport of As in groundwater is typically dictated by the mineralogy of the soil, pH, redox conditions, dissolved oxygen, and presence of series 4 transition metals (Fe, Mn, Pb, Cu, etc).



APPLIED SPECIATION
AND CONSULTING, LLC

Natural Sources of Arsenic

Lakes – Inflows from tributaries, industrial discharge, runoff, and wet and dry deposition have the greatest impact on the arsenic concentrations in lake and ponds. The molecular form and stratification of As in lakes and ponds is typically dictated by the depth (affecting light penetration), size, shape, aquatic foliage, microbial activity in the sediment, and seasonal temperature differences which can induce mixing. Since the aforementioned variables are different for every lake and pond mathematical models will only have limited success for predicting the fate and transport of As.

Rain – The most significant impact on the As concentration in rain is the atmospheric loading from coal fired power plants, volcanic activity, and incinerators.

Conclusion: Oxidized forms of As are thermodynamically favored in most aquatic systems. Arsenate is most prevalent in oxygenated waters; however, speciation becomes significantly more complex in reducing conditions. **Bioaccumulation and metabolism is species (plant and animal) specific**.

APPLIED SPECIATION AND CONSULTING, LLC

Anthropogenic arsenic uses / sources

mining and smelting (Au, Cu)
semiconductor production (Ga doping)
biocides
wood preservation (CCA)
defoliation (DMAs)
herbidices (cotton growing, weed control) (MMAs, DMAs, As_2O_3)
beetle control (MMAs)
orchards (Pb-arsenate)
feed additives for livestock (phenyl-As compounds):
fight intestinal parasites
stainless steel

coal combustion (fly ash)
phosphate detergents
phosphate fertilizers

APPLIED SPECIATION AND CONSULTING, LLC

What Arsenic Species Can We Expect?

- Arsenite
- Arsenate
- Monomethylarsonic acid
- Dimethylarsenic acid
- Trimethylarsonium
- Triphenylarsine
- Triphenylarsine oxide
- Tetramethylarsonium
- Arsenobetaine
- Arsenocholine
- Hexafluoroarsenate
- 3-Amino-4-hydroxyphenylarsonic acid
- 4-Aminophenylarsonic acid
- Nitarsone
- Thio-dimethylarsenite
- Arsenosugars (P & S) *see below*
- Arsenolipids (polar and non-polar)
- 4-Hydroxy phenlarsonic acid
- p-arsenilic acid
- Roxarsone

Arsenosugar-glycerol $(CH_3)_2AsO[(C_5H_4O)(OH)_2]OCH_2CHOHCH_2OH$
Arsenosugar-glycerol $(CH_3)_2AsS[(C_5H_4O)(OH)_2]\ OCH_2CHOHCH_2OH$
Arsenosugar- Phosphate $(CH_3)_2AsO[(C_5H_4O)(OH)_2]OCH_2CHOHCH_2HPO_4CH_2CHOHCH_2OH$
Arsenosugar-sulfonate $(CH_3)_2AsO[(C_5H_4O)(OH)_2]OCH_2CHOHCH_2SO_3$
Thioarsenosugar sulfonate $(CH_3)_2AsS[(C_5H_4O)(OH)_2]\ OCH_2CHOHCH_2SO_3$
Arsenosugar-sulfate $(CH_3)_2AsO[(C_5H_4O)(OH)_2]OCH_2CHOHCH_2OSO_3H$
Thioarsenosugar-sulfate $(CH_3)_2AsS[(C_5H_4O)(OH)_2]\ OCH_2CHOHCH_2OSO_3H$

APPLIED SPECIATION AND CONSULTING, LLC

Current Preparatory Methods for Arsenic Speciation Analysis

Regulatory (promulgated or close)
- Heated HCl extraction (EPA Method 1632 not recommended)
- Heated tetramethylammonium hydroxide (TMAH)
- HNO_3 Leach

Non-regulatory
- TBAH
- Acetone
- Mixed Solvent
- Enzymatic extraction (non-standardized)
- Methanol (MeOH)
- Nitric Acid (not recommended)
- Trifluoroacetic acid (TFA)
- Phosphoric acid

Hot plate
Hotblock
Microwave
Water bath
Sonicated water bath
Sonic wand
Inverted tumbler
Passive

APPLIED SPECIATION AND CONSULTING, LLC

Current Analytical Methods for Arsenic Speciation Analysis

- HG-CT-GC-AFS (hydride generation cryogenic trapping gas chromatography atomic fluorescence spectroscopy)
- IC-HG-AFS (ion chromatography hydride generation atomic fluorescence spectroscopy)
- IC-ICP-MS (ion chromatography inductively coupled plasma mass spectrometry) with and without DRC and CRC technology
- RP-ICP-MS (reverse phase chromatography inductively coupled plasma mass spectrometry)
- NP-ICP-MS (normal phase chromatography inductively coupled plasma mass spectrometry)
- SEC-ICP-MS (size exclusion chromatography inductively coupled plasma mass spectrometry)

- Some chromatography options compatible with soft ionization MS-MS

APPLIED SPECIATION AND CONSULTING, LLC

Problems with Current Approach

- Most industrial, commercial, and academic laboratories have limited knowledge and experience with different preparatory and chromatographic separation mechanisms

- Data objectives are built around "known" technology and not "available" technologies

- Limitations of extraction and analytical methods are overlooked and not considered "important" before widespread application

- Regulations have not kept up with demand – limited methods are available

- Standards can be VERY difficult to acquire

APPLIED SPECIATION AND CONSULTING, LLC

Solutions to Resolve Limitations

- Set data objectives independent of individual (person or laboratory) knowledge or experience
- Select preparatory methods in accordance with matrix type, detection limits, and target molecules
- Select analytical methods which can support resolution of arsenic species in extracts, detection limits, and extract solution
- Define quality control
  - Mass balance for extracts
  - Mass balance between total As and sum of species
  - Resolution between species (target and non-target species)
  - Mitigation of false positives
  - Spikes to monitor species conversion during extraction, storage, and analysis

APPLIED SPECIATION AND CONSULTING, LLC

New Method Approach
(Matrix and Species Specific)

Complex Carbohydrates, Lipids, Muscle, Simple and Complex Powders

Ionic

Inorganic → As(III), As(V) or TIAs → [MeOH, TFA, TMAH (TIAS), TBAH, Water, Enzyme, HNO_3]

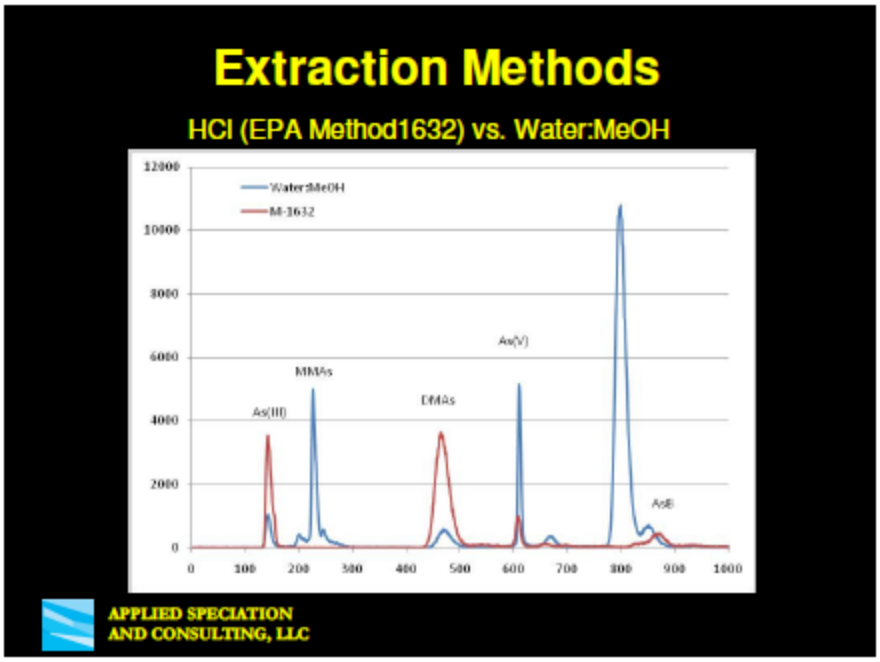
organic → Thiol, Sugars, Industrial waste, Feed additives, Primary metabolites, Intermediate metabolites → [MeOH, TFA, TMAH (TIAs), TBAH (TIAs)]

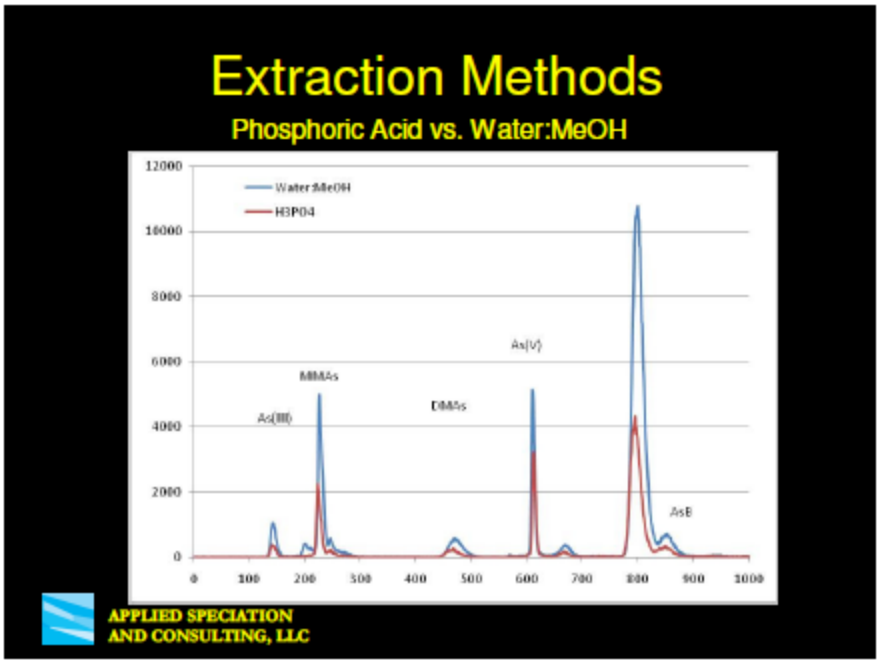
Non-Ionic

Industrial waste

Arsenolipids → Polar, Non-polar → [Mixed Solvent]

APPLIED SPECIATION AND CONSULTING, LLC


Extraction Methods
HCl (EPA Method1632) vs. Water:MeOH
Water:MeOH
M-1632
As(III)
MMAs
DMAs
As(V)
AsB
APPLIED SPECIATION
AND CONSULTING, LLC


Extraction Methods
Phosphoric Acid vs. Water:MeOH
Water:MeOH
H3P04
As(III)
MMAs
DMAs
As(V)
AsB
APPLIED SPECIATION
AND CONSULTING, LLC

Extraction Methods

Rice	Total As (HNO_3/H_2O_2)	Species (TFA Extraction)				Recovery
		$DMAs^{3}$	AsIII	AsV	Sum	
	mg kg^{-1}					% Tot. As
1	0.710 ± 0.028	0.572	0.168	<0.005	0.769	108
2	0.450 ± 0.021	0.32	0.116	<0.005	0.437	97
3	0.241 ± 0.003	0.068	0.157	0.011	0.236	98
4	0.258	0.069	0.142	0.008	0.218	85
5	0.242	0.171	0.049	0.023	0.242	100
6	0.253 ± 0.002	0.138	0.076	0.095	0.312	123
7	0.383 ± 0.003	0.302	0.071	0.003	0.382	100
8	0.369 ± 0.008	0.221	0.069	0.013	0.302	82
9	0.190 ± 0.002	0.061	0.122	0.008	0.192	101
10	0.203 ± 0.005	0.095	0.094	0.013	0.201	99
11	0.195 ± 0.017	0.106	0.086	0.014	0.207	106
12	0.270 ± 0.020	0.179	0.098	0.008	0.285	106
13	0.256	0.128	0.118	0.014	0.259	101
14	0.351	0.239	0.078	0.007	0.323	92
15	0.240 ± 0.014	0.171	0.081	0.013	0.265	111
16	0.222	0.143	0.084	0.003	0.230	104

APPLIED SPECIATION AND CONSULTING, LLC

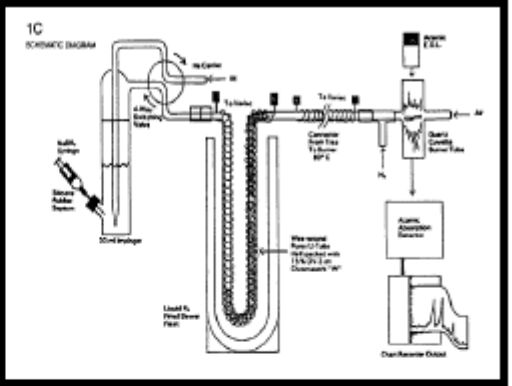
Extraction Methods

MeOH extract	mg/kg							Unknown Peaks (RT) mg/kg			
	Total with unknowns	As3	As5	MA/AsC/Tet	DMA	AsB/TriMat	Total	2.63	2.90	3.63	5.98
1	20.05	0.36	0.00	0.18	14.03	5.39	19.97	0.00	0.00	0.08	0.14
2	5.64	0.20	0.68	1.81	0.93	2.03	5.64	0.00	0.00	0.00	0.00
3	49.51	2.44	6.91	17.63	8.26	14.26	49.51	0.00	0.00	0.00	0.00
4	26.69	1.06	1.96	3.27	16.40	3.13	25.83	0.82	0.00	0.05	0.03
5	123.43	12.01	16.44	35.03	32.42	27.49	123.39	0.00	0.00	0.05	0.00
TMAH Extract								Unknown Peaks (RT) mg/kg			
	Total with unknowns	As3	As5	MA/AsC/Tet	DMA	AsB/TriMat	Total	2.63	2.90	3.63	5.98
1	27.01	0.08	0.03	0.09	8.26	6.58	15.05	11.71	0.00	0.25	0.23
2	6.82	0.17	1.39	1.92	0.90	2.36	6.74	0.00	0.09	0.00	0.09
3	56.28	0.88	14.04	17.13	7.74	15.63	55.42	0.00	0.86	0.00	0.60
4	31.58	0.04	3.10	3.88	18.94	4.74	30.70	0.00	0.01	0.88	0.04
5	140.42	0.23	30.10	41.04	34.82	33.36	139.55	0.00	0.00	0.87	0.00
Enzyme Extract								Unknown Peaks (RT) mg/kg			
	Total with unknowns	As3	As5	MA/AsC/Tet	DMA	AsB/TriMat	Total	2.63	2.90	3.63	5.98
1	19.21	0.13	0.40	0.09	12.96	5.55	19.13	0.00	0.00	0.08	0.12
2	6.45	0.65	0.94	1.81	0.91	2.14	6.45	0.00	0.00	0.00	0.03
3	55.06	6.19	7.80	18.09	8.08	14.90	55.06	0.00	0.00	0.00	0.00
4	25.50	0.93	2.29	3.75	12.68	3.26	22.91	2.59	0.00	0.00	0.00
5	134.02	13.12	18.15	39.71	30.28	30.87	132.13	1.90	0.00	0.00	0.00

APPLIED SPECIATION AND CONSULTING, LLC

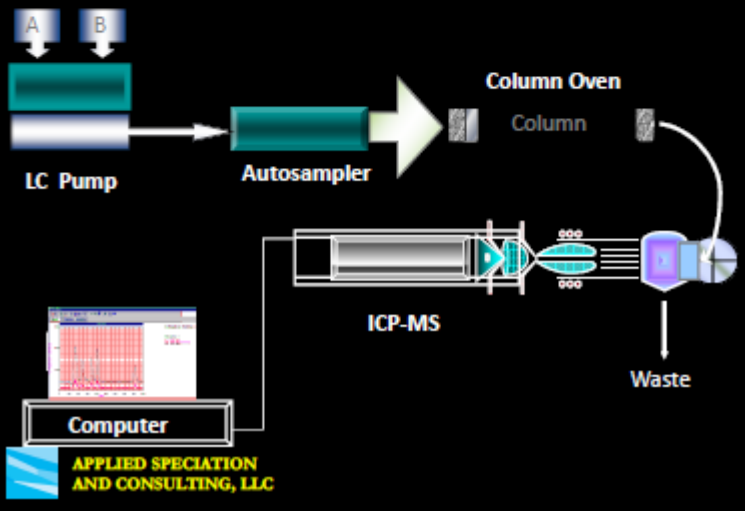
HG-CT-GC-AAS

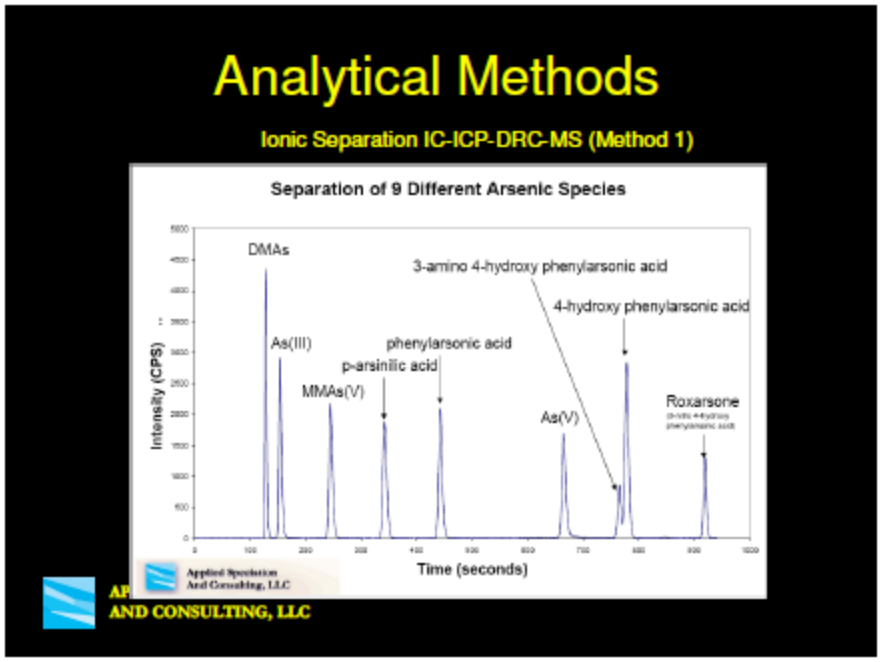
- The arsines are collected on a GC column placed in a LN_2 dewar.
  - bp: -55 ° C (AsH_3), 2 ° C ($MeAsH_2$) and 36 ° C (Me_2AsH)
- After collection, the Column is removed from the dewar and heated to thermally desorb and separate the arsines.
- The mobilized arsines are atomized by a H_2 flame and detected by AAS.

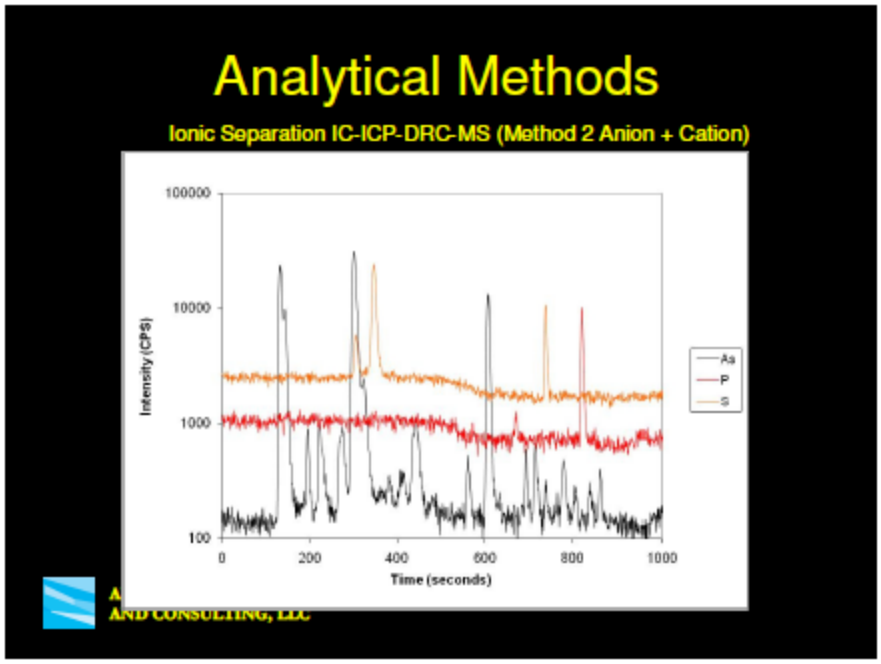


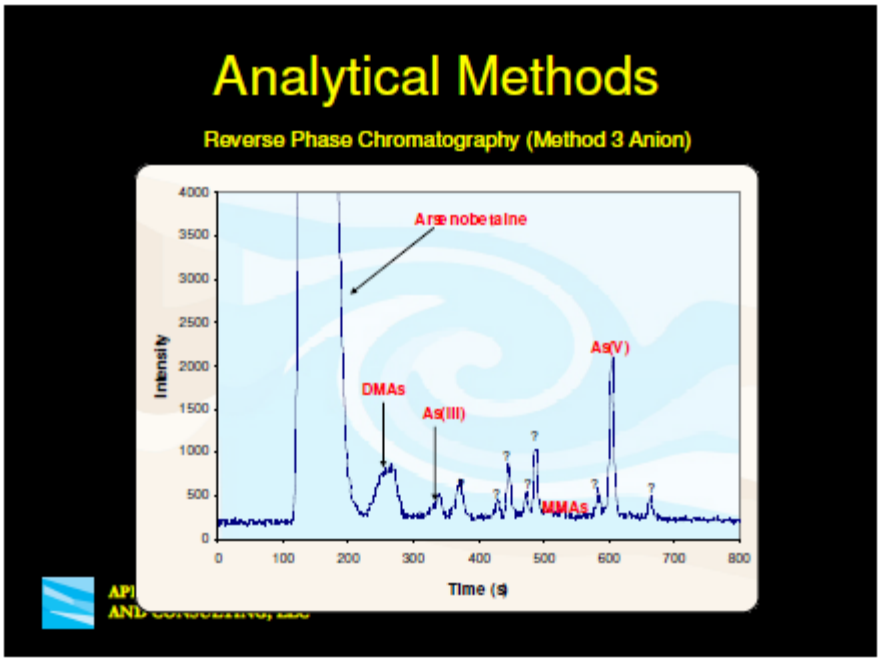
Reference: EPA Method 1632a

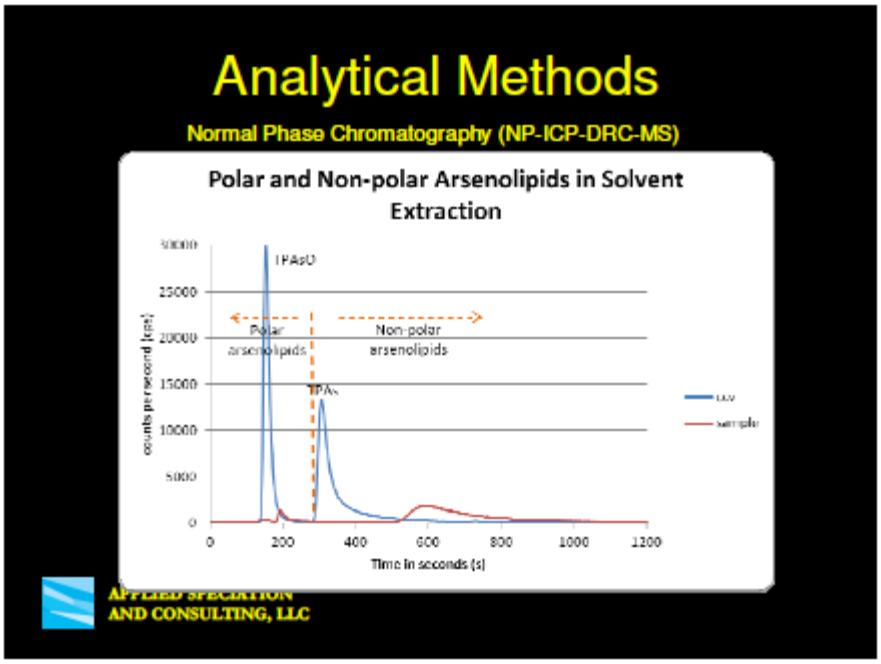
Schematic for HPLC-ICP-MS (RP, SEC,NP, or IC)




Analytical Methods
Ionic Separation IC-ICP-DRC-MS (Method 1)
Separation of 9 Different Arsenic Species
DMAs
3-amino 4-hydroxy phenylarsonic acid
4-hydroxy phenylarsonic acid
As(III)
phenylarsonic acid
p-arsinilic acid
MMAs(V)
As(V)
Roxarsone
Intensity (CPS)
Time (seconds)
Applied Speciation And Consulting, LLC
AND CONSULTING, LLC


Analytical Methods
Ionic Separation IC-ICP-DRC-MS (Method 2 Anion + Cation)
100000
10000
1000
100
Intensity (CPS)
0
200
400
600
800
1000
Time (seconds)
As
P
S
AND CONSULTING, LLC


Analytical Methods
Reverse Phase Chromatography (Method 3 Anion)
Arsenobetaine
DMAs
As(III)
As(V)
MMAs
Intensity
Time (s)


Analytical Methods
Normal Phase Chromatography (NP-ICP-DRC-MS)
Polar and Non-polar Arsenolipids in Solvent Extraction
TPAsO
Polar arsenolipids
Non-polar arsenolipids
TPAs
counts per second (cps)
Time in seconds (s)
AND CONSULTING, LLC

Conclusions

- Technology is available to support detailed characterization of arsenic in many matrices
- One size fits all approach has not been found to work
- Extraction and analytical methods must be specific to target molecules
  - Solvent extractions for non-ionic species
  - Water based extractions for ionic species
- Appropriate method must be available for total As confirmation in extracts for mass balance purposes
- Different approaches are available for quantitation ionic arsenic species
- Proper quality control must be employed to monitor species conversion, extraction efficiency, and retention time confirmation
- More work to be done with GC-ICP-MS for arsenolipids

APPLIED SPECIATION AND CONSULTING, LLC

Acknowledgements

All of our clients who make internal research possible – together we make the world a better place

The FDA – Science based regulations working to protect the citizens of the USA

APPLIED SPECIATION AND CONSULTING, LLC

Advances in Interference Removal for Accurate Arsenic Analysis in Food and Beverages

Steven Wilbur
Agilent Technologies

Abstract

Arsenic contamination of food and beverages has become a heated topic of discussion in media outlets and many households across the globe. Arsenic, like many other toxic analytes, exists in many forms, some of which are very toxic (As3+, As5+) while many others are inert. It has thus become very critical to identify the levels and types of species that exists in a particular sample in order to differentiate between the non-toxic and toxic species.

Challenges, however, exist in arsenic analysis due to the presence of isobaric interferences, which left uncontrolled, will bias the data. As such, collision/reaction cell (CRC) is employed for removal of these polyatomic interferences. Most polyatomic interferences are easily removed via a collisional or reactive mode however, doubly charged interferences are mostly left uncontrolled thus biasing the result. Critical to each analysis is understanding and ultimately identifying the types of interferences present, which would allow for their effective removal. Controlling what enters the cell is crucial to controlled chemical reactions thus allowing for accurate, precise and unbiased data in reaction mode.

Here we are providing a systematic approach to understanding the magnitude of these isobaric interferences and how to effectively approach their removal. Comparative analysis between single quad mass spectrometer and MS/MS technology will also be presented.

Advances in Interference Removal for Accurate Arsenic Analysis in Food and Beverages

National Environmental Monitoring Conference 2013
Austin TX
Steve Wilbur and Amir Liba
Agilent Technologies



Agilent Technologies

Let's Define the Problem -Medically, legally, analytically

Arsenic is toxic (but not all forms are toxic to the same degree)

Arsenic is present in drinking waters and many foods (but the form varies)

Toxicity depends on the form or species (but species conservation during sample prep is challenging)

Arsenic is challenging to determine by ICP-MS because it is monoisotopic, has a high ionization potential, and is subject to many common spectroscopic interferences.

Agilent Technologies

Inorganic arsenic-related health effects

Inorganic arsenic is a well-characterized Group 1 human carcinogen

- Lung, bladder, skin and others
- Transplacental carcinogen



Noncancer health effects

- Cardiovascular disease
- Diabetes mellitus
- Dermal effects
- Neurological effects/deficits
- Immunologic effects
- Fertility effects
- Birth defects
- Respiratory effects

Acute toxicity

- Irritation of lungs, throat, stomach, intestines and skin
- Death within hours after ingestion of sufficient dose

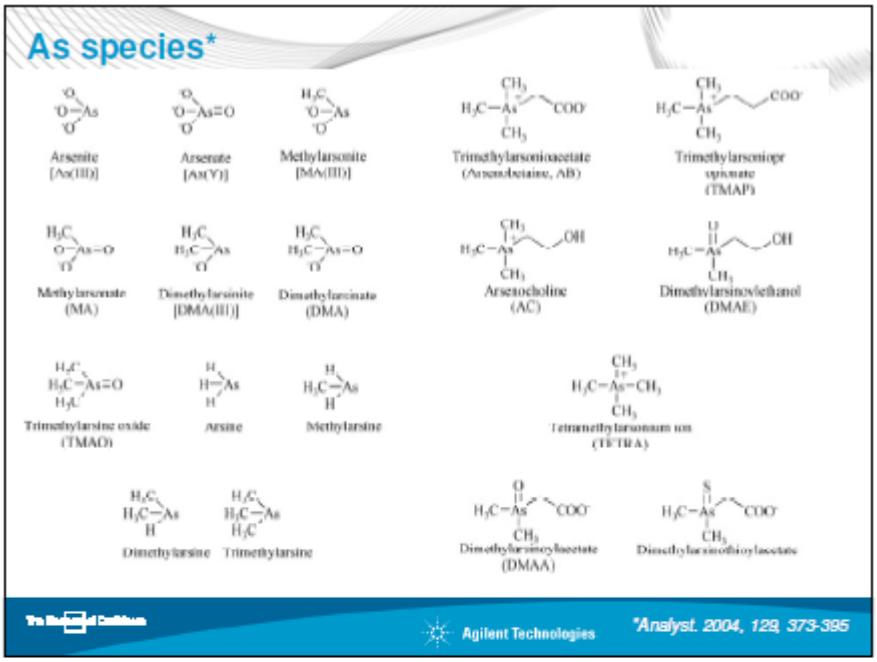
Agilent Technologies

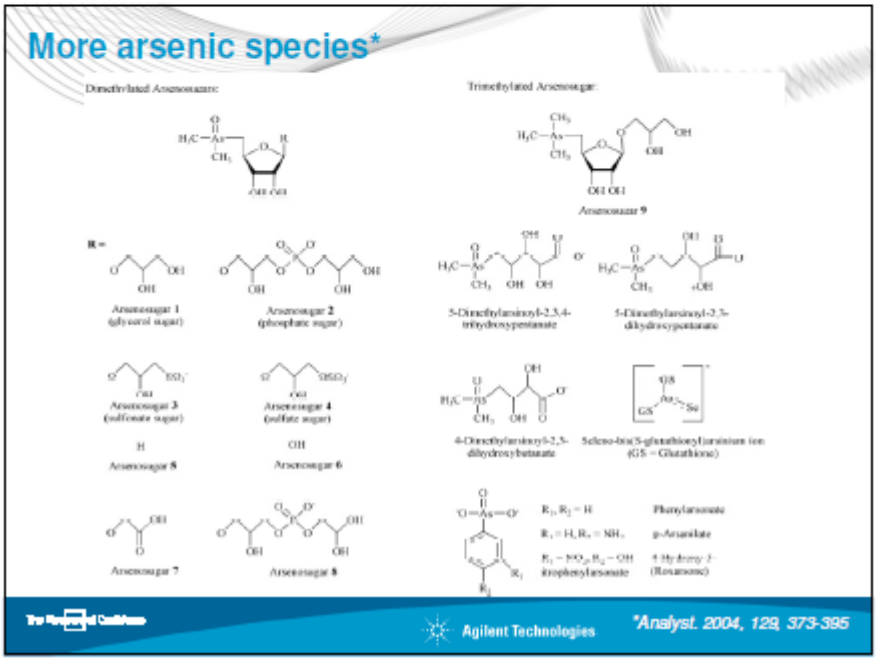
Arsenic in water – inorganic arsenic As(III) and As(V)



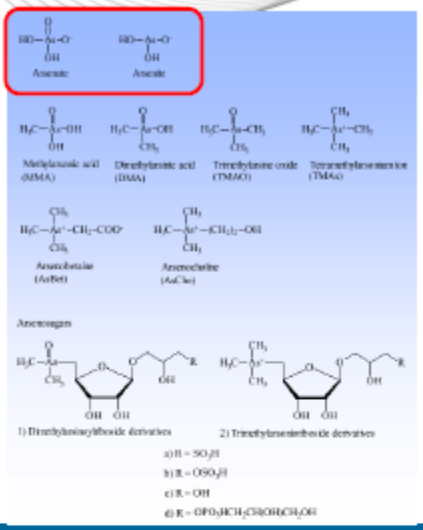
British Geological Survey

Agilent Technologies


As species*
Arsenite [As(III)]
Arsenate [As(V)]
Methylarsonite [MAs(III)]
Trimethylarsonioacetate (Arsenobetaine, AB)
Trimethylarsoniopr opionate (TMAP)
Methylarsonate (MA)
Dimethylarsinite [DMAs(III)]
Dimethylarsinate (DMA)
Arsenocholine (AC)
Dimethylarsinoylethanol (DMAE)
Trimethylarsine oxide (TMAO)
Arsine
Methylarsine
Tetramethylarsonium ion (TETRA)
Dimethylarsine
Trimethylarsine
Dimethylarsinoylacetate (DMAA)
Agilent Technologies
*Analyst. 2004, 129, 373-395


More arsenic species*
Dimethylated Arsenosugars:
Trimethylated Arsenosugar:
Arsenosugar 9
R =
Arsenosugar 1 (glycerol sugar)
Arsenosugar 2 (phosphate sugar)
5-Dimethylarsinoyl-2,3,4-trihydroxypentanate
5-Dimethylarsinoyl-2,3-dihydroxypentanate
Arsenosugar 3 (sulfonate sugar)
Arsenosugar 4 (sulfate sugar)
Arsenosugar 8
Arsenosugar 6
4-Dimethylarsinoyl-2,3-dihydroxybutanate
Seleno-bis(S-glutathionyl)arsinium ion (GS = Glutathione)
Arsenosugar 7
Arsenosugar 5
Phenylarsonate
p-Arsanilate
Agilent Technologies
*Analyst. 2004, 129, 373-395

As Speciation - Toxicity



Toxic!

Less-Toxic

Non-Toxic

?

Many As species exist – the inorganic As species are known to be toxic and most organic species are relatively harmless to humans.

The potential toxicity of some species, such as the huge variety of arsenosugars, has not yet been established.

Agilent Technologies

Arsenic in Food

Risk assessments are based on inorganic As

In food, high total As is not always equal to high inorganic As

Arsenic from water is 100% bioavailable; this might not be the case for food

Safe drinking water limits are set assuming long-term exposure

- Dietary choices are varied
- BUT rice-subsistence diets could be equal to or greater than 'safe' exposure limits
- Early life exposure is important, should limit exposure during this development period

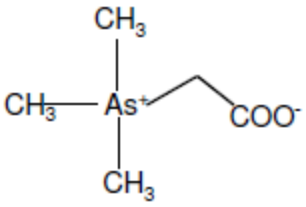
Agilent Technologies

Arsenic in seafood

Main source of total As to diet

- Fish can be > 1 ppm – 40 ppm total As

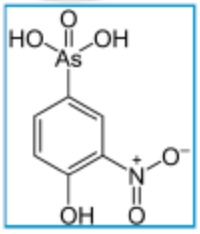
Arsenic is present almost exclusively as arsenobetaine: NON-TOXIC





Agilent Technologies

Arsenic in poultry

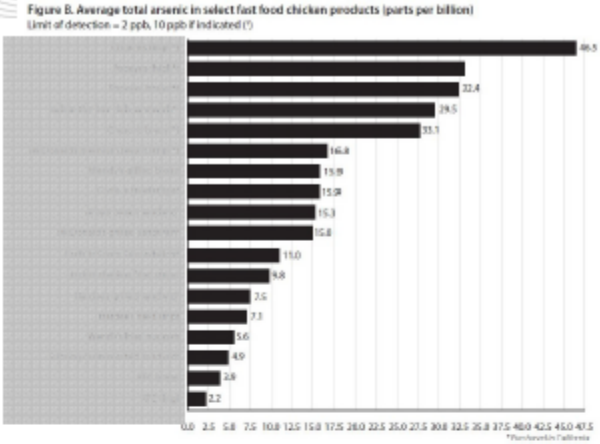


- **Roxarsone**
  - Also p-arsanilic acid, nitarsone, carbarsone, arsanilate sodium
- Additive in poultry and swine feed since mid-1940s
- Approved for growth promotion, improved pigmentation, coccidiostat, treatment of swine dysentery
- In poultry production: 88% raised using roxarsone
  - 2010 estimate
- In swine and turkey production: unknown %
- Single domestic producer
- July 8 2012 – Pfizer suspends marketing of roxarsone in the US

http://us.medage.net/upload/Roxarsone__USP24_20050704.jpg

Agilent Technologies

What about arsenic in chicken meat



2006 IATP: Playing Chicken: Avoiding Arsenic in Your Meat

Agilent Technologies

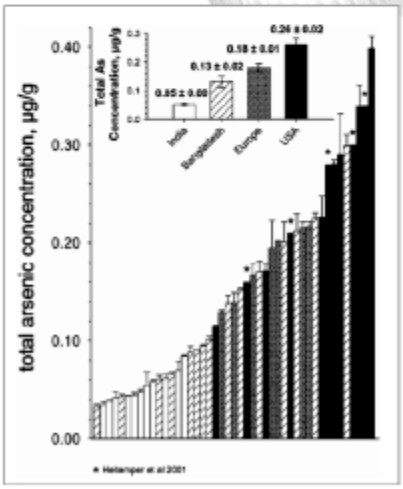
Arsenic in rice

Variation in Arsenic Speciation and Concentration in Paddy Rice Related to Dietary Exposure

P. N. WILLIAMS,† A. H. PRICE,† A. RAAB,‡ S. A. HOSSAIN,†,§ J. FELDMANN,‡ AND A. A. MEHARG*,†
School of Biological Sciences, University of Aberdeen, Aberdeen, AB24 3UU, UK, and ‡ Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, UK

"USA long grain rice had the highest mean arsenic level in the grain at 0.26 µg As g^{-1}"

"arsenic in rice contributes considerably to arsenic ingestion in subsistence rice diets"



Williams et al ES&T 39: 2005

Agilent Technologies

Surveys and 'market basket' studies

Survey of As and its speciation in rice products such as breakfast cereal, rice crackers and Japanese rice condiments.

Table 1
Summary of arsenic level in rice products total arsenic

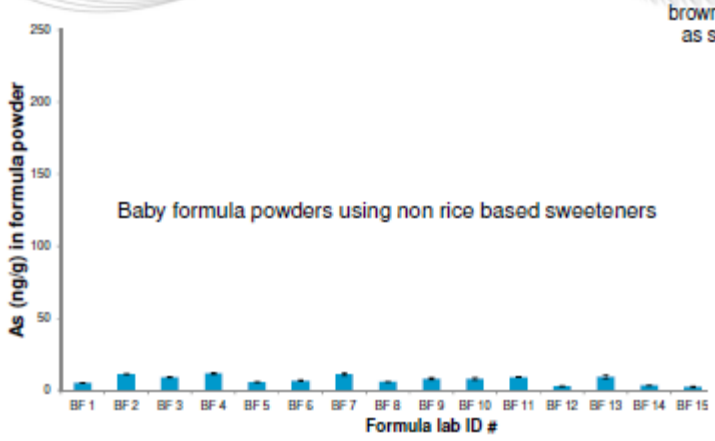
Product	*N*	Average concentration	Standard deviation
Crisped rice	3	0.21 mg/kg	0.01
Puffed rice	2	0.24 mg/kg	0.02
Rice malt	3	0.21 mg/kg	0.08
Noodles	6	0.12 mg/kg	0.09
Sweets	5	0.14 mg/kg	0.02
Rice cracker	11	0.28 mg/kg	0.03
Amazake	1	0.16 mg/kg	
Bran oil	3	0.03 mg/l	0.003
Vinegar	4	0.05 mg/l	0.023
Mirin	2	0.01 mg/l	0

Sun et al 2008, Environment International

Agilent Technologies

Arsenic in baby formula powder

Toddler formulas using organic brown rice syrup as sweetener



Agilent Technologies

Arsenic in Apple Juice



Agilent application note

New Limits for Arsenic Proposed by F.D.A.

By SABRINA TAVERNISE
Published: July 12, 2013

WASHINGTON — Nearly two years after an outcry about arsenic in apple juice touched off by a segment on "The Dr. Oz Show," the federal Food and Drug Administration is proposing a new limit on acceptable levels.

The new standard for arsenic, a carcinogen when consumed in large enough quantities, is 10 parts per billion, equal to the level that the Environmental Protection Agency has set for arsenic in drinking water. Experts said the allowable amount was relatively conservative since people typically drink far less apple juice than water.

Apple juice with arsenic levels that exceed the new target might be subject to action by the agency, including seizure, said Dr. Margaret Hamburg, the F.D.A. commissioner. The proposed target will be finalized only after comments from industry and the public, she said.

Agilent Technologies

Solving the Analytical Problems

- Separating the toxic from the non-toxic species with reliable species conservation and recovery
- Determining the concentration of toxic species (and others) in the presence of significant interferences and sometimes without access to species specific standards or reference materials
- Doing the above with sufficient accuracy, precision and method robustness

Agilent Technologies

ICP-MS as an LC detector for As



Specific and Selective:

ICP-QMS Arsenic is determined at mass 75 and the chloride interference is separated, in time, by the chromatographic system or removed by the collision cell.

ICP-QQQ Arsenic is determined as AsO (m/z=91) after the first quad removes all other potential interferences at m/z=91

Wide dynamic Range: the ICP-MS detector is linear over large concentration range (10e9)
- range limited by chromatographic system

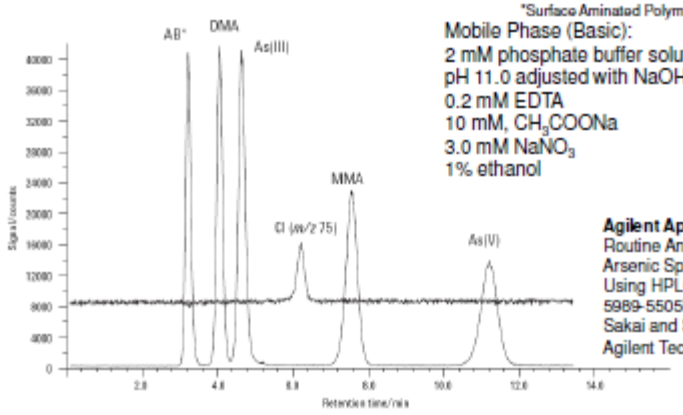
No structural information – ID by retention time

Accurate quantification for unknown As compounds possible using Compound Independent Calibration

Agilent Technologies

Arsenic Speciation with LC-ICP-MS

Complete isocratic separation of AsB & Cl from inorganic As



Column G3288-80000 (4.6 x 250 mm)
Guard Column G3154-65002
*Surface Aminated Polymer Substrate

Mobile Phase (Basic):
2 mM phosphate buffer solution (PBS)
pH 11.0 adjusted with NaOH
0.2 mM EDTA
10 mM, CH_3COONa
3.0 mM $NaNO_3$
1% ethanol

Agilent Application Note: Routine Analysis of Toxic Arsenic Species in Urine Using HPLC with ICP-MS, 5989-5505EN, by Tetsushi Sakai and Steven Wilbur, Agilent Technologies

Agilent Technologies

Arsenic species in apple juice
A simple, reliable method

A simple filtration (preserve the species, good recovery)

No sample digestion or stabilization was performed, as aggressive sample separation steps could cause species inter-conversion.

LC-ICP-MS Method	
Instrument	1200 LC
Column	G3288-80000 (4.6x250mm)
Mobile phase	2.0mM PBS, 0.2mM EDTA, 30mM CH3COONa, 2.0% EtOH pH 11.0 adjusted by 1M NaOH
Flow rate	1.0 mL/min
Injection Vol.	100µL
Oven Temp.	Ambient
Sample Preparation	
Filter1	Membrane filter: Millex-LH 0.45µm PTFE 25mm (Millipore corporation)
Filter2	DDS Cartridge: TOYOPAK ODS M (TOSOH corporation)
Dilution	1:2 with de-ionized water

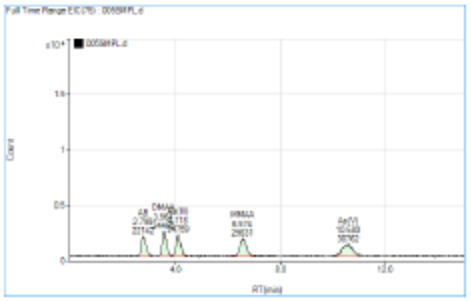
S/N for As Species in Apple Juice
Limit of Detection ~ 0.02ppb*

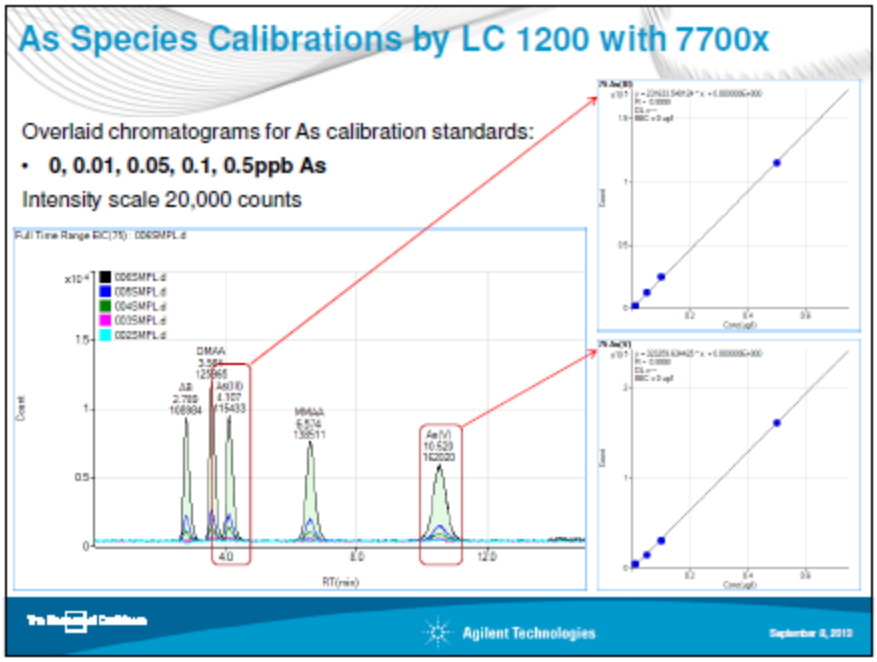
Peak#	Compound	RT[min]	Height	Area	Noise	S/N	Noise Type
1	AB	2.799	1797	22142	133	13.51	Peak-to-Peak
2	DMAA	3.564	2254	24465	133	16.95	Peak-to-Peak
3	As(III)	4.118	1910	24759	133	14.36	Peak-to-Peak
4	MMAA	6.574	1602	29631	133	12.04	Peak-to-Peak
5	As(V)	10.580	1082	30762	133	8.13	Peak-to-Peak

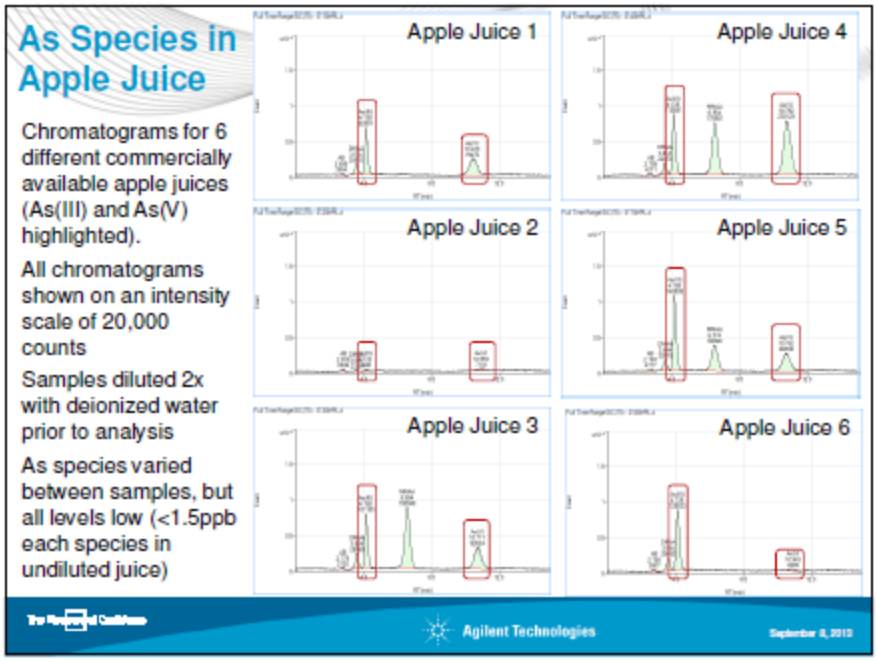
S/N report for 0.1ppb Standard – 7700x (intensity scale 20,000 counts)

S/N between 8 and 17 depending on compound

*proposed new FDA regulation is 10 ppb

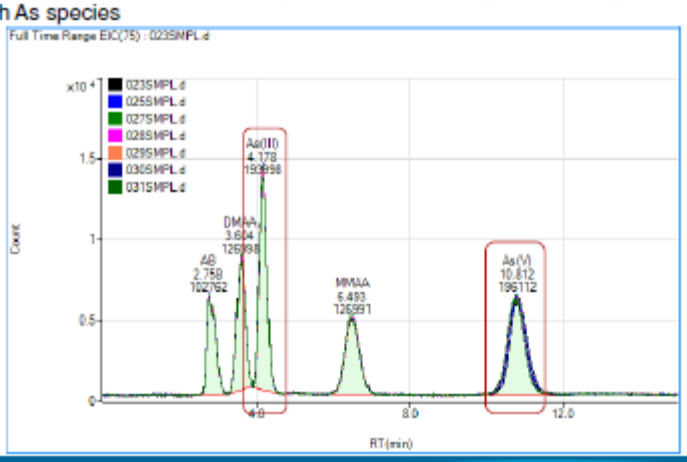



As Species Calibrations by LC 1200 with 7700x
Overlaid chromatograms for As calibration standards:
• 0, 0.01, 0.05, 0.1, 0.5ppb As
Intensity scale 20,000 counts
DMAA
MMAA
As(V)
RT(min)
Agilent Technologies


As Species in Apple Juice
Chromatograms for 6 different commercially available apple juices (As(III) and As(V) highlighted).
All chromatograms shown on an intensity scale of 20,000 counts
Samples diluted 2x with deionized water prior to analysis
As species varied between samples, but all levels low (<1.5ppb each species in undiluted juice)
Apple Juice 1
Apple Juice 2
Apple Juice 3
Apple Juice 4
Apple Juice 5
Apple Juice 6
Agilent Technologies

As Species Stability (precision and robustness)

Overlaid chromatograms for 7 separate injections of Apple Juice 1 spiked with 0.5ppb each As species



Quantitative Results for As Species in Apple Juice by single quad ICP-MS

		AB	DMAA	As(III)	MMAA	As(V)
Sample Name	Dilution	Conc. [ug/l]	Conc. [ug/l]	Conc. [ug/l]	Conc. [ug/l]	Conc. [ug/l]
Apple Juice 1	2	0.036	0.163	0.717	ND	0.492
Apple Juice 2	2	0.026	0.019	0.04	ND	0.044
Apple Juice 3	2	0.020	0.230	0.874	1.371	0.573
Apple Juice 4	2	0.039	0.179	0.982	1.266	1.479
Apple Juice 5	2	0.043	0.180	1.243	0.678	0.536
Apple Juice 6	2	0.036	0.203	1.086	ND	0.051

All individual species results less than 1.5ppb in the undiluted juice samples. Total inorganic As (sum of As(III) and As(VI) less than 2.5ppb in all samples

Precision for As Species in Apple Juice

Stability data (n=7) for spiked apple juice. RT and concentration results

RT stability around 0.2 to 0.3%RSD

Concentration stability ~1%RSD

	AB		DMAA		As(III)		MMAA		As(V)	
Sample Name	RT	Conc. [ug/l]	RT	Conc. [ug/l]	RT	Conc. [ug/l]	RT	Conc. [ug/l]	RT	Conc. [ug/l]
Spike 50-1	2.758	0.944	3.604	1.010	4.178	1.675	6.493	0.916	10.812	1.213
Spike 50-2	2.769	0.935	3.614	1.015	4.178	1.677	6.493	0.911	10.802	1.209
Spike 50-3	2.769	0.939	3.614	1.004	4.178	1.655	6.503	0.903	10.762	1.207
Spike 50-4	2.758	0.936	3.614	0.999	4.168	1.646	6.503	0.921	10.762	1.194
Spike 50-5	2.758	0.955	3.614	1.009	4.178	1.635	6.473	0.923	10.762	1.176
Spike 50-6	2.748	0.925	3.634	0.996	4.158	1.650	6.473	0.901	10.762	1.230
Spike 50-7	2.758	0.924	3.624	0.991	4.178	1.648	6.463	0.916	10.772	1.203
%RSD	0.265	1.149	0.263	0.851	0.189	0.936	0.247	0.927	0.199	1.387

Agilent Technologies

Preliminary Conclusion – not too bad
Can this be improved using ICP-QQQ?

Fast – the entire separation was complete in under 12 min, and sample to sample is about 14 min.

linearity – the MS detector shows excellent linearity across the analytical range

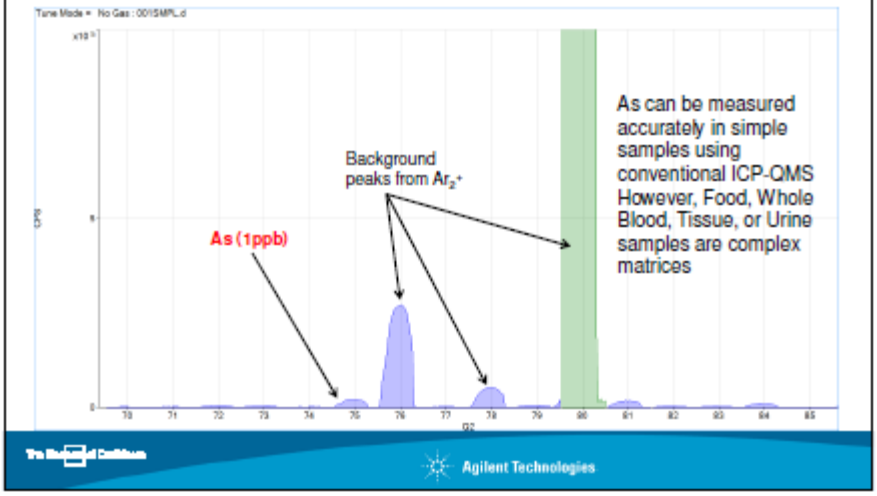
Specificity – the common non-toxic arsenic did not overlap with the species desired to be determined and the interfering peak from ArCl is also chromatographically separated.

Simplicity – the existing method used for As was modified to be tolerant of the changed matrix (apple juice) and was seen to be a very flexoble method.

Agilent Technologies

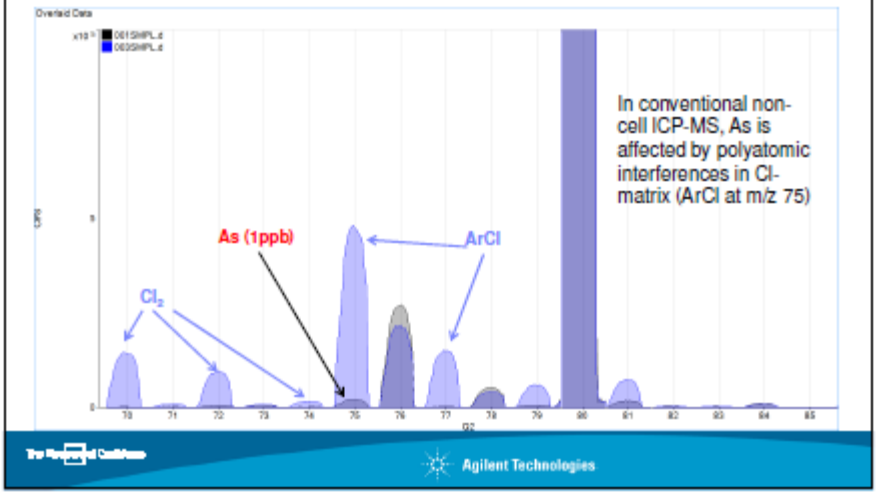
Reminder Why >90% of Quadrupole ICP-MS Have Collision/Reaction Cell – Interference Removal

Arsenic (mass 75) 1ppb Standard – No Gas Mode



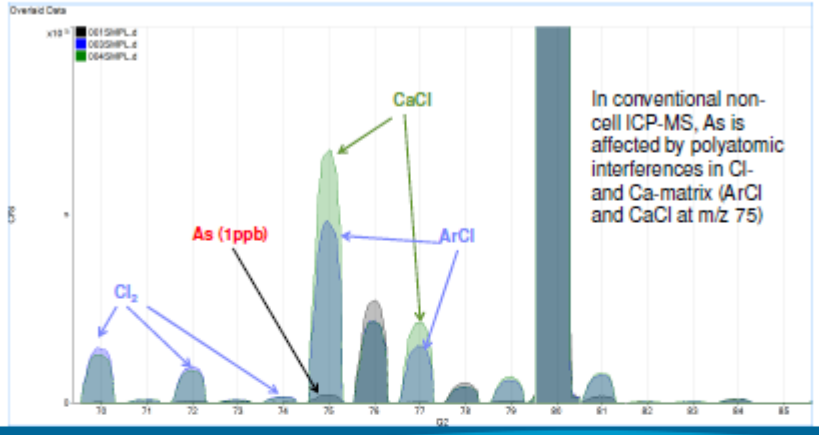
As Measured at m/z 75 in Cl-Matrix is Overlapped by ArCl Polyatomic Interference

1ppb As in 5% HCl



As Measured at m/z 75 in Cl & Ca-Matrix is Overlapped by ArCl/CaCl Polyatomic Interferences

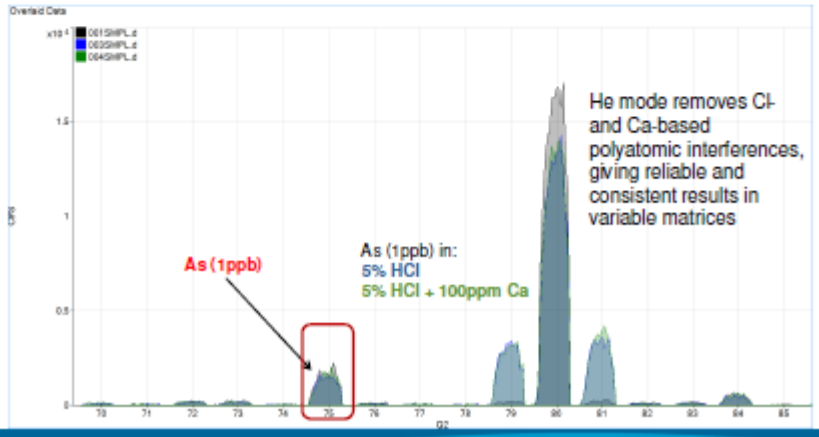
1ppb As in 5% HCl, 1ppb As in 5% HCl + 100ppm Ca



Agilent Technologies

As Measured at m/z 75 in Ca/Cl-Matrix – He Mode Removes ArCl/CaCl Polyatomic Interferences

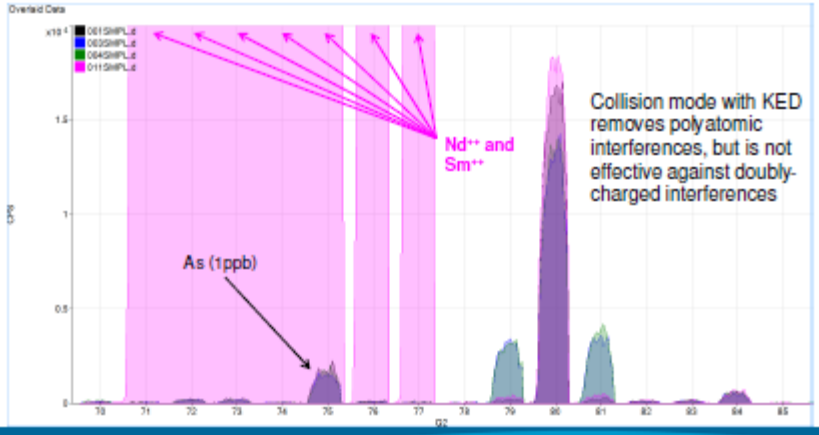
1ppb As in 5% HCl, 1ppb As in 5% HCl + 100ppm Ca – *all interferences removed – Problem solved...*



Agilent Technologies

However,… He Mode Can't Remove ALL Possible Interferences

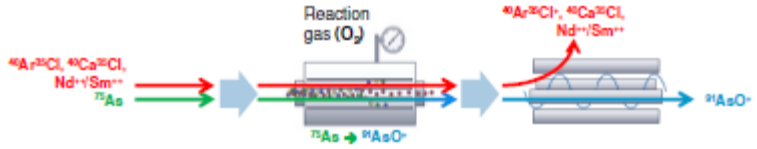
1ppb As + 1ppm Nd/Sm in He Mode – Nd & Sm form 2+ ions. Isotopes at mass 150 appear at 75 (half true mass) 2+ interferences not removed



Agilent Technologies

Conventional ICP-QMS Can Use Reaction Mode to Avoid 2+ Interferences on ^{75}As

$^{75}As^+ + O_2$ <cell gas> → $^{91}AsO^+$
$^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$, Sm^{++}, $Nd^{++} + O_2$ → no (or very slow) reaction



Analyte and interfering ions enter reaction cell

As^+ reacts with O_2 cell gas to form AsO^+ product ion

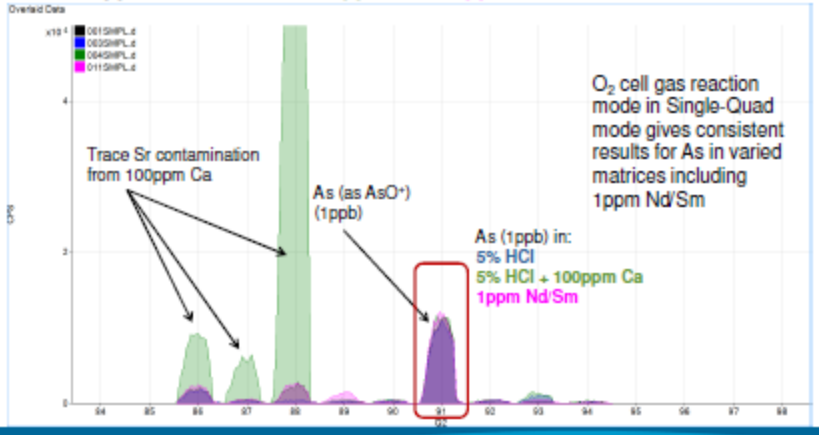
Quad set to AsO^+ product ion mass (m/z 91) – rejects original $^{40}Ar^{35}Cl^+$, $^{40}Ar^{35}Cl^+$, Nd^{++}/Sm^{++} interfering ions

Agilent Technologies

O_2 Reaction Mode on Conventional ICP-QMS - (8800 in single quad mode)

As^+ is converted to AsO^+ and moved to mass 91 – avoids interferences

1ppb As, + 5% HCl + 100ppm Ca, + 1ppm Nd/Sm

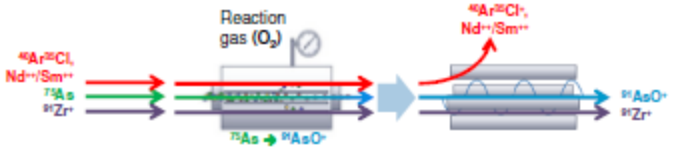


Agilent Technologies

So ICP-QMS Reaction Mode Solves the Problem?

Not Quite!

ICP-QMS with O_2 cell gas avoids $^{40}Ar^{35}Cl^+$ $^{40}Ca^{35}Cl^+$ and Nd^{++}/Sm^{++} overlap on $^{75}As^+$, but AsO^+ product ion at m/z 91 can be overlapped



Analyte and interfering ions enter reaction cell

As^+ reacts with O_2 cell gas to form AsO^+ product ion. Not all Zr^+ reacts to form ZrO^+ (some Zr^+ remains)

Quad set to AsO^+ product ion mass (m/z 91) – rejects original $^{40}Ar^{35}Cl^+$, $^{40}Ar^{35}Cl^+$, Nd^{++}/Sm^{++} interfering ions but cannot remove $^{91}Zr^+$

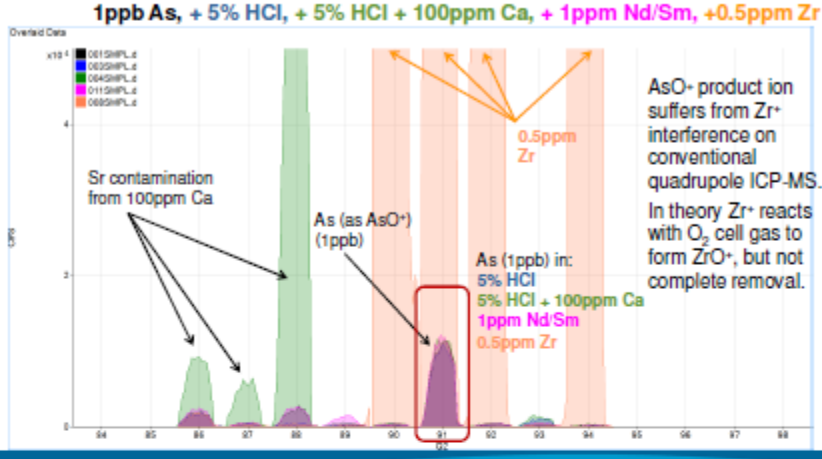
Conventional Quadrupole ICP-MS cannot reject on-mass interferences that overlap cell-formed analyte reaction product ions

Agilent Technologies

Product Ion Overlaps with Conventional ICP-QMS O_2 Mass-Shift Mode

As^+ is converted to AsO^+ and measured at mass 91 – overlap from $^{91}Zr^+$

1ppb As, + 5% HCl, + 5% HCl + 100ppm Ca, + 1ppm Nd/Sm, +0.5ppm Zr



AsO^+ product ion suffers from Zr^+ interference on conventional quadrupole ICP-MS.

In theory Zr^+ reacts with O_2 cell gas to form ZrO^+, but not complete removal.

Agilent Technologies

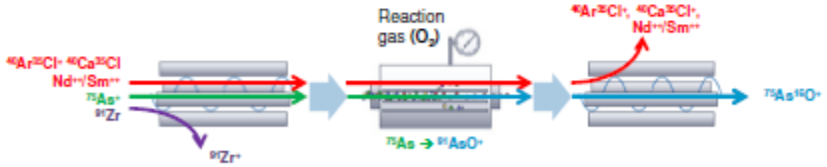
The solution: ICP-MS/MS Mass-Shift with O_2 Cell Gas

Same reaction with O_2 cell gas is also used on 8800 ICP-MS/MS:

$^{75}As^+ + O_2$ <cell gas> $\rightarrow$ $^{91}AsO^+$

$^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$, Sm^{++}, $Nd^{++} + O_2 \rightarrow$ no reaction

<u>BUT</u> Q1 of 8800 rejects $^{91}Zr^+$ ions that would overlap AsO^+ at mass 91



Q1 set to m/z 75, so rejects all ions except m/z 75. ^{91}Zr at mass 91 is rejected

As^+ reacts with O_2 cell gas to form AsO^+ product ion. $^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$, Nd^{++}/Sm^{++} don't react and stay at m/z 75

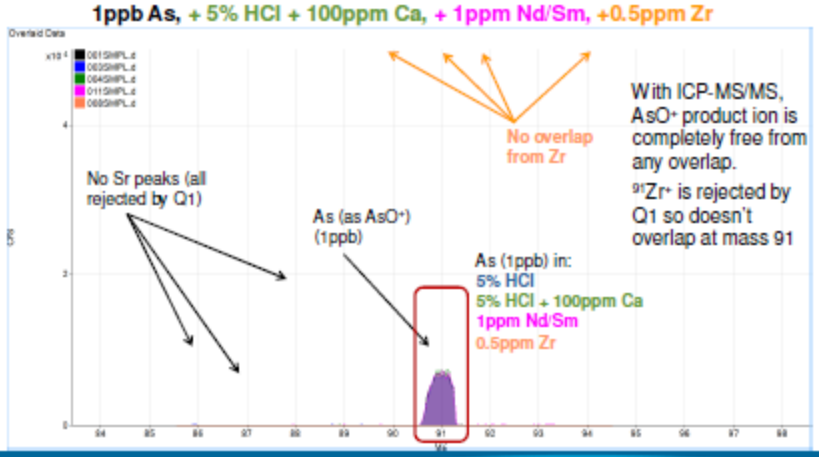
Q2 set to m/z 91, AsO^+ product ion mass – rejects original on-mass interferences

Agilent Technologies

ICP-MS/MS O_2 Mass-Shift Mode for As – Consistent Results in Any Matrix

Same matrices as before – ALL overlaps are removed by MS/MS

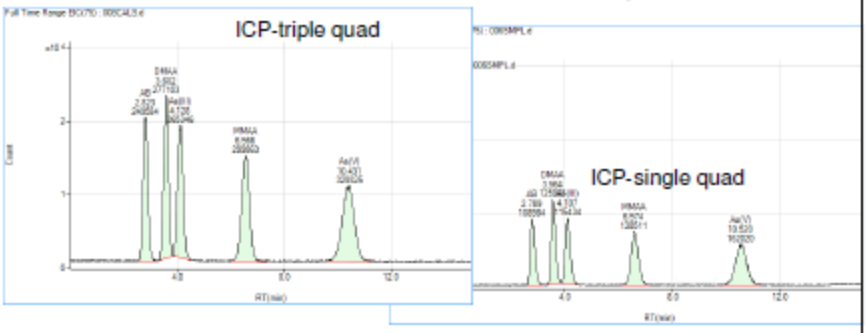
1ppb As, + 5% HCl + 100ppm Ca, + 1ppm Nd/Sm, +0.5ppm Zr



Agilent Technologies

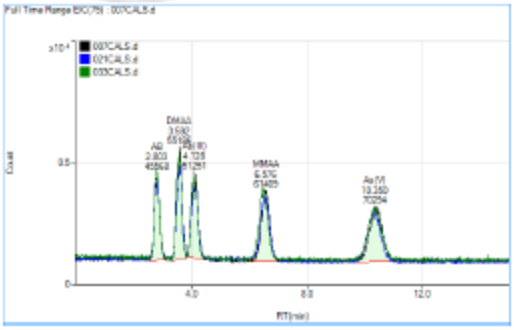
As Species Sensitivity with 8800 ICP-QQQ

Comparison of 0.5ppb As species standard with 8800 (left) and 7700x (right) –same intensity scale. Sensitivity ~ 2x higher with 8800 – significant improvement in S/N



Agilent Technologies

8800 ICP-QQQ – As Species at Low-Levels



Overlaid chromatograms and stability data (n=3) for 0.1ppb standard repeated start, middle and end of sequence (7 hours total)

RT %RSD: 0.2% to 0.6%

Conc %RSD: 2.5% to 4%

	75 AB			75 DMAA			75 As(III)			75 MMAA			75 As(V)		
	RT	Conc. [ug/l]	Area	RT	Conc. [ug/l]	Area	RT	Conc. [ug/l]	Area	RT	Conc. [ug/l]	Area	RT	Conc. [ug/l]	Area
0.1ppb	2.803	0.097	45568	3.592	0.098	55186	4.128	0.096	51251	6.576	0.100	61409	10.350	0.103	70294
0.1ppb	2.813	0.093	43686	3.602	0.093	52340	4.118	0.090	47972	6.546	0.098	59949	10.299	0.101	69028
0.1ppb	2.782	0.100	47263	3.592	0.100	56301	4.108	0.097	51792	6.495	0.105	64045	10.309	0.106	72305
%RSD	0.57	3.63	3.93	0.16	3.72	3.74	0.24	4.01	4.11	0.63	3.57	3.36	0.26	2.44	2.34

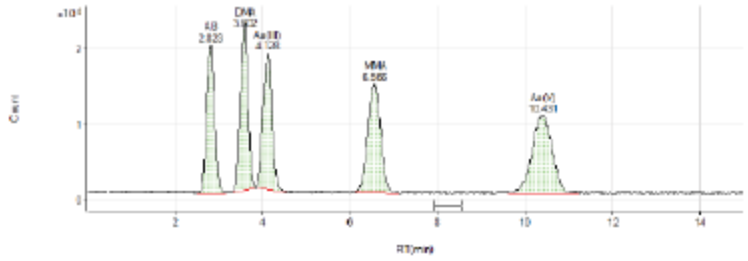
Agilent Technologies

September 8, 2013

As Speciation in Apple Juice by ICP-QQQ LOD ~ 2x better, and absolutely no interferences

Table 2. 3x S/N detection limits for arsenobetaine (AB), dimethylarsinic acid (DMA), As(III) (arsenite), monomethylarsonic acid (MMA), and As(V) (arsenate).
* Arsenobetaine (AB) elutes in the void volume and cannot be reliably quantified in the presence of some other co-eluting species.

Compound	RT (min)	Height	Area	Noise	S/N	LOD (ng/L)	Noise type
AB*	2.823	19584	246584	153	127.84	11.72	Peak-to-peak
DMA	3.602	22117	277103	153	144.34	10.38	Peak-to-peak
As(III)	4.128	18022	215346	153	117.78	12.74	Peak-to-peak
MMA	6.566	14421	295863	153	94.24	15.92	Peak-to-peak
As(V)	10.431	10295	328825	153	67.08	22.36	Peak-to-peak



Agilent Technologies

Conclusions

- LC-ICP-QMS is a simple, robust, sensitive technique for determining toxic arsenic species in foods and beverages
- Single quad ICP-MS using either He mode or O_2 reaction mode can be used effectively, but some risk of residual interferences remains
- LC-ICP-QQQ is just as simple and reliable as LC-ICP-QMS but has the added advantage of even lower LOD, and higher confidence that no unknown interferences are present.

Agilent Technologies

Thank you

Any questions?

Agilent Technologies

SECTION 18

COLLABORATIVE EFFORTS TO IMPROVE ENVIRONMENTAL MONITORING

Automated In-line Digestion and Analysis of Total Phosphorous (TP) and Total Nitrogen (TN) in Environmental Water Samples

William Lipps
OI Analytical

Abstract

A high proportion of the workload in environmental laboratories involves analysis of total phosphorous (TP) and total nitrogen (TN) in water samples for Clean Water Act compliance reporting. At the present time these analyses must be performed using manual or semi-automated methods as there are no U.S. EPA-approved automated methods.

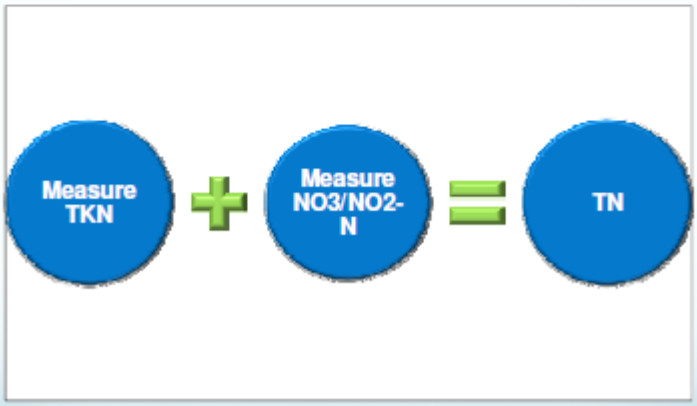
The U.S. EPA parameter for total nitrogen is the sum of Total Kjeldahl Nitrogen (TKN) and Nitrate plus Nitrite Nitrogen. Water samples that have undergone Kjeldahl digestion can be analyzed for total phosphorous as well as TKN which only partially mitigates sample handling and workload issues. Fully automated simultaneous analysis of TP and TN cannot be achieved because an approved method for determining TN as a single analyte is not available.

This presentation will examine the use of an alkaline persulfate digestion as an alternative to Kjeldahl digestion to support analysis of both total nitrogen and total phosphorous. Analytical results obtained from automated in-line digestion and simultaneous analysis of TP and TN will be presented and contrasted with results obtained by currently approved manual and semi-automated methods. Differences in analyst time, reagent consumption, sample throughput, and hazardous waste generated by each technique will also be summarized and reported.

Automated Digestion of Total Nitrogen and Total Phosphorus in Environmental Samples

William Lipps
OI Analytical

EPA definition of total nitrogen

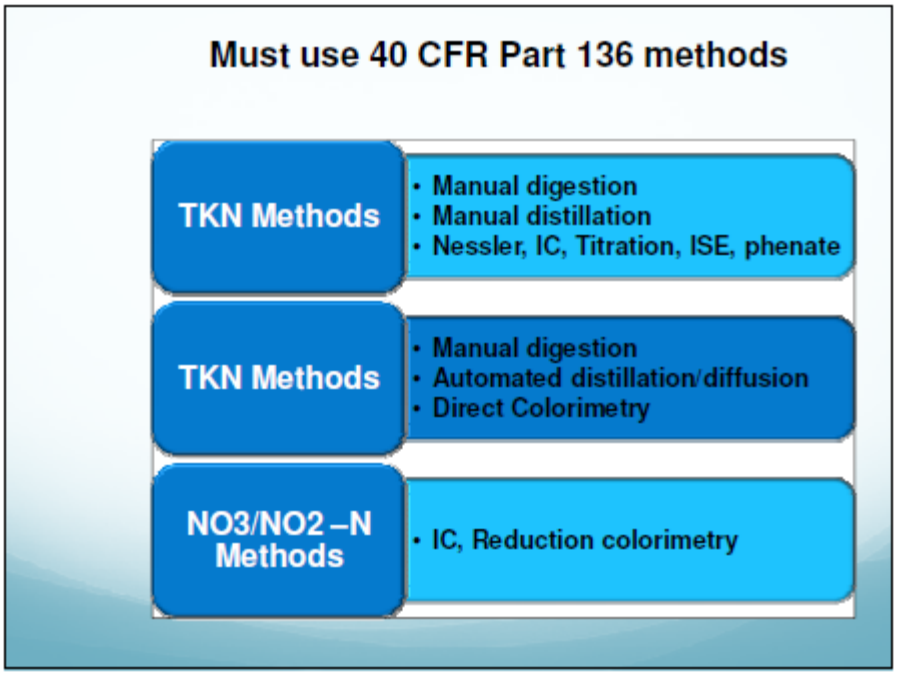


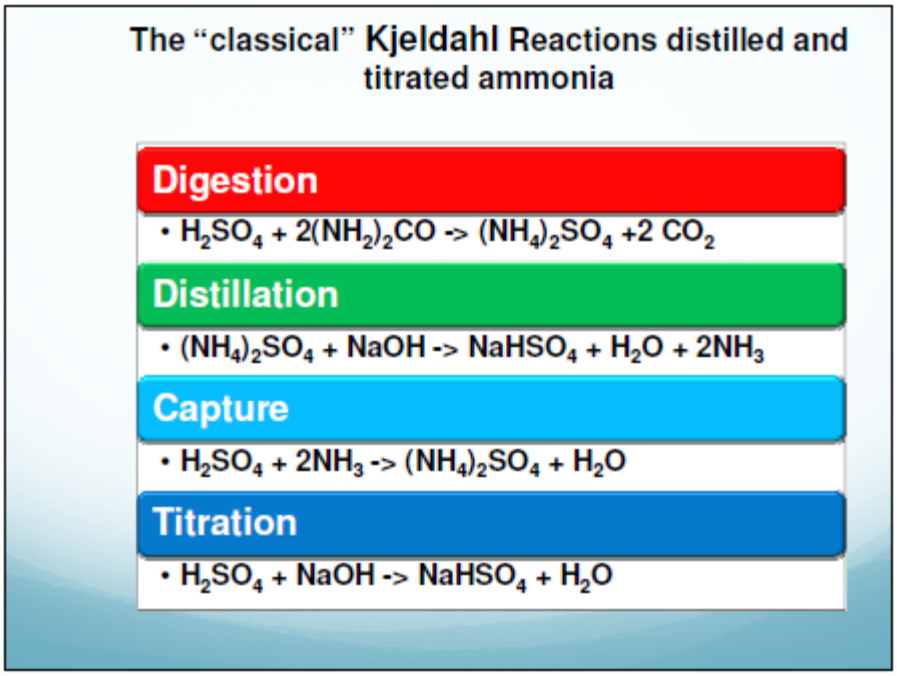
Measuring organic nitrogen requires a TKN and ammonia analysis



TKN is a "classical" analysis of total nitrogen

- TKN includes
  - Organic Nitrogen
  - Ammonia Nitrogen (NH_3-N)
- TKN does not include
  - Nitrate Nitrogen (NO_3-N)
  - Nitrite Nitrogen (NO_2-N)


Must use 40 CFR Part 136 methods
TKN Methods
• Manual digestion
• Manual distillation
• Nessler, IC, Titration, ISE, phenate
TKN Methods
• Manual digestion
• Automated distillation/diffusion
• Direct Colorimetry
NO3/NO2 –N Methods
• IC, Reduction colorimetry


The "classical" Kjeldahl Reactions distilled and titrated ammonia
Digestion
• $H_2SO_4 + 2(NH_2)_2CO \rightarrow (NH_4)_2SO_4 + 2\ CO_2$
Distillation
• $(NH_4)_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O + 2NH_3$
Capture
• $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 + H_2O$
Titration
• $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$

Present Day TKN methods can either distill (diffuse) or measure NH_4^+ in the matrix

Manual Digestion

- $H_2SO_4 + (NH_2)_2CO \rightarrow (NH_4)_2SO_4 + 2CO_2$
  - Must use catalyst

Distillation (required for some methods)

- $(NH)_4SO_4 + NaOH \rightarrow NaHSO_4 + H_2O + 2NH_3$

Detection

- Titration, ISE, manual colorimetry, automated colorimetry

The block digester methods for TKN do not require distillation

- Sodium Citrate is a better complexing agent
- Salicylic acid method
- Blue color measured at 640 – 660 nm
- Continuous Flow or Discrete Analyzer methods.

Digest multiple samples on a block and analyze them automatically

- Faster than titration
- Results in minutes
- Easy repeat of questionable results
- Dilute off scale samples
- No distillation
- Smaller volumes (25 ml)

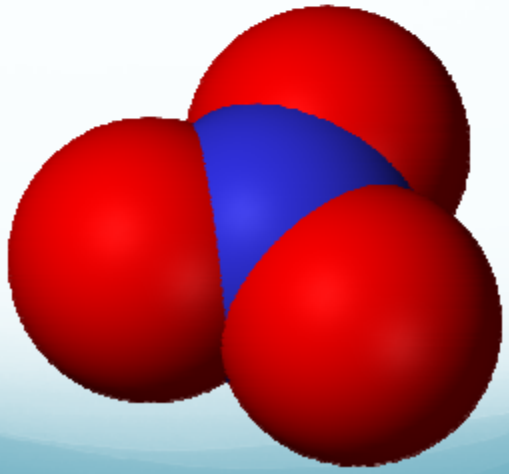
Operational Comparison of TKN methods

Manual Digestion & Distillation Followed By:	Require final digest volume	Require final distillate volume
Titration	no	no
Ion Selective Electrode	no	yes
Manual Phenate	no	yes
Automated Phenate	no	yes
Block Digestion		
Automated Salicylate	yes	N/A

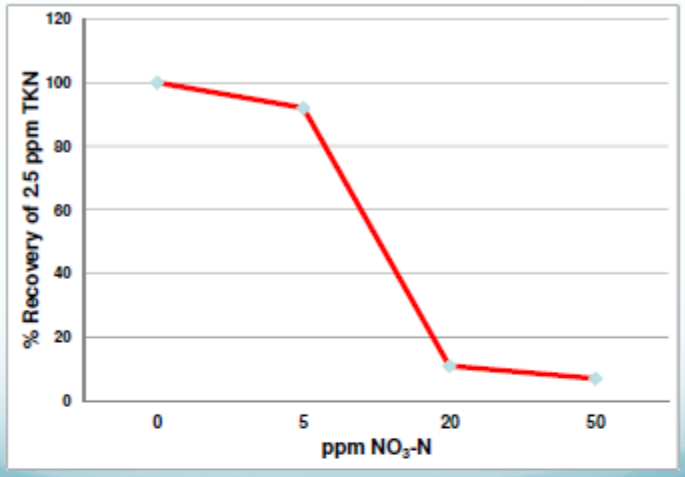
Techniques for the analysis of Total Nitrogen (EPA only approves TKN)

Manual Digestion & Distillation Followed By:	MDL (mg/L)
Titration	1.0
Manual Phenate	0.05 ?
Ion Selective Electrode	0.03
Automated Phenate	0.01
Block Digestion	
Automated Salicylate	0.1
Auto-GD/pH colorimetry	0.2
Auto-GD/Salicylate	0.02

Problem -TKN does not measure nitrate, and total nitrogen includes nitrate plus nitrite



Low Recovery of TKN in presence of NO_3-N



Schlueter 1977

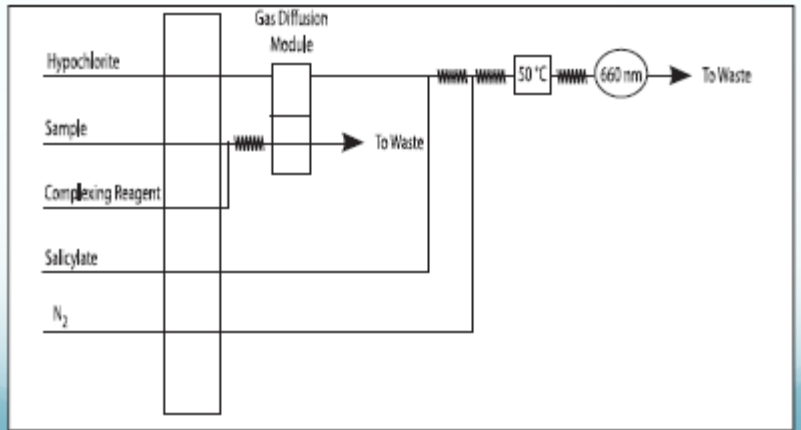
Typical N in influent and effluent

	Influent	Effluent
TKN (mg/L)	30	2
NO_3-N (mg/L)	0	17
TN (mg/L)	30	19

Minimize digestion time to maximize recovery when nitrate is present

1. 25 mL sample
2. 10 mL digestion reagent
3. 5 stones
4. 160 ° C for 1 hour
5. 380 ° C for 30 minutes
6. Cool, rinse sides, cool
7. Dilute to 25 mL (or 50 mL)

With EPA allowed method modifications, both ammonia and TKN can be determined with the same CFA method



EPA 351.2 TKN by Gas Diffusion Colorimetry

EPA	Modified
Direct Colorimetry	Automated Diffusion
Salicylate	Salicylate
Tartrate	Citrate
0.01 – 2.0 ppm	0.01 – 20 ppm

Low Level Organic Nitrogen Requires a TN analysis, not TKN

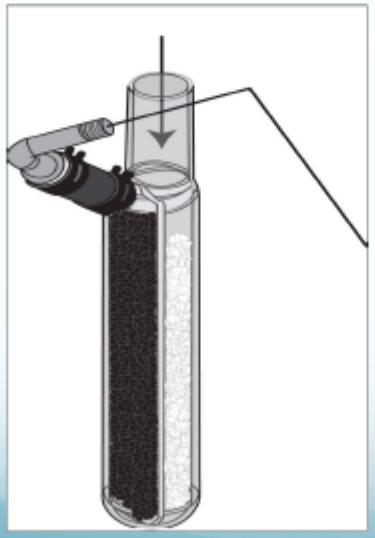


$NO_x\text{-}N = NO_3\text{-}N + NO_2\text{-}N$

Analysis of Total Nitrogen Compounds

- Filter preserved sample for DIN
- Do Not filter preserved sample for TN
- Analyze TN
- Analyze DIN (DIN=TIN)
  - NO3 + NO2
  - NH4
- TON = TN - DIN

HTCO Total Nitrogen Bound (TNb)



720° C reactor

TOC & TNb

Total Nitrogen Bound, or TNb is measured on a TOC analyzer

Oxidation

- $2(NH_2)_2CO + 7O_2 + \text{catalyst} \rightarrow 4NO_2 + 4H_2O + CO_2$

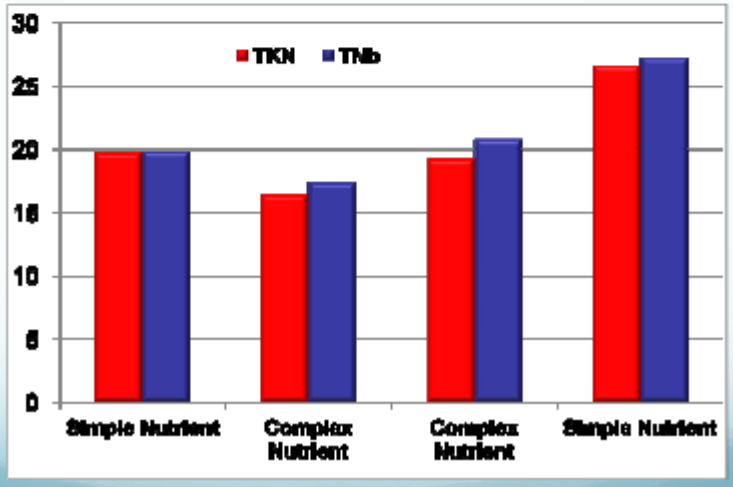
Reduction

- $2NO_2 + \text{catalyst} \rightarrow 2NO + O_2$

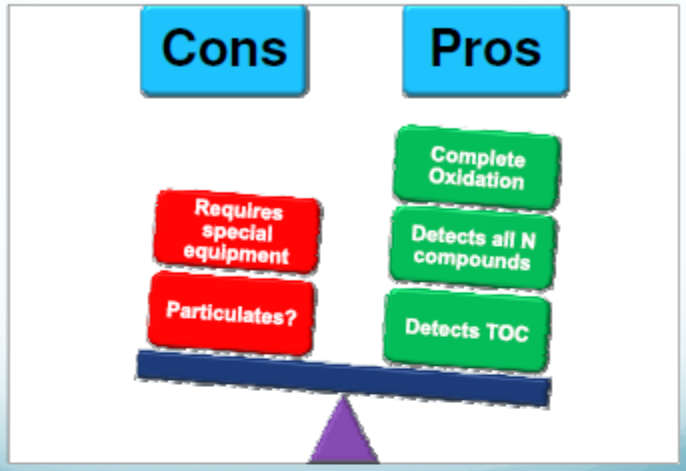
Detection

Chemiluminescence
Electrochemical

Comparison of TNb to TKN (QC samples)



Advantages and disadvantages of TNb



Alkaline Persulfate Digestions for TN do not require specialized equipment



Manually digest

Determine NO_3-N

Measures all TN

Manual Alkaline Digestion for TN can be done in an autoclave or with test tubes

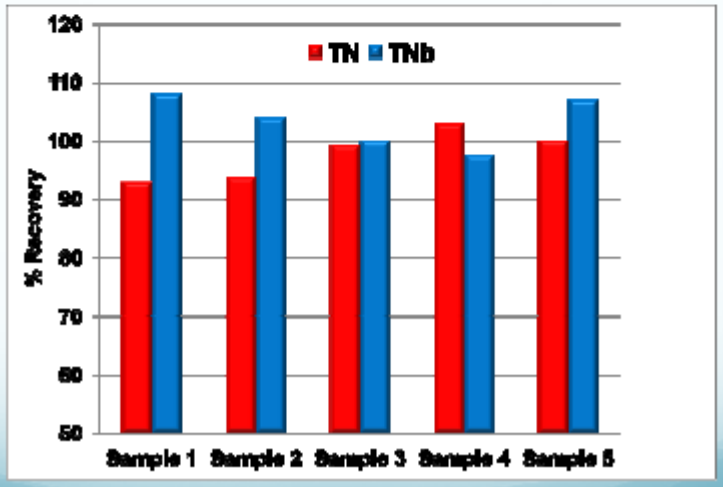
Alkaline Digestion

- $(NH_2)_2CO + 8\ S_2O_8^{-2} + 18\ OH^- \rightarrow 2\ NO_3^- + CO_2 + 16\ SO_4^{-2} + 11\ H_2O$

Colorimetry

- Any Nitrate or Nitrate + Nitrite method

Comparison of TN to TNb illustrates equivalent results on samples tested



Doyle 2004

Comparison of TN to TKN + NO_3/NO_2 -N

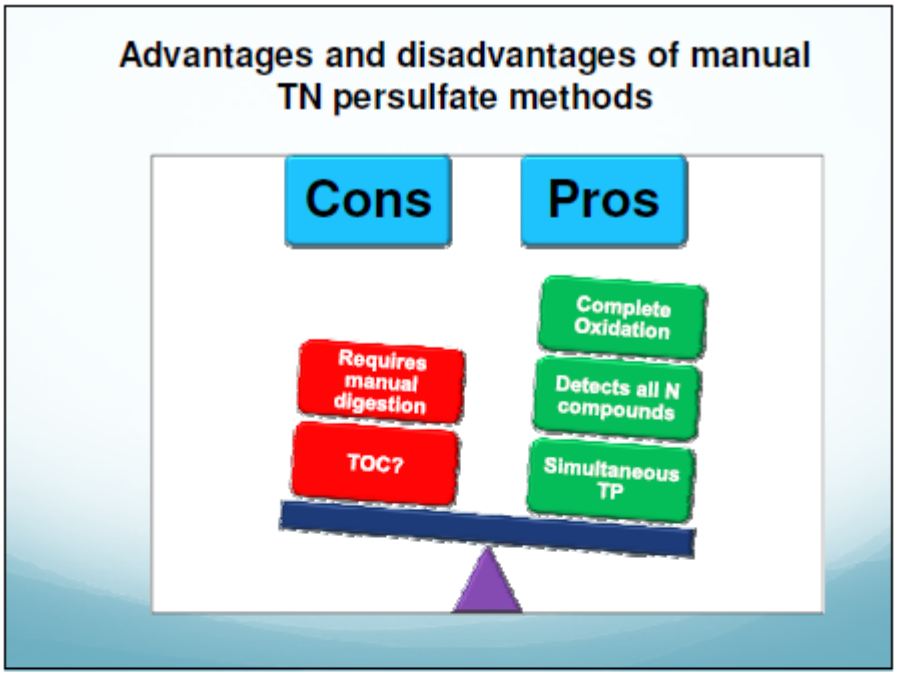
	TOC (mg/L)	TKN + NOx (mg/L)	TN (mg/L)
Cecil	17.5	2.9	2.9
Greenville 1	36.0	3.1	3.5
Hiwassee 2	59.0	8.8	8.9
Irwin	108	17.7	16.0

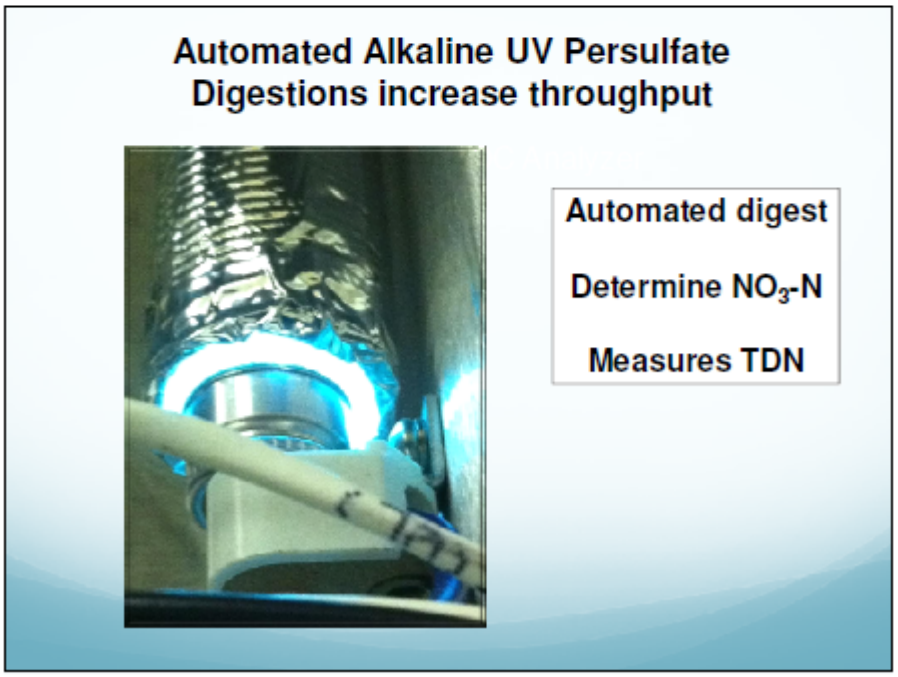
Cabrera 1993

Comparison of TN to TKN with % RSD

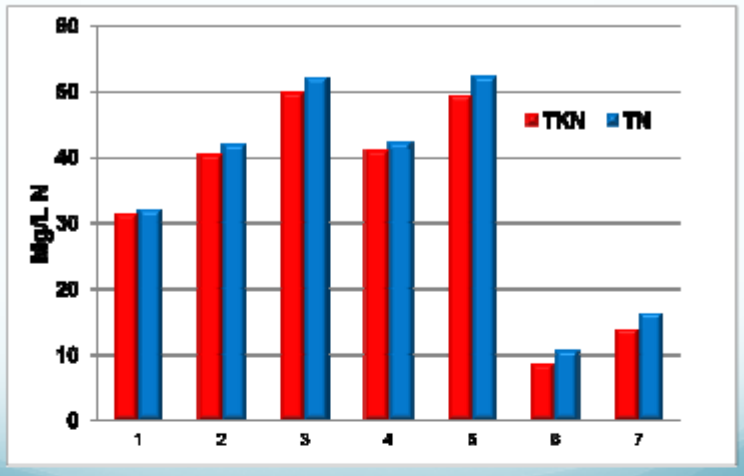
	TKN (mg/L)	TKN (%RSD)	TN (mg/L)	TN (%RSD)
Bear Creek	0.18	10.65	0.22	5.72
Silver Fork	0.36	19.29	0.41	6.49
Salt River	0.59	25.31	0.76	3.23
Ted Shanks	0.61	25.25	1.05	6.04

Smart 1981


Advantages and disadvantages of manual TN persulfate methods
Cons
Pros
Requires manual digestion
TOC?
Complete Oxidation
Detects all N compounds
Simultaneous TP


Automated Alkaline UV Persulfate Digestions increase throughput
Automated digest
Determine NO_3-N
Measures TDN

Comparison of Automated TN with TKN



Unknowns regarding the efficiency of Automated UV Alkaline Digestion



Particulates?

Advantages and disadvantages of automated TN persulfate methods



What samples for Total Nitrogen may look like



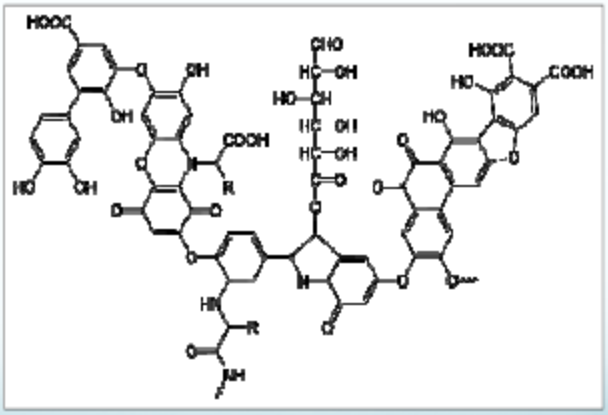
Organic matter consumes persulfate too

$(NH_2)_2CO + 8\ S_2O_8^{-2} + 18\ OH^- \rightarrow 2\ NO_3^- +$

$CO_2 + 16\ SO_4^{-2} + 11\ H_2O$

About 100 ppm C upper limit

A Humic acid molecule



Particulates consume persulfate and are hard to sample

~ 15 - 20% N attached to particulates

Particulates > ~ 30 ppm TSS N/A by CFA

Non quantitative transfer of particulates to HTCO

Fe^{+2} to Fe^{+3} = 1 e^-

Total Phosphorus Digestion Methods

Acid Persulfate (beaker or autoclave)

Kjeldahl (block digestion)

Both convert inorganic and organic phosphorus to orthophosphate

Acid persulfate digestion for total P can be done in a beaker, autoclave, or test tubes

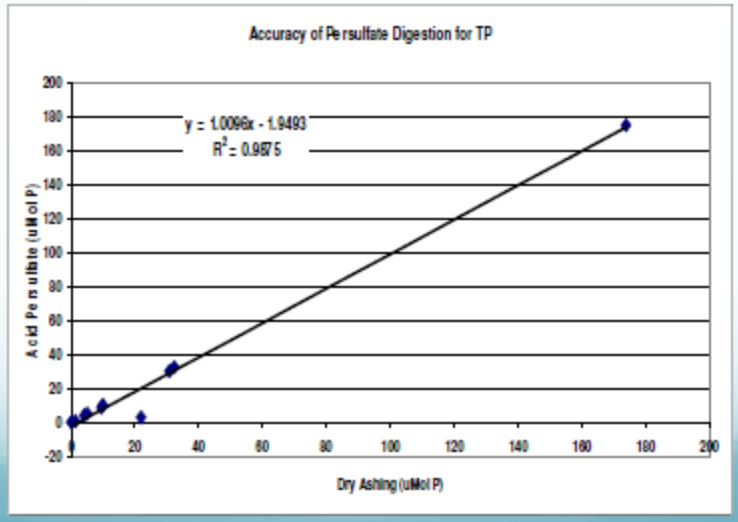
Acid Persulfate Digestion

- $R\text{-}HPO4 + S_2O_8^{-2} + H2SO4 \rightarrow H3PO4 + nCO_2 + nHSO_4^- + n\ H_2O$

Colorimetry

- Any Phosphate method

Comparison of Dry Ashing and Acid Persulfate for Total P



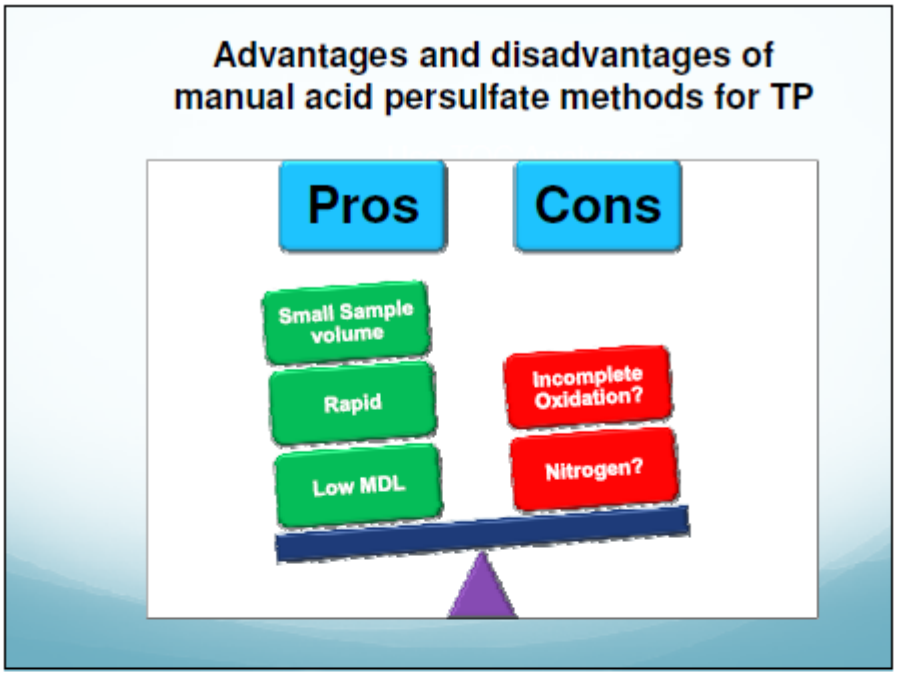
Outlier data on persulfate and wet oxidation comparison for TP digestion

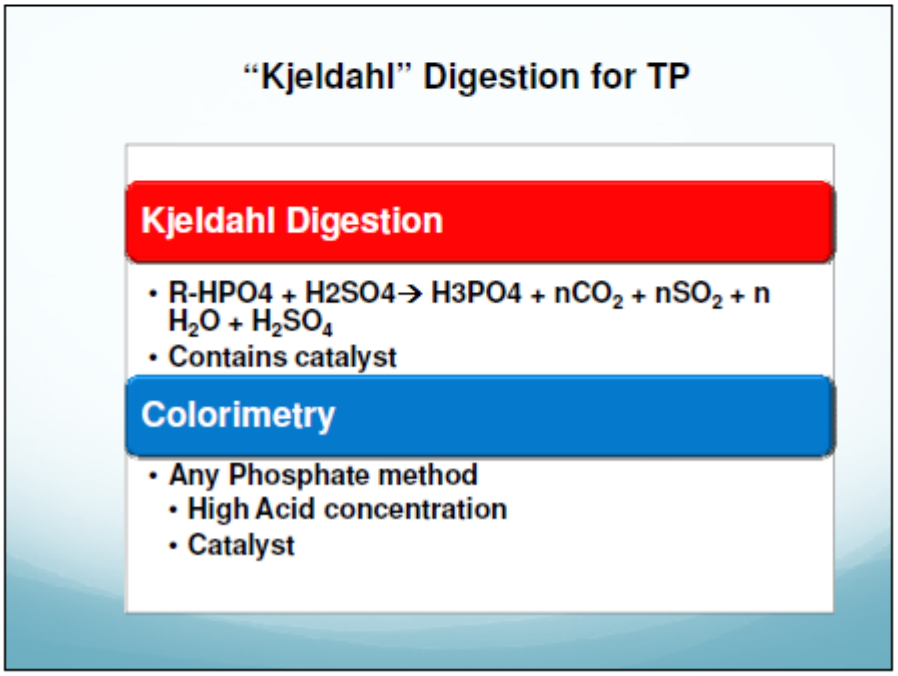
Material tested	Dry Ash uMol P	Persulfate uMol P
Montmorillonite	1.44	1.00
Kaolinite	22.0	3.04

Suzamura, Limnol. Oceanogr. Methods 6 2008, 619-629

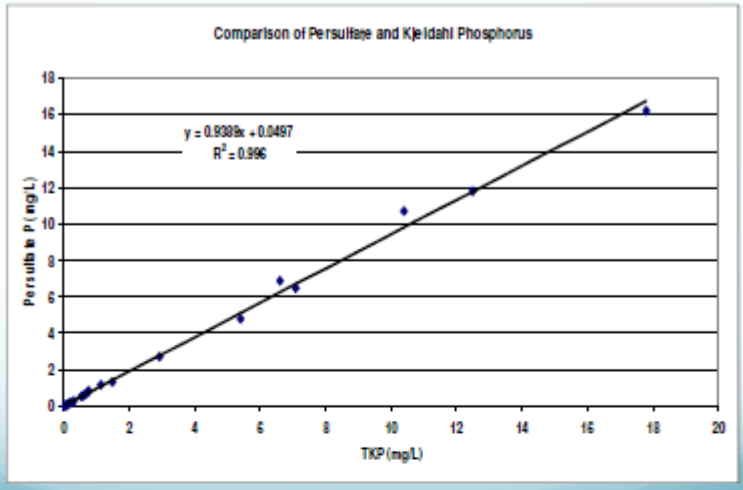
Potential problems with acid persulfate digestions for total phosphorus

- Too much acid
- High chloride
- Organic Matter
- Excess particulates
- Contamination


Advantages and disadvantages of manual acid persulfate methods for TP
Pros
Cons
Small Sample volume
Rapid
Low MDL
Incomplete Oxidation?
Nitrogen?


"Kjeldahl" Digestion for TP
Kjeldahl Digestion
• R-HPO4 + H2SO4→ H3PO4 + nCO2 + nSO2 + n H2O + H2SO4
• Contains catalyst
Colorimetry
• Any Phosphate method
• High Acid concentration
• Catalyst

Comparison of persulfate and Kjeldahl for TP



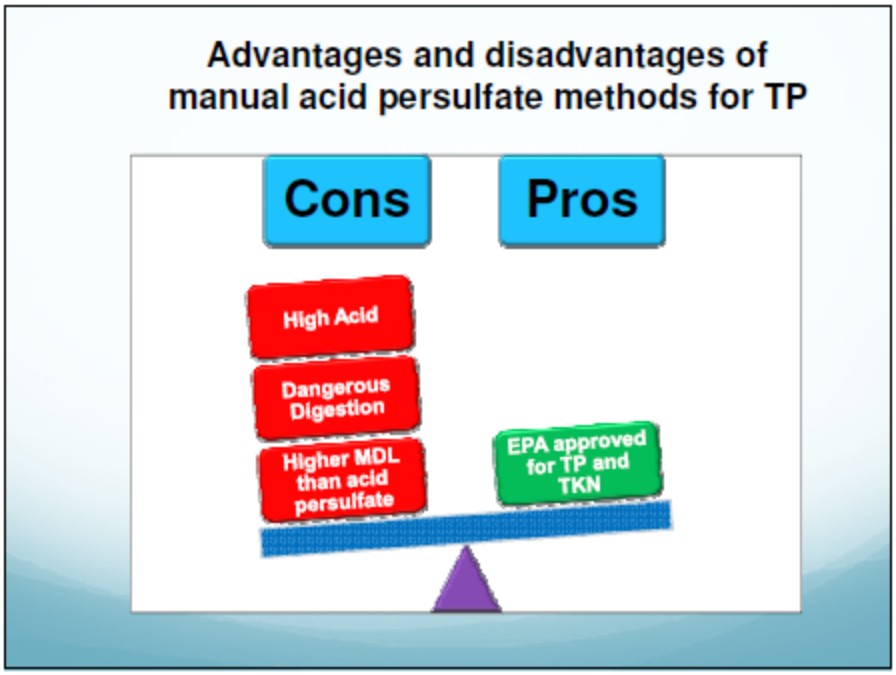
Potential problems with Kjeldahl digestions for total phosphorus

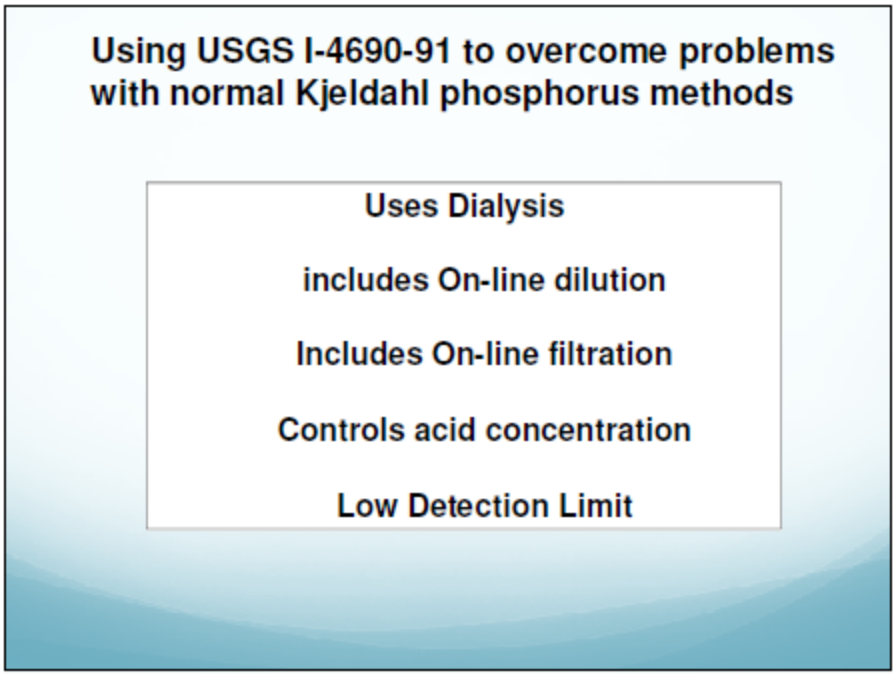
High Acid Concentration

Hazardous Digestion

Catalyst

May require dilution of acid


Advantages and disadvantages of manual acid persulfate methods for TP
Cons
Pros
High Acid
Dangerous Digestion
Higher MDL than acid persulfate
EPA approved for TP and TKN


Using USGS I-4690-91 to overcome problems with normal Kjeldahl phosphorus methods
Uses Dialysis
includes On-line dilution
Includes On-line filtration
Controls acid concentration
Low Detection Limit

Alkaline Persulfate Digestions for Total P



Manually digest

Determine PO_4^{-3}

Measures TP

Manual Alkaline Persulfate Digestion for TP

Alkaline Digestion

- $R\text{-}HPO_4$ + excess $S_2O_8^{-2}$ + 18 OH^- → H_3PO4 + CO_2 + HSO_4^{-2} + n H_2O

Colorimetry

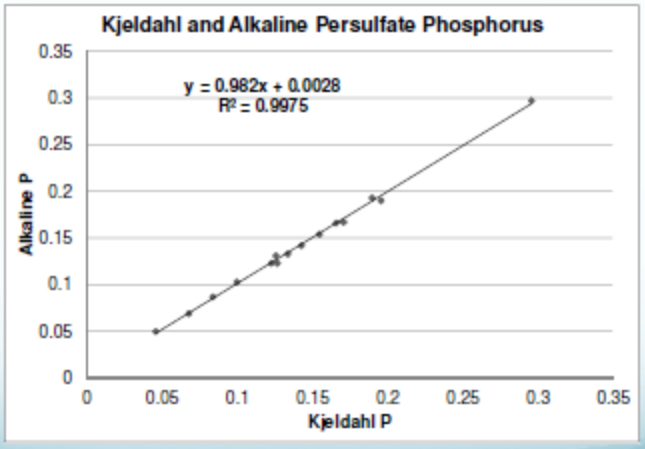
- Any phosphate method

Comparison of Alkaline Persulfate and Acid Persulfate Total Phosphorus

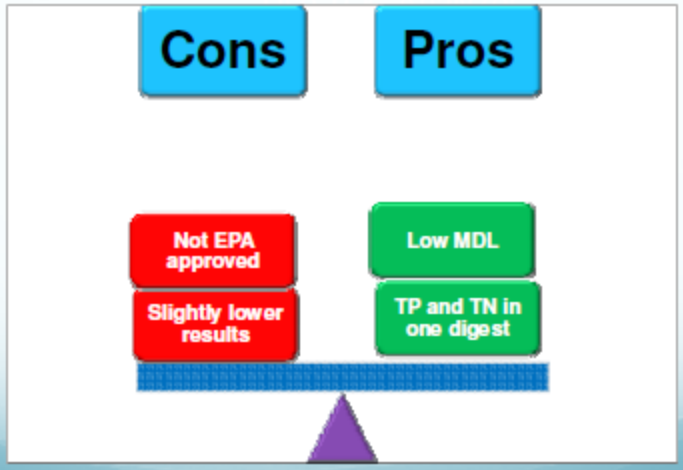
Compound	Alkaline (mg/L P)	Acid (mg/L P)
Adenosine tri-phosphate (ATP)	0.166	0.176
Glycerophosphate	0.196	0.204
Phenyl Phosphate	0.168	0.179
Phytic Acid	0.177	0.180

USGS Water Resources Investigative Report 03-4174 (2003)

Comparison of TKP and Alkaline Persulfate



Advantages and disadvantages of manual Alkaline persulfate method for TP



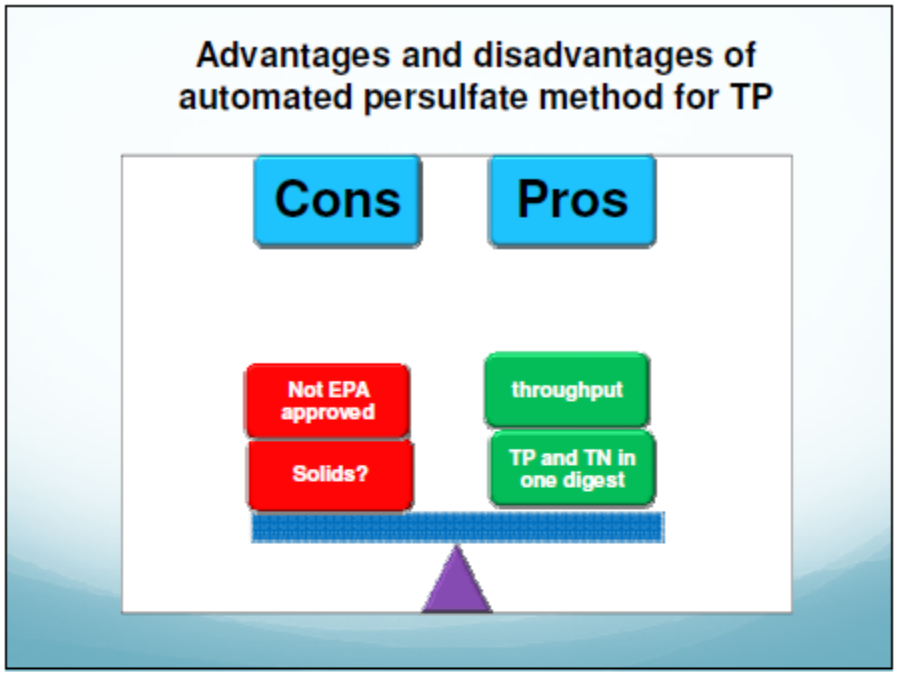
Automated Alkaline UV Persulfate Digestions

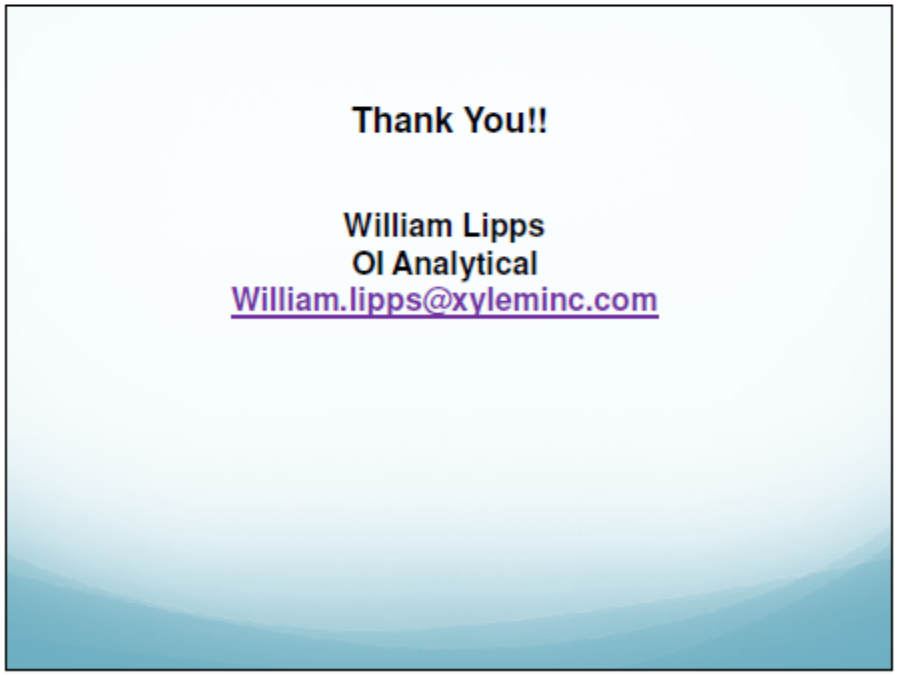


Automated digest

Determine PO_4^{-3}

Measures TDP


Advantages and disadvantages of automated persulfate method for TP
Cons
Pros
Not EPA approved
Solids?
throughput
TP and TN in one digest


Thank You!!
William Lipps
OI Analytical
William.lipps@xyleminc.com

Simplified Method for the Determination of Total Kjeldahl Nitrogen in Water and Wastewater

Cary Jackson
Hach Company

Abstract

Total Kjeldahl Nitrogen (TKN) is defined as the sum of organic nitrogen and ammonia present in a wastewater sample. A preliminary digestion is used to oxidize carbon compounds to carbon dioxide, and convert organic forms of any nitrogen present (amino acids, proteins, peptides) to ammonia. The traditional digestion uses sulfuric acid in combination with mercury or copper catalysts and salts. Maco-digestion (500 mL) of at least two hours is followed by addition of sodium hydroxide, where the ammonia is distilled into boric acid or buffer solution. The ammonia distillate is then measured by back titration or nesslerization.

In the simplified TKN method (s-TKN™), inorganic and organic nitrogen (total nitrogen) are oxidized to nitrate by micro-digestion with peroxodisulfate. The micro-digestion (<2 mL) takes one hour and requires no distillation. The nitrate ion from the distillate is reacted with 2,6-Dimethylphenol in a solution of sulfuric acid and phosphoric acid to form nitrophenol where it is measured colorimetrically. A second sample is analyzed for nitrate-nitrite by reacting with 2,6-Dimethylphenol, measured colorimetrically, then subtracted from the results of the digested sample. sTKN results are comparable to traditional macro digestion and analysis methods. This talk compares and contrasts the tow TKN methods, both in performance, cost of analysis, and green chemistry implications.

SIMPLIFIED METHOD FOR THE DETERMINATION OF TOTAL KJELDAHL NITROGEN IN WATER AND WASTEWATER

Dr. Cary B. Jackson
Director of Regulatory Affairs

GOALS OF THE PRESENTATION

- Review Traditional Total Kjeldahl Nitrogen
  - Advantages and Disadvantages
- Present New Simplified Total Kjeldahl Nitrogen System
  - Theory
  - Chemistry
  - Results
  - Advantages and Disadvantages

TOTAL KJELDAHL NITROGEN (TKN) HISTORY

- TKN Method first presented on 7-March-1883 by Johan Kjeldahl (1849-1900) as a novel method for analyzing protein
- Numerous Applications:
  - Wastewater Treatment for nitrogen testing and removal
  - Food and Beverage production for protein analysis
  - Agriculture
- One of the most challenging, dangerous and labor-intensive tests performed in wastewater treatment plant laboratories.

REGULATORY SIGNIFICANCE

- TKN is used as a indicator for wastewater treatment performance, pre-treatment loading fees, and is limited in discharge to receiving waters
- More than 3000 wastewater treatment plants in the United States have a NPDES discharged permit limiting TKN



TRADITIONAL TKN CHEMISTRY

TKN Method: Digestion, distillation, capture, and titration

Degradation: $Org\text{-}N + H_2SO_4 + Hg_{(catalyst)} + Heat_{(189°C)} \rightarrow (NH_4)_2SO_4 + CO_{2\ (gas)} + H_2O_{(gas)}$

Distillation: $NH_4^+ + (NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_{3\ (gas)}$

Capture: $B(OH)_3 + H_2O + NH_3 \rightarrow NH_4^+ + B(OH)_4^-$

Back Titration*: $B(OH)_3 + H_2O + Na_2CO_3 \rightarrow NaHCO_3 + NaB(OH)_4 + CO_{2\ (gas)} + H_2O$

* Typically Methyl Orange Indicator: <pH 3.1:RED; >pH 4.4:YELLOW

5

COLORIMETRIC DETECTION

- Nessler
  - Nessler reagent (K_2HgI_4) reacts with ammonia under strong alkaline conditions to produce a yellow-colored species. The intensity of the color is directly proportional to the ammonia concentration.
    - $2KsHgI4 + NH3 + 3KOH \rightarrow Hg_2OINH_2 + 7KI + 2H_2O$
    - Chemistry downside - Contains mercury

6

COLORIMETRIC DETECTION

- Phenate
  - Ammonia combines with hypochlorite (OCl^-) to form monochloramine (NH_2Cl) which then reacts with phenate to form 5-aminophenate.
  - The 5-aminophenate is oxidized in the presence of a catalyst (nitroprusside), which results in the formation of indophenol (a blue-colored compound).

Chloramination: $NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$

Phenate Reaction: $NH2Cl$ + phenate $\rightarrow H_2N$-phenol

Color Formation: H_2N-phenol + $Fe(CN)_5NO_2^-$ (nitroprusside) $\rightarrow$ Indophenol

Chemistry Downside: Phenol Odor

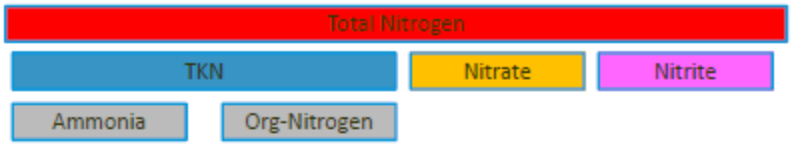
7

ELECTROCHEMICAL DETECTION

- Ion Selective Electrode (ISE)
  - Potentiometric sensor for ammonia measurement
  - Multi-point calibration curve must be generated and the ISE technology must be maintained.

8

TKN – WHAT IT IS / IS NOT?



Total Nitrogen = NH_3 + Org-N + NO_3^- + NO_2^-

By definition, TKN, which is a component of total nitrogen, is the sum of organic nitrogen and ammonia. Therefore, the above relationship may be re-written as:

Total Nitrogen = TKN + NO_3^- + NO_2^-

or

TKN = Total Nitrogen – (NO_3^- + NO_2^-)

9

SIMPLIFIED TOTAL KJELDAHL NITROGEN

- The simplified TKN (s-TKN™) method utilizes two simple measurements to calculate the TKN value as:
  - The difference between the concentration of TN and NO_3^- + NO_2^-.



10

S-TKN™ EQUATION

- TKN is a component of total nitrogen, and is the sum of organic nitrogen and ammonia. Therefore, the TKN equation may be re-written as:

$$\text{Total Nitrogen} = NH_3 + \text{Org-N} + NO_3^- + NO_2^-$$

- The s-TKN method is based on this nitrogen relationship. s-TKN is defined as the difference between the concentration of TN and Nitrate-Nitrite

$$\text{s-TKN} = \text{Total Nitrogen} - (NO_3^- + NO_2^-)$$

11

S-TKN CHEMISTRY

- TN is determined by digesting the sample for 1 hour at 100 º C with $K_2S_2O_8$ under alkaline conditions, oxidizing all forms of nitrogen to NO_3^-.

Digestion: $NH_3 + \text{Org-N} + NO_3^- + NO_2^- + K_2S_2O_8 + \text{NaOH} \rightarrow NO_3^-$

Analysis: TN digestate for NO_3^-

Undigested sample for $(NO_3^- - NO_2^-)$

$TN(NO_3^-) - (NO_3^- - NO_2^-) = \text{TKN}$

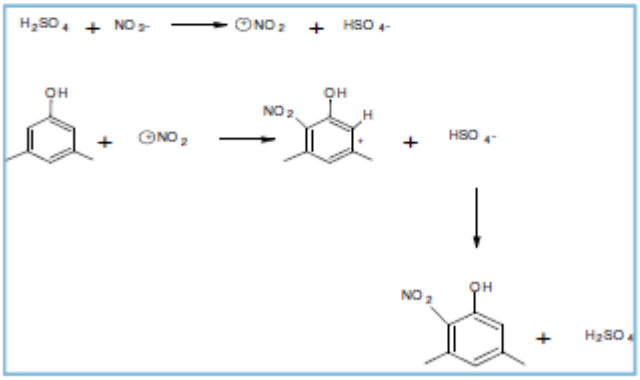
12

DIMETHYLPHENOL CHEMISTRY

- NO_3^- reacts with 2,6-dimethylphenol, forming a colored complex.
  - NO_3^- in the presence of sulfuric acid yields a nitronium ion (NO_2^+) and HSO_4^-.
  - Nitronium ions are electrophiles that attack the aromatic ring of the dimethylphenol reagent to form intermediate nitro-carbonium ions.
  - The basic HSO_4^- ion extracts a hydrogen ion from the nitro-carbonium intermediate to yield a stable substitution product (o, or p-nitro-dimethylphenol).

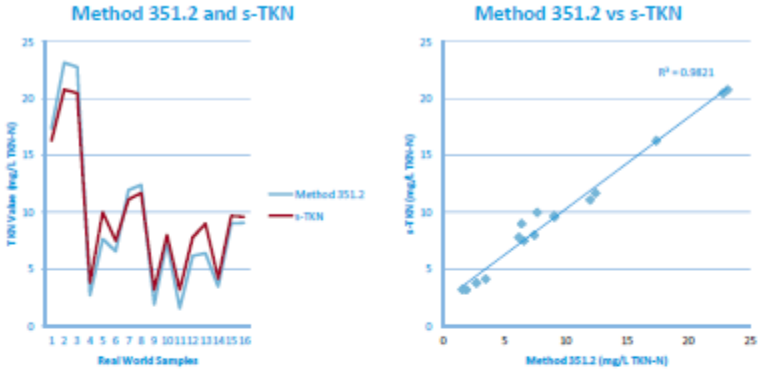
13

DIMETHYLPHENOL + NITRATE REACTION



14

METHOD PERFORMANCE CORRELATION PLOTS S-TKN WITH TKN



These matrices included wastes from dairy processing, brewing, photo-processing, and geographically dispersed municipal waste facilities.

15

AMMONIA NITROGEN MATRIX SPIKE RECOVERY OF S-TKN WITH TKN

Sample Matrix	% Recovery (s-TKN)	% Recovery (EPA 351.2)
Industrial Chemical Effluent 1	96.8%	102.8%
Municipal Waste Effluent 1	113.6%	99.2%
Municipal Waste Effluent 2	91.2%	105.3%
Municipal Waste Effluent 3	97.6%	107.5%
Industrial Food Effluent 1	102.4%	95.6%
Industrial Beverage Effluent 1	105.4%	107.0%
Average	**101.2%**	**102.9%**

These matrices included wastes from dairy processing, brewing, photo-processing, and geographically dispersed municipal waste facilities.

16

FOOTPRINT OF S-TKN DIGESTION BLOCK AND ANALYSIS EQUIPMENT



17

BENEFITS OF S-TKN METHOD

- Green Chemistry
- Eliminates the use of hazardous mercury
- One hour digestion, no need for fume hood
- Three results in one test (TKN, TN, (NO_2^- + NO_3^-))
- Performance equally effective to other EPA approved TKN methods
- Small lab space footprint (No Fume Hood Needed)
- Startup Cost - $4200 (digestion block and spectrophotometer)
- s-TKN Cost per test - $4 per test (Traditional TKN Cost - $25 - $50)

18

EPA ATP VALIDATION STUDY



19

QUESTIONS

20

BACKUP SLIDES

21

ORGANIC NITROGEN RECOVERY

TN Organic compounds

2 mg/L Nicotinic Acid, Urea , separate and equally combined
30 mg/L Nicotinic Acid, Urea, separate and equally combined
80 mg/L Nicotinic Acid, Urea, separate and equally combined

mg/L N Spike	Urea (%)	Nicotinic Acid (%)	Combined Urea/Nicotinic Acid (%)	Average % Recovery
2.00	97.5	99.5	99.5	102
2.00	102	104	105	
30.0	97	96.7	97.3	96.7
30.0	101	98.0	96.0	
80.0	94.1	93.8	93.9	95.3
80.0	96.3	94.4	96.6	
Average % Recovery	**98.0**	**97.7**	**98.0**	

22

Proposed Updates to the 40CFR Part 136 MDL Procedure

Richard Burrows
TestAmerica

Abstract

The TNI Chemistry Expert Committee has been working on a set of proposed updates to the 40 CFR Part 136 Method Detection Limit procedure. These proposed updates will soon be presented to EPA for consideration. This paper will describe the modifications and updates included, and the reasons for the modifications.

Collaboration on Detection and Quantitation

Draft Changes to MDL Determination

Richard Burrows, Brooke Conner

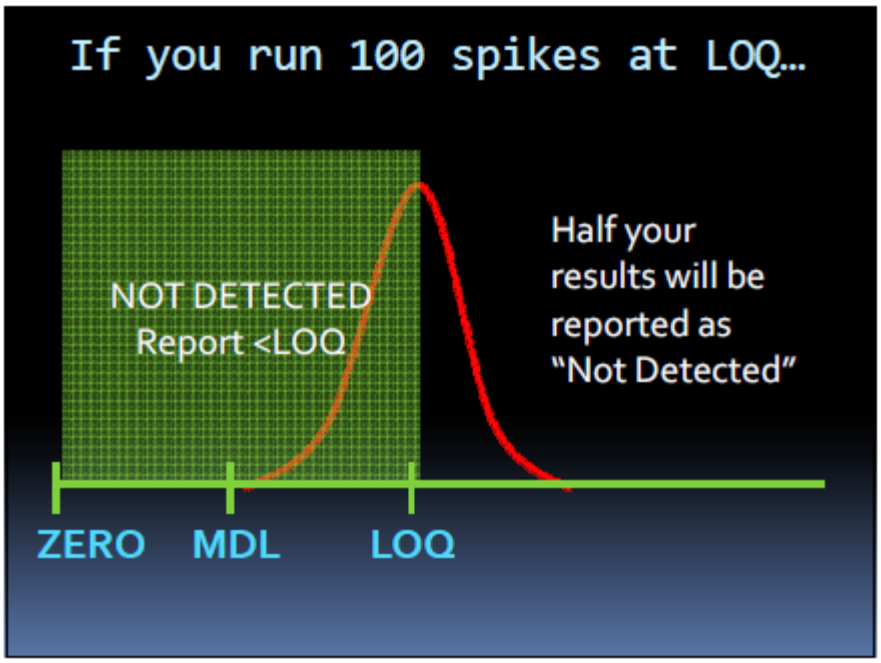


What can (should) we do?

- We have been doing it this way for 30 years, perhaps it is OK?
- Or are things getting worse?

What are our options?

- Replace the MDL
  - DQFAC procedure
  - ASTM IDE/WDE
- Stop reporting below the quantitation limit
- Leave the MDL alone
  - Improve things for TNI labs at least, through development of a standard by the EMMEC
- Modify the MDL
  - Based on principles from the DQFAC and learning from the Pilots



Chemistry Committee Tasks

Maintain as much original intent from the EPA 40 CFR Part 136 Appendix B - MDL procedure while assuring scientific integrity.

MDL Definition

Appendix B to Part 136

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

MDL Definition

Appendix B to Part 136

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

TNI

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Appendix B – Estimate MDL

- Estimate MDL
  - Signal to noise 2.5 – 5
  - 3x standard deviation of spikes
  - Change in slope of standard curve
  - Instrument limitations

Appendix B – Estimate MDL

- Estimate MDL
  - Signal to noise 2.5 – 5
  - 3x standard deviation of spikes
  - Change in slope of standard curve
  - Instrument limitations

TNI

- Signal to noise 3 - 5
- 3x standard deviation of method blanks, plus the mean
- 3x standard deviation of spikes
- Change in slope of standard curve
- Instrument limitations
- Previously determined MDL

Appendix B – MDL Procedure

- Prepare spikes close to estimated MDL (1-5 times estimated MDL)
- 7 aliquots through entire method.

Appendix B – MDL Procedure

- Prepare spikes close to estimated MDL (1-5 times estimated MDL)
- 7 aliquots through entire method.

TNI

- Spike at 2 – 10 times MDL_e
- Process 7 spikes and 7 blanks in 3 or more batches.
- Multiple instruments must analyze a minimum of 2 spikes and 2 blanks.

Appendix B – MDL Procedure

- Calculate the variance, standard deviation and the 95% Confidence Interval
  - Optional – iterate by spiking at the new MDL.

Appendix B – MDL Procedure

- Calculate the variance, standard deviation and the 95% Confidence Interval
  - Optional – iterate by spiking at the new MDL.

TNI

$$\boldsymbol{MDL_s} = t_{(n-1,1-\alpha=0.99)}S$$

$$\boldsymbol{MDL_b} = \overline{X} + t_{(n-1,1-\alpha=0.99)}S_b$$

MDL = larger of MDL_s or MDL_b

TNI – Ongoing Data Collection

- Minimum 2 spikes per quarter
- Collect method blanks

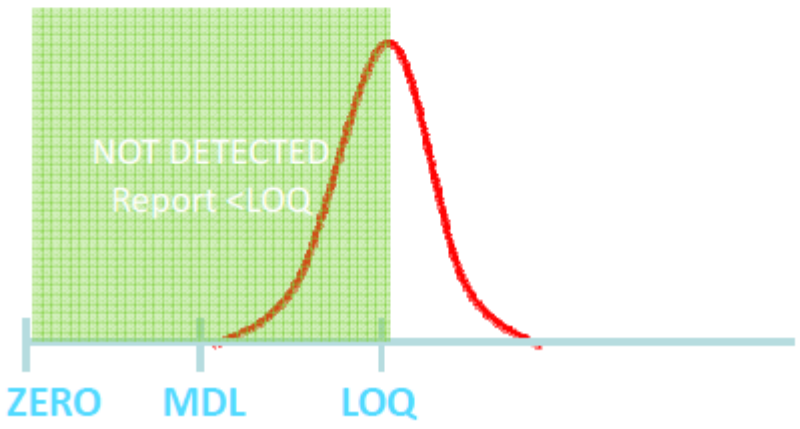
TNI – Annual Verification

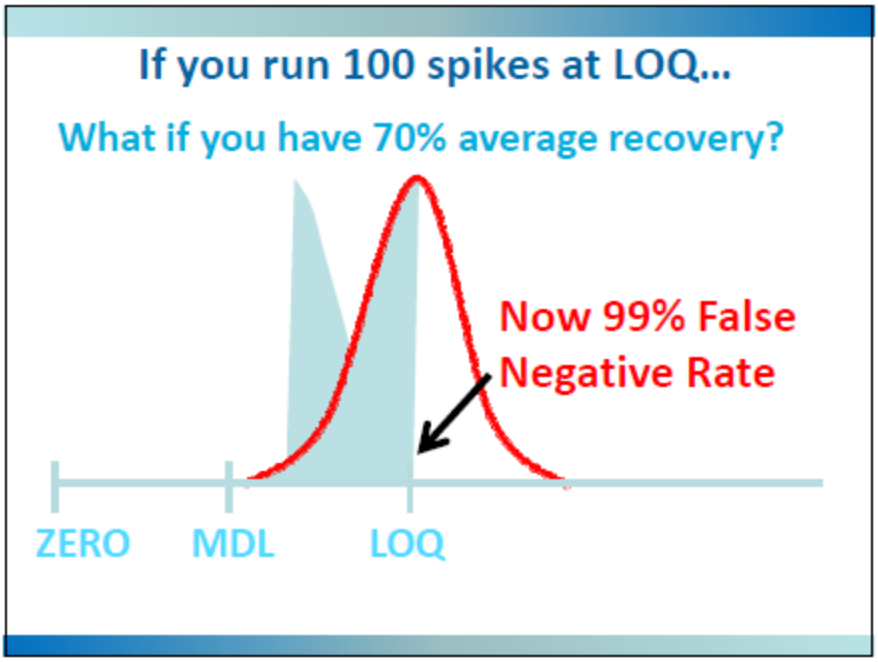
- Recalculate MDL_s and MDL_b (2 yrs data)
- Set MDL_b to highest blank if there are non-detects in the blank data set and n<100.
- Set MDL_b to 99th percentile if n>100
- If $MDL_{recalculated}$ is within 0.3 – 3 times existing, and <2% of method blanks are >MDL, then optionally leave MDL unchanged.

TNI – Spike Concentration

- Once per year, re-evaluation spiking concentration.
- If >5% of spikes are not detected, then raise spike concentration and re-determine MDL.

If you run 100 spikes at LOQ…



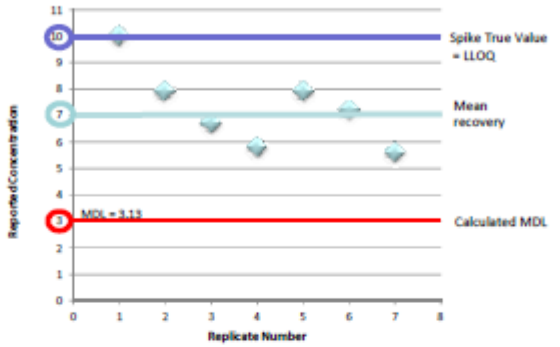


What if....

- LOQ = LLOQ from SW-846
  - Use the LLOQ spikes to calculate the MDL

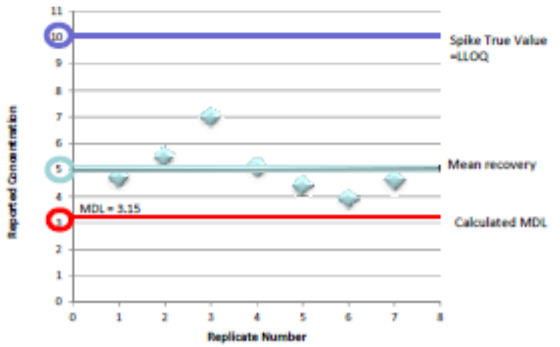
70% recovery, 10% RSD

Spike	#1	#2	#3	#4	#5	#6	#7	Mean	MDL
10	10	7.9	6.7	5.8	7.9	7.2	5.6	7.0	3.13



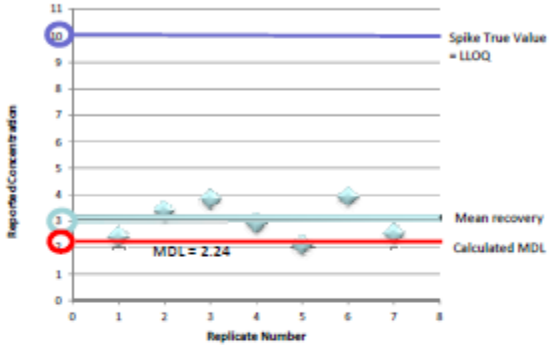
50% recovery, 20% RSD

Spike	#1	#2	#3	#4	#5	#6	#7	Mean	MDL
10	4.7	5.5	7	5.1	4.4	3.9	4.6	5.0	3.15



30% recovery, 25% RSD

Spike	#1	#2	#3	#4	#5	#6	#7	Mean	MDL
10	2.4	3.4	3.8	2.9	2.1	3.9	2.5	3.0	2.24

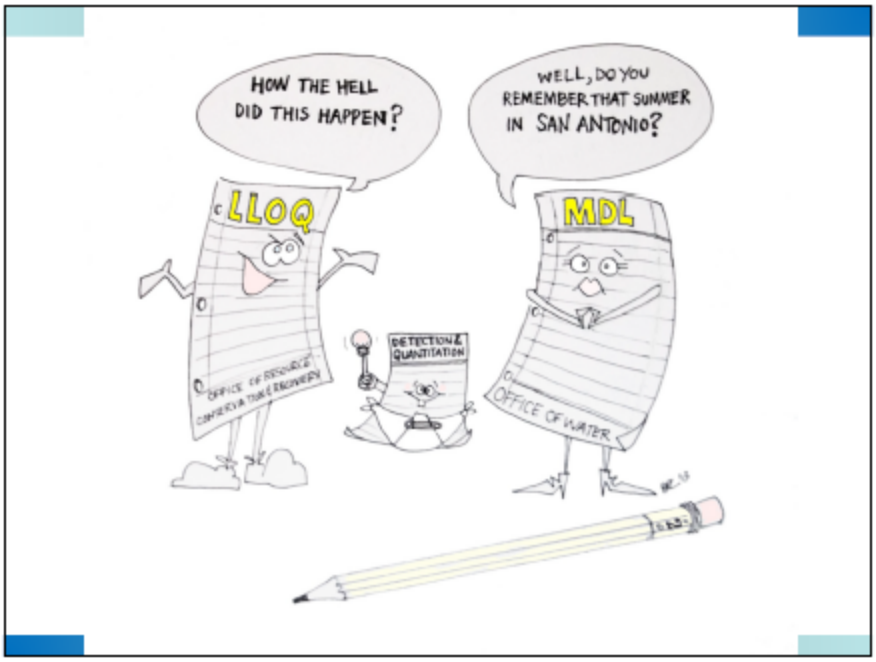


EPA Methods Harmonization

Office of Resource Conservation and Recovery
and
Office of Water

Detection and Quantitation Procedures

Harmonized!!


HOW THE HELL DID THIS HAPPEN?
WELL, DO YOU REMEMBER THAT SUMMER IN SAN ANTONIO?
LLOQ
MDL
DETECTION & QUANTITATION
OFFICE OF WATER

Questions?

Collaborative Efforts for Creating a Robust Trace Metals Analytical Procedure for Flue Gas Desulfurization Wastewater by ICP-MS

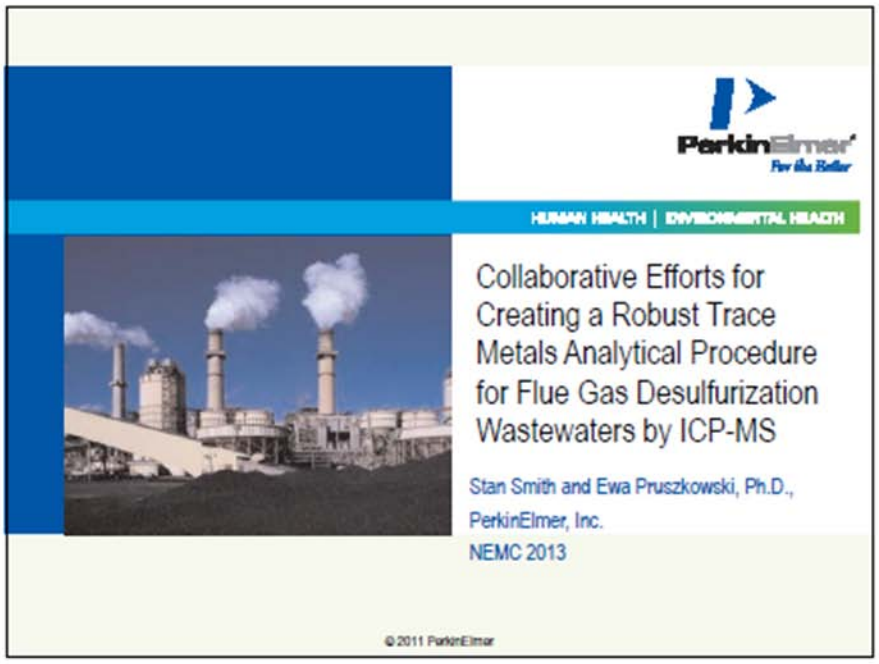
Stan Smith
PerkinElmer, Inc.

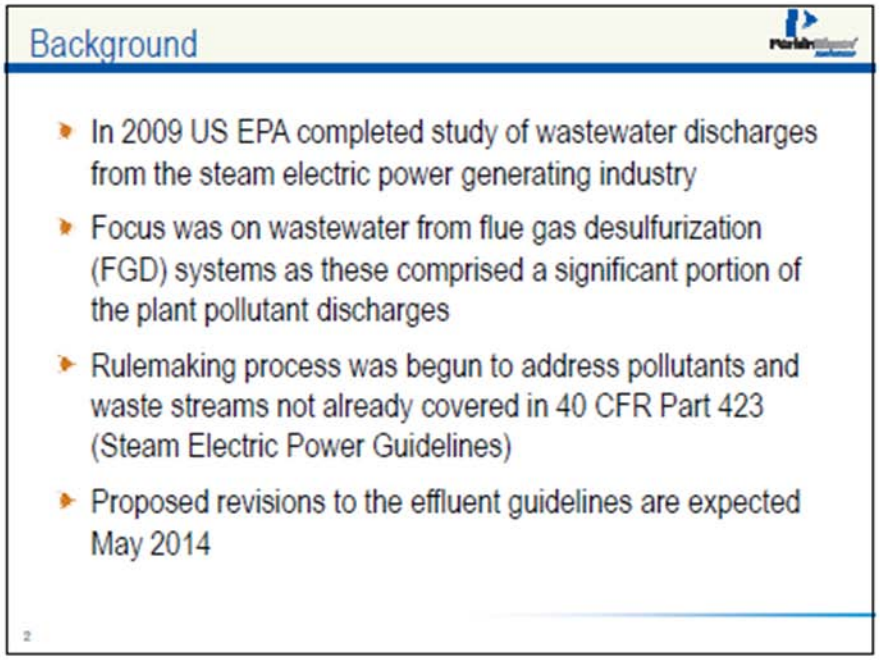
Abstract

The Unites States Environmental Protection Agency (EPA) continues to make progress toward promulgating regulations for the steam electric power generating industry. In particular, progress has been made in regards to creating and providing a robust analytical procedure for the analysis of flue gas desulfurization (FGD) wastewaters by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Through collaborative efforts, the EPA, its contractors, and Perkin Elmer have created a detailed procedure for the analysis of this complex wastewater matrix.

FGD wastewater can be one of the most challenging sample types to analyze by ICP-MS instrumentation. This wastewater stream can be extremely acidic and saturated with high concentrations of calcium sulfate (e.g., gypsum), and may contain high concentrations of heavy metals, alkali earth metals, chlorides and dissolved organic compounds. With the very high total dissolved solids and metals concentrations, current EPA Methods such as 200.8 and 1638 are inadequate to address the interferences encountered. As such, cell based technologies including interference removal techniques such as collision mode and/or reaction mode are needed.

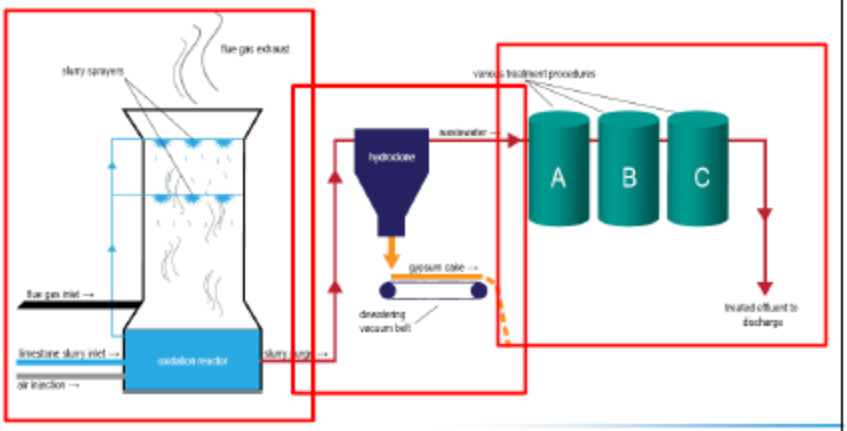
The procedure that will be discussed reflects the latest collaborative efforts and includes details on the entire analytical process from sample preparation, to instrument optimization, calibration, sample analysis, quality assurance procedures, and sample reporting. The entire procedure is geared specifically toward FGD wastewater and utilizes instrument accessories and analytical techniques to improve the analytical performance for this challenging matrix.


PerkinElmer
For the Better
HUMAN HEALTH | ENVIRONMENTAL HEALTH
Collaborative Efforts for Creating a Robust Trace Metals Analytical Procedure for Flue Gas Desulfurization Wastewaters by ICP-MS
Stan Smith and Ewa Pruszkowski, Ph.D.,
PerkinElmer, Inc.
NEMC 2013
© 2011 PerkinElmer


Background
In 2009 US EPA completed study of wastewater discharges from the steam electric power generating industry
Focus was on wastewater from flue gas desulfurization (FGD) systems as these comprised a significant portion of the plant pollutant discharges
Rulemaking process was begun to address pollutants and waste streams not already covered in 40 CFR Part 423 (Steam Electric Power Guidelines)
Proposed revisions to the effluent guidelines are expected May 2014
2

Background

Typical FGD treatment system using wet scrubber to remove SO_2 emissions from the flue gas



3

FDG Process

Background

- ICP-MS currently preferred technique for FGD due to sensitivity and wide availability (ICP-OES ?)
- Current methods 200.8, 6020, and 1638 lack detailed treatment for interferences associated with FGD
- May 2010 EPA proposed draft testing procedure specific to FGD through a collaborative effort with a contract lab (instrument-specific)
- Draft procedure largely based on 200.8 and 1638 with additional procedures on handling interferences
- Just what does FGD wastewater look like?

4

Analytical Techniques

Background

- Constituents of FGD wastewater come from the limestone used to make the slurry, the coal burned, and the water supply
- FGD wastewaters vary widely depending on above parameters as well as the efficiency of the FGD treatment system

Parameter	Range (mg/L)
Total Dissolved Solids	4000 - 68,000
Chloride	1000 - 35,000
Sulfate	1500 - 8000
Calcium	750 - 4000
Magnesium	1100 - 4800
Sodium	670 - 4800
Boron	10 - 800
Total Organic Carbon	5 - 1100

Nearly 7% Polyatomic TDS Interferences e.g., $^{34}S^{16}O^{16}O$ on ^{66}Zn

Also high ppm Al, Fe, and Mn

5 FGD Wastewater

Collaborative Goals

Merriam-Webster Definition of *COLLABORATE*

- 1. to work jointly with others or together especially in an intellectual endeavor
- ~~2. to cooperate with or willingly assist an enemy of one's country and especially an occupying force~~
- 3. to cooperate with an agency or instrumentality with which one is not immediately connected

6

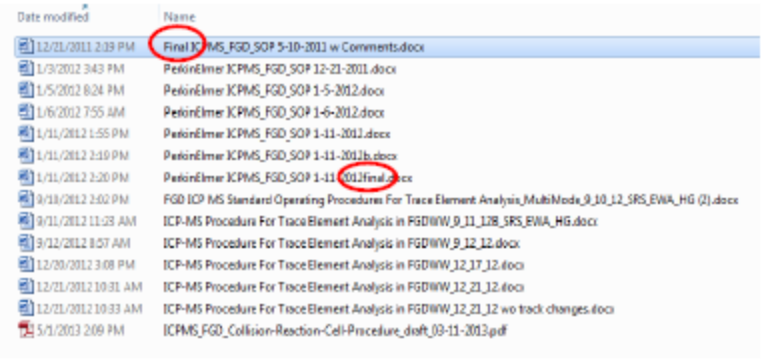
Collaborative Goals

- Create alternate test procedure for different instrument and interference removal technology
  - Along the way, opted to include significantly more detail; instrument hardware, interference removal techniques
  - Digestion procedure (1638); evaluate open vessel digestion vs closed vessel digestion
  - Minimal dilution needed for signal suppression for best DLs
    - Dilution via traditional liquid dilution vs gas dilution

7

Speaking of Collaboration

- Collaborative process involves a process where ideas are exchanged, rarely does the first draft survive as the final



8

A non-inclusive list

Procedure Development

- *Title: Standard Operation Procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure*
- *Introduction - 1.2 The ICP-MS spectrometer with the Universal Cell can operate in reaction, collision and standard modes…*

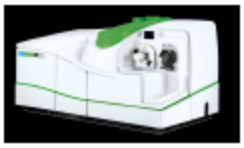
  The use of instrument configurations and/or accessories designed to accommodate samples with high dissolved solids levels is highly recommended…

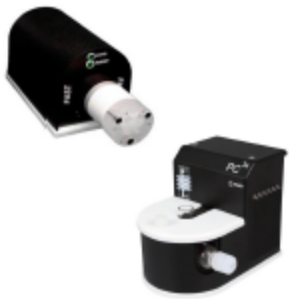
  This method was developed on a Perkin Elmer NexION 300D ICP/MS using an Environmental Scientific SC-DX FAST Automated Sample Introduction System.
- *1.3 …analysis of 13 elements… Al, As, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn*

9

Procedure Development, Hardware

- *2.4 A NexION 300D ICP-MS (Perkin Elmer, Shelton, CT) coupled to an SC DX FAST (ESI, Omaha, NE) automated sample delivery system is used for this procedure… The FAST portion of the delivery system uses a 6-port switching valve containing a Teflon sample loop…In this procedure, a 1.5 ml was adequate…*
- *2.5 …The baffled, cyclonic spray chamber used in the SC DX FAST introduction system is Peltier-cooled to 2ºC to ensure low oxides and greater stability of the instrument.*





10

Procedure Development, Hardware

- *6.1.2 The sample introduction system also includes a PFA ST concentric nebulizer, 2.0 mm quartz injector, and baffled cyclonic spray chamber with gas addition port (ESI, Omaha, NE)…*
- *6.1.3 PVC peristaltic pump tubing, orange-white, is used to produce a sample flow rate of 270 uL/min…*
- *6.1.4 A mixing tee is used to blend in the internal standards after the peristaltic pump and before the nebulizer… The peristaltic pump tubing used for the internal standard solution is orange-whitered and when used in combination with orange-white pump tubing for the carrier solution or sample, creates a minimum dilution of approximately 8.1%.*





11

Procedure Development, Sample Preparation

- *10.2.1 EPA Method 1638 was used as the reference for the digestion of the samples in which section 12.2 describes Aqueous Sample Preparation.*
- Block digestion with vials sealed or open with watch glass covers?
  - Sealed results in a dilution factor that must be accounted for
  - Open has the potential for contamination
- No contamination was noted in digestion blanks

12

Procedure Development, Sample Preparation

- *10.2.2 Transfer a 50mL (± 0.5 mL) aliquot from a well-mixed, acid-preserved sample to a 50mL block digestion tube.*
- *10.2.3 Add 1.0mL of concentrated nitric acid and 0.25mL concentrated hydrochloric acid…*
- *10.2.5 Place a ribbed disposable watch glass over the digestion tube.*
- *10.2.6 Place the digestion tube into a block digester adjusted to achieve a temperature of approximately 85°C.*
- *10.2.7 Heat for 2 hours after 85°C is obtained.*
- *10.2.8 Remove the tubes from the block and allow to cool.*
- *10.2.9 Add deionized water to digestates to bring them back to 50.0 ml.*

13

Synthetic FGD Solution

- 7.2.4 Mixed Interference Check Solution (Synthetic FGD Wastewater)
  - 7.2.4.2 The following solution is prepared in 1.6% HCl
  - 7.2.4.3 Calcium, 2,000 mg/L
  - 7.2.4.4 Magnesium, 1,000 mg/L
  - 7.2.4.5 Sulfate, 2,000 mg/L
  - 7.2.4.6 Sodium, 1,000 mg/L
  - 7.2.4.7 1-Butanol, 2000 mg/L

14

Simulates "Typical" FGD Samples

Synthetic FGD Solution

- Seemingly simple mixture
- Purchase custom solution from commercial supplier
- Prepare from neat reagents and stock elemental solutions
- Beware contamination in stock solutions
- *9.3.1.2 In some cases it may not be possible to obtain interference check solutions that are completely free of contamination. In these cases, results up to 5X the reporting limit are acceptable if it is possible to demonstrate that the isotopic ratios correspond to natural abundances…*

15

To Purchase Or To Prepare?

Procedure Development, Interference Removal

More detailed descriptions of interference removal techniques

- *2.0 Hardware Description*
- *2.1 The NexION 300D… allows the analyst to choose the most appropriate collision/reaction cell (CRC) conditions for each analyte in FGD wastewater…*
- ***Collision Mode**: In this mode, the instrument offers conventional collision cell capability with kinetic energy discrimination (KED). By using a non-reactive gas, such as helium, the collision mode with KED removes many of the simple solvent- and argon-based polyatomic spectral interferences. This makes it ideal for elements such as Co, Ni, Cu and Zn which are prone to the larger cross-sectional polyatomic interferences to be concerned about. It is also effective for other analytes, such as As and Se.*

16

Procedure Development, Interference Removal

- ***Reaction Mode:*** *A technique that offers the best available detection capability. This mode, known as DRC (Dynamic Reaction Cell™) technology, removes the majority of interferences with little or no loss of analyte sensitivity by using pure reaction gases like ammonia while not allowing any reaction byproducts to leave the cell which could cause further interferences. DRC technology features a scanning quadrupole with a bandpass that removes by-product reactions created in the Universal Cell. Therefore any reaction gas can be used and in its pure form… This would be the mode of choice for the lowest possible detection limits for elements such as Cr, V and Mn.*

17

Procedure Development, Interference Removal

- ***Attachment 1: Suggested Mass Choices and Analysis Mode***

Mass	Element of Interest	Analysis Mode
27	Aluminum	STD or He
75	Arsenic	He
111, 114	Cadmium	He
52, 53	Chromium	NH3 or He
63, 65	Copper	He
208, 207, 206	Lead	STD
55	Manganese	NH3 or STD
60, 62	Nickel	He
78, 82	Selenium	NH3 or He
107	Silver	STD or He
205, 203	Thallium	STD or He
51	Vanadium	NH3 or He
66	Zinc	He

18

Procedure Development, Detection Limits

- Important objective of analytical procedure; achieve detection limits to support FGD regulations
- Due to high TDS of typical FGD wastewaters, some dilution of samples is necessary to reduce signal suppression and to achieve minimum internal standard recovery of 60%
  - What is minimum dilution needed for typical FGD?
  - Traditional liquid dilution, approximately 1:10 needed
  - Gas dilution, approximately 1:3 needed
- *6.1.5 Automated sample dilution, liquid or gas, simplifies the dilution process and results in less matrix being deposited on the cones during analysis and minimizes the rinse times normally needed for difficult matrices…*

19

Procedure Development, Detection Limits

- *Developing MDLs for EPA's Draft Collision Cell ICP/MS Procedure for Determination of Metals in FGD Effluent Samples*
- Round Robin conducted by EPA and contractor with several participant labs
- Specific to subset of elements of particular interest to EPA; As, Cd, Cr, Pb, Se, and Tl

MDLs in Synthetic FGD (KED/Collision Mode)					
Cr 52 (ug/L)	As 75 (ug/L)	Se 78 (ug/L)	Cd 111 (ug/L)	Tl 205 (ug/L)	Pb 208 (ug/L)
0.168	0.520	1.102	0.032	0.003	0.036

20

Obtained Method Detection Limits

Attachment 10: Typical Method Detection Limits

Mass/Element	Int. Time (sec)	Mode	Internal Standard	MDL (µg/L)
27 Al	0.5	STD	Sc	0.54
51 V	0.5	NH3	In	0.02
52 Cr	0.5	NH3	In	0.09
55 Mn	0.5	NH3	In	0.27
60 Ni	0.5	He	Ge	0.28
63 Cu	0.5	He	Ge	0.30
66 Zn	0.5	He	Ge	1.20
75 As	1.5	He	Ge	0.30
78 Se	1.5	He	Ge	1.01
107 Ag	0.5	STD	In	0.03
111 Cd	0.5	He	Ge	0.03
205 Tl	0.5	STD	In	0.01
208 Pb	0.5	STD	In	0.04

21

Determined in Synthetic FGD

The Final Product

- The SOP is available on the Steam Electric/FGD web page:

http://water.epa.gov/scitech/wastetech/guide/steam-electric/fgd.cfme

EPA United States Environmental Protection Agency | Office of Water (4303T) Washington, DC 20460 | DRAFT March 2013

Standard Operation Procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure

1.0 Introduction

1.1 This document describes procedures used to measure elements in Flue Gas Desulfurization (FGD) wastewaters. One of the most widely used technologies for removing pollutants such as sulfur dioxide, from flue gas emissions produced by coal-fired power plants, is a flue gas desulfurization that typically involves spraying a limestone slurry or other sorbent into the flue gas stream to convert gaseous sulfur dioxide to calcium sulfate (gypsum) or calcium sulfite. Many of the contaminants from the coal, limestone and make-up water are concentrated in the circulating water of the scrubbing system. So in order to maintain appropriate plant operating conditions, a purge stream of water containing these contaminants often has to be discharged from the scrubbers. This purge stream can contain high concentrations of gypsum, heavy metals, alkali earth metals, chlorides and dissolved organic compounds.

1.2 The ICP-MS spectrometer with the Universal Cell can operate in reaction, collision and standard modes. The composition of Flue Gas Desulfurization wastewaters can

22

Procedure Highlights

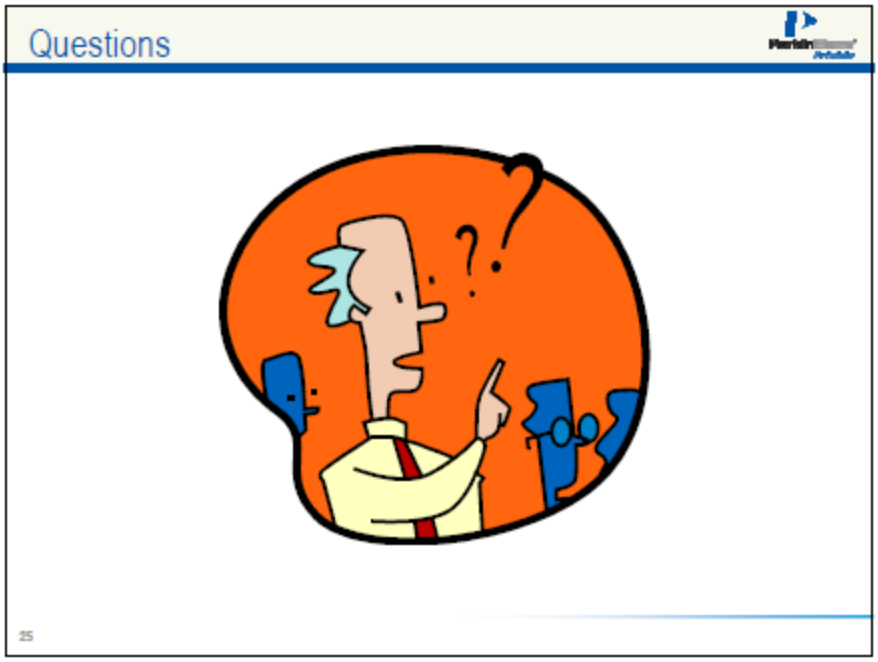
- Specific to FGD wastewater
- Addresses physical matrix issues (robust)
- Addresses interference removal techniques (UCT)
- Specific hardware
- Enough detail to run the procedure

23

Thanks

- Thanks to the Collaboration Team
  - U.S. Environmental Protection Agency
    Office of Science and Technology
    Engineering and Analysis Division (EAD)
    Washington, DC
  - CSC
    Engineering and Mission Support
    Alexandria, VA
  - Perkin Elmer, Inc.
    Shelton, CT

24

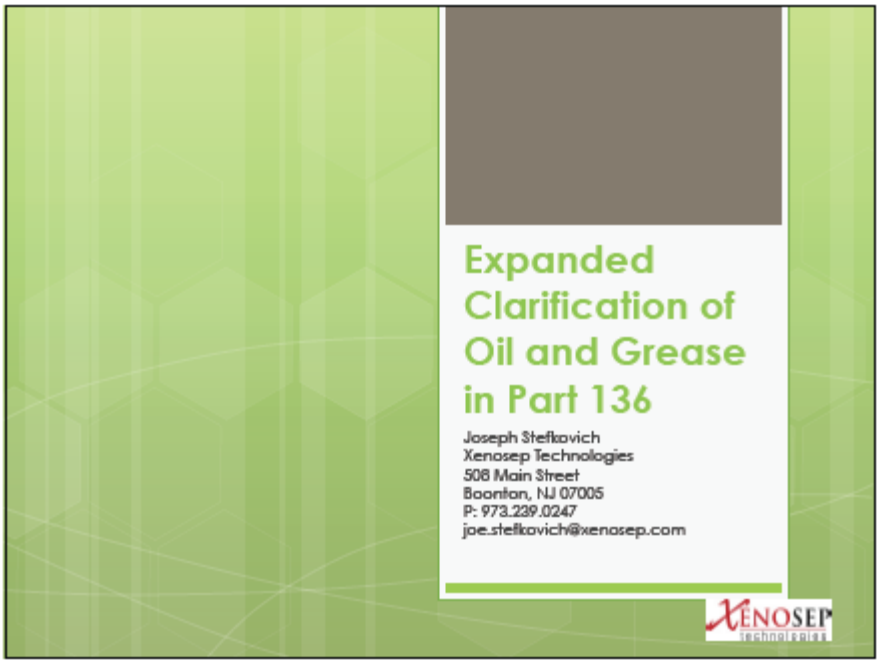

Questions
25

Expanded Clarification of Oil and Grease in Part 136

Joseph Stefkovich
Xenosep Technologies

Abstract

EPA Method 1664 Revision B was published in February 2010 and was included in Table IB as an approved inorganic test procedure for the measurement of oil and grease in the final Method Update Rule published on May 18th, 2012. EPA 1664B is an updated version of EPA 1664A and specifically identifies a list of allowable method modifications and other modifications that are not allowed. Now that laboratories, auditors and regulators are applying the requirements of EPA 1664B, certain clarifications may be needed due to a misunderstanding or misinterpretation of previous EPA 1664A requirements. The author will address a few of the hotter topics with EPA 1664A/B and will also clarify the requirements of the final decision on an alternative Oil and Grease method published on March 6, 2013.


Expanded Clarification of Oil and Grease in Part 136
Joseph Stefkovich
Xenosep Technologies
508 Main Street
Boonton, NJ 07005
P: 973.239.0247
joe.stefkovich@xenosep.com
XENOSEP


Abstract
EPA Method 1664 Revision B was published in February 2010 and was included in Table IB as an approved inorganic test procedure for the measurement of oil and grease in the final Method Update Rule published on May 18th, 2012. EPA 1664B is an updated version of EPA 1664A and specifically identifies a list of allowable method modifications and other modifications that are not allowed. Now that laboratories, auditors and regulators are applying the requirements of EPA 1664B, certain clarifications may be needed due to a misunderstanding or misinterpretation of previous EPA 1664A requirements. The author will address a few of the hotter topics with EPA 1664A/B and will also clarify the requirements of the final decision on an alternative Oil and Grease method published on March 6, 2103.
XENOSEP

Acknowledgement

- Xenosep Technologies would like to thank Mr. Lemuel Walker of the US EPA (Office of Science and Technology, Engineering and Analysis Division) for his review, comment and guidance of the following presentation. Any EPA related questions can be addressed to: Walker.Lemuel@epa.gov.

EPA 1664A – HEM & SGT-HEM (Oil and Grease)



Performance-Based Method

Method-Defined Analyte

40 CFR § 136.6 – Method Modifications

- Many potentially acceptable modifications but can not change chemistry or determinative technique
- "An analyst may not modify an approved analytical method for a method defined analyte." ((b)(3))
- Wastewater matrix issues
  - Can improve QC recovery with salts and inert surfactants
  - "must not react with or introduce the target pollutant into the sample"

Summary of EPA Methods 1664A and 1664B

- 1 L sample acidified to pH<2
- LLE – 3 x 30 mL extractions n-hexane
- Dry extract with sodium sulfate
- Distill solvent from extract
- HEM is desiccated and weighed
- Proportionate silica gel treatment
- SGT-HEM is desiccated and weighed

Types of Modifications

- Allowable (16)
- Unacceptable (5)
- Limited-Use ATP (1)
- All included in EPA 1664B – § 1.7 & 1.8

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Optimized Extraction Procedure	Included	Allowable
Alternate Determination Techniques	Not Allowed	Not Allowed
Analysis of < Collected Sample	Not Allowed	Not Allowed
Other Reference Standards	Not Allowed	Not Allowed
Spiking into Extractor	Not Allowed	Not Allowed
Method 1664 "Cu"	Included ATP	Allowable ATP

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Alternate Extraction Techniques	Included	Allowable
Alternate Concentration Techniques	Included	Allowable
Omit Oven Drying Step §11.4.4	Included	Allowable
Lower PAR Concentration (20mg/L)	Included	Allowable
Collect Smaller Sample Volume	Included	Allowable
Additional Balance Calibration	Included	Allowable

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Sample Acidification, pH<2	Included	Allowable
Prefilter, Filtration Aid Use	Included	Allowable
SPE Filter Use	Included	Allowable
Matrix Spike Selection	Included	Allowable
Silica Gel Treatments	Included	Allowable
Silica Gel Equivalence	Included	Allowable

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Solvent Phase Separation Paper	Included	Allowable
Polar Solvent Cleaning	Included	Allowable
Polar Solvent SPE Conditioning	Included	Allowable
Polar Solvent Rinsing/Extraction	Not Allowed	Not Allowed
Alternate Extraction Solvents	Not Allowed	Not Allowed
Methanol Rinse Exception	Included	Allowable

Summary of 1664A and 1664B Method Modifications

- 1 L sample acidified to pH<2
- LLE – 3 x 30 mL extractions n-hexane
- Dry extract with sodium sulfate
- Distill solvent from extract
- HEM is desiccated and weighed
- Proportionate silica gel treatment
- SGT-HEM is desiccated and weighed

Replace Sodium Sulfate with Methanol to Remove Water??



- Methanol in separatory funnel is not allowed
- How do you keep methanol or water out of aluminum pan?
- Must use sodium sulfate or equivalent

Replace Sodium Sulfate with Pipetting from Sep Funnel???



- Methanol in separatory funnel is not allowed
- How do you keep methanol or water out of aluminum pan?
- Must use sodium sulfate or equivalent

Replace Sodium Sulfate with Draining from Sep Funnel???

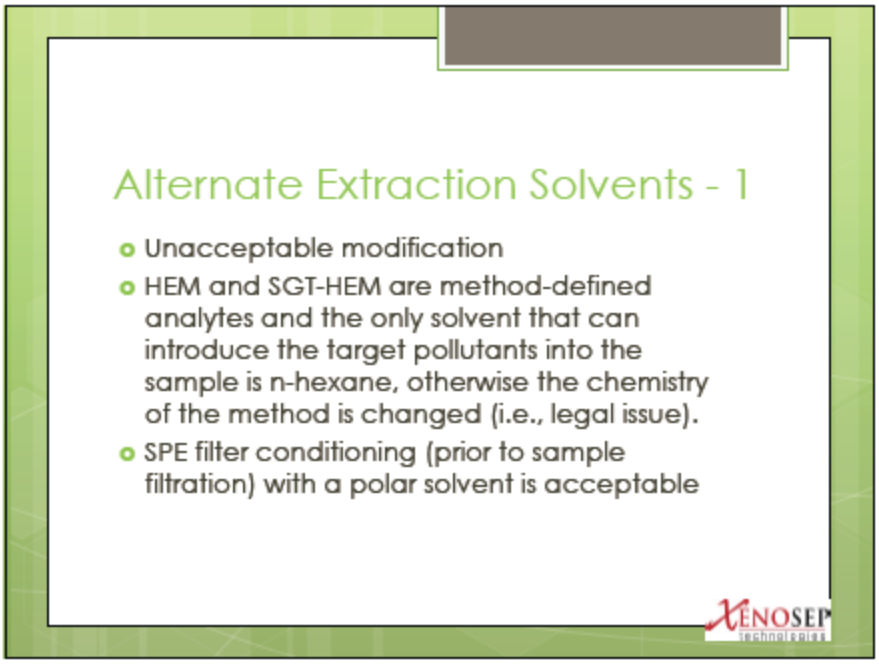


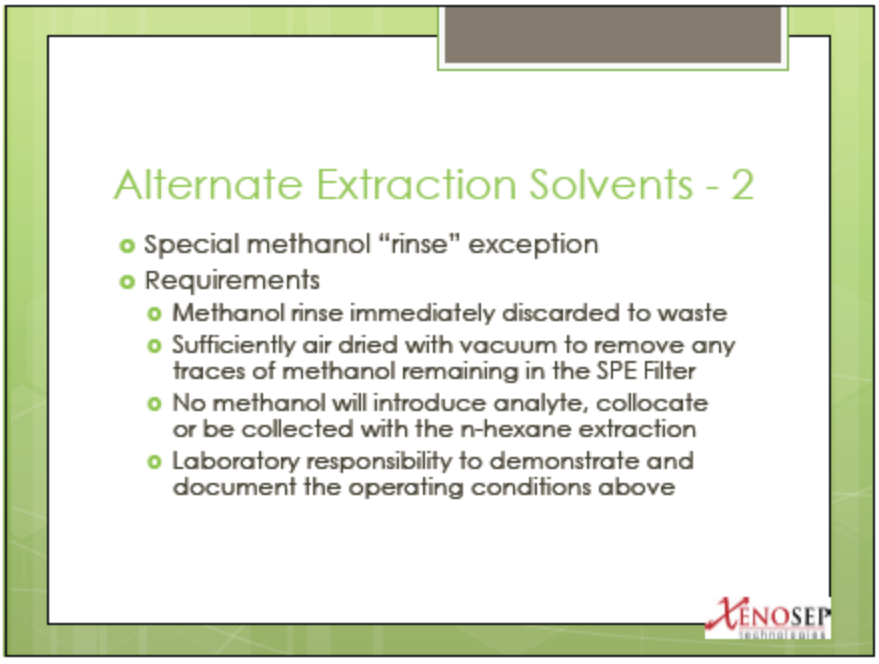
- Methanol in separatory funnel is not allowed
- How do you keep methanol or water out of aluminum pan?
- Must use sodium sulfate or equivalent

Replace Sodium Sulfate with Pouring from Sep Funnel???



- Methanol in separatory funnel is not allowed
- How do you keep methanol or water out of aluminum pan?
- Must use sodium sulfate or equivalent


Alternate Extraction Solvents - 1
Unacceptable modification
HEM and SGT-HEM are method-defined analytes and the only solvent that can introduce the target pollutants into the sample is n-hexane, otherwise the chemistry of the method is changed (i.e., legal issue).
SPE filter conditioning (prior to sample filtration) with a polar solvent is acceptable
XENOSEP


Alternate Extraction Solvents - 2
Special methanol "rinse" exception
Requirements
Methanol rinse immediately discarded to waste
Sufficiently air dried with vacuum to remove any traces of methanol remaining in the SPE Filter
No methanol will introduce analyte, collocate or be collected with the n-hexane extraction
Laboratory responsibility to demonstrate and document the operating conditions above
XENOSEP

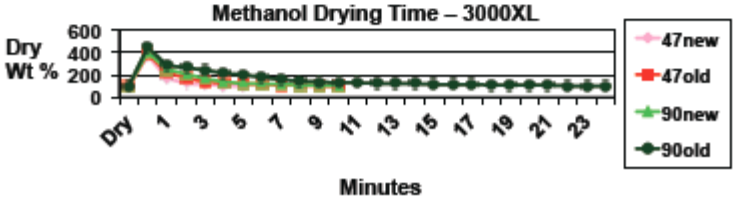
Methanol in Sep Funnel Vs. Methanol Rinse Requirements



- Methanol in separatory funnel is not allowed
  - Lab Responsibility
  - Co-Solvent
  - Collected
  - Collocated
  - Not discarded
  - Not dried to traces

Alternate Extraction Solvents - 3

- Meeting "exception" vacuum air dry requirements
  - 47mm SPE filter & 90mm SPE filter (Wet wt. = Dry wt.)
  - Many variables – vacuum, free air flow, SPE filter, etc.
- 2-3 Vacuum air dry steps & GC Analysis?

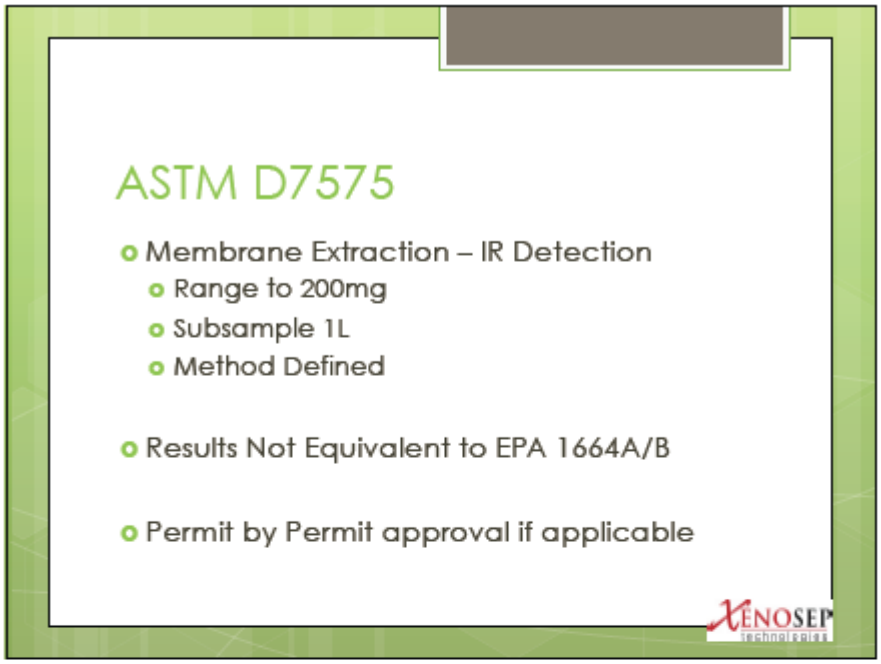


EPA 1664B Section 1.7.2.1 Note

- **NOTE:** The use of a polar solvent to condition an SPE filter or SPE device in a modified method prior to sample filtration is allowed. **The use of methanol or another polar solvent after sample filtration to remove water residual may be allowed provided the polar solvent is immediately discarded to waste and the SPE filter or SPE device is sufficiently air-dried with vacuum to remove any residual polar solvent to trace amounts so at no time will residual polar solvent introduce the target analyte into the sample, collocate with or be collected with the extraction solvent, n-hexane.** A simple test to determine sufficient residual polar solvent removal from an SPE filter by vacuum air drying would be to weigh and record the weight of a dry SPE filter to the nearest 0.1 mg. Then analyze a blank using the dry SPE filter, conditioning the SPE filter and filtering the blank sample per the modified SPE method. Immediately after discarding the polar solvent to waste (and prior to addition of the n-hexane extraction solvent), stop the vacuum, remove the SPE filter from the apparatus and weigh the wet SPE filter saturated with residual polar solvent to the nearest 0.1 mg. Record this wet SPE filter weight. Reassemble the wet SPE filter into the apparatus and **continue vacuum air drying the SPE filter until the weight of the wet SPE filter is less than 101% of the dry SPE filter weight.** For example, if the weight of the dry SPE filter is 1,000.0 mg, continue vacuum air drying the wet SPE filter until the final weight is less than or equal to 1,010.0 mg before contacting the SPE filter with the extraction solvent n-hexane. This simple test could be used by the laboratory to demonstrate and document removal of residual methanol from the SPE filter to trace amounts so as to ensure residual methanol will not introduce the target analyte into the sample and at no time will residual methanol collocate with the n-hexane extraction solvent or be collected in the collection flask.

Alternate Determinative Methods

- Unacceptable modification
- Examples listed at § 9.1.2 include:
  - Infrared spectroscopy
  - Immunoassay
  - Changes that degrade method performance
- Must be gravimetric determination


ASTM D7575
Membrane Extraction – IR Detection
Range to 200mg
Subsample 1L
Method Defined
Results Not Equivalent to EPA 1664A/B
Permit by Permit approval if applicable
XENOSEP


Questions?
More
information?
Joseph Stefkovich
Xenosep Technologies
508 Main Street
Boonton, NJ 07005
Tel: 973.239.0247
Joe.stefkovich@xenosep.com
XENOSEP

CWA and Degradation Product Analysis for Matrix-Specific Environmental Samples

Stuart Willison
USEPA, National Homeland Security Research Center

Abstract

Site characterization for clean-up of an area contaminated with chemical warfare agents (CWAs) will require testing of a variety of matrices (e.g., soil, surface, water, air), and may involve analysis of hundreds or thousands of samples. Sampling and analysis procedures for potentially hazardous CWA degradation products are of similar importance to analysis of the parent compound because the methods can provide the location of the most concentrated areas of contamination of the parent compound or identify any hazardous degradation products that may be present. There is still a need to improve the nation's laboratory capacity and capability to analyze environmental samples following an incident. A systematic analytical approach for all matrices of interest has been developed to avoid analytical complications inherent with analysis processes, including matrix suppression/enhancement effects, contamination, or interferents, which could lead to an incorrect conclusion about the presence/absence of a hazardous chemical. The same can be said for the decontamination stage of a remediation as well. As a result, proper analytical methods are needed not only for each matrix, but to ensure that an affected area is properly remediated prior to reoccupation. Depending on the properties of the analyte of interest, gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-tandem mass spectrometry (LC-MS/MS) detection may be the preferred analysis method. Analytical procedures developed to minimize complications will help to avoid delay for proper characterization.

The purpose of this work is to present method development for the detection of CWAs and their degradation products in various environmental matrices of interest. Matrix examples will include urban materials for surface sampling (from wipes), soil, and water samples. Experimentally, chemicals were deposited onto various matrices and determined via extraction, and analysis using either GC-MS or LC-MS/MS.

CWA and Degradation Product Analysis for Matrix-Specific Environmental Samples

Stuart A. Willison
U.S. EPA, National Homeland Security Research Center

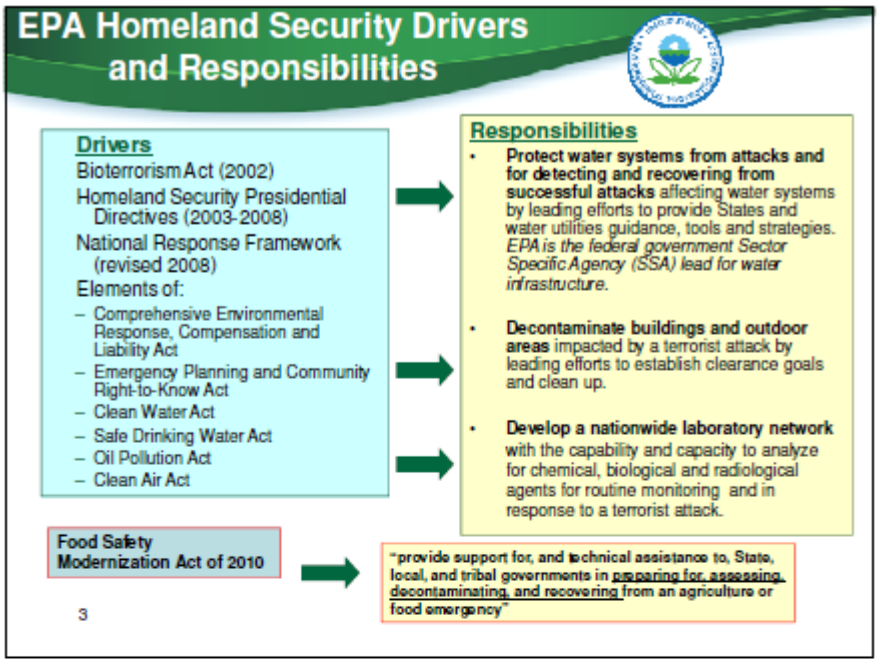
National Environmental Monitoring Conference, San Antonio, TX

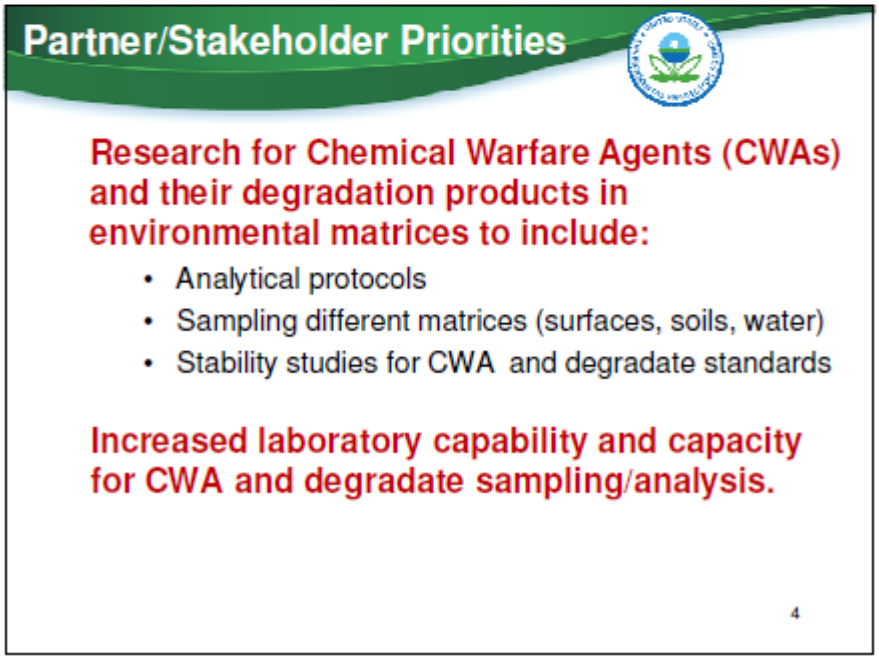


Outline

National Homeland Security Research Program

- **Drivers/Priorities**
- **Research Supporting EPA's Response to Contamination**
- **Analytical Capability for CWAs in Target Matrices (Sampling and Analysis)**
- **Analytical Capability for CWA Degradation Products in Target Matrices (Sampling and Analysis)**


EPA Homeland Security Drivers and Responsibilities
Drivers
Bioterrorism Act (2002)
Homeland Security Presidential Directives (2003-2008)
National Response Framework (revised 2008)
Elements of:
– Comprehensive Environmental Response, Compensation and Liability Act
– Emergency Planning and Community Right-to-Know Act
– Clean Water Act
– Safe Drinking Water Act
– Oil Pollution Act
– Clean Air Act
Responsibilities
• Protect water systems from attacks and for detecting and recovering from successful attacks affecting water systems by leading efforts to provide States and water utilities guidance, tools and strategies. EPA is the federal government Sector Specific Agency (SSA) lead for water infrastructure.
• Decontaminate buildings and outdoor areas impacted by a terrorist attack by leading efforts to establish clearance goals and clean up.
• Develop a nationwide laboratory network with the capability and capacity to analyze for chemical, biological and radiological agents for routine monitoring and in response to a terrorist attack.
Food Safety Modernization Act of 2010
"provide support for, and technical assistance to, State, local, and tribal governments in preparing for, assessing, decontaminating, and recovering from an agriculture or food emergency"
3


Partner/Stakeholder Priorities
Research for Chemical Warfare Agents (CWAs) and their degradation products in environmental matrices to include:
• Analytical protocols
• Sampling different matrices (surfaces, soils, water)
• Stability studies for CWA and degradate standards
Increased laboratory capability and capacity for CWA and degradate sampling/analysis.
4

Meeting Lab Throughput Requirements

Potential approaches

- Methods which can be applied to multiple labs for workload distribution by the Environmental Response Laboratory Network (ERLN) www.epa.gov/oemerln1



- High throughput sampling techniques and laboratory analysis techniques, including automated or rapid method capabilities

5

Research to Support EPA's Response to Contamination Events and Site-Specific Risk-Based Decisions



Sampling and Analysis

- To detect contaminants
- To determine extent of contamination

Risk assessment

- To assess potential risk of exposure, at harmful doses, and identify exposure pathways

Informs Risk Management Decisions

Research Focused Towards Chemical Warfare Agents

- **Analytes**
  - Tabun (GA), sarin (GB), soman (GD), cyclosarin (GF), sulfur mustard (HD), nitrogen mustards (HN-1 & HN-3), lewisite (L), VX and Russian VX (R-VX)
  - Nitrogen mustard degradates
  - Nerve agent degradates
- **Sample Types**
  - Soil
  - Water
  - Surface Analysis via Wipes
- **Analytical Techniques**
  - Gas Chromatography/Time-of-Flight Mass Spectrometry (GC/TOF-MS)
  - Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)





7

Method Detection Levels (MDL) for G-series, HD and VX by GC/TOF-MS

	Residential Soil (µg/kg)		Water (µg/L)		Wipe (ng/kg)
Agent	MDL		MDL		MDL
GB	0.22		0.14		0.0030
GD	0.67		0.11		0.0017
GF	0.12		0.14		0.0047
HD	0.12		0.10		0.0015
VX	0.41		0.23		0.0080

8

Method Detection Levels (MDL) for GA, HN-1, HN-3 and R-VX by GC/TOF-MS

	Residential Soil (mg/kg)		Water (µg/L)		Wipe (ng/kg)
Agent	MDL		MDL		MDL
GA	0.00033		0.13		11
HN1	0.00057		0.084		2.3
HN3	0.0016		0.72		35
R-VX	0.015		22		440

9

Stability Study for Ultra-Dilute CWA Standards

- One year stability study for 10 ppm standards of GB, GD, GF, HD and VX
  - Flame-sealed ampoules - one year shelf-life
  - Opened ampoules ~ 2-6 months depending on analyte
- Additional preservation study with only VX

IMPACT:

- Dilute concentrations allow for shipment to ERLN labs without special requirements.
- Provides stability of analyte standards over time in order to ensure availability of standard and reduce costs.

10

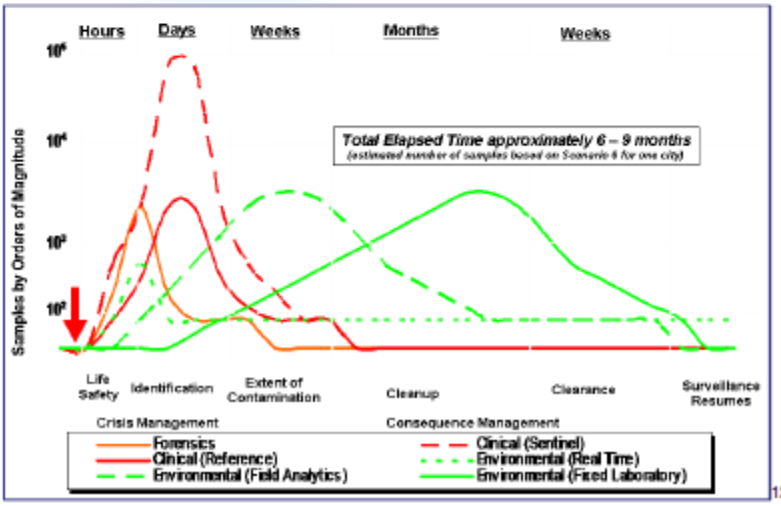
Japan Subway Attack by Use of a Nerve Agent



Kasumigaseki station was one of the ***many*** subway stations affected during the attack

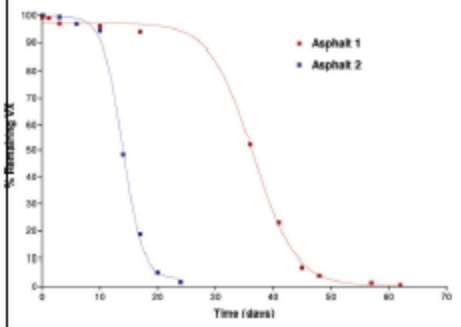
11

Sample Collection During an Incident

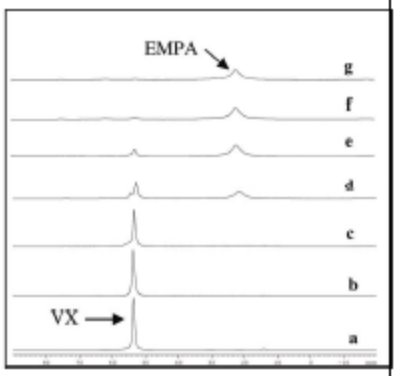


12

Persistence of VX and Degradation Product on Asphalt



Degradation profile of VX on ground asphalt.



^{31}P NMR results: (a) 0.1 days, (b) 6 days, (c) 10 days, (d) 14 days, (e) 17 days, (f) 20 days, and (g) 24 days after the contamination.

13

Columbus *et. al., Environ. Sci. Technol.*, 2012, **46**, 3921–3927

Importance of Degradate Analysis

IMPACT:

- Identifies potentially toxic degradates, which may persist
- Degradate analysis allows samplers to identify potentially concentrated areas of concern for parent compound
- Ensure remediation efforts can be completed

14

Challenges of Analysis Procedure for Degradation Products

- Most CWA degradation products are not amenable to gas-chromatography/mass spectrometry (GC-MS) analysis without a derivatization step
- Step can be time-consuming with often times incomplete conversion to the derivatized product
- Liquid chromatography/mass spectrometry (LC-MS) offers advantages over GC-MS because polar analytes can be directly analyzed

15

Optimization of Analysis Procedure for Degradation Products

- Optimal eluents, chromatography separation, mass spectrometric parameters were characterized with low (ppb) detection limits*
- Optimal wipe investigated: cotton gauze, non-woven polyester fiber cloth, pre-cleaned textile wipe, glass fiber filter, and filter paper
- Surface evaluation included the following surfaces: galvanized steel, glass, laminate, vinyl tile, treated wood, painted drywall



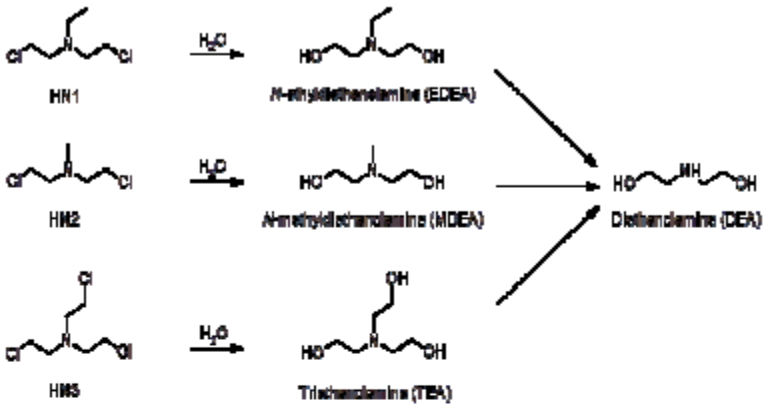




* EPA Reports: EPA 600/R-11/143 and EPA/600/R-12/581

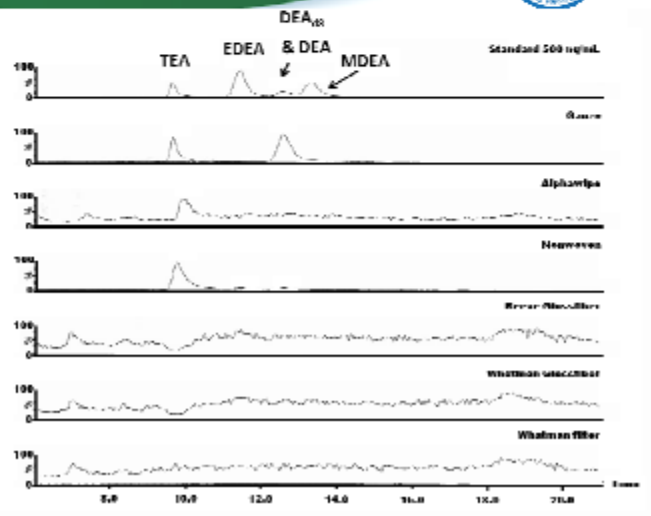
16

Hydrolysis Pathway of Nitrogen Mustards in the Environment



17

LC-MS/MS Chromatogram of Wipe Blanks*



18

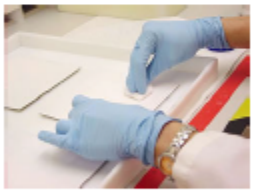
* EPA Reports: EPA 600/R-11/143 and EPA/600/R-12/581

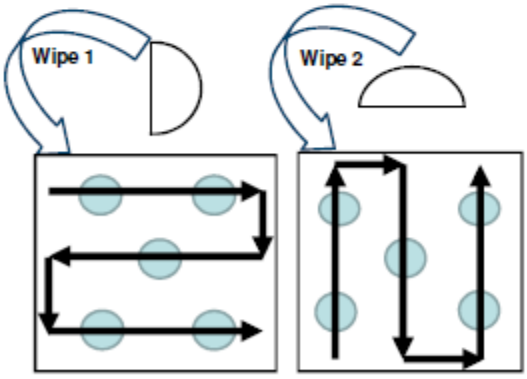
LC-MS/MS Chromatogram of Spiked Wipe Samples

Analyte	TEA		EDEA		MDEA		DEA	
Wipe	% Recovery (n=7)		% Recovery (n=7)		% Recovery (n=7)		% Recovery (n=7)	
Approximate Spike Concentration (ng/mL)	10	50	10	50	10	50	10	50
Cotton Gauze	680	150	35	28	49	30	1600	430
Non-woven polyester cloth	510	480	130	82	120	75	370	190
Alphawipe™	9	23	18	22	17	21	10	18
Filter Paper	74	82	87	100	76	83	62	77

9/8/2013 19

LC-MS/MS Chromatogram of Nitrogen Mustard Degradation Products





20

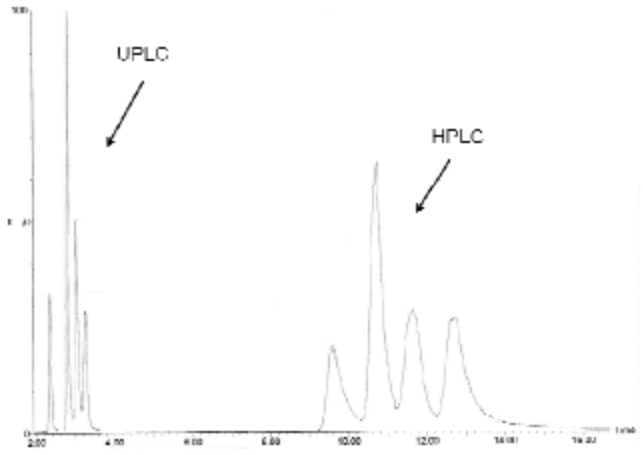
Analyte Recoveries from Surface Wiping*

Analyte	TEA[1]	EDEA	MDEA	DEA[1]
Surface	% Recovery (n=7)	% Recovery (n=7)	% Recovery (n=7)	% Recovery (n=7)
Laminate	81-99	47-71	66-80	71-81
Metal	20-46	49-56	54-74	62-79
Glass	91-150	31-36	52-61	59-81
Vinyl Tile	41-79	7-22	51-61	25-39
Painted Drywall[2]	19	8	17	13
Wood[2]	2	1	2	1

[1] Recoveries were subtracted from surface blanks for a representative recovery of target analytes
[2] Recoveries were only possible at highest spike concentration
* Results from surface wiping were performed using filter paper

21

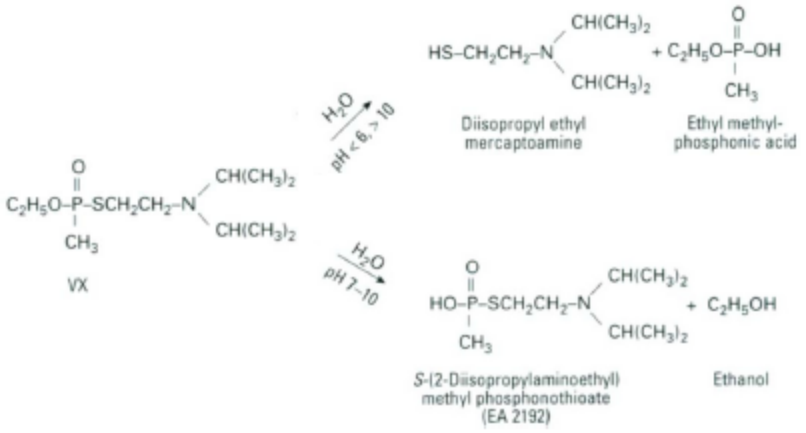
LC-MS/MS Chromatogram of Nitrogen Mustard Degradation Products*



22

* S.A. Willison, J. Chromatogr. A, *1270 (2012) 72–79*

Hydrolysis Pathway of VX in the Environment



23

LC-MS/MS Chromatogram of Spiked Wipe Samples

Wipe	Cotton Gauze	Non-woven Polyester Cloth	Alphawipe™	Glass Fiber Filter	Filter Paper
Analyte	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery
MPA	65	50	57	88	87
EMPA	67	54	57	89	89
IMPA	42	34	44	75	81
EHDMAP	56	59	74	75	78
PMPA	72	65	83	90	88

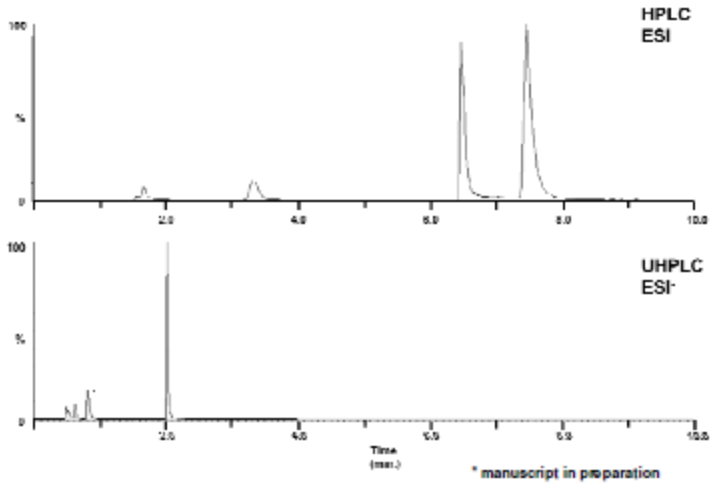
24

LC-MS/MS Chromatogram of Spiked Surface Samples

Laminate Surface				
	Filter Paper		Cotton Gauze	
Analyte	% Recovery	% Recovery	% Recovery	% Recovery
Ionization Mode	ESI +	ESI -	ESI +	ESI -
IMPA	67	98	72	79
MPA	102	55	122	35
EMPA	84	96	74	88
EHDMAP	57	67	53	71
PMPA	-	85	-	79

25

Enhancing Throughput for LC-MS/MS Analytical Methods*



* manuscript in preparation

26

Summary

- Sampling and analysis capabilities for CWA and their degradation products have been developed and tested for a variety of target matrices
- CWA ultra-dilute stability studies ensure quality and availability of standards during an incident
- Wipe selection may impact analysis capabilities due to the presence of native contaminants/interferences
- Rapid analysis methods will enhance laboratory throughput capability and capacity, improve detection levels, and generate less waste

27

Acknowledgements

Stuart Willison, Ph.D.
Research Chemist, Threat and Consequence Assessment Division
Willison.stuart@epa.gov; 513-569-7253

Co-authors/Collaborators:
Romy Campisano[1]
Tonya Nichols[1]
Terry Smith[2]
Carolyn Koester[3]
Bob Streicher[4]

[1]U.S. EPA, National Homeland Security Research Center
[2]U.S. EPA, Office of Emergency Management
[3]Lawrence Livermore National Laboratory
[4]National Institute for Occupational Safety and Health

DISCLAIMER: The U.S. EPA through its Office of Research and Development partially funded the research described in this presentation. It has been reviewed by the Agency but does not necessarily reflect the Agency's views. No official endorsement should be inferred. EPA does not endorse the purchase or sale of any commercial products or services.

SAM 2012
Published: July 2012



Website: www.epa.gov/sam

28

SECTION 19

DATA MANAGEMENT

Optimized Data Review and Management Tools

Nazy Abousaeedi
DatAssess Offering, CDC

Abstract

EPA continues to grow the scope of analytical methods supported and the range of reports and documents produced. At the same time, greater flexibility is being requested by users. Our data review and management tool (EXES & EDM) can provide support for new analytical methods in a timely manner, by using simplified user interfaces (UI), incorporating new programming technologies, and allowing the data users greater flexibility in managing their requirements.

The goal of the EXES system is to provide an application to efficiently evaluate analytical data regardless of the underlying method and data reporting requirements. The system provides users with advanced customization capabilities to review, edit, and add evaluation parameters, tests, Method Quality Objectives (MQOs), and Quality Assurance Project Plan (QAPP) requirements. Test rules will be consolidated and shared across methods where applicable, and new method support will be accomplished through user interfaces.

The updated features and capabilities provide all stakeholders with the following enhancements and new capabilities:

- Faster turnaround times for preliminary evaluations of Electronic Data Deliverables (EDD)
- Enhanced ”submit EDD” capabilities that offer a more intuitive User Interface (UI)
- Managed evaluation procedures to allow for a customized application of method requirements
- Tailored deliverable process flow to meet client-specific analytical evaluation needs
- Improved chemist review UI
- Better internal deliverable tracking UI
- Modular test rules for improved efficiency and faster roll out of new method support

The key architectural principals that CSC will incorporate into the new EXES are:

- Modern and simple
- Everything is (or can be) a component/service (i.e., easily extendable)
- Stateless (multiple EDDs can be processed at the same time)
- Optimized performance

Optimized Data Review and Management Tools

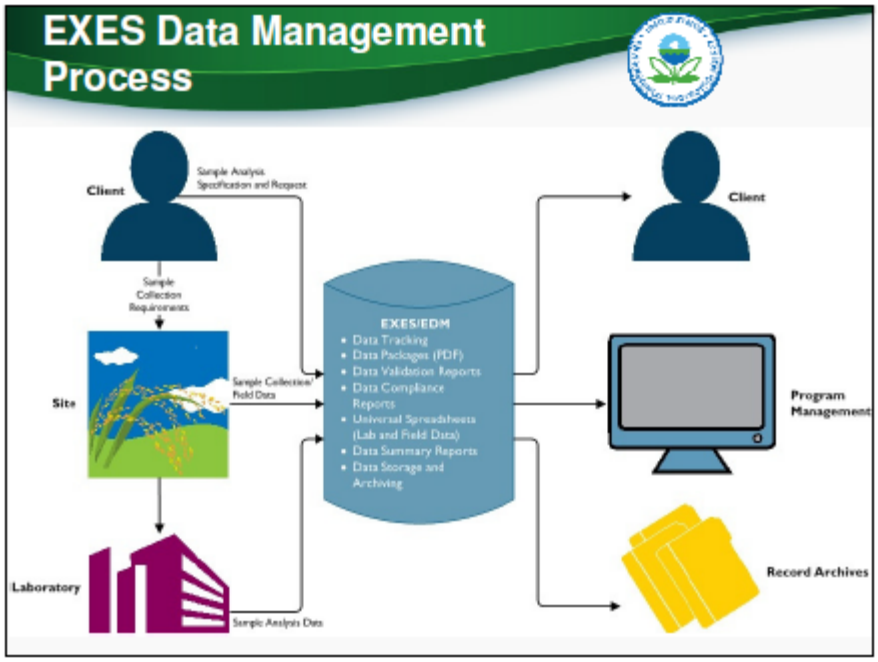


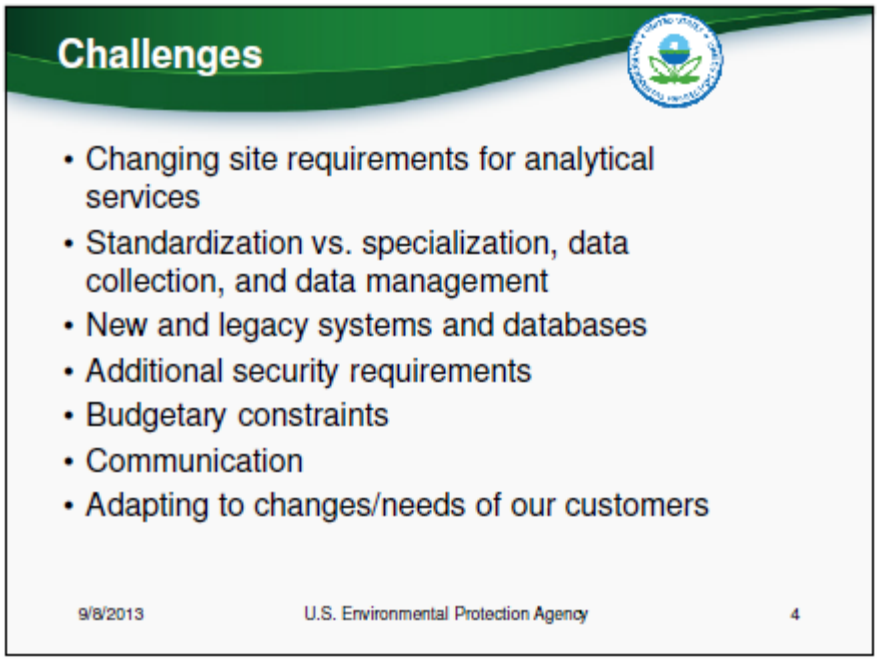
Nazy Abousaeedi, DatAssess Offering, CSC
Michael S. Johnson, USEPA HQ

U.S. Environmental Protection Agency

Data Management Overview Utilizing EXES

- Assist in defining analytical requirements
- Site and sample scheduling data
- Sample collection and tracking data
- Automated data assessment and reporting
- Data and record sharing, analysis, and archiving
- Management reporting


EXES Data Management Process
Client
Sample Analysis Specification and Request
Sample Collection Requirements
Site
Sample Collection/ Field Data
Laboratory
Sample Analysis Data
EXES/EDM
• Data Tracking
• Data Packages (PDF)
• Data Validation Reports
• Data Compliance Reports
• Universal Spreadsheets (Lab and Field Data)
• Data Summary Reports
• Data Storage and Archiving
Client
Program Management
Record Archives


Challenges
• Changing site requirements for analytical services
• Standardization vs. specialization, data collection, and data management
• New and legacy systems and databases
• Additional security requirements
• Budgetary constraints
• Communication
• Adapting to changes/needs of our customers
9/8/2013
U.S. Environmental Protection Agency
4

Examples of Variances

- Analysis
  - –Varying analyte detection requirements for projects
  - – Matrix issues
- Data Delivery
  - – Lateness
  - – Incomplete/non-compliant data
- Data Assessment
  - – Quality affected by laboratory errors, field errors, etc.
  - – Combination of special requirements (i.e., multiple formats)

9/8/2013 U.S. Environmental Protection Agency 5

Why Optimized Data Assessment?

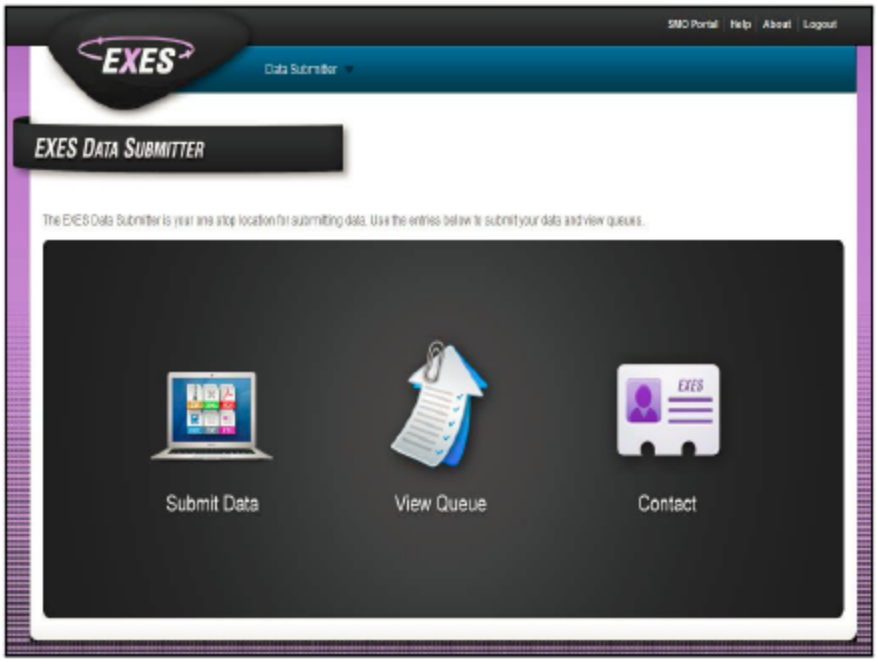
- Provides data users with confirmed results and confidence in usability of data
- Standardized protocols incorporate quality control procedures and criteria
- User can define any level of data validation or assessment
- Documented savings of 80% over manual data validation
- Efficient, consistent and timely

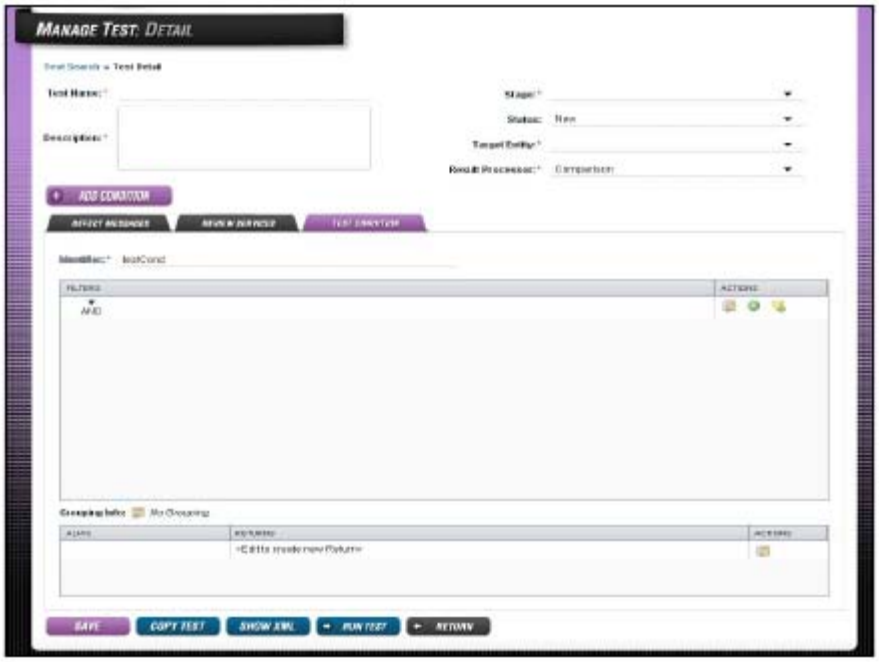
9/8/2013 U.S. Environmental Protection Agency 6

What is EXES?

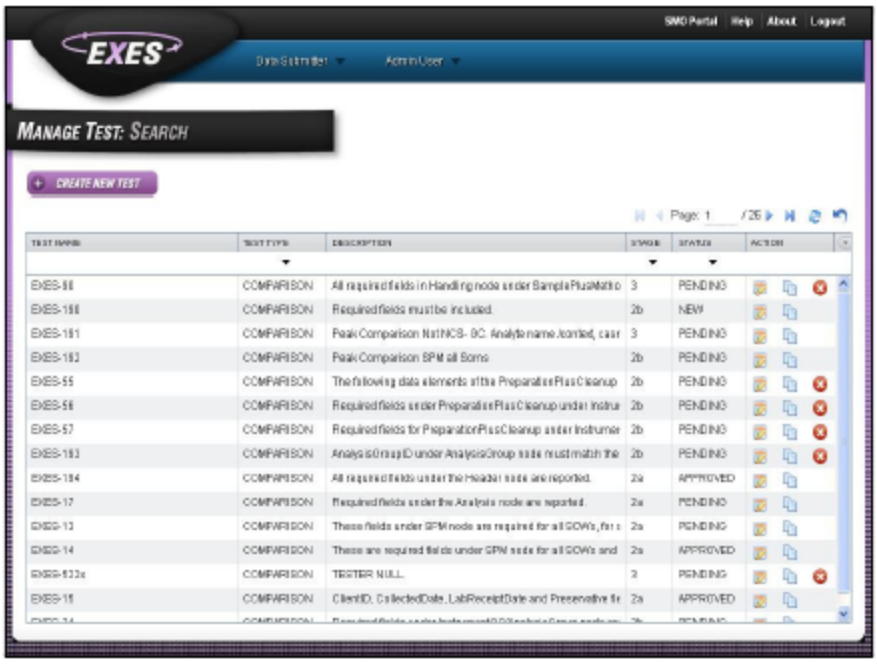
- The Web-based data assessment/validation and management tool that can evaluate analytical data based on method requirements, and provide users with advanced customization capabilities to review, edit, and add evaluation parameters, tests, Method Quality Objectives (MQOs), and Quality Assurance Project Plan (QAPP) requirements. It uses:
  - Format neutral domain and data model,
  - Re-usable Process Flow Libraries (PFL),
  - Method Evaluation Libraries (MELs); and
  - Method Evaluation Procedures (MEPs).

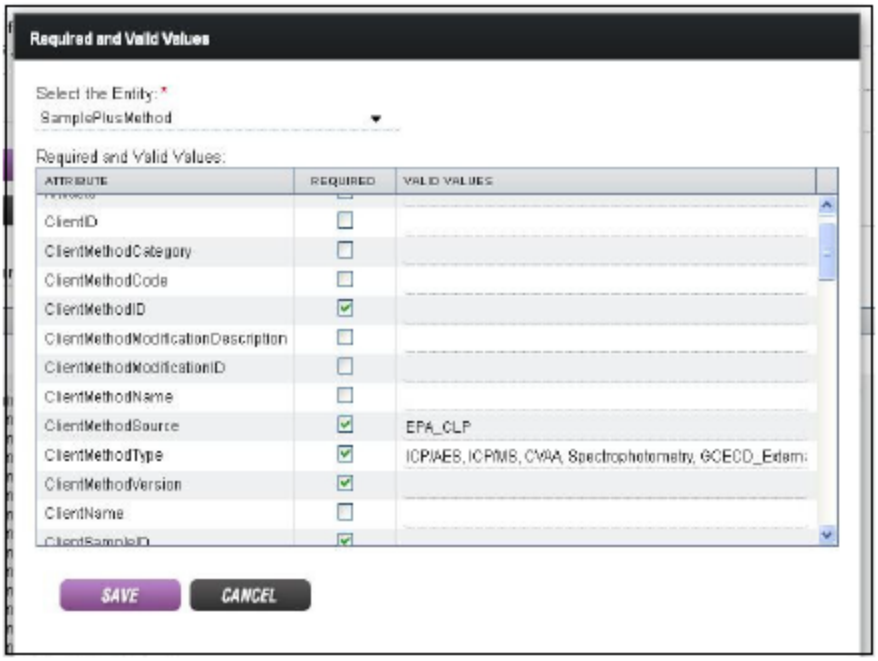
9/8/2013 U.S. Environmental Protection Agency 7




MANAGE TEST: DETAIL
ADD CONDITION
SAVE
COPY TEST
SHOW XML
RUN TEST
RETURN


Add Filter
LEFT VALUE
OPERATOR
RIGHT VALUE
Attribute
Condition Attribute
Function
Function: roundValue
PARAMETERS
NAME
VALUE
originalValue
Peak.RRF
precisionType
Decimal
precisionNumber
3
Function Attribute
Group
Equals
Not Equals
Greater Than
Less Than
Greater Than or Equal To
Less Than or Equal To
In List
Not In List
Between
Not Between
Is NULL
Is Not NULL
This is a Final Filter
Single Value
Function: roundCalValue
Multiplier:
in_eqd_id
HeaderNodeId
in_node_id
Peak
in_calc_name
RelativeResponseFactor
SAVE
CANCEL


EXES
SMO Portal
Help
About
Logout
Data Submitter
Admin User
MANAGE TEST: SEARCH
CREATE NEW TEST
Page: 1 /25
TEST NAME
TEST TYPE
DESCRIPTION
STAGE
STATUS
ACTION
EXES-88 COMPARISON All required fields in Handling node under SamplePlusMetho 3 PENDING
EXES-188 COMPARISON Required fields must be included. 2b NEW
EXES-181 COMPARISON Peak Comparison NotNICS- QC. Analyte name /control, case 3 PENDING
EXES-183 COMPARISON Peak Comparison SPM all Somo 2b PENDING
EXES-55 COMPARISON The following data elements of the PreparationPlusCleanup 2b PENDING
EXES-56 COMPARISON Required fields under PreparationPlusCleanup under Instru 2b PENDING
EXES-57 COMPARISON Required fields for PreparationPlusCleanup under Instrumer 2b PENDING
EXES-183 COMPARISON AnalysisGroupID under AnalysisGroup node must match the 2b PENDING
EXES-184 COMPARISON All required fields under the Header node are reported. 2a APPROVED
EXES-17 COMPARISON Required fields under the Analysis node are reported. 2a PENDING
EXES-13 COMPARISON These fields under SPM node are required for all SOW's, for t 2a PENDING
EXES-14 COMPARISON These are required fields under SPM node for all SOW's and 2a APPROVED
EXES-132e COMPARISON TESTER NULL 3 PENDING
EXES-15 COMPARISON ClientID, CollectedDate, LabReceiptDate and Preservative fo 2a APPROVED


Required and Valid Values
Select the Entity: *
SamplePlusMethod
Required and Valid Values:
ATTRIBUTE
REQUIRED
VALID VALUES
ClientID
ClientMethodCategory
ClientMethodCode
ClientMethodID
ClientMethodModificationDescription
ClientMethodModificationID
ClientMethodName
ClientMethodSource
EPA_CLP
ClientMethodType
ICP/AES, ICP/MS, CVAA, Spectrophotometry, GC/ECD_Extern
ClientMethodVersion
ClientName
SAVE
CANCEL

EXES Benefits – You Are in Control

- **Flexible** - user interfaces that enable you to create test rules data review criteria and reports dynamically, select and create their desired level of assessments.
- **Reusable** features allow **authorized** users the ability to create new libraries or search and modify existing libraries, saving time and effort, resulting in cost savings.
- **Consistent**, reproducible and independent electronic review improves overall project transparency.
- **Customizable**, tailored deliverable process flow to meet client-specific analytical evaluation needs.

9/8/2013 U.S. Environmental Protection Agency 13

The Key Architectural Principles

- **Modern and Simple to Use**
- **Easily Extendable Component**
- **Format Neutral** Accepts Staged Electronic Data Deliverables (SEDD) format (2a, 2b and 3) in both versions (5.1 and 5.2) and any other future format.
- **Optimized Performance**

9/8/2013 U.S. Environmental Protection Agency 14

What is Optimized Data Management?

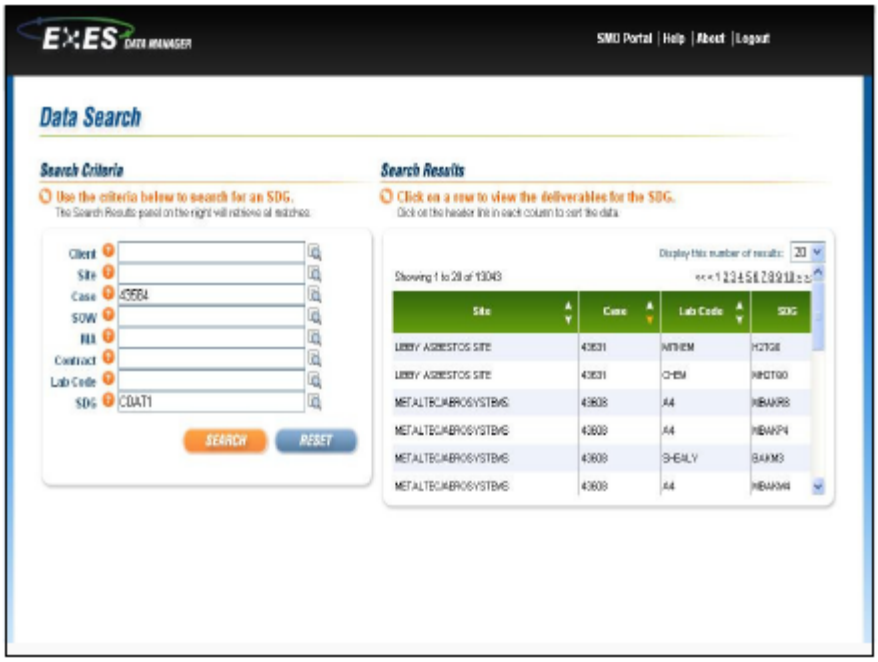
- Data assessment/validation reports can be available within minutes of data delivery.
- Spreadsheets and outputs include both field and analytical data ready for upload to databases and mapping tools.
- Web-based system allows access for all users with an appropriate level of access, based on their user role.

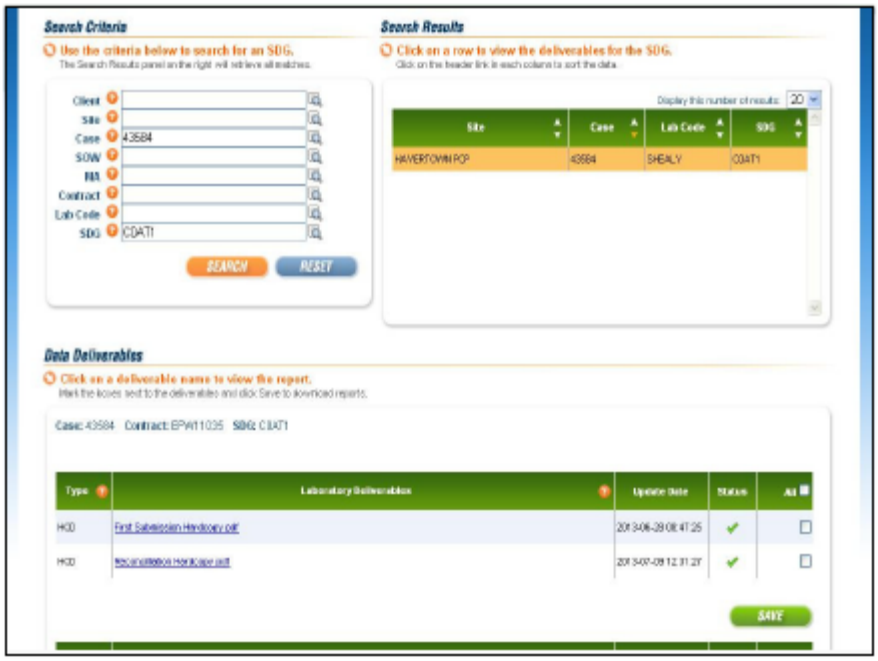
9/8/2013 U.S. Environmental Protection Agency 15

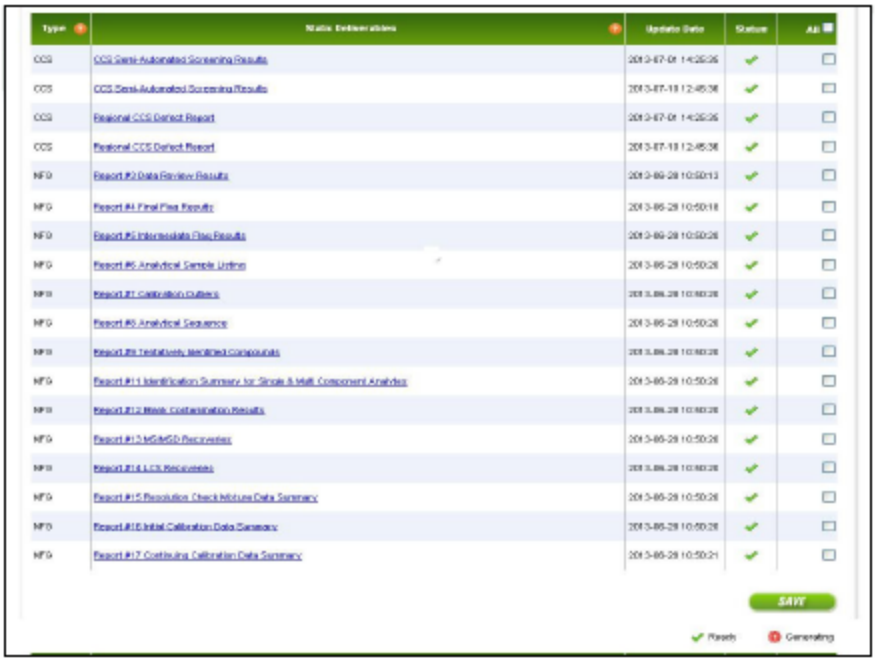
What is EDM?

- EXES Data Manager (EDM) provides a web based/centralized data management tool:
  - Stores all laboratory deliverables.
  - Provides a series of reports based on validation criteria.
  - Provides summary reports that includes final results, validation flags and level.
  - Provides results based on data user's validation criteria.
  - Allows users to edit and regenerate all dynamic reports.
  - Provides an audit tracking log of all changes made by user name and date/time.
  - Available within 24 hours of data delivery from laboratory.

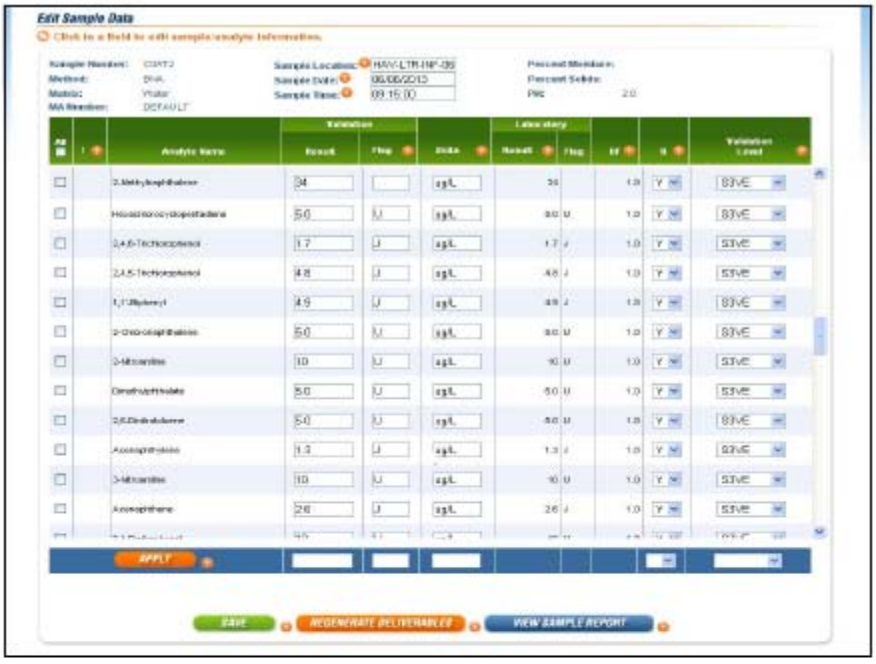
9/8/2013 U.S. Environmental Protection Agency 16

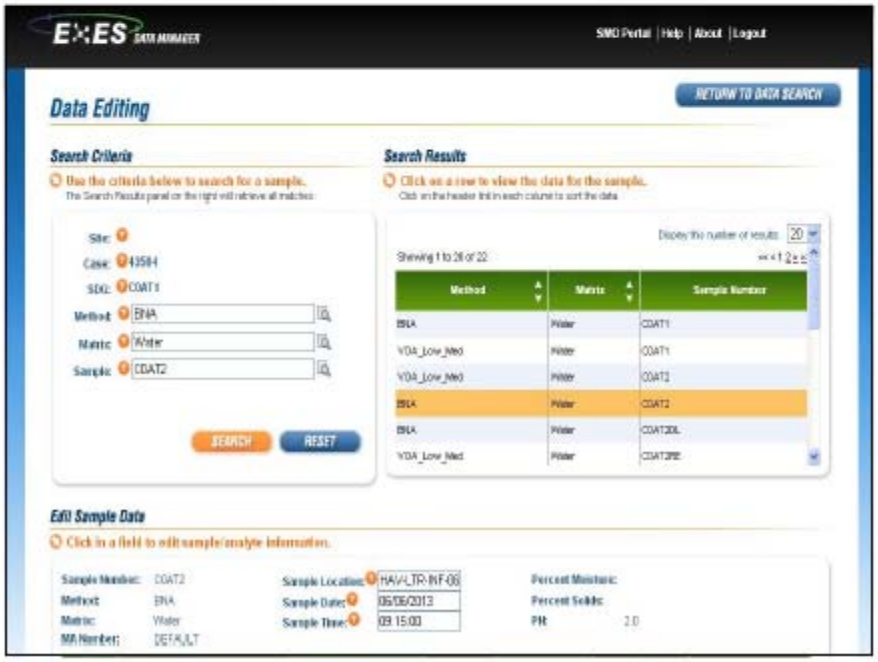

EXES DATA MANAGER
SMO Portal | Help | About | Logout
Data Search
Search Criteria
Use the criteria below to search for an SDG.
Client
Site
Case 43584
SOW
RA
Contract
Lab Code
SDG CDAT1
SEARCH
RESET
Search Results
Click on a row to view the deliverables for the SDG.
Site
Case
Lab Code
SDG

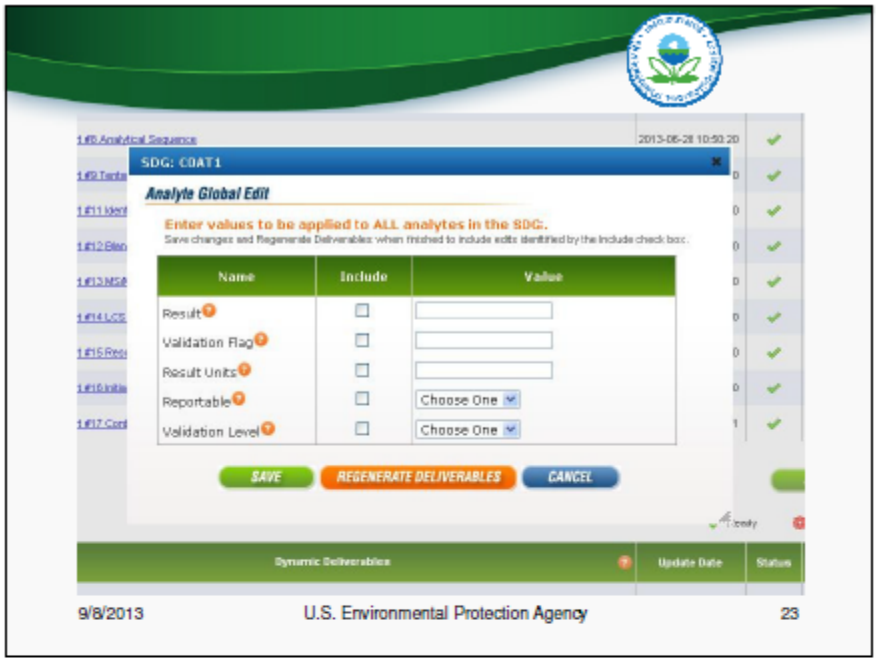

Search Criteria
Use the criteria below to search for an SDG.
Client
Site
Case 43584
SOW
RA
Contract
Lab Code
SDG CDAT1
SEARCH
RESET
Search Results
Click on a row to view the deliverables for the SDG.
Site
Case
Lab Code
SDG
HAVERTOWN PCP
43584
SHEALY
CDAT1
Data Deliverables
Click on a deliverable name to view the report.
Case: 43584 Contract: EPW11035 SDG: CDAT1
Type
Laboratory Deliverables
Update Date
Status
All
HCD
HCD
SAVE


Type
Static Deliverables
Update Date
Status
All
CCS
CCS Semi-Automated Screening Results
CCS
CCS Semi-Automated Screening Results
CCS
Regional CCS Defect Report
CCS
Regional CCS Defect Report
NFG
Report #2 Data Review Results
NFG
Report #4 Final Flag Results
NFG
Report #5 Intermediate Flag Results
NFG
Report #6 Analytical Sample Listing
NFG
Report #7 Calibration Outliers
NFG
Report #8 Analytical Sequence
NFG
Report #9 Tentatively Identified Compounds
NFG
Report #11 Identification Summary for Single & Multi Component Analytes
NFG
Report #12 Blank Contamination Results
NFG
Report #13 MS/MSD Recoveries
NFG
Report #14 LCS Recoveries
NFG
Report #15 Resolution Check Mixture Data Summary
NFG
Report #16 Initial Calibration Data Summary
NFG
Report #17 Continuing Calibration Data Summary
SAVE
Ready
Generating


Ready
Generating
Type
Dynamic Deliverables
Update Date
Status
All
DAT
Support Deliverable
EDM
Edit History Report
EDM
Sample Summary Report
SAVE
EDIT SAMPLE DATA
EDIT SDG DATA
9/8/2013
U.S. Environmental Protection Agency
20


Edit Sample Data
Click in a field to edit sample/analyte information.
Sample Number: COAT2
Method: ENA
Matrix: Water
MA Number: DEFAULT
Sample Location: HAV-LTR-INF-08
Sample Date: 06/06/2013
Sample Time: 09:15:00
Percent Moisture:
Percent Solids:
PH: 2.0
Analyte Name
Result
Flag
Units
Result
Flag
DF
Q
Validation Level
APPLY
SAVE
REGENERATE DELIVERABLES
VIEW SAMPLE REPORT

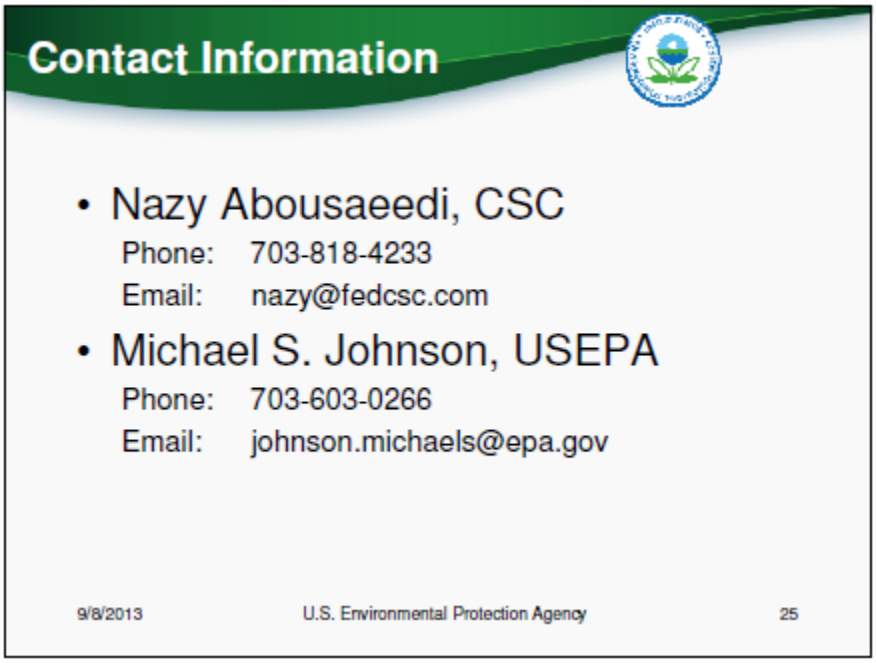

EXES DATA MANAGER
SMO Portal | Help | About | Logout
RETURN TO DATA SEARCH
Data Editing
Search Criteria
Use the criteria below to search for a sample.
The Search Results panel on the right will retrieve all matches.
Site:
Case: 43584
SDG: COAT1
Method: ENA
Matrix: Water
Sample: COAT2
SEARCH
RESET
Search Results
Click on a row to view the data for the sample.
Click on the header link in each column to sort the data.
Display the number of results: 20
Showing 1 to 20 of 22
Method
Matrix
Sample Number
ENA Water COAT1
VOA_Low_Med Water COAT1
VOA_Low_Med Water COAT2
ENA Water COAT2
ENA Water COAT2DL
VOA_Low_Med Water COAT2RE
Edit Sample Data
Click in a field to edit sample/analyte information.
Sample Number: COAT2
Method: ENA
Matrix: Water
MA Number: DEFAULT
Sample Location: HAV-LTR-INF-08
Sample Date: 06/06/2013
Sample Time: 09:15:00
Percent Moisture:
Percent Solids:
PH: 2.0



EDM Advantages Over Traditional Records Management

- Files available to all those given access on a Universal, Regional Contractor, site, or project level.
- Records will be retained and sent to Superfund Enterprise Management System (SEMS) for archiving.
- Easy access to data for later review or litigation.

9/8/2013 U.S. Environmental Protection Agency 24


Contact Information
• Nazy Abousaeedi, CSC
Phone: 703-818-4233
Email: nazy@fedcsc.com
• Michael S. Johnson, USEPA
Phone: 703-603-0266
Email: johnson.michaels@epa.gov
9/8/2013
U.S. Environmental Protection Agency
25

Reconciling EPA Approved Methods in a Database

Daniel Hickman
The NELAC Institute

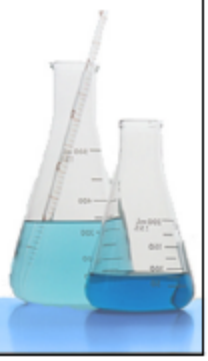
Abstract

The TNI National Laboratory Accreditation Database is used to track environmental laboratory accreditation by matrix, method, and analyte. In order to eliminate confusion and work efficiently in a database structure, methods are assigned method codes that include the specific method reference, revision, and revision date. Methods approved by EPA for compliance reporting under Drinking Water and Wastewater were identified. The process of method reconciliation exposed a number of conflicts and sources of confusion between the references in the CFR, on the web, and in the method source documents. This paper documents those challenges and offers a potential solution.

Reconciling EPA Approved Methods in a Database

Daniel Hickman
TNI Database Administrator

August 08, 2013



LAMS

- Laboratory Accreditation Maintenance System
  - Laboratory Demographics
  - Method Table
  - Analyte Table
  - Matrix Table
  - Technology Table
  - Fields of Accreditation Table



TNI Method Code Table

- TNI Method Codes established for each method which includes:
  - Method Reference
  - Revision or Edition
  - Revision Date
  - Technology



Accreditation

- Laboratories are accredited by Fields of Accreditation (FOA).
  - Matrix
  - Method
  - Analyte
- PTs are scored by method for DW and by technology for the other programs.



What we were trying to do

- Identify methods approved by EPA for Drinking Water and Wastewater, including:
  - Method Reference
  - Method Revision
  - Method Date
  - Method Source
- List them in a database format.
- Assumed that the methods would be listed in the Federal Register.



What we Found

- Wastewater MUR did not include Table 1E or Table 1F.
- Problems with CFR.
- Problems with method listing on Web pages
- EPA DW and EPA Wastewater sometimes approve different versions.



Difficulties in CFR

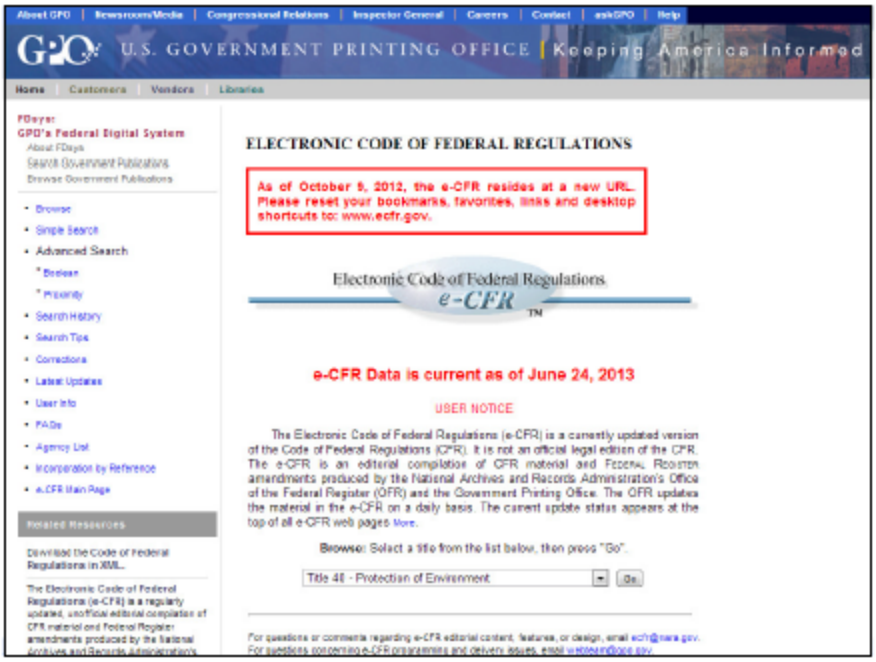
- Important information contained in footnotes:
  - Method Source
  - Method requirements
  - Non-EPA methods
- CFR published with missing footnotes.
- Formatting errors such as misplaced columns.

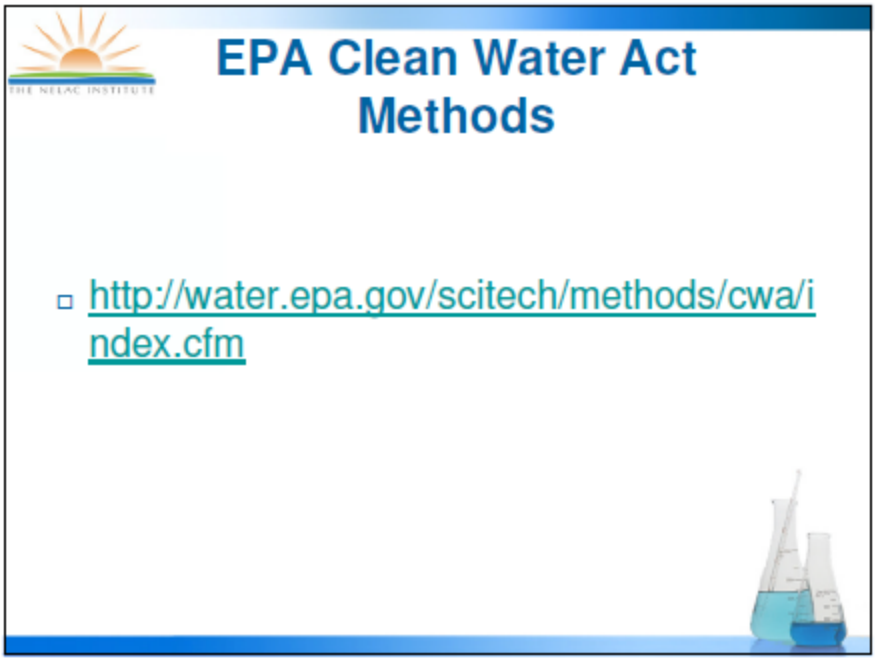


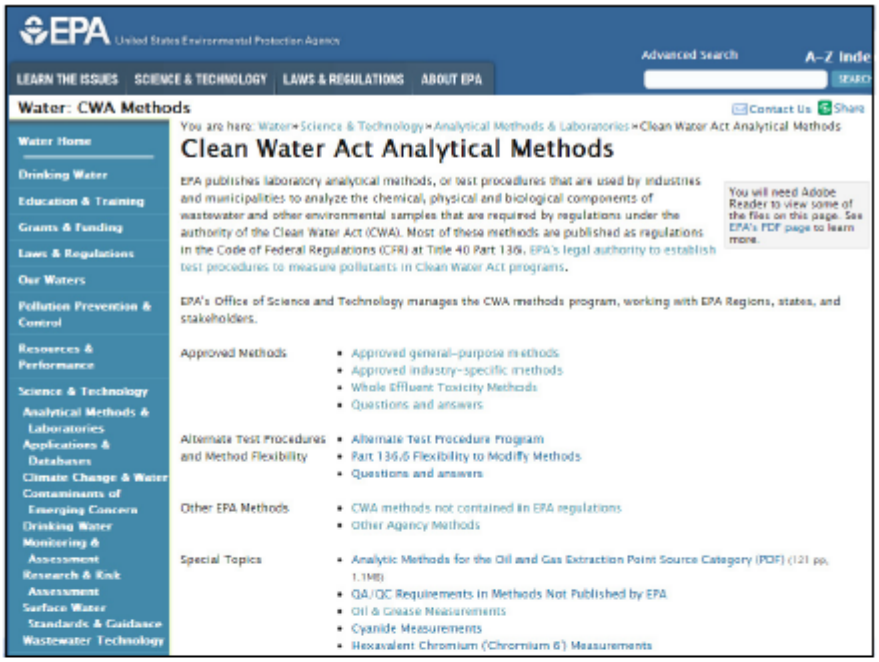
Electronic CFR

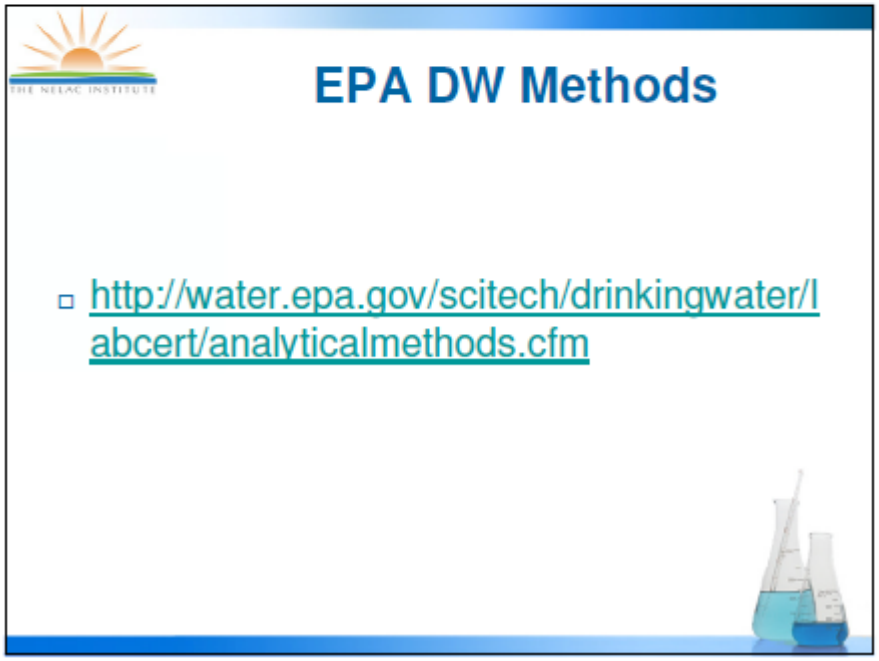
WWW.ecfr.gov

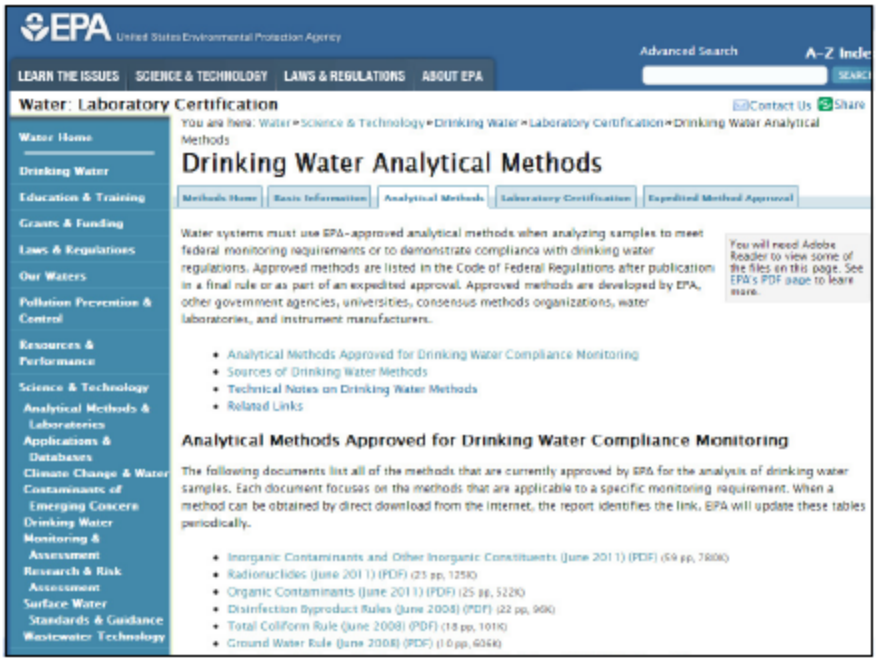



About GPO | Newsrooms/Media | Congressional Relations | Inspector General | Careers | Contact | askGPO | Help
GPO U.S. GOVERNMENT PRINTING OFFICE | Keeping America Informed
Home | Customers | Vendors | Libraries
FDsys.gov
GPO's Federal Digital System
About FDsys
Search Government Publications
Browse Government Publications
Browse
Simple Search
Advanced Search
Boolean
Proximity
Search History
Search Tips
Corrections
Latest Updates
User Info
FAQs
Agency List
Incorporation by Reference
e-CFR Main Page
Related Resources
Download the Code of Federal Regulations in XML.
The Electronic Code of Federal Regulations (e-CFR) is a regularly updated, unofficial editorial compilation of CFR material and Federal Register amendments produced by the National Archives and Records Administration's
ELECTRONIC CODE OF FEDERAL REGULATIONS
As of October 9, 2012, the e-CFR resides at a new URL. Please reset your bookmarks, favorites, links and desktop shortcuts to: www.ecfr.gov.
Electronic Code of Federal Regulations
e-CFR
e-CFR Data is current as of June 24, 2013
USER NOTICE
The Electronic Code of Federal Regulations (e-CFR) is a currently updated version of the Code of Federal Regulations (CFR). It is not an official legal edition of the CFR. The e-CFR is an editorial compilation of CFR material and Federal Register amendments produced by the National Archives and Records Administration's Office of the Federal Register (OFR) and the Government Printing Office. The OFR updates the material in the e-CFR on a daily basis. The current update status appears at the top of all e-CFR web pages More.
Browse: Select a title from the list below, then press "Go".
Title 40 - Protection of Environment
Go
For questions or comments regarding e-CFR editorial content, features, or design, email ecfr@nara.gov.
For questions concerning e-CFR programming and delivery issues, email webmaster@gpo.gov

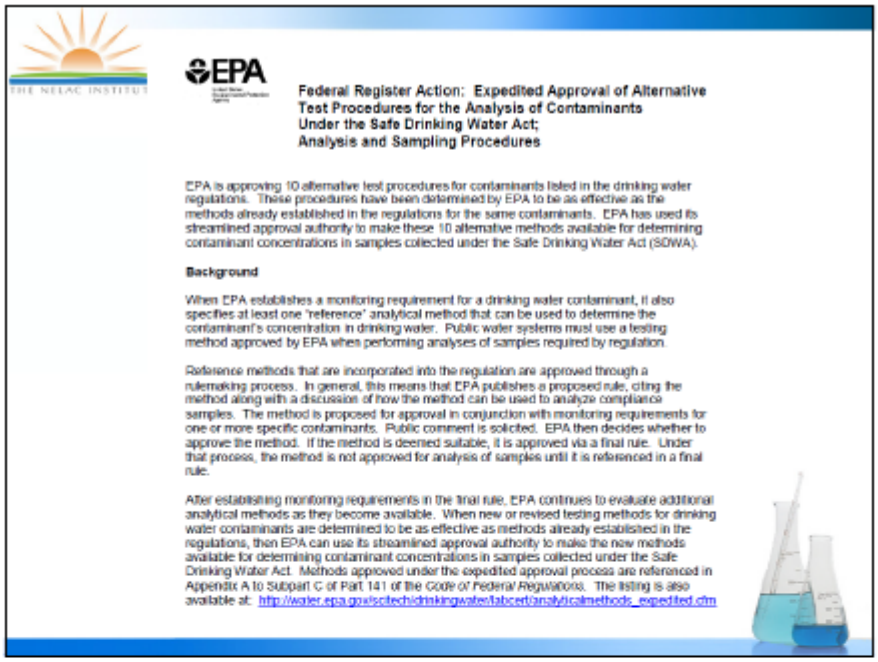

THE NELAC INSTITUTE
EPA Clean Water Act Methods
http://water.epa.gov/scitech/methods/cwa/index.cfm

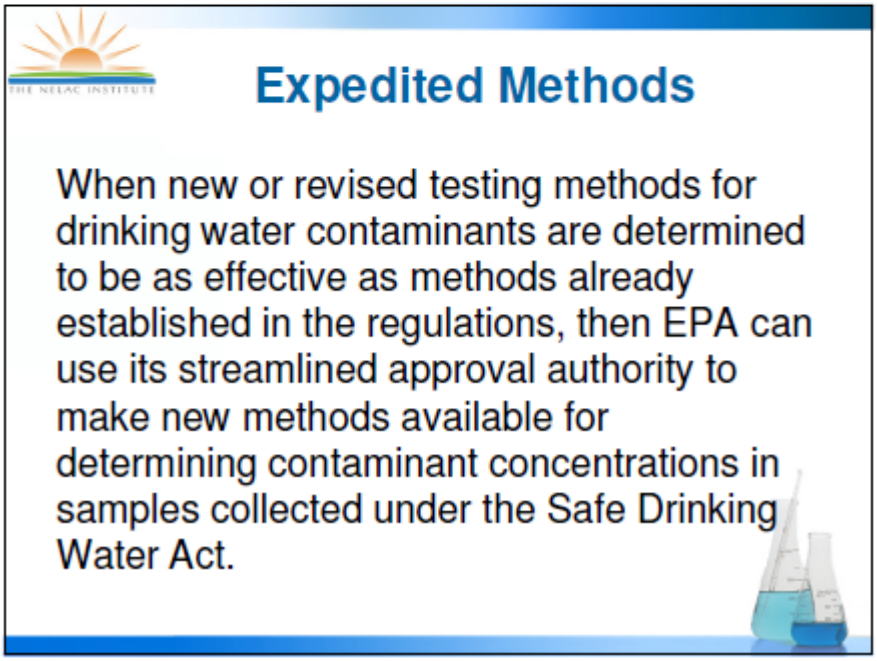

EPA United States Environmental Protection Agency
Advanced Search
A–Z Inde
LEARN THE ISSUES
SCIENCE & TECHNOLOGY
LAWS & REGULATIONS
ABOUT EPA
SEARCH
Water: CWA Methods
Contact Us
Share
You are here: Water» Science & Technology» Analytical Methods & Laboratories »Clean Water Act Analytical Methods
Water Home
Drinking Water
Education & Training
Grants & Funding
Laws & Regulations
Our Waters
Pollution Prevention & Control
Resources & Performance
Science & Technology
Analytical Methods & Laboratories
Applications & Databases
Climate Change & Water
Contaminants of Emerging Concern
Drinking Water
Monitoring & Assessment
Research & Risk Assessment
Surface Water Standards & Guidance
Wastewater Technology
Clean Water Act Analytical Methods
EPA publishes laboratory analytical methods, or test procedures that are used by industries and municipalities to analyze the chemical, physical and biological components of wastewater and other environmental samples that are required by regulations under the authority of the Clean Water Act (CWA). Most of these methods are published as regulations in the Code of Federal Regulations (CFR) at Title 40 Part 136. EPA's legal authority to establish test procedures to measure pollutants in Clean Water Act programs.
You will need Adobe Reader to view some of the files on this page. See EPA's PDF page to learn more.
EPA's Office of Science and Technology manages the CWA methods program, working with EPA Regions, states, and stakeholders.
Approved Methods
Approved general-purpose methods
Approved industry-specific methods
Whole Effluent Toxicity Methods
Questions and answers
Alternate Test Procedures and Method Flexibility
Alternate Test Procedure Program
Part 136.6 Flexibility to Modify Methods
Questions and answers
Other EPA Methods
CWA methods not contained in EPA regulations
Other Agency Methods
Special Topics
Analytic Methods for the Oil and Gas Extraction Point Source Category (PDF) (121 pp, 1.1MB)
QA/QC Requirements in Methods Not Published by EPA
Oil & Grease Measurements
Cyanide Measurements
Hexavalent Chromium (Chromium 6) Measurements


THE NELAC INSTITUTE
EPA DW Methods
http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods.cfm


EPA United States Environmental Protection Agency
Advanced Search
A–Z Index
LEARN THE ISSUES
SCIENCE & TECHNOLOGY
LAWS & REGULATIONS
ABOUT EPA
Water: Laboratory Certification
Contact Us
Share
Water Home
Drinking Water
Education & Training
Grants & Funding
Laws & Regulations
Our Waters
Pollution Prevention & Control
Resources & Performance
Science & Technology
Analytical Methods & Laboratories
Applications & Databases
Climate Change & Water
Contaminants of Emerging Concern
Drinking Water Monitoring & Assessment
Research & Risk Assessment
Surface Water Standards & Guidance
Wastewater Technology
You are here: Water » Science & Technology » Drinking Water » Laboratory Certification » Drinking Water Analytical Methods
Drinking Water Analytical Methods
Methods Home
Basic Information
Analytical Methods
Laboratory Certification
Expedited Method Approval
Water systems must use EPA-approved analytical methods when analyzing samples to meet federal monitoring requirements or to demonstrate compliance with drinking water regulations. Approved methods are listed in the Code of Federal Regulations after publication in a final rule or as part of an expedited approval. Approved methods are developed by EPA, other government agencies, universities, consensus methods organizations, water laboratories, and instrument manufacturers.
You will need Adobe Reader to view some of the files on this page. See EPA's PDF page to learn more.
Analytical Methods Approved for Drinking Water Compliance Monitoring
Sources of Drinking Water Methods
Technical Notes on Drinking Water Methods
Related Links
Analytical Methods Approved for Drinking Water Compliance Monitoring
The following documents list all of the methods that are currently approved by EPA for the analysis of drinking water samples. Each document focuses on the methods that are applicable to a specific monitoring requirement. When a method can be obtained by direct download from the Internet, the report identifies the link. EPA will update these tables periodically.
Inorganic Contaminants and Other Inorganic Constituents (June 2011) (PDF) (59 pp, 780K)
Radionuclides (June 2011) (PDF) (25 pp, 125K)
Organic Contaminants (June 2011) (PDF) (25 pp, 522K)
Disinfection Byproduct Rules (June 2008) (PDF) (22 pp, 96K)
Total Coliform Rule (June 2008) (PDF) (18 pp, 101K)
Ground Water Rule (June 2008) (PDF) (10 pp, 636K)


THE NELAC INSTITUTE
ATP Expedited Approval
http://water.epa.gov/scitech/drinkingwater/labcert/upload/epa815r12003.pdf


EPA
Federal Register Action: Expedited Approval of Alternative Test Procedures for the Analysis of Contaminants Under the Safe Drinking Water Act; Analysis and Sampling Procedures
EPA is approving 10 alternative test procedures for contaminants listed in the drinking water regulations. These procedures have been determined by EPA to be as effective as the methods already established in the regulations for the same contaminants. EPA has used its streamlined approval authority to make these 10 alternative methods available for determining contaminant concentrations in samples collected under the Safe Drinking Water Act (SDWA).
Background
When EPA establishes a monitoring requirement for a drinking water contaminant, it also specifies at least one "reference" analytical method that can be used to determine the contaminant's concentration in drinking water. Public water systems must use a testing method approved by EPA when performing analyses of samples required by regulation.
Reference methods that are incorporated into the regulation are approved through a rulemaking process. In general, this means that EPA publishes a proposed rule, citing the method along with a discussion of how the method can be used to analyze compliance samples. The method is proposed for approval in conjunction with monitoring requirements for one or more specific contaminants. Public comment is solicited. EPA then decides whether to approve the method. If the method is deemed suitable, it is approved via a final rule. Under that process, the method is not approved for analysis of samples until it is referenced in a final rule.
After establishing monitoring requirements in the final rule, EPA continues to evaluate additional analytical methods as they become available. When new or revised testing methods for drinking water contaminants are determined to be as effective as methods already established in the regulations, then EPA can use its streamlined approval authority to make the new methods available for determining contaminant concentrations in samples collected under the Safe Drinking Water Act. Methods approved under the expedited approval process are referenced in Appendix A to Subpart C of Part 141 of the Code of Federal Regulations. The listing is also available at: http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_expedited.cfm


Expedited Methods
When new or revised testing methods for drinking water contaminants are determined to be as effective as methods already established in the regulations, then EPA can use its streamlined approval authority to make new methods available for determining contaminant concentrations in samples collected under the Safe Drinking Water Act.

Expedited Methods

http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_expedited.cfm



EPA United States Environmental Protection Agency

Advanced Search A–Z Index

LEARN THE ISSUES | SCIENCE & TECHNOLOGY | LAWS & REGULATIONS | ABOUT EPA

Water: Laboratory Certification

Contact Us Share

You are here: Water » Science & Technology » Drinking Water » Laboratory Certification » Expedited Method Approval Process

Water Home
Drinking Water
Education & Training
Grants & Funding
Laws & Regulations
Our Waters
Pollution Prevention & Control
Resources & Performance
Science & Technology
Analytical Methods & Laboratories
Applications & Databases
Climate Change & Water
Contaminants of Emerging Concern
Drinking Water Monitoring & Assessment
Research & Risk Assessment
Surface Water Standards & Guidance
Wastewater Technology

Expedited Method Approval Process

Methods Home | Basic Information | Analytical Methods | Laboratory Certification | Expedited Method Approval

EPA can use an expedited process to announce the approval of new drinking water analytical methods in the Federal Register. The process provides laboratories and water systems more timely access to new alternative testing methods than the traditional rulemaking process.

You will need Adobe Reader to view some of the files on this page. See EPA's PDF page to learn more.

- Expedited Method Approval Requirements
- New! Expedited Method Approval Federal Register Notices
- New! Methods Approved Under the Expedited Process

Expedited Method Approval Requirements

There are several requirements that must be met before a new method can be approved using the expedited process.

- Public water systems must be required by federal regulation to monitor for a contaminant that is an analyte in the new method.
- Drinking water regulations must list at least one approved method for the contaminant (i.e., a method that was approved using the rulemaking process).
- A comparison of the new alternative method to the approved method(s) must show the new method to be equally effective in determining the concentration of the contaminant.

New methods may be submitted for evaluation under the Alternate Test Procedure (ATP) program. A new method can be considered for approval using the expedited process, if it has performance characteristics that fall within the range of performance characteristics obtained by the methods listed in regulation for the same contaminant.

↑Top of page

WWW.NEMI.GOV

- Lots of good information on title, source, citation, summary, analyte list, detection limit, cost, etc.
- Most non-EPA Methods are missing.
- Does not list all approved EPA methods.
- Not all EPA methods listed are approved.



EXAMPLES



CFR/Web Examples

40 CFR 136, 1F	EPA Web	Document
EPA 1666	EPA 1666	EPA 1666A
EPA 1667	EPA 1667	EPA 1667A
EPA 1671	EPA 1671	EPA1671A
EPA 502.2	EPA 502.2	EPA 502.2, Rev 2.0
EPA 524.2	EPA 524.2	EPA 524.2, Rev 4.0
EPA 551	EPA 551	EPA 551, 1990
EPA 1624C	EPA 1624C	EPA 1624C
EPA 1625C	EPA 1625C	EPA 1625C



Examples

- With last MUR, EPA Wastewater dropped use of editions for Standard Methods and began using the format used in the online versions
  - SM 2540 B-1997
  - SM 3113 B-1999
  - SM 4500 H+ B-2000
  - SM 9223 B-2004



FR Vol. 77, No. 97, p 29767

"This approach clearly identifies the version of the standard method approved under Part 136 and no longer ties it to a particular compendium printing or edition of Standard Methods. For example, the exact method, Standard Method 3113B–2004 appears in the 18th, 19th, and 20th edition of Standard Methods. Because this method is the same in all of these editions, a laboratory may refer to any of these editions when using Standard Method 3113B–2004 to measure the analytes listed in Table IB that are approved for this method."



Examples

40 CFR Part 136.3 Table 1C, footnote 2

- "The full text of Methods 601-613, 624, 625, 1613B, 1624B, and 1625B are provided at Appendix A."
  - None of the methods have revisions or revision dates.
  - New method codes created with revision dates of CFR each time they were issued.



Examples

- EPA CW approved SM-2011 methods (22nd Edition)
- EPA DW approved SM 22nd Ed



Examples

- SM 9223 B (multiple editions)
  - Colilert
  - Colilert-18
  - Colisure
  - Colisure Quantitray
- Each method also listed separately in 40 CFR 136.3, Table 1A



Examples

Method	EPA CWA	EPA DW
ASTM D1067-92B		X
ASTM D1067-02B		X
ASTM D1067-06B	X	X



Examples

Method	EPA CWA	EPA DW
ASTM D1179-93B		X
ASTM D1179-99B		X
ASTM D1179-04B	X	X
ASTM D1179-10B		X



Examples

Method	EPA CWA	EPA DW
ASTM D1253-95	X	
ASTM D1253-08	X	X



Examples

Method	EPA CWA	EPA DW
EPA 150.1		X
EPA 150.2	X	X



Examples

Method	EPA CWA	EPA DW
EPA 1623	X	
EPA 1623.1		X



Examples

Method	EPA CWA	EPA DW
EPA 245.2	X	
EPA 245.2 Rev 2.0		X



Examples

Method	EPA CWA	EPA DW
EPA 300.1, Rev 1, 2000		X
EPA 300.1, Rev 1, 1997	X	



Examples

Method	EPA CWA	EPA DW
EPA 515.2, Rev 1.1		X
EPA 515.2 Rev 1.0	X	



Examples

Method	EPA CWA	EPA DW
SM 2120 B-2001	X	
SM 2120 B-2011	X	
SM 2120 B 21st Ed (2001)	X	X
SM 2120 B 22st Ed (2011)	X	X



Examples

Method	EPA CWA	EPA DW
SM 2130 B-2001	X	
SM 2130 B-2011	X	
SM 2130 B 21st Ed (2001)	X	X
SM 2130 B 22st Ed (2011)	X	X



Solutions ?

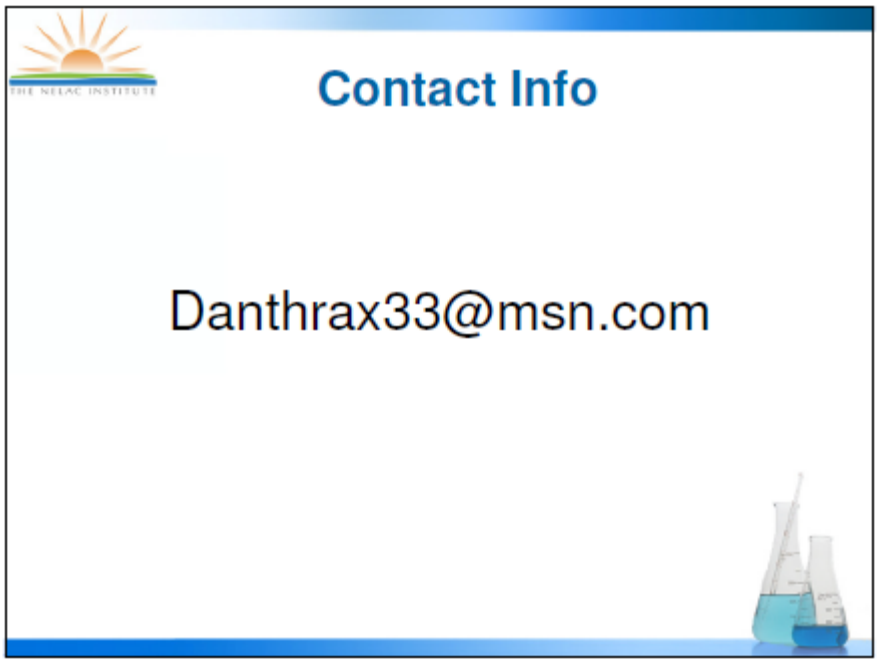
- Work together on common method nomenclature.
- Coordinate timing with MUR releases.
- Consider advanced notice to states of intention to list new expedited methods.
- Better identification of method revision and revision dates on methods themselves.



Solutions ?

- Use TNI database or create new one to keep track of which methods and revisions are currently approved.
- Use DB to list approval by Method-Analyte rather than Analyte-Method.
- Use DB to search for approved method by matrix, technology, and/or analyte.




Contact Info
Danthrax33@msn.com

Understanding End-Users' Approaches to Ensuring the Quality of Environmental Data

Christina Hiegel
Trihydro Corporation

Abstract

Federal and state environmental regulatory and governing bodies have developed protocols or requirements for ensuring the quality of laboratory produced data. These protocols can vary widely and may be dependent upon the decision of the regulator governing the project. Sources for data validation standards include: the United States Environmental Protection Agency (USEPA) National Functional Guidelines (NFG) documents, USEPA Solid Waste – 846 methodology, Department of Defense regulations, National Environmental Laboratory Accreditation Program (NELAP) requirements, and other methods and regulatory guidance documents. Consistently, the regulatory guidance documents are more or at times less stringent than the promulgated methods or SOPs which causes conflicting views between the laboratory and end-user on the quality of the data. The differences between sources make it extremely difficult for the laboratory and data end-user to determine when analytical data is in fact accurate, precise, compliant, and representative.

One of the largest problems with differing data quality requirements is that the laboratories and data end-users are not familiar with each other's expectations of quality. Often times an end user's validation or review will result in rejection of data that would be considered valid by the laboratory. Additionally, the end-user's objectives may not have been met by the laboratory. Understanding the evaluation of quality by the end user will help to improve the quality of results and provide acceptable data that meets both the laboratories and end users' obligations.

The laboratories process for ensuring quality includes the use of promulgated analytical methods that are used to develop standard operating procedures (SOPs). The SOPs address everything from bottle preparation, analyst training, sample storage, and sample preparation and analyses to data calculations and final report preparation. In addition, most environmental laboratories are under scrutiny of state and third party accrediting agencies who provide certification or accreditation for a given method or process. These agencies evaluate the laboratory processes, SOPs, and data to determine if the laboratory is able to meet the quality requirements set by the accrediting organizations.

In contrast, end users of the analytical reports provided by the laboratories evaluate the quality of the data in a slightly different manner than the laboratory. The overall quality of the data to the end-user is determined by the usability of the data with respect to the project objectives. Therefore, the end-user is looking at more than the individual data results to determine if the objectives of the regulatory agency or client were met. These objectives would include the reporting limits, required quality assurance samples, comparison of blind duplicate samples, condition of samples when they arrived at the laboratory, any major non-conformances that would not allow the data to be reported, or results that are dissimilar to expected results or different than previous results. The end user may perform limited to very complex reviews of the data from basic screening to complex data validation.

Therefore, due to the increased demand for data validation and adherence to the quality standards, it is important for both the laboratories and end users to realize what is required to ensure quality data and more importantly to understand that the requirements that each entity are trying to meet are different. Preparing for and understanding the end-users goals and how they are reviewing the data will help to ensure greater satisfaction by the end-user in the data received from their laboratory.

Understanding End-Users' Approaches to Ensuring the Quality of Environmental Data

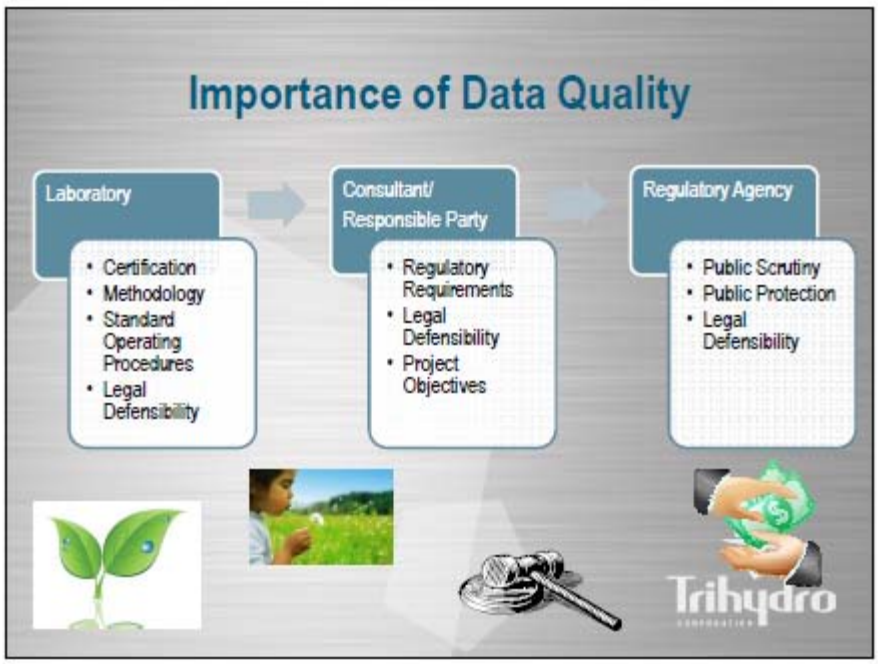
By Christina Hiegel, P.E.
Civil/Environmental Engineer

Introduction

Christina has over 11 years' experience in the environmental industry. She is a registered civil/environmental engineer and manages the chemistry group at Trihydro. Her primary responsibilities include providing technical support for projects in data defensibility, data quality, and leading data quality efforts.

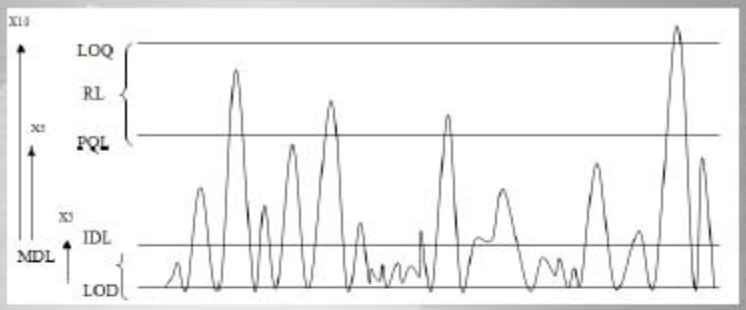


Christina Hiegel


Importance of Data Quality
Laboratory
• Certification
• Methodology
• Standard Operating Procedures
• Legal Defensibility
Consultant/ Responsible Party
• Regulatory Requirements
• Legal Defensibility
• Project Objectives
Regulatory Agency
• Public Scrutiny
• Public Protection
• Legal Defensibility
Trihydro


Differing Quality Standards
Trihydro

Reporting Limits



Holding Times



Preservations







Trihydro

Choosing Analytical Methods

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ASTM INTERNATIONAL

STANDARDMETHODS

Trihydro

Data Validation Standards

Batch number: 12345AAB	Sample number(s): 100000-100005		UNSPK:	MW-1 BKG:	MW-1		
Antimony	173*	169*	75-125	5	20	N.D.	N.D.	0 (1)
Arsenic	169*	173*	75-125	2	20	N.D.	N.D.	0 (1)
Beryllium	93	99	88-117	3	20	N.D.	N.D.	0 (1)
Lead	111	113*	81-120	164*	20	N.D.	N.D.	0 (1)
Nickel	100	121*	85-117	13	20	21.2	26.3	20 (1)
Silver	98	106	82-114	7	20	N.D.	N.D.	0 (1)



Data Validation Standards

Table 18. Spike Sample Actions for ICP-MS Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R < 30% Post-digestion spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R < 30% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) affected non-detects as estimated (UJ)
Matrix Spike %R > 125% Post-digestion spike %R > 125%	Qualify affected results that are ≥ MDL as estimated high (J+)
Matrix Spike %R > 125% Post-digestion spike %R ≤ 125%	Qualify affected results that are ≥ MDL as estimated (J)
Matrix Spike %R < 30% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R > 125% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated high (J+) Non-detects are not qualified

USEPA. 2010. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review (USEPA-540-R-10-011). Available from: http://www.epa.gov/superfund/programs/clp/download/functguid.pdf



Data Validation Standards

Batch number: 2120000B Sample number(s): 1000001 - 100005 UNSPK: MM-6

Acenaphthene	93	96	71-115	8	30
Di-n-butylphthalate	90	94	79-118	8	30
Dibenz(a,h)acridine	99	101	78-128	7	30
1,2-Dichlorobenzene	88	89	72-111	7	30
1,3-Dichlorobenzene	88	90	68-111	7	30
1,4-Dichlorobenzene	89	91	67-106	9	30
Diethylphthalate	86	89	69-119	9	30
2,4-Dimethylphenol	94	98	36-122	9	30
Dimethylphthalate	95	97	42-132	7	30
2,4-Dinitrophenol	94	97	20-168	7	30
1,4-Dioxane	69	73	21-84	11	30
bis(2-Ethylhexyl)phthalate	99	101	73-129	6	30
Fluoranthene	94	98	71-123	8	30
Fluorene	97	98	71-123	6	30
Indene	89	91	75-115	9	30
2-Methylnaphthalene	92	93	77-113	8	30
2-Methylphenol	19	20	19-126	5	30
4-Methylphenol	88	88	13-128	5	30
4-Nitrophenol	63	67	10-109	11	30
Phenanthrene	94	98	76-112	8	30
Phenol	76	76	8-83	5	30
Pyridine	67	67	19-83	5	30



Data Validation Standards

Table 36. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Semivolatiles Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	Use professional judgment
Lower Acceptance Limit ≤ %R, RPD ≤ Upper Acceptance Limit	No qualification	

USEPA. 2008. *USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review* (USEPA-540-R-08-01). Available from: http://www.epa.gov/superfund/programs/clp/download/functfg.pdf.

TABLE 16. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ACTIONS FOR TRACE VOLATILES LOW-LEVEL VOLATILES, SEMIVOLATILES, PESTICIDES, AND AROCLOR ANALYTES

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R above the Upper Acceptance Limit	J	No Qualification
RPD value above the Upper Acceptance Limit	J	UJ
%R Less than 30%	J	UJ and R*



Calibration Standards

ANALYTE	CURVE TYPE	AVE RRF	RRF	MIN RRF	CALC AMOUNT	SPIKE AMOUNT	%D	MAX %D
1,2-Dichloroethene, Total	Ave	0.3126	0.2737		97.6	100	-12.4	35.0
Xylenes, Total	Ave	2.007	1.767		132	150	-11.9	35.0
Chlorotrifluoroethene	Ave	0.1251	0.1890		75.6	50.0	51.1*	35.0
Dichlorodifluoromethane	Ave	0.4192	0.4666		55.7	50.0	11.3	35.0
Chloromethane	Ave	0.2670	0.2531	0.1000	47.4	50.0	-5.2	35.0
Vinyl chloride	Ave	0.2689	0.2550		47.4	50.0	-5.2	35.0
2-Chloro-1,1,1-Trifluoroethane	Ave	0.3652	0.3670		50.2	50.0	0.5	35.0
Bromomethane	Ave	0.2299	0.1958		42.6	50.0	-14.8	35.0
Chloroethane	Ave	0.1734	0.1575		45.4	50.0	-9.2	35.0
Trichlorofluoromethane	Ave	0.5605	0.5571		49.7	50.0	-0.6	50.0
Acrolein	Ave	0.0240	0.0335		450	500	30.1	55.0
Acetone	Ave	0.0577	0.0574		199	200	-0.6	55.0

Trihydro CORPORATION



Calibration Standards

Table 17. Continuing Calibration Verification (CCV) Actions for Low/Medium Volatiles Analyses

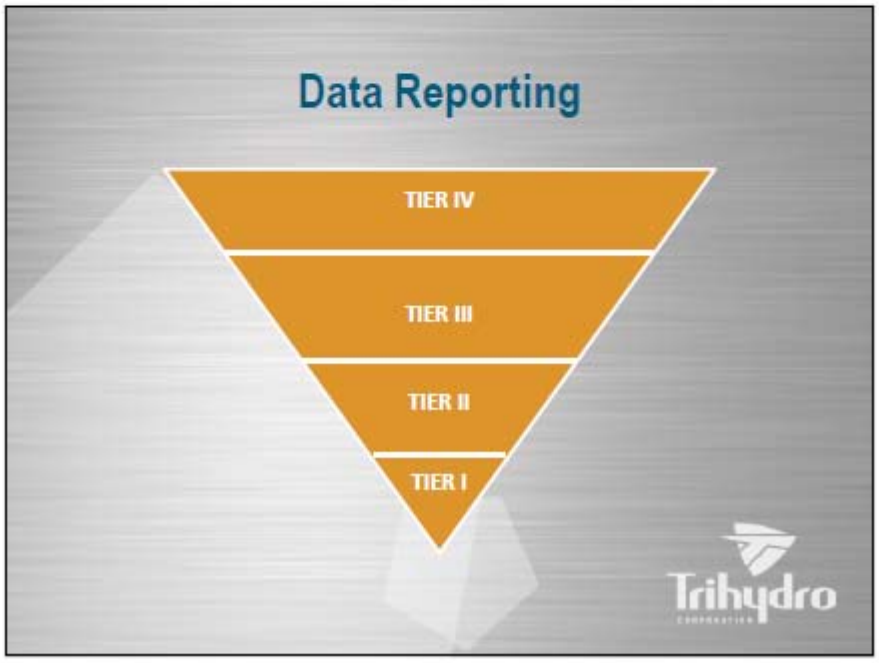
Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.0050 (advisory for 1,4-Dioxane) RRF < 0.010 (target compounds listed in Table 15) RRF < 0.050 (all other target compounds)	RRF < 0.0050 (advisory for 1,4-Dioxane) RRF < 0.010 (all volatile target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.0050 (advisory for 1,4-Dioxane) RRF ≥ 0.010 (target compounds listed in Table 15) RRF ≥ 0.050 (all other target compounds)	RRF ≥ 0.0050 (advisory for 1,4-Dioxane) RRF ≥ 0.010 (all volatile target compounds)	No qualification	

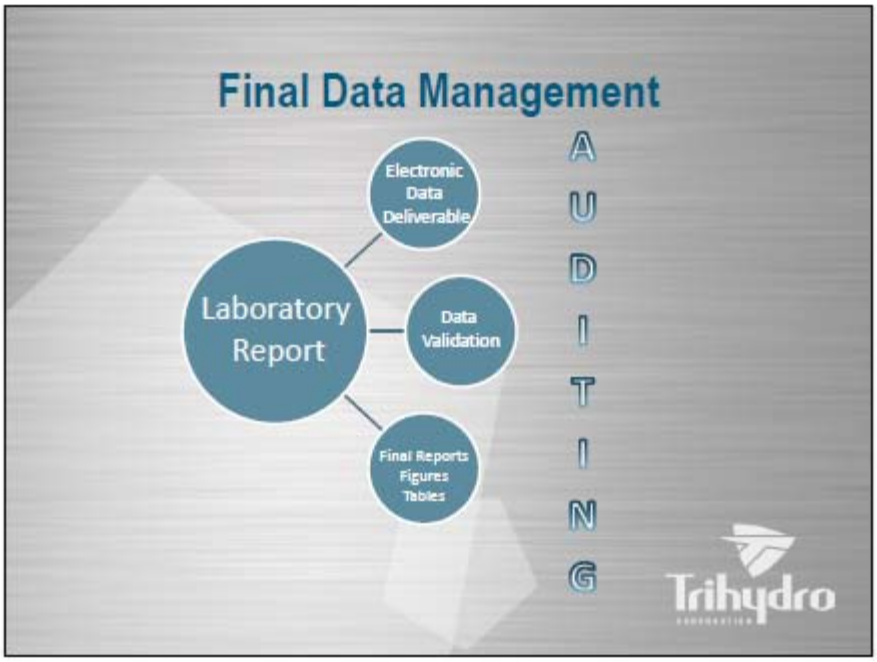
USEPA. 2008. USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (USEPA-540-R-08-01). Available from: http://www.epa.gov/superfund/programs/clp/disposal/guide.pdf

Trihydro CORPORATION




Precision
Trihydro


Data Reporting
TIER IV
TIER III
TIER II
TIER I
Trihydro



Meeting Quality Objectives

Communicate:

- General project information
- Regulatory requirements
- Reporting limits and analyses requirements
- Analyses, constituents of concern, target analytes
- Subcontracting requirements
- How to communicate with each other
- Validation objectives
- Audit changes to the data
- Other information (e.g., sampling requirements, blanks, turn, and special reporting packages)

Trihydro


Trihydro

Web-based Chain of Custody Service & LIMS Integration

Scot Cocanour
Promium

Abstract

A web-based service provides an efficient, accurate, and reliable process to replace paper-based chains of custody. Scot and Jim will describe the components and benefits of EnviroChain from Promium, an online chain of custody service for laboratories and their clients.

For at least the last forty years, laboratories have been using paper chains of custody (CoC) to manage samples. Thousands of paper CoCs are handled every year in most labs. That paper-based system is inefficient—data must be entered on the paper and then again in the LIMS, inaccurate—every time data is hand-written and then transcribed repeatedly creates potential for data entry errors, and unreliable—with paper CoCs getting damaged or lost.

A web-based electronic chain of custody service not only addresses those issues, it also delivers a rich source of data in near real-time for laboratory project planning and sample management. The result is a reduction in costs and headaches. With the explosion in the use of smartphones and tablets, there is finally a field technology that can truly leverage web applications for managing chains of custody. Coupled with a tight integration with a LIMS, the flow of data is accelerated from the field to final report.

NEMC 2013 PROMIUM

Web-based Chain of Custody Service

Scot Cocanour | CEO, Promium

AMAZING TECHNOLOGICAL ADVANCES PROMIUM



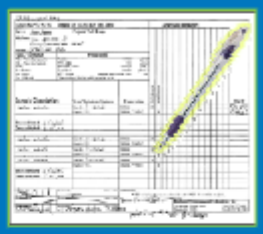
CoC EVOLUTION

PROMIUM

1970s



40 Years Later



PROBLEMS WITH ALL THOSE PAPER CoCs

PROMIUM

1. Double entry of data
2. Transcription errors
3. Confusing & Hard to read



Undermines the integrity of chain of custody

TRANSLUCENT COSTS

PROMIUM

You see the costs but look right through them

Data entry: 15 min? 20? for every CoC

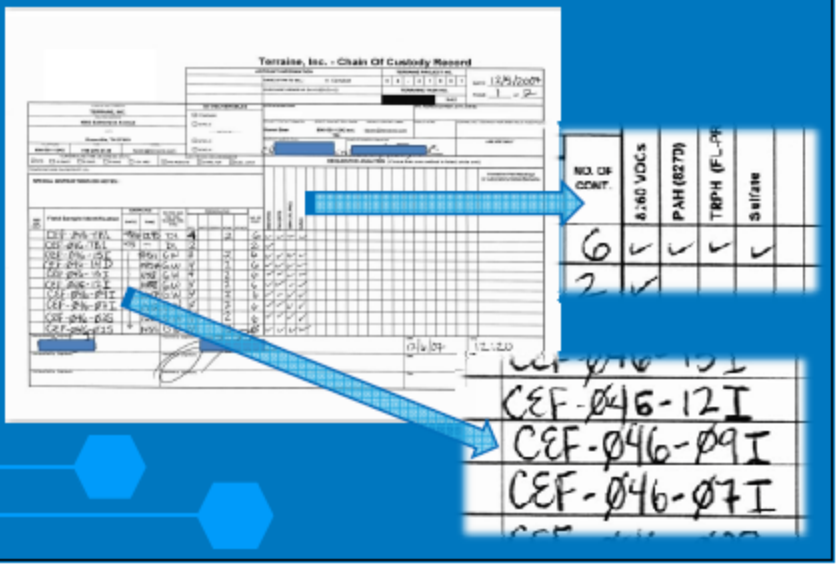
Correcting the errors? 20 min? 45?

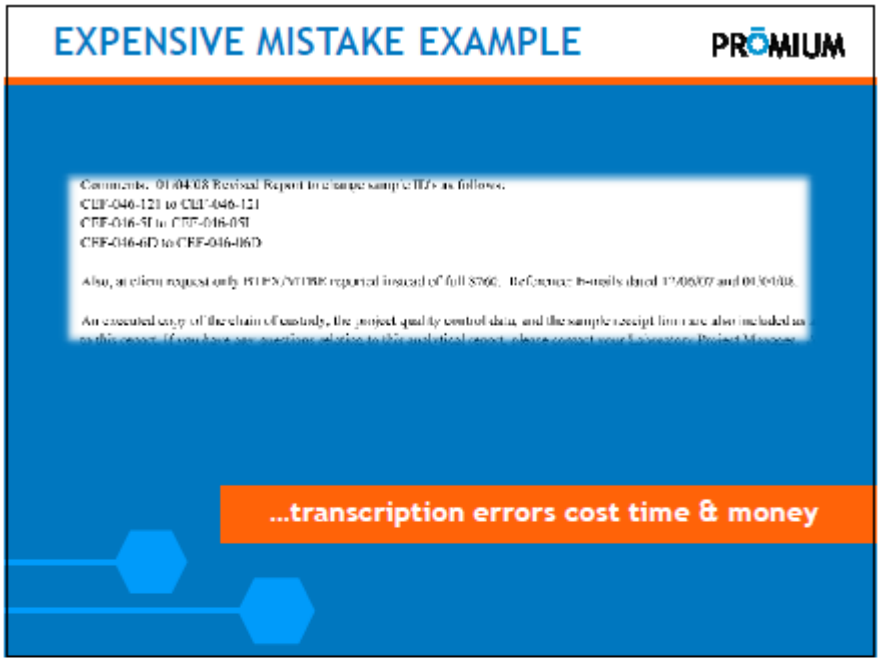
$5.00 - $10.00 for each paper CoC

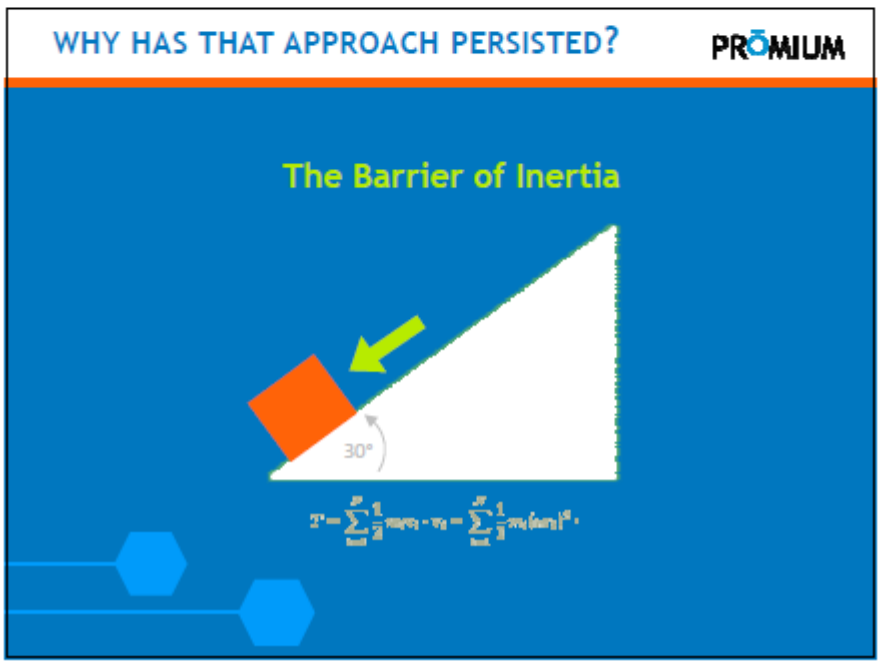
...for thousands of CoCs every year

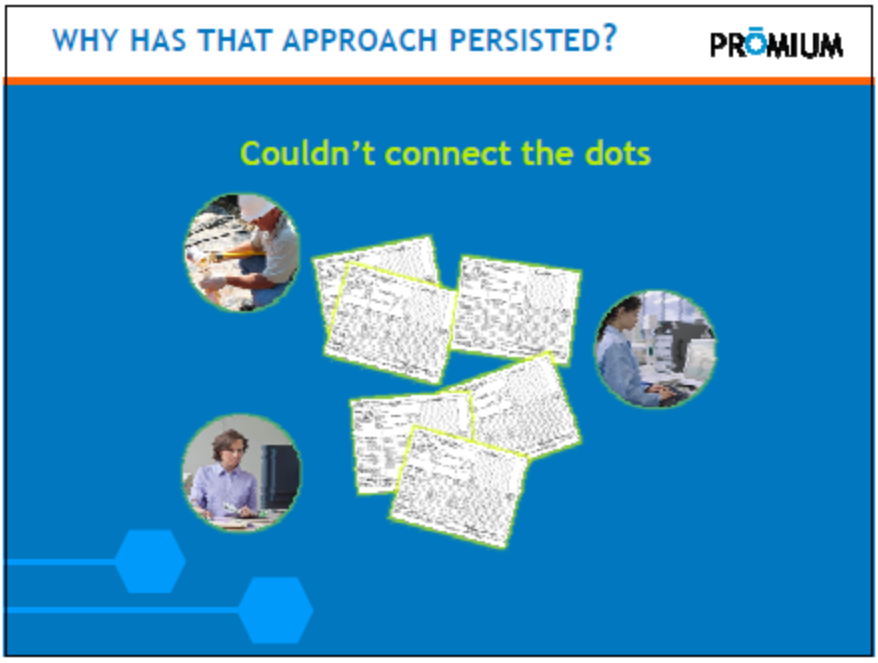
EXPENSIVE MISTAKE EXAMPLE

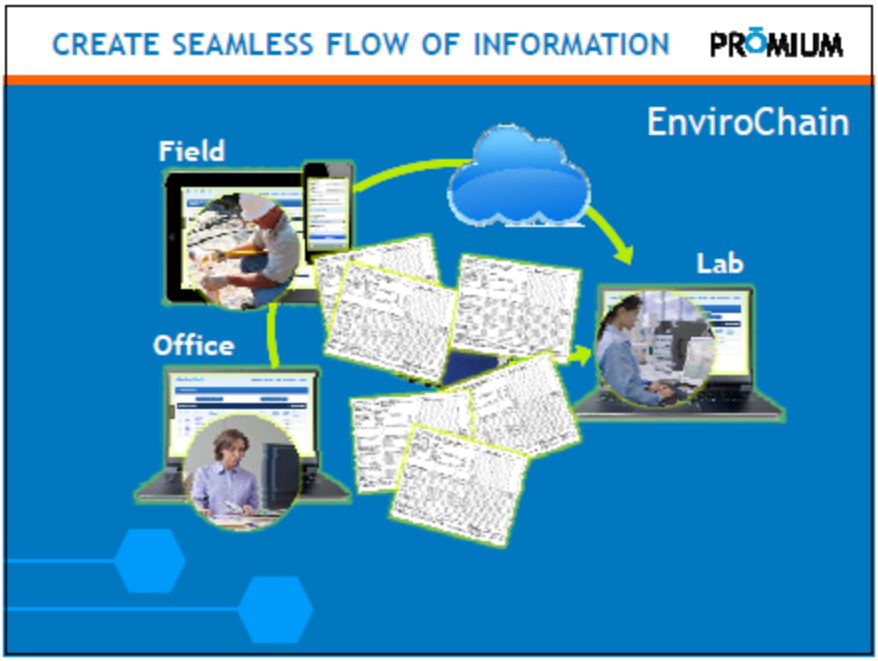
PROMIUM




EXPENSIVE MISTAKE EXAMPLE
PROMIUM
Comments: 01/04/08 Revised Report to change sample ID's as follows:
CEF-046-121 to CEF-046-121
CEF-046-5I to CEF-046-05I
CEF-046-6D to CEF-046-06D
Also, at client request only BTEX/MTBE reported instead of full $760. Reference: E-mails dated 17/06/07 and 01/04/08.
An executed copy of the chain of custody, the project quality control data, and the sample receipt limits are also included as
...transcription errors cost time & money


WHY HAS THAT APPROACH PERSISTED?
PROMIUM
The Barrier of Inertia
30°


WHY HAS THAT APPROACH PERSISTED?
PROMIUM
Couldn't connect the dots


CREATE SEAMLESS FLOW OF INFORMATION
PROMIUM
EnviroChain
Field
Lab
Office

AUTOMATE THE PROCESS

PROMIUM

EnviroChain

Efficiency, Accuracy and Reliability

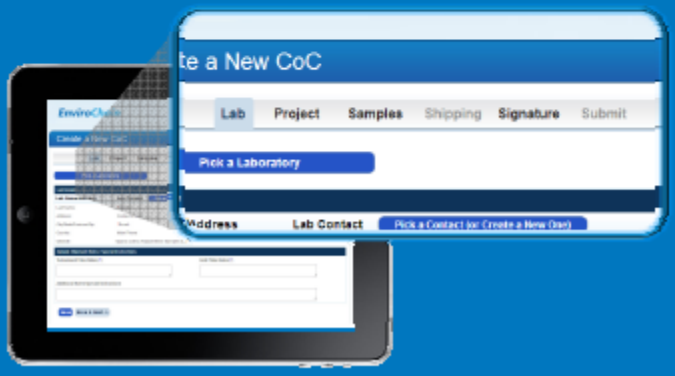
- Secure transfer of data
- Pre-entered analysis methods
- Previous CoCs used to create new ones
- Lab preview of incoming workload
- Direct upload of CoCs into the LIMS

Eliminate confusion, error, and delay.

BETA DEMONSTRATION

PROMIUM

EnviroChain



Managing Environmental Monitoring Information in Cloud

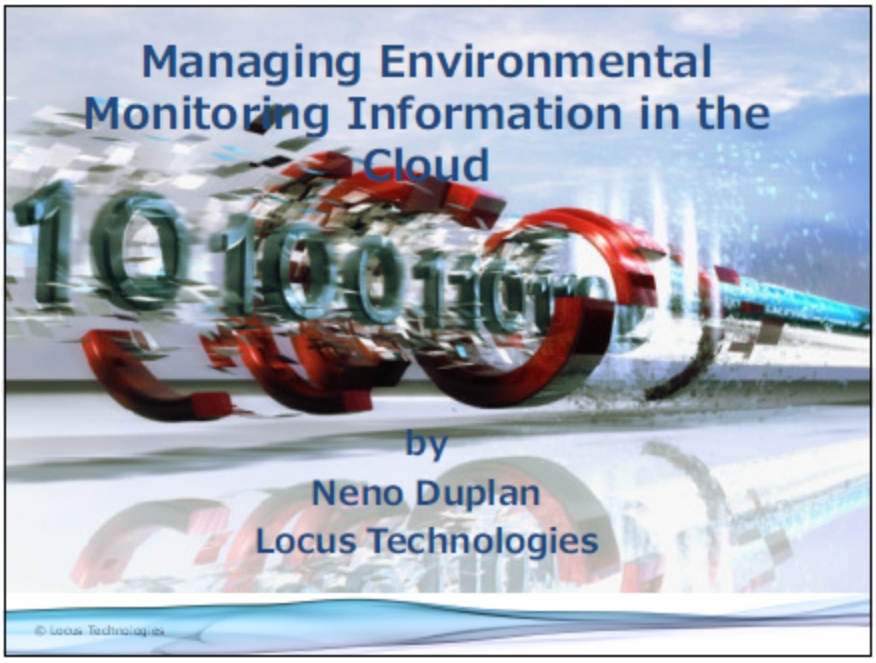
Neno Duplan
Locus Technologies

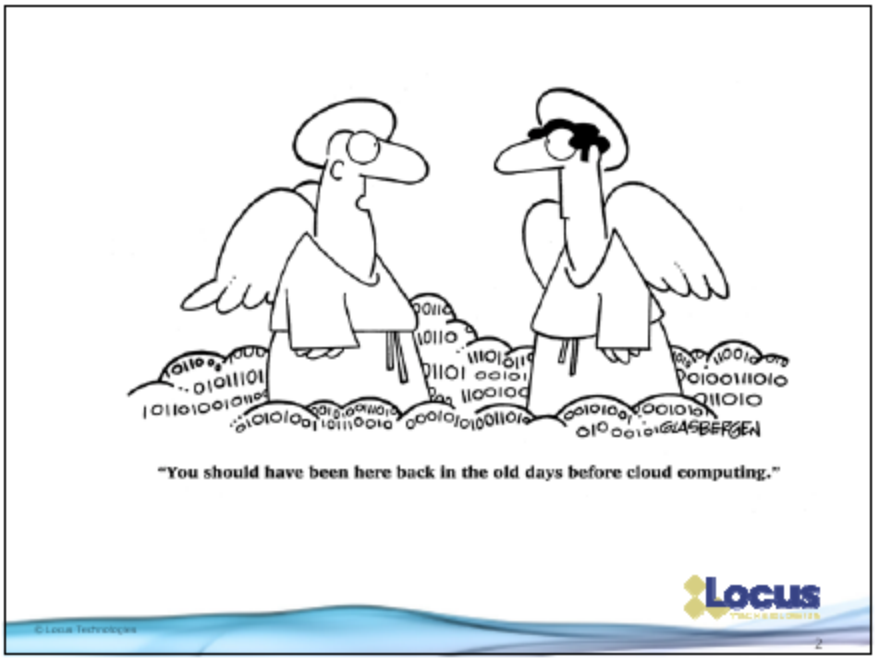
Abstract

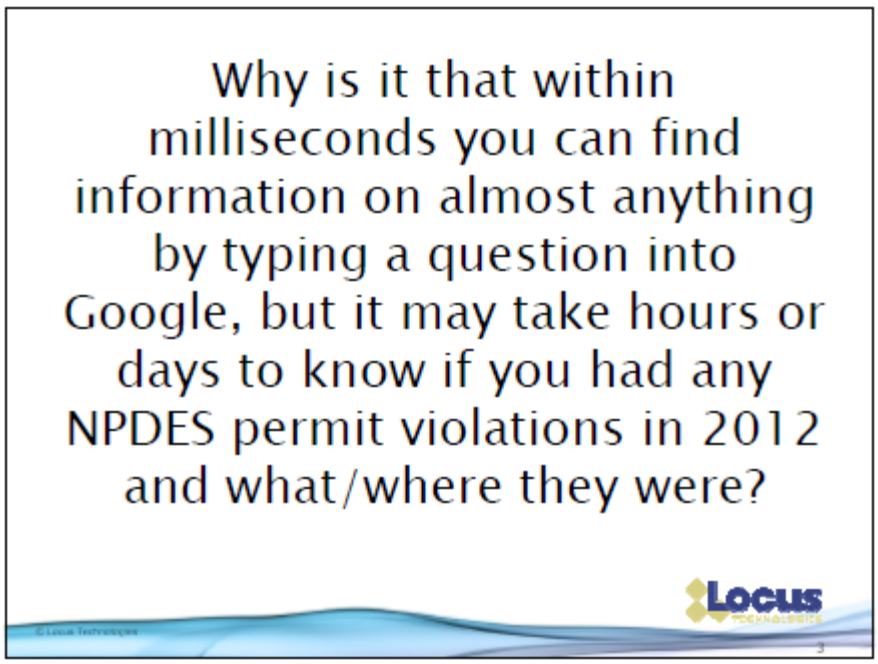
The concept of cloud computing has been steadily growing in popularity over the past decade or two. The many benefits that Software as a Service (SaaS) offers include simple, web-based accessibility, a quick set-up time, less maintenance required, and less effort needed from IT. However, despite the Cloud's glowing reviews and increasing presence in the corporate world, some companies still remain in the past.

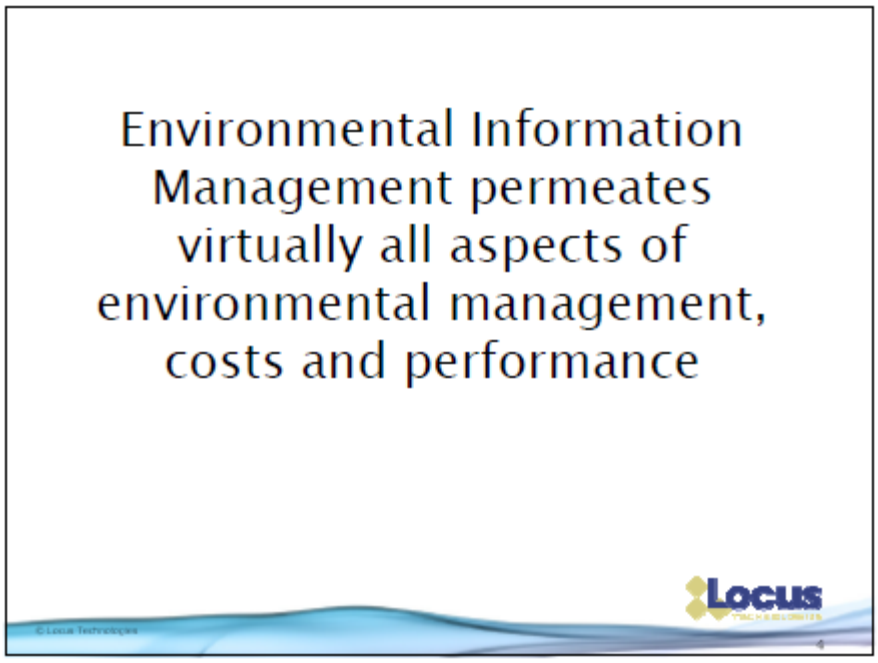
Switching to the Cloud can be an especially detrimental decision to organizations responsible for managing their environmental data across multiple sites. For industries ranging from energy and utilities to food production and services, the millions of records and numerous regulations companies deal with every day makes this a highly complex process. Even though multifaceted and difficult, countless companies still choose to use spreadsheets or access databases to collect, analyze, and report on their environmental, compliance, and sustainability data. Information management is the key driver behind all aspects of environmental management, costs and performance. This is why the proper management of environmental data is essential. If a company has records scattered across various silo systems that neither the company nor their consultants can easily access, this data cannot be effectively mined for actionable information, and what can't be measured can't be managed.

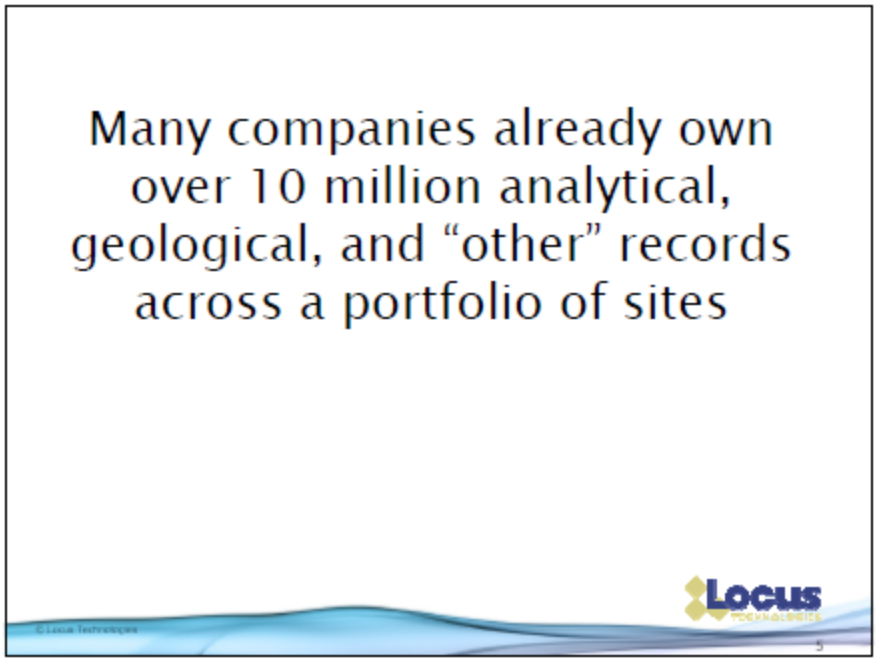
By managing environmental information in the Cloud, cost benefits can be reached. By capturing and analyzing data in one centralized, easily accessible place, you can analyze information at portfolio level a thousand times faster, providing actionable insight in real time. This feature allows you to easily identify opportunities for cost savings.

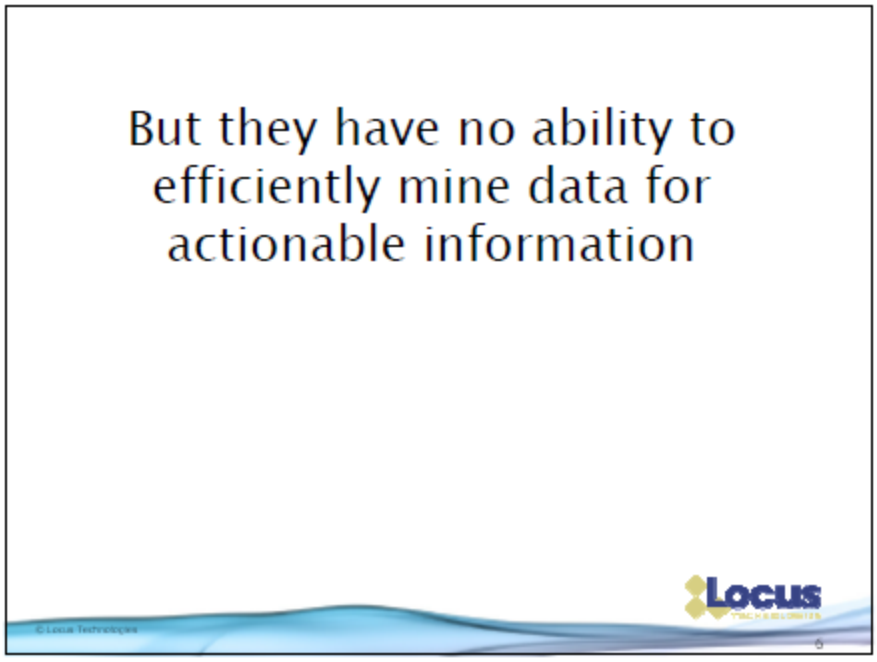

Managing Environmental Monitoring Information in the Cloud
by
Neno Duplan
Locus Technologies
© Locus Technologies

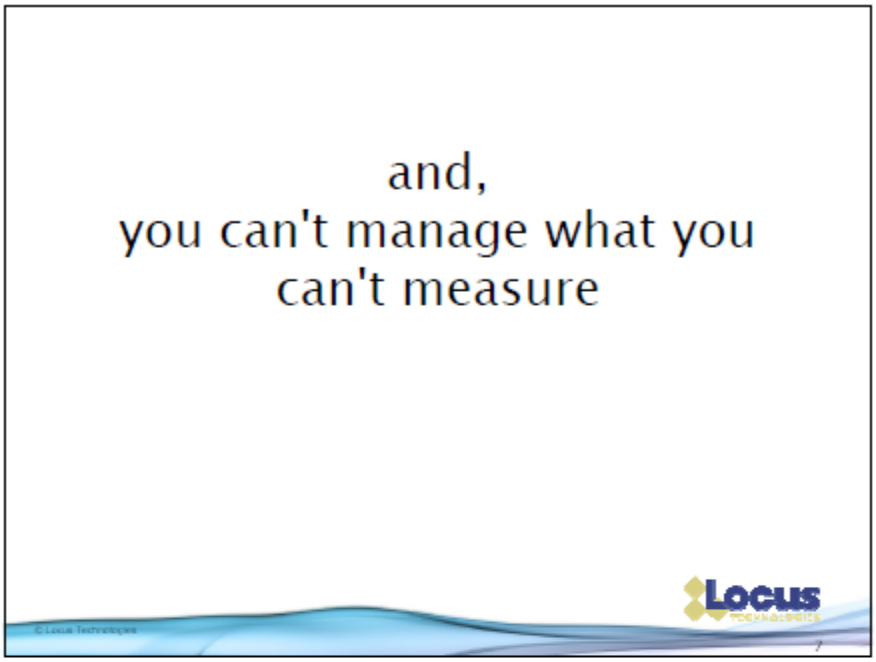

"You should have been here back in the old days before cloud computing."
Locus
© Locus Technologies
2

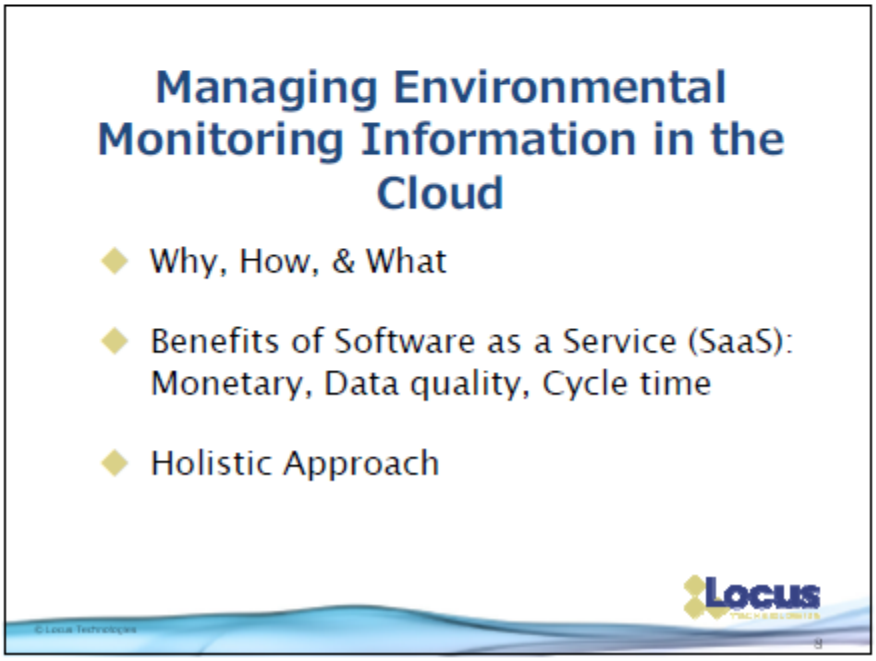

Why is it that within milliseconds you can find information on almost anything by typing a question into Google, but it may take hours or days to know if you had any NPDES permit violations in 2012 and what/where they were?
Locus


Environmental Information Management permeates virtually all aspects of environmental management, costs and performance
Locus


Many companies already own over 10 million analytical, geological, and "other" records across a portfolio of sites
Locus
5

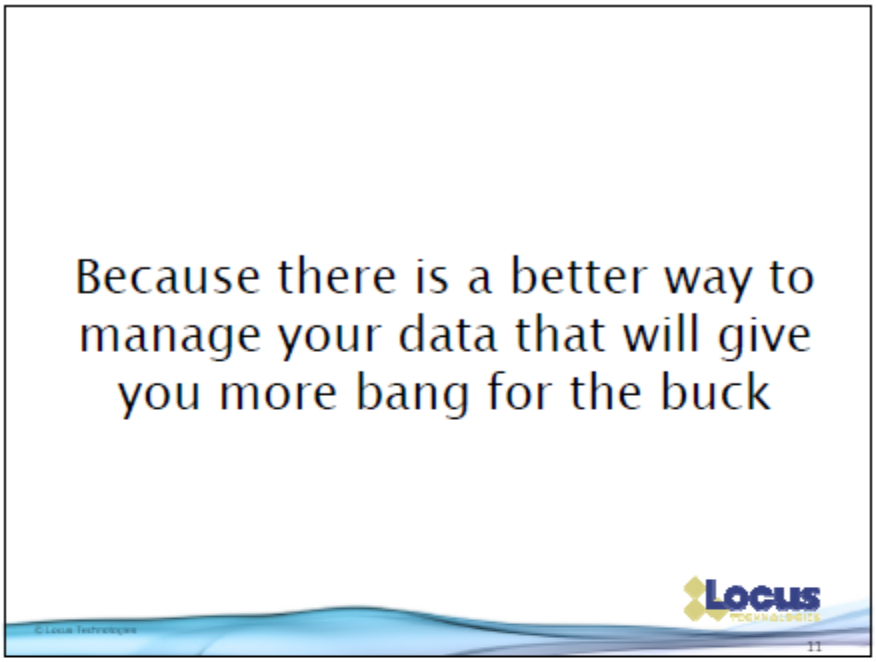

But they have no ability to efficiently mine data for actionable information
Locus
6

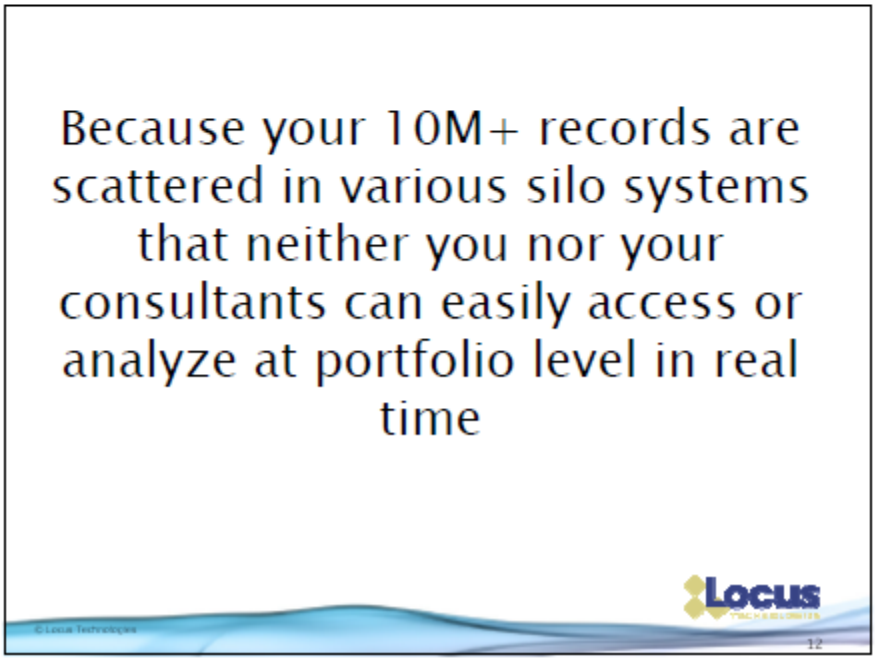

and,
you can't manage what you
can't measure
Locus


Managing Environmental Monitoring Information in the Cloud
Why, How, & What
Benefits of Software as a Service (SaaS): Monetary, Data quality, Cycle time
Holistic Approach
Locus


WHY
HOW
WHAT
Locus
9


Money
Time
Quality
Locus
10


Because there is a better way to manage your data that will give you more bang for the buck
Locus
11


Because your 10M+ records are scattered in various silo systems that neither you nor your consultants can easily access or analyze at portfolio level in real time
Locus
12



Plethora of hard to use applications hosted inside or outside the enterprise

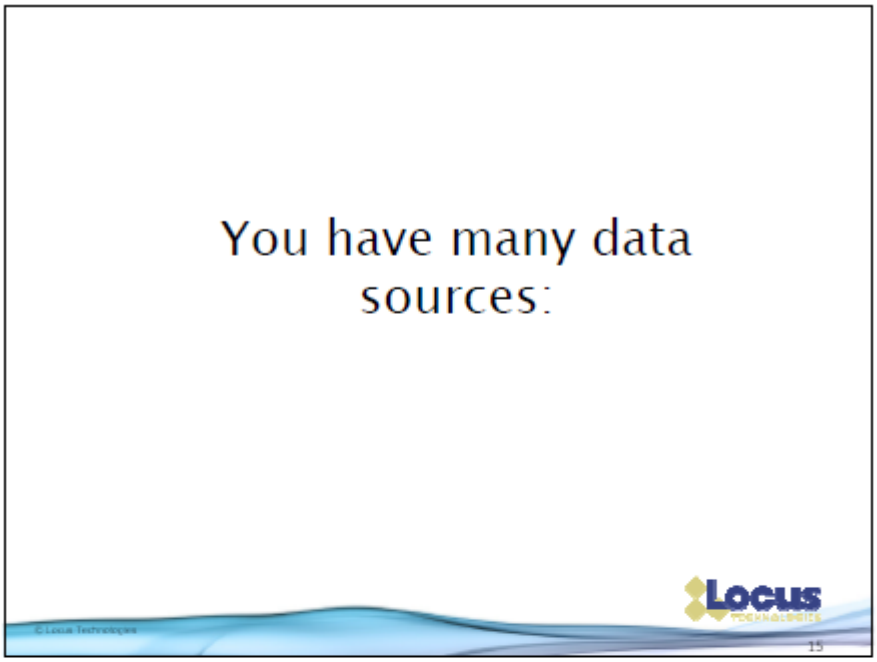
© Locus Technologies

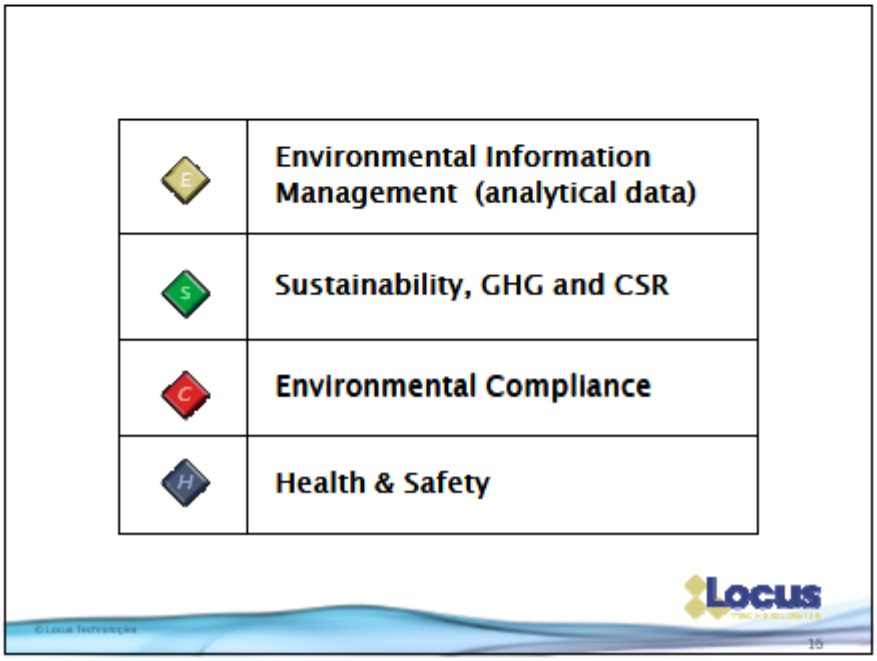
13

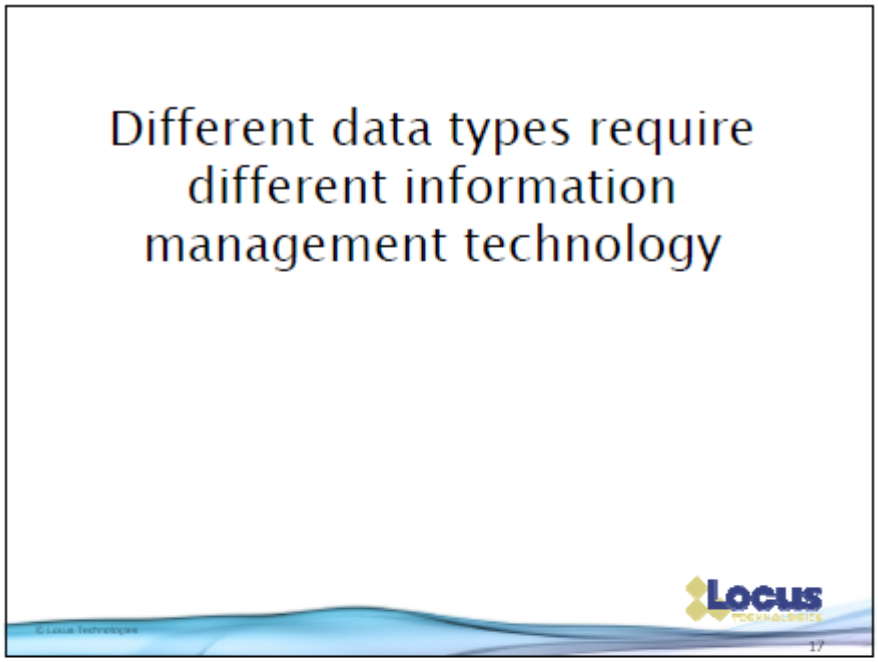
Different navigation systems and user experiences

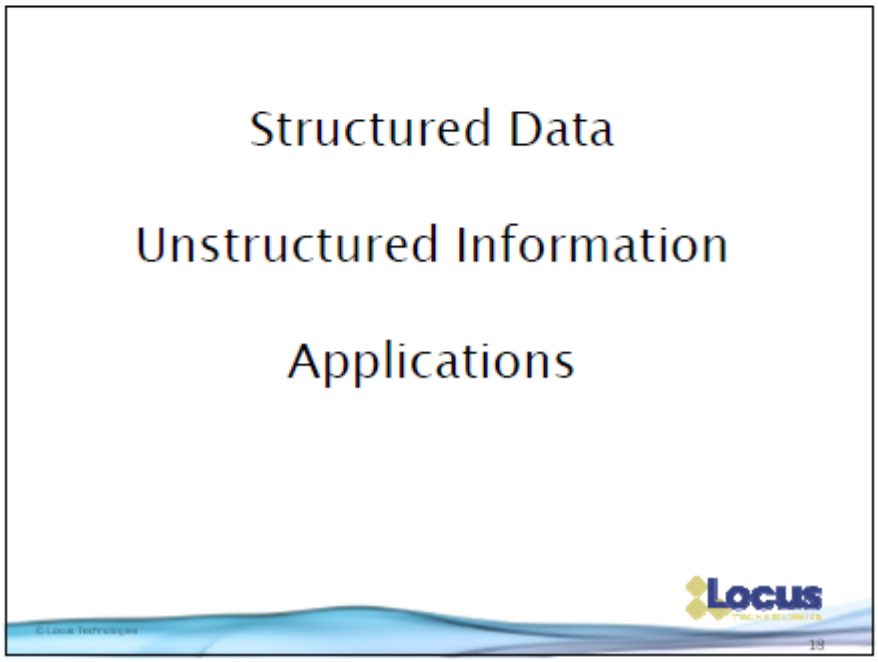
© Locus Technologies

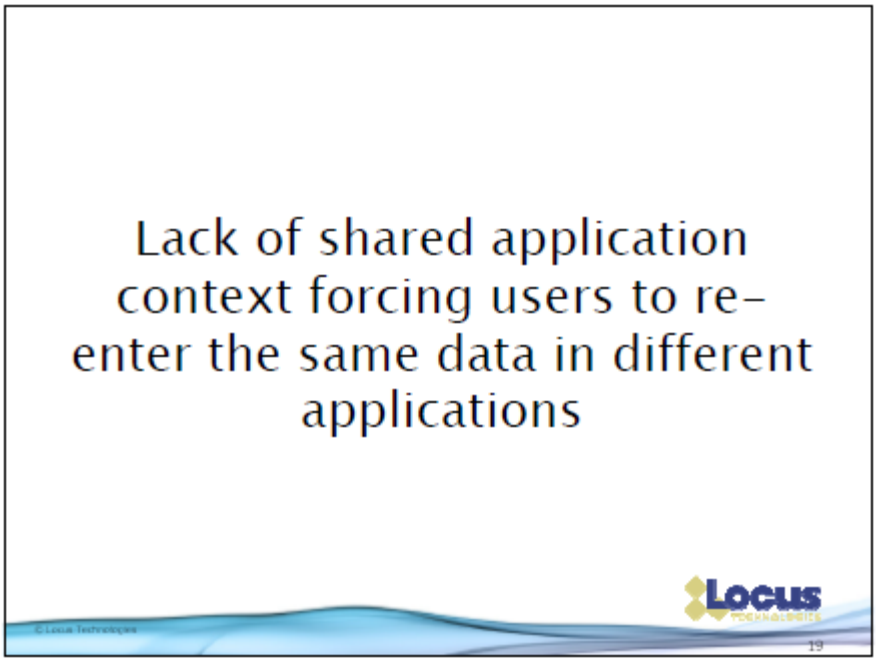
14

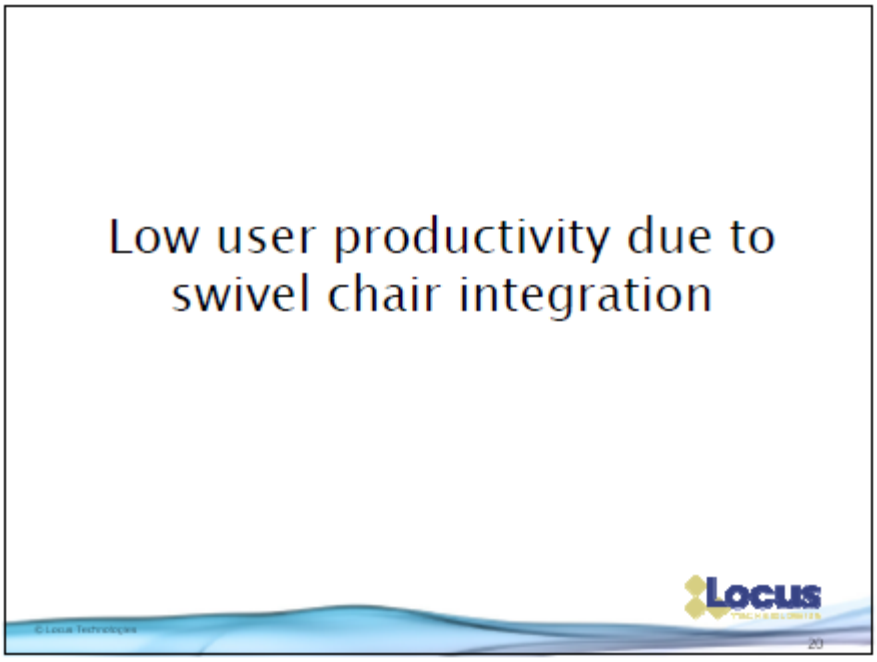

You have many data sources:
Locus
15

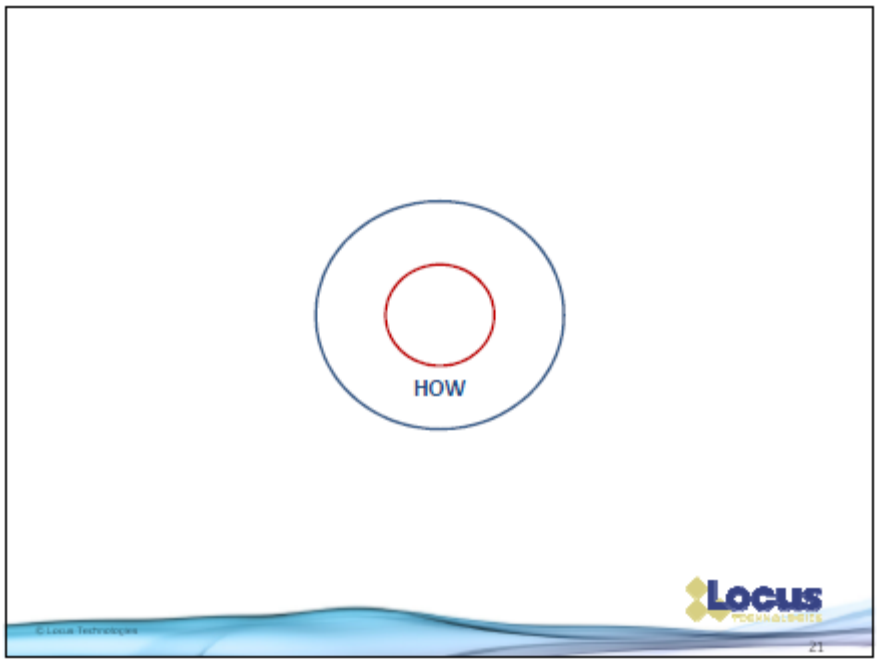

E
Environmental Information Management (analytical data)
S
Sustainability, GHG and CSR
C
Environmental Compliance
H
Health & Safety
Locus
16


Different data types require different information management technology
Locus
17


Structured Data
Unstructured Information
Applications
Locus
18

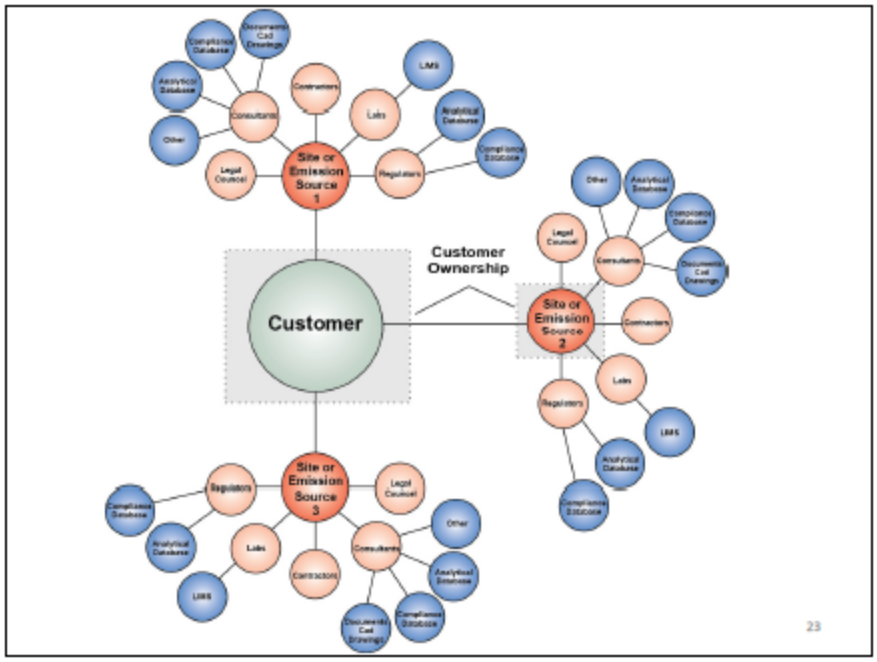

Lack of shared application context forcing users to re-enter the same data in different applications
Locus
19

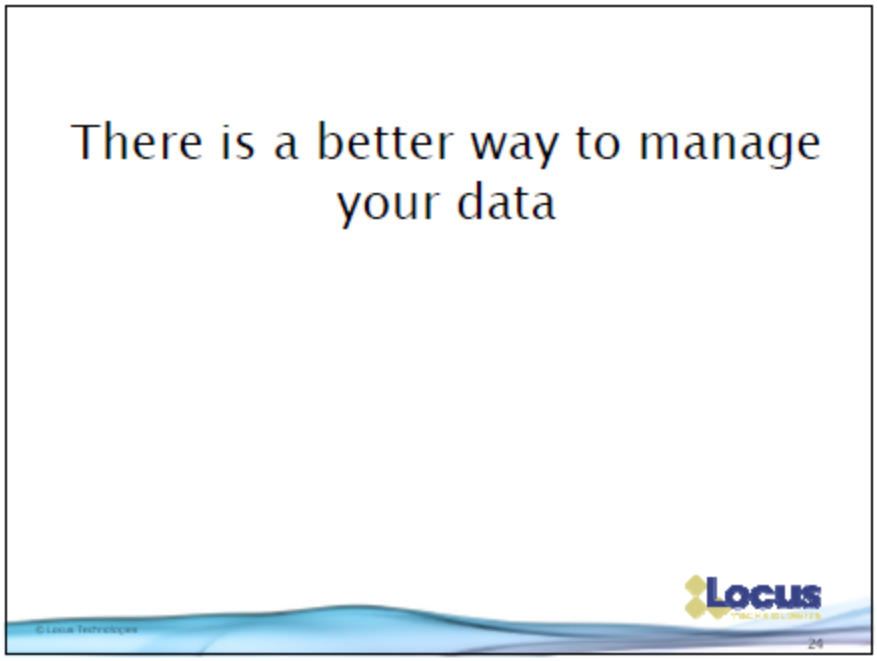

Low user productivity due to swivel chair integration
Locus
20

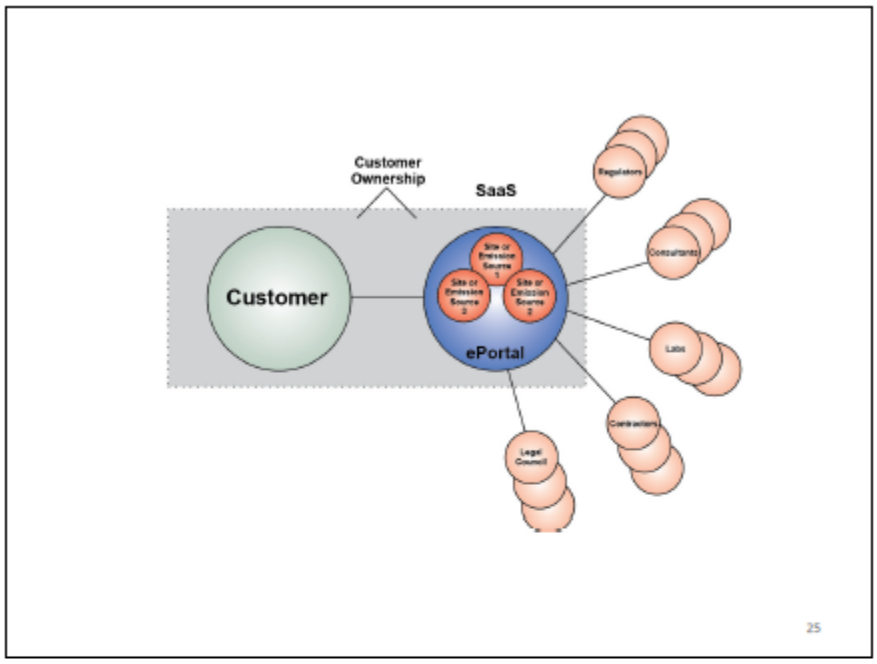


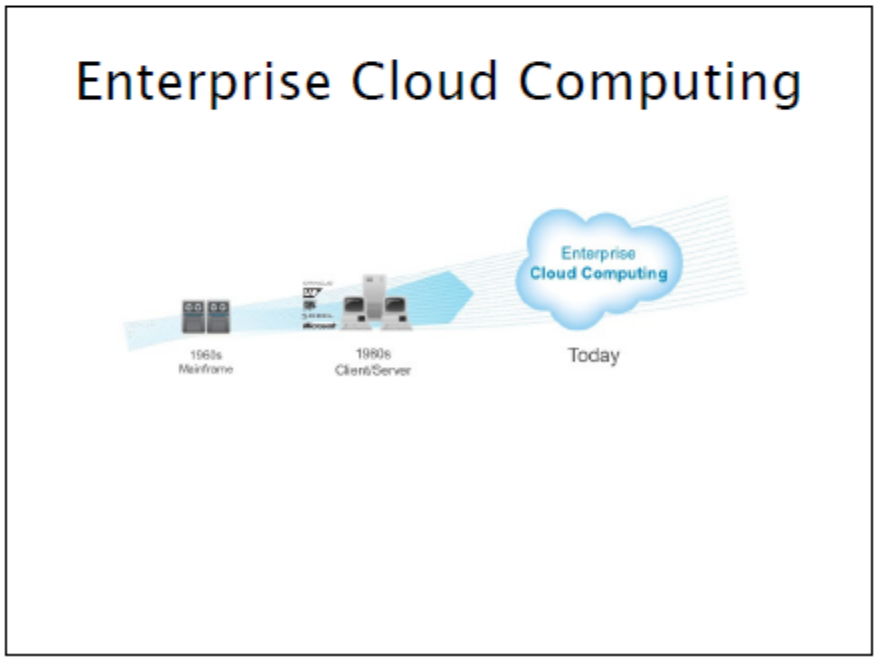
We believe companies should own and have easy access to their own environmental data in one centralized and integrated system in the Cloud.

Locus
22

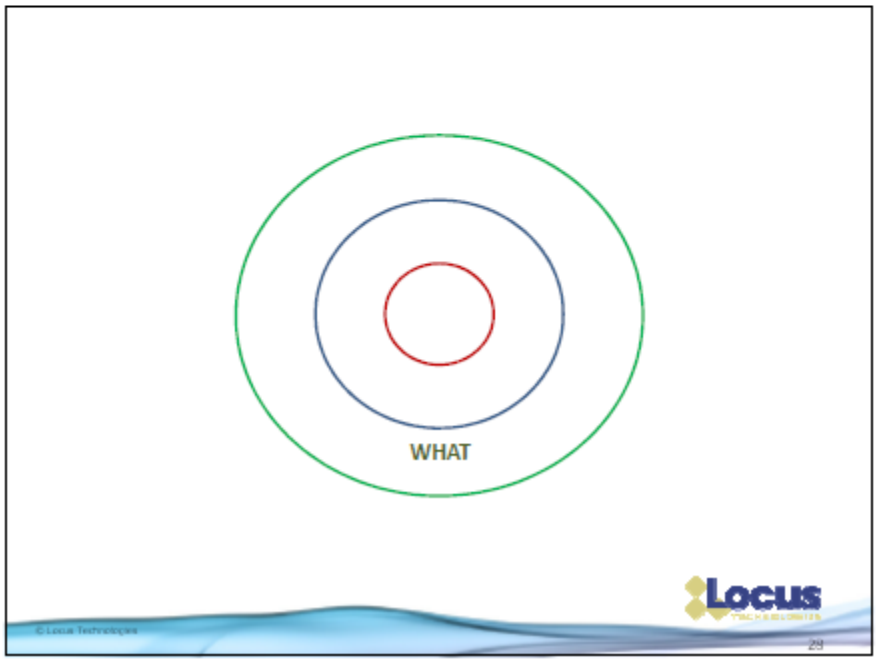

Customer
Customer Ownership
Site or Emission Source 1
Site or Emission Source 2
Site or Emission Source 3
Consultants
Labs
Regulators
Legal Counsel
Other
LIMS
Contractors
23


There is a better way to manage your data
Locus
24


Customer Ownership
SaaS
Customer
ePortal
Regulators
Consultants
Labs
Contractors
Legal Counsel
25


Enterprise Cloud Computing
Enterprise
Cloud Computing
1960s
Mainframe
1980s
Client/Server
Today


Your customers and employees are in the Cloud.
What about your company?
Locus
27

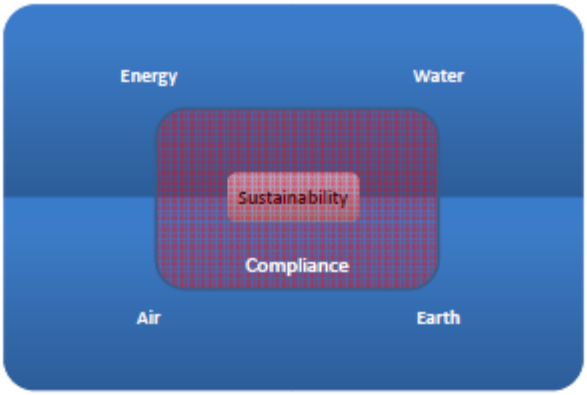

WHAT
Locus
29

Use a software platform that integrates applications across media and regulatory frameworks in the Cloud.

© Locus Technologies

29

Holistic Approach Across Organization



© Locus Technologies

30

Why SaaS Solution

- Significant cost reduction
- Pay only for what you consume
- Gain ownership of data
- Convenience and ease of use
- Rolling upgrade program
- Gain access to applications much faster
- Focus on innovation, not infrastructure





Locus TECHNOLOGIES

© Locus Technologies

31

SaaS shifts the cost of upgrades from the customer to the vendor, resulting in the rolling (and free) upgrade program.

Locus TECHNOLOGIES

© Locus Technologies

32

One change benefits all users instantly

Capitalize on the wisdom of the crowd

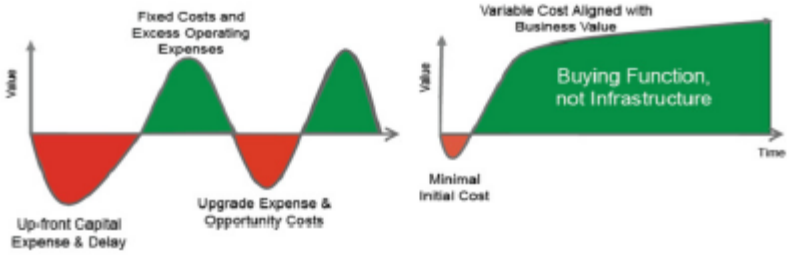
© Locus Technologies

33

Faster Results; Lower Risks; Predictable Costs

On-Premise Operations:
53% of software projects cost
189% of original estimate[1]

Cloud Computing:
Average 49% ROI
within 10 Months[2]



1 Standish Group, Chaos Report 2009

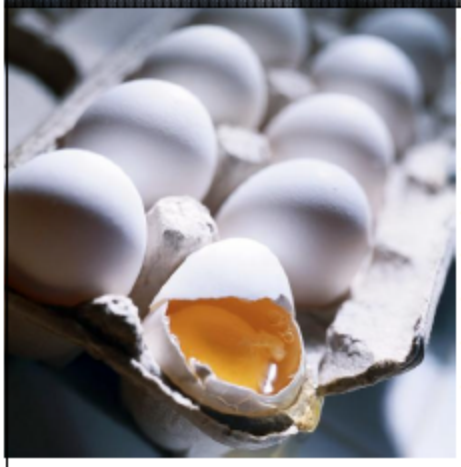
© Locus Technologies

34

But not all clouds are created equal

True SaaS	Other "Clouds"
Single instance of software—all customers	ASP
Multitenancy Databases	Web-based
Rolling and instant upgrade for all customers	Internet accessible
Seamless integration on demand	Separate instance, separate code base
Business-Driven Configurability	Separate upgrades
	Hardware and licensing costs

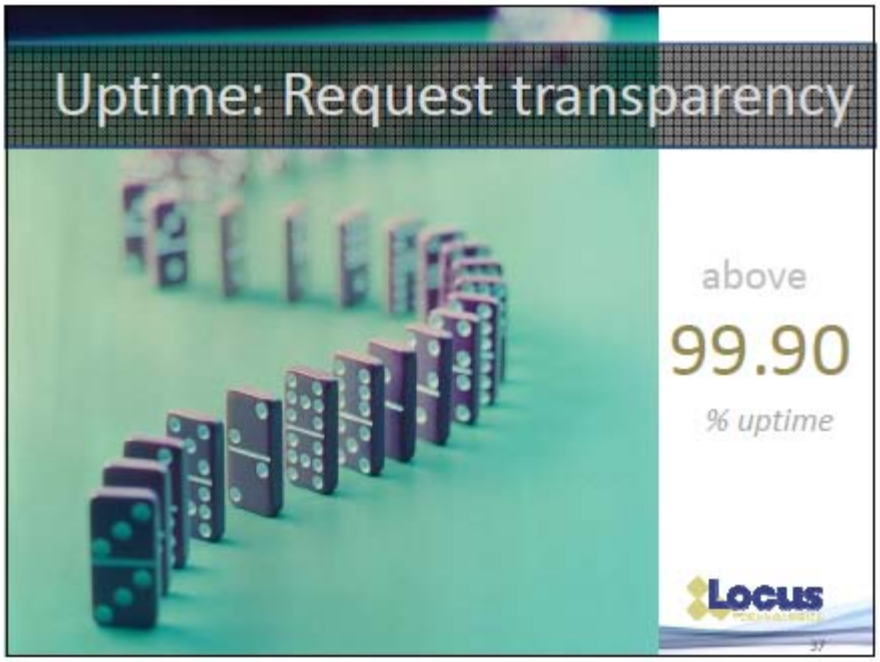
What is important for SaaS



- Time in the cloud
- Customer Installed base
- Certification (SAS70/SSAE-16)
- Monitoring transparency
- Data replication and storage
- Network Outage
- Catastrophic events
- Backups and Security
- Network Intrusion

Locus

© Locus Technologies


Uptime: Request transparency
above
99.90
% uptime
Locus


Monetary Benefits
Locus

Significant cost reduction, ROI, ROO

© Locus Technologies

Data Quality Benefits



© Locus Technologies

Corporations realize significant qualitative benefits from a centralized web-based system. Although more difficult to quantify, they are equally or more important than quantitative savings.

© Locus Technologies

41

Every decision you make about your sites hinges on the quality of your data.

If you don't own it, you cannot access it, so how do you know how good or bad it is?

© Locus Technologies

42

Reduce Cycle Time



Locus TECHNOLOGIES

© Locus Technologies

43

Reduce cycle time for data loading, validation, management, and reporting—all error free with zero defects

Locus TECHNOLOGIES

© Locus Technologies

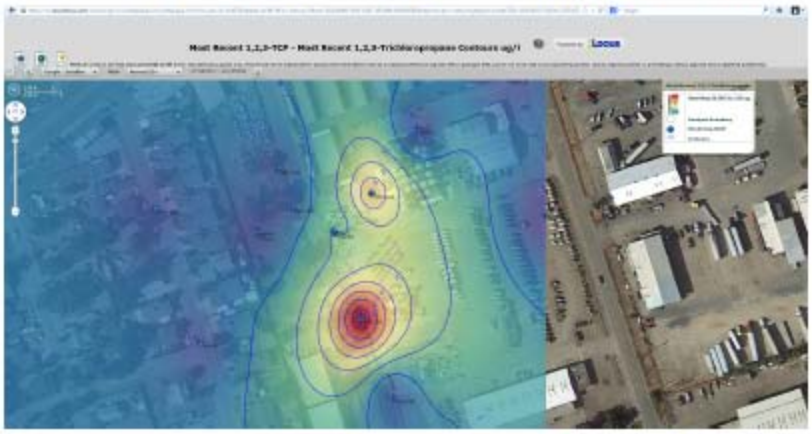
44

Automate regulatory reporting

With a single click if possible



Extent of 1,2,3-TCP contamination?





We've been down this road many times before

It's a struggle at first,
but in the end,
You will come ahead

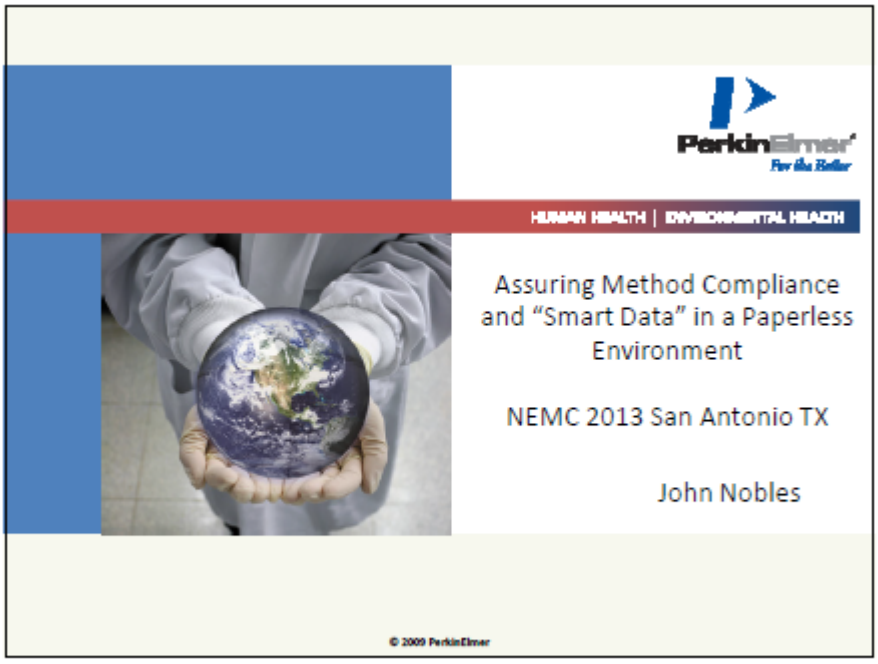

For more information contact
info@locustec.com
+1-650-960-1640
Locus
TECHNOLOGIES
Locus
TECHNOLOGIES
© Locus Technologies
49

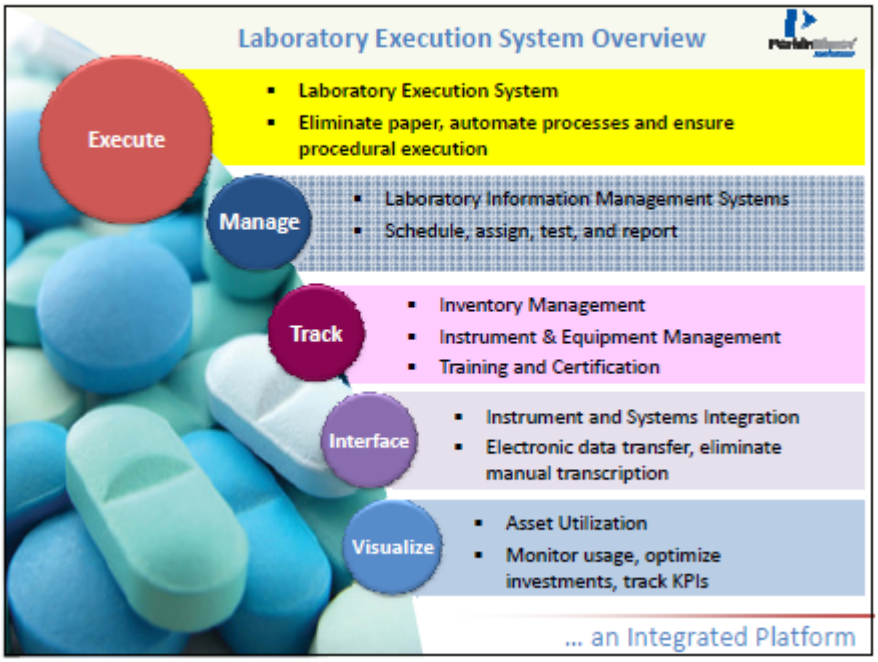
Making Informed Decisions through LIMS Data Exploration and Visualization

John Nobles
PerkinElmer, Inc.

Abstract

New data mining and visualization tools offer a unique approach to extracting and compiling data from disparate databases and electronic files. Users are empowered to create dynamic dashboards on-the-fly and evaluate data across different agencies at the federal, state and local levels. The software can also be configured to provide the same access from databases at a specific site, and provide mashup without having to write custom interfaces between various applications in use.


PerkinElmer
For the Better
HUMAN HEALTH | ENVIRONMENTAL HEALTH
Assuring Method Compliance and "Smart Data" in a Paperless Environment
NEMC 2013 San Antonio TX
John Nobles
© 2009 PerkinElmer


Laboratory Execution System Overview
Execute
Laboratory Execution System
Eliminate paper, automate processes and ensure procedural execution
Manage
Laboratory Information Management Systems
Schedule, assign, test, and report
Track
Inventory Management
Instrument & Equipment Management
Training and Certification
Interface
Instrument and Systems Integration
Electronic data transfer, eliminate manual transcription
Visualize
Asset Utilization
Monitor usage, optimize investments, track KPIs
... an Integrated Platform

Procedures based LES dramatically enhances lab productivity

Problems with paper



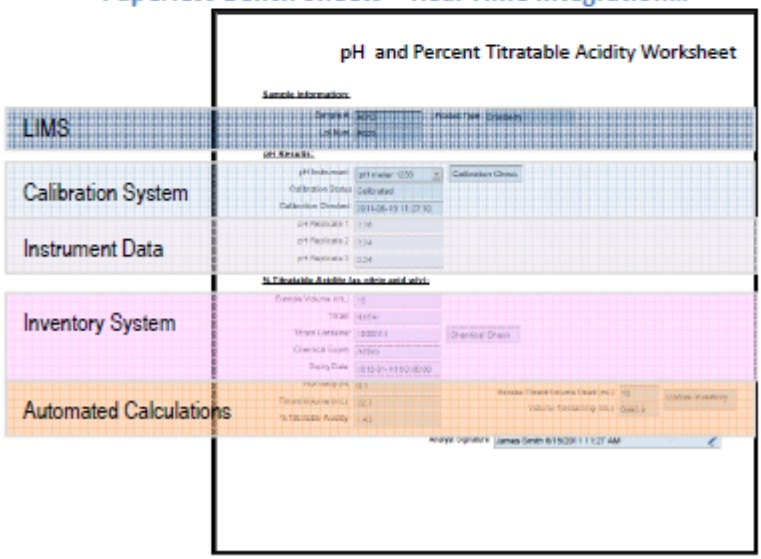
- Illegible handwriting/transcription errors
- Information recorded where it should not be
- Image printed/pasted onto page
-Storage and Retrieval Concerns
- Ultimately no control

Benefits of Automation

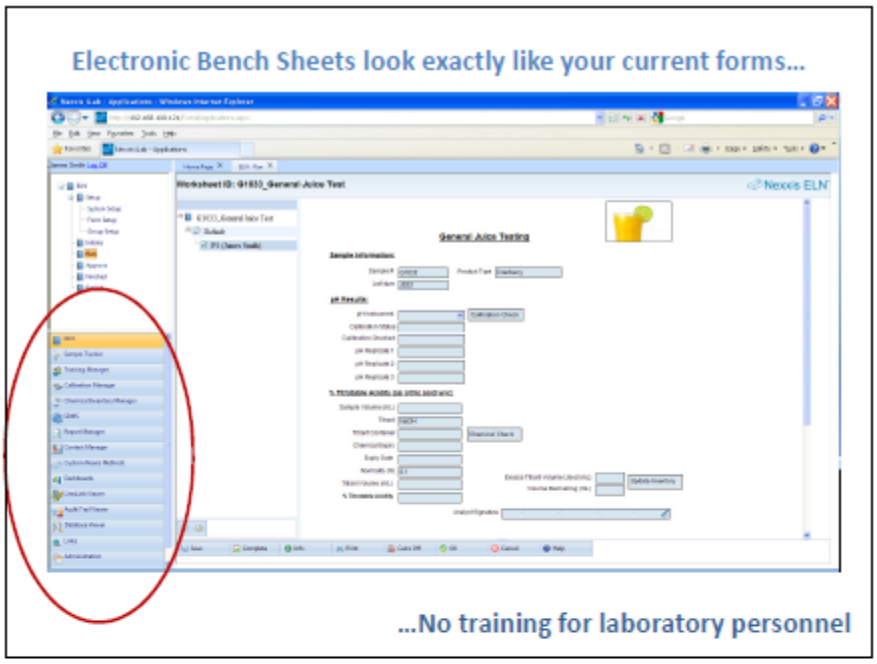


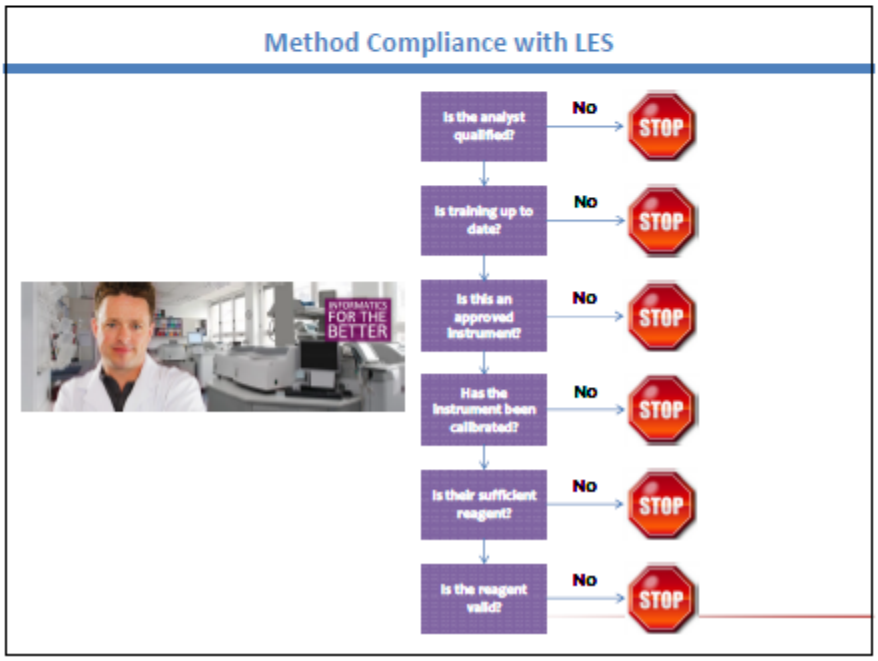
- Legible text
- All information electronically traced
- Selection from pre-defined lists
- Electronic signature
- Insert image electronically (Easily and Quickly retrieved)
- Controlled execution –step by step

Paperless Bench Sheets – Real Time Integration…

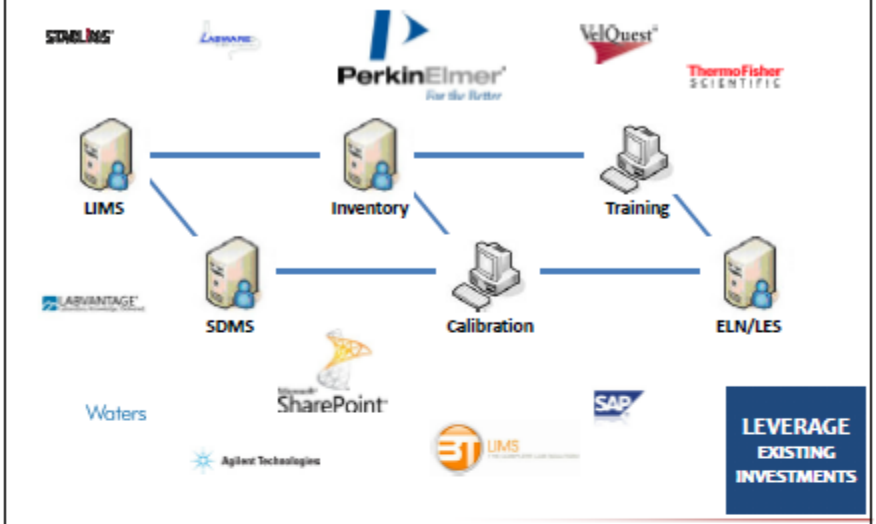


…ENFORCE EVERY STEP OF THE SOP/METHOD


Electronic Bench Sheets look exactly like your current forms...
...No training for laboratory personnel


Method Compliance with LES
Is the analyst qualified?
No
STOP
Is training up to date?
No
STOP
Is this an approved instrument?
No
STOP
Has the instrument been calibrated?
No
STOP
Is their sufficient reagent?
No
STOP
Is the reagent valid?
No
STOP
INFORMATICS FOR THE BETTER

Truly Vendor Neutral



Work with any existing technologies

Scenario One – Disparate Databases

THE SAGA OF A HAMBURGER

- A significant obstacle to the consistent data exchange deliverables are the sheer number of networks and reporting requirements. Following public consumption of a tainted hamburger, a laboratory must:
- Send the data to FDA if it's the lettuce, ketchup, mayo, or bun
- Send the data to USDA if it's the meat
- Send the data to CDC and the state lab if someone became ill
- If it is a biological contamination, send the data to one CDC network
- If it is a chemical contaminant, send the data to a different CDC network
- Send the data to EPA if the food was contaminated due to environmental concerns
- Different EPA networks exist for water, waste, air and response mitigation.
- Lab data must be formatted for each program and then sent through multiple networks.
- A single laboratory section in EPA RTP, NC has over 50 disparate segmented databases.
- How many does your lab have?

APHL White Paper

Laboratory Information Management Systems (LIMS) use variable formats to meet the various reporting requirements of federal agencies. There is a critical need for the creation of a "standard" for reporting analytical data including quality control data associated with the analysis of environmental samples. Such a format will allow data receivers to quickly check submissions from multiple laboratories for analytical data quality prior to decision making.

Jack Krueger, APHL Informatics Consultant

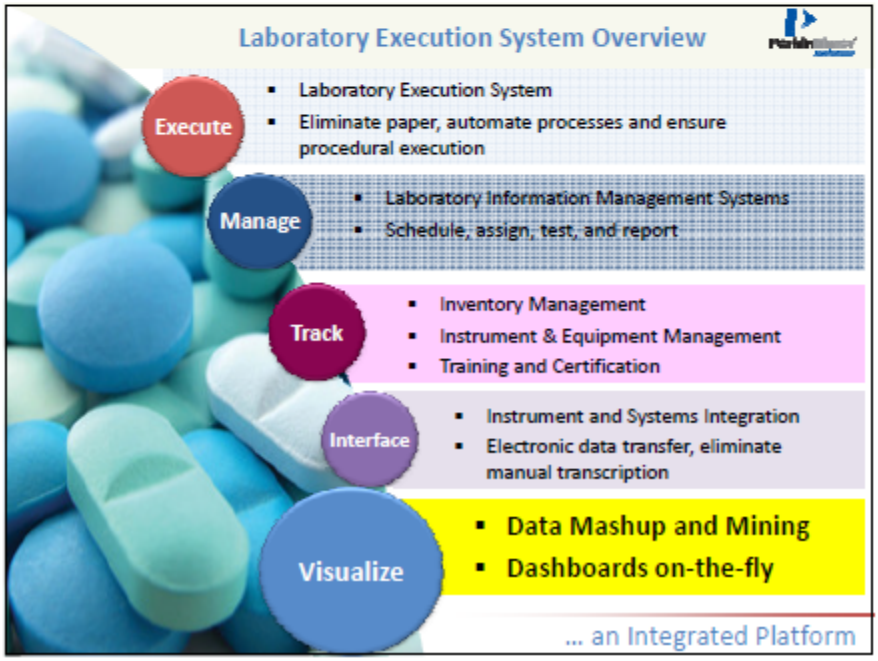
APHL White Paper

- Environmental health laboratories support many local, state and federal programs, such as:

- **emergency preparedness and response,**
- **biomonitoring,**
- **food safety,**
- **radiation exposure assessment,**
- **drinking water quality,**
- **waste water treatment,**
- **solid waste testing,**
- **environmental exposure assessment.**

APHL White Paper

- In 2010, a verbal survey of the APHL Environmental Health Committee, Environmental Laboratory Subcommittee and Informatics Committee members indicated that few are capable of automatically producing an electronic data deliverable used by EPA for emergency response.
- A goal of this project is to provide a standard electronic data deliverable that can meet multiple agency/client needs. Laboratories participate in multiple federal response networks, requiring them to communicate analytical results in a standardized, interoperable and secure format. Such communication is particularly important during times of emergency. Each of the federal agency laboratory response networks (CDC, FDA, USDA, EPA) require different EDDs from laboratories.



Without a common deliverable format, how do we..



Emergence of Data Discovery and Visualization "SMART DATA"



Spotfire for data mining



Freely explore data without the need for IT tasks such as creating complex queries, modeling dimensions, or defining navigational paths.

Combine data from disparate sources to gain a comprehensive view of the business & make better decisions faster

The Spotfire Approach

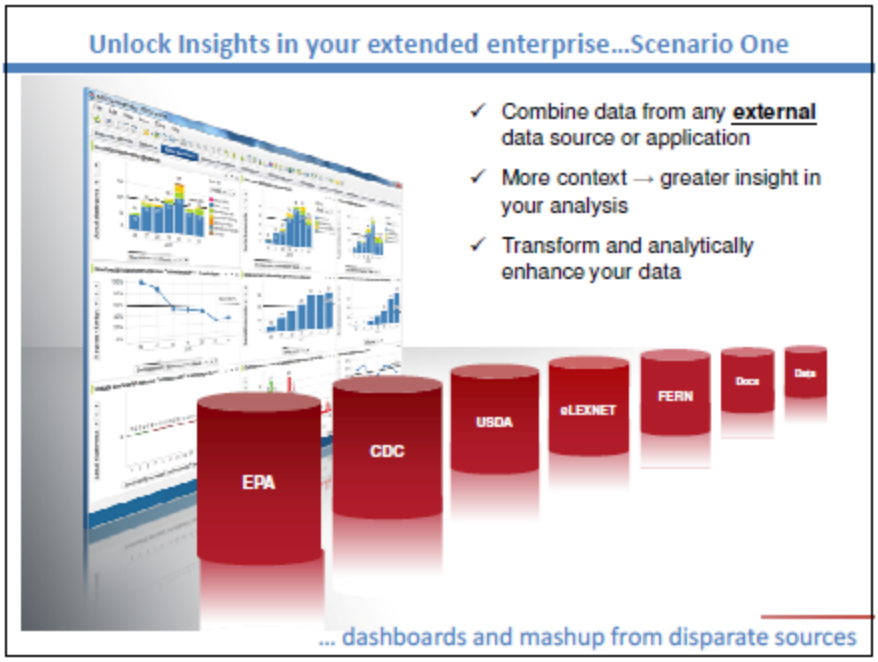
Empowers users to freely explore their data
- *Not limited by predefined views or aggregations*
- *No barriers or delays—no IT programming required*

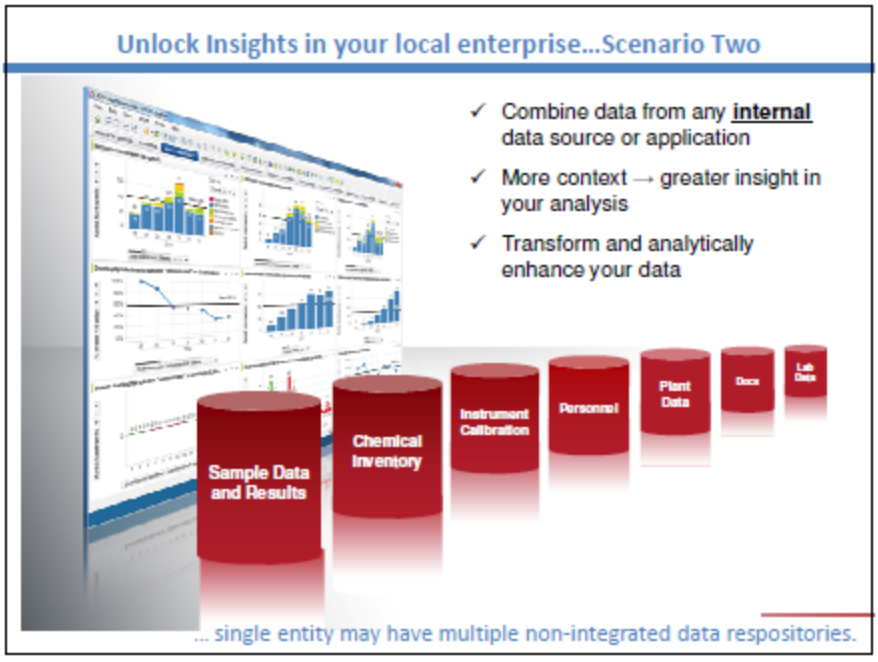
Users can answer their questions without restriction
- *Ad hoc data analysis*
- *Freely move from known to unanticipated questions*
- *Fastest to actionable insight*

Universal analytics platform
- *Applicable across any process, function, or use case*
- *Data visualization, predictive analytics, event-driven analytics*
- *Analytic Dashboards for better decision making across the organization*

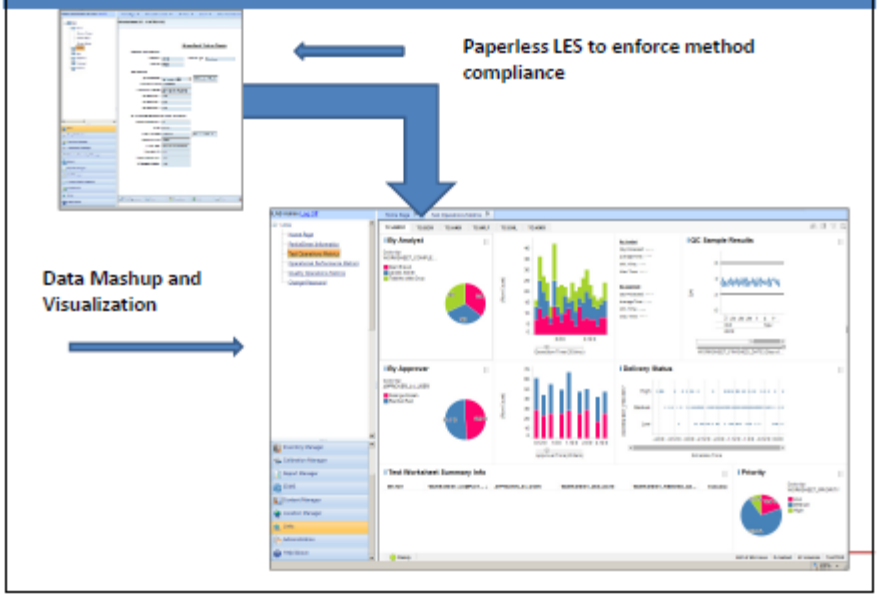


First to insight. First to Action.


Unlock Insights in your extended enterprise...Scenario One
✓ Combine data from any external data source or application
✓ More context → greater insight in your analysis
✓ Transform and analytically enhance your data
EPA
CDC
USDA
eLEXNET
FERN
... dashboards and mashup from disparate sources


Unlock Insights in your local enterprise...Scenario Two
✓ Combine data from any internal data source or application
✓ More context → greater insight in your analysis
✓ Transform and analytically enhance your data
Sample Data and Results
Chemical Inventory
Instrument Calibration
Personnel
Plant Data
... single entity may have multiple non-integrated data respositories.

Lab Execution System & Data Mining



Analytic Dashboards

Key Features

- Interactive Summary Views with
  - Dynamic Values
  - Wide range of Conditional Icons
  - Sparklines
- Drill-down navigation
- Driven by filters, user control



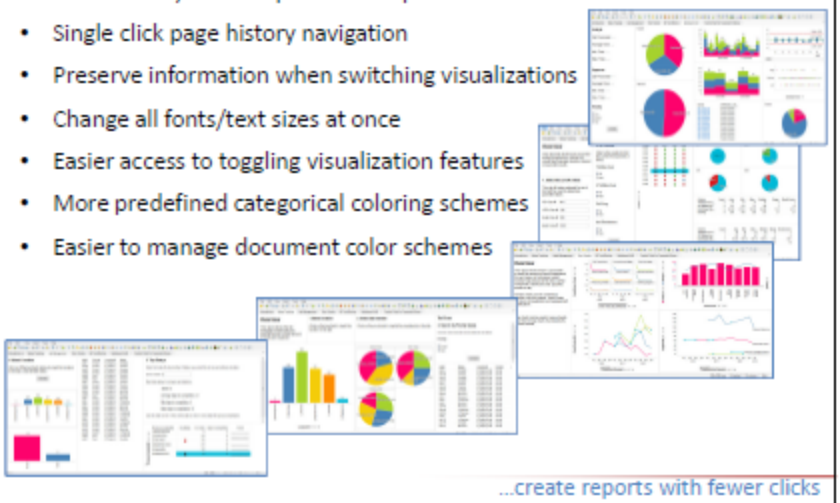
Key Benefits

- Key metrics at a glance
- Quickly see everything needed on a single screen
- Easily & intuitively spot patterns, exceptions, trends and outliers
- Quickly drill into details when needed

...increase productivity and improve data-driven decision making!

Easy to Build Dashboards

- Fixed size layouts to optimize for specific devices and screens
- Single click page history navigation
- Preserve information when switching visualizations
- Change all fonts/text sizes at once
- Easier access to toggling visualization features
- More predefined categorical coloring schemes
- Easier to manage document color schemes



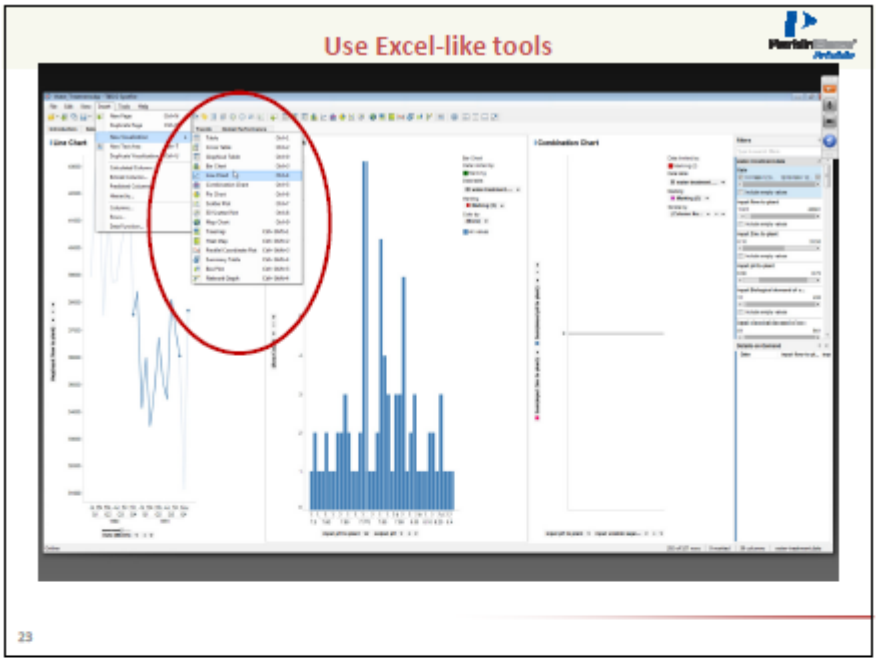
...create reports with fewer clicks

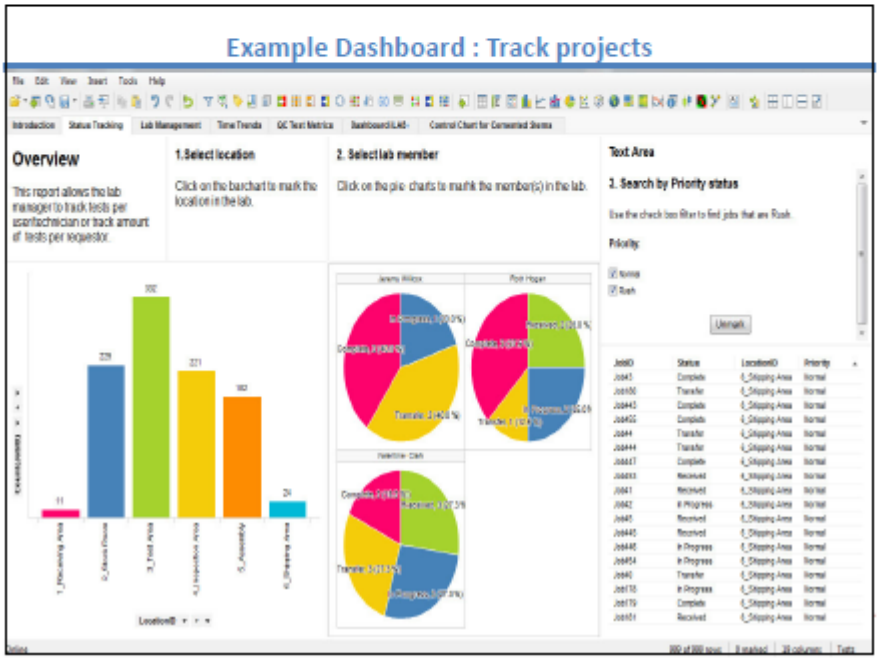
... can be used to create Lab Management Dashboards

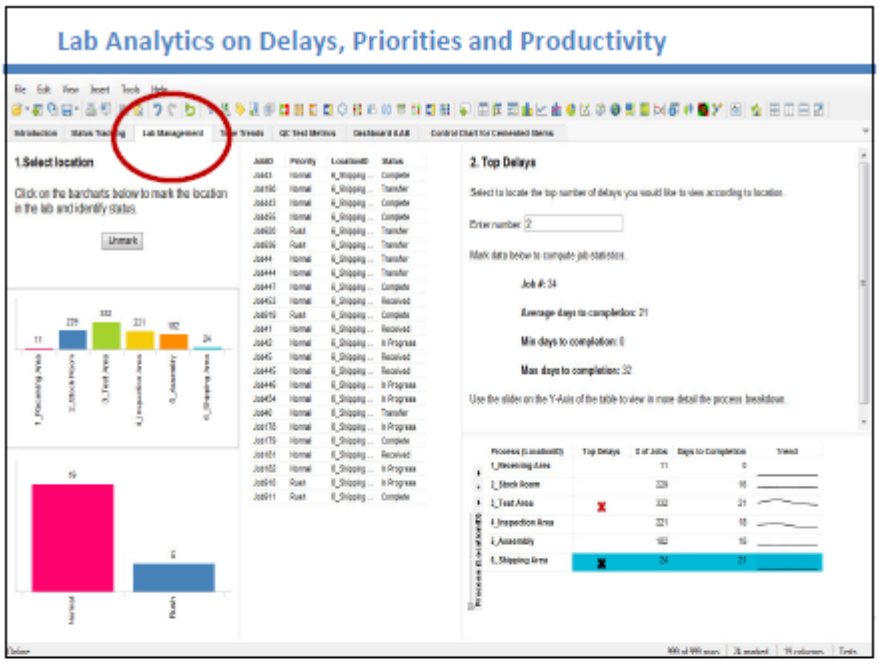
- Efficiently organize day-to-day work in the Lab
  - Track, assign & manage requests & report the results
  - Monitor testing progression
  - Monitor backlogs
- Test Metrics
  - Track tests per user/technician
  - Track amount of tests per requestor
- Lab Management
  - Transparence system to track amount of work requested for each piece of instrument
  - Monitor total amount of the time when instrument is down per year
  - Prioritize limited number of requests per requestor
- Project Management
  - Assign est. cost to each test to understand value of tests
  - Track total cost of spend per project
  - Project/test priority capability
  - Track amount of tests per project

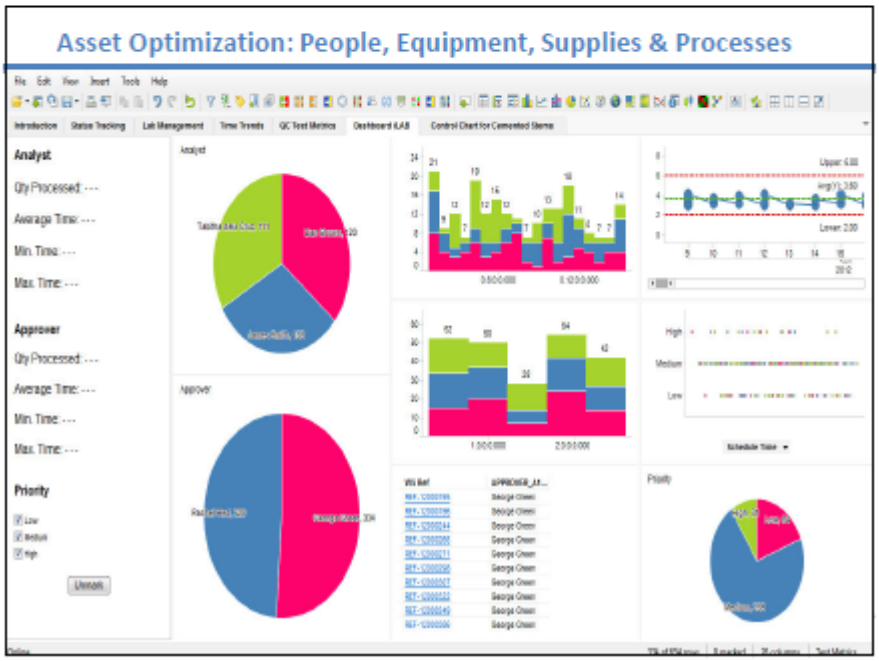
22

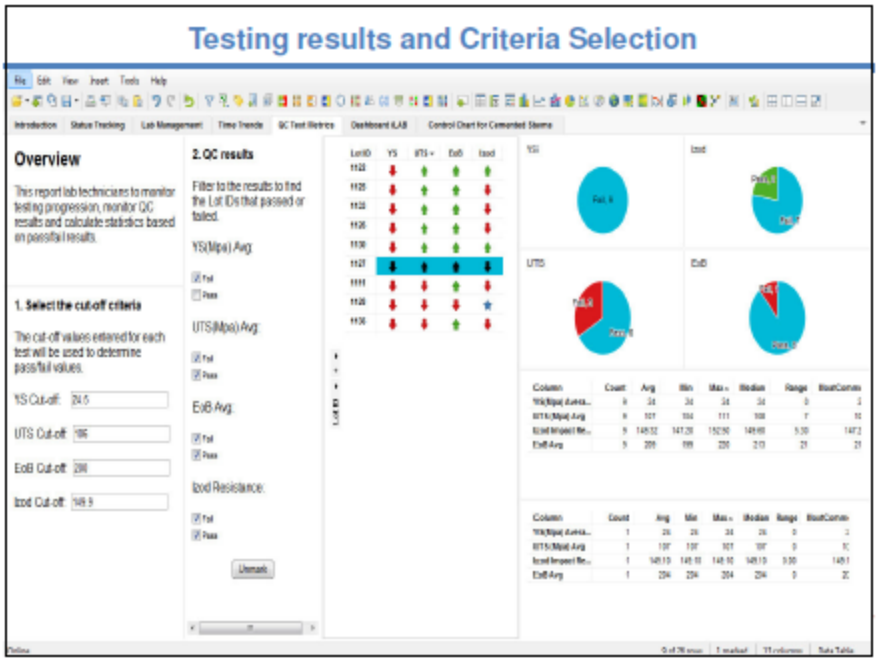
...quick insight to the data

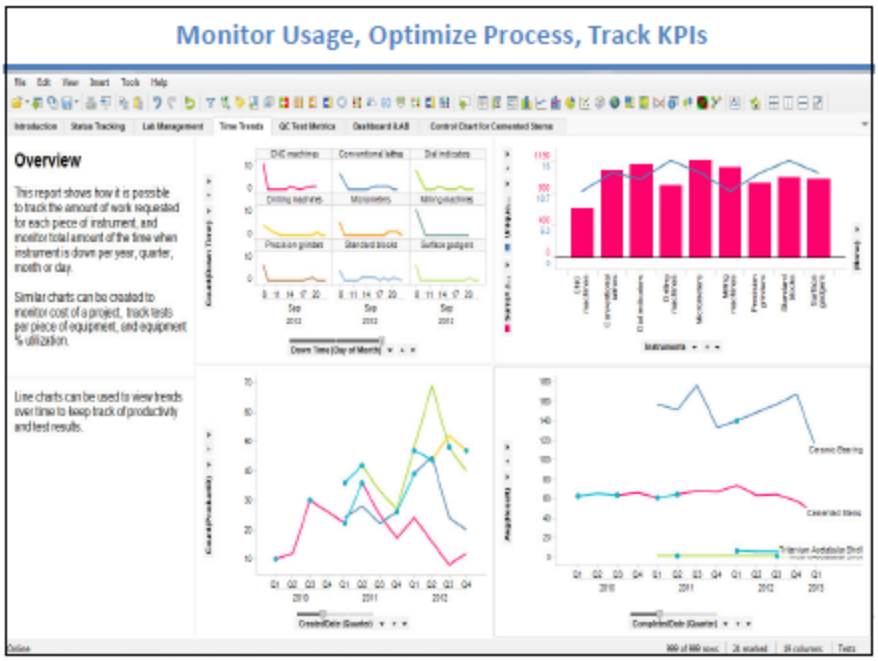

Use Excel-like tools
23


Example Dashboard : Track projects
Overview
1.Select location
2. Select lab member
Text Area
3. Search by Priority status

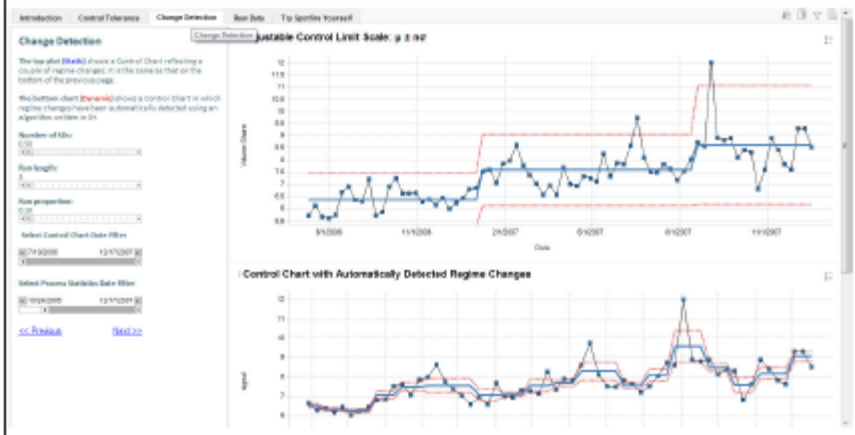

Lab Analytics on Delays, Priorities and Productivity
1.Select location
Click on the barcharts below to mark the location in the lab and identify status
Unmark
2. Top Delays
Select to locate the top number of delays you would like to view according to location
Enter number: 2
Mark data below to compute job statistics
Job #: 34
Average days to completion: 21
Min days to completion: 0
Max days to completion: 32
Use the slider on the Y-Axis of the table to view in more detail the process breakdown


Asset Optimization: People, Equipment, Supplies & Processes
Analyst
Qty Processed: ---
Average Time: ---
Min. Time: ---
Max. Time: ---
Approver
Qty Processed: ---
Average Time: ---
Min. Time: ---
Max. Time: ---
Priority
Low
Medium
High
Unmark


Testing results and Criteria Selection
Overview
This report lab technicians to monitor testing progression, monitor QC results and calculate statistics based on pass/fail results.
1. Select the cut-off criteria
The cut-off values entered for each test will be used to determine pass/fail values.
YS Cut-off:
UTS Cut-off:
ExB Cut-off:
Izod Cut-off:
2. QC results
Filter to the results to find the Lot IDs that passed or failed.
YS(Mpa) Avg:
UTS(Mpa) Avg:
ExB Avg:
Izod Resistance:
Unmark

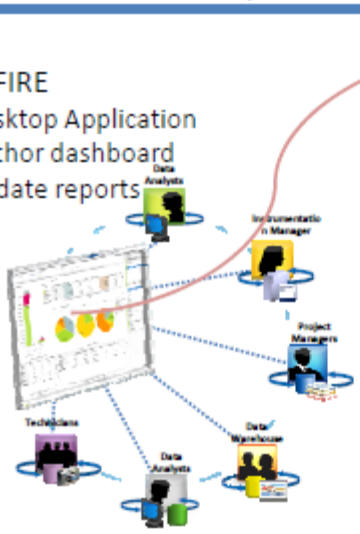

Monitor Usage, Optimize Process, Track KPIs
Overview
This report shows how it is possible to track the amount of work requested for each piece of instrument, and monitor total amount of the time when instrument is down per year, quarter, month or day.
Similar charts can be created to monitor cost of a project, track tests per piece of equipment, and equipment % utilization.
Line charts can be used to view trends over time to keep track of productivity and test results.

Control Charts



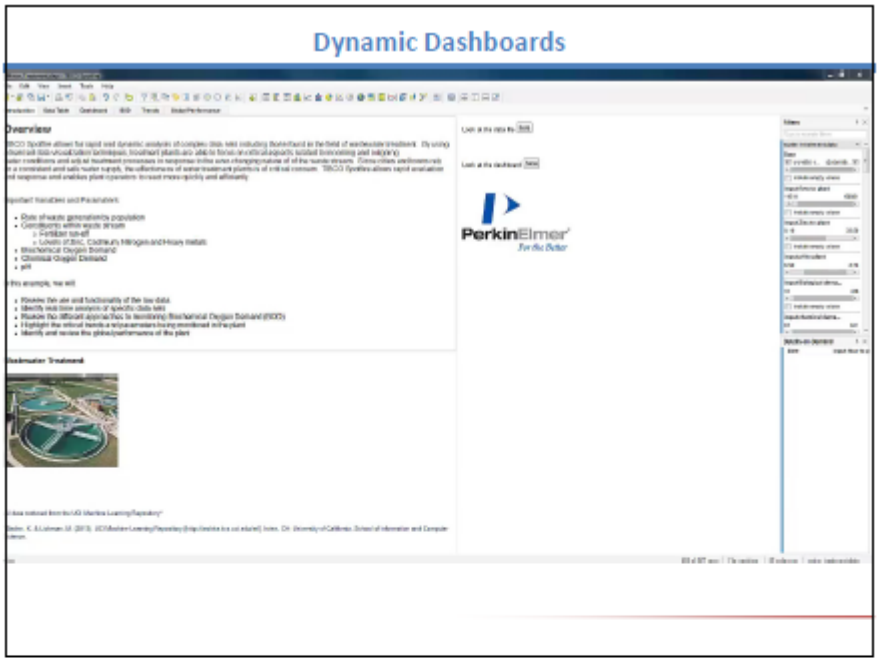
Easy Collaboration and Report Generation All-in-One Solution

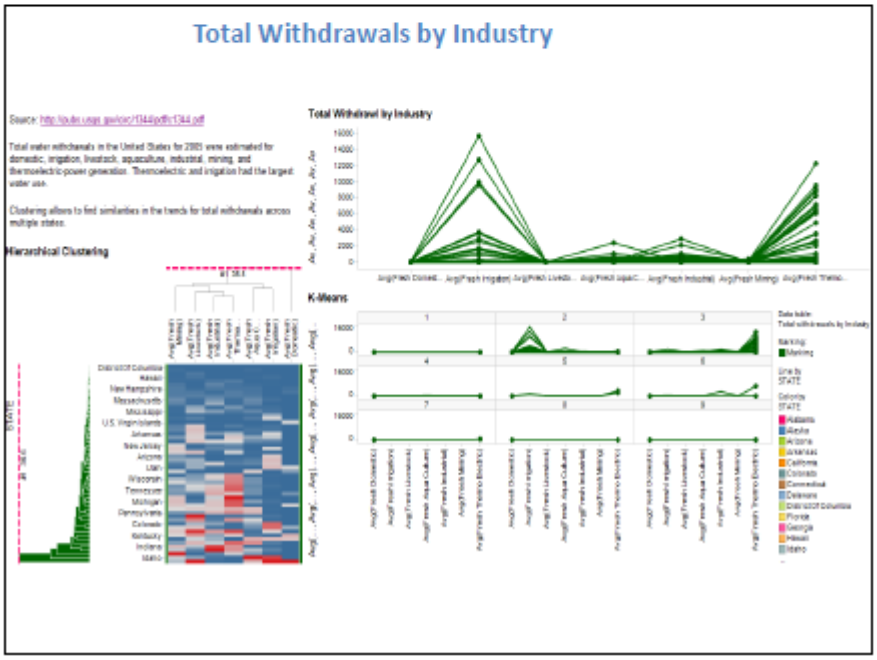
- SPOTFIRE
  - Desktop Application
  - Author dashboard
  - Update reports

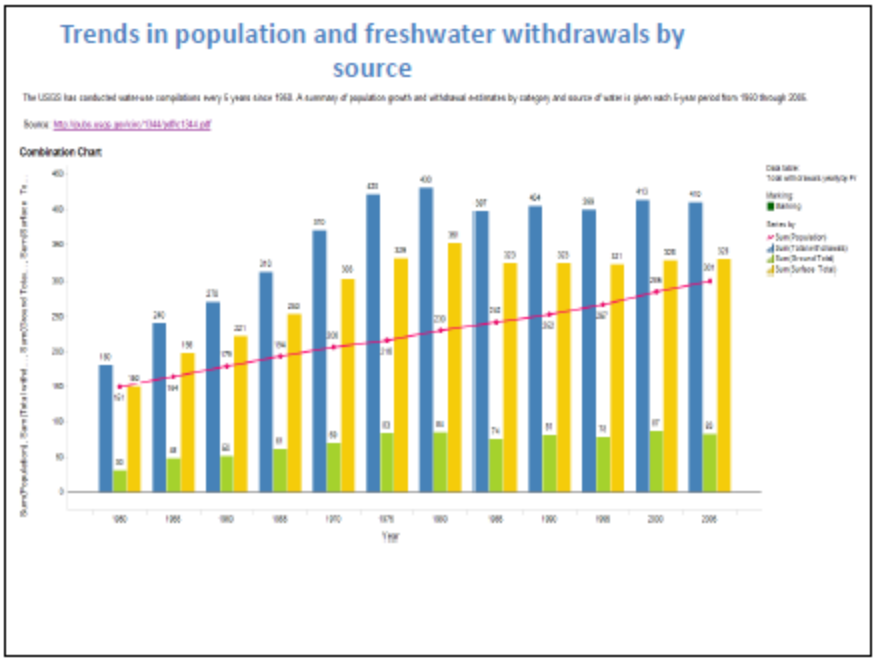


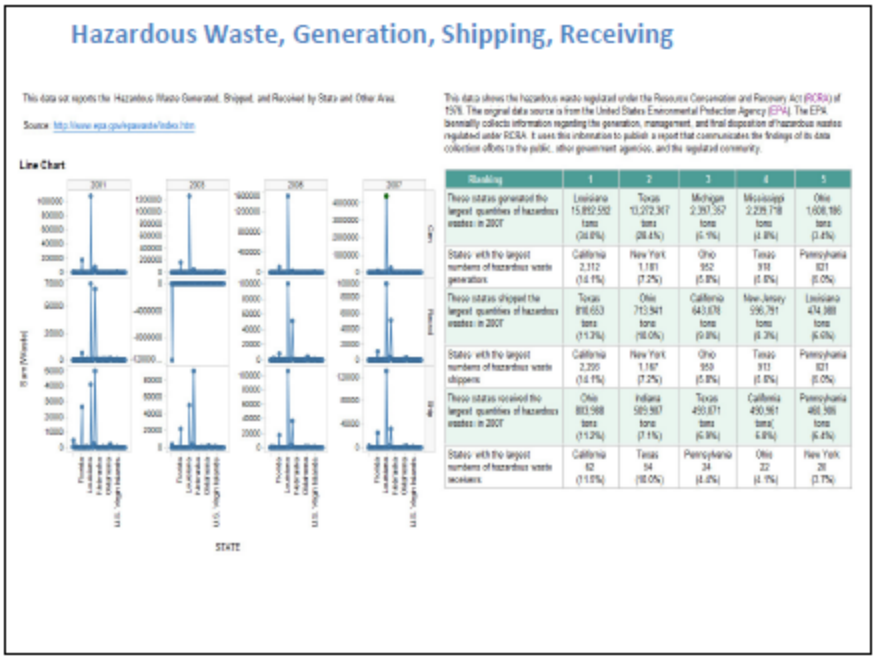


- WebPlayer
  - Online report
  - Zero-Installation
  - Read-only Views
  - Interactive interface

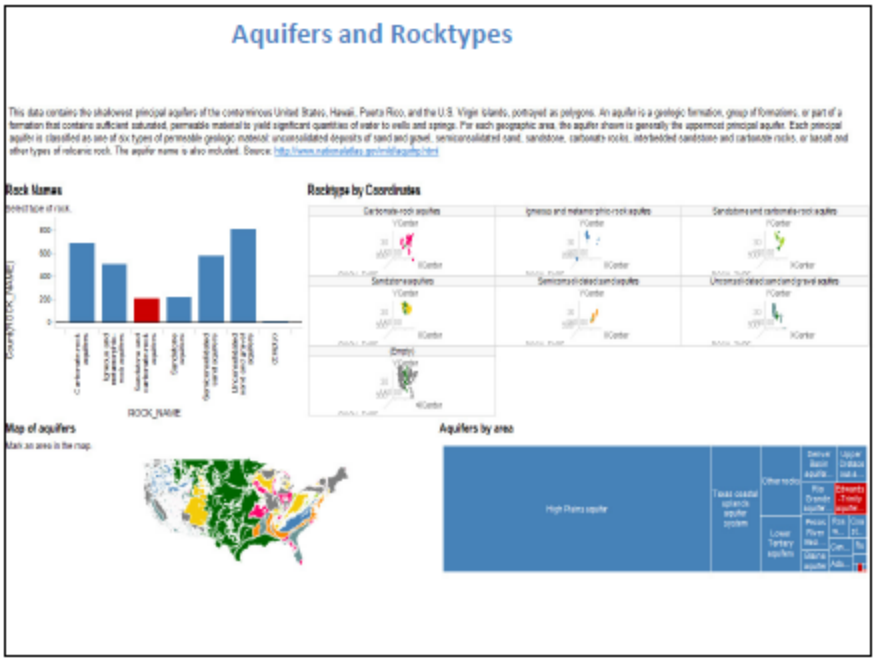

Dynamic Dashboards
Overview
PerkinElmer
To Be Better

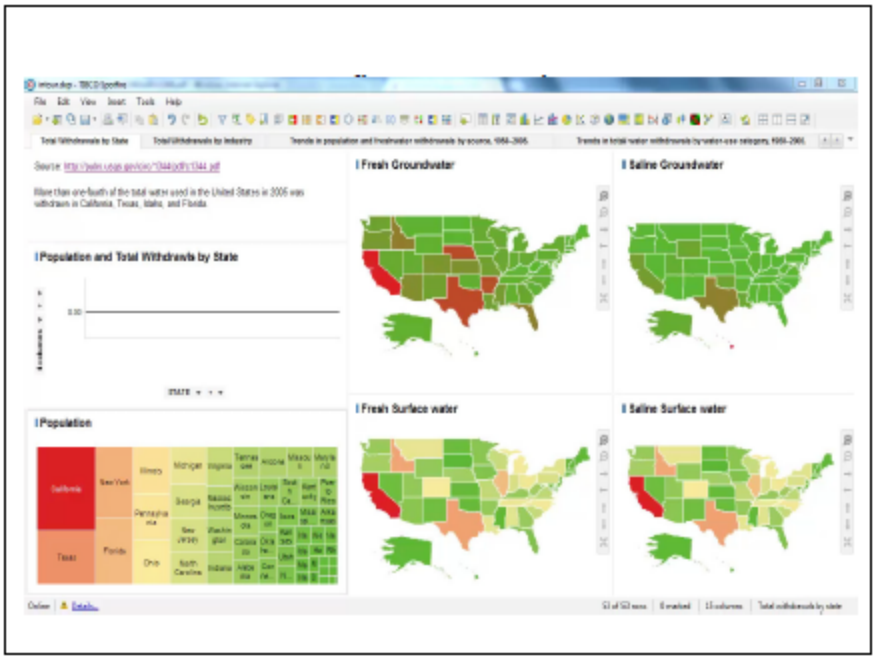

Total Withdrawals by Industry
Total Withdrawal by Industry
Hierarchical Clustering
K-Means



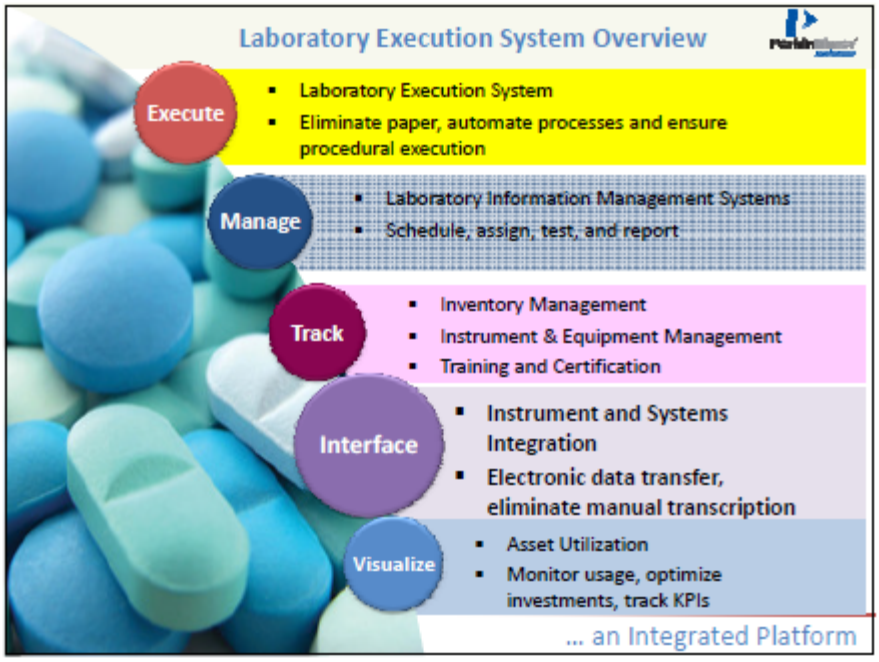


Ranking	1	2	3	4	5
These states generated the largest quantities of hazardous wastes in 2007	Louisiana 15,892,592 tons (36.8%)	Texas 13,272,367 tons (30.4%)	Michigan 2,297,357 tons (5.1%)	Mississippi 2,239,718 tons (4.8%)	Ohio 1,608,186 tons (3.4%)
States with the largest numbers of hazardous waste generators	California 2,312 (14.1%)	New York 1,181 (7.2%)	Ohio 952 (5.8%)	Texas 918 (5.6%)	Pennsylvania 821 (5.0%)
These states shipped the largest quantities of hazardous wastes in 2007	Texas 818,653 tons (11.3%)	Ohio 713,941 tons (10.0%)	California 643,078 tons (9.8%)	New Jersey 590,751 tons (8.3%)	Louisiana 474,988 tons (6.6%)
States with the largest numbers of hazardous waste shippers	California 2,295 (14.1%)	New York 1,167 (7.2%)	Ohio 959 (5.8%)	Texas 911 (5.6%)	Pennsylvania 821 (5.0%)
These states received the largest quantities of hazardous wastes in 2007	Ohio 883,988 tons (11.2%)	Indiana 589,907 tons (7.1%)	Texas 490,671 tons (6.9%)	California 450,561 tons (6.8%)	Pennsylvania 466,589 tons (6.4%)
States with the largest numbers of hazardous waste receivers	California 62 (11.6%)	Texas 54 (10.0%)	Pennsylvania 34 (6.4%)	Ohio 22 (4.1%)	New York 20 (3.7%)


Aquifers and Rocktypes
This data contains the shallowest principal aquifers of the conterminous United States, Hawaii, Puerto Rico, and the U.S. Virgin Islands, portrayed as polygons. An aquifer is a geologic formation, group of formations, or part of a formation that contains sufficient saturated, permeable material to yield significant quantities of water to wells and springs. For each geographic area, the aquifer shown is generally the uppermost principal aquifer. Each principal aquifer is classified as one of six types of permeable geologic material: unconsolidated deposits of sand and gravel, semiconsolidated sand, sandstone, carbonate rocks, interbedded sandstone and carbonate rocks, or basalt and other types of volcanic rock. The aquifer name is also included. Source:
Rock Names
Select type of rock.
ROCK_NAME
Rocktype by Coordinates
Carbonate-rock aquifers
Igneous and metamorphic rock aquifers
Sandstone and carbonate-rock aquifers
Sandstone aquifers
Semiconsolidated sand aquifers
Unconsolidated sand and gravel aquifers
(Empty)
YCenter
XCenter
Map of aquifers
Mark an area in the map.
Aquifers by area
High Plains aquifer
Texas coastal uplands aquifer system
Other rocks
Lower Tertiary aquifers


Source:
More than one-fourth of the total water used in the United States in 2005 was withdrawn in California, Texas, Idaho, and Florida.
Population and Total Withdrawls by State
STATE
Population
Fresh Groundwater
Saline Groundwater
Fresh Surface water
Saline Surface water


SEPAView
The magazine of the Scottish Environment Protection Agency
Spotfire – a new, innovative way to display water quality information
A new, web-based application is transforming the way Scotland's public bodies display their information about Scotland's environment.
SEPA
Scottish Environment Protection Agency
37


Laboratory Execution System Overview
Execute
Laboratory Execution System
Eliminate paper, automate processes and ensure procedural execution
Manage
Laboratory Information Management Systems
Schedule, assign, test, and report
Track
Inventory Management
Instrument & Equipment Management
Training and Certification
Interface
Instrument and Systems Integration
Electronic data transfer, eliminate manual transcription
Visualize
Asset Utilization
Monitor usage, optimize investments, track KPIs
... an Integrated Platform

Automating Data Collection and Review

Without a LIMS that can manage and link this data, laboratories must manually input the quality control data into the results message. This adds a significant burden not only on the reporting laboratory but also on the data user, and increases the chances of errors in the data.

Typical QC Parameters

The analytical results associated with the analysis of a batch of targets and quality control samples is known as the analytical sequence. Different methods and different programs or clients may require different analytical sequences. Below is an inclusive example of what might be included in one analytical sequence:

- Instrument Blank
- Initial Calibration
- Initial Calibration Validation
- Lab Reagent Blank or Method Blank
- Lab Fortified Blank or Laboratory Control Sample
- Matrix Spike
- Matrix Spike Duplicate
- Target Samples (typically 10)
- Continuing Calibration Verification
- Continuing Calibration Blank
- Target Samples (typically 10)
- Continuing Calibration Verification
- Continuing Calibration Blank

Data Elements for Type 2 Submission

- Project Details
- Date Format
- Laboratory Qualifiers Definition
- Organization Details
- Method Details
- Sample Details
- Sample Chain of Custody Identifier
- Sample Matrix
- Analysis Details
- Analysis End Date
- Analysis Type
- Laboratory Analysis Identifier
- Substance Identification Details
- Reporting Limit
- Reporting Limit Units
- Result Units
- Substance Type
- Data Package Identifier
- Laboratory Narrative
- Project Identifier
- Organization Identifier
- Method Identifier
- Sample Identifier
- Sample Collection End Date
- Sample Type
- Analysis Batch Identifier
- Analysis Start Date
- Instrument Identifier
- Method Identifier
- Exclusion Indicator
- Reporting Limit Type
- Result
- Substance Name
- Run Batch Identifier

Any Instruments, Any LIMS, Any Metadata

- Uni-Directional Interfaces
  - One way transfer of data from instrument to LIMS
  - Simplest to implement
  - Eliminates transcription errors

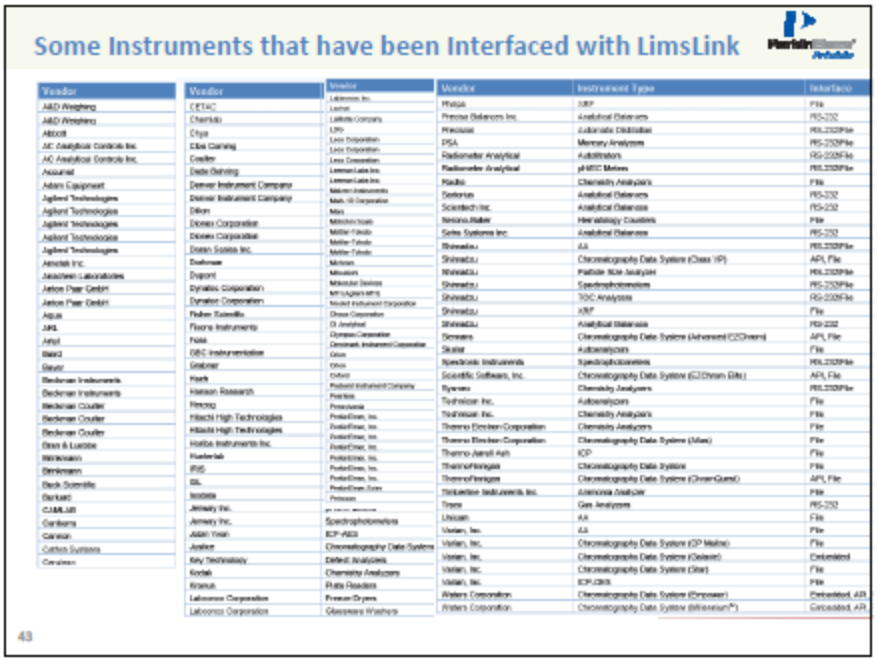


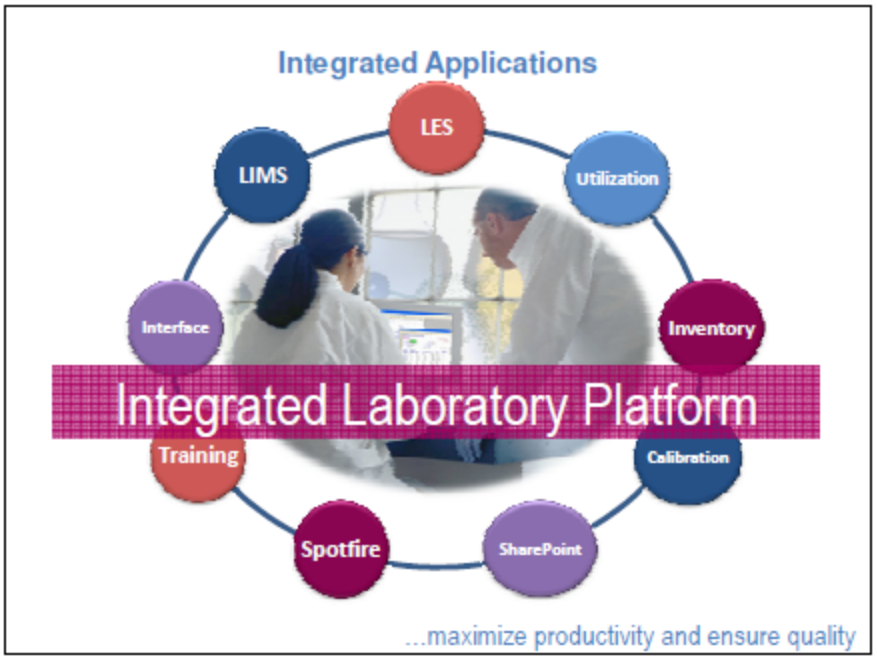
- Bi-Directional Interfaces
  - Two way transfer of data between instrument and LIMS
  - Leverages sample and test information that resides in LIMS
    - Reduces effort and errors



- Integration with CDS – TotalChrom, Chemstation, Empower
  - Two way transfer of data between CDS and LIMS
  - All interaction is initiated from within the CDS client




Some Instruments that have been Interfaced with LimsLink
43


Integrated Applications
LES
LIMS
Utilization
Interface
Inventory
Integrated Laboratory Platform
Training
Calibration
Spotfire
SharePoint
...maximize productivity and ensure quality

SECTION 20

AIR METHODS/MONITORING: INDOOR AIR QUALITY AND VAPOR INTRUSION

The Use of "Green" Thermal Techniques to Simplify Analyses for the Protection of Human Health

Ben Peters
CDS Analytical

Abstract

Traditionally, monitoring of water, soil, solids, air and consumer products (including food) involves numerous analytical techniques many involving the use of hazardous chemicals as extraction solvents. Methylene Chloride, Hexane, Carbon Disulfide, Benzene, Acetonitrile, and many other organic solvents can be used to extract organics from solids or liquids. Air monitoring can be done by collecting air in bulky, difficult to handle canisters, or with the use of dangerous and problematic liquid cryogens. Product emissions can be evaluated by solvent extraction or water based leaching.

Greener, cleaner Analytical techniques exist that are rarely used. Thermal desorption, Thermal Extraction and Pyrolysis are all techniques that involve the use of heat to free analytes from their matrix for analysis by GC. These techniques are used in mission-critical situations, like health & safety monitoring in many of the world's most dangerous venues. Thermal desorption is used to monitor air for chemical agents like mustard, Sarin and VX, and in industrial facilities to detect toxic industrial chemicals (TICS) and ozone precursors. Versions of Headspace and Pyrolysis techniques are used throughout the world for evaluating polymers in all forms (Paints, adhesives, plastics, bio mass, even looking for life on Mars)

This Presentation will show the latest in thermal techniques and discuss several advantages over the more popular techniques involving solvents, canisters, and liquid cryogens.

CDS Analytical, Inc.

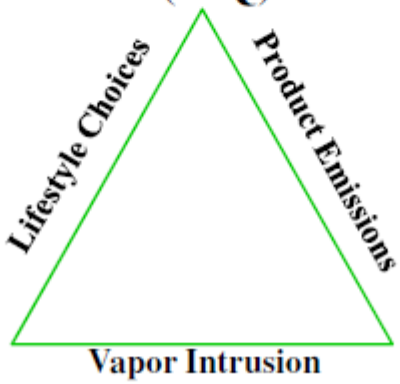
The Use of "Green" Techniques to Simplify Analyses for the Protection of Human Health (Focus on Indoor Air Quality)

Presented by:
Ben Peters
Regional Sales Manager
CDS Analytical – Oxford, PA



CDS Analytical, Inc.

The Three Sides of Indoor Air Quality (IAQ)



CDS Analytical, Inc.

- **Product Emissions:** Off gassing of volatiles from liquid and solid products around the house. Can include:
  - Chemicals (Gasoline, Cleaners, Detergents, Solvents, Pesticides…)
  - Scented products (Air fresheners!, Candles, Potpourri)
  - Combustion Sources (Wood stoves, fire place(s))
  - Cosmetics
  - Paints
  - Carpets
  - Furniture
  - Wall board/ceiling tiles/other building materials
  - Just about every item purchased in your house

NEMC: 08/2013 3

CDS Analytical, Inc.

- **Vapor Intrusion:**



USEPA: Diagram

NEMC: 08/2013 4

CDS Analytical, Inc.

- **Lifestyle Choices:** Things that we do around the house. Can include:
  - Smoking
  - Cooking styles (Grilling, Frying, types of foods we eat)
  - Pets (Fur, Dander, Urine (and other waste products)
  - Cleanliness
  - Where we live
  - Daily, weekly, Seasonal habits
  - Choice of using air conditioner or opening windows
  - Choice of products we purchase (See Product Emissions)

NEMC: 08/2013 5

CDS Analytical, Inc.

Typical IAQ Investigation

- Define objectives
- Conduct pre-sampling survey of the three sides of the IAQ:
  - Indoor sources, building materials, lifestyle choices, vapor intrusion concerns, ventilation, meteorology.
- Establish sampling objectives, methods, and duration
- Sample
- Evaluate data and calculate heath & safety risks

NEMC: 08/2013 6

CDS Analytical, Inc.

Typical Analytical techniques

- Air
  - Thermal Desorption (Active and/or Passive)
  - Summa Canisters
  - Bags
- Soil/Solids
  - Solvent extraction
- Water
  - Purge & Trap
  - Solvent extraction
- Product Emissions
  - Headspace
  - Solvent extraction

Let's focus on these Green techniques

NEMC: 08/2013 7

CDS Analytical, Inc.

The use of heat to perform Thermal Desorption, Thermal Extraction and Pyrolysis

I wonder if there is a better way to analyze Solids for Organics



NEMC: 08/2013 8

CDS Analytical, Inc.

COOL

WARM

HOT

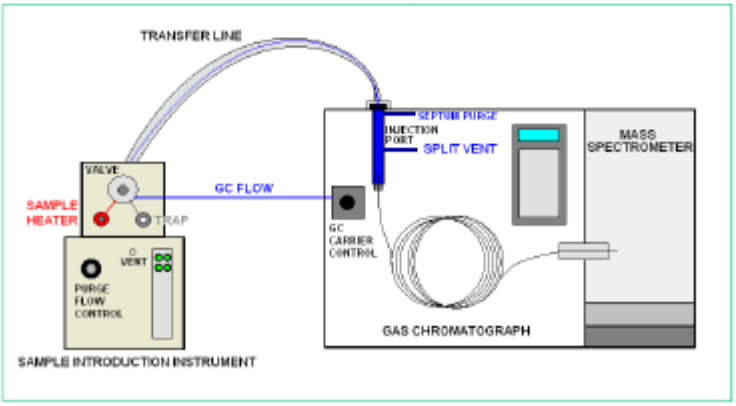
- **Purge & Trap-** A liquid sample is purged with an inert gas to order to remove volatile organics
- **Thermal Desorption-** Typically used to desorb "sorbent tubes" of analytes or very small solid samples by using temperature.
  - Sample is typically a gas or solid
- **Dynamic Head Space-** The controlled application of an elevated temperature and purged gas on a sample for a predetermined time to desorb any trapped analytes.
  - Samples are typically solids and often relatively large.
- **Pyrolysis-** The use of controlled heating to break down large organic polymers for GC-MS analysis

NEMC: 08/2013 9

CDS Analytical, Inc.

System for Thermal Sampling-GC/MS

Including thermal desorption, headspace, pyrolysis and oxidation

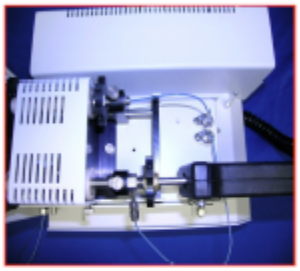


NEMC: 08/2013 10

CDS Analytical, Inc.

Pyroprobe 5200





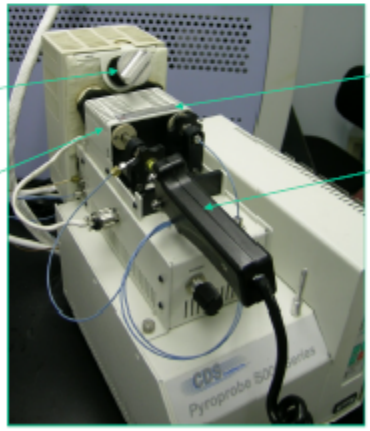
- Multiple steps with GC start
- Programmable interface
- Automatic on-line valve
- Transfer line to GC
- Direct to GC or with trapping
- Options include:

Thermal desorption probe
Test tube desorber
High-Pressure
Catalytic reactor

NEMC: 08/2013 11

CDS Analytical, Inc.

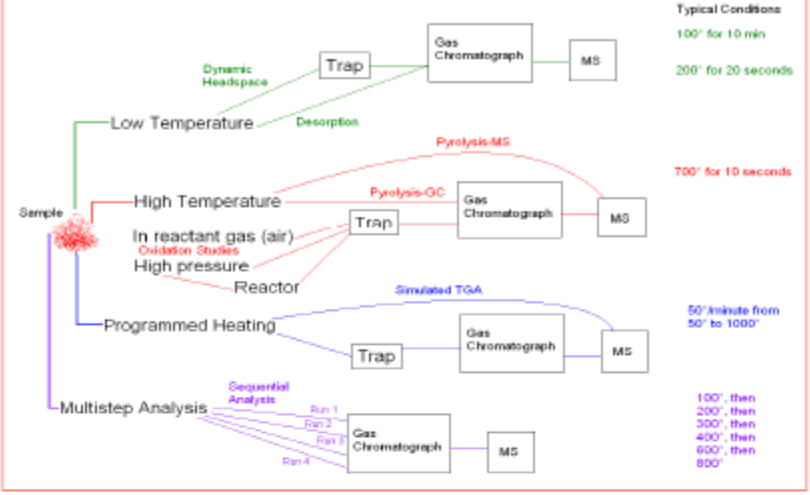
Direct to GC or with Trapping



NEMC: 08/2013 12

CDS Analytical, Inc.

THERMAL SAMPLING OPTIONS

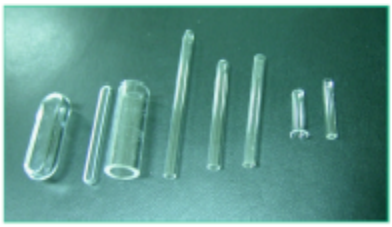


NEMC: 08/2013 13

CDS Analytical, Inc.

Probes and Tubes



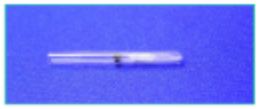


NEMC: 08/2013 14

CDS Analytical, Inc.

Sample Capacities

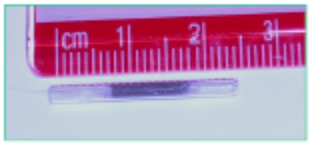
For pyrolysis, usually ~100 ug of Organic Material
Can use Larger Samples for Thermal Extraction



1 mg tobacco



10 mg cellulose

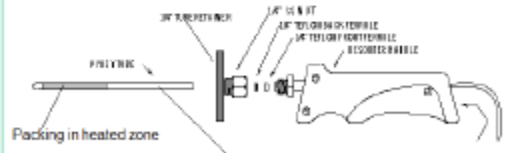


25 mg soil

NEMC: 08/2013 15

CDS Analytical, Inc.

Thermal Desorption Probe Replaces Pyroprobe Filament Rod



Pyras tube dimensions 1/4" OD with 2" heated length.
Useable volume 0.75 ml.
(4 mm ID x 60 mm sample zone)

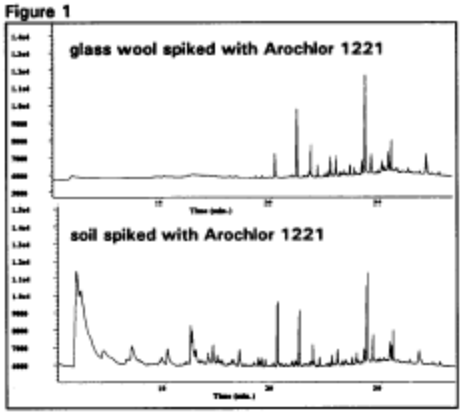


NEMC: 08/2013 16

CDS Analytical, Inc.

Soil Direct to GC (PCBs)

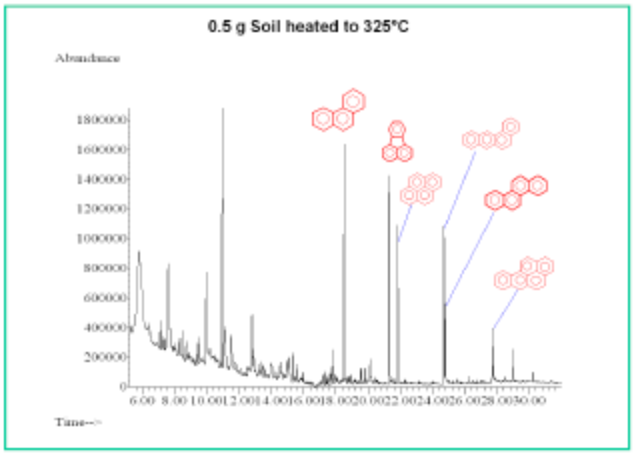
Figure 1



NEMC: 08/2013 17

CDS Analytical, Inc.

PAHs in Soil, Direct to GC

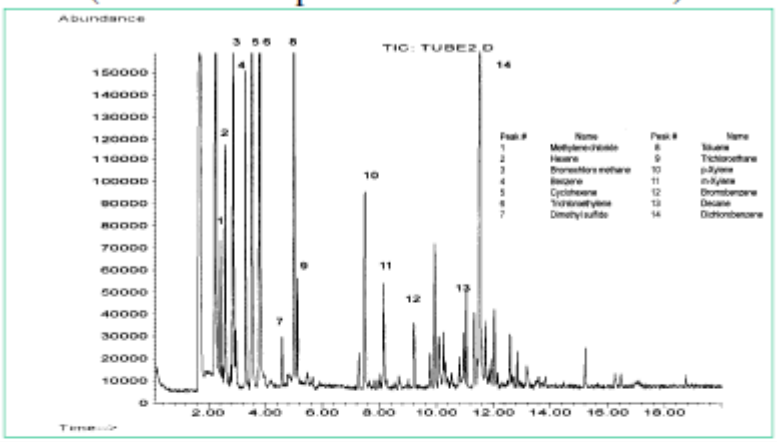


NEMC: 08/2013 18

CDS Analytical, Inc.

Air Sampling

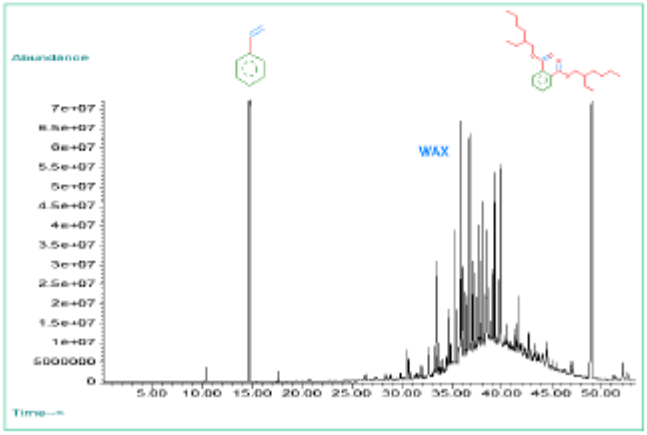
(Thermal desorption tube filled with Tenax)



NEMC: 08/2013 19

CDS Analytical, Inc.

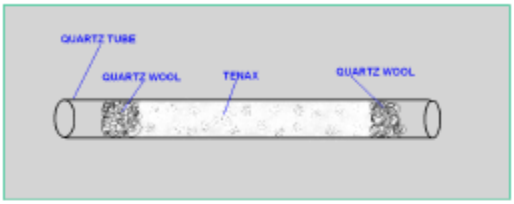
Dynamic Headspace of Rubber (200°C)



NEMC: 08/2013 20

CDS Analytical, Inc.

Mini-trap

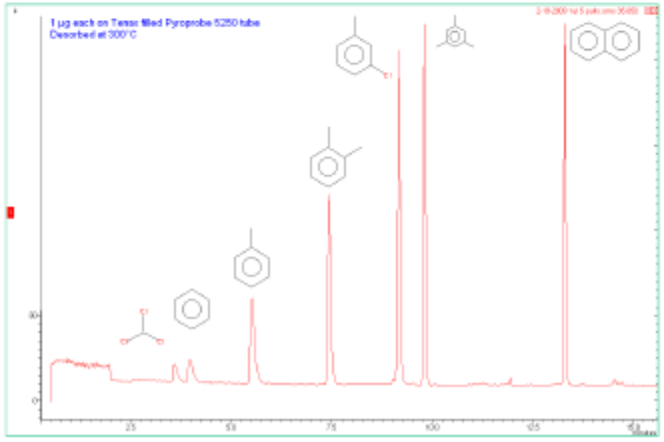




NEMC: 08/2013 21

CDS Analytical, Inc.

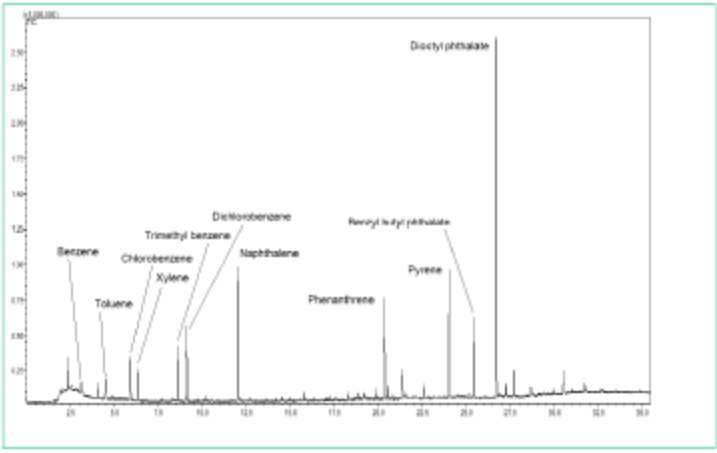
Standard Desorbed from Mini-trap



NEMC: 08/2013 22

CDS Analytical, Inc.

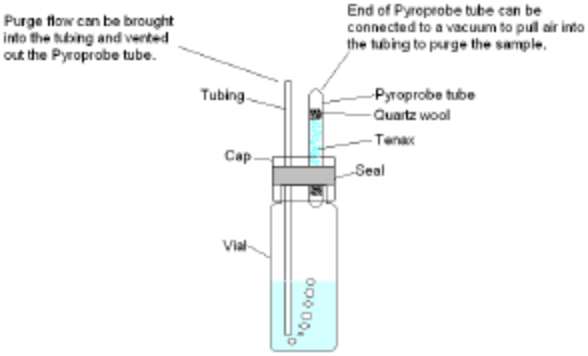
Water through Mini-trap



NEMC: 08/2013 23

CDS Analytical, Inc.

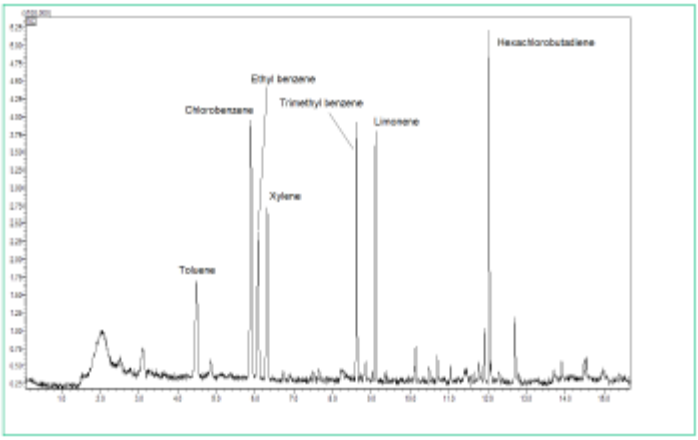
Mini-Purge & Trap



NEMC: 08/2013 24

CDS Analytical, Inc.

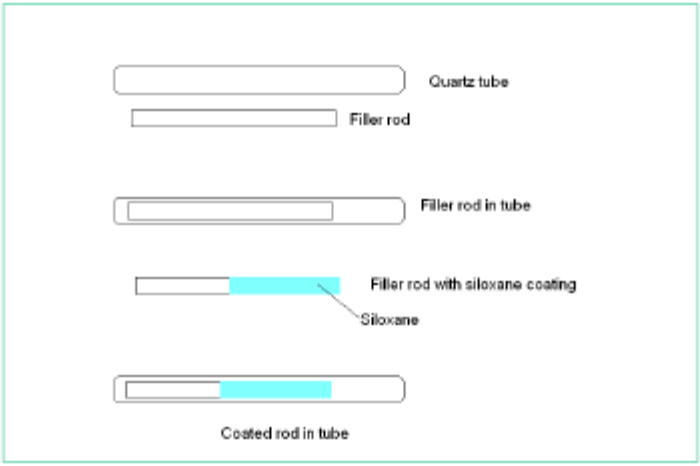
Mini-Sparge of Water



NEMC: 08/2013 25

CDS Analytical, Inc.

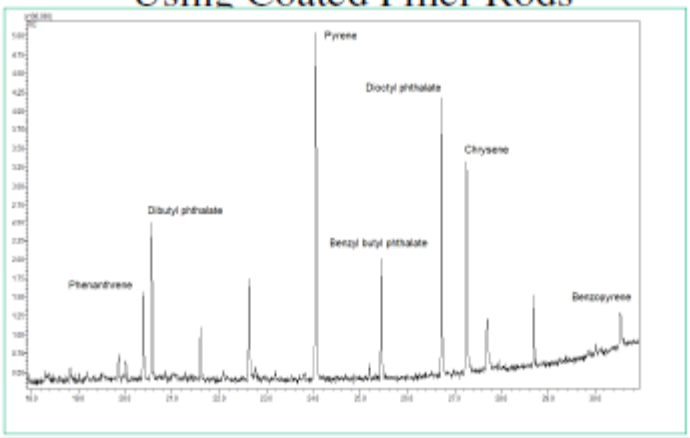
Coated Tube Inserts



NEMC: 08/2013 26

CDS Analytical, Inc.

40 ppb PAH/Plastcizer in Water Using Coated Filler Rods



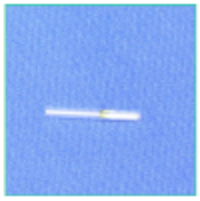
NEMC: 08/2013 27

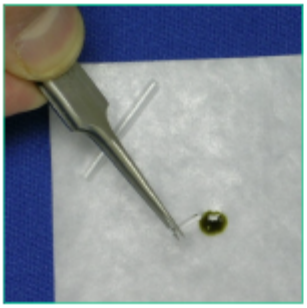
CDS Analytical, Inc.

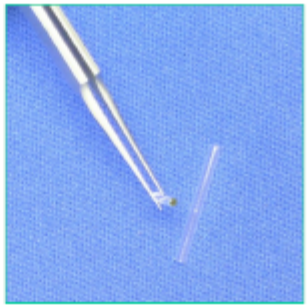
Sampling oils



Quartz rod inside tube



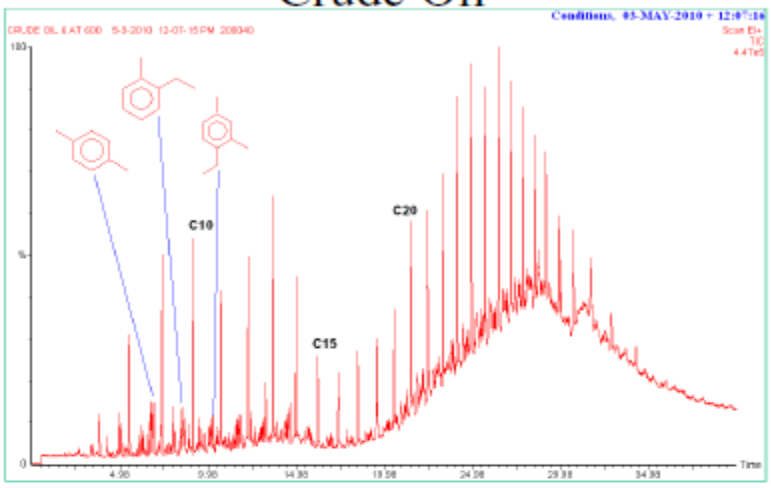




NEMC: 08/2013 28

CDS Analytical, Inc.

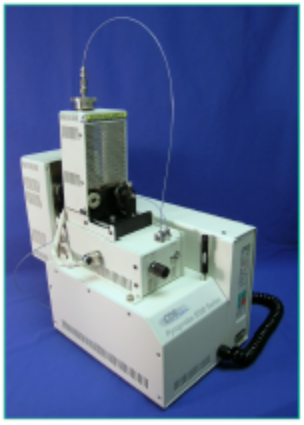
Crude Oil



NEMC: 08/2013 29

CDS Analytical, Inc.

Test-Tube Desorber



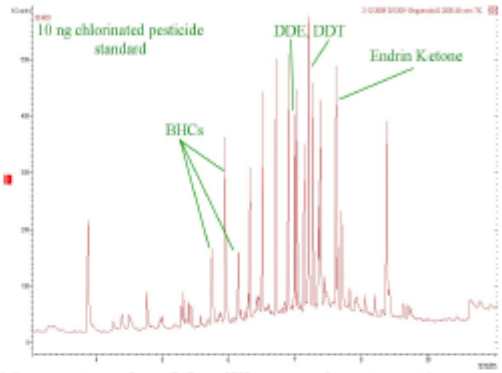


NEMC: 08/2013 30

CDS Analytical, Inc.

Pesticides in Soils

- Extract at 325° C
- 2 grams in Test-tube desorber
- Tenax Trap
- Desorb trap at 300° C
- GC/MS
- DB-5 column



10 ng standard by Thermal extraction

NEMC: 08/2013 31

CDS Analytical, Inc.

Characterization of Indoor Dust

- Dust consists of a mixture of natural & synthetic polymers and smaller more volatile molecules from the "environment"

Can we analyze the dust samples from different locations and get as much or more information than just doing air samples?

NEMC: 08/2013 32

CDS Analytical, Inc.

Experimental

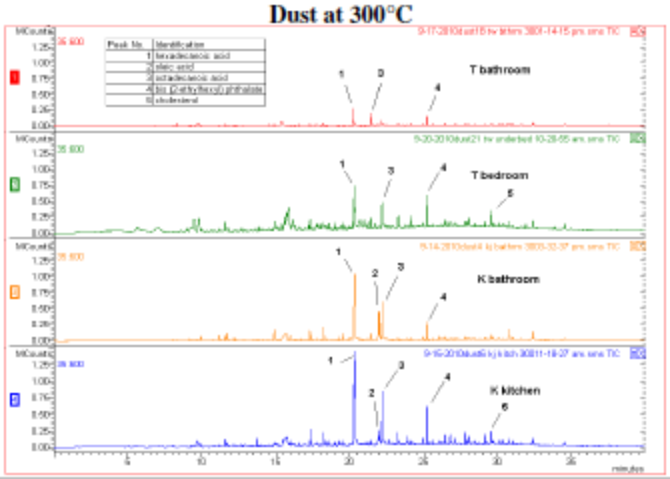
- We looked at dust collected from several rooms in 2 different homes.
- Using the 5200 Pyroprobe we thermally extracted (300ºC) and then Pyrolyzed (750ºC) the samples.
- Reviewing the data for Semi-volatile contaminants and Polymer components.

NEMC: 08/2013 33

CDS Analytical, Inc.

Desorption to GC

Dust at 300°C



NEMC: 08/2013 34

CDS Analytical, Inc.

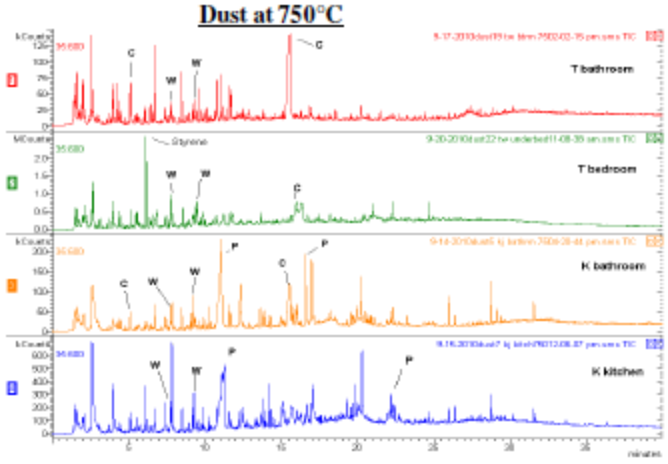
Pyrolysis to GC

Dust at 750°C

C – Cotton

W – Wool

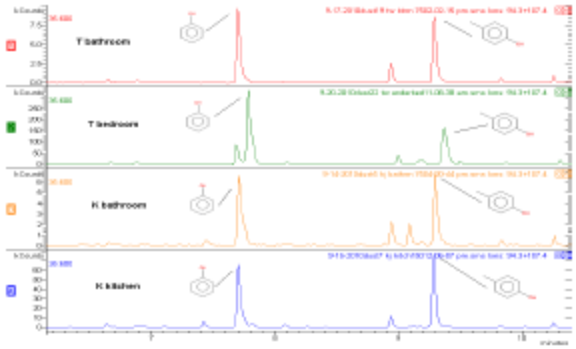
P - Polyester



NEMC: 08/2013 35

CDS Analytical, Inc.

Using SIM to confirm polymers



Phenol and Methyl-Phenol from Wool or Hair. Direct pyrolysis of source material can be used to confirm original sources of dust.

NEMC: 08/2013 36

CDS Analytical, Inc.

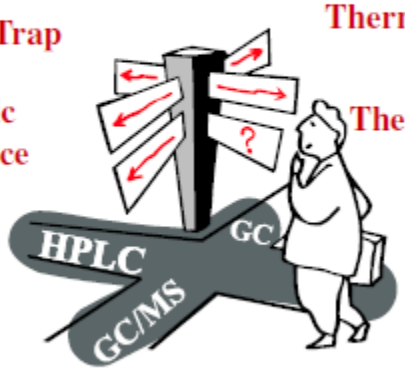
Questions

Purge & Trap

Thermal Desorption

Dynamic Headspace

Thermal Extraction



NEMC: 08/2013 37

Calibration of Adsorbent Based Passive Vapor Samplers for Concentration Reporting in Air, Soil Gas, and Water for Vapor Intrusion Investigations

James Whetzel
Amplified Geochemical Imaging, LLC

Abstract

Passive Vapor Samplers have been used for indoor and outdoor air monitoring as a quantitative tool for a number of years. Various consensus standards exist to describe how these samplers are to be calibrated according to considerations of Fick's First Law of Diffusion. These principles have been extensively applied to volatile organic compound (VOC) detection with passive samplers designed with a two dimensional diffusion surface for air sampling, but have not generally been applied to samplers that have a three dimensional diffusion surface or for passive sampler measurements in water.

Determination of VOCs in air, water, and soil gas are critical for determining the potential for vapor intrusion into structures. Interest in the use of passive samplers for VI investigation stems from their ease of use and potential for longer term sampling and relatively low detection limits. Using a hydrophobic inert membrane to protect adsorbents allows the application of passive sampling to air, water, and soil vapor. This presentation will describe methods to calibrate the compound uptake rates and subsequent determination of VOC concentrations in air, water, and soil gas using a membrane protected adsorbent based passive sampler.

Calibration of Adsorbent Based Passive Vapor Samplers for Concentration Reporting in Air, Soil Gas, and Water for Vapor Intrusion Investigations

Jim Whetzel, Harry Anderson, Ian McMullen,
and Don D'Apolito
Amplified Geochemical Imaging, LLC

2013 NEMC
August 8, 2013

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC Slide 1

Overview

- Notable benefits/use of passive sampling
- Membrane-based passive sampler
- Concentration Calibration: Lab & Field
  - Air
  - Soil Gas
  - Water
- Conclusions

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC Slide 2

Benefits of Passive Sampling

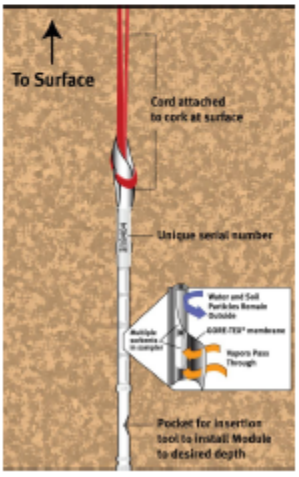
- Rapid, cost-effective, unobtrusive deployment
- Minimal access limitations
- Time-integrated sampling
  - Sensitivity to low concentrations
  - Sensitivity to broad range of compounds: VOCs, SVOCs, PAHs
- Virtually any soil and moisture condition
- Not affected by turbidity or inorganic additives (e.g. oxidizers)
- No mechanical parts, connections, controller calibration
  - Reduced possibility of sampling error
- Single use – no residual signal

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 3

AGI Universal Sampler
(formerly the GORE® Module or GORE-SORBER)





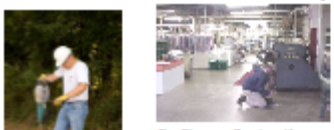


- GORE-TEX® Membrane (ePTFE)
  - Waterproof, gas-permeable
  - Designed for diffusion – no adsorption
  - Chemically-inert – no off-gassing
  - Protects sorbent integrity
- Hydrophobic, engineered sorbents
  - VOCs, SVOCs, PAHs
  - Duplicate samples

GORE, GORE-TEX, and GORE-SORBER are registered trademarks of W.L. Gore and Associates, Inc.
www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 4

Installation & Use

Soil Gas | Subslab Vapor | Air | Water



Dry Cleaner - Courtesy Kansas Department of Health & Environment













VI Investigation– Courtesy of Ecology & Environment





Vertical Profiling in Wells

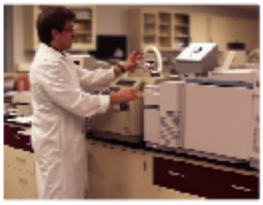
- Surface to any depth
- Permanent sampling ports
- Vertical profiling

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 5

Analysis

- Dedicated laboratory
- Minimal sample handling
- US EPA Method 8260 (TD\GC\MS)
  - Modified for thermal desorption
  - Screening method
  - 8260M - extended QC method
    - ISO 17025, DoD ELAP accreditation by A2LA



ACCREDITED
Cert.# 3062.01

- Mass and concentration data
  - air, soil gas, water, sediment

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 6

References – Passive Air Sampling



- ASTM D 6306-98 Standard Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air
- ASTM D 4597-03 Standard Practice for Sampling Workplace Atmospheres to Collect Gases or Vapors with Solid Sorbent Diffusive Samplers
- ASTM D 6246-02 Standard Practice for Evaluating the Performance of Diffusive Samplers
- ASTM D 5314-93 Standard Guide for Soil Gas Monitoring in the Vadose Zone
- MDHS 27, 70, 80 Methods for the Determination of Hazardous Substances, Volatile Organic Compounds in Air

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 7

Conversion to Concentration

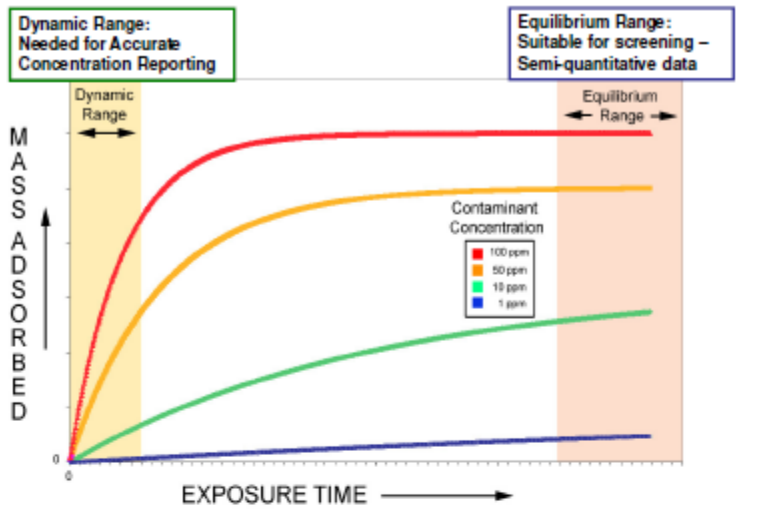
Select Method for Determining S

Dynamic or

Static uptake

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 8

Dynamic v. Static



www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 9

Dynamic Uptake

Fick's 1st Law of Diffusive Flux
(simplified)

S=sampling rate vol/t

$$\frac{dm}{dt} = -D\left(\frac{A}{L}\right)(C_x - C_0^{\,0})$$

$$C_x = \left[\left(\frac{1}{S}\right)\left(\frac{dm}{dt}\right)\right]$$

m = mass
t = time
D = diffusion coefficient
(A/L) = geometric parameter describing shape of sampler
C_x = concentration of analyte in the module at time, t = x
C_o = concentration at time, t = 0

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 10

Sampling Rate, S

Measure S for one or two compounds then extrapolate based on compound diffusivity and Fick's first law

or

Measure S directly for each target compound

- More accurate
- Industry standard method

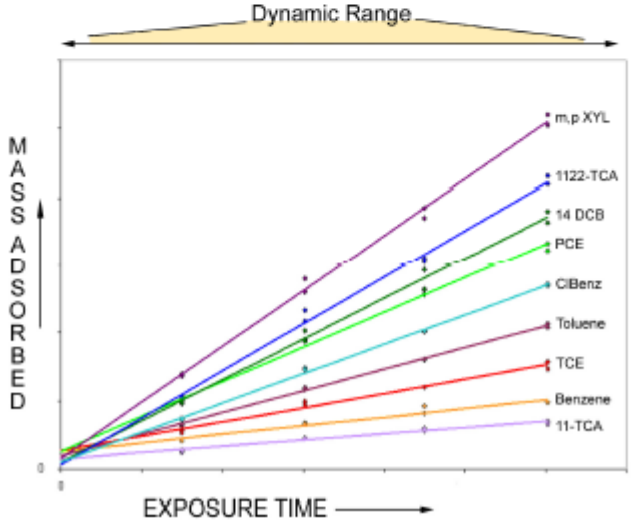
ASTM D 4597-03

Advances in Air Sampling, AICHG (1990), ISN 0-87371-115-7, Chapter 9, "Recent Developments in Passive Sampling Devices," James D. Mulik and Robert G. Lewis

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 11

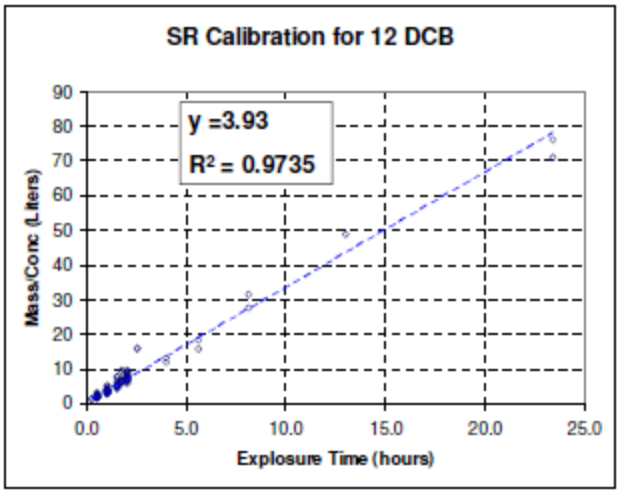
Sampling Rate, S



www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 12

Sampling Rate, S (L/hr)



1,2-Dichlorobenzene Sampling Rate = 3.93 L/Hr

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 13

Sampling Rate - Air

SR @298.94 K			
	L/ Hr		L/ Hr
MTBE	1.1	PCE	2.33
t12DCE	1.08	ClBENZ	3.05
c12DCE	1.51	EtBENZ	3.02
CHCl3	1.18	mpXYL	3.02
111TCA	0.75	oXYL	3.1
12DCA	1.87	1122TetCA	3.35
BENZ	1.91	135TMB	3.19
CCl4	0.93	124TMB	3.35
TCE	1.83	13DCB	3.97
112TCA	2.4	14DCB	4.09
TOL	2.54	12DCB	3.93

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 14

Other Factors to Consider

- Temperature
- Mass adsorbed
- Humidity
- Matrix properties



www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 15

Factors to Consider

FACTOR	AIR	SOIL GAS	WATER	SEDIMENT
Analyte	Important	Important	Important	Important
Exposure Time	Conditionally Important	Conditionally Important	Conditionally Important	Conditionally Important
Sorbed Mass	Important	Important	Important	Important
Temperature	Important	Important	Important	Important
Concentration*				
			Important	Important
Media Velocity	Conditionally Important		Conditionally Important	
pH				
% RH				
Salt Level				

Effects are Sorbent and Sampler Dependent

Important indicates SR changes continuously by that factor

Conditionally Important indicates that at certain levels or ranges of the factor SR may be affected

Blank cells indicate that factor does not have a significant affect on SR or concentration calc.

* Concentration is not an important factor, for time can be limited to prevent sorbent saturation.

pH, %RH, and Salinity were evaluated within "normal" sampling conditions and found "not important."

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 16

Factors to Consider

- **Determine valid ranges for "conditionally important" factors**



- **Account for the "important" factors in model**







www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 17

Calculating Concentrations - Air

Regression Approach
- Accounts for subtle non-linear effects in mass, time and temperature

$$C_x = (m)^b / (t)^d / [Sr \times \exp(-Ea/R/(1/Tr-1/T))]$$

b & d = exponents accounting for non-linear response
-Ea/R = correction for deviation from ref. temp
Sr = sampling rate at reference temperature
Ea/R = derived activation energy component
T = temperature °K
Tr = reference temperature
C_x = concentration of analyte in the module at time, t = x

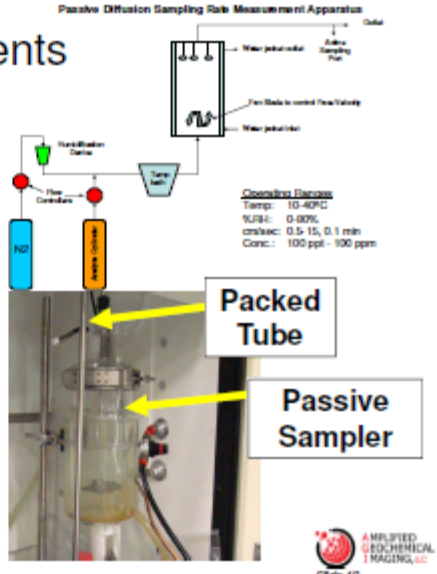
www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 18

Laboratory Measurements

Chamber experiments

- 30+ compounds
- Varied conc., humidity, temperature, face velocity
- Chamber conc. verified using TO17 sampling



www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 19

Valid Ranges for Conditional Factors

Air

Temperature 5 to 35°C

Time and Concentration*

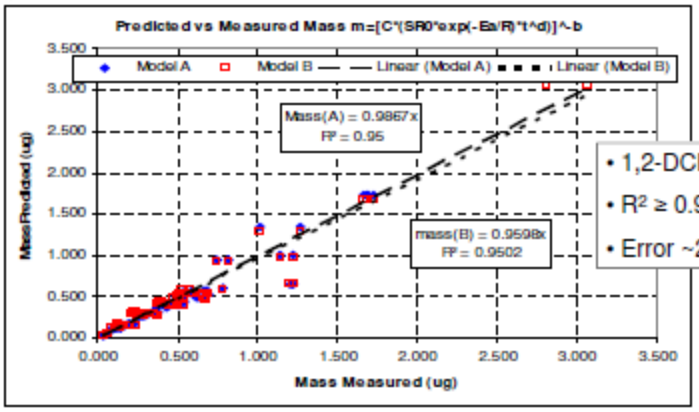
- **Mass within calibration range**
- **Total mass < ~1mg**

Example – Trichloroethene	
4 Hours	4 to 1600ug/m^3
24 Hours	1 to 560ug/m^3

*Dependent on compound and adsorbents

www.agisurveys.net
©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 20

Equation Predicted v. Measured - Air



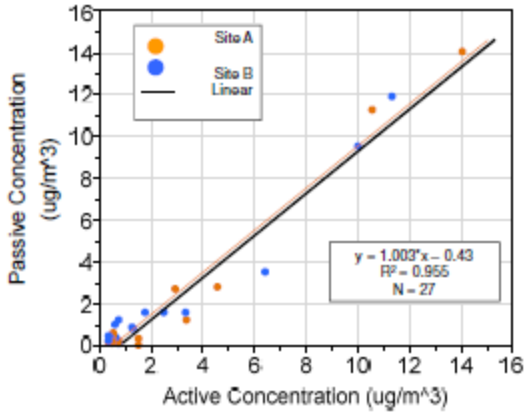
- 1,2-DCB
- $R^2 \geq 0.9$
- Error ~25%

- **Mass calculated using 2 models**
- **Inputs – concentration, exposure time, and temp.**

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 21

Comparing Concentrations

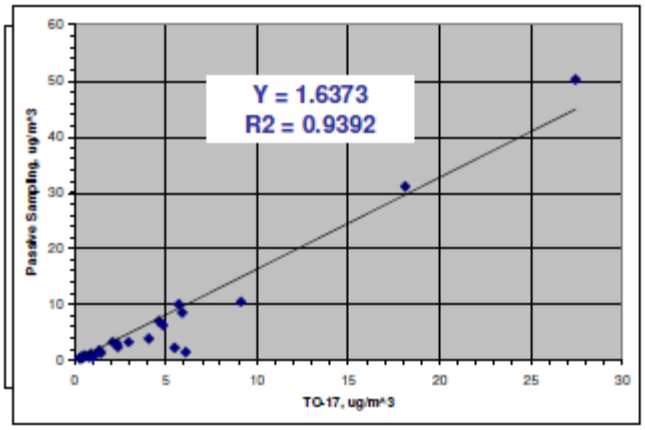
Home Air – 24 hours





www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 22

Comparing Concentrations
Home Air – 24 hours



- TO-17 Comparison
- BTEX, TMBs, DCB, Naphthalene

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 23

Soil Gas
Simplified version of equation

- $Conc_{Air} = \frac{(Mass/\ t)\ /SF}{S_x}$
- $Conc_{Air} = \frac{ug/hr}{L/hr} = ug/L$

$Conc_{air}$ = ug/L
$Conc_{soil\ gas}$ = ug/L
Mass = mass desorbed (ug)
SF = desorption efficiency (dimensionless)
S_x = measured sampling rate (L/hr)
t = time (hr)
E = soil diffusion correction (dimensionless)

Soil matrix retards diffusion from soil pore space to sampler

passive sampler

Effects of soil

- $Conc_{soil\ gas} = Conc_{air}/E = ug/L$

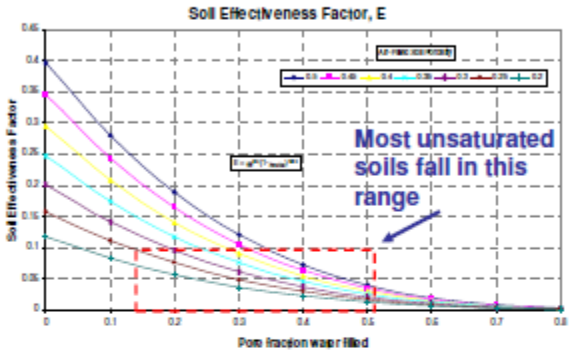
www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 24

Calculating Concentrations – Soil Gas

Adjust for soil diffusion resistance (E)

- $E = D_{eff}/D_{air} = \Theta^{(4/3)}(1-\varepsilon)^{(10/3)}$
- $Conc_{Soil\ Gas} = \frac{Conc_{Air}}{E}$

Θ = total soil porosity
ε = water-filled porosity
D_{eff} = effective diffusion coefficient in soil
D_{air} = diffusion coefficient in air

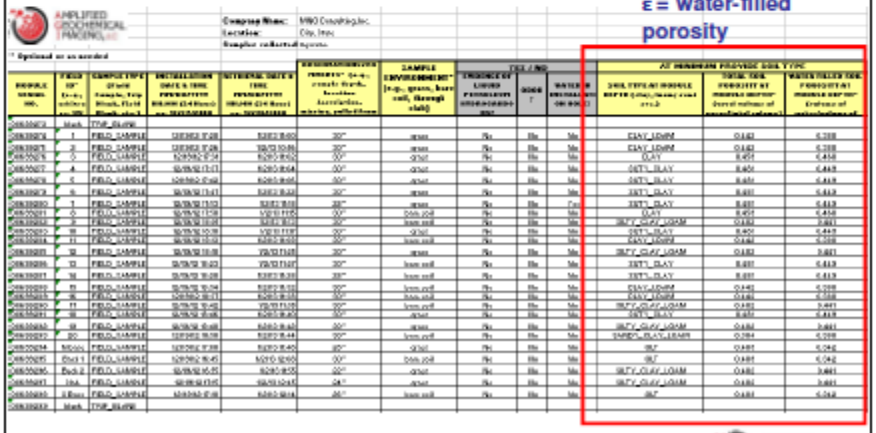


Millington, R. J., "Gas Diffusion in Porous Media", Science, (1959), Vol. 130, 100-102

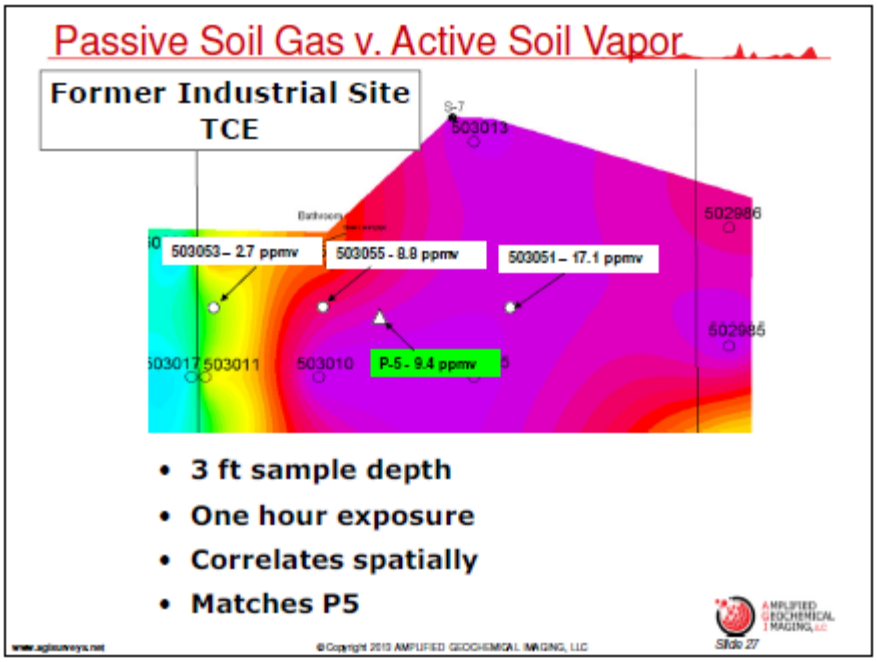
www.agiusveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 25

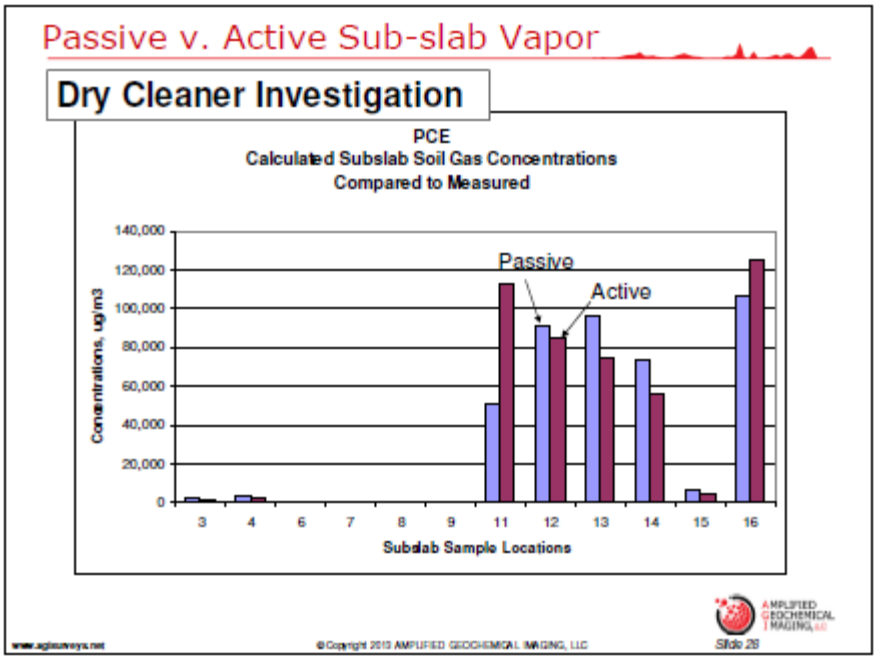
Example Installation & Retrieval e-Log

Θ = total soil porosity
ε = water-filled porosity



www.agiusveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 26

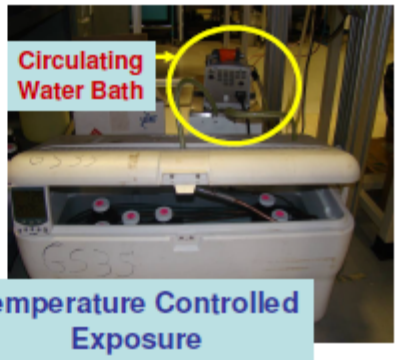

Passive Soil Gas v. Active Soil Vapor
Former Industrial Site
TCE
503013
502986
503053 – 2.7 ppmv
503055 - 8.8 ppmv
503051 – 17.1 ppmv
502985
503017
503011
503010
P-5 - 9.4 ppmv
• 3 ft sample depth
• One hour exposure
• Correlates spatially
• Matches P5
Slide 27


Passive v. Active Sub-slab Vapor
Dry Cleaner Investigation
PCE
Calculated Subslab Soil Gas Concentrations
Compared to Measured
Passive
Active
Concentrations, ug/m3
140,000
120,000
100,000
80,000
60,000
40,000
20,000
0
3
4
6
7
8
9
11
12
13
14
15
16
Subslab Sample Locations
Slide 28

Concentration Calculations in Water



Mixing Water Solutions





Passive Samplers in Filled 1L bottles

Temperature Controlled Exposure

Concentrations, Temperatures, Exposure Times Varied

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 29

Concentration Calculations in Water

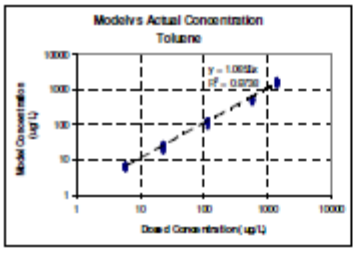
Simplified equation for water

- Single conc., time, temp

Conc (ug/L) = mass(ug)/time(Hr)/SR(L/Hr)

Multiple times, temps, and sorbed mass

Conc = $(mass)^b$ /$(time)^{-d}$ /[-SRo x exp(-Ea/R(1/Tr - 1/T))]



Regression output from ln(conc) versus ln(mass), ln(time), 1/temp

b & d = exponents accounting for non-linear response

-Ea/R = correction for deviation from ref. temp

SRo = Sampling rate

Other inputs

T = water temp (K),

Tr = reference water temp (K)

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC

Slide 30

Sampling Rate Table - Water

SR @293.24 K			
	L/ Hr		L/ Hr
MTBE	0.00246	PCE	0.00615
t12DCE	0.00431	CIBENZ	0.00542
c12DCE	0.00459	EtBENZ	0.00603
CHCl3	0.00459	mpXYL	0.00636
111TCA	0.00659	oXYL	0.00658
12DCA	0.00448	1122TetCA	0.00442
BENZ	0.00504	13STMB	0.00787
CCl4	0.00677	124TMB	0.00784
TCE	0.00517	13DCB	0.00721
112TCA	0.00434	14DCB	0.00708
TOL	0.00557	12DCB	0.00695

www.agisurveys.net © Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 31

Valid Ranges for Conditional Factors Water – AGI Sampler

Temperature 9 to 26°C

Flow < 10m/day*

Pressure < 35 feet below water*

Concentration* and Time

Expected concentration of Primary Contaminant (ppb)*	Residence time in well (Hr.)
30 to 6500	0.5 (30 min.)
15 to 3000	1
7 to 1500	2
5 to 1000	3

* Values based on detection limits and upper range of majority of standard VOCs/ SVOCs (Aquifer temp ~10C, flow <10m/day, depth <35 feet below water surface)

*** Range can be extended using different model and/or reduced exposure**

www.agisurveys.net © Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 32

Passive v. Active Water Sampling
Gas Station

Well No.	Sample Depth (ft)	Benzene	Toluene	Ethylbenzene	Xylenes (total)	MtBE	TAME	TBA
MW-2	4.2 (to water)	*	*	2	*	*	*	*
MW-2 (Passive)	5.7	*	13	4	2	*	*	*
MW-9	4.8 (to water)	50	*	*	*	1360	*	1250
MW-9 (Passive)	5.6	42	57	7	10	1350	710	3350
MW-10	3.8 (to water)	*	*	*	*	66	*	*
MW-10 (Passive)	5.7	*	100	*	13	20	*	*
MW-11	7.8 (to water)	*	*	*	*	84	*	*
MW-11 (Passive)	8.5	*	24	*	2	67	*	*
MW-13R	7.7 (to water)	*	*	*	*	44	*	*
MW-13R (Passive)	14.0	*	21	*	2	13	*	*
MW-14	8.3 (to water)	*	*	*	*	3930	*	*
MW-14 (Gore)	10.0	*	100	*	10	1450	*	2310

* - reported as below analytical detection limits

- Compared favorably
  - Some volatile loss observed
- AGI Sampler detected more compounds

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 33

Conclusions

Adsorbent based passive samplers

- Simple and cost effective to deploy and retrieve
- After proper calibration
  - Provide comparable measurement of concentrations in air, soil gas, and water
- "Important" factors must be determined and accounted for during calibration
- Ranges of use for "Conditional" factors need to be established

www.agisurveys.net ©Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 34


Thank You!
Jim Whetzel
Amplified Geochemical Imaging, LLC
100 Chesapeake Blvd.
Elkton, MD 21921
410-506-4779
whetzel@agisurveys.net
www.agisurveys.net
© Copyright 2013 AMPLIFIED GEOCHEMICAL IMAGING, LLC
Slide 35

NH Mold Task Force Standard of Care

Guy Sylvester
Absolute Resource Associates

Abstract: The New Hampshire Mold Task Force Presents the NH "Standard of Care"

Background

In 2008, a group of NH business leaders and health professionals came together with the same concern: few states have laws in place to protect citizens when it comes to mold and poor indoor air quality. They had seen how lack of regulation in the industry was creating a variety of problems for citizens and the industry itself, and were motivated to find a way to get mold legislation on the books. The group worked with lawmakers for several months to write and propose NH House Bill 482, relative to mold assessment, testing and remediation, which lost by just one vote.

Not ready to give up, the group was encouraged by the lawmakers involved to form a "Mold Task Force," with the goal of creating a Standard of Care for the state's mold industry. Published in December, 2012, the New Hampshire Mold Task Force (NHMTF) Standard of Care is now a public document which provides detailed information to citizens about the causes of indoor mold, possible health risks, prevention measures, and about the mold industry in general, including best practices and tips for hiring consultants and contractors. This document was created for the citizens of NH, but the information is being distributed nationwide because of its broad appeal. Charlie Wiles, the Executive Director of ACAC (American Council for Accredited Certification), upon reviewing the document, stated, “I have seen few documents that are as well written as this one.”

The NHMTF views the Standard of Care as just the first step toward protecting our citizens when it comes to mold and poor indoor air quality. The document, sponsored by the American Lung Association, is being seen as a very helpful tool by health professionals and indoor air quality experts alike. Their work is starting to cause a buzz in the industry; they made a presentation a few weeks ago at the 2013 ACAC National Conference in Phoenix, and are have been asked to speak at various professional conferences on the East Coast in the coming months.

Conclusion

This presentation summarizes the findings of the NHMTF and the process which paved the way for the “Standard of Care’ and future legislation. The group is sharing their story with other states in the hopes that the document will be shared nationwide, providing valuable information to those who are affected by mold as well as those in the mold industry. Their ultimate hope is that Mold Legislation takes root across the country, protecting the health and well-being of our citizens.

Members of the NHMTF:

Chair and Presenter: Guy Sylvester, Absolute Resource Associates
Chair: Philip Alexakos, Manchester Health Department, Chair: Rick Rumba, Keene State University, Tim Carr, Able Restoration, David Choate III, Grubb & Ellis Real Estate, Cathy Coe, Environmental Health Inc., Dennis Francoeur, RPF Environmental, Lee Gilman, American Lung Association, Scott Knightly, Envirovantage, Jeff May, May Indoor Air Investigations, Ed Miller, American Lung Association, and Chris Sullivan, Certrex LLC.

nhmtf
New Hampshire Mold Task Force

AMERICAN LUNG ASSOCIATION.
Fighting for Air
lungne.org

New Hampshire Mold Task Force
and the American Lung Association Present:

Standard of Care

for the New Hampshire Mold Industry

A Guide for Citizens Affected by
Mold & Moisture in NH Buildings

NHMTF Standard of Care
History

A Group of NH Professionals Came Together With Concerns about Mold

- Lack of Regulation
- Lack of Consumer Protection
- Brainstormed Ideas for Legislation



BUYER BEWARE!

NHMTF Standard of Care
Legislation Proposal- Highlights

- No person shall perform mold assessment services for remuneration unless that person is a board certified IAQ professional.
- No person shall develop mold remediation specifications for remuneration unless that person is a board certified IAQ professional. Written mold remediation specifications shall adhere to industry standards accredited by the American National Standards Institute (ANSI).
- Mold remediation contractors shall follow the specifications and protocols written by a board certified IAQ professional. Deviations from any specification shall be in writing and approved by the board certified IAQ professional.
- Board certified IAQ professionals who write mold remediation specifications for projects shall not conduct mold remediation activities for the same project for a period of at least one year.

NHMTF Standard of Care
2009 Legislation

NH House Bill 482

- NH House, Commerce and Consumer Affairs Committees supported the Bill
- Sub-committee vote unanimous
- Full Committee - Lost by just 1 vote
- Committee Chair: *"bill would cost NH home buyers additional $$"*

NHMTF Standard of Care

Discouraged, But Not Defeated!

NH House Reps ask for a "Mold Task Force" to create a "Standard of Care" for NH

- Industry Experts
- Industry Associations
- Consultants
- Contractors
- Health Professionals



NHMTF Standard of Care

AMERICAN LUNG ASSOCIATION®

Fighting for Air

lungne.org

NHMTF Standard of Care

The Process

Creating a Standard of Care

- What is a Standard of Care?
- Once it becomes published, legislators have a "Best Practices" legal document for the industry.



NHMTF Standard of Care

The Process

Creating a Standard of Care

- Brainstorming
- Research other States
- All ideas welcome
- Multi-vote on ideas



NHMTF Standard of Care
What's this all about?

- Consumer Protection
- Ethics
- Certifications
- Training
- Health
- The Industry
- Pro's and Con's?



Section II
Minimum Qualifications for a Mold Consultant

NHMTF Standard of Care
Protecting Consumers

- Currently anyone can practice Consulting or Contracting in the Mold Industry, within NH.
- An "expert" can be sold as an individual with:
  - No Education
  - No Training
  - No Certifications
  - No Experience



- No Protection or Direction for Consumers

The NHMTF Recommendations for hiring a Mold Consultant

ACAC

- Certification by The American Council for Accredited Certifications, ACAC
  - CIEC, Board Certified Indoor Environmental Consultant
  - CIE, Board Certified Indoor Environmentalist
  - CMC, Board Certified Microbial Consultant
  - CMI, Bard Certified Microbial Investigator

The NHMTF Recommendations for hiring a Mold Consultant (contd)



- CIH Board Certified Industrial Hygienist
- Other 3rd Party Certifications approved by ANSI and CESB





3rd Party Certification: What it means

- Must be administratively independent of other organizations in matters pertaining to certification.
- Certifying body must consist of a majority of certified individuals.
- Must provide the public and consumers with an opportunity for input into its policies and decisions.
- Must follow strict rules for public disclosure of certification-related activities.
- Must follow strict rules for test development, evaluation and administration.
- Must enforce stringent eligibility requirements for all candidates, including 8 yrs of education and/or field experience for engineering-related designations, such as CIEC and CMC, and 2 to 5 yrs education and/or field experience for engineering-technician designations, such as CIE, CMR, CMRS, CIAQM, CMI and CRMI.

3rd Party Certification: Why It's Important!

- Indoor Environmental Professionals (IEPs) have been thoroughly trained & educated in:
  - Threats to health
  - Containment / Engineering Controls
  - Clean-up standards, recognition and investigations
  - Industry guidance documents (EPA, OSHA, AIHA, DES, etc.)
  - Data Interpretation

NHMTF Declares That IAQ Testing is Inadequate by Itself

- A "mold expert" collects sample data & sends their client the data results (and a bill). Problem? There's no interpretation of the results!
- Mold is ubiquitous, the consumer sees mold on a data sheet and "FREAKS OUT."
- Sending the test result without a physical investigation is inappropriate
- Reports should, at a minimum have: Written findings, recommendations and conclusions, scope of work for clean up, recommend follow up "CLEARANCE" tests and investigation.

NHMTF Standard of Care

3rd Party Certification:

Why It's so Important!



Educate Yourself!



The Pro's of 3rd Party Certification

- Third party Certification provides:
  - Experience
  - Education
  - Performance
  - Testing
- VERY VERY IMPORTANT:
  - Third party organizations can "take action!"



NHMTF Standard of Care
More About 3rd Party Certification

- IAQA Position Statement on Certification

Indoor Air Quality Association Inc.

ACAC

Council of Engineering and Scientific Specialty Boards 1990

ANSI American National Standards Institute

NCCA National Commission for Certifying Agencies NCCA Accredited Program

NHMTF Standard of Care

Ethics

- Very Important for the Consumer

Indoor Air Quality ASSOCIATION INC.

ACAC

COUNCIL OF ENGINEERING AND SCIENTIFIC SPECIALTY BOARDS CESB 1990

ANSI American National Standards Institute

ABIH american board of industrial hygiene

Does Mold Make You Sick?



NHMTF Standard of Care

Mold's Affect on Health: A Myth?

Statements about Mold & Health collected from

- AIHA "Recognition, Evaluation and Control of Indoor Mold."
- World Health Organization study on indoor dampness and related health effects.
- EPA Report on Mold and Moisture in Schools and Commercial Buildings.
- Indoor Environment Connections Articles.



NHMTF Standard of Care

A Major Hurdle in the Battle

This document brings to the table

a credible published document that can be a baseline for all to follow and reference:

Citizens
IAQ Professionals
Landlords
Lawyers
Lawmakers

nhmtf
New Hampshire Mold Task Force



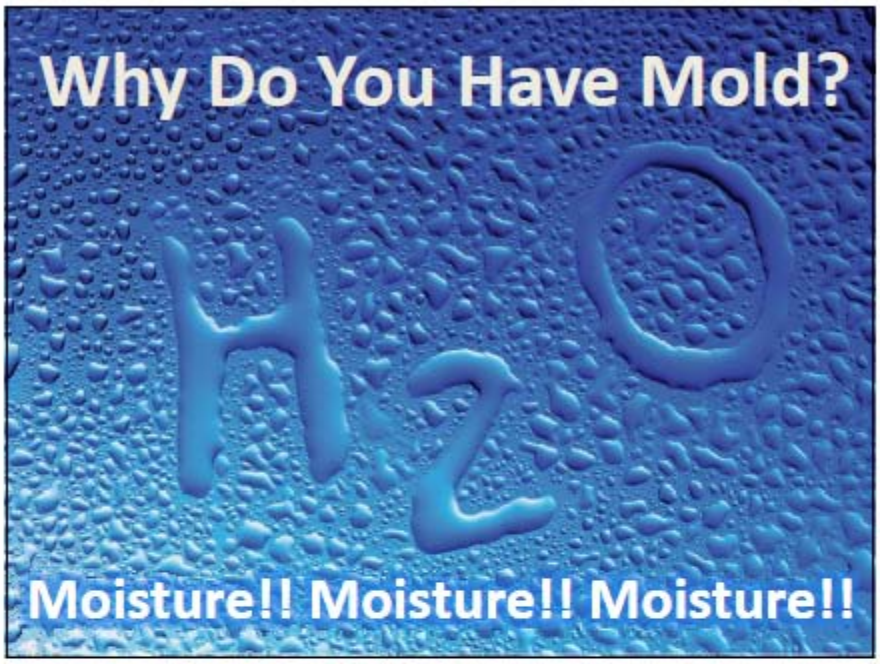
Mold & Moisture



25

I'm Thriving Baby!!!





Why is it in Your Basement?



Why is it in Your Living Space?



Moisture Gets Trapped!



Moisture by Accident!

Pipes, Appliances, Showers



Why is Mold in Your Attic?



How to hire A Professional!

- Where to go to find a Remediation Firm?
- Where to go to find a qualified professional and more information?

ACAC

IICRC
Institute of Inspection Cleaning and Restoration Certification

ABIH
american board of industrial hygiene

AIHA
Protecting Worker Health

Section III Contractors

nhmtf
New Hampshire Mold Task Force

Minimum Qualifications for Contractors

- Insurance, specific to environmental coverage
- Experience in industry, IICRC S520 is and ANSI Standard
- List of references, more than a few and not just homeowners
- Certifications; ACAC offers several levels of Certification for remediators.
- Application of an "Biocide" requires a Pesticide license
- Depth of staff
- Will they be around if there is a problem down the road (warrantee coverage)?



NHMTF Standard of Care

Red Flags when hiring a remediation firm:

- Offer to do both the initial investigation and the remediation
- No Pollution Liability Insurance
- No References
- No proof of Certification or IICRC Training
- No specific classes in Mold Remediation



Section IV
NHMTF and Legislation
What's Next?

nhmtf
New Hampshire Mold Task Force

NHMTF Standard of Care
Back to Legislation

What We've Learned:

- Legislators want bills that protect the consumer!
- Legislators do not want more legislation that restricts business or costs the state $$!
- Legislators do not want "CERTIFICATION BILLS"



NHMTF Standard of Care
In Summary

We Believe….

- Exposure to indoor mold is a health risk to our citizens
- 3rd party certifications should be required of IEPs
- We must educate Consumers
- Mold Testing & Remediation should be performed by two separate parties
- IAQ Testing alone is inadequate in most situations
- All Mold Abatement workers should have professional training



NHMTF Standard of Care
Recommendations to NH Legislators

- Adopt Legislation for Mold
- Amend NH Building Codes
- Protect rights of NH citizens affected by mold
- Provide educational information to NH citizens regarding IAQ, mold, health effects, rights and resources.



NHMTF Standard of Care

Stay Tuned!

You can find the NH Standard of Care pdf here:

- American Lung Association:
  www.lung.org, (search on NH Standard of Care)
- ACAC: **www.acac.org**, in the NH forms section
- Absolute Resource Associates home page:
  www.absoluteresourceassociates.com

nhmtf
New Hampshire Mold Task Force



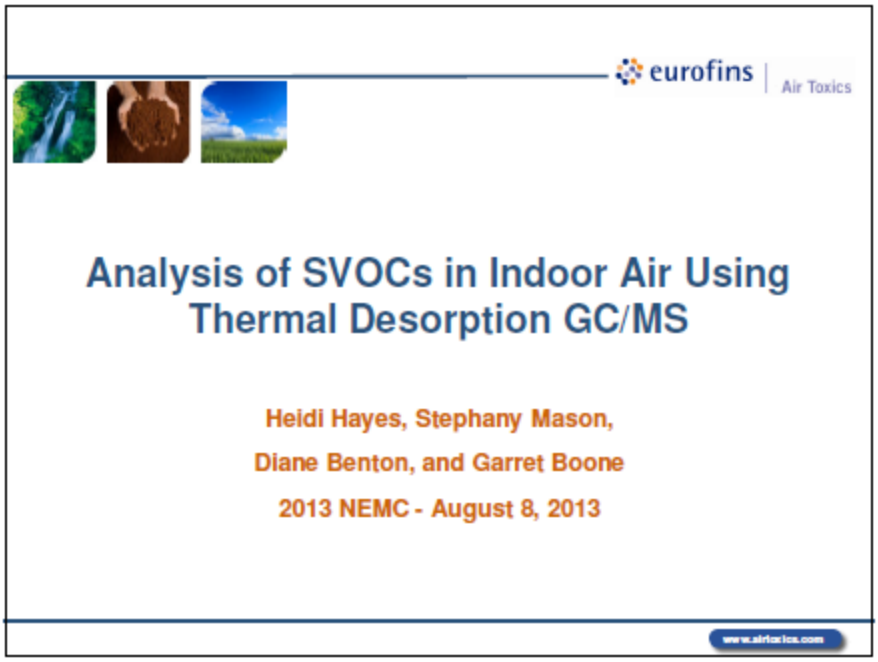
Analysis of Particulate and Vapor Phase Semi-Volatile Organic Compounds in Indoor Air Using Thermal Desorption Gas Chromatography-Mass Spectrometry

Heidi Hayes
Eurofins Air Toxics, Inc.

Abstract

Identifying and measuring semi-volatile organic compounds (SVOCs) are of increasing interest in assessing indoor air quality and quantifying human health risks. Sources of SVOCs in indoor air include household activities such as cooking, use of fireplaces, and smoking as well as emissions from building materials and household products, and intrusion of outdoor air. The conventional methods for measuring SVOCs in indoor air use a combination of filters to collect the particulate-associated fraction and sorbents such as XAD resin to capture gas-phase contaminants. Both the filter and sorbent cartridge are extracted together as one sample using an organic solvent. While effective, these methods require a large volume of air to provide the desired sensitivity, and the solvent extraction step requires significant labor and resources in the laboratory. As an alternative to solvent extraction, thermal desorption techniques allow for the direct analysis of the collection media, thereby eliminating the off-line preparation steps and providing improved sensitivity since a large portion of the sample is transferred to the analytical unit. Despite the advantages of thermal desorption, the low vapor pressure of SVOC compounds present a challenge in selecting the appropriate collection media and desorption parameters. The media must retain the most volatile compounds at the desired sampling volume while efficiently releasing the least volatile particulate-associated compounds during the thermal desorption step. Desorption parameters must be optimized to insure complete transfer of the target compounds from the media through the secondary trap and transfer line to the GC.

A method using thermal desorption coupled with GC-MS was developed to measure indoor air SVOCs in the vapor and particulate phase. The SVOCs evaluated by this method include a list of PAHs ranging from naphthalene to 5- and 6-ringed PAHs, such as benzo(a)pyrene and benzo(ghi)perylene. Several combinations of filters and sorbents are evaluated for recovery and ease of use, and analytical performance data including sensitivity, linearity, and precision are presented. Performance of the thermal desorption method is compared to the conventional solvent extraction technique by collecting concurrent indoor air samples. Advantages and limitations of the thermal desorption method are presented.


eurofins | Air Toxics
Analysis of SVOCs in Indoor Air Using Thermal Desorption GC/MS
Heidi Hayes, Stephany Mason,
Diane Benton, and Garret Boone
2013 NEMC - August 8, 2013


Outline
• Background
• SVOCs in Indoor Air
• Conventional Sampling and Analysis Methods
• EPA Method TO-17 Validation - SVOCs
• Aroclors
• PAHs
• Next Steps
• Conclusions
eurofins | Air Toxics
2

Indoor Air Quality Investigations



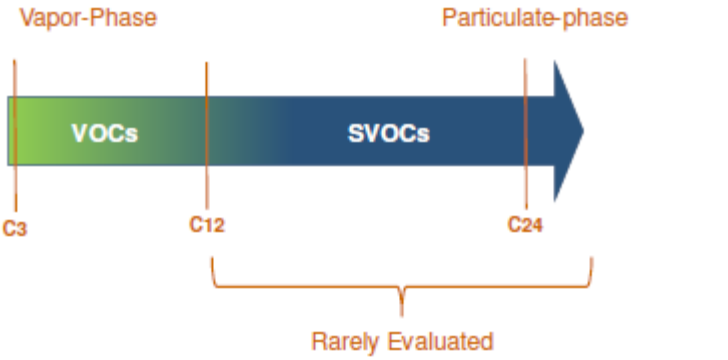
Commonly monitored pollutants

- Inorganic gases
  - CO, CO_2, NO_2
- Particulates
  - $PM_{2.5}$, PM_{10}
- Molds/Allergens
- Volatile organic compounds (VOCs)

eurofins | Air Toxics

3

Indoor Air Quality Investigations



eurofins | Air Toxics

4

Indoor Air Quality Investigations



SVOCs

- Polychlorinated Biphenyls (PCBs)
- Polycyclic aromatic hydrocarbons (PAHs)
- Flame Retardants
- Plasticizers

eurofins | Air Toxics

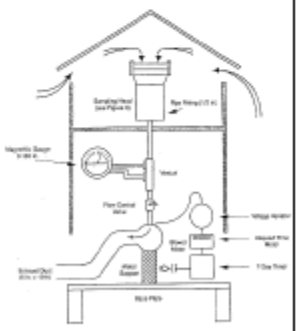
5

Conventional Air Methods - SVOCs



TO-4 (PCBs), TO-13 (PAHs)

- PUF or PUF/XAD sorbent cartridge
- High Volume sampler
- Solvent Extraction: Analytical RLs = 100 to 1000 nanograms
- Large volumes collected = 300 m^3 = 300,000 Liters
- Sample RL ≈ 0.3 to 3 ng/m^3



High volume samplers are not practical for indoor air measurements.

eurofins | Air Toxics

6

Conventional Air Methods - SVOCs

TO-10 (PCBs) and TO-13 (modified)

- Use standard sample vacuum pump
- Typical achievable flow rates 1 to 5 LPM
- 'Low flow' sorbent cartridge
- 24 hour duration = 1500 to 7200 Liters
- Sample RLs ≈ 10 to 100 ng/m³



eurofins | Air Toxics 7

SVOCs – Screening Level (SL)

SVOC	SL (ng/m³)*	Solvent-extracted RL (ng)	Sample Volume (L)	Duration (min)	Duration (days)
Aroclor 1242	4.3	1000	232,000	46,400	32
Benzo(a)pyrene	0.87	100	115,000	23,000	16

Screening Level = 10^{-6} Cancer Risk,
Residential Indoor Air, May 2013 ORNL

eurofins | Air Toxics 8

Proposed Approach



EPA Compendium TO-17



- Collect on sorbent tube using a personal pump
- Thermally desorb and analyze by GC/MS
- Thermal Desorption sample introduction is several orders of magnitude more sensitive than Solvent Extraction

SVOC	SL (ng/m^3)	TO-17 RL (ng)	Sample Volume (L)	Duration (min)	Duration (days)
Aroclor 1242	4.3	1.0	232	464	0.32
Benzo(a)pyrene	0.87	0.50	574	1,149	0.80

eurofins | Air Toxics

9

TO-17 Validation Objectives



Optimize for SVOC compounds

- Sorbent Tube Selection
  - Dual Bed – very weak sorbent combination
- ATD Desorption Parameters
  - Specialized secondary trap
  - Primary Desorption = 375°C
  - Secondary Desorption = 400°C

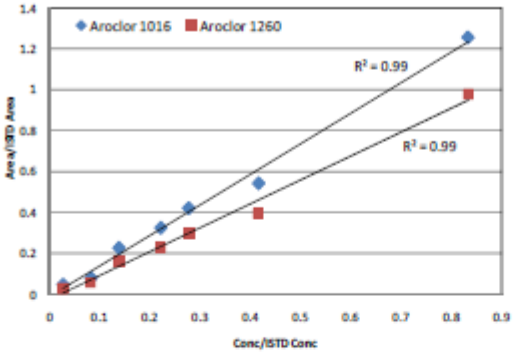


eurofins | Air Toxics

10

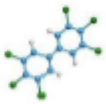
TO-17 Aroclor Linearity





Concentration Range 1.0 ng to 30 ng

Aroclor	Average %RSD
1016	8.25
1260	8.41

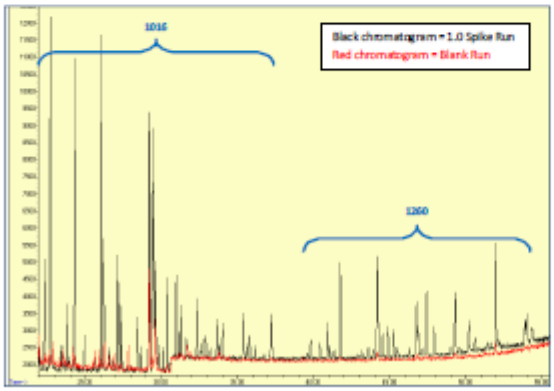


eurofins | Air Toxics

11

TO-17 Aroclor Sensitivity





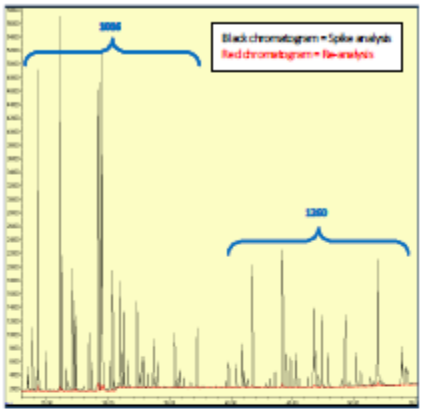
Method Detection Limit Study – 8 replicates spiked at 1.0 ng

Aroclor	MDL (ng)
1016	0.31
1260	0.21

eurofins | Air Toxics

12

TO-17 Aroclor Desorption Efficiency



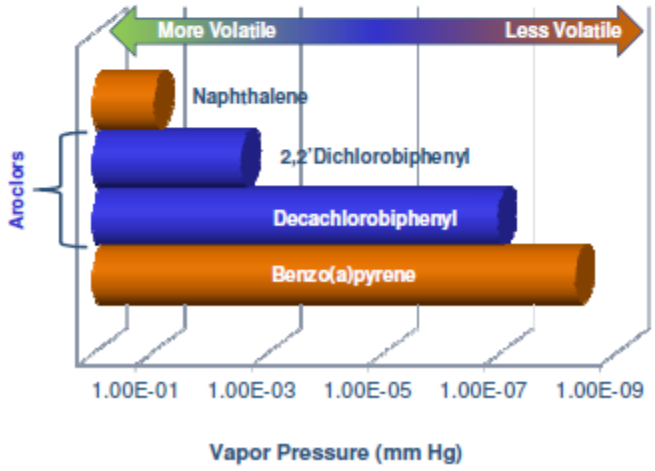
Aroclor	%DE
1016	99.7
1260	100.0
1221	100.0
1232	98.4
1242	97.1
1248	97.5
1254	100.0
1268	100.0

All Aroclors met performance criterion of >95% DE

eurofins | Air Toxics

12

TO-17 PAHs - 'Widening' the challenge



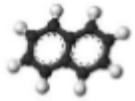
eurofins | Air Toxics

14

TO-17 PAHs Method Validation



- Retention of Naphthalene
  - Safe Sampling Volume (SSV) Determination
- Desorption efficiency of Benzo(a)pyrene and 6-ringed PAHs
- Linearity
- Sensitivity
- Particulate filter evaluation
- Field evaluation





eurofins | Air Toxics

15

TO-17 PAHs SSV Determination



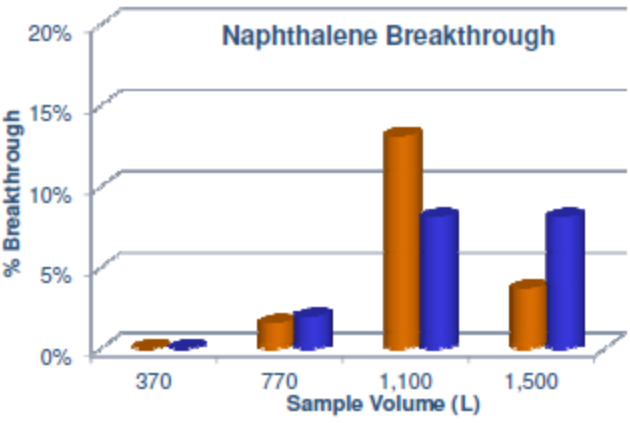
~0.25 LPM ~24 hours	Front	Back	~ 370 Liters
	Front	Back	
~0.50 LPM ~24 hours	Front	Back	~ 770 Liters
	Front	Back	
~0.75 LPM ~24 hours	Front	Back	~ 1,100 Liters
	Front	Back	
~1.0 LPM ~24 hours	Front	Back	~ 1,500 Liters
	Front	Back	

Naphthalene spiked at 10 ng on front tube
Sampled filtered air, conditioned at 50%RH and 23 deg C

eurofins | Air Toxics

16

TO-17 PAHs SSV Determination



eurofins | Air Toxics

17

TO-17 PAHs Method Validation – Next Steps

- Retention of Naphthalene
  - Safe Sampling Volume (SSV) Determination
  - Outcome = 0.5 LPM for 24 hours = 770 Liters
- *Desorption efficiency of Benzo(a)pyrene and 6-ringed PAHs – In progress*
- *Linearity – In progress*
- *Sensitivity – In progress (0.1 to 0.5 nanograms)*
- *Particulate filter evaluation (Initial Studies with glass wool plug)*
- *Field evaluation (In progress - initial proof of concept)*

eurofins | Air Toxics

18

TO-17 PAHs Method Validation

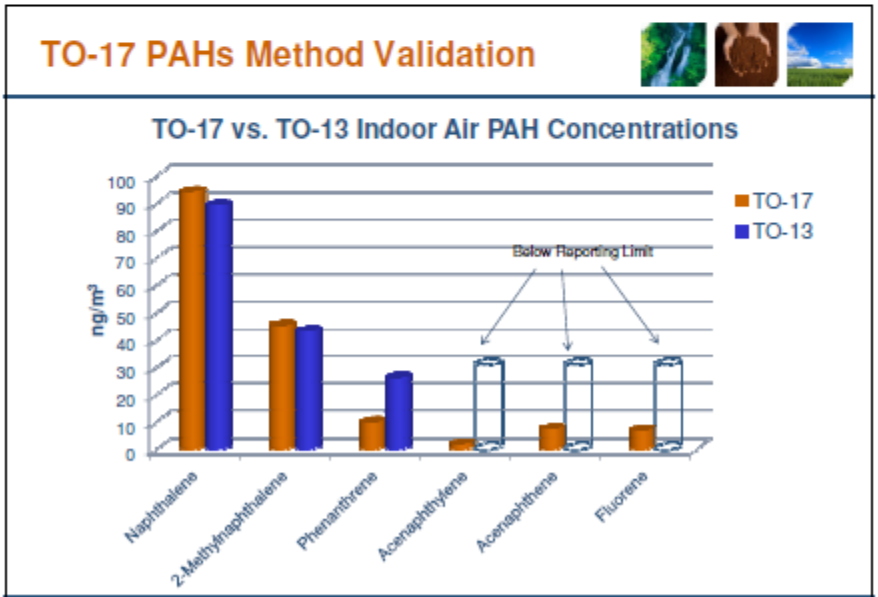
- Proof of concept – Field comparison
- Indoor air sample
  - TO-13 and TO-17 concurrent samples
  - 24-hour sample duration

Method	Flow Rate (LPM)	Duration (min)	Volume (L)
TO-17	0.5	1304	617
TO-13	2.5	1304	3,260

eurofins | Air Toxics

19

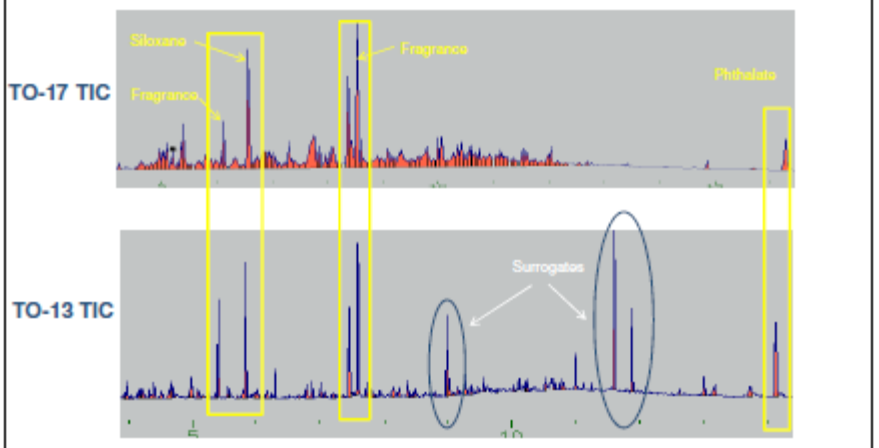
TO-17 PAHs Method Validation



eurofins | Air Toxics

20

TO-17 Method Validation



eurofins | Air Toxics

21

Conclusions

EPA Method TO-17 can successfully be applied to Aroclor measurements and is promising technique for PAHs.

- Sensitivity is beneficial for the Indoor Air Quality investigations
- Additional lab and field validation is required, specifically for the 5 and 6-ringed PAHs which are challenging due to their low vapor pressures.
- Evaluation of particulate filter as part of the TO-17 sampling train required for compounds largely associated with particulates.

eurofins | Air Toxics

22


eurofins
Air Toxics
Questions
Heidi Hayes, Technical Director
hhayes@airtoxics.com
916-985-1000 x 3341
www.airtoxics.com

Developing a National Standard for Health Based Emissions

Jessica Evans
NSF International

Abstract

NSF International and Underwriters Laboratories are partnering in the development of an American National Standard on health based emissions. The standard will expand on criteria detailed in CA/DHS/EHLB/R-174 (CDPH Standard Practice), and establish procedures for sample collection and preparation, emission testing, concentration modeling, performance criteria, and compliance verification for specific chemicals of interest. The scope includes volatile organic compound (VOC) emissions from building products and interior furnishings including, but not limited to, wall coverings, paints, adhesives, furniture, and floor coverings. The standard will apply to the use of these products in commercial, institutional, and residential building types. Our presentation will provide an update regarding the standards development effort to date, and provide information regarding how interested stakeholders can participate in this important project.

Developing a Health Based National Standard for Chemical Emissions into Indoor Environments

Jessica Evans
Director, Standards
NSF International

Scott Steady
Product Manager – Indoor Air Quality
UL Environment

What is a Consensus Standard?

- Standards are documented agreements containing technical specifications or other precise criteria to be used consistently as rules, guidelines, or definitions of characteristics, to ensure that materials, products, processes and services are fit for their purpose.
- Consensus has 2 main components
  - A numerical requirement
  - Effort to resolve objections

Use of ANSI Standards

- ANSI National Standards are referenced in regulations and legislation throughout the U.S. and internationally.
- Examples of references include:
  - Model Plumbing and Building Codes
  - State regulations governing treatment and distribution of drinking water
  - FDA Model Food Code
  - USDA/FSIS regulations for food processing equipment
  - Various regulations in Canada, Israel, Taiwan, Australia, Brazil and other countries

Joint Committee



- Consensus body that oversees a specific standard or set of related standards
- Balanced membership of external stakeholders
  - Public Health
  - Manufacturers
  - Users
  - Other categories as indicated by the standards project
- Membership is based on applicant's experience and expertise

Task Group

- Formed by Chairperson or Joint Committee based on need
- Chairperson of JC selects the TG Chair
- Maximum size 15 people, membership is open to all, not only JC members
- NSF/UL 440 Task Groups
  - Toxicology
  - Environment and Products

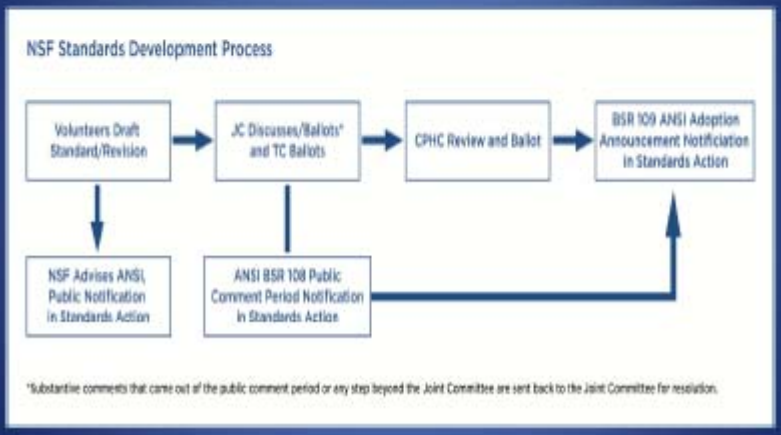
Information Flow



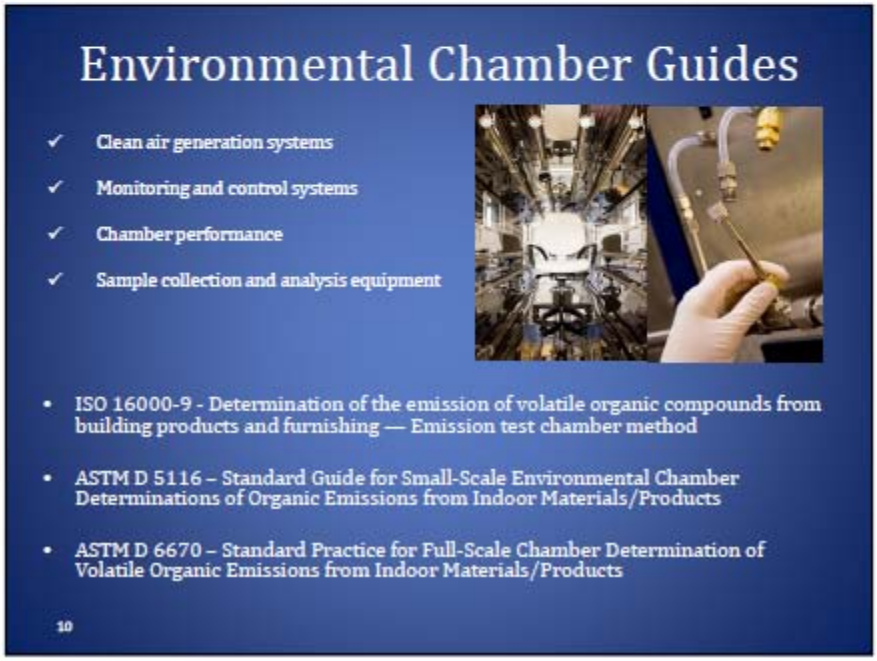
Council of Public Health Consultants

- NSF advisory body for standards development and program implementation
- Ensure public health issues addressed
- Review & ballot all standards or revisions
- Elects its own membership
  - Leaders in public health, environment and academics
- Technical Committee Role
  - Conduct review of proposed revisions utilizing technical expertise in the field or area covered by the ballot

NSF/UL 440 Standards Process




Product Emissions Testing
Air Purification and Conditioning
Environmental Chamber Testing
Predicting Indoor Exposure Levels
Sample Preparation
Analysis and Reporting


Environmental Chamber Guides
✓ Clean air generation systems
✓ Monitoring and control systems
✓ Chamber performance
✓ Sample collection and analysis equipment
• ISO 16000-9 - Determination of the emission of volatile organic compounds from building products and furnishing — Emission test chamber method
• ASTM D 5116 – Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
• ASTM D 6670 – Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products
10

Chemical Measurement

- VOC Measurements
  - ✓ ASTM D 6196 / EPA TO-17 / ISO 16000 Part 6
  - ✓ Collect chamber air on Tenax Sorbent Media, thermally desorb chemicals and analyze by GC/MS
  - ✓ Applicable to 1,000's of chemicals



- Aldehyde Measurement
  - ✓ ASTM D 5197 / EPA TO-11 / ISO 16000 Part 3
  - ✓ Collect chamber air on DNPH Cartridge, elute with acetonitrile and analyze by HPLC
  - ✓ Primarily for formaldehyde and acetaldehyde

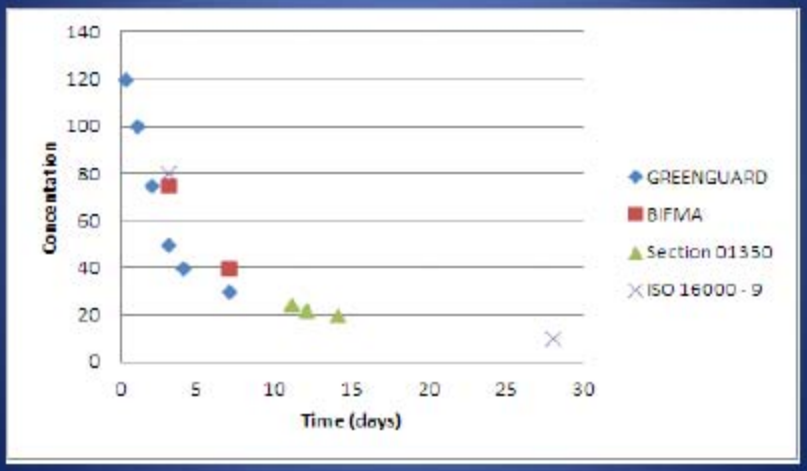


11

Existing Furniture and Building Product Test Methods

- UL 2821 GREENGUARD Certification Program Method for Measuring and Evaluating Chemical Emissions From Building Materials, Finishes and Furnishings (and UL 2818 Standard)
- California Department of Public Health Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers Version 1.1 (California Section 01350)
- BIFMA M7.1 Standard Test Method for Determining VOC Emissions (and X7.1 Standard)
- ISO 16000-9 Determination of the emission of volatile organic compounds from building products and furnishing -- Emission test chamber method

Comparison of Sampling Time Points



Predicting Exposure Concentrations

Health based toxicology benchmarks are defined in terms of breathing concentration (µg/m^3 or ppm)

Chamber methods are designed to measure emission rates (µg/m^2*hr)

Need to define the product use environment

- Room Volume
- Product loading (m^2/m^3)
- Ventilation



Health Based Exposure Limits

Existing standards have limits for relatively few chemicals emitted from indoor products

Toxicology reference values exist for many chemicals but most were developed for occupational exposure



15

Toxicology Work Group Approach

- Identify VOCs emitted from indoor products
- Identify qualifying authoritative bodies as sources of toxicological reference values
- Determine appropriate TRVs for noncancer health effects and carcinogens
- Adjustments to TRV-derived air concentrations to determine acceptance criteria
  - address uncertainties, decay rates, exposure durations, sensitive sub populations and reporting limits
- Standing Committee – Authority and Procedures
- Formaldehyde


Questions?
Jessica Evans
NSF International
Phone: 734-913-5774
Email: jevans@nsf.org
Scott Steady
UL Environment
Phone: 678-444-4056
Email: Scott.Steady@ul.com

Developing ASTM Standards for Test Specimen Preparation and Measuring Emissions of Volatile and Semi-Volatile Organic Compounds (VOCs and SVOCs) from Spray Polyurethane Foam (SPF) Insulation Products

John Sebroski
Bayer MaterialScience, LLC

Abstract

This presentation will discuss the ongoing development of ASTM standard practices and test methods to measure potential chemical emissions from spray polyurethane foam (SPF) insulation designed for on-site application in buildings. The consensus standards are being developed to evaluate SPF products for their impact on indoor air quality after installation in order to establish re-occupancy times for residents and re-entry times for trade workers. A standard practice is currently being developed for spraying, sampling, packaging, and test specimen preparation of SPF insulation samples for environmental chamber emissions testing. The prepared specimens are placed into micro-scale test chambers which are optimized to recover the emissions of semi-volatile organic compounds (SVOCs), e.g., flame retardant and amine catalysts, since these compounds have been shown that they can adhere to the walls of conventional small-scale test chambers that are commonly used for product emission testing. The VOC and SVOC emissions are captured from the chambers onto stainless steel thermal desorption tubes containing the appropriate sorbents, then analyzed with thermal desorption and GC/MS. The measured values are reported as emission factors to estimate the mass emitted per unit time and surface area. The consensus standards are being developed by ASTM Committee D22 on Air Quality through Subcommittee D22.05 on Indoor Air.

Developing ASTM Standards for Measuring VOC and SVOC Emissions from Spray Polyurethane Foam Insulation Products

John Sebroski

Bayer MaterialScience LLC

American Chemistry Council | Center for the Polyurethanes Industry

CPI Emissions Task Force Objective

Develop methods for SPF standardization that can be used by manufacturers to evaluate potential emissions released from SPF insulation samples.

Participate in research to support the development of SPF product emissions standards through ASTM Subcommittee D22.05 on Indoor Air Quality.

ASTM Subcommittee D22.05 on Indoor Air

SPF Emissions Task Group Members

- Industry (CPI, III)
- Regulatory (US EPA, CPSC, etc.)
- Instrument Vendors
- Consultants
- Air Quality Testing Labs
- Certification Programs
- Other Stakeholders

ASTM Work Items

- ASTM WK30960 (Recently published as D7859-13e1)

  Standard Practice for Spraying, Sampling, Packaging, and Test Specimen Preparation of Spray Polyurethane Foam (SPF) Insulation Samples for Environmental Chamber Emissions Testing

- ASTM WK40293

  New Practice for Estimating Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation using Micro-Scale Environmental Test Chambers

- ASTM WK40292

  New Test Method for Measuring Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Samples in Environmental Test Chambers with Thermal Desorption and Gas Chromatography / Mass Spectroscopy (TD-GC-MS)

Generic SPF Formulations

Three generic SPF formulations were developed by CPI to evaluate the test methods for measuring emissions.

The formulations represent the following sample types:

Spray Polyurethane Foam
Open-cell 1/2 pound
High Pressure

Spray Polyurethane Foam
Closed-cell 2 pound
High Pressure

Spray Polyurethane Foam
Kit Formulation
2 Component, Low Pressure

ASTM Standard Practice D7859-13e1





Standardizes the procedures for spraying, sampling, packaging and test specimen preparation of SPF insulation for testing of emissions using environmental chambers.

Practice is applicable to both closed-cell and open-cell SPF insulation.





Spraying, Packaging and Transport

Spraying Parameters

- Specialized equipment with trained operators
- Samples are sprayed in spray booth under controlled conditions
- Samples sprayed onto sheets of HPDE as substrate
- Sample thickness specified for both open-cell and closed-cell SPF

Packaging and Transport

- Samples allowed to cure for 1-hour
- Samples are wrapped with aluminum foil then placed into layered polyethylene terephthalate (PET) bags with minimal headspace
- Samples shipped in insulated secondary container
- Electronic data loggers can be used to monitor temperature, pressure and relative humidity during transport
- Samples and data record shipped to laboratory via overnight delivery service

Laboratory Requirements

General Knowledge of SPF Formulations

- Define target compounds for emission monitoring
- Surface skin may need to be removed to simulate trimming of SPF insulation to wall studs or other structural elements

Sample Receipt and Storage

- Chain of custody
- Samples are stored in unopened bags at typical indoor office conditions (no refrigeration or freezing)

Holding Time

- Chamber testing must begin within 20 minutes of opening the PET bag and within 48-hours from spraying

Preparation of Specimens

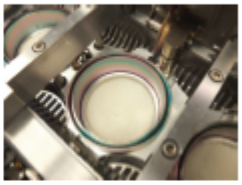
- Samples are cut to tightly fit into stainless steel sample holders or micro-scale chambers

ASTM Work Item WK40293

Describes the procedures to collect chemical emissions from SPF insulation samples using micro-scale environmental test chambers

Operating conditions minimize wall adhesion (sink effects) and maximize recovery of the SVOCs, which are captured onto sorbent tubes from the outlet of the micro-scale chamber



Micro-Scale Chamber Apparatus

Apparatus shown below holds four micro-scale chambers, controls gas flow and temperature

After equilibration, samples are collected from exhaust ports at various times



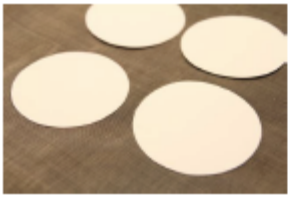

Sampling from Micro-Scale Chamber



Internal 58mm internal glass-fiber filter with 1-(2-pyridyl)piperazine (PP)



Flow calibrator



90mm glass-fiber filters with PP to wipe chamber walls



Thermal desorption tubes



Silica gel with DNPH tube

ASTM Work Item WK40292

Analytical methodology utilizing thermal desorption GC/MS to measure the chemical emissions of semi-volatile and volatile organic compounds (SVOCs and VOCs) from SPF insulation samples

Thermal desorption tubes are used to collect air samples from:

- Micro-scale or conventional test chambers
- Buildings to monitor indoor air concentrations



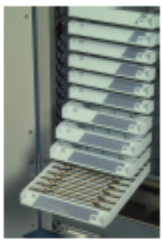
What is Thermal Desorption GC/MS?

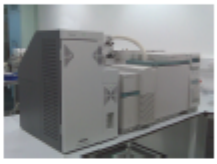
VOCs and SVOCs are sampled onto thermal desorption tubes packed with a specific combination of sorbents containing glass wool, graphitized carbon and porous polymer adsorbent.

Samples can be stored in sealed containers prior to analysis.

Captured organic compounds are released during a two-stage thermal desorption process and are identified and quantified by gas chromatography/ mass spectrometry.

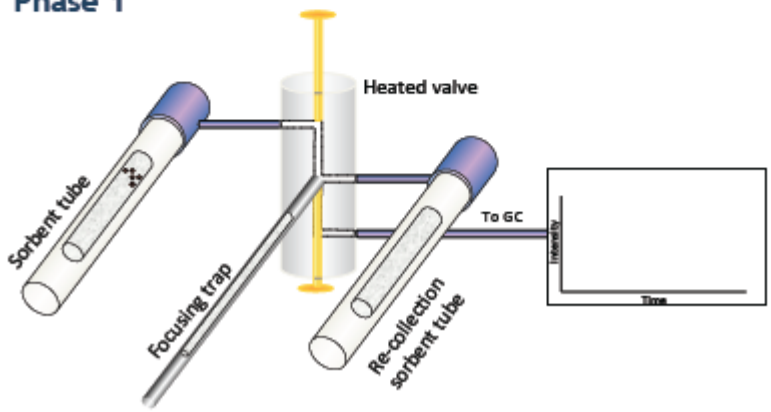
Target compounds compared with reference standards; unknown compounds are tentatively identified with NIST Mass Spectral Library.





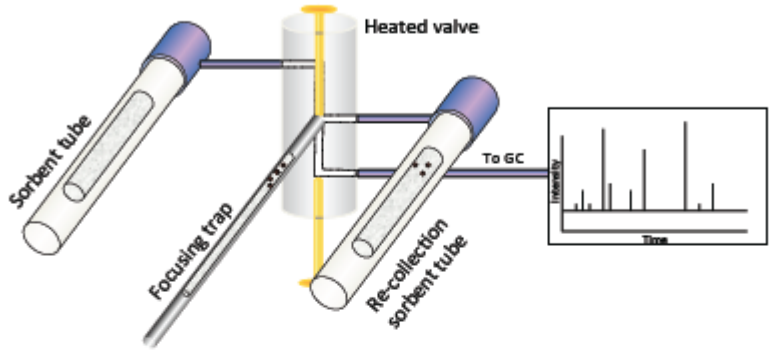
Two-Stage Thermal Desorption

Phase 1

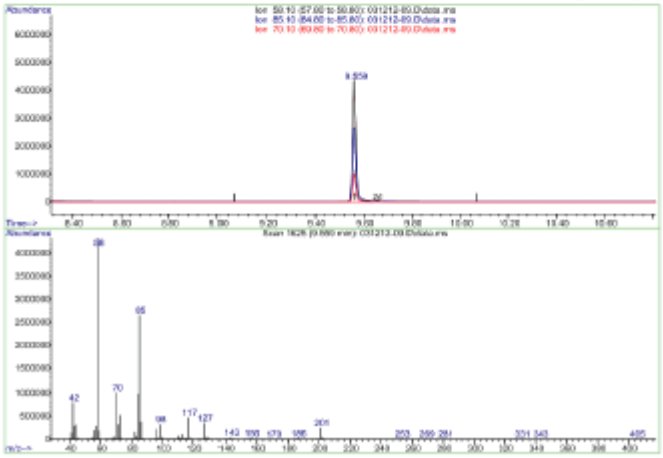


Two-Stage Thermal Desorption

Phase 2



Extracted Ion Chromatogram Mass Spectrum



Generic SPF Target Compounds with Thermal Desorption GC/MS

Compound Name	Compound Type	Retention Time, minutes	Estimated Quantitation Limit, ng	Mean Recovery, %	Precision RSD, %
HFC-245a	Blowing Agent	1.48	20	89.7	10.9
TMAEEA	Amine Catalyst	7.69	200	71.5	24.6
BDMAEE	Amine Catalyst	7.72	20	94.5	4.10
PMDTA	Amine Catalyst	8.26	50	92.9	3.52
DAPA	Amine Catalyst	9.56	100	96.2	3.38
TMIBPA	Amine Catalyst	9.65	200	68.1	13.3
TCPP	Flame Retardant	12.5	50	92.6	2.94

Evaluation of Data

Emissions factors

- Mass per surface area and time, µg / m^2 hour

Predicted building concentrations

- Loading factor in building, area /volume, m^2/m^3
- Air exchange rate (ventilation rate), fresh air exchanges / hour
- Predicted concentration values are typically calculated in $\mu g/m^3$

Evaluation of Data

Re-entry time

- Compare predicted concentrations at a given time with Occupational Exposure Limits (OELs)

Re-occupancy time

- Compare predicted concentration at a given time with Chronic Reference Exposure Limits (CRELs) or 1/100 OEL

Evaluate ventilation rates

- Evaluate ventilation rates to meet exposure limits or odor threshold limits

Research and Collaboration

Current Research Projects

- **Center for Polyurethane Industry (CPI)**
  - Further support development of analytical test methods
  - Optimize recovery of flame retardant and amine catalysts using micro-scale test chambers
- **International Isocyanate Institute (III)**
  - Evaluate prototype micro-scale test chambers optimized for MDI emissions

US EPA, Office of Research and Development

- Ongoing CPI and US EPA meetings to discuss current activities in each organization

ASTM D22.05 on Indoor Air

Subcommittee Ballot

- WK40292 Standard Test Method for Measuring SPF Chemical Emissions with Thermal Desorption Tubes and GC/MS
- WK40293 Standard Practice for Using Micro Chamber to Measure SPF Emissions

Scheduled Meetings

- October 22, 2013, Jacksonville, Florida
- April 8, 2014, Toronto, Ontario, Canada

Acknowledgments

ASTM International Committee D22 on Air Quality

- Subcommittee D22.05 on Indoor Air

Bayer MaterialScience LLC

- Environmental Analytics Laboratory
- Product Safety and Regulatory Affairs

Center for Polyurethane Industry (CPI)

- SPF Emissions Task Force
- SPF Ventilation Task Force


Questions?

SECTION 21

LABORATORY ACCREDITATION

When You Cannot Travel to Conduct a Required TNI Audit, What Are Your Options?

Stuart Nagourney, Retired
NJ Department of Environmental Protection

Abstract

What do you do when you cannot travel to conduct required TNI audits of laboratories that do more than $1M of analytical work annually for your State?

The New Jersey Department of Environmental Protection, Office of Quality Assurance faces just such a dilemma regarding two laboratories located in Mississaugua, Ontario Canada that have primary TNI certification with our accrediting authority. This talk will describe how technology can be employed to perform audits remotely when administrative obstacles prevent traditional operations.

The talk will include excerpts from a “mock” remote audit.

WHEN YOU CANNOT TRAVEL TO CONDUCT A REQUIRED TNI AUDIT, WHAT ARE YOUR OPTIONS?

Stuart Nagourney

NJDEP (ret.)

609-558-2012

stunag@aol.com

DISCLAIMER

- The content of this presentation reflects my views and not those of any other organization or individual

STATUS OF NJDEP, OQA

- Certify >900 laboratories worldwide; ~150 are "full-service" labs.
- Currently assess all labs. biennially
- Operate a "dual program" - State & TNI
- Also responsible for Dep't.-wide QA duties
- Once had 19 auditors; as of 7/1/13, 11 remain (2 eligible to retire); no replacements
- Processing contract for utilizing 3rd party assessors to assist w/out-of-state audits

TRENTON, WE HAVE A PROBLEM

- Maxxam and ALS are both NJDEP primary TNI labs.
- Location of both labs.: Mississauga, Ontario, CAN
- NJDEP has conducted multiple audits of each lab.
- Travel approval to assess both in Oct. 2012 was denied since this was defined as "foreign travel"

NJDEP OPTIONS

- Do nothing and hope no one notices
- Retire before someone notices (works for some, not for others)
- Force TNI responsibilities on another AB
- Be creative

CREATIVE OPTION: REMOTE AUDITS

- Training, customer interactions, … are now increasingly done on-line via interactive software such as Citrix® GoToMeeting®
- Features:
  - Real-time sharing of documents & files
  - Audio and video connectivity
  - Ability to record & archive results

PROCESS FOR EVALUATING POTENTIAL FOR REMOTE AUDITS

- Administrative Restrictions - None in N.J.A.C. 7:18, TNI or ISO
- Management and Lab. Support - Obtained
- Costs - Minimal
  - GoToMeeting® is free
  - Webcams are inexpensive
  - Most labs. have broadband connectivity

PROCESS FOR EVALUATING POTENTIAL FOR REMOTE AUDITS

- Evaluate technology limitations
- Start small: choose a lab. that has only a few certified methods in one area of analysis
- Conduct "mock audits" under controlled conditions
- Try it and see how it goes

TEST CASE - AECOM

- AECOM (Harvard, MA) is a willing NJ State-certified lab.; has a minimal # of certified methods (Methods 5 & 201)
- Travel from NJ-MA would have involved 5 hrs. on the train each way for a ~1.5-hr. assessment
- NJDEP rigorously reviewed SOPs and other records prior to remote assessment

AECOM AUDIT RESULTS

- Audit conducted May 7, 2013 following prior demonstration of internet connectivity
- AECOM submitted SOPs and other documentation to the NJDEP in advance
- NJDEP audit checksheets used for audit shared in advance with AECOM
- Time: ~1.5 hrs.
- Findings: 3 deficiencies, all minor

AECOM AUDIT ISSUES

- Audio worked well, but we could not record audio (using external phone and not VIOP) or WebCam video
- WebCam video screen size was very small and resolution was limited
- AECOM had low bandwith connection and limited wireless capability

CLIENT FEEDBACK

"I was impressed by the remote audit of our air lab this morning; there were clearly some limitations in the technology at that particular facility, but overall the process seemed to accomplish the goals. The concept garnered a great deal of interest among our chemistry staff when we first heard about it since we face some of the same limitations that you do regarding on-site audits. This is a very innovative approach and is an option we will likely consider."

Mary O'Connell Kozik
Senior Project Chemist
AECOM

ADD'L. TECHNOLOGICAL ISSUES

- Non-Citrix® software needed to display full-screen HD video (Windows Media Encoder or similar). Use Citrix® in "record" mode
- Need high-speed WIFI w/sufficient bandwidth (4G USB Modem, ⌑ 4-5 Mbps)
- These could be the minimal requirements for clients to conduct remote audits

ADMINISTRATIVE CONCERNS

- Audit files are likely subject to OPRA; does that impact client confidentiality?
- Remote audits will almost certainly be an option rather than a requirement
- Can NJDEP or TNI require minimum technology requirement for remote audits?

HOW ABOUT REMOTE AUDITS OF "FULL-SERVICE" LABS.?

- LOTS more up-front review of QM, SOPs, … needed prior to remote audit
- Initial audits and audits of "problem" labs. should be done on-site
- QS should be easy to do remotely
- Would require multiple webcams on both ends to audit various parts of the lab. concurrently as is now done
- If lab. sections are audited sequentially, time for the audit could take ~2 weeks
- Remote audits would be much less expensive for the lab.

NEXT STEPS

- Learn more about the technology to enhance video
- Explore application to more diverse and complex audits
- Evaluate experience of other ABs
- Develop written TNI guidance

ACKNOWLEDGEMENTS

- Marty Hackman NJDEP
- Dr. Bernie Wilk NJDEP
- Paul Taverna AECOM
- Danielle Wineberg AECOM

The Benefits of a Public/Private Partnership on Laboratory Accreditation

Chris Gunning
A2LA Environmental Sciences

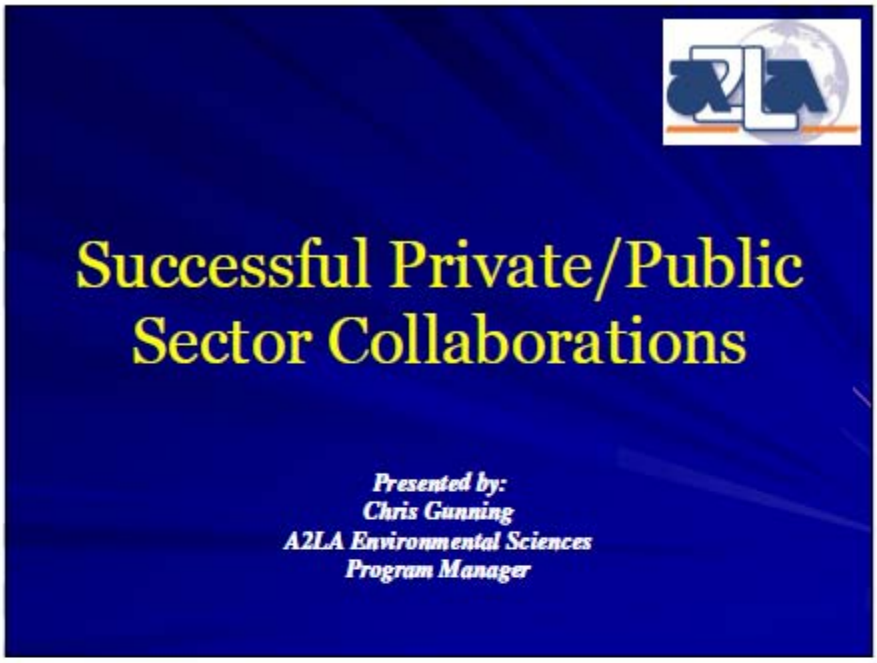
Abstract

In order to protect public health and the environment, regulators need data of known and documented quality. The public needs to have confidence in the data regulators are relying on. The future of the commercial laboratory industry depends on the public having confidence in the data being generated. A level playing field requires that all laboratories adhere to recognized quality standards.

In this age of increasing national debt and shrinking state budgets, there is a large amount of pressure on state accrediting bodies to maintain a high level of service and ensure data quality emerging from their accrediting labs with less and less resources at their disposal. One proposed solution to this problem is to work towards public and private partnerships that would shift some of the burden of performing the assessments and managing the day to day accreditation programs to mutually recognized third party accrediting bodies. The state programs could then focus on supervising the program and shifting resources towards method development and implementation. This partnership would allow the state programs to retain primacy in the issuance of licenses based on the third part accreditation thereby continuing to follow state regulations.

There are many examples of successful public and private partnerships that have been mutually beneficial. These include federal programs such as the EPA asbestos and lead programs, and state programs such as Georgia, Kentucky, Wyoming, and Washington. The partnerships have been successful due to the fact that they have been tailored to specific regulatory needs but are generally based on consensus standards ISO/IEC 17011 and ISO/IEC 17025. The programs require minimal agency resources while still being flexible enough to handle varying service demands.

In summary, the main goal of the accreditation process is to ensure (attest) that labs can competently demonstrate their abilities to perform their scope of accreditation in relation to the standard and accreditation requirements. This goal can be successfully realized in a growing market with limited resources by utilizing a successful public/private partnership model.


Successful Private/Public Sector Collaborations
Presented by:
Chris Gunning
A2LA Environmental Sciences
Program Manager


Why Collaborations are Successful
Programs can be catered to specific regulator needs but are based on common international consensus standards ISO/IEC 17011 and ISO/IEC 17025.
Collaborations enable varying degrees of oversight by the state and federal agencies based on their comfort level.
These collaborations place the costs of accreditation on the laboratories being assessed/audited.

Collaborations

1. State of Washington Department of Ecology
2. Kentucky Underground Storage Tank Laboratory Accreditation Program (UST)
3. State of Georgia Environmental Protection Division (EDP)
4. Wyoming Leaking Aboveground & Underground Storage Tank (LAUST)
5. Department of Defense Environmental Laboratory Accreditation Program (DoD ELAP)
6. National Environmental Field Activities Program (NEFAP)

Washington Department of Ecology

- Environmental laboratories that prepare data for submission to certain state agencies and programs are required to be accredited by WAC 173-50.
- Environmental Assessment Program (EAP) Lab Accreditation Unit (LAU) is charged with implementing this regulation.
- WAC 173-50-010: The purpose of this chapter is to establish a state program for accreditation of environmental laboratories which conduct tests and submit data to the Department of Ecology, the Department of Health, and other entities which require the use of accredited laboratories.

Washington Department of Ecology

- Standard Operating Procedure for the Accreditation of Environmental Laboratories
- Accreditation by a recognized third party (such as A2LA or Army Corps of Engineers).

Kentucky UST

- Under Kentucky statute KRS 224.60-130(2)(a), the Office of the Petroleum Storage Tank Environmental Assurance Fund has established criteria to accredit laboratories that contract with owners or operators of underground storage tanks (UST) to perform analytical testing related to Kentucky's underground storage tank program .
- UST owners and operators must have analytical testing performed at an accredited laboratory.
- This program was initiated in 1999.

Georgia EDP Background

- Section 12-2-9 of the Official Code of Georgia requires that "all commercial analytical laboratories submitting data for regulatory purposes shall be accredited or approved as specified in the EDP rules and regulations."
- Chapter 391-3-26-.04 in the EDP rules and regulations requires the EDP to establish an MOU with accrediting agencies for recognition of laboratories in Georgia.
- Original Memorandum of Understanding (MOU) was entered into on February 18, 2000 between the Georgia EDP and private Accrediting Body (AB). MOU is valid for 4 year intervals.

Georgia EDP Oversight

- EDP recognition is dependent upon a satisfactory evaluation of the AB.
- AB must assess to the requirements of ISO/IEC 17025 and any specific environmental requirements.
- When accrediting for drinking water analysis, the assessment shall follow guidelines contained in the "Manual for Certification of Laboratories Analyzing Drinking Water-Criteria and Procedures Quality Assurance."

Georgia EDP Oversight

- AB must maintain a list of accredited laboratories (scope of accreditation, date that accreditation is valid, and expiration date).
- AB must assess laboratory at least once every 2 years.
- AB must provide information (records of onsite assessment, information used to make accreditation decision, and any complaints against accredited laboratory) to the EDP upon request.
- AB must allow EDP associates to accompany assessors during on-site assessments.

Wyoming LAUST Background

- On March 1, 2001 the Wyoming Department of Environmental Quality/Water Quality Division's (WDEQ) Leaking Aboveground and Underground Storage Tank (LAUST) Program notified laboratories that they would begin use of the Program's Policy Number 35.
- LAUST Policy 35 requires WDEQ to establish criteria to accredit laboratories to perform testing under the LAUST Remediation Program.
- Required that laboratories wishing to continue work under LAUST to become accredited by December 31, 2011.

Wyoming LAUST Oversight

- Laboratories are required to submit an "Application for Certification for the Wyoming LAUST Program".
- Laboratories must submit proof of their current accreditation.
- Certification is valid for 2 years.
- AB must keep current on the list of approved analytes issued by LAUST.

DoD ELAP Background

- On December 24, 2008 the Assistant Deputy Under Secretary of Defense (Environment, Safety, and Occupational Health) issued a memorandum establishing the Department of Defense (DoD) Environmental Laboratory Accreditation Program (DoD ELAP).
- DoD Environmental Data Quality Workgroup (EDQW) was tasked with providing oversight of this program.
- 4 ABs were recognized based on signatory status to ILAC MRA (International Laboratory Accreditation Cooperation Mutual Recognition Agreement), and agreement to abide by the conditions and criteria set for by DoD ELAP.

DoD ELAP Conditions and Criteria

- AB must maintain ILAC MRA signatory status.
- AB must operate in accordance with ISO/IEC 17011 "Conformity assessment: General requirements for accreditation bodies accrediting conformity assessment bodies."
- AB must allow EDQW to attend its ILAC MRA peer evaluation.
- AB informs EDQW of upcoming assessments and must submit to observation by EDQW personnel.

DoD ELAP Conditions and Criteria

- AB must participate in meetings with the EDQW (monthly teleconference and yearly face to face) as part of continual improvement efforts for the DoD ELAP.
- AB must assess to the requirements for ISO/IEC 17025, 2003 NELAC Chapter 5, and the DoD Quality Systems Manual (QSM).
- AB must provide the EDQW with assessment reports and accreditation information.
- AB must maintain DYNEX spreadsheet of accredited laboratories on EDQW website.

DoD ELAP Successes

- 4 ABs have combines to accredit over 100 laboratories to the DoD ELAP requirements.
- Now more labs accredited for use by the DoD than when the individual armed forces branches performed the accreditations.
- More time and resources for the associated DoD personnel that were involved in performing assessments to focus on development and revision of regulations as well as project specifications.
- Greater consistency of accredited laboratories.

NEFAP/FSMO

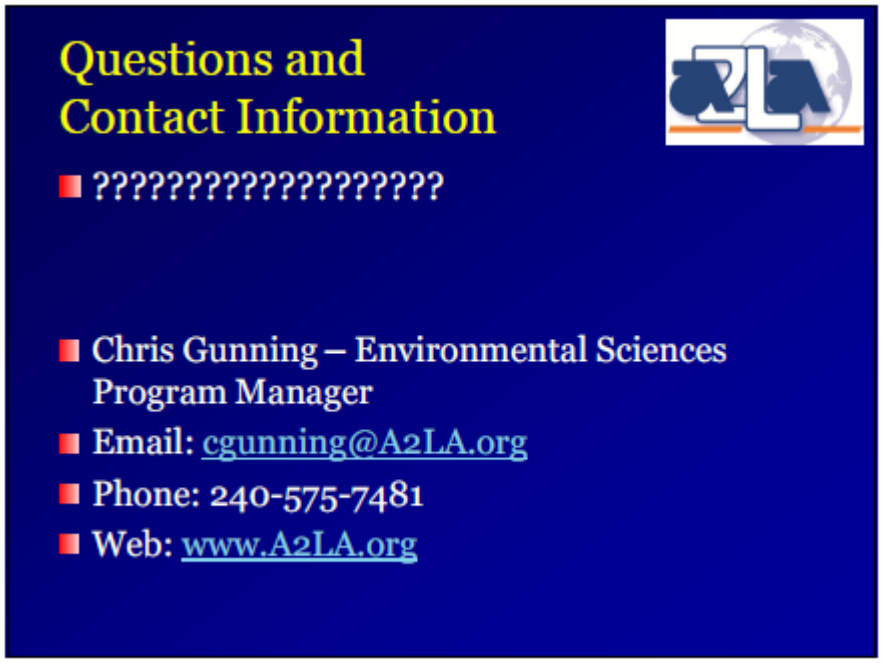
- National Environmental Field Activities Program (NEFAP) Executive Committee is to establish and implement an accreditation program for field sampling and measurement organizations (FSMOs).
- The NELAC Institute (TNI) Standard for FSMOs is modeled after ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories."
- TNI Standard Volume 1 is the FSMO Competency Standard.
- TNI Standard Volume II is the FSMO Accreditation Body (AB) Requirements to Accredit FSMOs.

NEFAP/FSMO

- ABs are required to apply for recognition to the NEFAP Executive Board.
- ABs must submit to periodic review by the NEFAP Executive Boards of its implementation of the program.

Benefits of Collaborations

- Greater consistency between assessments.
- High level of technical competence of assessors.
- High level of confidence in ABs based on the requirement for peer evaluations.
- State and Federal agencies maintain oversight of their individual programs.
- Increase in state resources that were dedicated to performing assessments and managing accreditations.


Questions and
Contact Information
???????????????????
Chris Gunning – Environmental Sciences Program Manager
Email: cgunning@A2LA.org
Phone: 240-575-7481
Web: www.A2LA.org

An Independently Prepared Second Source Lot Reference Material – Where Did This Come From and What Does It Really Mean?

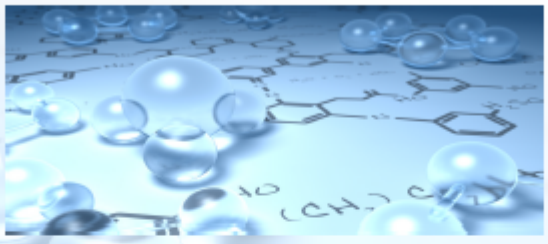
Joseph Konschnik
RESTEK Corporation

Abstract

For years environmental laboratories throughout the US have been required to verify the calibration standards they use for their instrument initial calibration using an independently prepared second source lot reference standard. The description of this second source lot is contained in various national and state-published standards and quality assurance program manuals. Laboratories are audited for compliance to such written standards; however there is ambiguity in terms of what a "second source lot" means. The definition of second source is typically determined by the auditors representing accrediting bodies, state regulatory agencies, or federal program quality assurance manuals. Since the interpretation is left to the auditing professional based on the information available and to a large extent, their own professional opinion, the definition may vary from one auditor to another, or among different programs for the same laboratory. This creates confusion for the laboratory and complicates the quality assurance procedures they must follow in order to remain compliant with multiple program requirements.

This presentation will provide an overview of the origin of the second source requirement and examine the published statements describing it. Viewpoints of the auditors, accrediting bodies, laboratories and reference standard manufacturers will be included with the intent to raise awareness of the ambiguity of current definitions and proposed universal definitions of what a "true independent second source lot" reference standard represents. Also presented is an actual case study where a reference standard manufacturer either procured, or attempted to procure independently manufactured raw material sources for organic compounds used in the manufacture of Certified Reference Materials. Their findings will be shared with regard to the impacts on the quality and cost of their reference standards manufacturing processes, and the products themselves.

An Independently Prepared Second Source Lot Reference Material - Where Did this Come From and What Does it Really Mean?



Joe Konschnik
RESTEK Corporation

NEMC

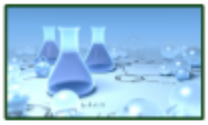
Presentation Content Outline

Second Source Lot Reference Material (RM)



- Purposes
- History
- Definitions & References to Use of Manufacturers of Starting Materials (MSMs)
- Case Study
- Conclusions & Recommendations
- Future Work

Second Source Lot RMs



Purposes of a Second Source Lot

1. Qualitative Agreement: Confirm Identity of Compounds in Primary Standard
2. Quantitative Agreement: Confirm Concentrations of Primary Standard Compounds
3. Degradation: Monitor and identify if occurring during analytical sequences

Second Source Lot RMs History

1994	ICV / QCS appears in Methods 200.8 / 6020
1994	NELAC Draft Standard requires second source
1997	NELAC requires 15% QC limit; AFCEE & ACoE adopt into their Manuals
1997	AFCEE requires 15% for inorganics and 25% for organics

Second Source Lot RMs History

1998	*Benzidine? Really?* Presented at WTQA
1999	NELAC drops 15% limit
2005	ACoE Manual publishes verification limits of 90-110% for Inorganics and 80-120% for Organics.
2009	TNI Standard still requires with laboratory established limits

Second Source Lot RMs
Definitions

Source	Definition
SW-846 Method 6020, 1994	… a standard composed of the analytes from a source different from those used in the standards for instrument calibration
EPA Method 200.8, 1994	… - The QCS should be obtained from a source outside the laboratory
AFCEE V.2.0, 1997	A second source standard is a standard purchased from a different vendor than the vendor supplying the material used in the initial calibration standards.

Second Source Lot RMs
Definitions

Source	Definition
EPA Method 1666, 1998	Standard solutions - Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition
EPA CLP, OLM04.2, Appendix E, 1999	Purchased solutions or mixtures must be verified by MS ID & purity confirmation, Chromatographic and quantitative documentation that the solution standard was QC checked

Second Source Lot RMs
Definitions

Source	Definition
ACE EM 200-1-10	An *initial calibration verification (ICV)* refers to the use of a mid-level, second-source, instrumental standard to verify the accuracy of the standards used to perform the initial calibration
FEM Glossary	The ICV is obtained from a separate source than the calibration standards, but may be from a different source from the same vendor

Second Source Lot RMs
Definitions

Source	Definition
NELAC, 2003 Standard	5.5.5.2.2.1.d – "…a standard obtained from a second manufacturer or lot if the lot can be demonstrated from the manufacturer as prepared independently from other lots."



Second Source Lot RMs
References

Source	Reference To Use of
EPA Method 625, Section 6.7	Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source
NELAC, 1994	All initial calibrations shall be verified with standards of high quality obtained from a second or different source
Standard Methods, 6410, Section 4.g (2000)	Prepare from pure standard materials or purchased as certified solutions

Second Source Lot RMs
References

Source	Reference to Use of
NELAC, 1997	When available, all initial calibrations shall be verified with a standard obtained from a second or different source
NELAC, 1999	All initial instrument calibrations must be verified with a standard obtained from a second source and traceable to a national standard, when available



Second Source Lot RMs
Conclusion

Many methods from sources such as:

- *ASTM*
- *Standard Methods*
- *SW-846*



do not contain a reference to either the use or definition of a Second Source Lot while many more do

Second Source Lot RMs

Purchasing Two Lots from Reference Material Producers (RMPs)

	Purchase from Same RMP	Purchase from Different RMPs
Perceived Advantages 	• Better Quantitative agreement between lots • Lower cost to purchase • Ease of purchase • CRMs containing same compounds for both lots	• Greater trust that systematic error did not occur • Greater trust that poor technique is not repeated • Meets auditor/QA Plan requirements Example: DoD QSM

Requirements for Manufacturers of Starting Materials (MSMs)



ISO Guide 34:

- …there are internationally recognized requirements and an assessment processes for the evaluation of RMPs in which the competence to produce a RM is determined
- Similar requirements exist for the testing and calibration laboratories that are the users of the RMs some of which may be these second source RMs

Requirements for Manufacturers of Starting Materials (MSMs)

ISO Guide 34:

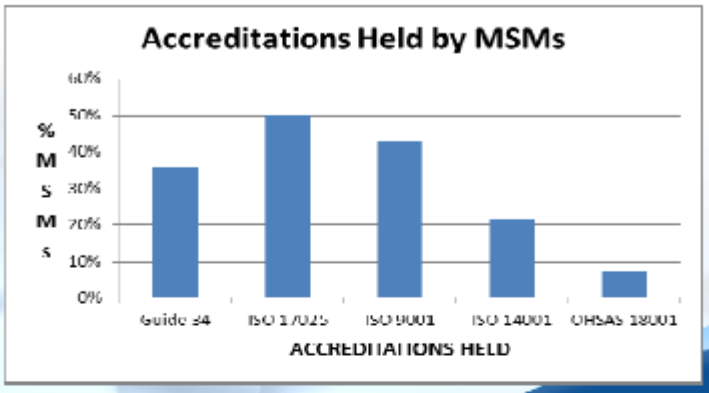


- There are no similar requirements for the MSMs (of chemicals, pesticides, etc.) from which the RMs are being produced that assess their competency to produce that starting material(SM)
- MSMs are not typically in the business of producing a product with the intent of it being used as a SM for a RM

Accreditations of MSMs

Accred.	Covers	Specifically addresses chemical identity and purity
ISO 9001	Quality Management Systems	No
ISO Guide 34	Competence of Reference Material Producers	Yes
ISO 17025	Competence of Laboratories	Yes
ISO 14001	Environmental Management Systems	No
OHSAS 18001	Occupational Safety and Health	No

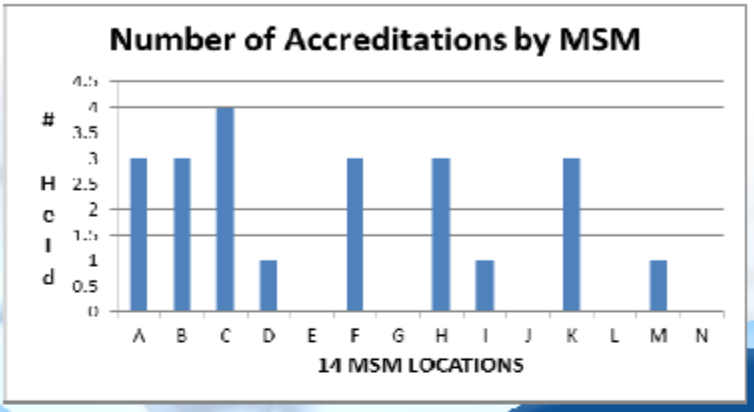
Accreditations of MSMs



Accreditations of MSMs

- 50% accredited for purity and identify of material (ISO Guide 34 and 17025)
- 40% accredited for Management Systems (ISO 9001)
- 20% accredited for Environmental Management (ISO 14001)
- 7% for Occupational Health (OHSAS 18001)
- **35% of 14 MSMs hold no accreditations that assess the competency to produce a SM**

Accreditations of MSMs



Second Source Lot Certified Reference Materials (CRMs) Case Study

- RESTEK created a series of second source organic compound CRM mixtures with the intent of manufacturing an independently prepared lot using a different SM lot from different MSMs
- EPA Methods 8260, 8270, 8081, 8140, 8151



Second SM Sourcing Challenges

- 41 SM Challenges out of 350 Total Compounds
  - 13 Failed % Purity Criteria of 98%
  - 10 Were cost-prohibitive
  - 4 Failed Qualitative Match with Primary
  - 2 Delivery Failure (i.e. Customs, delivery time)
  - 12 No Second SM Available

- **Had to Use Single Source SM for both Lots for 22 of the 41 Compounds**

Reasons for Quantitative Disagreement Between Two RMPs

- Blunder
  - E.g., dilution error
- Poor Technique or Wrong Procedure
  - Reactivity with other compounds
  - Non-quantitative transfer (e.g., techniques for viscous liquids or gases)
  - Solubility (wrong solvent used)
- Instability - Breakdown

Reasons for Quantitative Disagreement Between Two RMPs

- Re-setting %Purity of SM based on analytical determination of impurities – final concentration based on new purity vs. MSM's %purity value
- Policy on assigning expiration dates for products may vary among RMPs

Reasons for Qualitative Disagreement Between Two RMPs

- Wrong SM
  - Mislabeling Error
  - Handling Error
  - Non-Specific Analytical Identification
    - Melting point, FID



- SM Manufacture Variations
  - E.g.: Toxaphene, Aroclors
- Instability
  - Artifacts, Impurities

Reasons for Disagreement Between Two RMPs

- Custom vs. Stock RMP Products
  - Are ***Custom*** RMs tested to the same QA specifications as ***Stock*** RMs?
  - Does the RMP's ISO Accreditation or Certification include their ***Custom*** RMs?
  - Varying Levels of Quality offered for Custom CRMs, or RMs
    - Level A – Gravimetric Only
    - Level B – Qualitative
    - Level C – Quantitative

Conclusions & Recommendations

- Need a better & more consistent definition
- Additional specifications are needed to ensure qualitative and quantitative accuracy of CRMs among RMPs, e.g.
  - Verification procedures for identity & % Purity
  - Validate correct concentration by independent checks
  - Policy on setting expiration dates
- Who does this?
- **Second SMs are not the best solution**

Future Work on This Topic

- Need for consistent Laboratory requirements for use of second source RMs
- Need for laboratories to validate their RMs for purity, identity and concentration based on Data Quality Objectives.
- Need for industry-standard manufacturing specifications for the manufacture of RMs

A Better Definition of True Second Source RM - Proposal

Hierarchy of Options:

Tier I: A different RM from a second RMP

Tier 2: Either Two different RMPs from same SM
or Same RMP used two different SMs

Tier 3: Two independently prepared RM lots from same RMP

(All are acceptable options)

A Better Definition of True Second Source RM - Proposal

Hierarchy of Options:

The NELAC definition:

"*a standard obtained from a second manufacturer or lot if the lot can be demonstrated from the manufacturer as prepared independently from other lots*"

allows for the use of the three tiers with exception of "prepared independently from other lot"

A Better Definition of True Second Source RM - Proposal

Hierarchy of Options:

"prepared independently from other lot" is defined as:

- Prepared by a different chemist
- On a different day
- Used a different balance, or volumetric glassware


Co-Authors
J. Parr, Catalyst Information Resources, 210 S. Lamar St., Weatherford, TX, 76086 jparr@catalystinforesources.com
R. Vitale, L. Dupes, Environmental Standards, Inc. 1140 Valley Forge Rd., Valley Forge, PA 19482 rvitale@envstd.com , ldupes@envstd.com
R. Knake, Chris Gunning , A2LA, 5301 Buckeystown Pike, Suite 350, Frederick, MD 21701 rknake@a2la.org , cgunning@a2la.org
J. Konschnik, J. Fisher, RESTEK Corporation, 110 Benner Circle, Bellefonte, PA 18623 joe.konschnik@restek.com jason.fisher@restek.com

Development of a PT National Average

Matthew Sica
ANSI-ASW National Accreditation Board

Abstract

It has been 15 years (1997) since the USEPA has directly operated the drinking water and waste water PT programs. At that time, it was rather straight forward to calculate national averages of laboratory performance. Essentially, their data set included all the participants. Today, it is a somewhat more complicated as there are more analytes, matrices, providers and more than one data complicating the issue. Within the NELAC-TNI program there are 2 PTPA's pooling data. This report will analyze the values from ACLASS - PTPA which holds data for 3 major PT providers (Absolute Standards, Inc., NSI, RTC-Sigma Aldrich. The database schema, calculations and ways to improve the model will be discussed. Finally, oversight benefits to the NELAC-TNI program will be shown.



Developing a PT National Average of ANSI ASQ National Accreditation Board ACLASS Accredited PT Providers TNI

Presented By: Matt Sica

ANSI-ASQ National Accreditation Board

NELAC 2003

- Proficiency Testing A.7
  - A PTOB/PTPA is required to investigate any PT Provider whose pass/fail rate is Statistically different from the national average.

TNI EL-V4 6.3.2

- The PTPA shall investigate any situation where a PT Provider's pass/fail rate for any analyte or overall is statistically different from the national average at a 95% level, as determined by appropriate statistical techniques.

Challenges

- A PT Standard
  - Can be highest level standard in lab
- No TNI Standard requirement for use of RMs or CRMs from accredited sources
  - Homogeneity

Challenges

- Standard Prep for Methods
  - Metals: Standard from Salts
  - Organics: Preparation from Neats
- Data Collection
  - Analyte Group Names (optional field)
    - Did not calculate % Pass by Group
      - i.e. Metals

Challenges

- Small Datasets
  - N<30
- PTs not technology specific
- Labs report multiple methods with same result per study
  - Skews pass/fail rates with failure

Weighted Average

- Calculated in Filemaker Pro
- Verified accuracy of calculation
  - Excel
  - Hand Calculations

Weighted Average

- w=number of participants
- x=Study Pass Rate

$$\bar{x} = \frac{\sum w \cdot x}{\sum w}$$

Data Collection

- 124,483 Reported Values to PTPs (2012)
- 6532 Database Records Evaluated

9

Method

- While all data has been evaluated for calendar year 2012, only presenting:
- Sampling of Regulated DW analytes based on TNI FoPT Analyte Groups
- Charted DW, NPW, SCM solids
  - Same Analyte Code

10

Trace Metals: Lead

Analyte Code	Program	Average Pass Rate (%)	Total number of Records
1075	DW	99	243
1075	WW	93	837
1075	SCM	97	243

11

Nutrients: Nitrate + Nitrite as N

Analyte Code	Program	Average Pass Rate (%)	Total number of Records
1810	DW	95	290
1810	NPW	95	602

12

Minerals: Fluoride

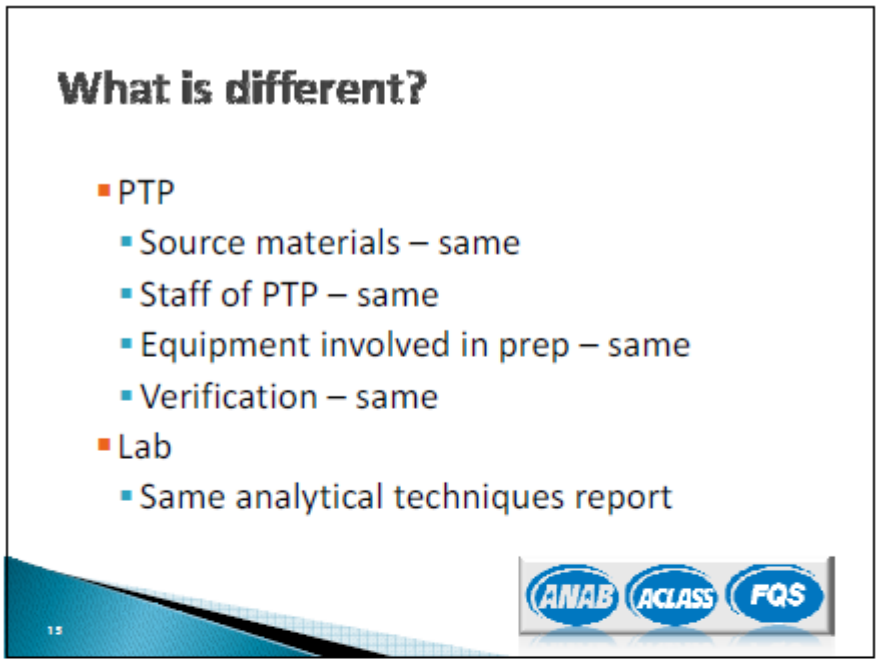
Analyte Code	Program	Average Pass Rate (%)	Total number of Records
1730	DW	85	449
1730	NPW	95	486
1730	SCM	97	103

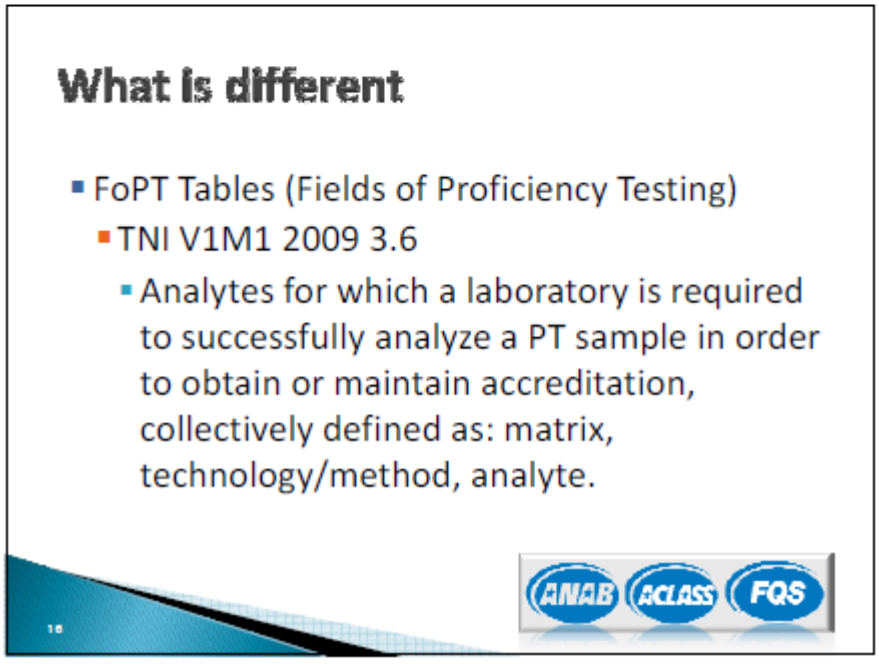


Why is Drinking Water Data lower?

Analyte Code	Program	Average Pass Rate (%)	Total number of Records
1730 (Fluoride)	DW	85	449
1730 (Fluoride)	NPW	95	486
1730 (Fluoride)	SCM	97	103
1635 (Cyanide)	DW	88	43
1635 (Cyanide)	NPW	96	347
1635 (Cyanide)	SCM	90	72
1870 (Ortho-phosphate)	DW	91	326
1870 (Ortho-phosphate)	NPW	96	698




What is different?
PTP
Source materials – same
Staff of PTP – same
Equipment involved in prep – same
Verification – same
Lab
Same analytical techniques report
15
ANAB
ACLASS
FQS


What is different
FoPT Tables (Fields of Proficiency Testing)
TNI V1M1 2009 3.6
Analytes for which a laboratory is required to successfully analyze a PT sample in order to obtain or maintain accreditation, collectively defined as: matrix, technology/method, analyte.
16
ANAB
ACLASS
FQS

FoPT

- http://www.nelac-institute.org/fopt.php
- DW
  - Chemistry
  - Microbiology
  - Radio Chemistry

17

ANAB ACLASS FQS

FoPT

- http://www.nelac-institute.org/fopt.php
- NPW
  - Chemistry
  - Microbiology
  - Whole Effluent Testing

18

ANAB ACLASS FQS

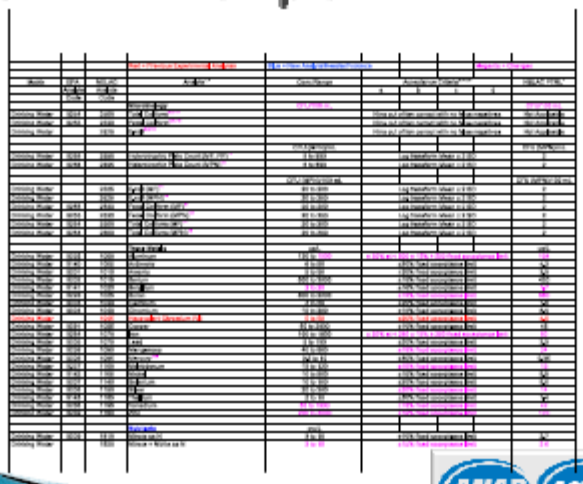
FoPT

- http://www.nelac-institute.org/fopt.php
- SCM Solid and Chemical Materials
  - Accreditation Analytes
    - Chemistry

19

ANAB ACLASS FQS

FoPT DW Example



20

ANAB ACLASS FQS

What is different?

- 1730 SCM Fluoride (F) **97**
- 1730 WP Fluoride **95**
- 1730 WS Fluoride **85**
- ±10% fixed acceptance limit for WS

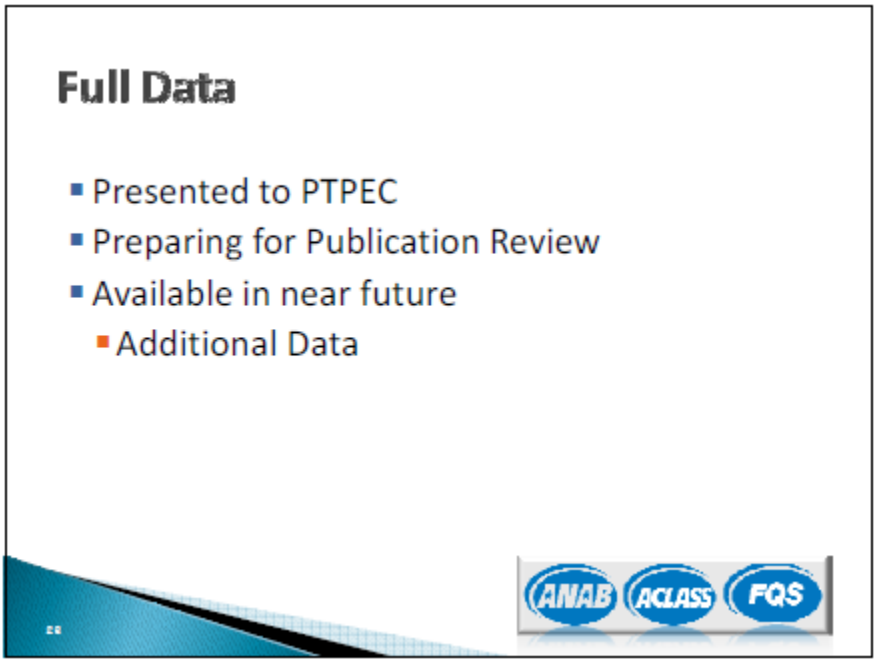
- Other programs
  - Different Criteria

21

Overall

- Weighted Mean Average for all data was:
- 96.1 % Pass Rate (124,483 reported records)
  - Data Includes:
    - Non TNI PT Analytes (State)
      - Accredited to ISO/IEC 17043

22


Full Data
Presented to PTPEC
Preparing for Publication Review
Available in near future
Additional Data
ANAB
ACLASS
FQS

Difficulties Encountered in Gaining Acceptance of Newly Approved Methodology

William Lipps
OI Analytical

Abstract

We have experienced a reluctance among laboratories to adopt to the new methods recently approved at 40 CFR Part 136. This presentation will discuss problems we have seen and examine potential solutions.

Difficulties Encountered in Gaining Acceptance of Newly Approved Methodology

William Lipps
OI Analytical

NEMC August 2013

Updates to 40 CFR Part 136 proposed September 23, 2010

Updates to 40 CFR Part 136 promulgated
May 18, 2012

Effective June 18, 2012





There is still misunderstanding about the rule



6

There is hesitation to make any changes



Commercial and Municipal Laboratories

- Unaware of new methods
- Do not know clients permits
- Misinterpret the new rules
- Are scared to make a change



8

States, Regions, and Local regulatory agencies

- Interpret the new rules differently
- Are concerned how new methods affect old data
- Existing regulations
- More paperwork



Accreditation Authorities

- Unaware of the new methods
- New methods to learn
- Interpret the new rules differently
- Concerned how new methods affect old data
- May have new QC requirements / check lists
- Need to create new codes and new lists



Instrument Manufacturers



Need adequate ROI

11

What are some things we can do?



12



13

Discussion

william.lipps@xyleminc.com

14

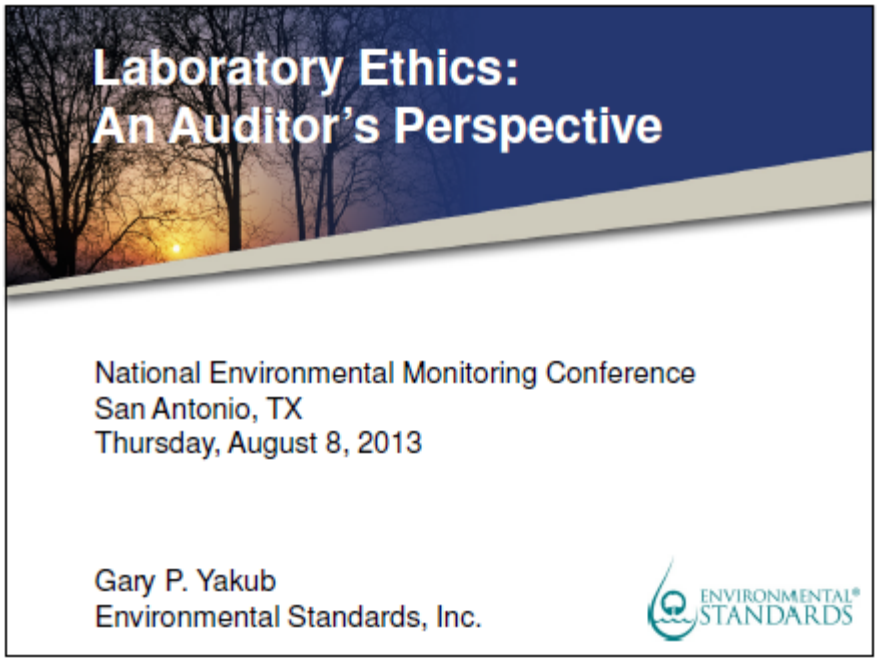
Laboratory Ethics: An Auditor's Perspective

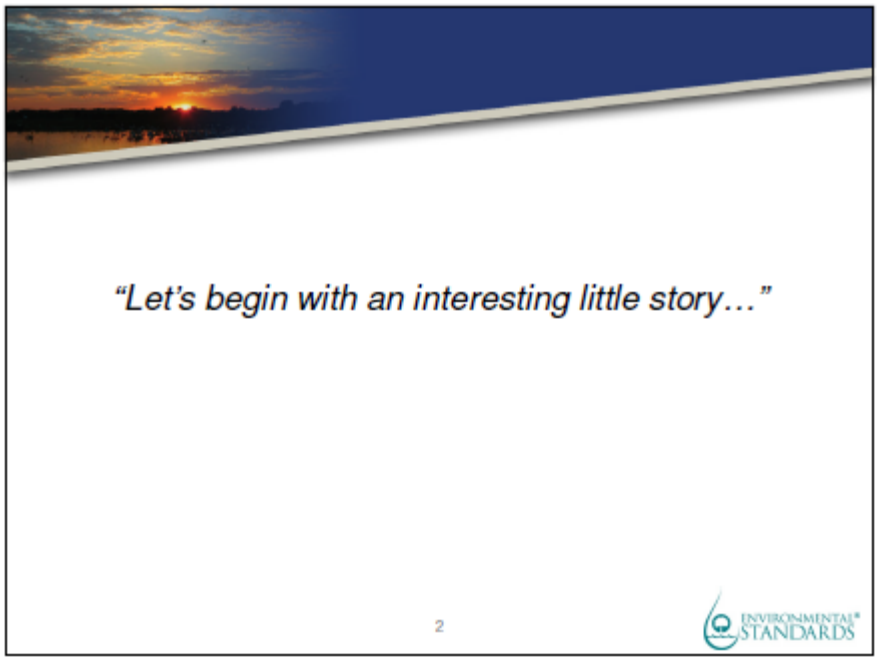
Gary Yakub
Environmental Standards, Inc.

Abstract

This presentation deals with personal, first-hand accounts of Laboratory Ethics and Data Integrity issues that I have encountered during my career as an Environmental Laboratory Auditor. Discussions include what I look for as an auditor to detect potential ethics and integrity issues, tools and strategies that Laboratory Managers and Quality Personnel can use to detect and deter laboratory fraud in their own facilities, and a discussion of how a laboratory can recover from ethics issues.

Current Laboratory Ethics and Data Integrity training has focused on concepts of ethics, behaviors to avoid, and potential punishments for unethical behavior. This presentation represents the next step in the Laboratory Ethics and Data Integrity education process, that of providing real-world examples of the information learned in the initial training phase, putting these important concepts into practice, and providing an insight into what auditors look for and how to perform your own ethics audit.


Laboratory Ethics:
An Auditor's Perspective
National Environmental Monitoring Conference
San Antonio, TX
Thursday, August 8, 2013
Gary P. Yakub
Environmental Standards, Inc.
ENVIRONMENTAL STANDARDS


"Let's begin with an interesting little story…"
2
ENVIRONMENTAL STANDARDS

Questions

- What does an auditor look for to identify potential ethics violation?
- What could have helped the QA Manager recognize potential ethics violation?



- Can we develop a list of tools that can help us evaluate our laboratories?

3

ENVIRONMENTAL STANDARDS

Data Surveillance

- Internal Surveillance
- External Surveillance



4

ENVIRONMENTAL STANDARDS

What Does an Auditor Look for?

- Evaluation Starts in the Pre-Audit Meeting
- Strong Ethics Program
- Does the Laboratory have:
  - Ethics Policy – Written Program?
  - Ethics Agreement – Signed by Everyone?
  - Ethics Support – Upper Management?
  - Ethics Training – Employee Understanding?
  - Ethics Audits – Specifically Target Ethics?
  - Corrective Actions – Ethics Violations?

5

ENVIRONMENTAL STANDARDS

What Does an Auditor Look for? (Cont.)

- Uniformity
- Perfection
- Following Written Procedures & SOPs
- Gaps in Continuity
- Trained, Knowledgeable Personnel
- Adequate Equipment, Glassware
- Adequate Amount of Consumables
- Preparation of Standards and Reagents



6

ENVIRONMENTAL STANDARDS

What Does an Auditor Look for? (Cont.)

- Raw Data Evaluations
  - Timelines, Sample Through-Put
  - Calibration Records and Responses
  - Instrument Output
  - Manual Data Management
  - Related Analytical Results

7

ENVIRONMENTAL STANDARDS

What Can Management Do?

- Assign Someone to Perform Surveillance
  - Someone separate from laboratory operations
- Develop an Internal Audit Schedule
  - Specifically Target Data Integrity/Ethics
- Think Like an Auditor
- Develop and Utilize Tools to Detect Issues
- Practice What You Preach



8

Data Surveillance Tools

- Data Audit
- Records Audit
- Purchase Order Audit
- Double-Blind Studies
- Split Samples
- Confidential Reporting Mechanism
- Frequent Training and Discussions
- Knowing Right from Wrong



9

ENVIRONMENTAL STANDARDS

"The rest of the story…"

10

ENVIRONMENTAL STANDARDS

Positive Factors

- Strong Ethics Program
- Dedicated, Educated Analysts & Managers
- Strong Performance
- Isolated Incident
- Acceptable, Prompt Corrective Action
  - Discipline
  - Re-training
  - Sample Qualification & Client Notification



11

ENVIRONMENTAL STANDARDS

BONUS SLIDES!

Don't tell anyone that you heard it from me, but here are some things I commonly see when I audit a laboratory…

12

ENVIRONMENTAL STANDARDS

"Guess We Weren't Paying Attention..."

- Expired Standards and Reagents
- Solids Oven Temperatures
- Thermometer Calibrations
- Application of Correction Factors
- BOD – Chlorine Removal & Sample Pretreatment



13

ENVIRONMENTAL STANDARDS

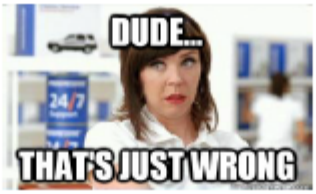
"Close, But No Cigar"

- QC Tests Analyzed, Results Ignored
- Balance Calibration Verifications
- Incomplete Records
- Indirect Traceability vs. Direct Traceability
- Incomplete or Ineffective Corrective Actions

14

ENVIRONMENTAL STANDARDS

"That's Just Wrong"



- Metals PE Study Samples
- Assorted Ethics Violations
- Undertrained/Inexperienced Analysts
- Incomplete Demonstrations of Capability

15

ENVIRONMENTAL® STANDARDS

Contact

ENVIRONMENTAL® STANDARDS
www.envstd.com

Gary Yakub
gyakub@envstd.com | 610.935.5577

Environmental Standards, Inc.
"Setting the Standards for Innovative Environmental Solutions"

Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577
Virginia 1208 East Market Street | Charlottesville, VA 22902 | 434.293.4039
Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590
Texas 11200 Richmond Avenue, Suite 350 | Houston, TX 77082 | 281.752.9782
Web www.envstd.com | E-mail solutions@envstd.com

16

SECTION 22

TOPICS IN DRINKING WATER

Coconut Charcoal Solid Phase Extraction - Large Volume Splitless Injection - GC-MS for Analysis of Dioxane, Tetrahydrofuran, Nitrosamines, Ethylene Dibromide, Trichloropropane, Dibromochloropropane, Chlorinated Solvents, and Disinfection Byproducts in Drinking Water: The Possibility for a Single Comprehensive Method

Christopher Rattray
RESTEK Corporation

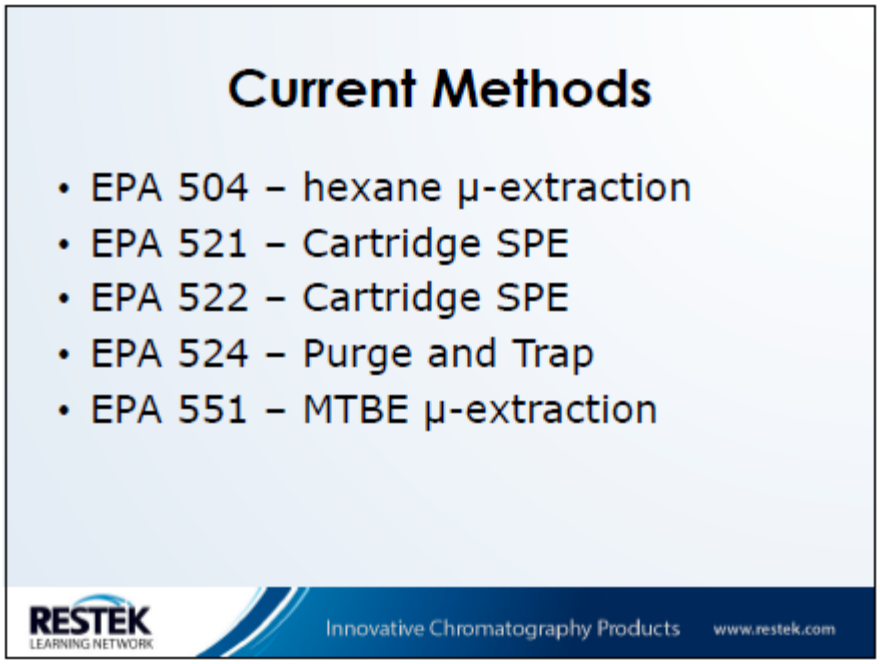
Abstract

Currently there are multiple EPA methods for the analysis of 1,4-dioxane, tetrahydrofuran, nitrosamines, ethylene dibromide (1,2-dibromoethane), 1,2,3-trichloropropane, 1,2-dibromo-3-chloropropane, chlorinated solvents, and disinfection byproducts in drinking water (e.g. 504.1, 521, 522, 524.3, 551.1), all requiring different sample preparation methods including solid phase extraction (SPE), liquid-liquid extraction, and purge-and-trap. We looked at combining these methods into one by extracting drinking waters with coconut charcoal SPE, eluting with an appropriate organic solvent, followed by concurrent solvent recondensation – large volume splitless injection (CSR-LVSI) – gas chromatography – mass spectrometry (GC-MS).

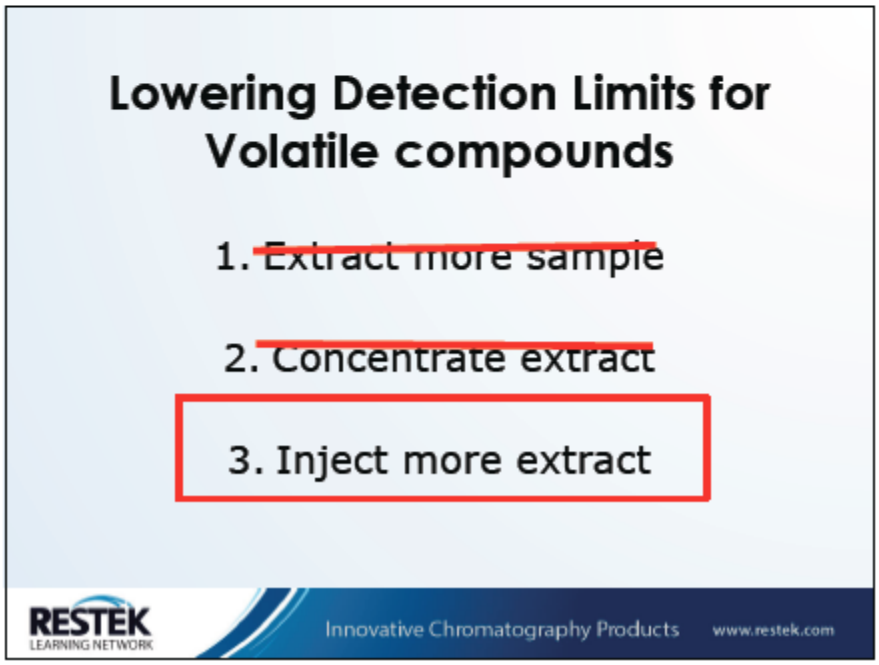
The benefits of a combination method include fewer samples for collecting and shipping and extracting, and less instrumental time. Because the final SPE extract cannot be concentrated via evaporation due to volatile compound loss, we employed CSR-LVSI, which uses a standard splitless injector to deliver as much as 50µL extract to a retention gap connected to a typical GC column for separation and then MS analysis. This large volume injection allows the low detection limits needed for drinking water analysis, especially for selected ion monitoring, but also even for full scan MS, which provides a better qualitative confirmation of the compounds of interest.

Data will be shown for spiked and unspiked drinking water samples analyzed by the proposed method and for more conventional 500 series methods.


Coconut Charcoal Solid Phase Extraction - Large Volume Splitless Injection - GC-MS for Analysis of Dioxane, Tetrahydrofuran, Nitrosamines, Chlorinated Solvents, and Disinfection Byproducts in Drinking Water: The Possibility for a Single Comprehensive Method
C. Rattray, J. Cochran, J. Herrington, M. Misselwitz
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


Current Methods
• EPA 504 – hexane µ-extraction
• EPA 521 – Cartridge SPE
• EPA 522 – Cartridge SPE
• EPA 524 – Purge and Trap
• EPA 551 – MTBE µ-extraction
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

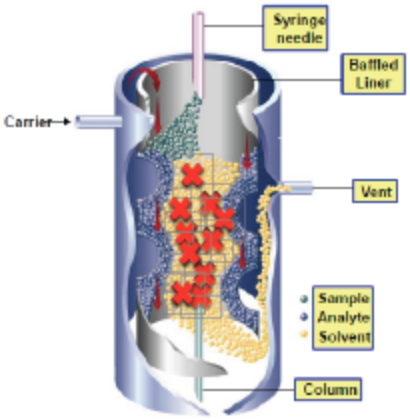

0.07 µg/L
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


Lowering Detection Limits for Volatile compounds
1. Extract more sample
2. Concentrate extract
3. Inject more extract
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

Analyte	CAS Registry Number	Boiling Point (°C)	Molecular Mass (AMU)	Vapor Pressure (mm Hg 20°C)	IRIS 1x10^-6 cancer risk concentration (ng/L)	UCMR Study
Tetrahydrofuran (THF)	109-99-9	66	72	143	-	-
1,4-Dioxane	123-91-1	101.1	88	30	350	3
N-nitrosodimethylamine (NDMA)	62-75-9	153	74	2.7	0.7	2
N-nitrosomethylethylamine (NMEA)	10595-95-6	154.4	88	1.1	2.0	2
N-nitrosodiethylamine (NDEA)	55-18-5	173.9	102	0.86	0.2	2
N-nitrosodi-n-propylamine (NDPA)	621-64-7	206	130	0.086	5.0	2
N-nitrosodi-n-butylamine (NDBA)	924-16-3	116 (a)	158	0.05 (b)	6.0	2
N-nitroso-pyrrolidine (NPYR)	930-55-2	214	100	0.06	20	2
N-nitroso-piperidine (NPIP)	100-75-4	219	114	0.092	-	-
N-nitroso-morpholine (NMOR)	59-89-2	224	116	0.036	-	-

a. 14 mm Hg
b. 25 °C

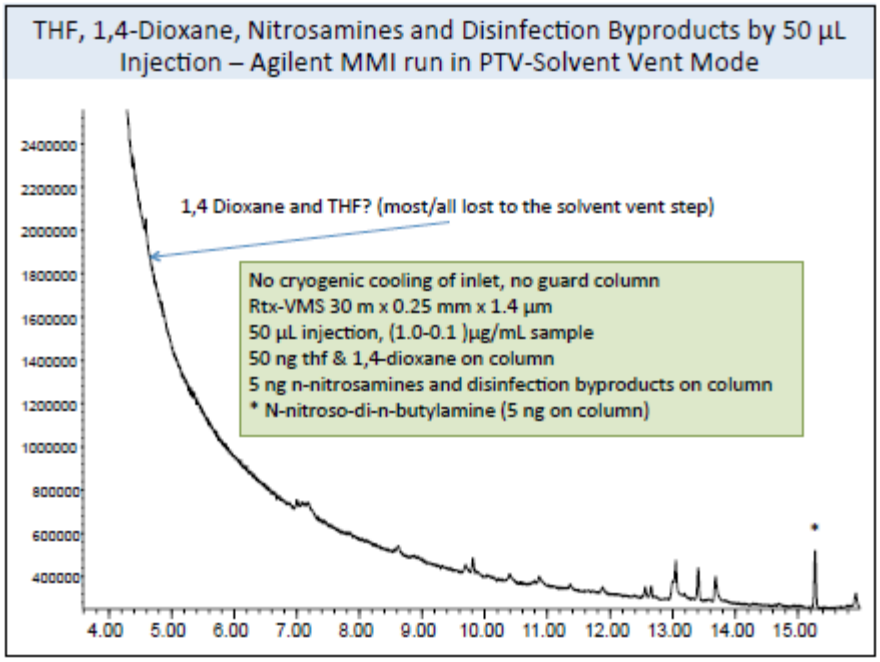
RESTEK LEARNING NETWORK Innovative Chromatography Products www.restek.com

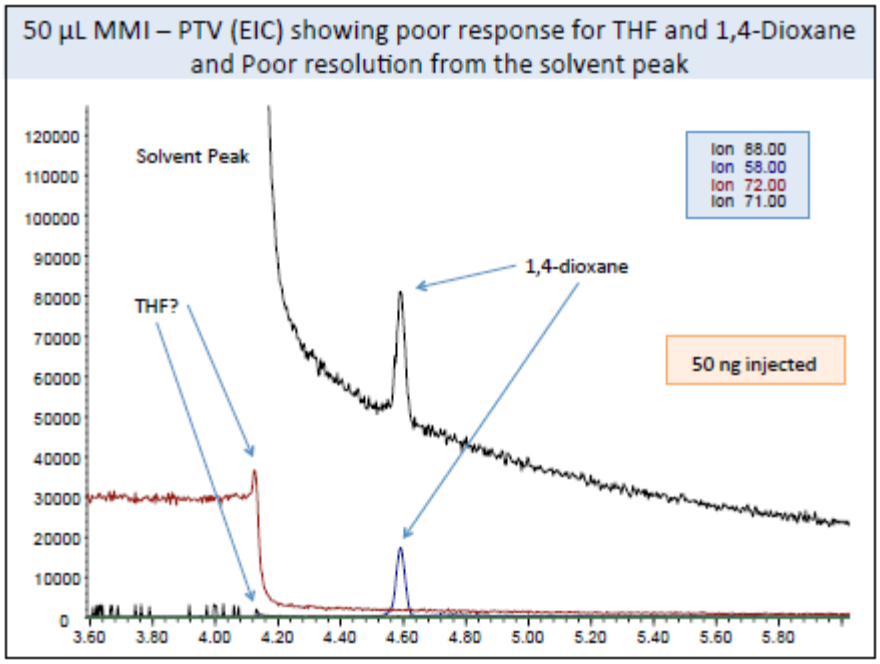


- Set inlet temperature at or below solvent boiling point
- Set high split ratio
- Inject sample very slowly into PTV
- Solvent evaporates through split vent
- Close split vent and ramp PTV temperature
- Carry out separation on analytical column

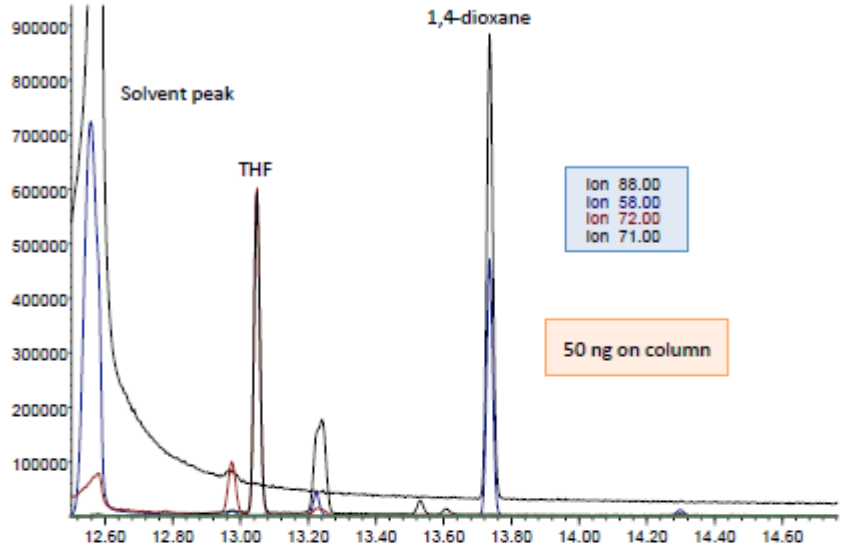
Volatile compounds are lost during solvent elimination

RESTEK LEARNING NETWORK Innovative Chromatography Products www.restek.com


THF, 1,4-Dioxane, Nitrosamines and Disinfection Byproducts by 50 µL Injection – Agilent MMI run in PTV-Solvent Vent Mode
1,4 Dioxane and THF? (most/all lost to the solvent vent step)
No cryogenic cooling of inlet, no guard column
Rtx-VMS 30 m x 0.25 mm x 1.4 µm
50 µL injection, (1.0-0.1)µg/mL sample
50 ng thf & 1,4-dioxane on column
5 ng n-nitrosamines and disinfection byproducts on column
* N-nitroso-di-n-butylamine (5 ng on column)
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00


50 µL MMI – PTV (EIC) showing poor response for THF and 1,4-Dioxane and Poor resolution from the solvent peak
Solvent Peak
Ion 88.00
Ion 58.00
Ion 72.00
Ion 71.00
1,4-dioxane
THF?
50 ng injected
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
3.60
3.80
4.00
4.20
4.40
4.60
4.80
5.00
5.20
5.40
5.60
5.80

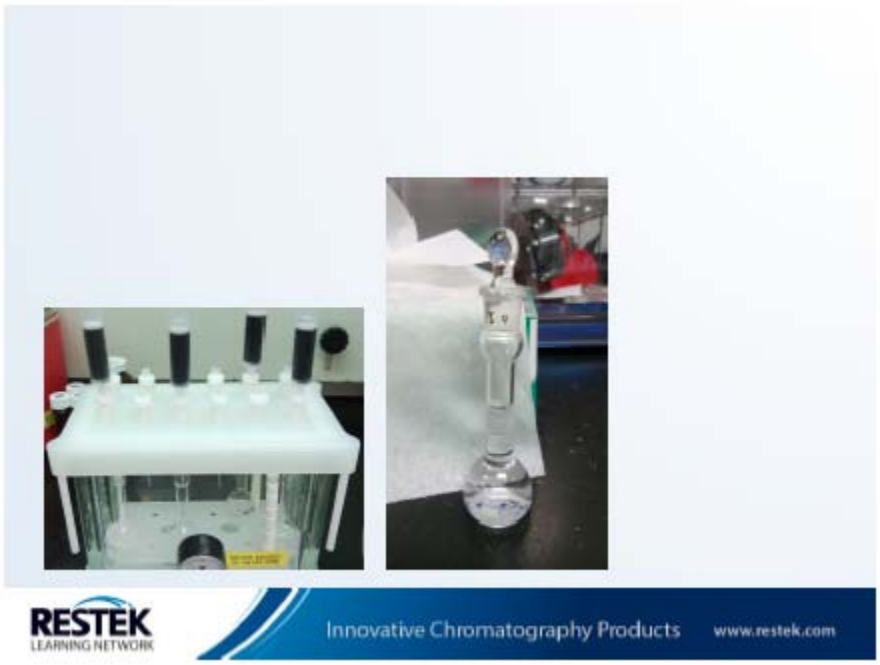
50 µL (1 ng/µL) CSR-LVSI (EIC) showing excellent response for THF and 1,4-Dioxane, as well as resolution from the solvent peak.

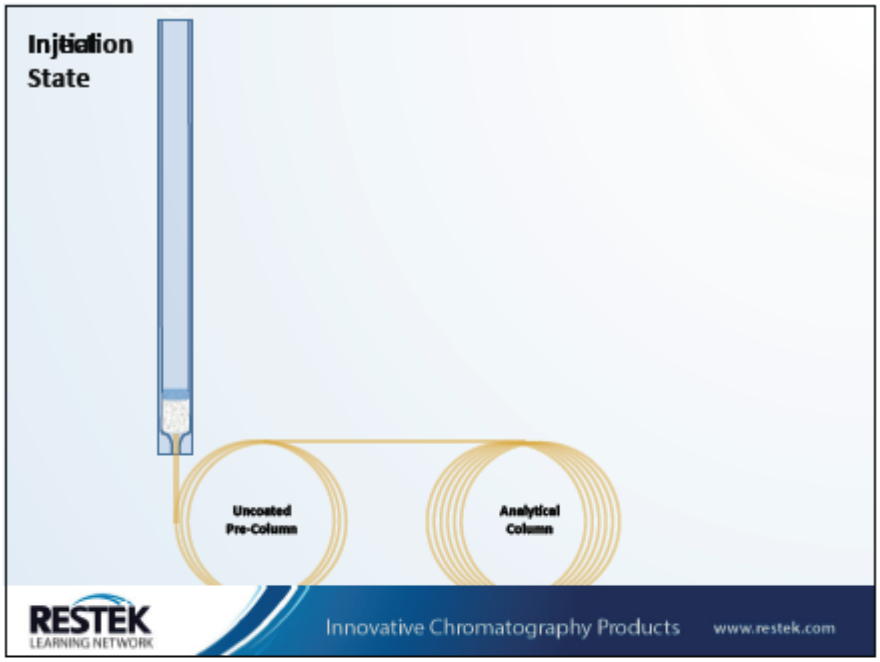


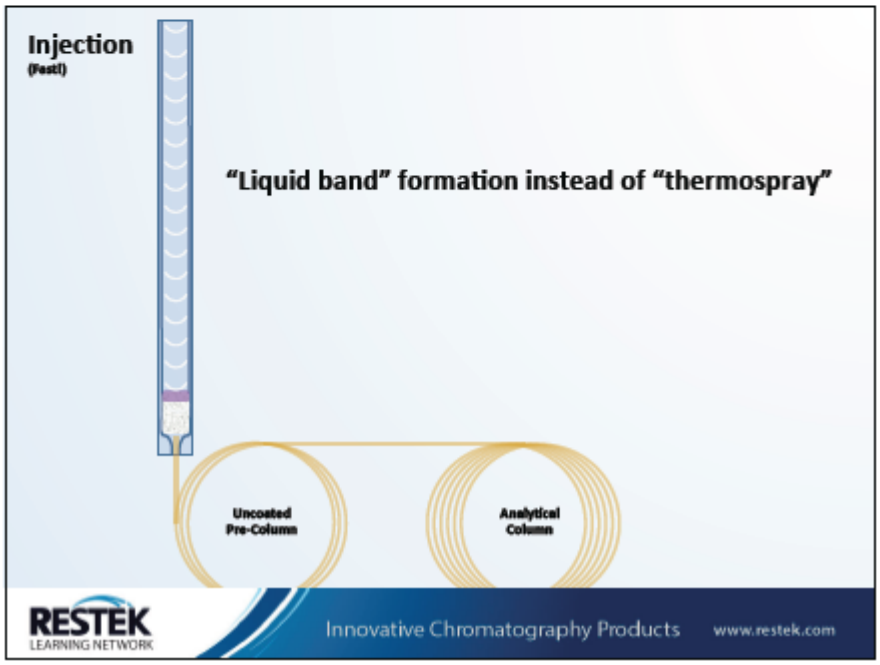
521 522 Combination method - 50 µL injection CSR-LVSI

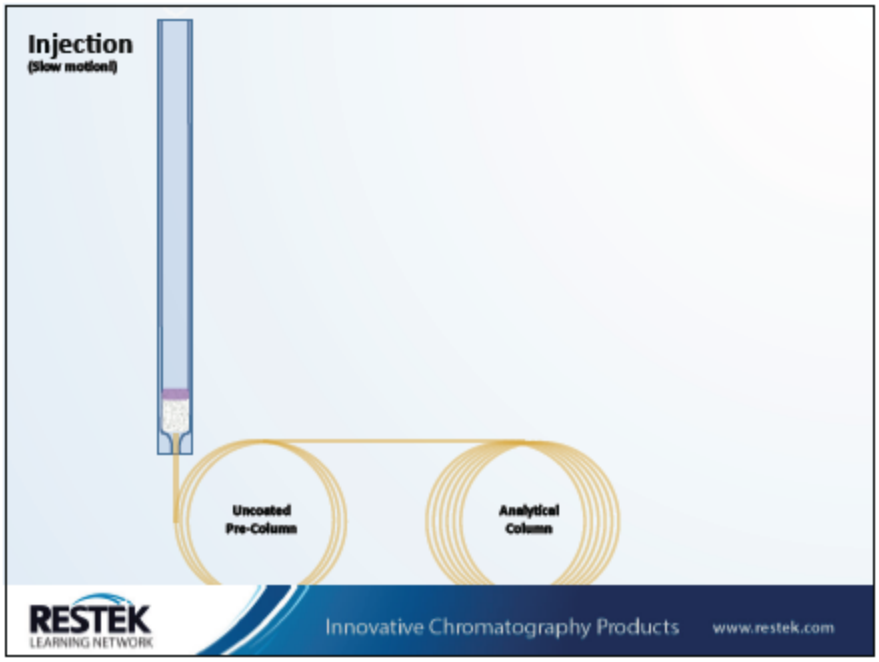
water (extract)	Blank		Low		Mid		High	
	ng/L	ng/mL	ng/L	ng/mL	ng/L	ng/mL	ng/L	ng/mL
THF	0.0	0.0	10	0.50	50	2.5	500	25
1,4-Dioxane-d8	4000	200	4000	200	4000	200	4000	200
1,4-dioxane	0.0	0.0	50	0.50	50	2.5	500	25
n-nitrosodimethylamine-d6	400	20	400	20	400	20	400	20
n-nitrosodimethylamine	0.0	0.0	0.50	0.025	2.5	0.13	25	1.3
n-nitrosomethylethylamine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5
n-nitrosodiethylamine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5
n-nitrosopyrrolidine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5
n-nitrosodi-n-propylamine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5
n-nitrosomorpholine	0.0	0.0	0.50	0.025	2.5	0.13	25	1.3
n-nitrosopiperidine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5
n-nitrosodi-n-butylamine	0.0	0.0	1.0	0.050	5.0	0.25	50	2.5

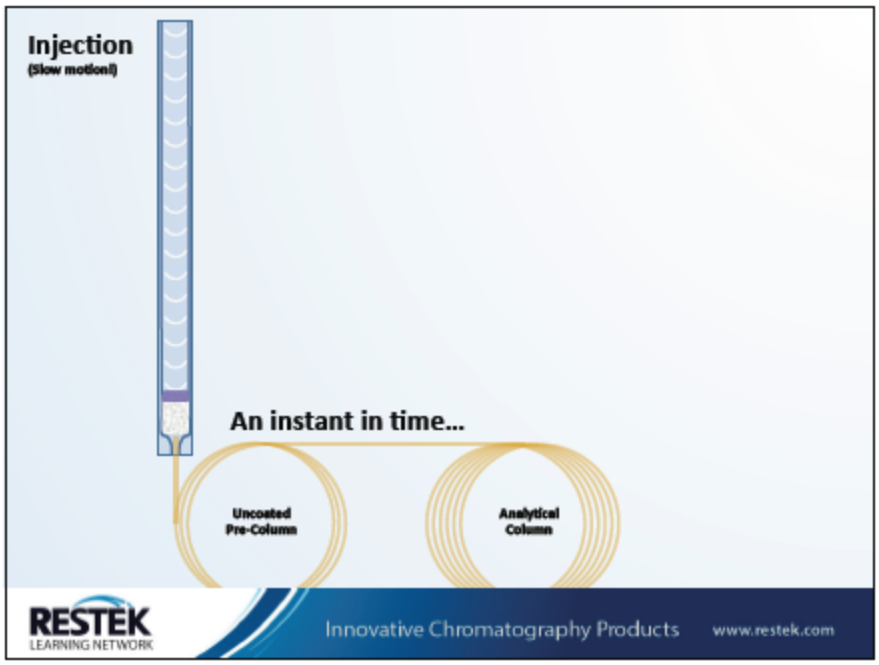
RESTEK LEARNING NETWORK Innovative Chromatography Products www.restek.com

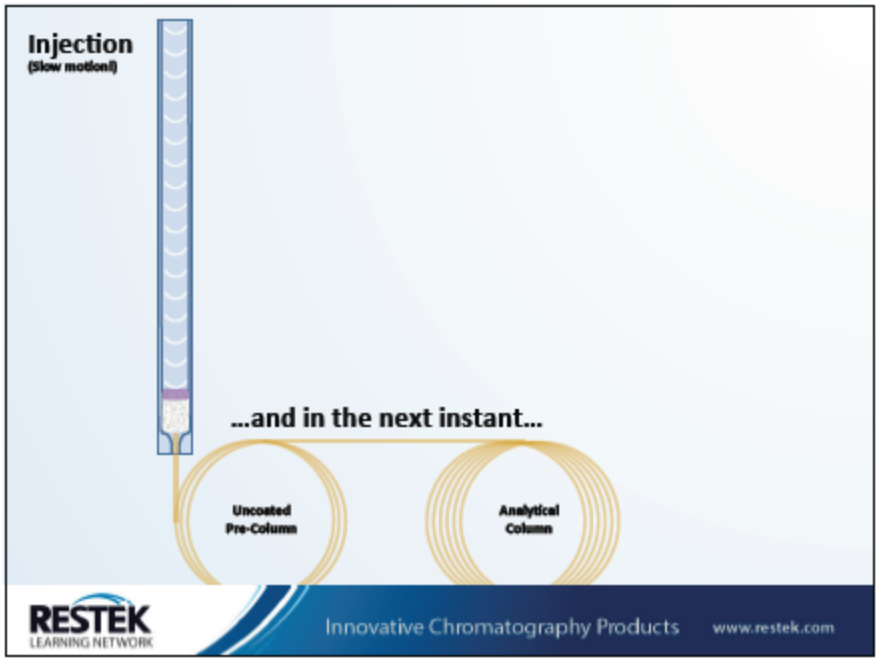

RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

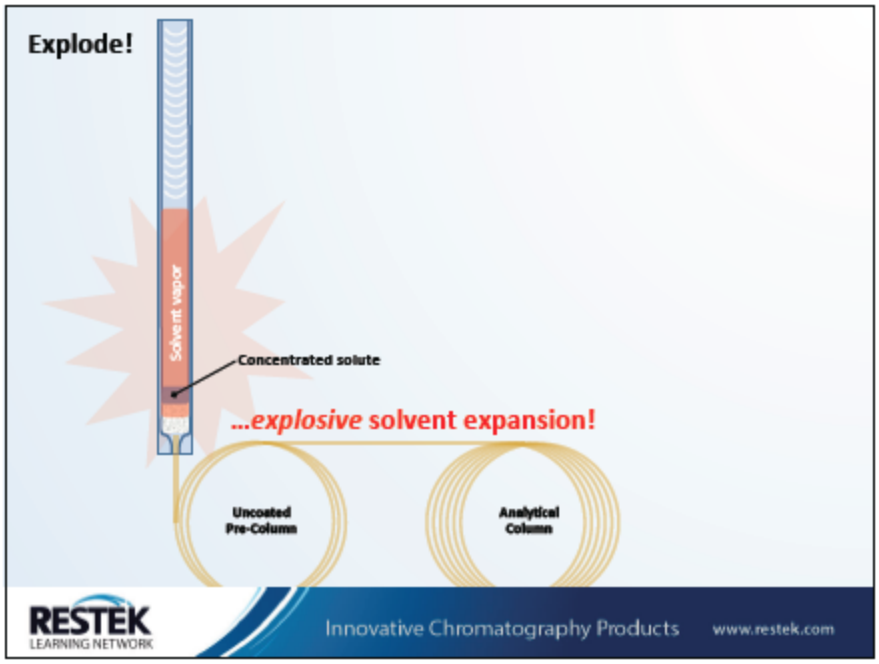

Injection
State
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

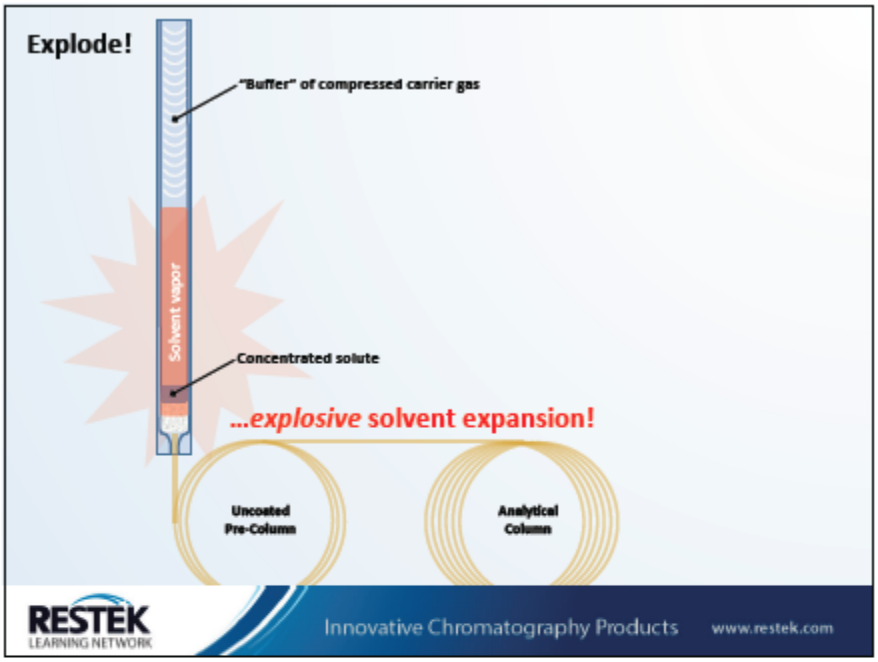

Injection
(Fast!)
"Liquid band" formation instead of "thermospray"
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

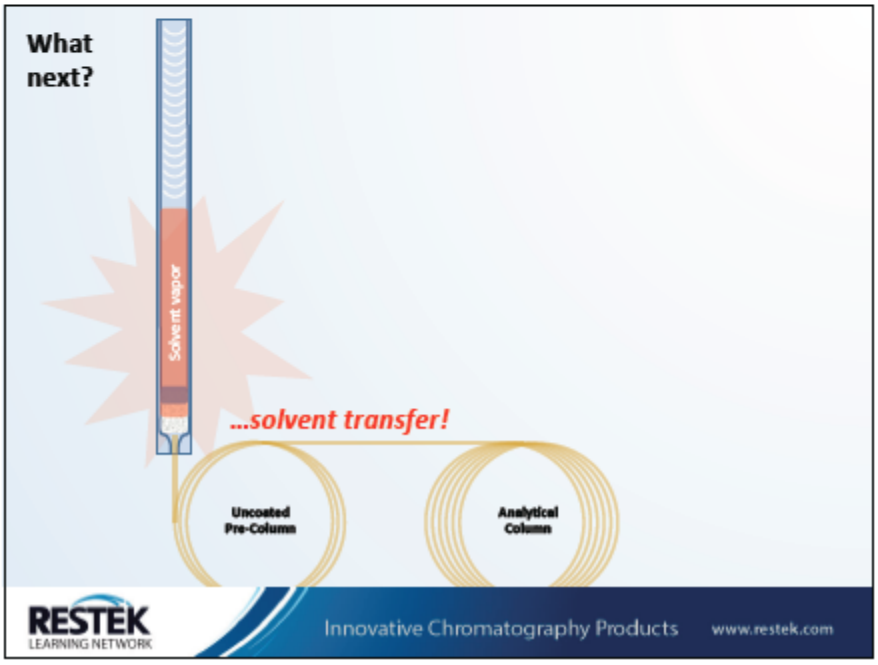

Injection
(Slow motion!)
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

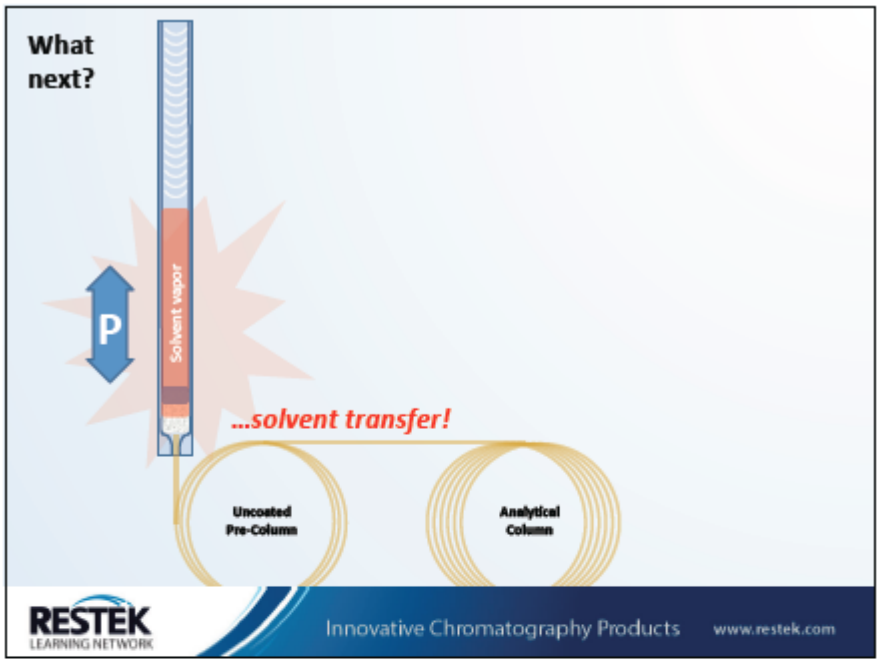

Injection
(Slow motion!)
An instant in time...
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

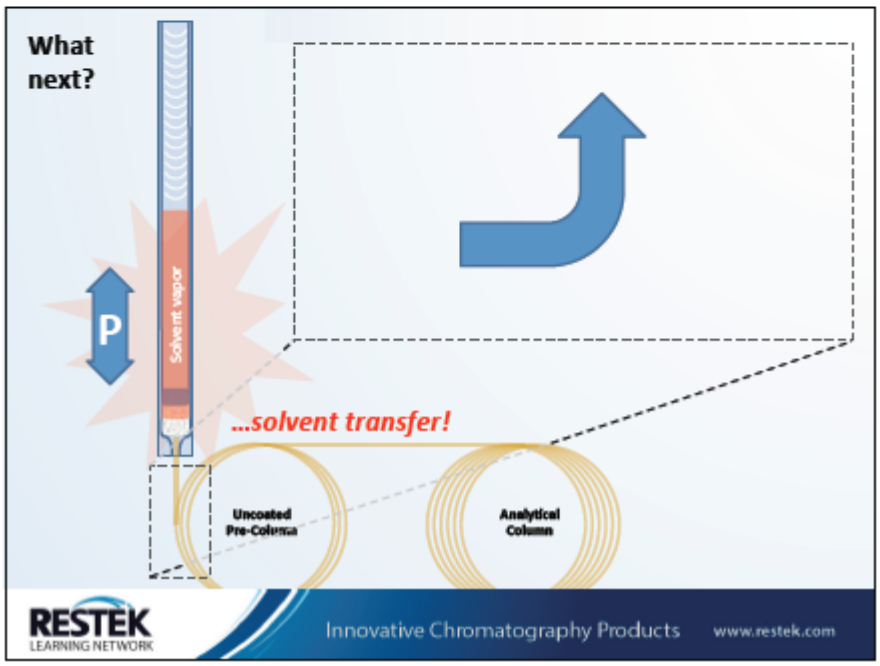

Injection
(Slow motion!)
...and in the next instant...
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

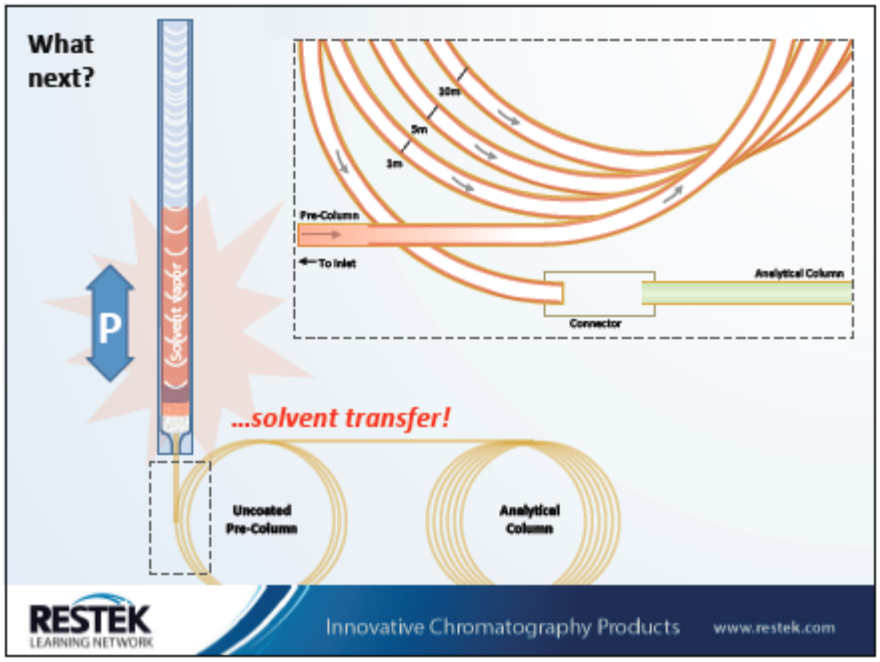

Explode!
Solvent vapor
Concentrated solute
...explosive solvent expansion!
Uncoated
Pre-Column
Analytical
Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

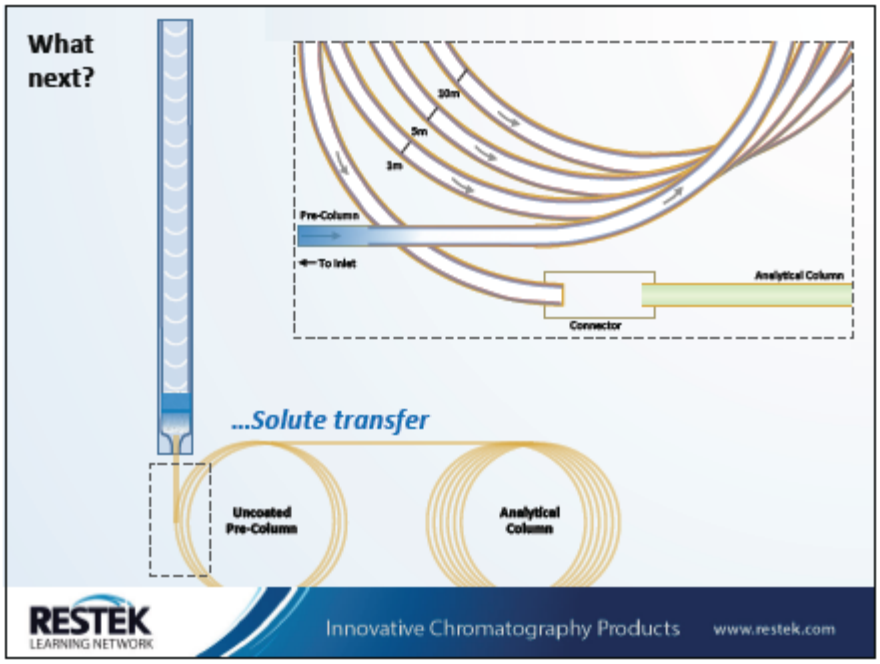

Explode!
"Buffer" of compressed carrier gas
Solvent vapor
Concentrated solute
...explosive solvent expansion!
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

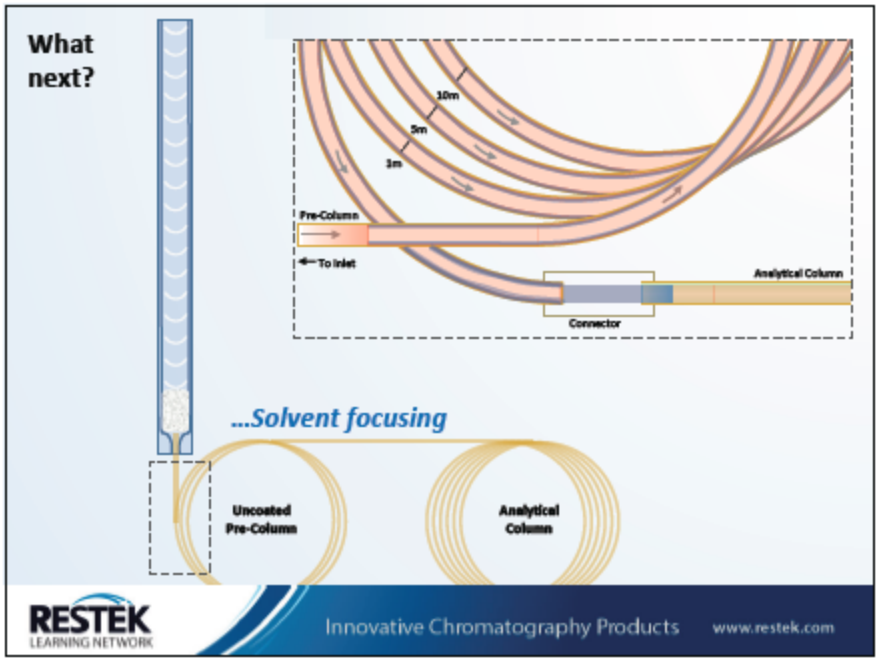

What next?
Solvent vapor
...solvent transfer!
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

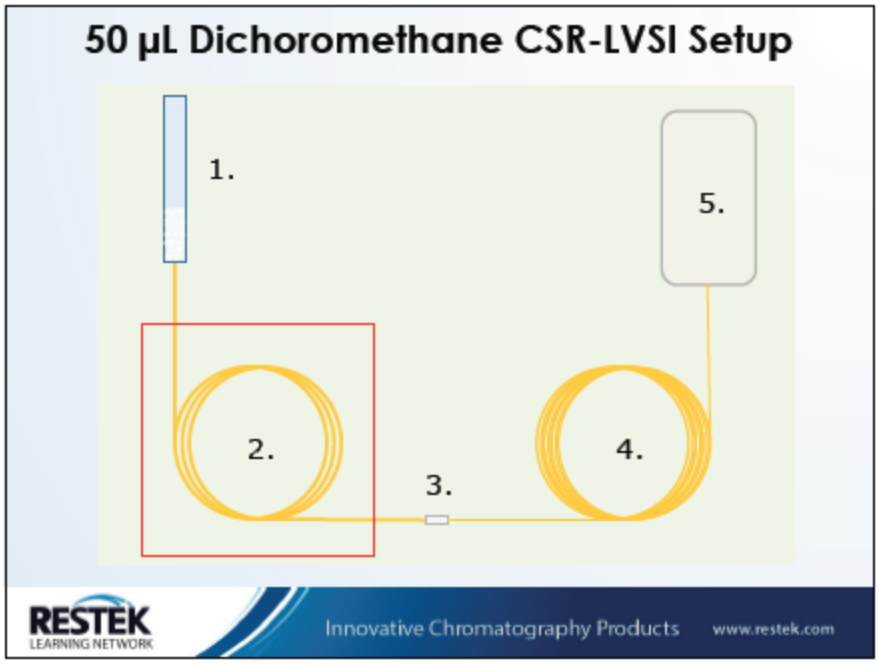

What next?
P
Solvent vapor
...solvent transfer!
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

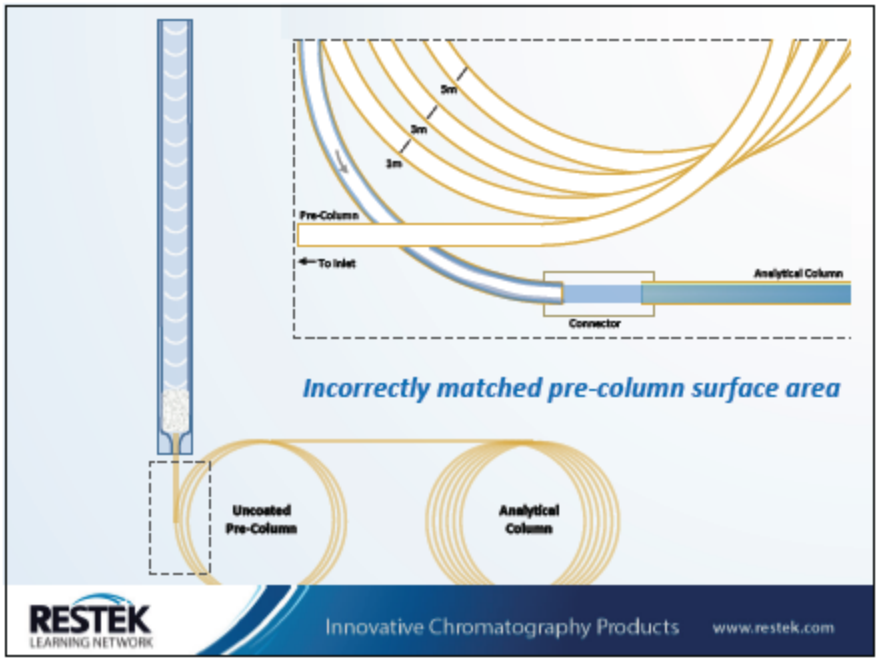

What next?
P
Solvent vapor
...solvent transfer!
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

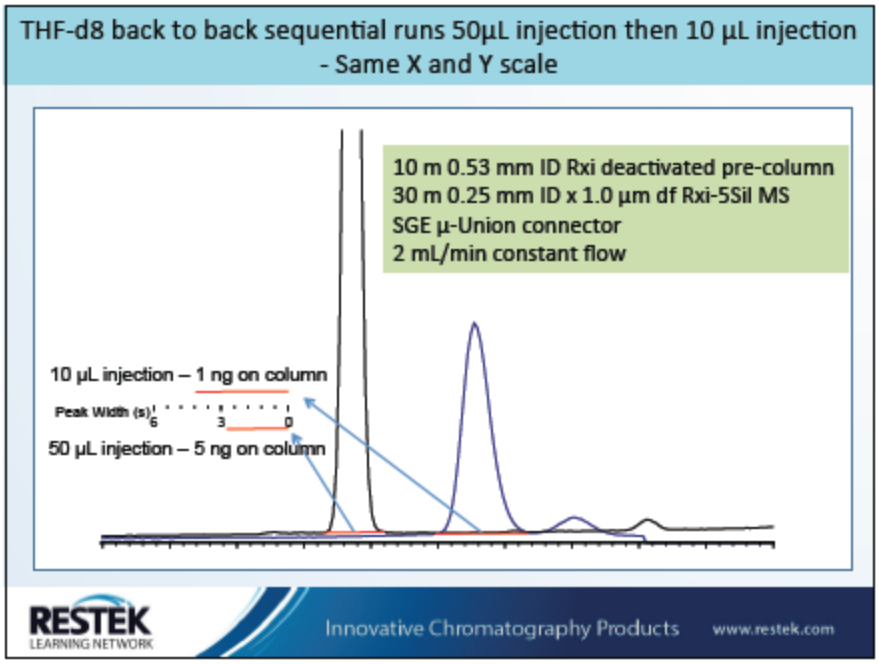

What next?
30m
5m
3m
Pre-Column
To inlet
Analytical Column
Connector
P
...solvent transfer!
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

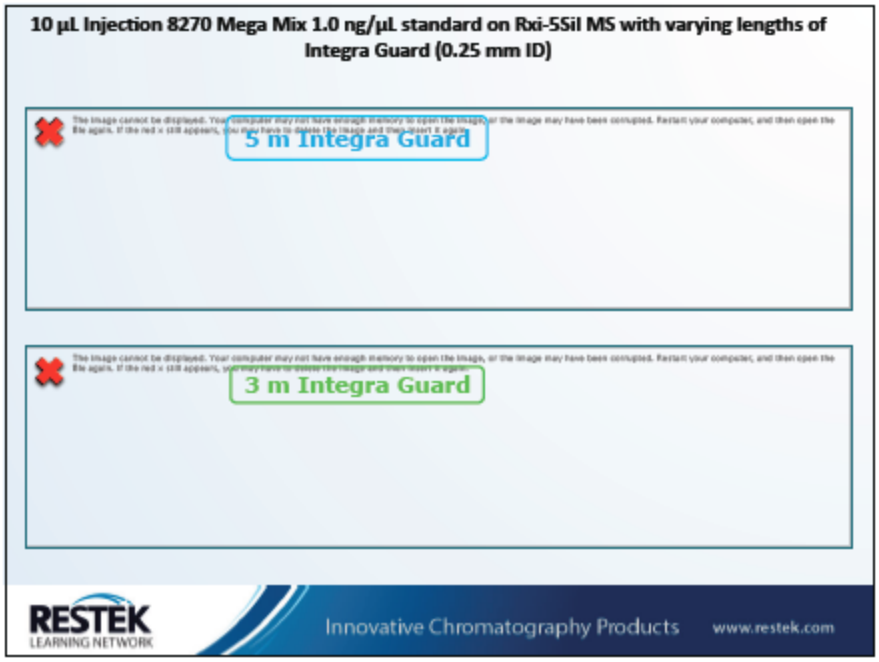

What next?
30m
5m
3m
Pre-Column
To inlet
Analytical Column
Connector
...Solute transfer
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

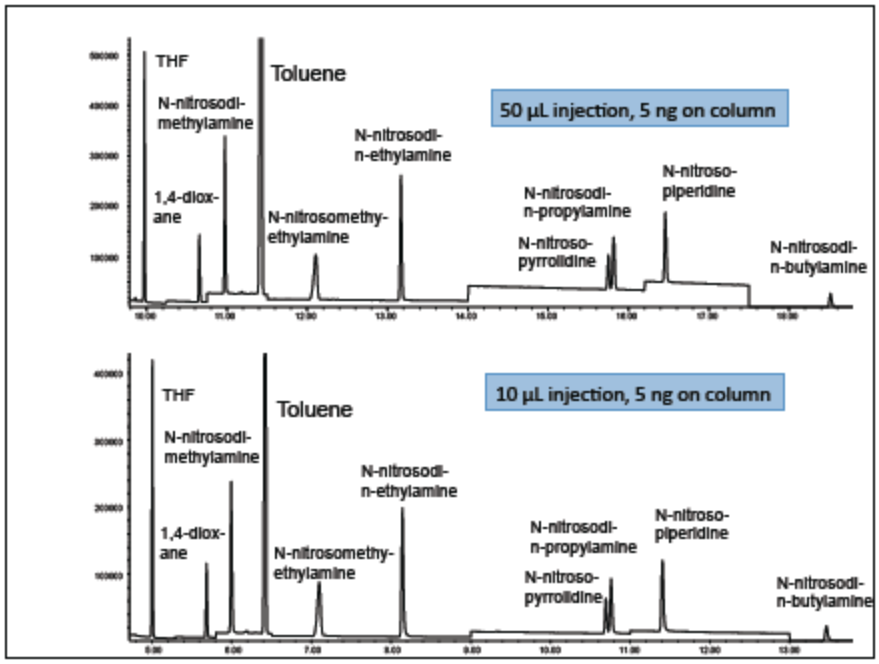

What next?
10m
5m
3m
Pre-Column
To Inlet
Analytical Column
Connector
...Solvent focusing
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


50 µL Dichoromethane CSR-LVSI Setup
1.
2.
3.
4.
5.
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

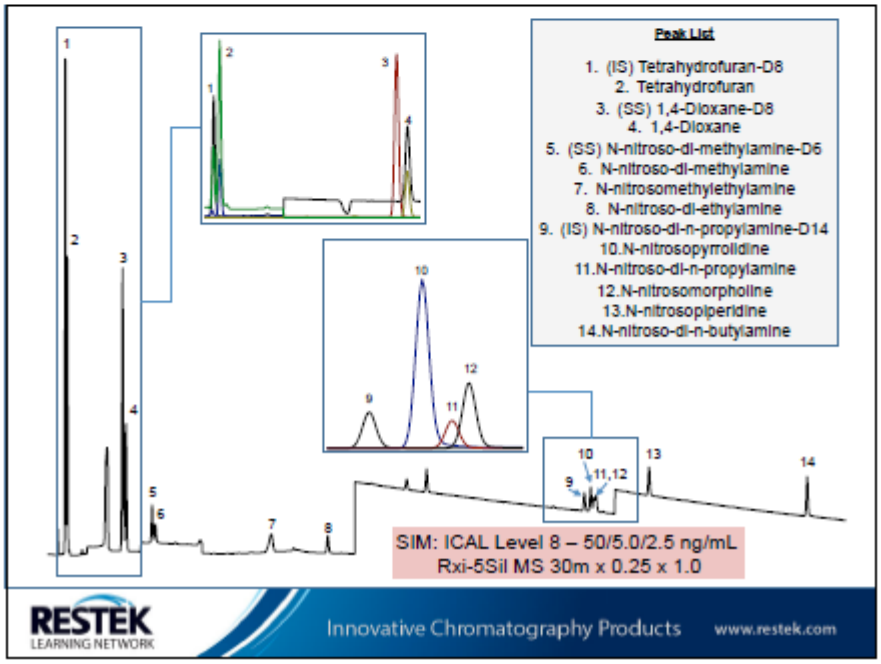

5m
3m
1m
Pre-Column
To Inlet
Analytical Column
Connector
Incorrectly matched pre-column surface area
Uncoated Pre-Column
Analytical Column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

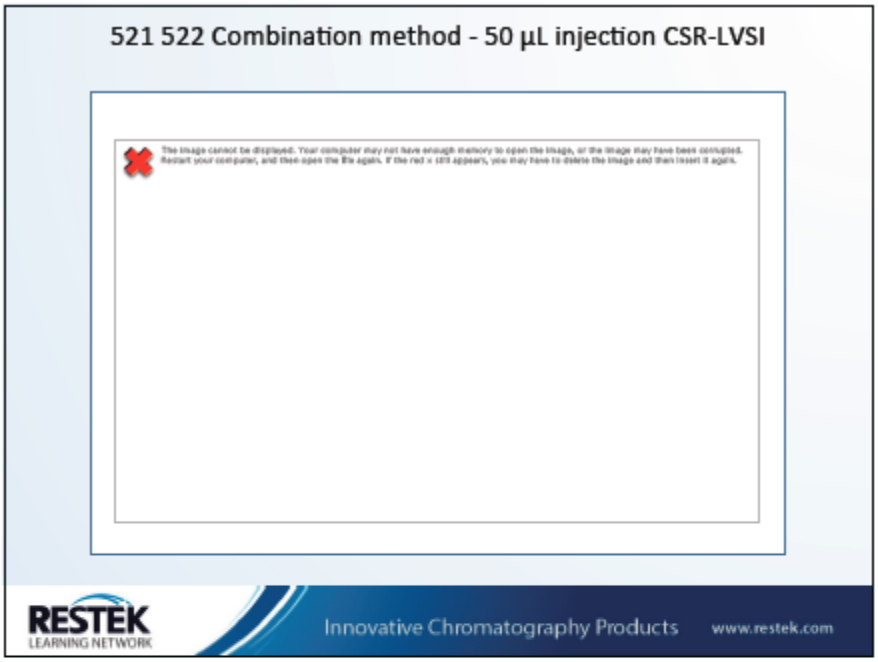

THF-d8 back to back sequential runs 50µL injection then 10 µL injection
- Same X and Y scale
10 m 0.53 mm ID Rxi deactivated pre-column
30 m 0.25 mm ID x 1.0 µm df Rxi-5Sil MS
SGE µ-Union connector
2 mL/min constant flow
10 µL injection – 1 ng on column
Peak Width (s)
6
3
0
50 µL injection – 5 ng on column
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

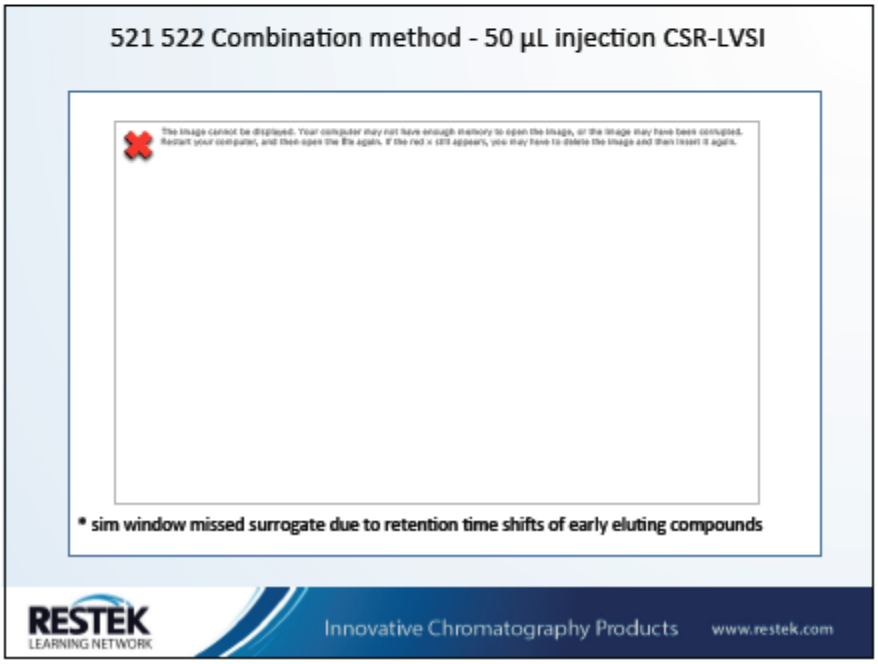

10 µL Injection 8270 Mega Mix 1.0 ng/µL standard on Rxi-5Sil MS with varying lengths of Integra Guard (0.25 mm ID)
5 m Integra Guard
3 m Integra Guard
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


50 µL injection, 5 ng on column
THF
Toluene
N-nitrosodi-methylamine
1,4-dioxane
N-nitrosomethyethylamine
N-nitrosodi-n-ethylamine
N-nitrosodi-n-propylamine
N-nitroso-pyrrolidine
N-nitroso-piperidine
N-nitrosodi-n-butylamine
10 µL injection, 5 ng on column
THF
Toluene
N-nitrosodi-methylamine
1,4-dioxane
N-nitrosomethyethylamine
N-nitrosodi-n-ethylamine
N-nitrosodi-n-propylamine
N-nitroso-pyrrolidine
N-nitroso-piperidine
N-nitrosodi-n-butylamine


RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


Peak List
1. (IS) Tetrahydrofuran-D8
2. Tetrahydrofuran
3. (SS) 1,4-Dioxane-D8
4. 1,4-Dioxane
5. (SS) N-nitroso-di-methylamine-D6
6. N-nitroso-di-methylamine
7. N-nitrosomethylethylamine
8. N-nitroso-di-ethylamine
9. (IS) N-nitroso-di-n-propylamine-D14
10.N-nitrosopyrrolidine
11.N-nitroso-di-n-propylamine
12.N-nitrosomorpholine
13.N-nitrosopiperidine
14.N-nitroso-di-n-butylamine
SIM: ICAL Level 8 – 50/5.0/2.5 ng/mL
Rxi-5Sil MS 30m x 0.25 x 1.0
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


521 522 Combination method - 50 µL injection CSR-LVSI
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com


521 522 Combination method - 50 µL injection CSR-LVSI
* sim window missed surrogate due to retention time shifts of early eluting compounds
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

521 522 Combination method - 50 µL injection CSR-LVSI

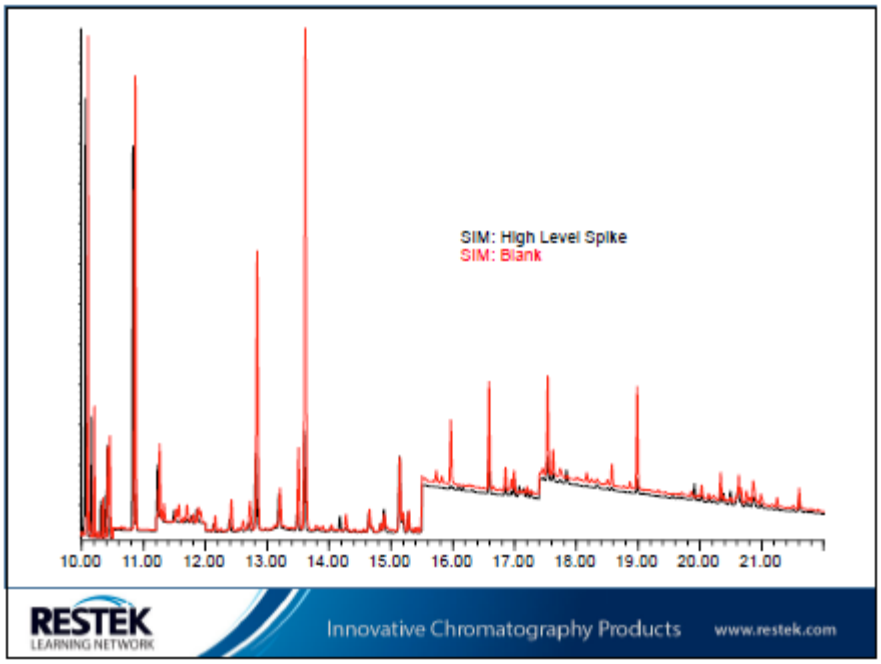
	Low Spike Amount [ng/L]	Average Concentration (n=3) [ng/L]	Percent Error (%)	% RSD (n=3)
THF	10	110	1000	71
1,4-Dioxane-d8	4000	4100	2.5	0.40
1,4-dioxane	10	16	58	27
n-nitrosodimethylamine-d6	400	320	20	2.3
n-nitrosodimethylamine	0.50	0.63	26	14
n-nitrosomethylethylamine	1.0	<2.0	--	--
n-nitrosodiethylamine	1.0	0.75	25	18
n-nitrosopyrrolidine	1.0	2.0	99	17
n-nitrosodi-n-propylamine	1.0	3.8	280	21
n-nitrosomorpholine	0.50	0.60	20	87
n-nitrosopiperidine	1.0	1.1	10	5.8
n-nitrosodi-n-butylamine	1.0	6.4	540	6.2

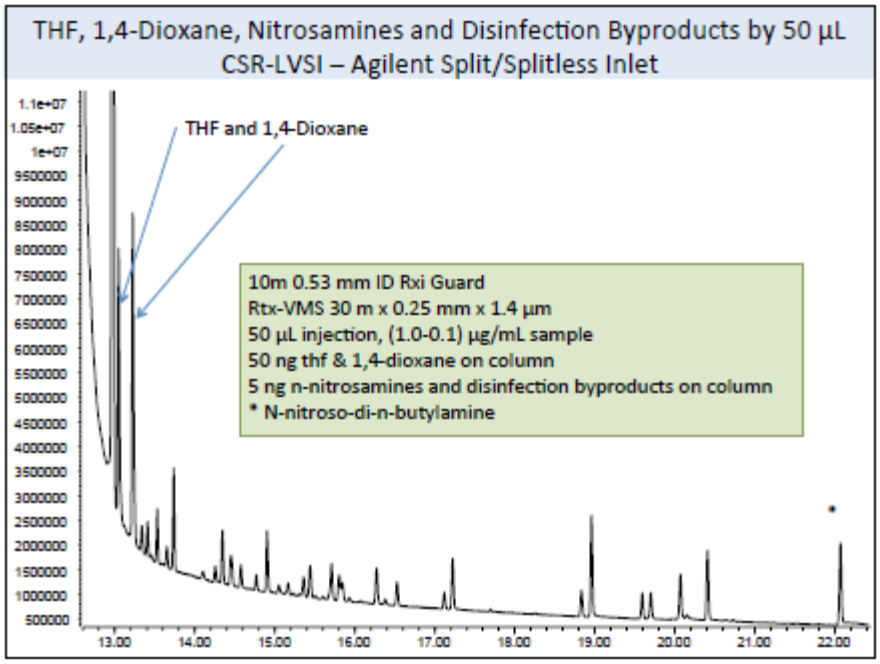
RESTEK LEARNING NETWORK Innovative Chromatography Products www.restek.com

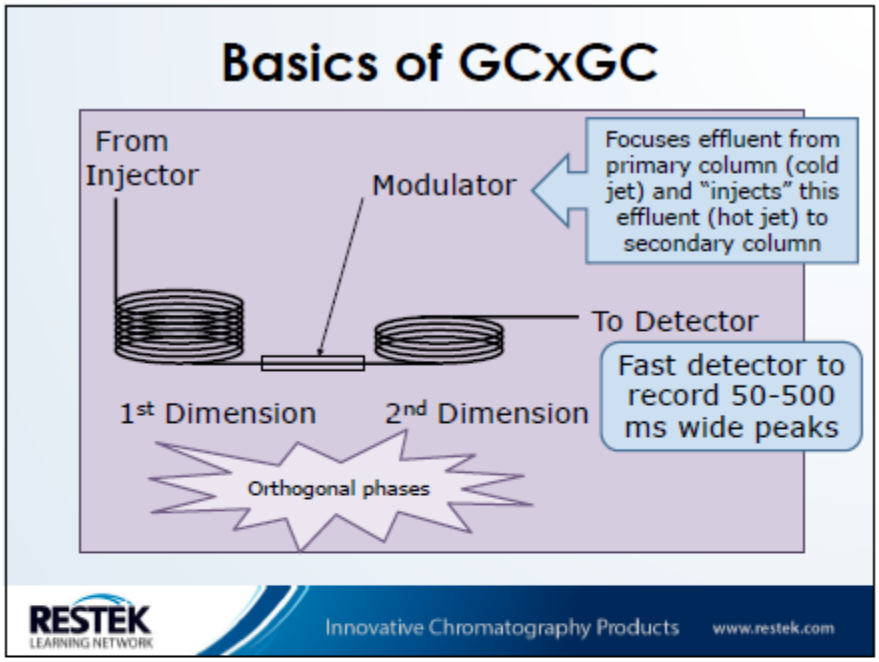
521 522 Combination method - 50 µL injection CSR-LVSI

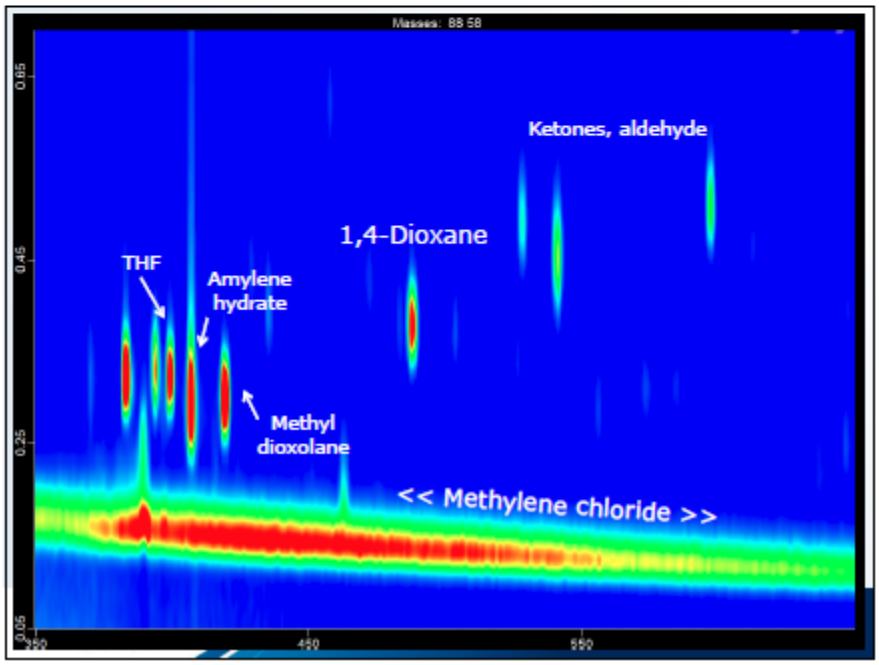
	Blank Amount [ng/L]	Average Concentration (n=3) [ng/L]	% RSD (n=3)
THF	0.0	170	69
1,4-Dioxane-d8	4000	4300	5.0
1,4-dioxane	0.0	12	87
n-nitrosodimethylamine-d6	400	350	6.4
n-nitrosodimethylamine	0.0	<0.50	--
n-nitrosomethylethylamine	0.0	<2.0	--
n-nitrosodiethylamine	0.0	0.095	173
n-nitrosopyrrolidine	0.0	1.4	3.6
n-nitrosodi-n-propylamine	0.0	2.2	87
n-nitrosomorpholine	0.0	0.37	87
n-nitrosopiperidine	0.0	0.68	44
n-nitrosodi-n-butylamine	0.0	7.0	16

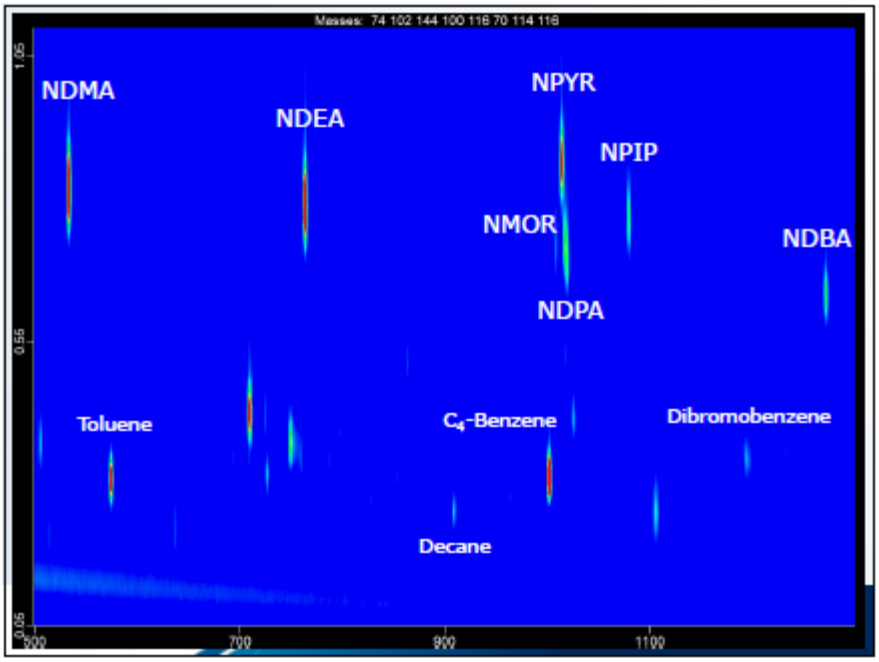
RESTEK LEARNING NETWORK Innovative Chromatography Products www.restek.com

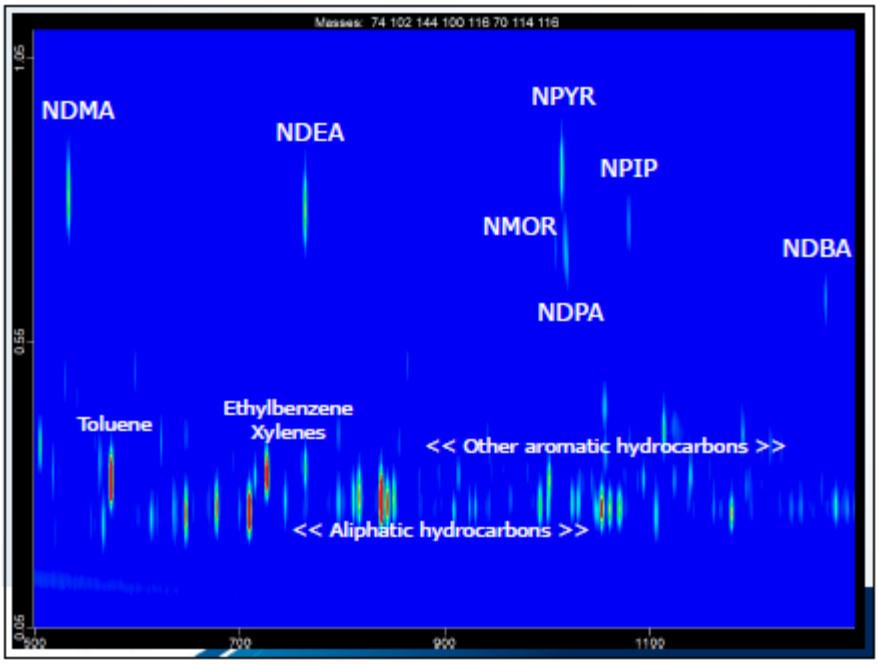

SIM: High Level Spike
SIM: Blank
10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

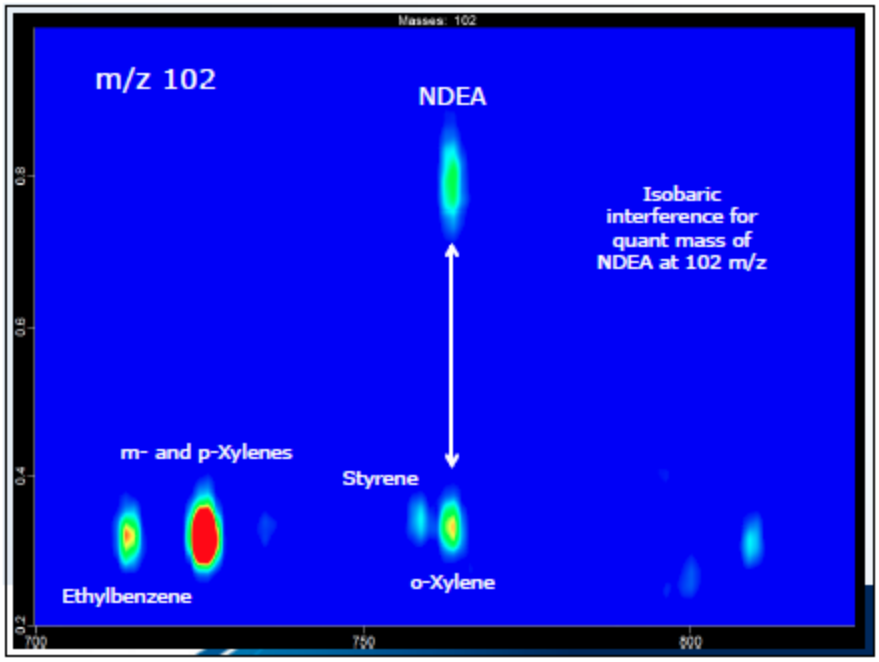

THF, 1,4-Dioxane, Nitrosamines and Disinfection Byproducts by 50 µL
CSR-LVSI – Agilent Split/Splitless Inlet
THF and 1,4-Dioxane
10m 0.53 mm ID Rxi Guard
Rtx-VMS 30 m x 0.25 mm x 1.4 µm
50 µL injection, (1.0-0.1) µg/mL sample
50 ng thf & 1,4-dioxane on column
5 ng n-nitrosamines and disinfection byproducts on column
* N-nitroso-di-n-butylamine
1.1e+07
1.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00

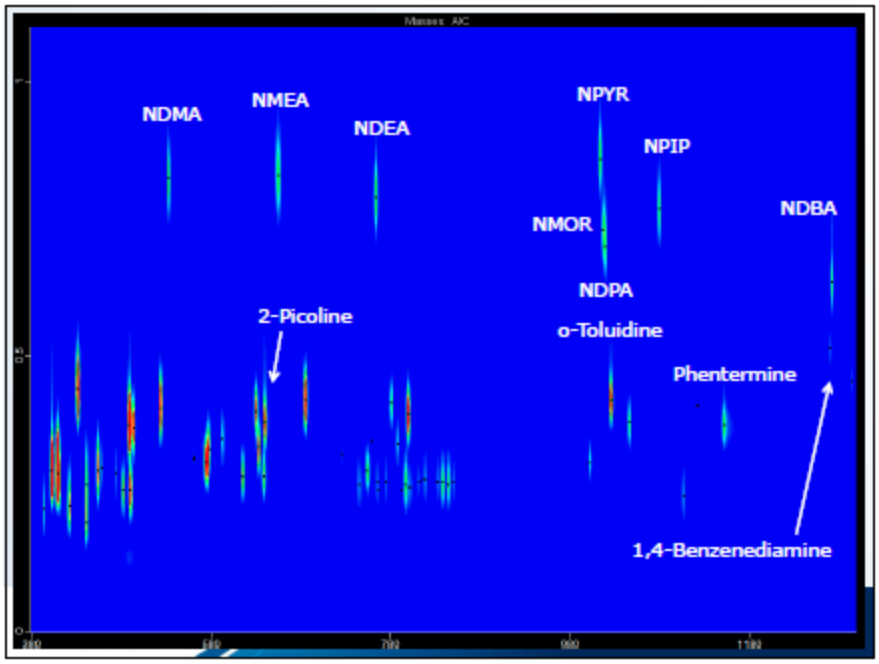

Basics of GCxGC
From Injector
Modulator
Focuses effluent from primary column (cold jet) and "injects" this effluent (hot jet) to secondary column
To Detector
Fast detector to record 50-500 ms wide peaks
1st Dimension
2nd Dimension
Orthogonal phases
RESTEK
LEARNING NETWORK
Innovative Chromatography Products
www.restek.com

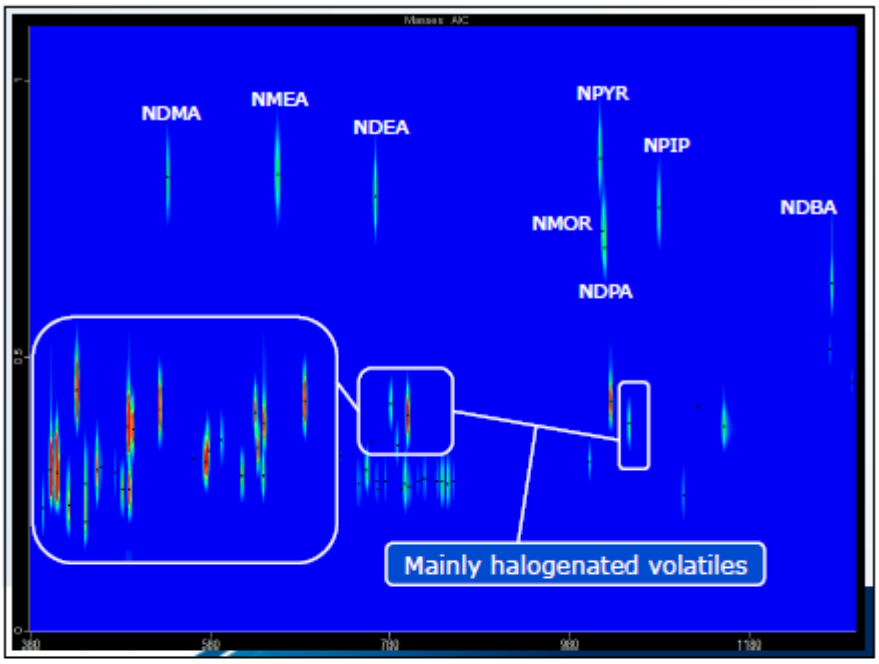

Ketones, aldehyde
1,4-Dioxane
THF
Amylene hydrate
Methyl dioxolane
<< Methylene chloride >>

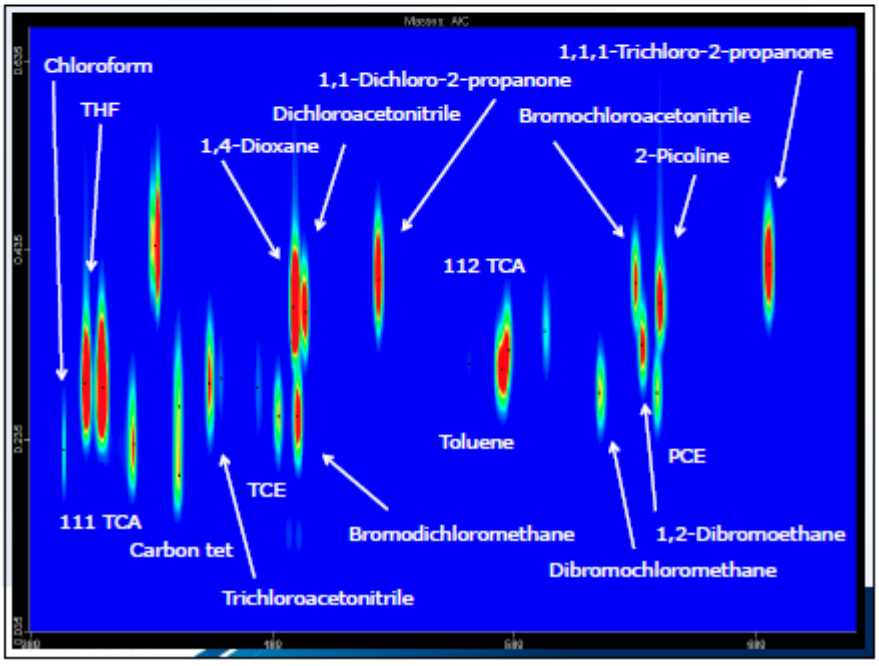

Masses: 74 102 144 100 116 70 114 116
1.05
0.55
0.05
NDMA
NDEA
NPYR
NPIP
NMOR
NDBA
NDPA
Toluene
C4-Benzene
Dibromobenzene
Decane
500
700
900
1100

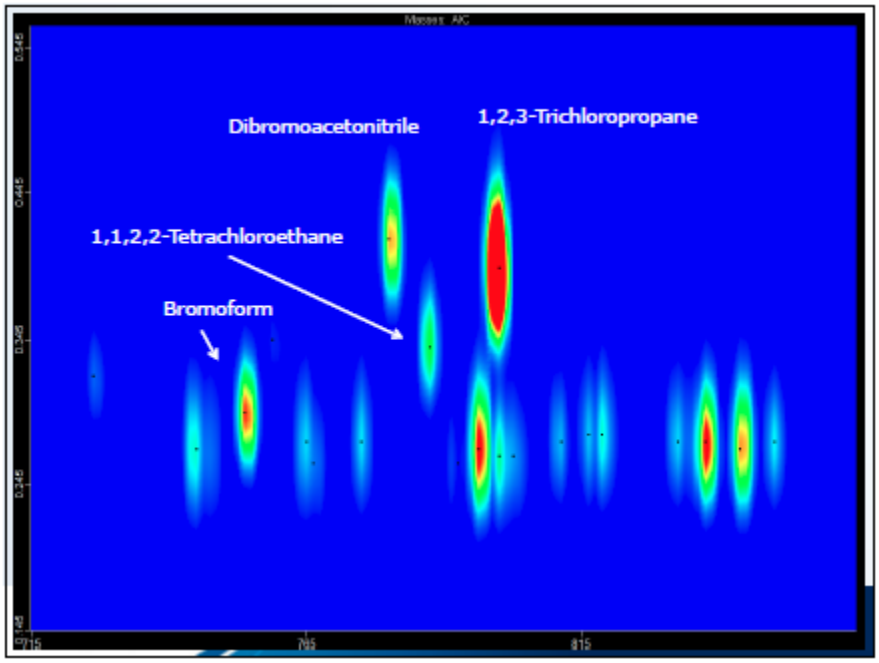

Masses: 74 102 144 100 116 70 114 116
1.05
0.55
0.05
NDMA
NDEA
NPYR
NPIP
NMOR
NDBA
NDPA
Toluene
Ethylbenzene
Xylenes
<< Other aromatic hydrocarbons >>
<< Aliphatic hydrocarbons >>
500
700
900
1100


Masses: 102
m/z 102
NDEA
Isobaric interference for quant mass of NDEA at 102 m/z
m- and p-Xylenes
Styrene
Ethylbenzene
o-Xylene
700
750
800


NDMA
NMEA
NDEA
NPYR
NPIP
NMOR
NDBA
NDPA
2-Picoline
o-Toluidine
Phentermine
1,4-Benzenediamine


NDMA
NMEA
NDEA
NPYR
NPIP
NMOR
NDBA
NDPA
Mainly halogenated volatiles


Chloroform
THF
1,1-Dichloro-2-propanone
1,1,1-Trichloro-2-propanone
Dichloroacetonitrile
Bromochloroacetonitrile
1,4-Dioxane
2-Picoline
112 TCA
Toluene
PCE
TCE
111 TCA
Carbon tet
Bromodichloromethane
1,2-Dibromoethane
Dibromochloromethane
Trichloroacetonitrile


Dibromoacetonitrile
1,2,3-Trichloropropane
1,1,2,2-Tetrachloroethane
Bromoform

Water and Wastewater Analysis Following Catastrophic Events

Matthew Magnuson
USEPA, Office of Research and Development

Abstract

The US Environmental Protection Agency (EPA) is the lead federal agency for clean-up after catastrophes, regardless of their cause. Whether the releases are intentional (e.g. terrorist attack or criminal activity) or unintentional (e.g. natural disaster or industrial accident), analysis of water and wastewater samples will be an integral part of EPA's activities. There are several ways water can become contaminated. For example, any point in a drinking water distribution systems may be contaminated. A wide area contamination release could affect open water sources. Further, water can become contaminated not only from the initial release, but also as a result of decontamination activities. Billions of gallons of water may be used when decontaminating wide areas. Much of the contaminated water may enter the storm or wastewater collection system, ultimately impacting the wastewater treatment plant and waters receiving the effluent. Thus, analysis of many types of water samples, each presenting distinct analytical challenges, will be necessary.

This presentation will discuss the technical aspects of some of the US EPA's Homeland Security Research Program's efforts to meet the many analytical challenges for water samples related to catastrophic events, including the potential need to analyze thousands of samples in a short period of time while maintaining analytical quality. Analytical method development for drinking water samples for contaminants such as chemical warfare agents (e.g. VX), biotoxins (e.g., botulinum toxin and ricin), and unregulated toxic industrial chemicals (e.g. pesticides and their degradates) will be presented. Examples of methods for the analysis of wastewater and wastewater treatment plant sludge will also be included.

Water and Wastewater Analysis Following Catastrophic Events

Matthew L. Magnuson & Hiba S. Ernst
US Environmental Protection Agency/Office of Research and Development
National Homeland Security Research Center/Water Infrastructure Protection Division

National Environmental Monitoring Conference
San Antonio, TX, August 5-8, 2013



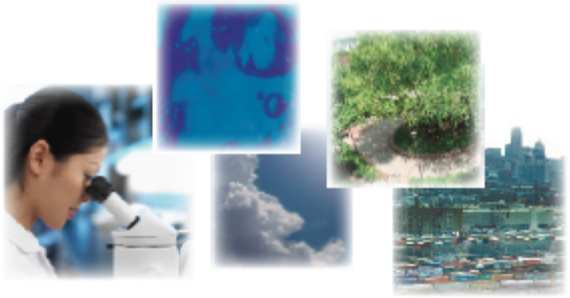
Presentation Overview

- Lab analysis during catastrophic events - Is there a difference?
- What is being done?
  - Lab Networks
  - Pre-selected and verified methods
  - Biotoxin research projects
  - Chemistry research projects

NHSRC Mission

To conduct research and develop scientific products that improve the capability of the Agency to carry out its homeland security responsibilities

ADVANCING OUR NATION'S SECURITY THROUGH SCIENCE



EPA Homeland Security Roles

- Protecting water and wastewater infrastructure
- Indoor and outdoor clean-up following attack or natural disaster
  - can use millions of gallons of water
  - can result in even more contaminated wastewater
- Development of a nationwide laboratory network
- Reducing vulnerability of chemical & hazardous materials
- Cyber security





NHSRC Research Projects

Multi Use →
- Homeland Security
- Cross Agency
- "Normal" Environmental Operations

Many homeland security practices may also benefit day to day operation. For example, emerging analytical techniques useful for water emergencies and/or clean-up after contamination might also be useful for monitoring water quality.

Water Security & Sustainability

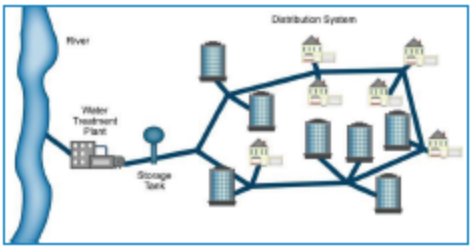


Water Security Threats



Water Distribution Networks

- Multiple points of access over thousands of miles of pipe
- Vulnerable to insider, physical, and cyber threats
- Vulnerable to intentional or accidental contamination (e.g., injection at hydrant or cross-connection)
- Contamination might not be detected until people are sick or in the hospital
- Intelligence information on adversary capabilities



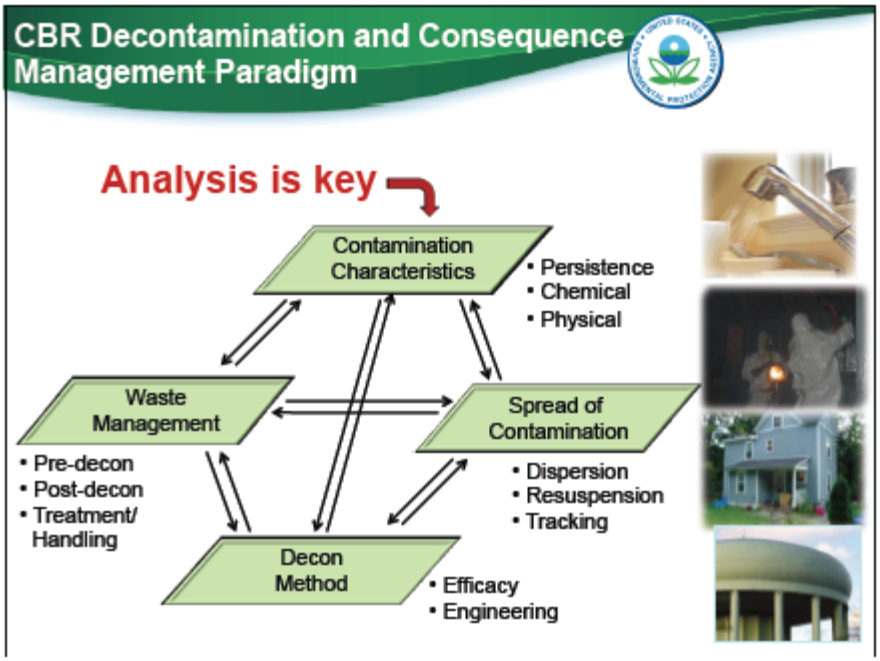
7

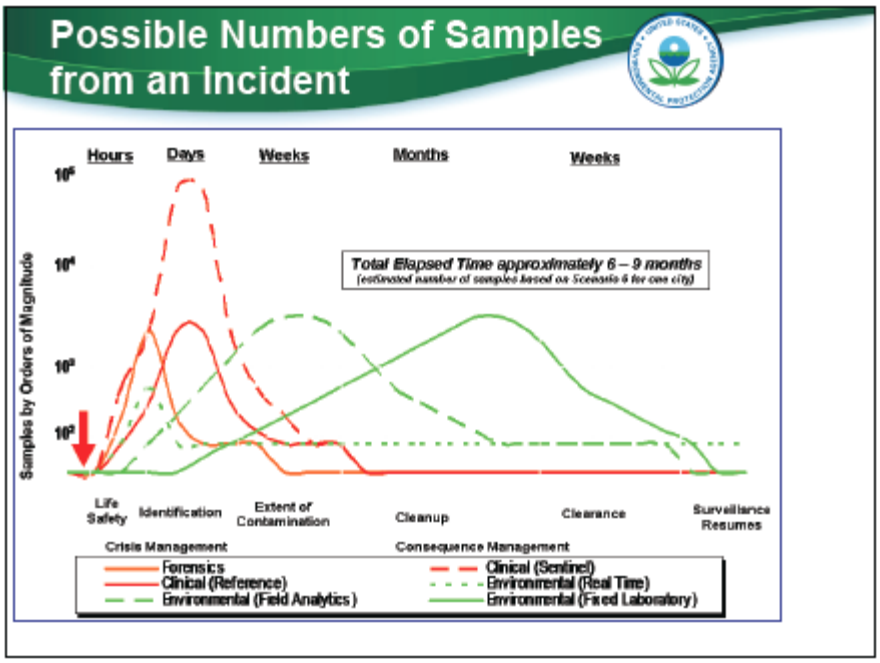
Why Waste Water?



- Wide area contamination release could affect water sources.
- Water can become contaminated not only from the initial release, but also as a result of decontamination activities.
- Millions of gallons of water may be used for decon.
- Contaminated water may enter the storm or wastewater collection system, impacting the wastewater treatment plant and receiving waters.

8


CBR Decontamination and Consequence Management Paradigm
Analysis is key
Contamination Characteristics
• Persistence
• Chemical
• Physical
Waste Management
• Pre-decon
• Post-decon
• Treatment/ Handling
Spread of Contamination
• Dispersion
• Resuspension
• Tracking
Decon Method
• Efficacy
• Engineering


Possible Numbers of Samples from an Incident
Hours
Days
Weeks
Months
Weeks
Samples by Orders of Magnitude
Total Elapsed Time approximately 6 – 9 months
Life Safety
Identification
Extent of Contamination
Cleanup
Clearance
Surveillance Resumes
Crisis Management
Consequence Management
Forensics
Clinical (Reference)
Environmental (Field Analytics)
Clinical (Sentinel)
Environmental (Real Time)
Environmental (Fixed Laboratory)

Meeting Lab Throughput

Potential approaches

- High throughput sampling techniques and laboratory analysis techniques, including automated or rapid method capabilities
- Methods which can be applied to multiple labs by Environmental Response Laboratory Network (ERLN) and Water Laboratory Alliance



ERLN



Selected Analytical Methods (SAM)



SAM 2012

Published: July 2012

Chemical Methods
142 analytes
5 matrices

Pathogen Methods
31 analytes
4 matrices

Radiochemical Methods
25 analytes
6 matrices

Biotoxin Methods
18 analytes
5 matrices

www.epa.gov/sam

Laboratory Method Development

- Methods aim to have data quality objectives (DQOs) fit for their intended use by
  - EPA/Water Security Division through the Water Laboratory Alliance
  - EPA/Office of Emergency Management through the Environmental Response Laboratory Network
- Availability of Method and Study Reports
  - Availability announced on website, and we also maintain a list of stakeholders who are specifically informed
  - **Register at http://www.epa.gov/nhsrc**

NHSRC Research Products

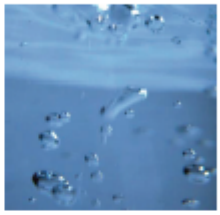
- Results presented many other ways—stakeholder meetings, symposia, workshops, etc.
- Products and research plans receive rigorous quality reviews



Most scientists regarded the new streamlined peer-review process as 'quite an improvement.'

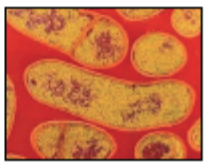
Method Development in Water Matrices (Biotoxins and Chem)





Method Development for Biotoxins

- Protein
  - Abrin, Ricin, Botulinum neurotoxin (A, B, E, F), Shiga 1 & 2, Staphylococcal Enterotoxin (A, B, C)
- Small molecule
  - Aflatoxin B1, α-Amanitin, anatoxin-a, brevetoxin B, α-Conotoxin, Cylindrospermopsin, Diacetoxyscirpenol, microcystins (LA, LR, LW, RR, YR), picrotoxin, saxitoxins, T2 mycotoxin, tetrodotoxin





Detection of Biotoxins

- Analytical techniques
  - Antibody-based detection schemes
    - Enzyme Linked Immunosorbant Assay (ELISA)
    - Lateral flow devices
    - Various antibody-capture-release detectors (fluorescence, electrochemiluminescence, etc.)
  - Instrumental analysis
    - Liquid chromatography-mass spectrometry
    - Gas chromatography-mass spectrometry
    - others

Meeting Throughput Requirements

Multi-tier analysis approach

- Environmental restoration hopefully is effective, so while there are many samples, fewer will be positive after initial decontamination activities
- Samples initially subjected to higher throughput screening methods
- Followed by analysis of selected samples with lower throughput, but more definitive, techniques
- Application approach of techniques listed will appear in future version of SAM (e.g. see techniques of ricin in table below)

Ricin	9009-86-3 (ricin)	Presumptive	Immunoassay[7]	Adapted from lateral flow immunoassay kits
	60 kDa glycoprotein composed of two subunits (~32 kDa A chain and ~34 kDa B chain); an agglutinin of MW 120 kDa may be present in crude preparations	Complementary Presumptive (ricinine)	LC-MS	Adapted from Journal of Analytical Toxicology 25(3): 145-150
	5254-40-3 (ricinine)	Confirmatory	Immunoassay	Adapted from Journal of AOAC International 91(2): 375-382
	small molecule, ricin marker	Biological Activity	Enzyme activity[7]	Adapted from Analytical Biochemistry 376(1): 87-89

Biotoxin Detection Projects

Centers for Disease Control and Prevention

- Quantitation of biotoxins via methods adapted from clinical matrices such as urine
- LC/MS/MS methods, as used in chemical laboratory response network (LRN) for clinical samples
  - Adaptation to drinking water matrices
  - Stability, extraction, chromatography, MS tuning
  - High throughput, small samples, automation, IT
- Enzyme Linked Immunosorbant Assay (ELISA) for Botulinum toxin in clinical samples and food adapted to water
- Endopep-MS (enzymatic activity) method adapted to water samples
- Ability of the ultrafiltration (UF) technique to concentrate botulinum toxin in water samples

Features of Adapted Methods

- 100-1000 samples/day
- Analytes
  - Alpha amanitin
  - TETS
  - Biomarkers for ricin and abrin
- Stable Isotopic Internal Standards

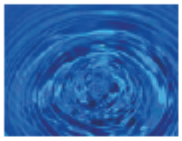






Method Development for Chemicals



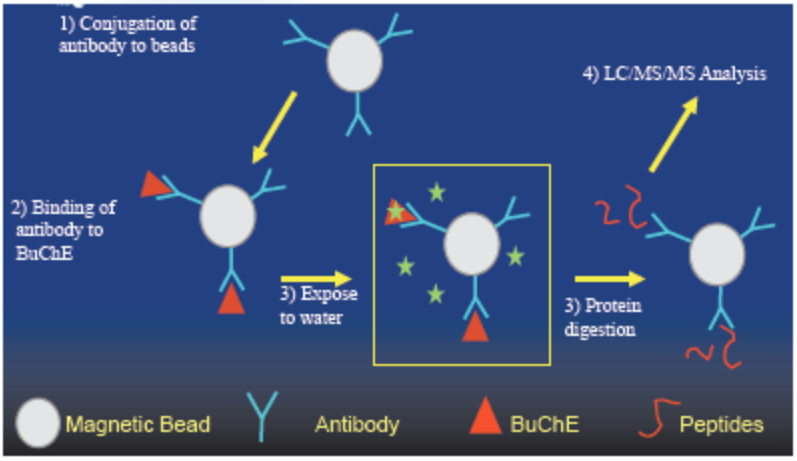




Verification of Chemicals in Existing Method

- Use methods as written, for lab familiarity
- Understand performance, demonstrate all steps including QC
- Examples
  - Semi-volatiles (e.g. pesticides)
  - CWA transformation products
  - Metals

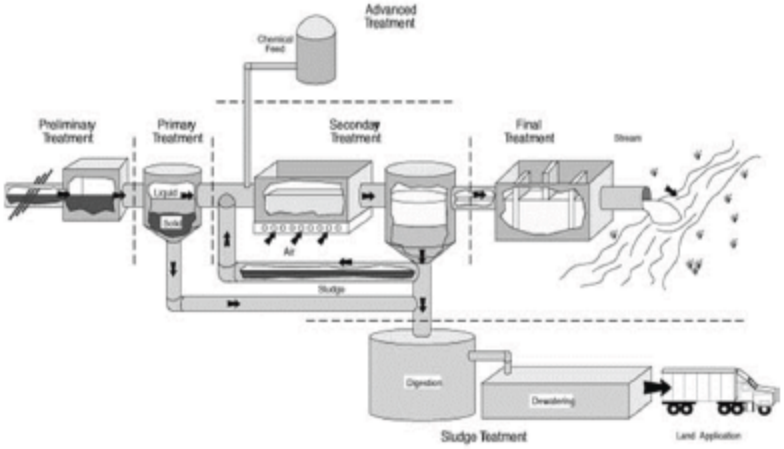
Immunomagnetic Scavenging and LC/MS Detection of VX in Water



IMSc LC-MS/MS Method for Detection of VX in Water

- Method sensitivity down to the ppt level
  - Calculated method detection limit = 5.6 ng/L
  - Minimum reportable level = 25 ng/L
  - Small sample size (100 µL)
- Can be used to analyze up to 500 samples per day
- Low concentrations of VX can be detected in preserved tap water 91 days after spiking
  - Suggests applicability of this method for determining water contamination with VX and verifying environmental remediation

Wastewater Treatment Process



Analysis for System Studies

Degradation of contaminants by activated sludge

Example contaminants:

- EMPA (ethyl methyl phosphonic acid) : Environmental and decon product of VX, determined by LC/MS/MS
- Malathion: Simulant for VX, determined by GC/MS
- Evaluated total suspended solid concentration and contact time

Conclusions:

- If nitrifiers are active, they might degrade the analyte of concern (less than 25 percent)
- EMPA, malathion, and similarly sorbed and biodegraded compounds may pass through an activated sludge wastewater treatment plant largely unchanged

Future Directions

- Extension to "All-hazard" catastrophes –natural disasters, industrial accidents, etc
- Analysis approaches for other matrices
- Additional biotoxins and chemicals
- Refinement of existing methods
- Application-focused studies (decontamination, system operations, etc.)
- Enhanced collaborations
  - Federal (e.g. recent EPA, DHS, and DOD agreement)
  - Other: **maybe YOU?!**

Acknowledgements

- Centers for Disease Control and Prevention
  - Rudy Johnson, Ph.D.
  - Jennifer Links, Ph.D.
  - Stephen Morse, Ph.D.
  - CT method development group
- Food Safety Inspection Service
  - Mark Campbell, Ph.D.
  - Marcus Head, Ph.D.
  - Jim Jones, Ph.D.
  - Anne Hurley, DVM, MPH
- US Air Force Institute of Technology
  - Maj. LeeAnn Racz, Ph.D.
  - Lt. Allen Janeckso, M.S.
  - Maj. Edward Walters, M.S.
- Naval Surface Warfare Center
  - Elaine Strauss, Ph.D.
  - Wynn Vo
  - Andrew Slaterbeck, Ph.D.
  - Bradford Gutting, Ph.D.
- Environmental Protection Agency
  - Michelle Burgess, Ph.D., EPA
  - Sanjiv Shah, Ph.D., NHSRC
  - Gene Rice, Ph.D., NHSRC
  - Hiba Ernst, Ph.D., NHSRC
  - Alan Lindquist, Ph.D., NHSRC
  - Frank Schaefer, Ph.D., NHSRC
  - Vince Gallardo
  - Tonya, Nichols, Ph.D., NHSRC

Acknowledgements

Matthew Magnuson, Ph.D.
Acting Associate Director/Chemist
Water Infrastructure Protection Division
magnuson.matthew@epa.gov; 513-569-7321

Co-authors/Collaborators:
Romy Campisano
Erin Silvestri
Stuart Willison

U.S. EPA, National Homeland Security Research Center

DISCLAIMER: The U.S. EPA through its Office of Research and Development partially funded the research described in this presentation. It has been reviewed by the Agency but does not necessarily reflect the Agency's views. No official endorsement should be inferred. EPA does not endorse the purchase or sale of any commercial products or services.

SAM 2012
Published: July 2012



Website: www.epa.gov/sam

Screening Environmental Samples for a Diverse Range of Compound Classes and Structures with Accurate Mass LC-MS and an Integrated Scientific Information System

Kenneth Rosnack
Waters Corporation

Abstract

Introduction

The presence of an increasingly complex array of pharmaceuticals and personal care products (PPCPs) in water bodies throughout the world is placing a greater demand on techniques used to screen for these compounds. Using a high resolution screening technique employing MSe where high and low energy switching enables the acquisition of precursor and fragments ion in a single injection, provides information rich data that can be used to reduce the large number of false detects that arise from the use of accurate mass alone. In combination with an integrated scientific information system, the ability to screen for the presence of PPCPs, their adducts and potential metabolites in a single injection is now possible in a routine laboratory.
Methods

Owing to the wide chemical diversity of the compounds described as PPCPs, the extraction and separation of the many classes and structures pose a major analytical challenge. Depending on detection level required, two alternative approaches could be taken for sample preparation. The first involves simple filtration followed by large volume injection of the water sample. If lower levels of detection were required, a method employing mixed mode solid phase extraction was used. UPLC separation on a 2.1 x 100 mm HSS T3 analytical column (1.7um) was found to provide optimum chromatographic conditions to resolve the range of chemically diverse PPCPs. Experiments were performed on a high resolution LC coupled to a quadrupole time of flight mass spectrometer. Simultaneous acquisition of accurate mass precursor and accurate mass fragment ions provided information rich data with excellent sensitivity. All data was collected and processed with an integrated Scientific Information System.

Preliminary Data

Processing the accurate mass precursor and fragment ion data through a new scientific information system, enabled low level detection of PPCPs, their adducts and metabolites in drinking and environmental water samples. The use of retention time information as well as fragment ions for confirmation resulted in a reduction in the number of false detection from the samples. Simultaneous identification and quantification can be performed on the samples and the results reviewed and reported using a single, integrated platform. This work demonstrates the applicability of accurate mass LC-MS in order to expand the scope of contaminant testing in water samples.

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

SCREENING ENVIRONMENTAL SAMPLES FOR A DIVERSE RANGE OF COMPOUND CLASSES AND STRUCTURES WITH ACCURATE MASS LC-MS AND AN INTEGRATED SCIENTIFIC INFORMATION SYSTEM

Ken Rosnack
Business Development Manager
ken_rosnack@waters.com

Food & Environmental | Business Operations

©2013 Waters Corporation 1

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Overview

- **The requirements for screening assays**
  - Introduction & background to screening analysis
  - Challenges and regulatory considerations
  - Performance criteria
- **Pesticide screening solution with UNIFI**
- **An overview of UNIFI 1.6 software via a well water example**
- **Summary and conclusions**





©2013 Waters Corporation 2

The purpose of residue screening?

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

Goals
- To eliminate the compliant samples (≥95% samples?)
- To identify the non-compliant samples for subsequent confirmation and quantification (~5%?)

Needs
- Applicable for **high-throughput multi-residue** analysis
- **Sensitivity** in line with the relevant Regulatory limits in complex matrices
- **Validated** in accordance with legislative requirements

Process
- **Rapid, cost effective** and **"user friendly"** from sample preparation to results reporting...

©2013 Waters Corporation

Residue Screening Classification

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- **Targeted screening (QQQ)**
  - Well defined target list of analytes
  - Selective acquisition &/or processing modes
  - Analytical standards available for every compound



- **Non-targeted (suspect) screening (Tof)**
  - Non targeted relates to the acquisition type
  - Screen against a comprehensive library of known compounds
  - Analytical standards available for most compounds



- **Unknown screening (Tof)**
  - No defined target list
  - Compound not present in the library, maybe a ne chemical structure
  - Structural elucidation required



©2013 Waters Corporation

Challenges/Needs Facing Environmental Monitoring Laboratories

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- Laboratories have to screen for larger numbers of compounds at very low concentrations *(<ppb, ppt)*
- Increase in the number of samples =
  - Shorter turn-around times required to keep pace with demand
  - Simple access
- With longer lists of priority substances, better understanding of the transformation of pesticides and POPs in the environment, many laboratories wish to extend the scope of their analytical methods beyond the compounds listed in the drinking water methods.
- Trend for **generic, multi-residue** methods
  - Trade off between selectivity and sensitivity…



©2013 Waters Corporation

SANCO/12495/2011 – performance criteria - high resolution, accurate mass

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- Sensitivity in line with the relevant Regulatory limits
  - MRLs / MRPLs / RCs / ALs / ADIs etc…
- Applicability of the **screening** method is defined by the false non-compliant (positive) and false compliant (negative) rates
  - A low false negative rate is critical for screening assays to avoid missing MRL violations
  - **Tolerance ≤ 5% false negative rate**
  - A low false positive rate is important for screening assays to reduce costly quant / confirmatory analysis
  - **Desirable ≤ 5% false positive rate**
- Mass accuracy tolerance = ≤5 ppm
- Mass resolution tolerance = ≥20k (FWHM)



©2013 Waters Corporation

SANCO/12495/2011 criteria for chromatography

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- .....the minimum acceptable **retention time** should be at least twice the void volume of the column...
- .....the retention of the analyte, should correspond to that of the calibration solution .....with a tolerance of ±0.5% for GC and ±2.5% for LC.

Chromatography is still important !!!!

©2013 Waters Corporation

SANCO/12495/2011 – Requirements for the confirmation of the results

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

Table 4. Identification requirements for different types of mass spectrometers

MS mode:	Single MS (standard mass resolution)	Single MS (high resolution/high mass accuracy)	MS/MS
Typical systems (examples)	quadrupole, ion trap, time-of-flight (TOF)	TOF, Orbitrap, FTMS, magnetic sector	Triple quadrupole ion trap, hybride MS (e.g. Q-TOF, Q-trap)
Acquisition:	Full scan, Limited m/z range, Selected ion monitoring (SIM)	Full scan, Limited m/z range, Selected ion monitoring (SIM)	Selected/multiple reaction monitoring (SRM/MRM), full scan product-ion spectra
Requirements for identification:	≥ 3 diagnostic ions, (preferably including quasi molecular ion)	≥ 2 diagnostic ions (preferably including the quasi molecular ion). Mass accuracy < 5 ppm. At least one fragment ion.	≥ 2 product ions
Ion ratio(s):	according to Table 5		

- **A variety of MS analysers and configurations including HR-MS are recognised with differing requirements for identification depending on the inherent analytical power**

©2013 Waters Corporation

Why High Resolution Accurate Mass Screening?

Waters
THE SCIENCE OF WHAT'S POSSIBLE.



©2013 Waters Corporation

Advantages of accurate mass screening?

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- Over recent years high resolution mass spectrometry has gained in popularity as a screening tool in the food and environmental sector

✓ **Ability to perform non-targeted analysis**
- The freedom to measure compounds without prior compound specific tuning

✓ **Ability to perform historical (retrospective) data review**
- The capability of performing structural elucidations of unknowns or suspected compounds

✓ **Ability to perform full spectral analysis**
- Providing greater insight into the composition of a complex sample

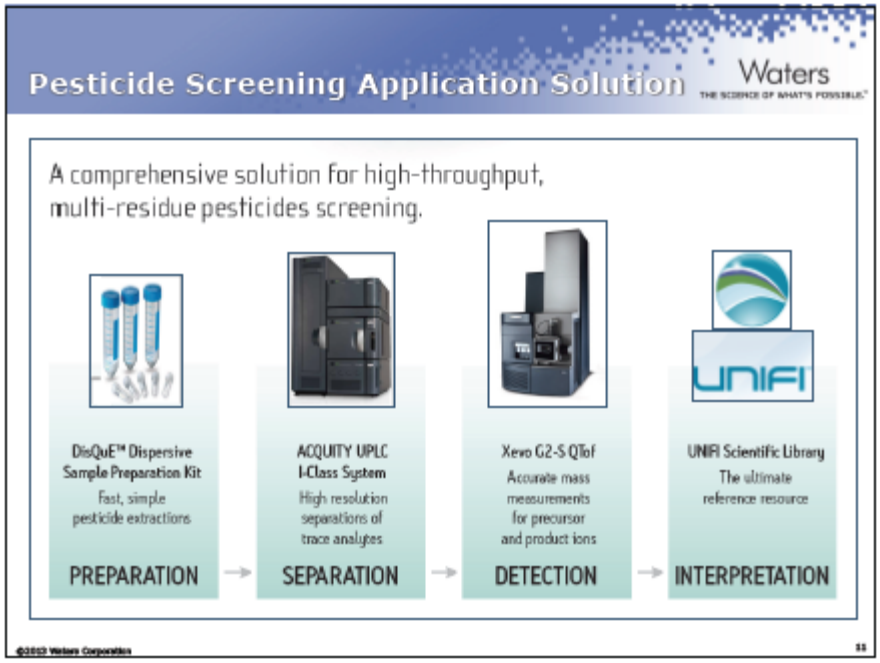
✓ **Ability to screen for larger number of compounds and adducts**
- Compared to QqQ based screening

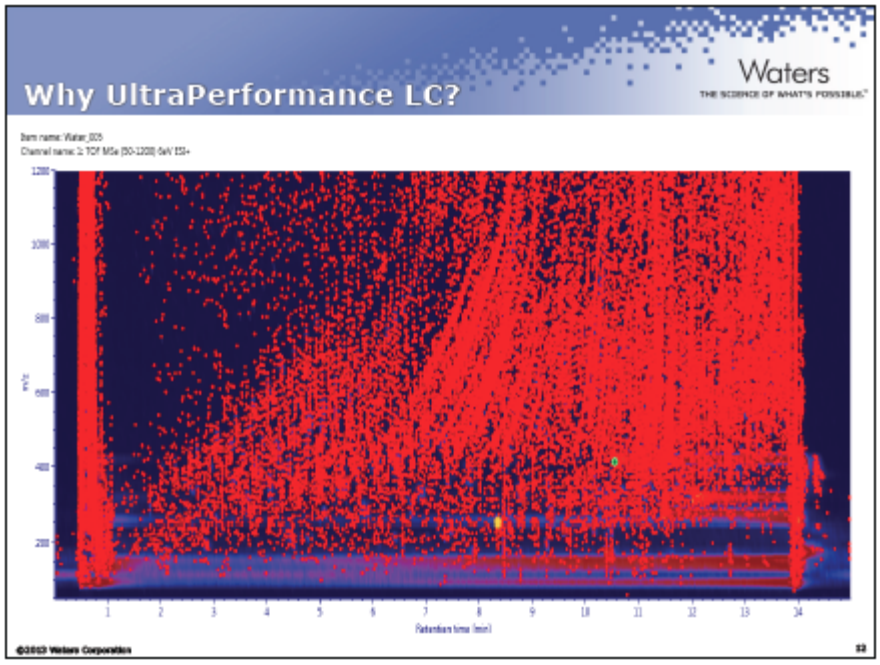
✓ **Increased specificity in complex matrices**
- Accurate mass, diagnostic fragment ions...

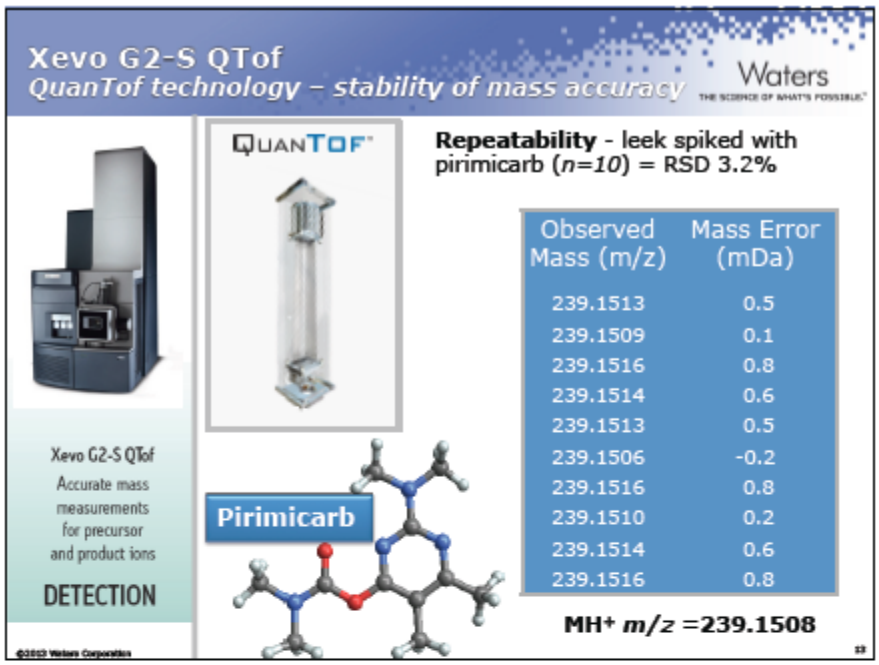
"HRMS strongly competes with classical tandem mass spectrometry in the field of quantitative multiresidue methods (e.g., pesticides and veterinary drugs). It is one of the most promising tools when moving towards nontargeted approaches..."

Kaufman A., Anal BioAnal Chem 2011 Dec 17

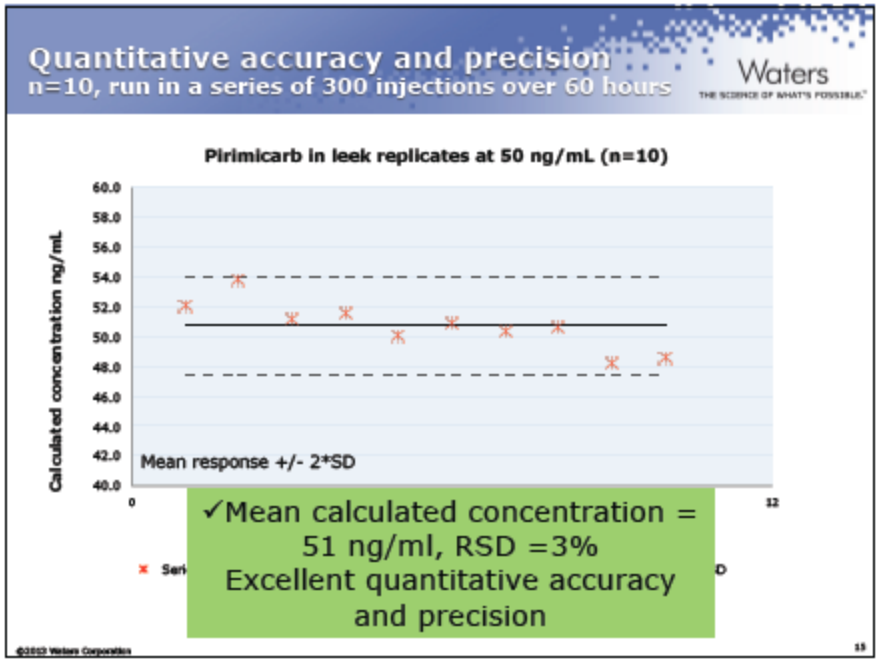
©2013 Waters Corporation

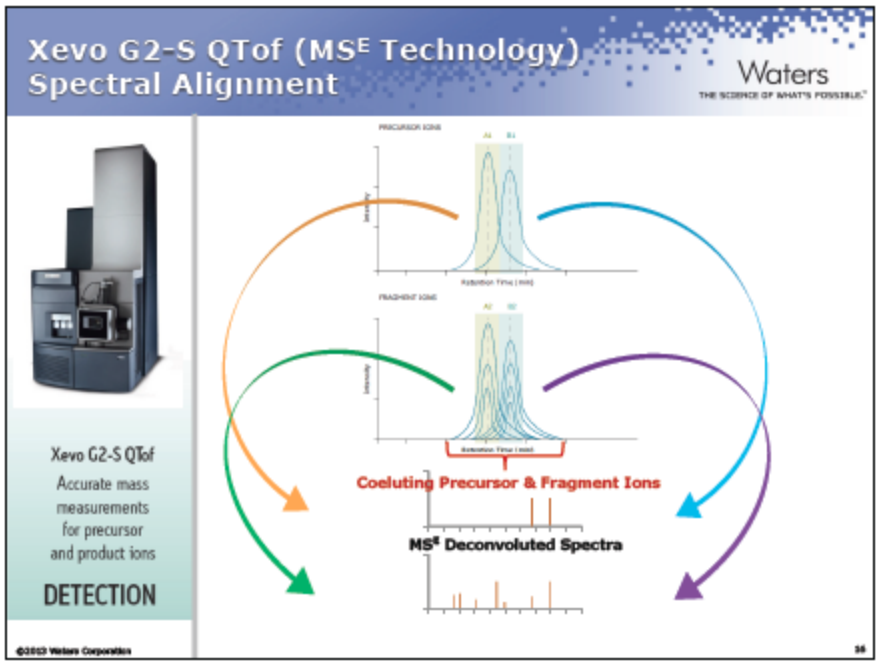

Pesticide Screening Application Solution
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
A comprehensive solution for high-throughput, multi-residue pesticides screening.
UNIFI
DisQuE™ Dispersive Sample Preparation Kit
Fast, simple pesticide extractions
PREPARATION
ACQUITY UPLC I-Class System
High resolution separations of trace analytes
SEPARATION
Xevo G2-S QTof
Accurate mass measurements for precursor and product ions
DETECTION
UNIFI Scientific Library
The ultimate reference resource
INTERPRETATION
©2013 Waters Corporation
33


Why UltraPerformance LC?
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
m/z
Retention time (min)
©2013 Waters Corporation
32


Xevo G2-S QTof
QuanTof technology – stability of mass accuracy
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
QUANTOF
Repeatability - leek spiked with pirimicarb (n=10) = RSD 3.2%
Observed Mass (m/z)
Mass Error (mDa)
239.1513 0.5
239.1509 0.1
239.1516 0.8
239.1514 0.6
239.1513 0.5
239.1506 -0.2
239.1516 0.8
239.1510 0.2
239.1514 0.6
239.1516 0.8
Pirimicarb
MH+ m/z =239.1508
Xevo G2-S QTof
Accurate mass measurements for precursor and product ions
DETECTION


Xevo G2-S QTof
QuanTof technology –Accurate & Quantitative
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
QUANTOF
STEPWAVE
Quantitative Performance
Matrix Matched Calibration Series
(mandarin extract): Imazalil: 1 – 1000 ng/g
Xevo G2-S QTof
Accurate mass measurements for precursor and product ions
DETECTION


Quantitative accuracy and precision
n=10, run in a series of 300 injections over 60 hours
Waters
Pirimicarb in leek replicates at 50 ng/mL (n=10)
Calculated concentration ng/mL
60.0
58.0
56.0
54.0
52.0
50.0
48.0
46.0
44.0
42.0
40.0
0
12
Mean response +/- 2*SD
✓Mean calculated concentration = 51 ng/ml, RSD =3%
Excellent quantitative accuracy and precision

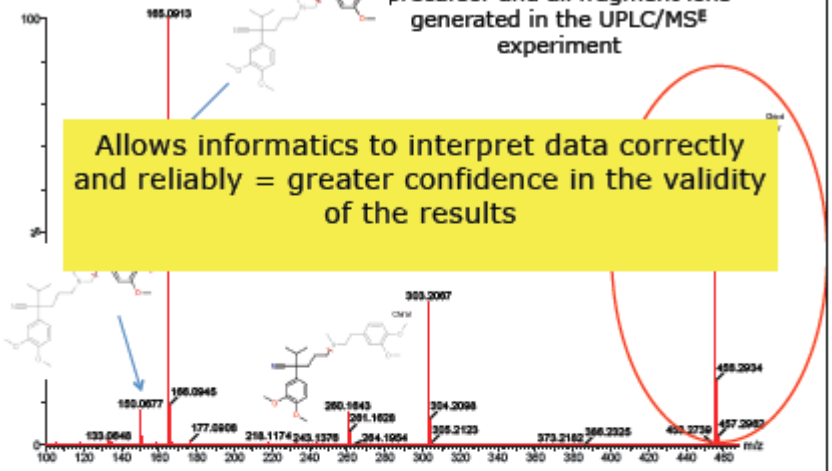

Xevo G2-S QTof (MSE Technology)
Spectral Alignment
Waters
Xevo G2-S QTof
Accurate mass measurements for precursor and product ions
DETECTION
Coeluting Precursor & Fragment Ions
MSE Deconvoluted Spectra

Fragment ion information with UPLC/MS^E

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

Exact mass performance for precursor and all fragment ions generated in the UPLC/MS^E experiment

Allows informatics to interpret data correctly and reliably = greater confidence in the validity of the results



©2013 Waters Corporation

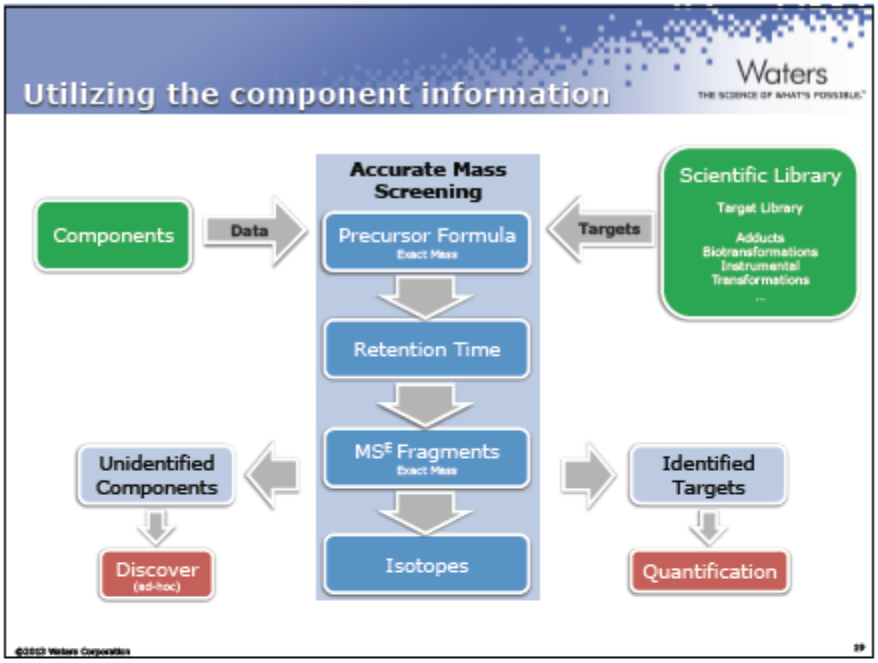
Comprehensive Data Set and Scientific Library

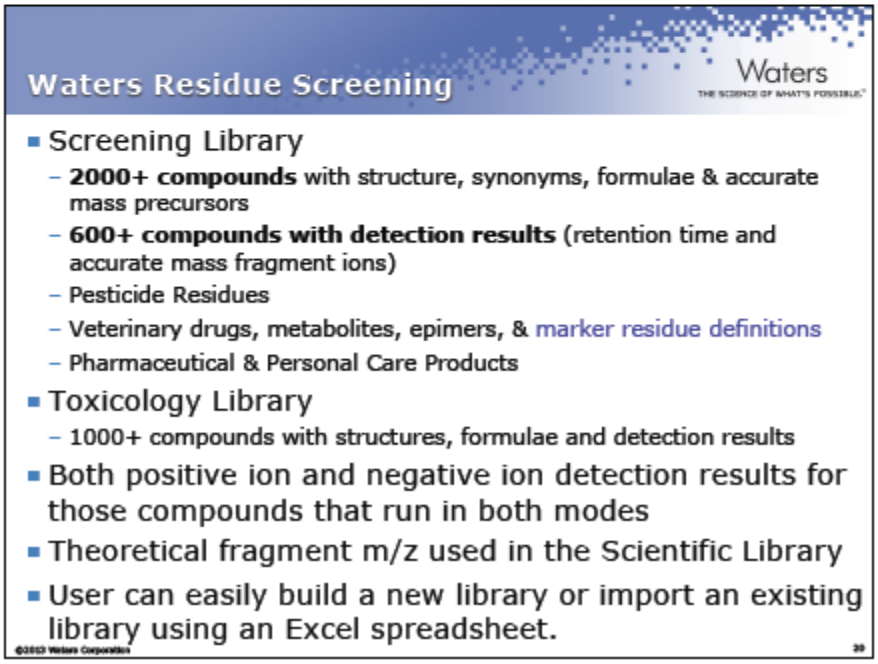
Waters
THE SCIENCE OF WHAT'S POSSIBLE.

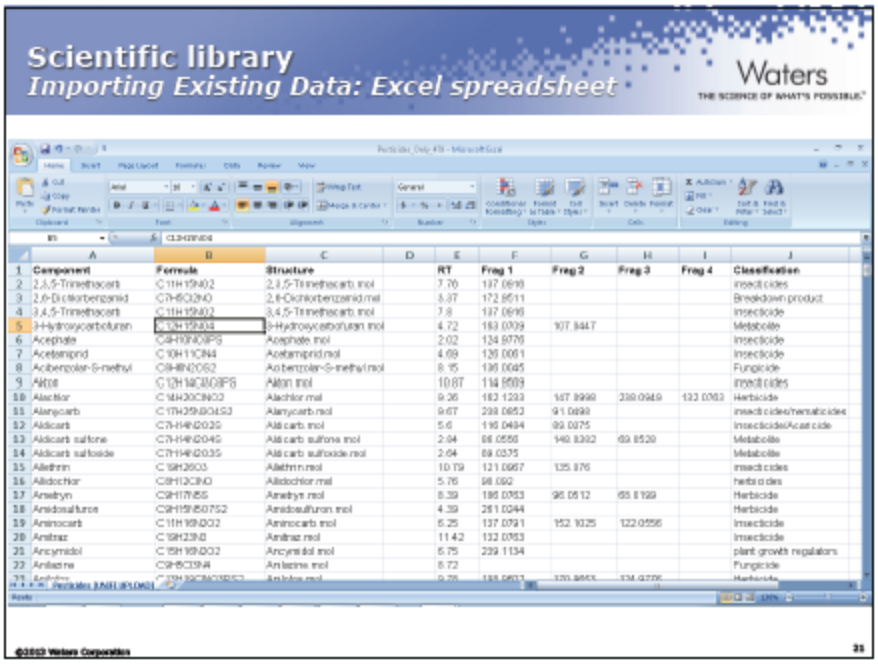
- Screening experiments are dependent on the **quality** of data and libraries.
- Critical information that is used for ID process
  - **Name** *(chemical, common, synonyms, marker residue definition)*
  - **Chemical formula**
  - **Structure**
  - **Retention time**
  - **Accurate mass precursor ions**
  - **Accurate mass fragment ions**
  - **Isotopic patterns**
  - **Isotope intensity**
  - Expected ion ratios
  - Theoretical spectra
  - Drift Time

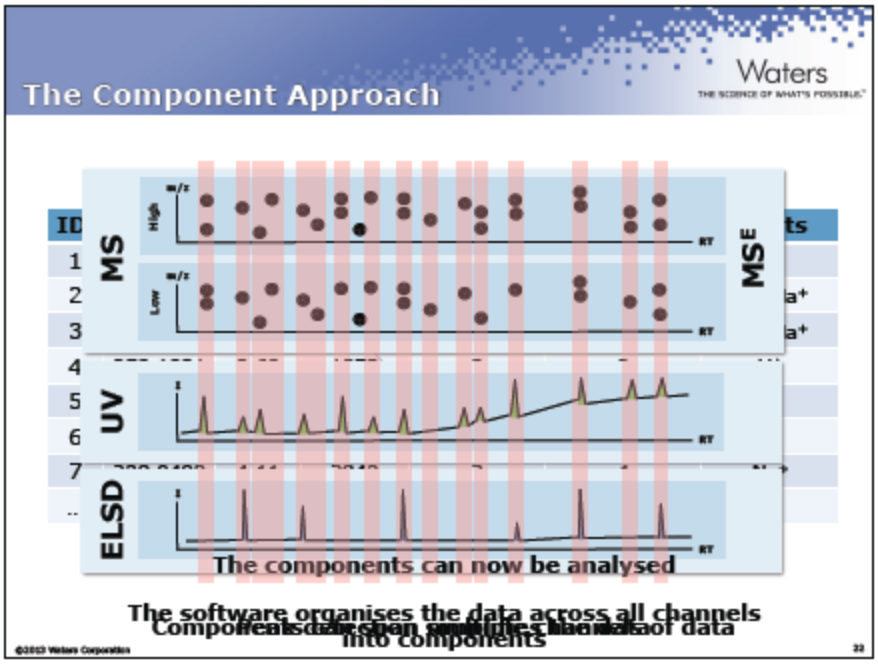


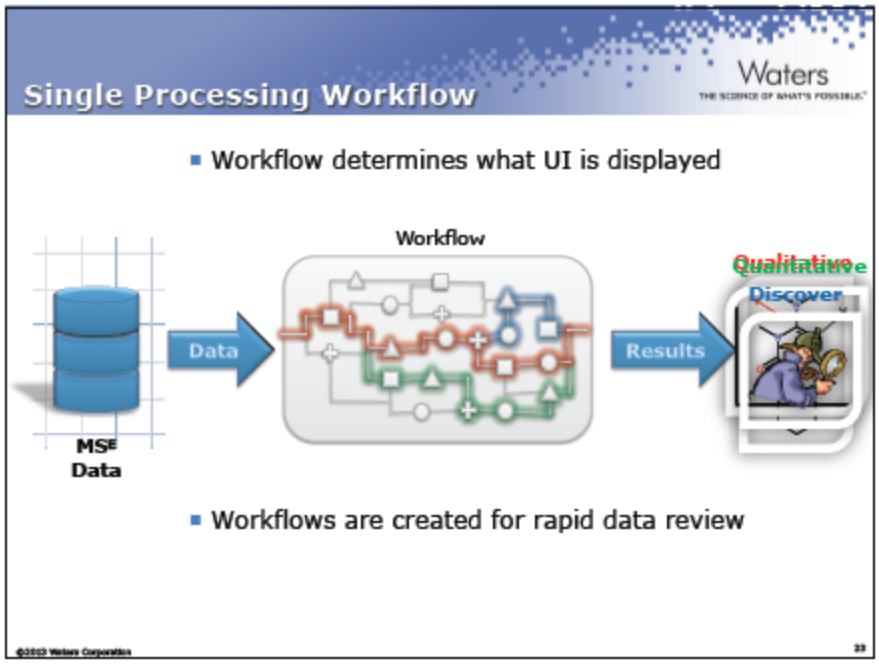
©2013 Waters Corporation

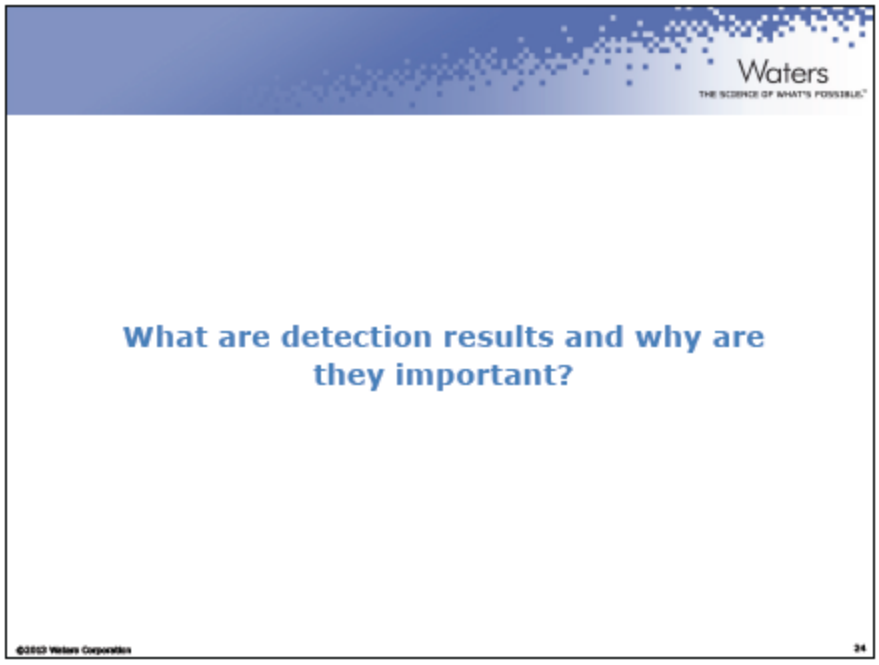

Utilizing the component information
Waters
Components
Data
Accurate Mass Screening
Precursor Formula
Exact Mass
Retention Time
MS^E Fragments
Exact Mass
Isotopes
Targets
Scientific Library
Target Library
Adducts
Biotransformations
Instrumental
Transformations
Unidentified Components
Discover
(ad-hoc)
Identified Targets
Quantification

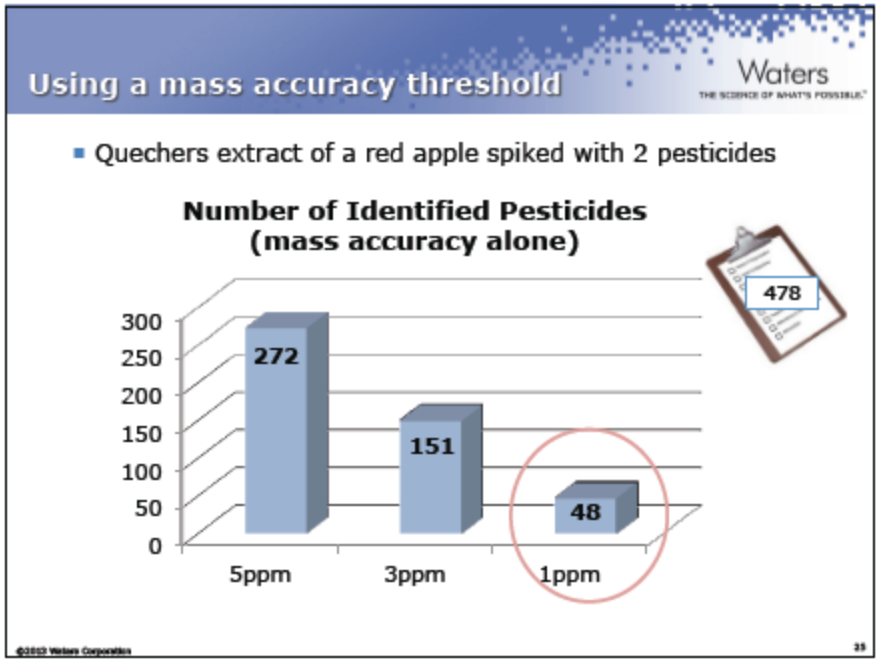

Waters Residue Screening
Waters
Screening Library
2000+ compounds with structure, synonyms, formulae & accurate mass precursors
600+ compounds with detection results (retention time and accurate mass fragment ions)
Pesticide Residues
Veterinary drugs, metabolites, epimers, & marker residue definitions
Pharmaceutical & Personal Care Products
Toxicology Library
1000+ compounds with structures, formulae and detection results
Both positive ion and negative ion detection results for those compounds that run in both modes
Theoretical fragment m/z used in the Scientific Library
User can easily build a new library or import an existing library using an Excel spreadsheet.

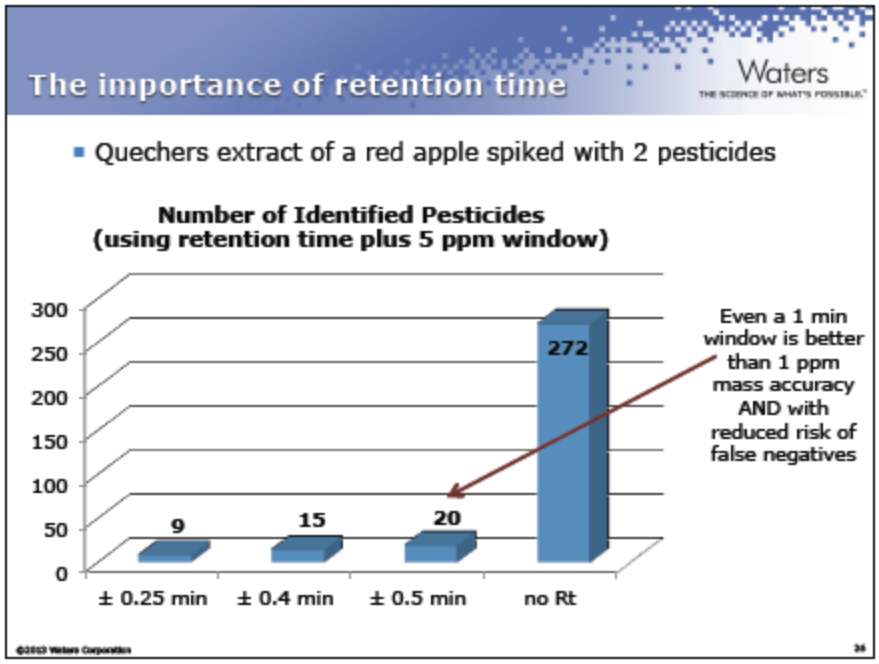

Scientific library
Importing Existing Data: Excel spreadsheet
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
©2013 Waters Corporation
21

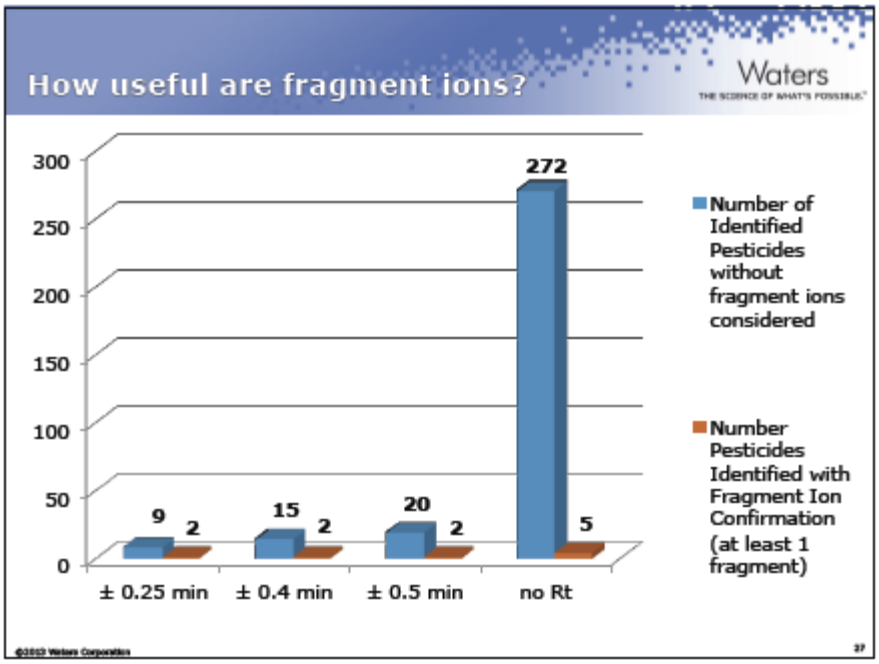

The Component Approach
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
MS
High
Low
m/z
RT
MSE
UV
ELSD
The components can now be analysed
The software organises the data across all channels
into components
©2013 Waters Corporation
22

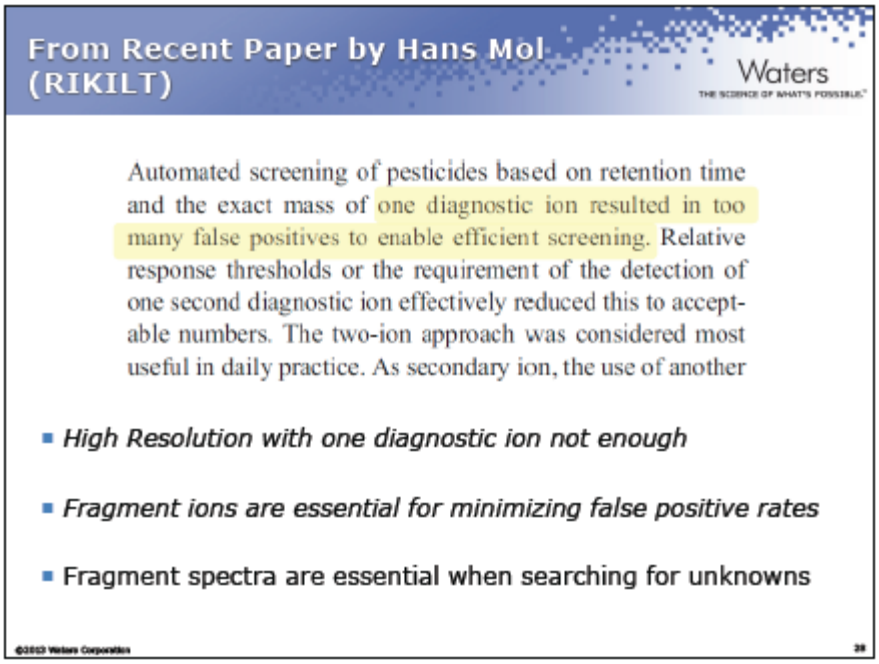

Single Processing Workflow
Waters
Workflow determines what UI is displayed
Workflow
Data
Results
Qualitative
Quantitative
Discover
MSE
Data
Workflows are created for rapid data review

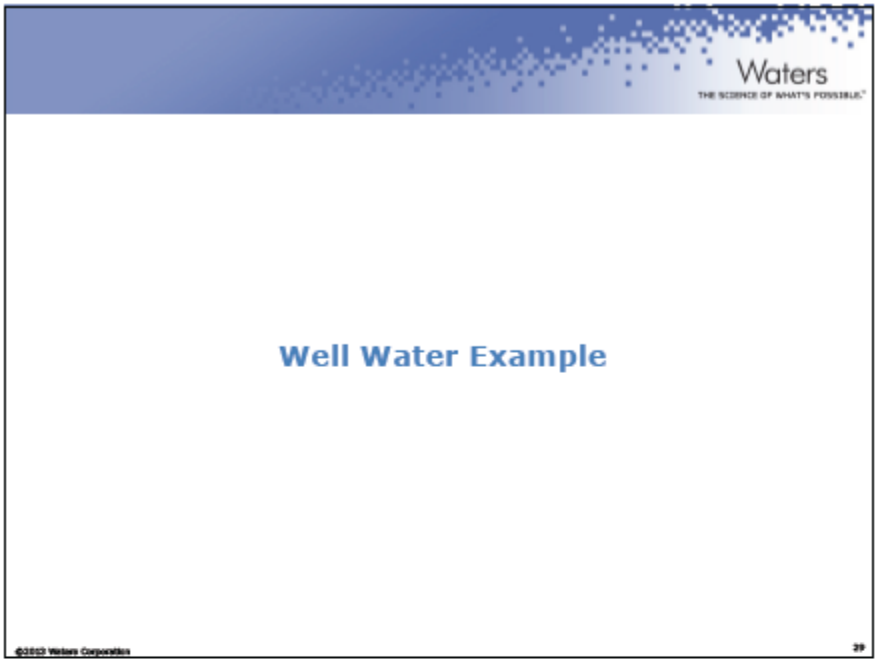

Waters
What are detection results and why are they important?


Using a mass accuracy threshold
Waters
Quechers extract of a red apple spiked with 2 pesticides
Number of Identified Pesticides
(mass accuracy alone)
478
300
250
200
150
100
50
0
272
151
48
5ppm
3ppm
1ppm


The importance of retention time
Waters
Quechers extract of a red apple spiked with 2 pesticides
Number of Identified Pesticides
(using retention time plus 5 ppm window)
300
250
200
150
100
50
0
9
15
20
272
± 0.25 min
± 0.4 min
± 0.5 min
no Rt
Even a 1 min window is better than 1 ppm mass accuracy AND with reduced risk of false negatives


How useful are fragment ions?
Waters
300
250
200
150
100
50
0
9
2
15
2
20
2
272
5
± 0.25 min
± 0.4 min
± 0.5 min
no Rt
Number of Identified Pesticides without fragment ions considered
Number Pesticides Identified with Fragment Ion Confirmation (at least 1 fragment)


From Recent Paper by Hans Mol (RIKILT)
Waters
Automated screening of pesticides based on retention time and the exact mass of one diagnostic ion resulted in too many false positives to enable efficient screening. Relative response thresholds or the requirement of the detection of one second diagnostic ion effectively reduced this to acceptable numbers. The two-ion approach was considered most useful in daily practice. As secondary ion, the use of another
High Resolution with one diagnostic ion not enough
Fragment ions are essential for minimizing false positive rates
Fragment spectra are essential when searching for unknowns



UPLC Acquisition Parameters

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

LC System:	Waters ACQUITY I-Class
Column:	ACQUITY UPLC HSS C_{18}, 1.8 mm, 2.1x150 mm
Column Temp:	50°C
Flow Rate:	0.40 mL/min.
Mobile Phase A:	$H_2O$with 5 mM NH_4HCO_2 (pH 3.0 with formic acid)
Mobile Phase B:	Acetonitrile with 0.1 % (v/v) formic acid.
Total run time:	17 min
Injection volume:	100 µL

Gradient Conditions

Time	Flow rate	Composition A	Composition B	Curve
0.00	0.400	87.0	13.0	Initial
0.50	0.400	87.0	13.0	6
10.00	0.400	50.0	50.0	6
10.75	0.400	5.0	95.0	6
12.25	0.400	5.0	95.0	6
12.50	0.400	87.0	13.0	6
15.00	0.400	87.0	13.0	6

©2013 Waters Corporation
39

MS conditions

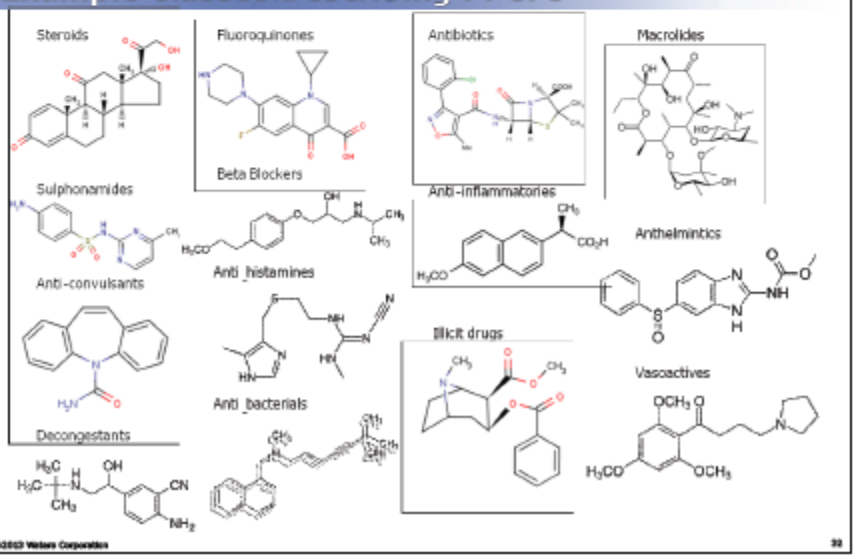
Waters
THE SCIENCE OF WHAT'S POSSIBLE.

MS system:	Xevo G2-S QTof MS
Resolution:	30,000 FWHM
Ionisation mode:	ESI+
Capillary voltage:	1 kV
Sample cone:	20 V
Source temp:	120 °C
Desolvation temp:	550°C
Desolvation gas:	1000 L/H
Reference Mass:	Leucine Enkephalin $[M+H]^+$ = 556.2766
Acquisition range:	*m/z* 50-1200
Acquisition rate:	10 spectra/second
MS^E Low collision energy:	4.0 V
Collision energy ramp:	10-45 V

©2013 Waters Corporation

Example Classes Describing PPCPs

Waters
THE SCIENCE OF WHAT'S POSSIBLE.



©2013 Waters Corporation

Sample Preparation

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

- ***PPCP Standards***: High Level Standards (10 µg/L) in UPLC water.
- ***Extracted Blank*** - Treated as a reference. A UHPLC-grade water sample (Fisher Optima™), enriched using SPE protocol (next slide).
- ***Extracted well water sample*** - Treated as the unknown. A well

Atenolol	Corticosterone	Ofloxacin	Ticlopidine
Azithromycin	Cortisone	Oxprenolol	Tolbutamide
Benzocaine	Cotinine	Procaine	Triamcinolone acetonide
Bromhexine	Digoxigenin	Promethazine	Trimethoprim
Buflomedil HCl	Ketoprofen	Pyrimethamine	Tripolidine
Chlorpheniramine	Levamisole	Ranitidine	Warfarin
Cimetidine	Metoprolol	Roxithromycin	Xylazine
Cocaine	Miconazole	Salbutamol (albuterol)	

- ***Non-extracted well water*** - Well water sample neither enriched nor spiked.
- ***Extracted calibration standards*** - Eight levels (1.0, 2.0, 2.5, 5.0, 10.0, 25.0 and 50.0 ng/L) of the 35 PPCPs were spiked into an extracted UPLC-grade water sample.

©2013 Waters Corporation

SPE Sample Preparation Protocol - *1:1000 enrichment*

Waters
THE SCIENCE OF WHAT'S POSSIBLE.



Loading
- Condition 1: 5 mL MeOH
- Condition 1: 5 mL Water
- Load: 1 Litre @ 10mL/min

Washing
- Disconnect Stack
- Wash MAX: 5 mL 100 % H_2O + 2 % NH_4OH
- Wash MCX: 5 mL 100% H_2O + 2 % Formic acid

Eluting
- Elute 1 MAX: 5 mL 100 % MeOH
- Elute 2 MAX: 5 mL 100 % MeOH + Formic acid
- Elute 3 MCX: 5 mL 100 % MeOH + NH_4OH

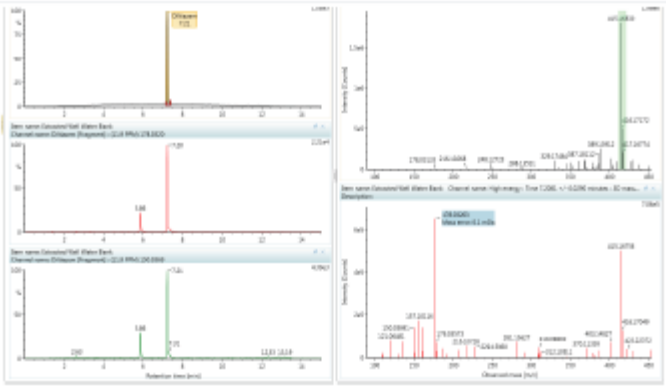
Post Elution
- Pool all 3 elutions
- Evaporate to dryness (N_2)
- Reconsitute 1000 uL 100 % H_2O + 10 mM NH_4Formate
- Inject 100 uL

©2013 Waters Corporation

Ditiazem Spiked into Well Water

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

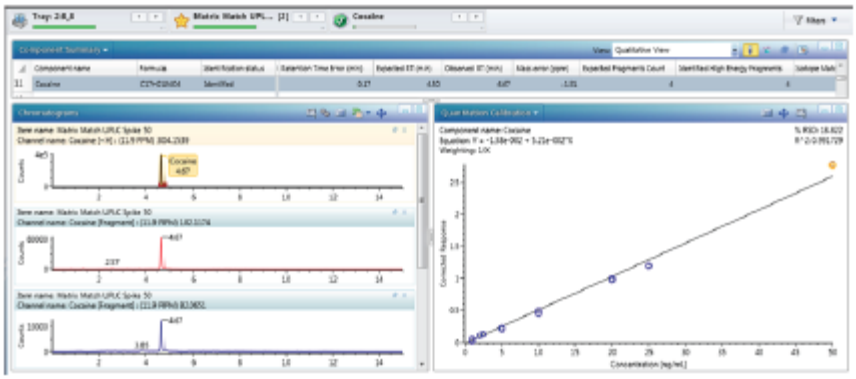
Expected Fragments Count	Identified High Energy Fragments	Isotope Match Mz RMS PPM	Isotope Match Intensity RMS Percent
3	3	1.05	6.48
5	5	0.63	8.32
1	1	0.82	6.64



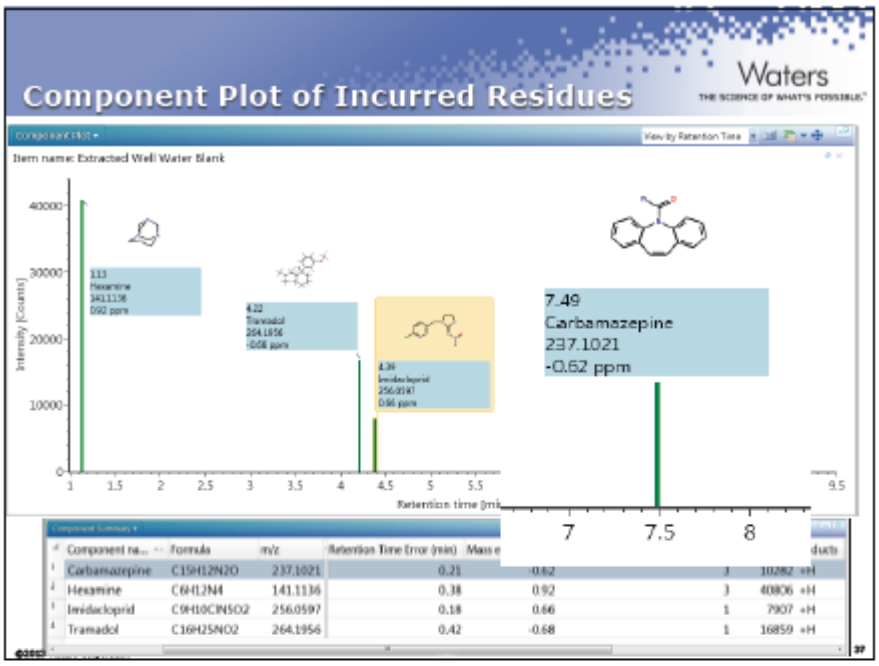
©2013 Waters Corporation

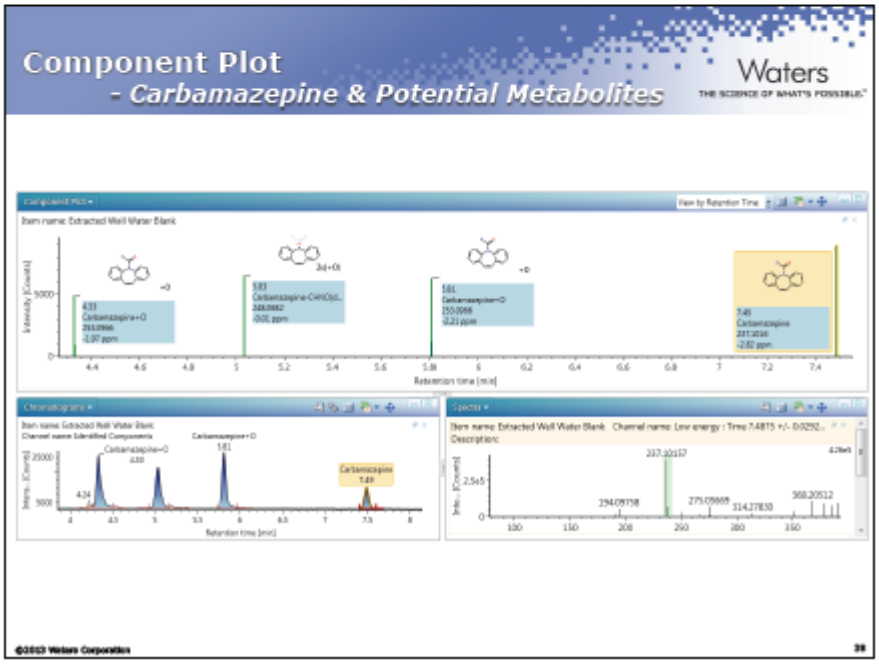
Cocaine Spiked into Well Water - *Quantitation*

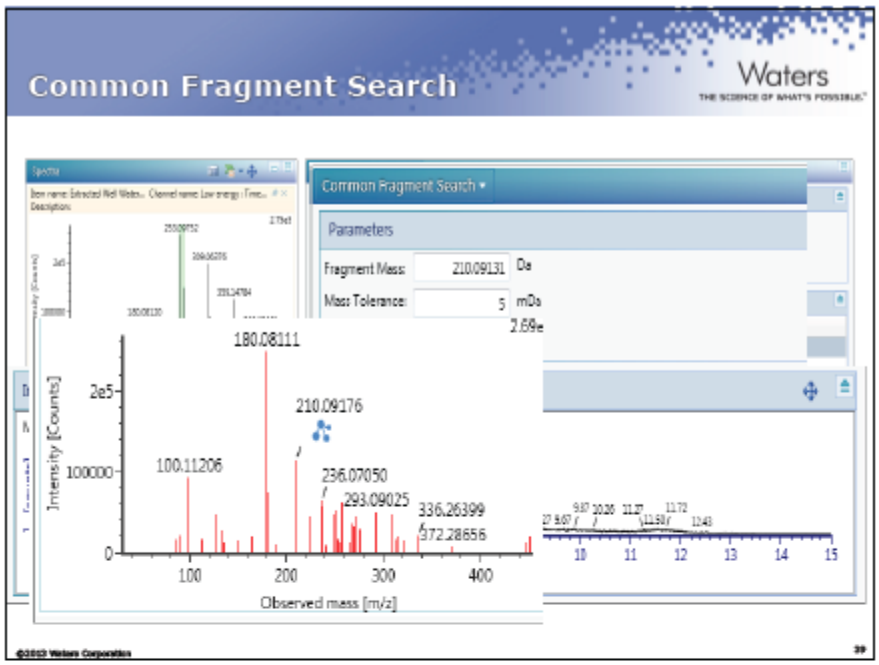
Waters
THE SCIENCE OF WHAT'S POSSIBLE.

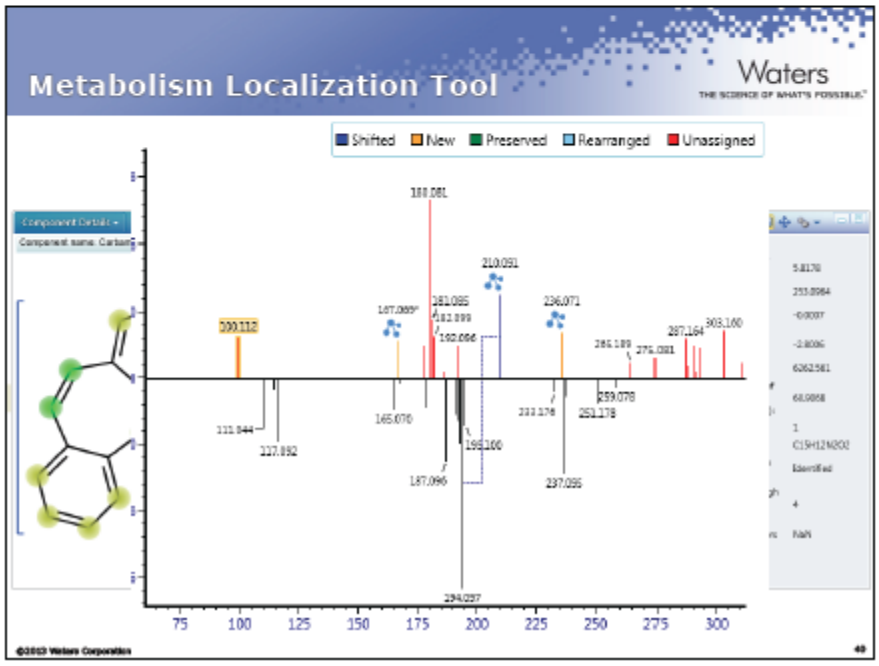


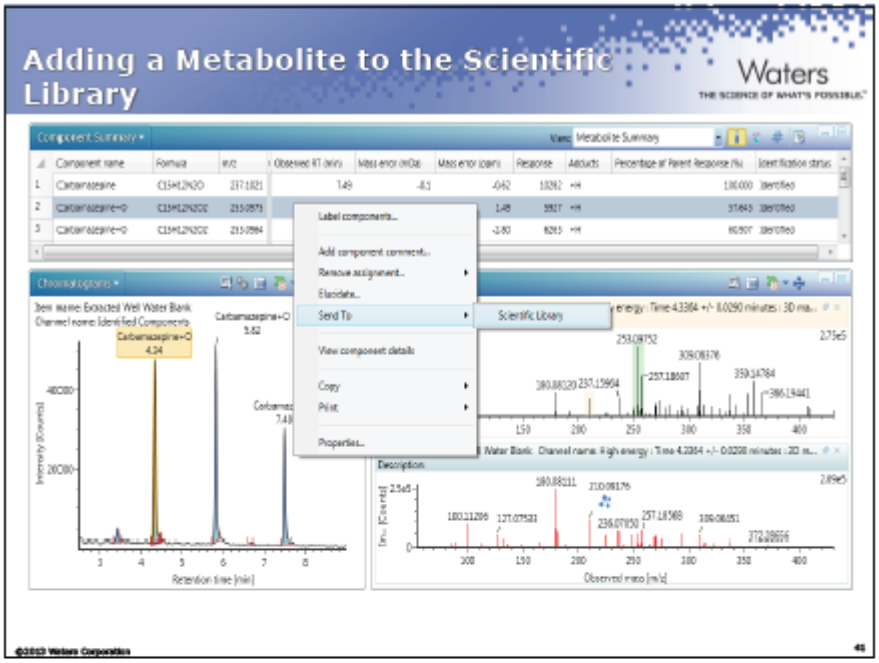
©2013 Waters Corporation

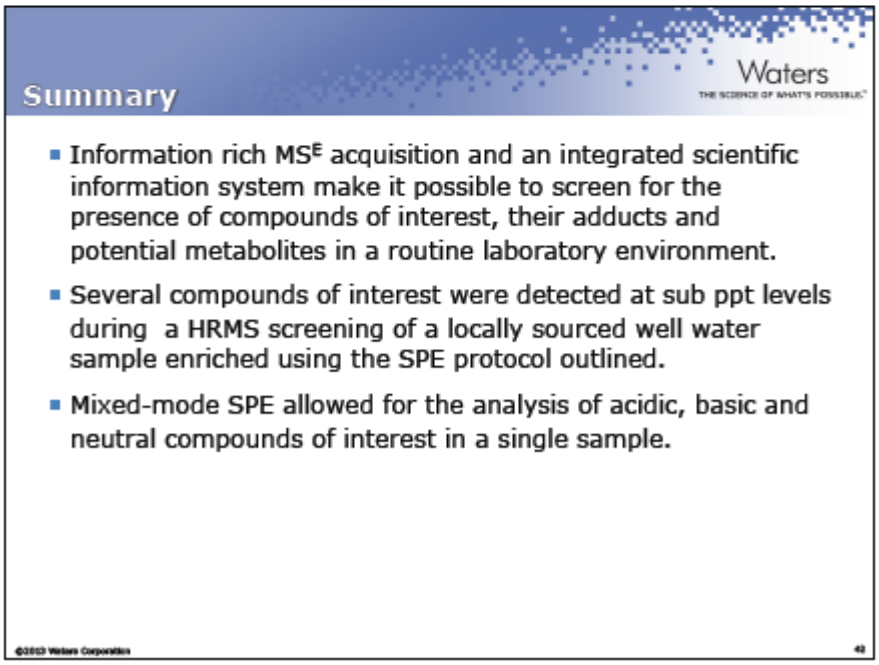

Component Plot of Incurred Residues
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
Item name: Extracted Well Water Blank
7.49
Carbamazepine
237.1021
-0.62 ppm
Component Summary
Component na...
Formula
m/z
Retention Time Error (min)
Carbamazepine
C15H12N2O
237.1021
0.21
-0.62
Hexamine
C6H12N4
141.1136
0.38
0.92
Imidacloprid
C9H10ClN5O2
256.0597
0.18
0.66
Tramadol
C16H25NO2
264.1956
0.42
-0.68


Component Plot
- Carbamazepine & Potential Metabolites
Waters
THE SCIENCE OF WHAT'S POSSIBLE.


Common Fragment Search
Waters
Common Fragment Search
Parameters
Fragment Mass: 210.09131 Da
Mass Tolerance: 5 mDa
180.08111
210.09176
100.11206
236.07050
293.09025
336.26399
372.28656
Intensity [Counts]
Observed mass [m/z]


Metabolism Localization Tool
Waters
Shifted
New
Preserved
Rearranged
Unassigned


Adding a Metabolite to the Scientific Library
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
Component Summary
Metabolite Summary
Component name
Formula
Label components...
Add component comment...
Remove assignment...
Elucidate...
Send To
Scientific Library
View component details
Copy
Print
Properties...
Carbamazepine+O
Retention time [min]
Observed mass [m/z]
©2013 Waters Corporation
41


Summary
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
Information rich MSE acquisition and an integrated scientific information system make it possible to screen for the presence of compounds of interest, their adducts and potential metabolites in a routine laboratory environment.
Several compounds of interest were detected at sub ppt levels during a HRMS screening of a locally sourced well water sample enriched using the SPE protocol outlined.
Mixed-mode SPE allowed for the analysis of acidic, basic and neutral compounds of interest in a single sample.
©2013 Waters Corporation
42

Summary

- The presence of retention times and accurate mass fragment ions in Scientific Libraries within UNIFI allowed identifications to be made on more information than accurate mass of the precursor ions alone. This proves critical for reducing false detection rates and enabling rapid data review for screening experiments.
- Using the metabolite identification functionality of UNIFI, several metabolites of carbamazepine were identified in an environmental water, in addition to the parent.
- Subsequent scientific library additions of identified metabolites is simplified, enabling the user to expand identification information for multi residue screening experiments.

©2013 Waters Corporation

Thanks

Questions???

Ken Rosnack
Business Development Manager
ken_rosnack@waters.com

Food & Environmental | Business Operations

©2013 Waters Corporation

Simultaneous Determination of Paraquat and Diquat in Environmental Water Samples by HPLC-MS/MS

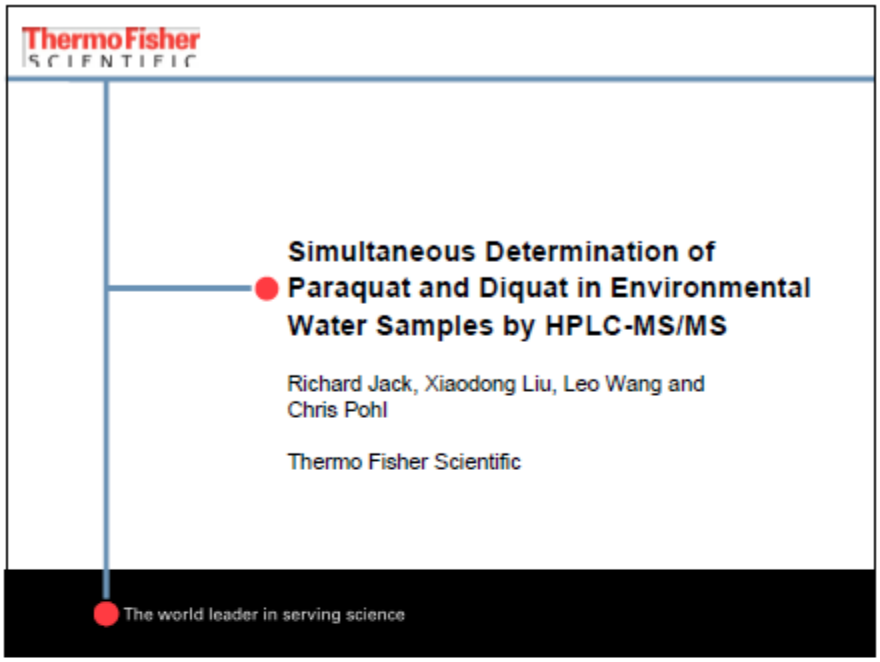
Richard Jack
ThermoFisher Scientific

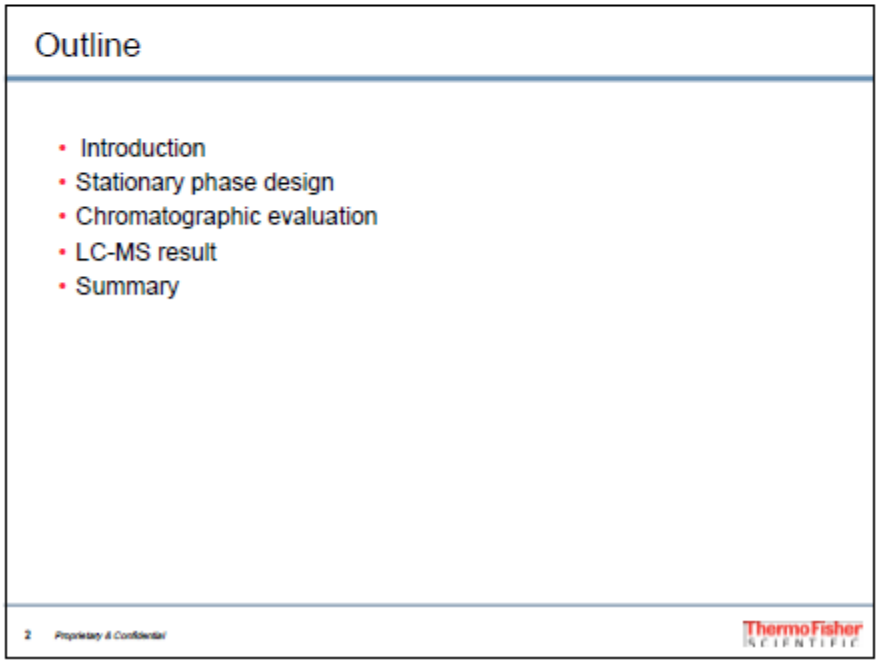
Abstract

Paraquat (1,1'-dimethyl-4,4'-bipyridylium ion) and Diquat (1,1'-ethylene-2,2' -bipyridyliumion) are quaternary amines widely used as herbicides for both terrestrial and aquatic plants. Due to their wide usage and moderate toxicities, their presence in runoff from application areas and in agricultural consumer products has been a major concern for aquatic life and human health. Diquat is currently regulated by the United States Environmental Protection Agency (US EPA) at 20 ?g/L in drinking water. Paraquat is not currently regulated. Commonly used methods for Paraquat and Diquat analysis include ion pairing liquid chromatography (IP-LC)2,3, capillary electrophoresis4 (CE) with various detectors such as ultraviolet (UV) and mass spectrometry (MS).

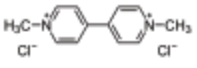
This study describes an HPLC-MS/MS method for high throughput, sensitive and selective quantitation of Paraquat and Diquat in environmental waters. Without using an ion pairing reagent, sensitivity was significantly improved and detection limit scan be extended to low ng/L levels. Environmental water samples were prepared offline via anion exchange cleanup or injected directly for online solid phase extraction (SPE) using a weak anion exchange cartridge. Sufficient retention and improved chromatographic resolution were achieved with isocratic elution on a mixed mode column featuring reversed-phase, anion/cation exchange retention mechanisms. Analytical time was within 5 minutes per sample ensuring routine high throughput. SRM was used for quantitation with isotope labeled internal standards to achieve quantitation accuracy.

In this method, Paraquat and Diquat were separated within 5 minutes with chromatographic resolution greater than 7 to avoid SRM interferences and thus enhance the detection selectivity and sensitivity. Two SRM transitions for each analyte were used for quantitation and confirmation. The lower limit of quantitation (LLOQ) was determined to be 100 ng/L for both analytes. Quantitation precision was within 10% at 500 ng/L and 4% at 50 ?g/L. Good linearity was achieved from 100 ng/L to 100 ?g/L with a coefficient of determination (r2) greater than 0.999 for both analytes with using 1/x weighting factor. Other performance parameters such as specificity, carry over, accuracy, and matrix effect were also evaluated and are presented below. This method has been applied for various samples including drinking water and ground water.

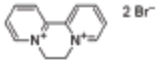

ThermoFisher
SCIENTIFIC
Simultaneous Determination of Paraquat and Diquat in Environmental Water Samples by HPLC-MS/MS
Richard Jack, Xiaodong Liu, Leo Wang and Chris Pohl
Thermo Fisher Scientific
The world leader in serving science


Outline
• Introduction
• Stationary phase design
• Chromatographic evaluation
• LC-MS result
• Summary
2
Proprietary & Confidential
ThermoFisher
SCIENTIFIC

Paraquat (Pq) and Diquat (Dq)



Paraquat (Pq)



Diquat (Dq)

- Non-selective, nonsystematic contact herbicides
- Environmental & safety concerns
  - Toxic to humans through contact (e.g. oral, respiratory, dermal)
  - Moderately hazardous: LD50 ~35 mg/kg for human
  - Banned or restricted in several European countries and in Japan
- Regulation
  - The U.S. EPA regulation: < 20 µg/L for Dq in drinking water
  - European Union (EU)'s general rule for pesticides in drinking water (98/83/EC):
    - < 0.1 µg/L of each individual pesticide
    - < 0.5 µg/L for the total concentration
- Food safety concerns in developing countries

Analytical Methods

- Colorimetric spectrophotometry
- Enzyme linked immunosorbent assay (ELISA)
- Liquid scintillation counting (LCS)
- HPLC – wide acceptance
  - Ion exchange column – post-column derivatization – fluorescence detection
  - Reversed-phase column – UV, PDA, or MS

U.S. EPA Method 549.2

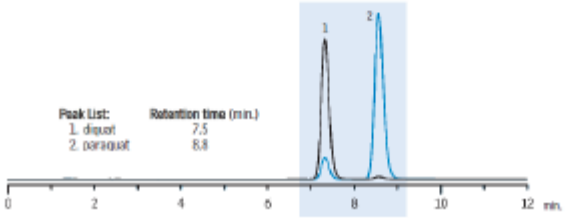
- A HPLC method for the determination of diquat and paraquat in drinking water sources and finished drinking water
- Summary of the method
  - Offline SPE
  - RPLC/ion-pairing
  - UV or PDA detection
  - Detection limit: 0.72 µg/L for Dq; 0.68 µg/L for Pq
- Challenges
  - Poor reproducibility
  - Time consuming
  - Complex mobile phase: water, phosphoric acid, acetonitrile, heptane or hexane sulfonic acid (ion pairing agent), and diethylamine (DEA)
  - Separation and peak shape

5 Proprietary & Confidential

ThermoFisher SCIENTIFIC

An Improved Method

- Specialty column – good separation and peak shape
- Special mobile phase additive
- Challenges
  - Poor reproducibility
  - Time consuming
  - Complex mobile phase
  - Incompatible with MS

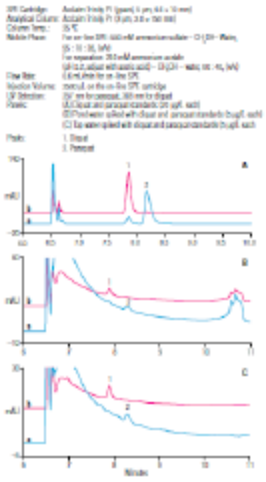


6 Proprietary & Confidential

ThermoFisher SCIENTIFIC

A Method Not Requiring Ion-Pairing Agent

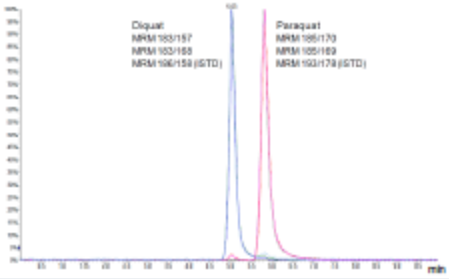
- RP/AEX/CEX tri-mode column
- No ion-pairing agent required
- On-line SPE
- Challenges
  - High concentration buffer (not MS-friendly)
  - Peak shape



ThermoFisher SCIENTIFIC

LC/MS – Greater Sensitivity w/o Sample Preparation

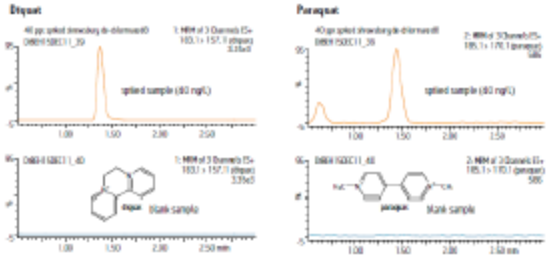
- Specialty RP column
- No sample enrichment
- LOQ: 0.1 µg/L for diquat and 5 µg/L for paraquat (10-µL)
- Challenges
  - HFBA as ion-pairing agent – not desirable for MS
  - High aqueous mobile phase (95%) – lower sensitivity



ThermoFisher SCIENTIFIC

UHPLC HILIC Column – Off-line SPE – LC/MS

- UHPLC HILIC column
- Off-line sample preparation (20x)
- LOQ: ~ 40 ppt for diquat and paraquat (10-µL)
- Challenges
  - Dipuat and paraquat co-elution
  - High buffer concentration – lower sensitivity



ThermoFisher SCIENTIFIC

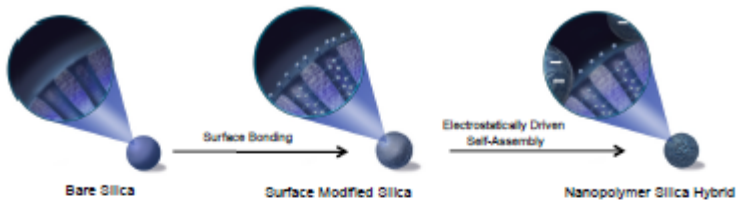
Objective

To develop a method for determination of diquat and paraquat :

1.	Retain	k' > 2
2.	Resolve	Rs > 2 (Dq/Pq)
3.	Behave	As < 1.5 (UV)
4.	LC-MS compatible	No ion-pairing agent Solvent > 50% (v/v) Buffer concentration < 50 mM
5.	Simple	Isocratic method
6.	Fast	< 5 min
7.	Sensitive	Better than reported

ThermoFisher SCIENTIFIC

Nano-polymer-Silica-Hybrid (NSH) Technology



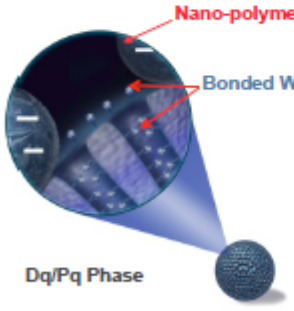
Benefits:

- Versatile chemistry platform
- Cation-exchange and anion-exchange function simultaneously
- Distinctive spatial separation of the anion-exchange and cation-exchange regions, which results in maximum flexibility in method development.
- Chromatography can be easily optimized by adjusting mobile phase buffer concentration, pH, and solvent content, concurrently or independently.
- Ideal selectivity for simultaneous separation of basic, neutral, and acidic analytes
- Separation of hydrophilic ionic and ionizable analytes without ion-pairing reagent

11 Proprietary & Confidential

ThermoFisher SCIENTIFIC

Stationary Phase Design



Retention mechanism:
WCX: Carboxylate
WAX: Tertiary amine
RP: Alkyl

Silica Substrate:
3 µm, high-purity, spherical, porous

Surface Area
100 m^2/g

Pore Size
300 A

Operating Pressure limit
4000 psi

Operating flow rate range
0.3 – 0.9 mL/min for 3mm I.d.
0.15- 0.45 mL/min for 2.1 mm I.d.

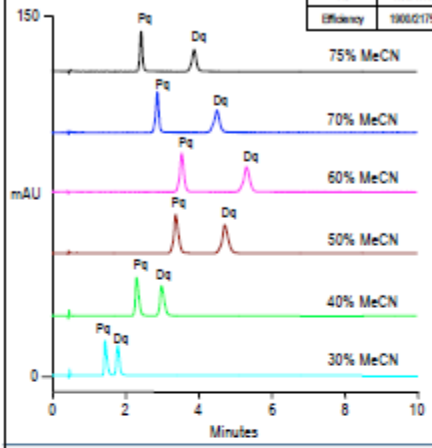
pH range
2.5-7.0

12 Proprietary & Confidential

ThermoFisher SCIENTIFIC

Organic Solvent Effect

Pq/Dq	30% MeCN	40% MeCN	50% MeCN	60% MeCN	70% MeCN	75% MeCN
Rs	2.45	3.69	5.5	7.5	8.0	8.8
As	1.88/1.18	1.17/1.35	1.15/1.07	1.03/0.98	0.93/0.96	1.08/0.96
Efficiency	1900/2175	3060/3370	4090/4680	5550/5560	6030/4840	6230/5670

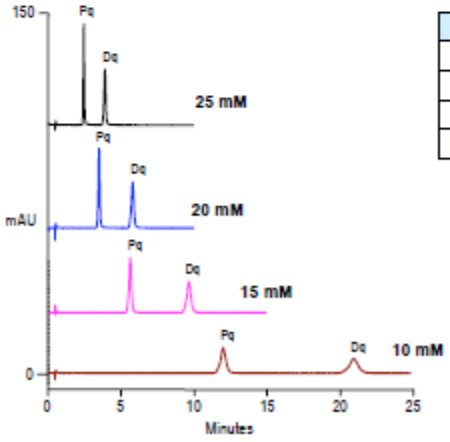


Column: Dq/Pq prototype, 3 µm
Dimensions: 3.0 x 50 mm
Mobile Phase: MeCN/ 25 mM (total) NH_4OAc, pH5
Temperature: 30 °C
Flow Rate: 0.60 mL/min
Inj. Volume: 2 µL
Detection: UV, 290 nm
Sample: Dq and Pq (0.1 mg/mL each)

13 *Proprietary & Confidential*

ThermoFisher SCIENTIFIC

Buffer Concentration Effect



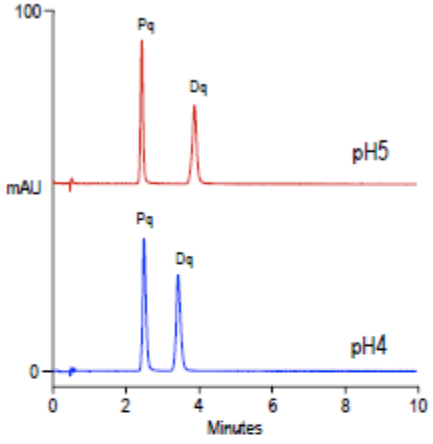
Pq/Dq	10 mM	15 mM	20 mM	25 mM
Rs	10.7	10.3	9.5	8.8
k	26.4/46.8	11.8/21.0	6.9/12.2	4.5/7.9
As	1.02/0.96	1.02/0.93	1.03/0.97	1.08/0.96
Efficiency	5900/6160	5860/6170	5760/5770	6230/5670

Column: Dq/Pq prototype, 3 µm
Dimensions: 3.0 x 50 mm
Mobile Phase: 75/25 v/v CH_3CN/ various conc. NH_4OAc, pH5
Temperature: 30 °C
Flow Rate: 0.60 mL/min
Inj. Volume: 2 µL
Detection: UV, 290 nm
Sample: Dq and Pq (0.1 mg/mL each)

14 *Proprietary & Confidential*

ThermoFisher SCIENTIFIC

pH Effect



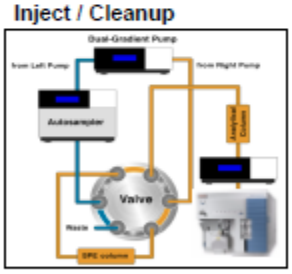
Column: Dq/Pq prototype, 3 µm
Dimensions: 3.0 x 50 mm
Mobile Phase: 75/25 v/v CH_3CN/ 25 mM (total) NH_4OAc, pH5
Temperature: 30 °C
Flow Rate: 0.60 mL/min
Inj. Volume: 2 µL
Detection: UV, 290 nm
Sample: Dq and Pq (0.1 mg/mL each)

Pq/Dq	pH4	pH5
Resolution (Rs)	5.1	8.8
Retention (k)	4.7/6.8	4.5/7.9
Asymmetry (As)	1.31/1.18	1.08/0.96
Efficiency	3900/4800	6200/5600

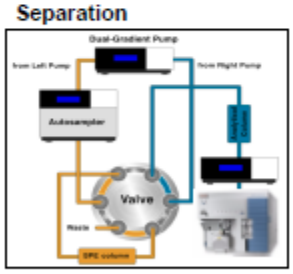
ThermoFisher SCIENTIFIC

LC/MS configuration

Inject / Cleanup



Separation



ThermoFisher SCIENTIFIC

MS and Test Matrix parameters

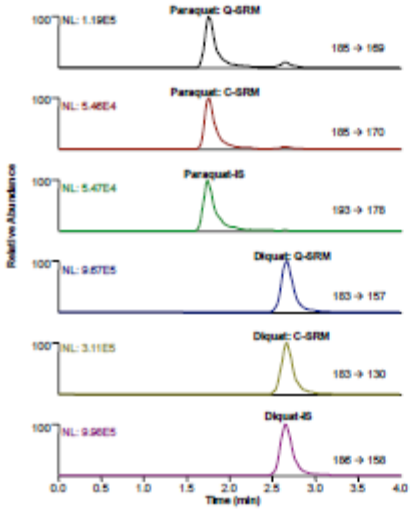
SRM Scan Events	Precursor	Quantitative SRM (CID)	Confirmative SRM (CID)
Paraquat	185	169 (27)	170 (17)
Paraquat-d_8	193	178 (17)	
Diquat	183	157 (22)	130 (31)
Diquat-d_3	186	158 (22)	

Matrix	Conc.
Na^+ and K^+	> 5000 mg/L
NH_4^+	1000 mg/L
NO_3^-	200 mg/L
HCO_3^-	1500 mg/L
SO_4^{2-}	2500 mg/L
Cl^-	3500 mg/L

17 Proprietary & Confidential

ThermoFisher SCIENTIFIC

LC-MS-MS: Paraquat and Diquat at 10 ppb



Chromatographic Conditions

System:	UltiMate 3000 RS UHPLC System
Column:	Dg/Pg
Column Temp.:	Ambient
Mobile Phase:	25% Ammonium Acetate (100 mM, pH 5.0) 75% Acetonitrile
Flow Rate:	0.5 mL/min
Injection:	5 µL

Mass Spectrometric Conditions

System:	Quantum TSQ Access MAX Triple Quad
Interface:	Heated Electrospary Ionization with HESI II probe
Spray Voltage:	1500 V
Vaporizer Temperature.:	400 °C
Sheath Gas Pressure:	70
Aux Gas Pressure:	10
Capillary Temperature:	350 °C
Quantitation Mode:	Selected Reaction Monitoring (SRM)

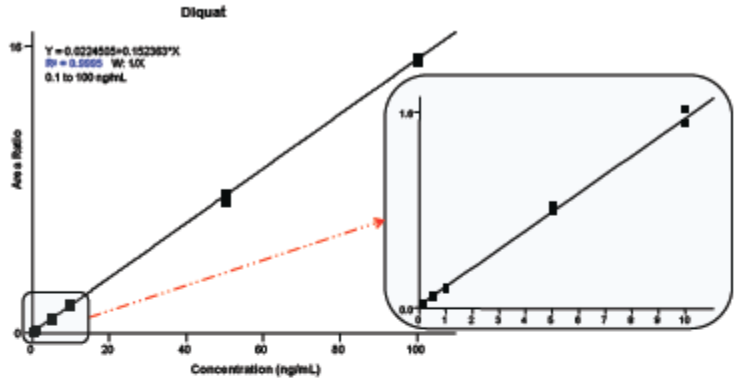
Scan Events	Precursor	Quantitative SRM (CID)	Confirmative SRM (CID)
Paraquat	185	169 (27)	170 (17)
Paraquat-d_8	193	178 (17)	
Diquat	183	157 (22)	130 (31)
DiQuat-d_3	186	158 (22)	

18 Proprietary & Confidential

ThermoFisher SCIENTIFIC

Quantitation: Diquat from 0.1 to 100 ng/mL

LOQ – 100 ppt (10-µL) or 1 pg



ThermoFisher SCIENTIFIC

Spike Recoveries

ng/mL	Replicates	Paraquat			Diquat		
		Observed	%Recovery	%RSD	Observed	%Recovery	%RSD
Creek Water	0.50 (n=3)	0.39	78.0	1.73	0.44	88.0	3.14
	5.0 (n=2)	5.12	102	3.17	5.37	107	1.30
	50 (n=3)	47.2	94.4	0.52	52.1	104	1.04
Heavy Matrix	10 (n=30)	10.5	105	3.48	9.43	94.3	1.09

ThermoFisher SCIENTIFIC

Summary

- Nanopolymer Silica Hybrid (NSH) technology allows for tailoring column chemistry to meet specific needs.
- A column for diquat and paraquat analysis has been developed
  - Adequate retention — k' > 2
  - Excellent resolution — Rs > 4 (Dq/Pq)
  - Good peak shape — As < 1.5
  - MS-compatible — No ion-pairing agent; Acetonitrile > 50% (v/v); Buffer concentration < 25 mM
  - Simple — Isocratic method
  - Fast — 5 min
  - Sensitive — 1 pg (or 0.1 ppb with 10-µL injection)
  - Robust — Recoveries in real and synthetic matrices

Update in the Development of a Drinking Water Method for the Measurement of Select Organic Contaminants in Drinking Water Using Hydrophilic-Modified Polymeric SPE and GC/MS

Paul Grimmett
USEPA, Office of Research and Development

Abstract

In October 2009, the USEPA's Office of Ground Water and Drinking Water (OGWDW) published its latest Drinking Water Contaminant Candidate List (CCL 3). This list contains potential drinking water contaminants that the agency will consider for regulation. One of the key pieces of information necessary to make a regulatory determination for a contaminant is its nationwide occurrence. Historically, OGWDW has collected the necessary occurrence data under its Unregulated Contaminant Monitoring Regulations (UCMRs). In order for a contaminant to be included in a UCMR, a standardized analytical method for its measurement in drinking water must be available. A group of compounds from CCL 3, which were not amenable to any current EPA method, were evaluated for grouping into a new method. The group consists of two industrial compounds (o-toluidine and quinoline), a pesticide (dimethipin), a fungicide (captan), and a food additive (butylated hydroxyanisole, BHA). The current procedure requires preservation of a 1-L drinking water sample with L-ascorbic acid, EDTA, Trizma buffer, and diazolidinyl urea, followed by solid phase extraction (SPE) with a hydrophilic-modified polymeric (divinylbenzene, 500 mg) sorbent. Sample analyses were then performed using gas chromatography/mass spectrometry (GC/MS). Extraction efficiencies of all compounds in fortified laboratory reagent water (LRW) ranged from 92-123% in low level spikes (0.1 µg/L), 94-112% in mid-level spikes (1 µg/L), and 85-99% in high level spikes (5 µg/L). Extraction efficiencies of all compounds in fortified groundwater source drinking water (hardness > 350 mg/L) ranged from 117-133% in low level spikes (0.1 µg/L), 86-113% in mid-level spikes (1 µg/L), and 86-101% in high level spikes (5 µg/L). Extraction efficiencies of all compounds in fortified surface water source drinking water ranged from 86-108% in mid-level spikes (1 µg/L) and 76-109% in high level spikes (5 µg/L). Future work will include challenging the extraction and analysis process with laboratory created waters high in total organic carbon (TOC ~ 2 mg/L) and challenging the preservation scheme with a 28 day holding time study. Ideally, this method will contain the option for selected ion monitoring (SIM), to achieve a Lowest Concentration Minimum Reporting Level (LCMRL) below the health reference level (HRL) for quinoline (0.01 µg/L).

(Related Session: Topics in Drinking Water)

Update in the Development of a Drinking Water Method for the Measurement of Select Organic Contaminants in Drinking Water Using Hydrophilic-Modified Polymeric SPE and GC/MS

Paul E. Grimmett



Disclaimer: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

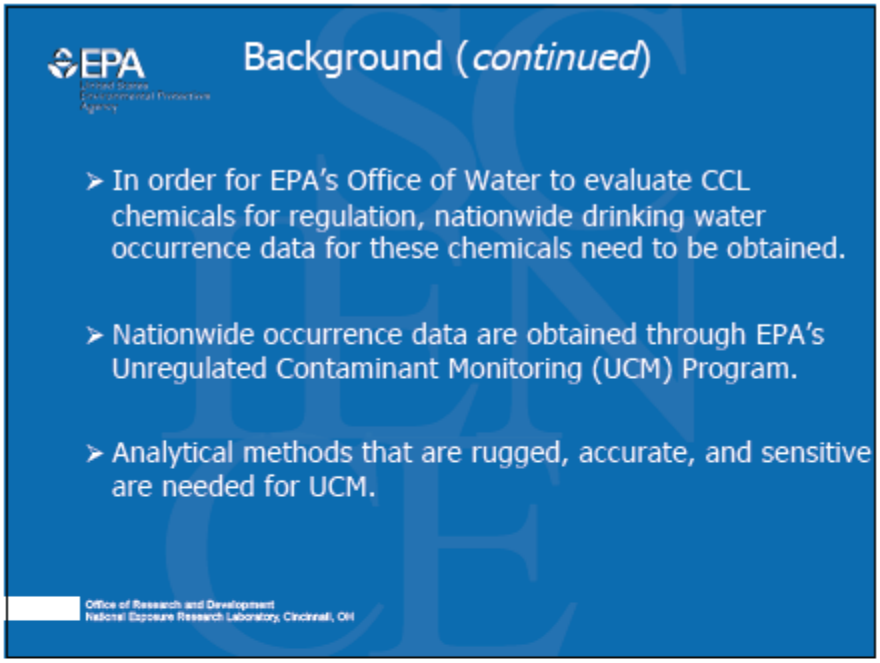
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

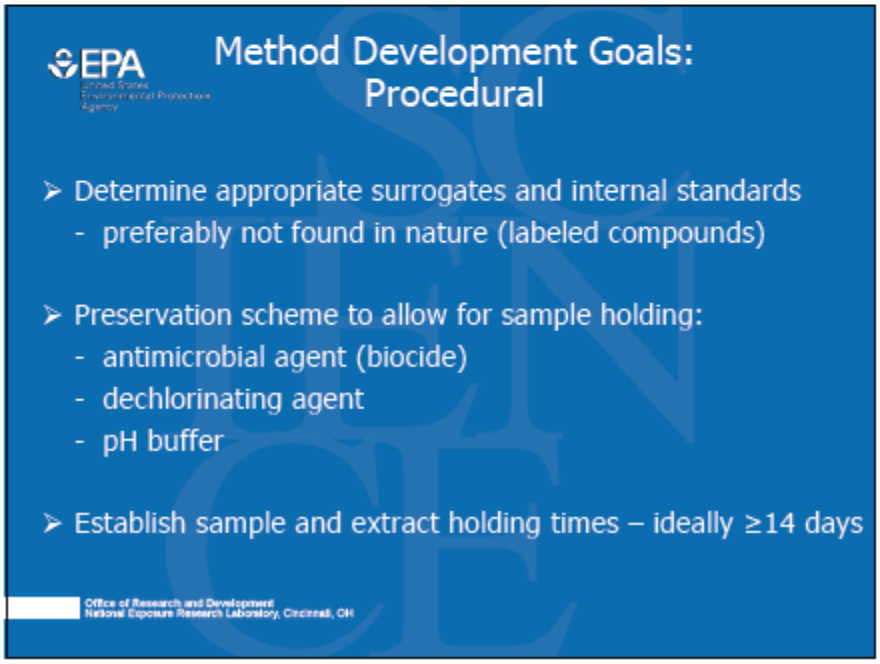
NEMC
Aug. 8, 2013

Background

- The Safe Drinking Water Act, as amended in 1996, requires EPA to execute a program that identifies, monitors and considers for regulation new and emerging chemicals that may pose a risk to drinking water consumers.
- EPA notifies the public of chemicals it is investigating by publishing the drinking water Contaminant Candidate List (CCL).
- Current list is CCL 3 (final version published in 2009)

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Background (*continued*)
➢ In order for EPA's Office of Water to evaluate CCL chemicals for regulation, nationwide drinking water occurrence data for these chemicals need to be obtained.
➢ Nationwide occurrence data are obtained through EPA's Unregulated Contaminant Monitoring (UCM) Program.
➢ Analytical methods that are rugged, accurate, and sensitive are needed for UCM.
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

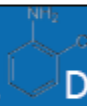

EPA
Method Development Goals: Procedural
➢ Determine appropriate surrogates and internal standards
- preferably not found in nature (labeled compounds)
➢ Preservation scheme to allow for sample holding:
- antimicrobial agent (biocide)
- dechlorinating agent
- pH buffer
➢ Establish sample and extract holding times – ideally ≥14 days
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

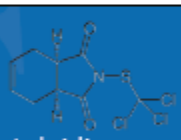
Method Development Goals: Quality Control

- Establish Data Quality Objectives (DQOs)
  - normally 70-130% recovery with <30% RSD
  - 50-150% recovery at concentrations near the Minimum Reporting Limit (MRL)
- Establish detection limits (DLs) and lowest concentration minimum reporting levels (LCMRLs) below health reference levels (HRLs)

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Current Method Development Work





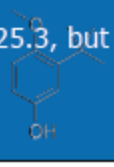
- Development of drinking water method for *o*-toluidine, quinoline, dimethipin, captan, and butylated hydroxyanisole (BHA)

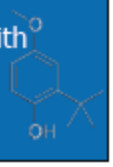




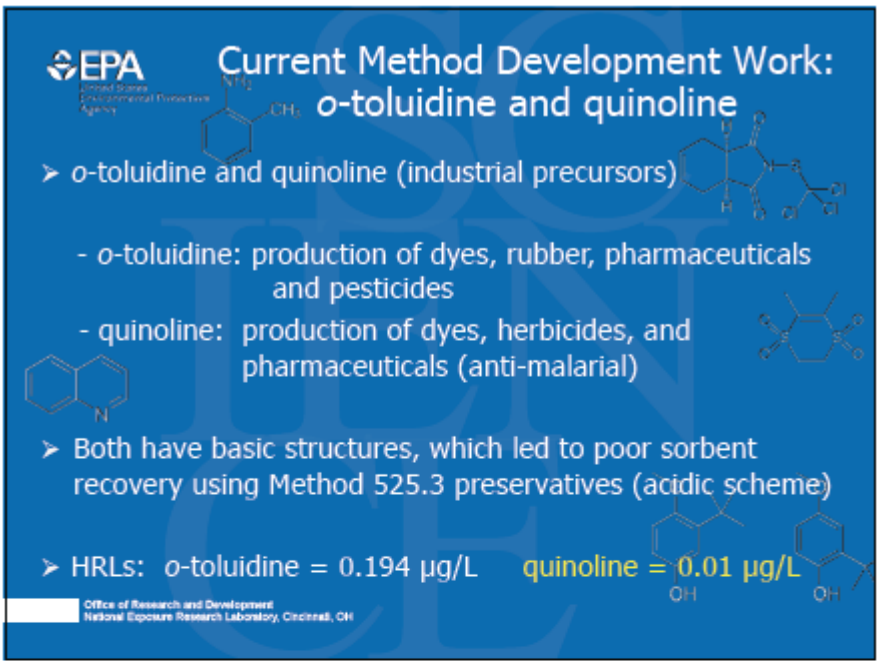
- CCL3 compounds, classified as semivolatiles (SVOCs)
- All were originally evaluated for inclusion into EPA Method 525.3 (SVOCs by GC/MS), but were removed due to performance issues.

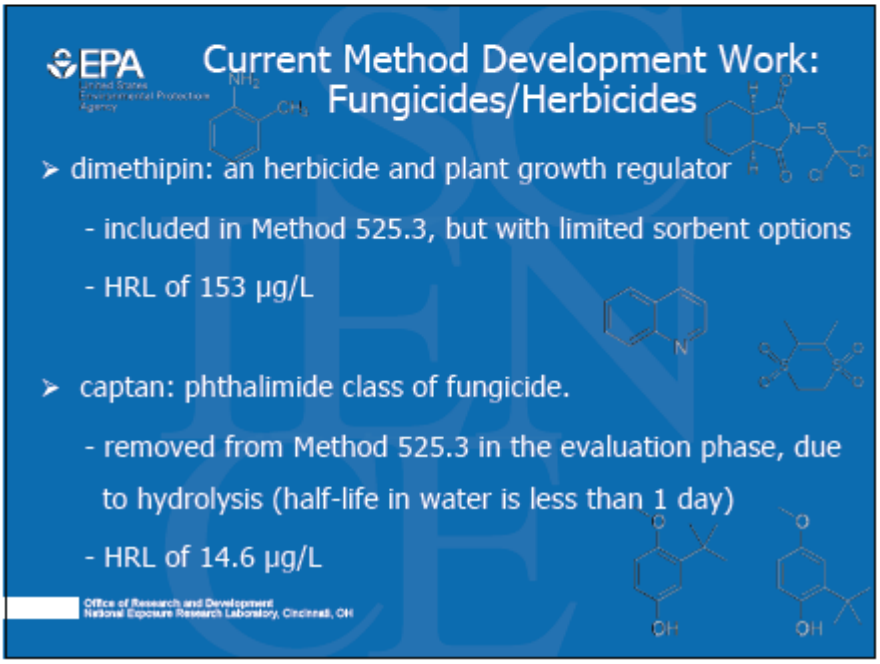
Note: dimethipin remained in EPA Method 525.3, but with limited sorbent options

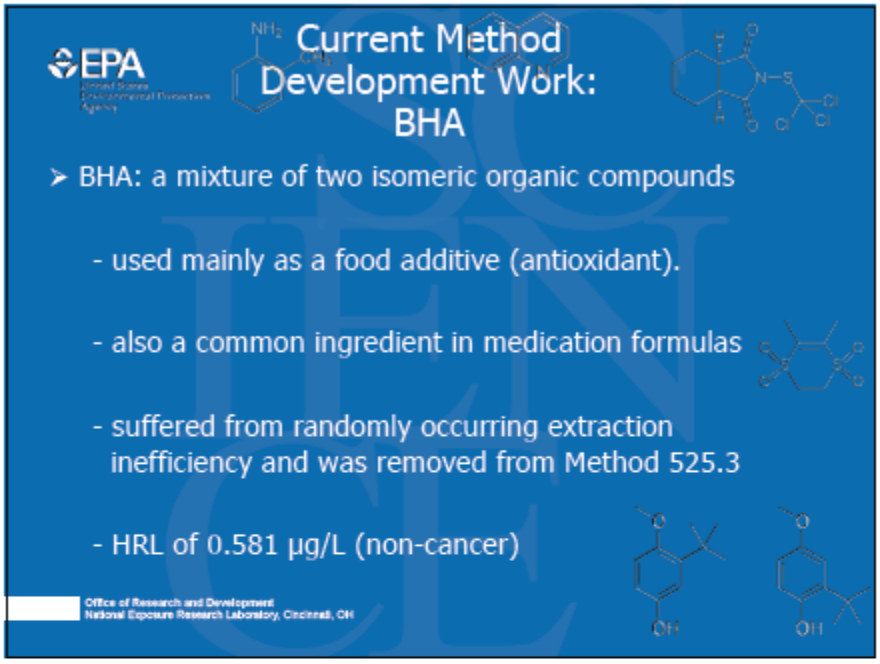


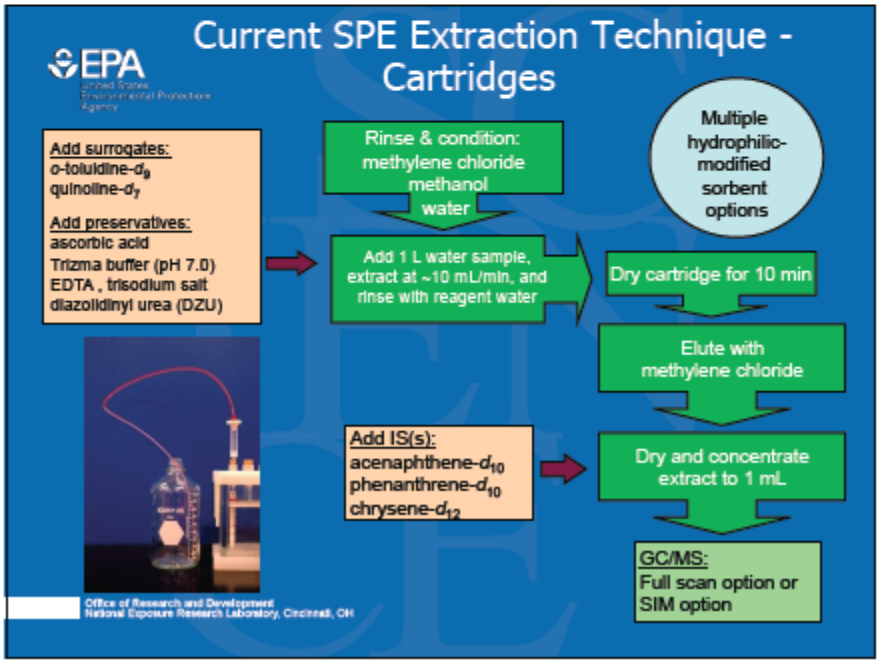


Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Current Method Development Work:
o-toluidine and quinoline
o-toluidine and quinoline (industrial precursors)
- o-toluidine: production of dyes, rubber, pharmaceuticals and pesticides
- quinoline: production of dyes, herbicides, and pharmaceuticals (anti-malarial)
Both have basic structures, which led to poor sorbent recovery using Method 525.3 preservatives (acidic scheme)
HRLs: o-toluidine = 0.194 µg/L
quinoline = 0.01 µg/L
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Current Method Development Work:
Fungicides/Herbicides
dimethipin: an herbicide and plant growth regulator
- included in Method 525.3, but with limited sorbent options
- HRL of 153 µg/L
captan: phthalimide class of fungicide.
- removed from Method 525.3 in the evaluation phase, due to hydrolysis (half-life in water is less than 1 day)
- HRL of 14.6 µg/L
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Current Method Development Work: BHA
BHA: a mixture of two isomeric organic compounds
- used mainly as a food additive (antioxidant).
- also a common ingredient in medication formulas
- suffered from randomly occurring extraction inefficiency and was removed from Method 525.3
- HRL of 0.581 µg/L (non-cancer)
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Current SPE Extraction Technique - Cartridges
Add surrogates:
o-toluidine-d_9
quinoline-d_7
Add preservatives:
ascorbic acid
Trizma buffer (pH 7.0)
EDTA , trisodium salt
diazolidinyl urea (DZU)
Rinse & condition:
methylene chloride
methanol
water
Multiple hydrophilic-modified sorbent options
Add 1 L water sample, extract at ~10 mL/min, and rinse with reagent water
Dry cartridge for 10 min
Elute with methylene chloride
Add IS(s):
acenaphthene-d_{10}
phenanthrene-d_{10}
chrysene-d_{12}
Dry and concentrate extract to 1 mL
GC/MS:
Full scan option or SIM option
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

GC/MS Full Scan Analysis Specs

Column: Restek RXI-5sil-MS and J&W DB-1701
30 m x 0.25 mm x 0.25 μm column

Injector: 275 °C (splitless mode), 20 psi pulse

Inj. vol: 1 μL

Flow: 1 mL/min, helium carrier gas

Oven: 60 °C for 1 min, to 300 °C at 10 °C/min, hold 2 min. Total time = 27 min.

MS Transfer Line: 275 °C

MS: scan 50-350 amu, full scan





Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

GC/MS SIM Analysis Specs (Preliminary)

Column: Restek RXI-5sil-MS

Injector: 275 °C (splitless mode), 20 psi pulse

Inj. vol: 1 μL

Flow: 1 mL/min, helium carrier gas

Oven: 60 °C for 1 min, to 300 °C at 10 °C/min, hold 2 min. Total time = 27 min.

MS Transfer Line: 275 °C

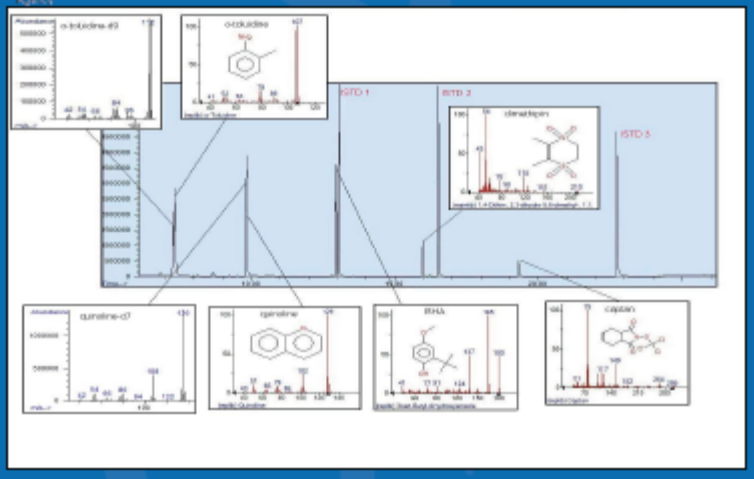
MS SIM: 6 windows (amu, dwell time)
WIN1, 5.00 min: (106.10, 25) (107.10, 25) (112.10, 25)(114.10, 25)
WIN2, 7.64 min: (102.00, 25) (108.10, 25) (129.10, 25)(136.10, 25)
WIN3, 10.62 min: (137.10, 25) (162.10, 25) (164.10, 25)(180.10, 25)
WIN4, 13.76 min: (54.10, 75) (118.00, 75) (188.10, 25)
WIN5, 17.16 min: (79.00, 75) (149.00, 75)
WIN6, 20.37 min: (236.20, 25) (240.20, 25)





Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Sample Total Ion Chromatogram (TIC) with Mass Spectra, 5 µg/mL standard



Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Internal Standards acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} labeled as ISTD 1, ISTD 2, and ISTD 3, respectively.

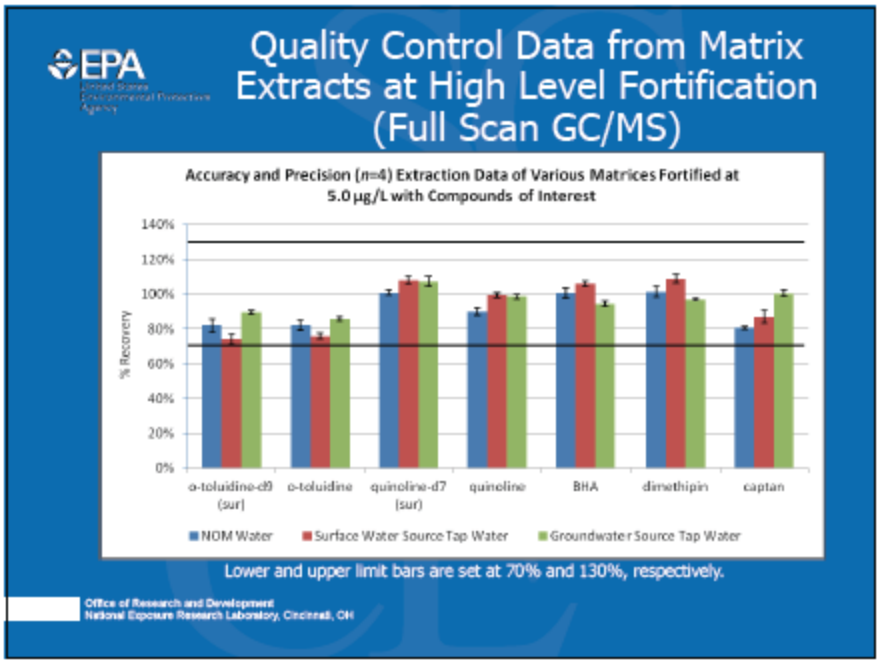
Quality Control Data at Various Concentrations, Drinking Water Matrices

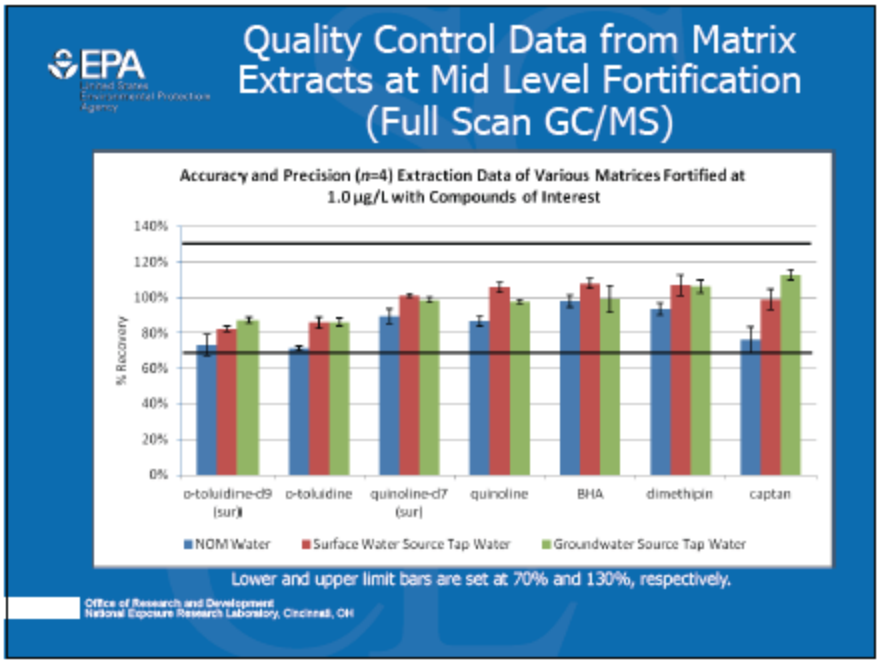
- Three different water matrices were fortified with CCL 3 compounds, then extracted and analyzed.

1. Drinking water – surface water source
2. Drinking water – groundwater source (hardness ~ 350 mg/L)
3. Natural Organic Material (NOM) water – lab water spiked with concentrated organic matter from the Ohio River (TOC @ 1.8- 2.2 mg/L)

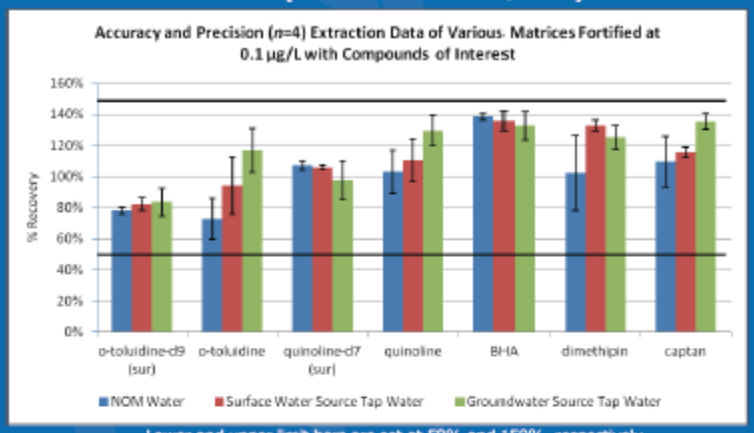
- Fortification performed at 5 µg/L, 1 µg/L, and 0.1 µg/L.
- Each matrix was extracted in 4x replicates.

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Quality Control Data from Matrix Extracts at High Level Fortification (Full Scan GC/MS)
Accuracy and Precision (n=4) Extraction Data of Various Matrices Fortified at 5.0 µg/L with Compounds of Interest
% Recovery
140%
120%
100%
80%
60%
40%
20%
0%
o-toluidine-d9 (sur)
o-toluidine
quinoline-d7 (sur)
quinoline
BHA
dimethipin
captan
NOM Water
Surface Water Source Tap Water
Groundwater Source Tap Water
Lower and upper limit bars are set at 70% and 130%, respectively.
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Quality Control Data from Matrix Extracts at Mid Level Fortification (Full Scan GC/MS)
Accuracy and Precision (n=4) Extraction Data of Various Matrices Fortified at 1.0 µg/L with Compounds of Interest
% Recovery
140%
120%
100%
80%
60%
40%
20%
0%
o-toluidine-d9 (sur)
o-toluidine
quinoline-d7 (sur)
quinoline
BHA
dimethipin
captan
NOM Water
Surface Water Source Tap Water
Groundwater Source Tap Water
Lower and upper limit bars are set at 70% and 130%, respectively.
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Quality Control Data from Matrix Extracts at Low Level Fortification (Full Scan GC/MS)



Lower and upper limit bars are set at 50% and 150%, respectively.

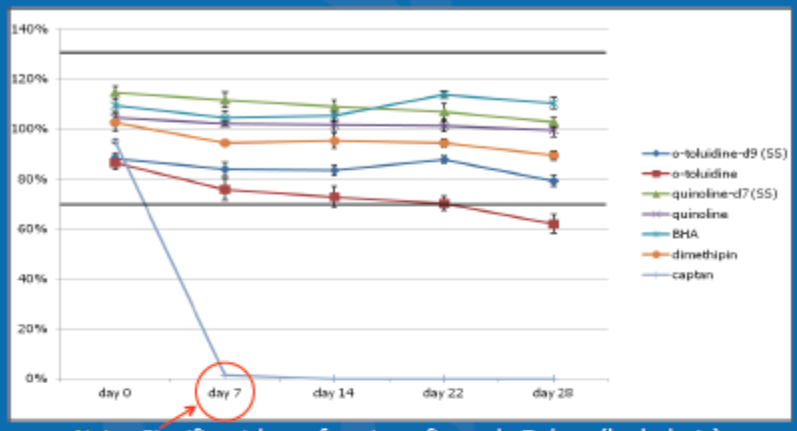
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Sample Holding Time Study

- Stability study of compounds in preserved drinking water stored at 10 °C for 48 hours (simulated shipping), then stored at 6 °C over a 28-day time period.
- Replicate samples (n = 4) were fortified at 2.5 μg/L for each compound, then extracted and analyzed at selected time points.
- Lower and upper control limit bars set at 70% and 130%, respectively.

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Sample Holding Time Study Results



Note: Significant loss of captan after only 7 days (hydrolysis)

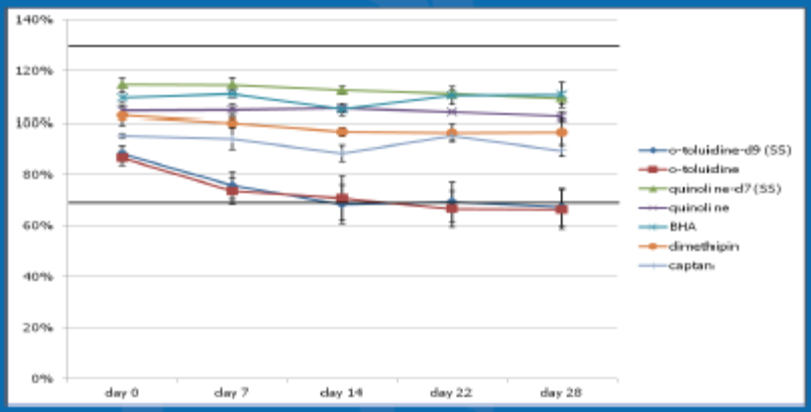
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Sample Extract Holding Time Study

- Stability study of compounds in sample extracts stored at -5 °C over a 28-day time period.
- Replicate samples (n =4) were fortified at 2.5 μg/L for each compound on Day 0, then analyzed at selected time points.
- Lower and upper control limit bars set at 70% and 130%, respectively.

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Sample Extract Holding Time Study

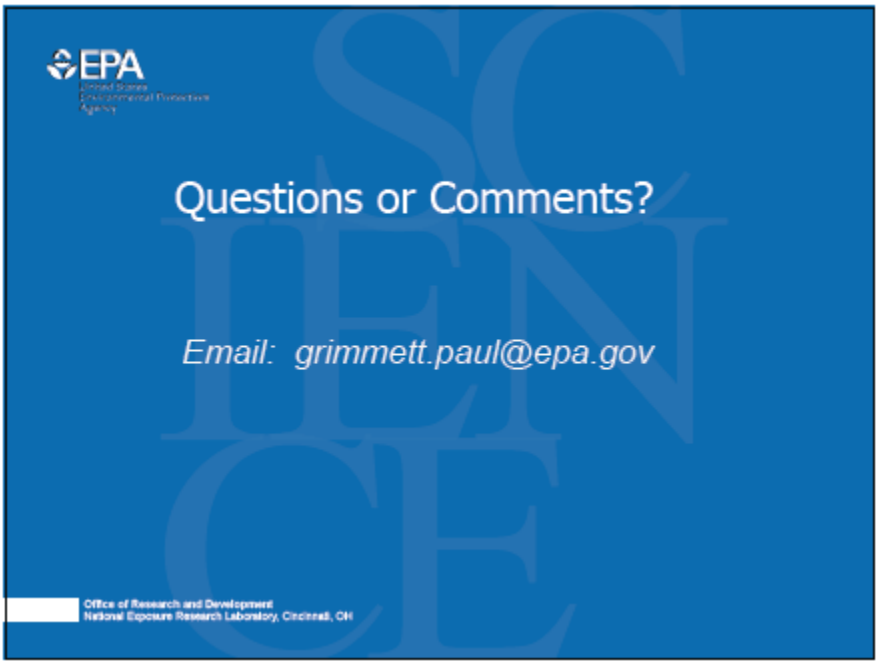


Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Remaining Laboratory Work with Current Method

- LCMRL and MDL analysis and calculations
- Repeat sample matrix challenges, holding time studies, and LCMRL/MDL calculations in SIM
  - work has been initiated
  - quinoline: HRL of 0.010 µg/L
- Multi-laboratory verification
  - LCMRL data
  - matrix data

Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH


EPA
Questions or Comments?
Email: grimmett.paul@epa.gov
Office of Research and Development
National Exposure Research Laboratory, Cincinnati, OH

Ultra-Sensitive Detection of Pharmaceutical and Personal Care Products (PPCPs) in Water with an Integrated On-Line Extraction-UHPLC-MS/MS System

Helen Sun
Bruker Corporation

Abstract

The occurrence of pharmaceutical and personal care products (PPCPs) in the environment water is of growing concern due to their potential harmful effects on environmental and human. The conventional methods based on the "template" of EPA 1694 method require pre-concentration of large volume of water sample and tedious SPE cleanup, followed by LC-tandem mass spectrometer analysis in order to achieve the low ng/L (ppt) level detection. In this study, we introduce an UHPLC system with an integrated online extraction option coupled to a Bruker EVOQ Elite triple quadrupole mass spectrometer for detection of PPCP's in water. The Bruker Advance UHPLC OLE system consists of one binary pump and an integrated third pump for online sample preparation. The built-in online extraction requires no additional hardware assembly (LC pump and valve), and can readily detect 1-5 ppt of PPCPs in water by rapidly pre-concentrating 0.5 mL drinking water sample. The current ongoing work is focused on expanding the targeted PPCP list in one analytical run by further optimizing the pre-concentration step and improving chromatographic separation, which will be applied on the water samples from the local lakes in the bay area.



Ultra-sensitive Detection of Pharmaceutical and Personal Care Products (PPCPs) in Water with an Integrated On-Line Extraction-UHPLC-MS/MS System

Helen Sun, Ph.D.
Bruker Corporation,
Chemical and Applied Markets (CAM)

Chemical and Applied Markets

Copyright 2013 Bruker Corporation. All Rights Reserved.

Pharmaceutical and Personal Care Products (PPCPs)



PPCP category:

- Prescription medicine
- Over-the-counter drugs
- Veterinary drugs
- Fragrances
- Cosmetics
- Sun-screen products
- Diagnostic reagents
- Nutraceuticals (e.g., Vitamins)

Chemical and Applied Markets

Copyright 2013 Bruker Corporation. All Rights Reserved.

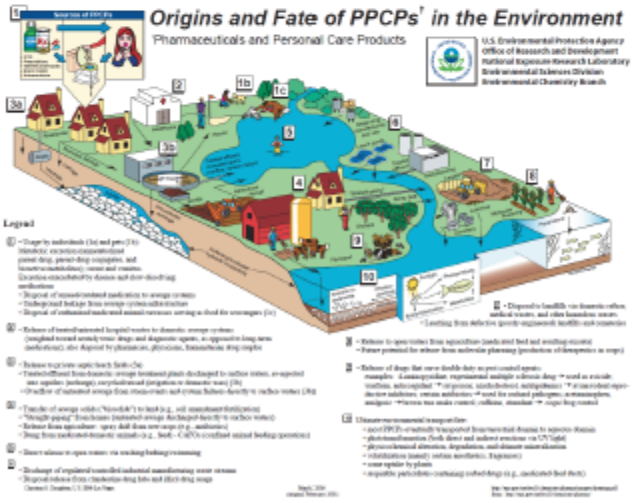
Examples of PPCPs

PPCP name	Classification
Ibuprofen	Analgesic
Gemfibrozil	Antilipemic
Cimetidine	Anti-acid reflux
Acetaminophen	Antipyretic, Analgesic
Thiabendazole	Fungicide and parasiticide
Sulfadimethoxine	Sulfonamide antibiotic
Caffeine	Stimulant
Bisphenol A	Plasticizer
Cholesterol	Sterol
Testosterone	Sex Hormone
Estrogen	Sex Hormone
Benzylecgonine	Cocaine metabolite, drug of abuse

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Source of PPCPs



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

PPCPs: impact to the planet



Potential risk to environment





Potential risk to ecological system



Potential risk to water resource



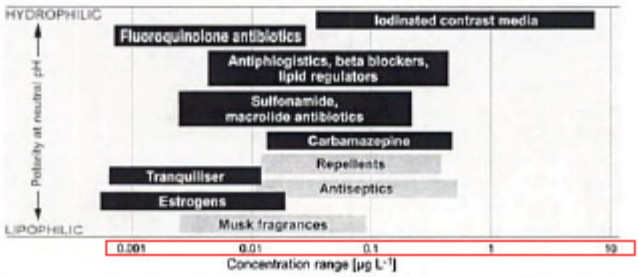
Potential risk to human

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Monitoring PPCPs in water

Levels of PPCPs detected in the treated municipal waste water



Analytical challenges for PPCP monitor in water:

- Trace amount of analyte
- Multi-residue analysis

It requires a sensitive instrument with high speed analysis capability

Ternes, Thomas A. Human Pharmaceuticals, Hormones And Fragrances: The Challenge of Micropollutants in Urban Water Management, IWA Publishing

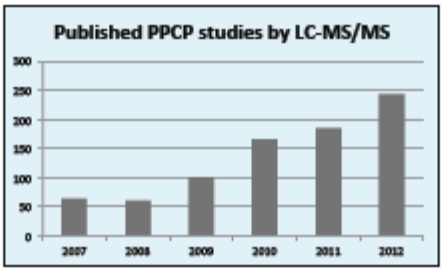
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

LC-MS/MS for PPCP analysis in water

EPA **Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS**

December 2007

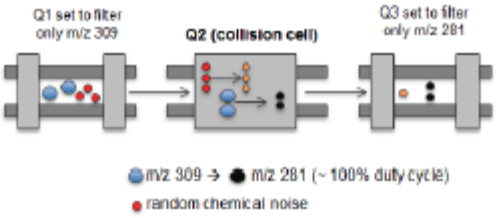


Chemical and Applied Markets

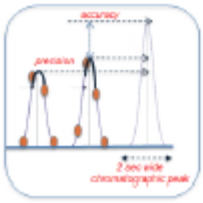
Copyright 2012 Bruker Corporation. All Rights Reserved.

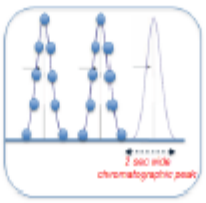
LC-MS/MS for PPCP quantitation

MRM mode of LC-MS/MS for quantitation



targeted analysis, high accuracy







Chemical and Applied Markets

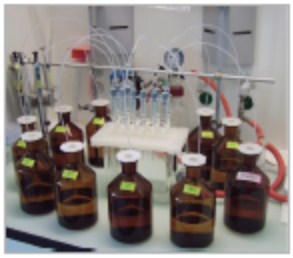
Copyright 2012 Bruker Corporation. All Rights Reserved.

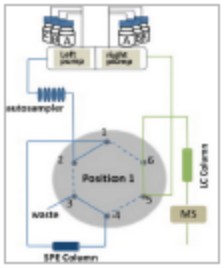
Sample preparation for PPCP analysis in water

Pre-concentration step: improve sensitivity

Offline solid phase extraction
- Labor intensive
- High consumable cost

HPLC online extraction
- Automatic, less labor intensive
- Two pump systems, complicates plumbing diagram





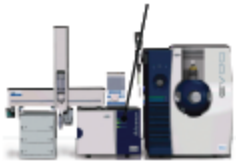
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

EVOQ LC-TQ online extraction (OLE)



- On-Line Extraction (OLE)
- Binary + Loading pump
- Same foot-print



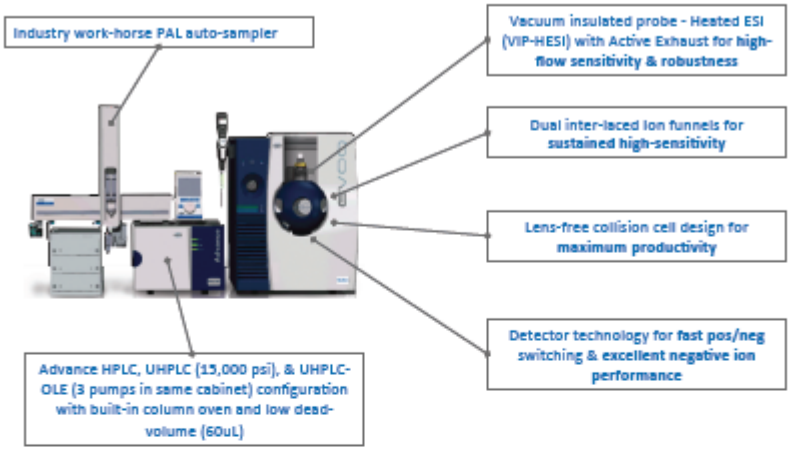
- Bruker Advance™ UHPLC^{OLE}: The first UHPLC with an integrated third pump for online extraction
- Maximum Performance and Flexibility
- OLE Applications:
  - Sample online pre-concentration
  - Dual trap capability
  - Matrix elimination

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Bruker LC-TQ Advantage

Designed for a singular purpose – to reliably quantify thousands of real samples in the fastest 'sample-to-report' time possible



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

The Bruker LC-TQ Advantage

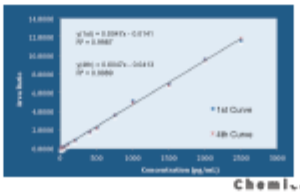
Food Testing –Clenbuterol as a contaminant in meat

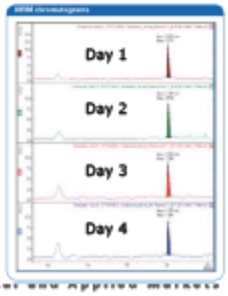
- Clenbuterol is a sympathomimetic amine (beta-2 agonist).
- Side-effect is an increases in basal metabolism rates, which helps build muscle mass, while reducing body-fat.
- Major outbreak in China which sickened over 900 people
- Over 17 livestock houses closed in Mexico due to 100% of samples testing positive for clenbuterol



- EVOQ LC-TQ Advantage
  - Turn-key method on the EVOQ LC-TQ
  - Sustained high sensitivity –proof statement available
  - Available in Compound Based Screening library

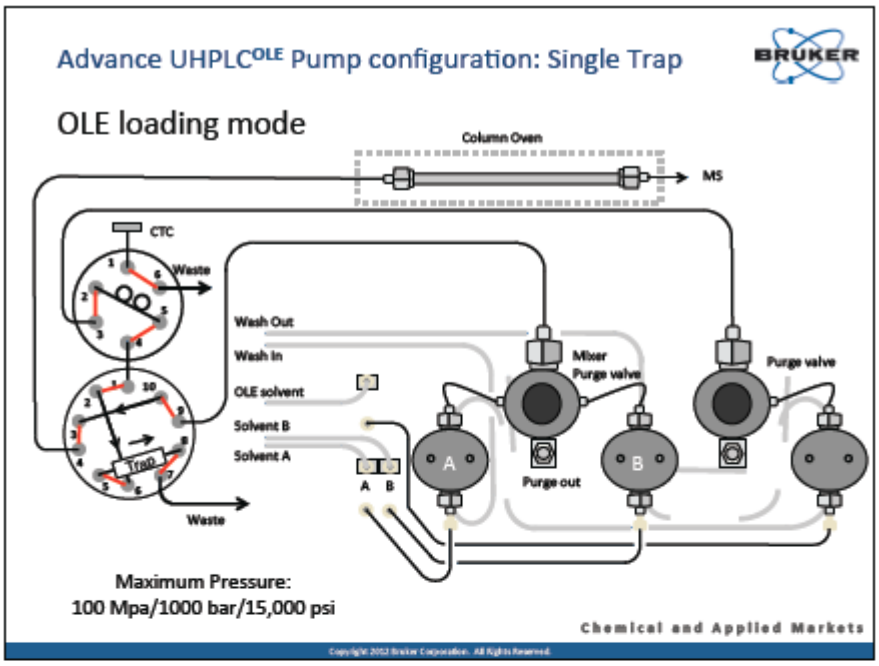


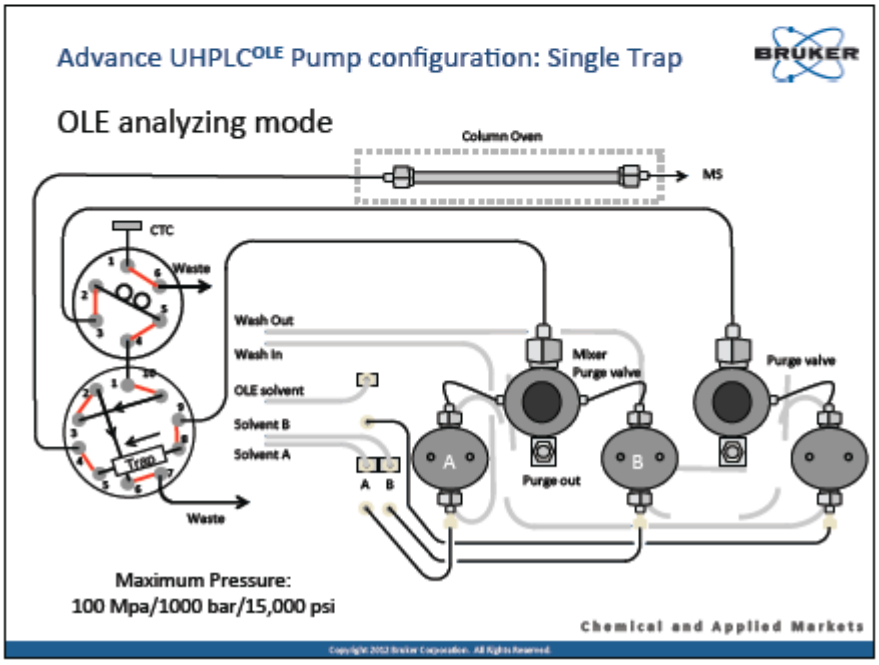


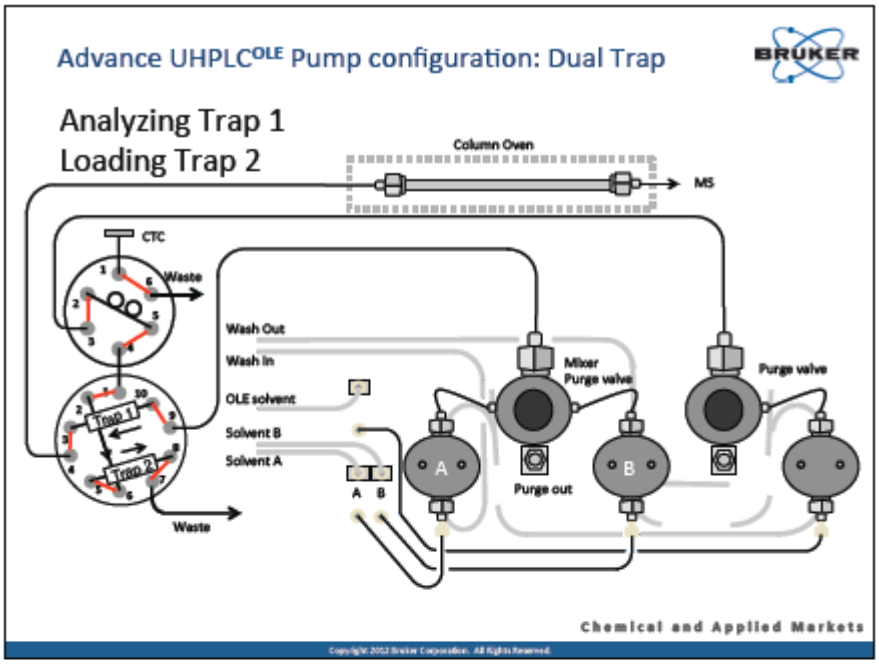


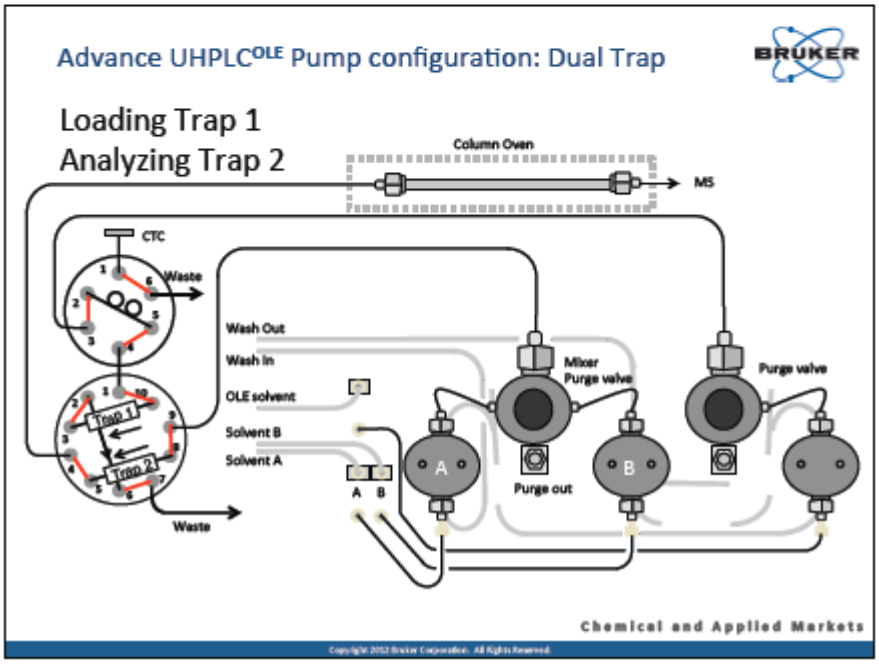
Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

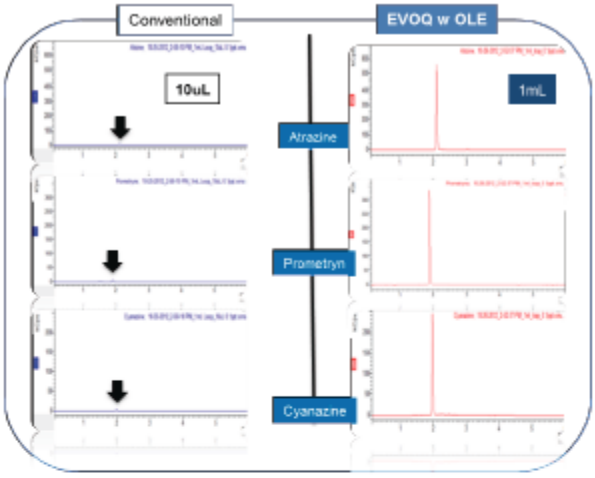

Advance UHPLC^OLE Pump configuration: Single Trap
BRUKER
OLE loading mode
Column Oven
MS
CTC
Waste
Wash Out
Wash In
OLE solvent
Solvent B
Solvent A
Trap
Waste
A B
Mixer Purge valve
Purge out
Purge valve
Maximum Pressure:
100 Mpa/1000 bar/15,000 psi
Chemical and Applied Markets


Advance UHPLC^OLE Pump configuration: Single Trap
BRUKER
OLE analyzing mode
Column Oven
MS
CTC
Waste
Wash Out
Wash In
OLE solvent
Solvent B
Solvent A
Trap
Waste
A B
Mixer Purge valve
Purge out
Purge valve
Maximum Pressure:
100 Mpa/1000 bar/15,000 psi
Chemical and Applied Markets


Advance UHPLC^OLE Pump configuration: Dual Trap
BRUKER
Analyzing Trap 1
Loading Trap 2
Column Oven
MS
CTC
Waste
Wash Out
Wash In
OLE solvent
Solvent B
Solvent A
Trap 1
Trap 2
Waste
A B
Mixer Purge valve
Purge out
Purge valve
A
B
Chemical and Applied Markets


Advance UHPLC^OLE Pump configuration: Dual Trap
BRUKER
Loading Trap 1
Analyzing Trap 2
Column Oven
MS
CTC
Waste
Wash Out
Wash In
OLE solvent
Solvent B
Solvent A
Trap 1
Trap 2
Waste
A B
Mixer Purge valve
Purge out
Purge valve
A
B
Chemical and Applied Markets

EVOQ OLE – lowering detection limit



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.



EVOQ OLE application – PPCP quantitation in city tap water samples and river water



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

PPCP list

PPCP compounds	Category
Alprazolam	anxiolytic
Ciproxacin	antibiotic
Sulfamethoxazole	antibiotic
Trimethoprim	antibiotic
Carbamazepine	anticonvulsant
2,4-D	pesticide/herbicide
Ametryn	pesticide/herbicide
Atrazine	pesticide/herbicide
Bentazone	pesticide/herbicide
Carboxine	pesticide/herbicide
Cyanazine	pesticide/herbicide
Diuron	pesticide/herbicide
Hexazinone	pesticide/herbicide
Hydroxy Atrazine	pesticide/herbicide
MCPA	pesticide/herbicide
Mecoprop	pesticide/herbicide
Metolachlor	pesticide/herbicide
Metribuzin	pesticide/herbicide
Prometryn	pesticide/herbicide
Pyriproxyfen	pesticide/herbicide
Simazine	pesticide/herbicide
Thiabendazole	pesticide/parasiticide
Dapoxetine	prescription drug
Sildenafil	prescription drug
Caffeine	stimulant

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Experimental condition

- **LC**
  - Bruker Advance UHPLC^{OLE}

  OLE pump
  - Flow rate: 500 µL/min
  - Gradient: isocratic, 100% H_2O + 0.1% FA
  - Column: YMC-Pack Pro ODS-AQ, 35mm × 2.0 mm, 3 µm
  - Injection volume: 400 µL

  UHPLC binary pump
  - Flow rate: 400 µL/min
  - Solvent A: H_2O + 5mM NH_4OAc
  - Solvent B: MeOH
  - Column: YMC-Pack Pro C18 RS, 50mm × 2.0 mm, 3 µm
  - Gradient run: 1 5 min

- **MS condition**

  Instrument
  - Bruker EVOQ Elite

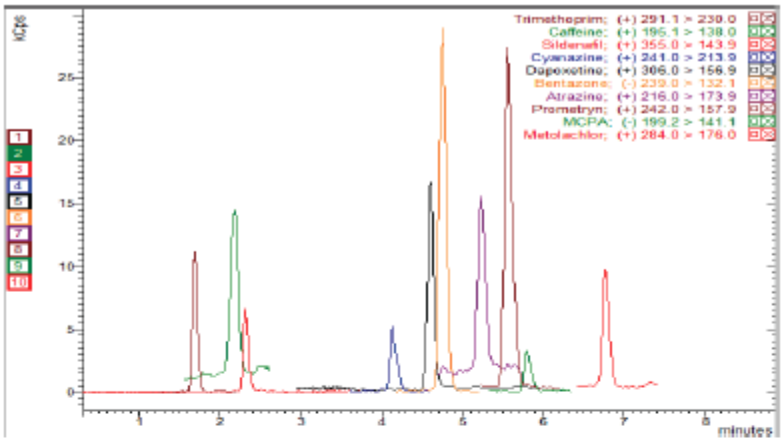
  Ion source condition
  - HESI: ±4000 V
  - Cone gas flow: 15 unit
  - Cone temp: 300 °C
  - Heated Probe gas: 50 unit
  - Heated Probe temp: 450 °C
  - Nebulizer gas flow: 50 unit
  - Exhaust gas: on

- **Sample preparation**
  - Water sample acidified to 0.1% FA and filtered (0.45µm)

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

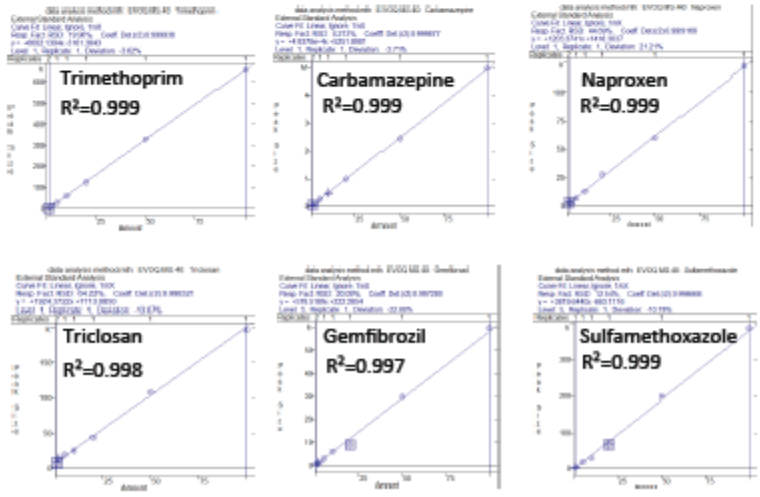
Selected PPCPs at 2 ppt



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Linearity, 1 ppt – 100 ppt



Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Summary of PPCPs in Water

Compound Name	RT (min)	ESI	R^2	S/N (p/p) 2 ppt	RSD% n=10 (5ppt)	Tap Water 1	Tap Water 2	Creek Water	Bottled Water
						pg/mL (ppt)			
Trimethoprim	1.66	+	0.994	389	5.80%	<2	<2	5	<2
Hydroxy Atrazine	1.88	+	0.997	61	9.20%	4	<2	7	<2
Thiabendazole	1.93	+	0.996	408	8.70%	ND	<2	<2	<2
Ciproxacin	2.03	+	0.999	25	4.90%	ND	ND	ND	ND
Caffeine	2.19	+	0.995	68	8.00%	ND	<2	<2	10
Sildenafil	2.33	+	0.998	132	6.60%	ND	ND	ND	<2
Sulfamethoxazole	2.51	+	1	68	5.00%	<2	<2	ND	<2
Cyanazine	4.1	+	0.998	201	8.70%	ND	ND	ND	<2
Simazine	4.38	+	1	56	9.40%	3	<2	5	ND
Metribuzin	4.39	+	0.999	26	12.50%	ND	ND	ND	ND
Hexazinone	4.42	+	0.997	553	4.90%	17	3	3	ND
Dapoxetine	4.62	+	0.999	268	6.00%	ND	ND	ND	ND
Bentazone	4.69	-	0.999	360	6.20%	ND	ND	ND	ND
Ametryn	4.73	+	0.997	404	5.70%	ND	ND	<2	ND
Carboxine	4.8	+	0.999	217	6.20%	ND	ND	ND	ND
Carbamazepine	4.85	+	0.999	485	4.50%	<2	<2	<2	ND
Atrazine	5.2	+	0.996	39	6.90%	<2	ND	ND	ND
Alprazolam	5.38	+	0.998	178	5.90%	ND	ND	ND	ND
Diuron	5.54	+	0.999	56	3.60%	9	<2	6.2	ND
Prometryn	5.56	+	0.994	376	8.40%	ND	ND	ND	<2
2,4-D	5.7	-	1	26	5.60%	9	<2	13	<2
MCPA	5.81	-	1	56	3.80%	<2	<2	<2	ND
Mecoprop	6.39	-	1	27	2.90%	<2	<2	11	2
Metolachlor	6.76	+	0.996	177	9.20%	22	<2	<2	<2
Pyriproxifen	8.36	+	1	23	3.50%	ND	<2	ND	<2

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Hexazinone



- Broad spectrum herbicide
- Inhibits photosynthesis
- Used to control grasses, wood plants
- High water solubility
- A pervasive groundwater contaminant

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.

Metolachlor



- Chloroacetanilide herbicide
- Has been detected in ground and surface water through out US (0.08 – 4.5 ppb)
- Category C pesticide by US EPA
- Bioaccumulation of metolachlor in edible species of fish
- US EPA health advisory level (HAL): 0.525 ppm

Chemical and Applied Markets

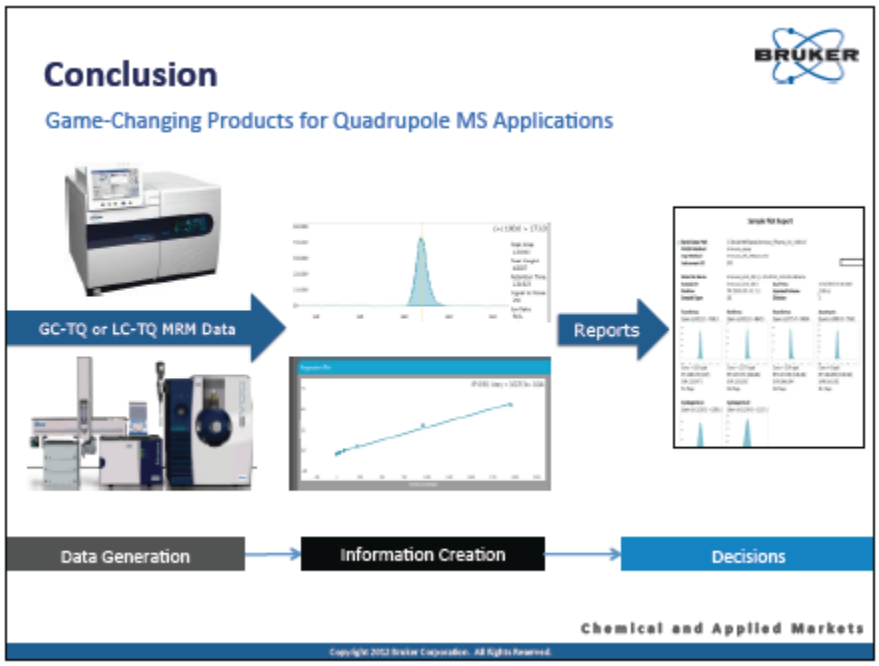
Copyright 2012 Bruker Corporation. All Rights Reserved.

Summary

- EVOQ OLE system provides a total solution for trace PPCP quantitation in water samples: automatic online extraction followed by LC-MS/MS targeted analysis
- An MRM based LC-MS/MS method has been developed for PPCP quantitation in city water, creek water and bottled water samples
- Quantitation result shows that the water quality between cities is slightly different, weed killer herbicides were screened in the tested water samples, but the concentration is still within safety range
- EVOQ OLE system is a ease-of-use, sensitive and robust instrument for PPCP analysis in water samples

Chemical and Applied Markets

Copyright 2012 Bruker Corporation. All Rights Reserved.


Conclusion
Game-Changing Products for Quadrupole MS Applications
GC-TQ or LC-TQ MRM Data
Reports
Data Generation
Information Creation
Decisions
Chemical and Applied Markets

SECTION 23

POSTER PRESENTATIONS

A Convenient Alternative for Low Level VOC Sampling

Linda Coyne, C. Kuhlman

Abstract

Environmental health professionals are being called upon to measure ppb levels of volatile organic compounds (VOCs) for many new applications. Current applications include vapor intrusion, fence line monitoring, community impact studies, and indoor air quality/green buildings. Stainless steel canisters have historically been the primary collection device for low level VOC sampling, but these devices are not always convenient or suitable for the current requirements. Canisters do not effectively collect semi-volatile compounds. Sample times are typically limited to 24 hours or less with canisters and they are bulky and impractical for emergencies or other situations where you need to place a lot of samplers. Passive diffusive samplers specifically designed for (sub) ppb level VOC sampling are a convenient alternative to canisters. Diffusive samplers are small, quiet, and easy to use. They are well suited for long-term studies up to 30 days and for sampling of semi-volatiles with proper sorbent selection. Passive samplers can be conveniently placed indoors, on fence lines, and in urban areas for ambient air studies. This study describes the use of the ULTRA III passive sampler for indoor and ambient air sampling of VOCs with analysis by gas chromatography (GC). The ULTRA III sampler contains two sorbent beds: one is for sample collection and the other serves as a blank for quality assurance. In this study, ULTRA III passive samplers containing three different sorbents, Anasorb GCB1, Carbograph 5, and activated carbon were used to sample various VOCs in indoor air for sample times of 1 to 30 days and the results were compared to co-located canister samples. The data showed correlation coefficients of 0.95, 0.98, 0.985, 0.999, and 0.981 for benzene, toluene, m,p-xylene, o-xylene, and perchloroethylene, respectively. The laboratory and field data also showed consistent uptake rates for 1 to 30 days for benzene, ethyl benzene, methyl-t-butyl ether, toluene, o-xylene, m-xylene, p-xylene and toluene. In conclusion, passive diffusive badges are a reliable collection device for low level VOC sampling and they provide a convenient alternative to canisters for many indoor and ambient air applications.

An Inert Flow Path GC: A Vital New Tool for Trace Environmental Analyses

Fred Feyerherm, Agilent Technologies

Abstract

Increasing sample complexity, lower limits of detection and the need to reliably analyze active analytes demand a highly inert flow path for modern gas phase analyses. As GC instrumentation improves in terms of resolving power and achievable limits of detection with techniques such as GC/MS, GC/MS/MS and GC-TOF MS, flow path inertness became a critical factor. Analytes must survive the tormented trip from injection through detection. Flow path activity, or lack of inertness, has a dramatic impact on the analysis of active analytes. The analytes that tend to stick to exposed silanols or even decompose on heated chemically active sites in the flow path include: organic acids and bases, sulfur species, alcohols, amines, aldehydes, phenols, and pesticides. Accurate and reproducible measurements of these target analytes play important roles in environmental preservation, water quality monitoring and human health risk assessment.

Prior efforts to eliminate active sites throughout the sample's flow path have focused primarily on column and liner deactivation strategies. These strategies have succeeded to the point where a laser focus on additional components in the flow path is the next logical step toward achieving a totally inert flow path. Inlet weldments, surface deactivated gold seals, micro-fluidic plates and ferrules used to make gas tight connections are all flow path components that come in contact with analytes of interest. Drinking water and contract laboratory pesticides application examples highlighting the impact a truly inert flow path has on environmental analytes are shown verses standard flow path results.

Application of Incremental Sampling Methodology to Sediments

Mark Bruce, TestAmerica

Abstract

Background
The Interstate Technology and Regulatory Council (ITRC) team on Incremental Sampling Methodology (ISM) spent three years developing guidance to improve the quality of site characterization. The ITRC ISM guidance document was publically released in February 2012, with internet given several time throughout 2012. This original guidance addressed terrestrial surface and subsurface soil situations. The same principles can be applied to sediments. However, the actual processes need to be modified for this aquatic environment and the higher moisture content typical in sediments. The state of Hawaii has already begun adapting the ISM principles to the aquatic sediment environment.

Incremental Sampling Methodology (ISM) is a sampling and analysis protocol that is designed to reduce data variability and to increase sample representativeness. ISM helps to minimize the sampling errors associated with sampling by providing a systematic approach to project planning and field work, as well as an emphasis on quality assurance/quality control measures throughout the sampling effort and not just in the laboratory. Similar resources applied to an ISM project will often reduce uncertainty far more than a project conducted using discrete sampling methods. This reduced uncertainty in some instances can reduce remediation or environmental liability insurance costs.

Approach
This presentation will primarily focus on the modifications needed to accommodate the laboratory processing of ISM sediment samples. The topics include moisture management, particle size selection, particle size reduction and subsampling.

Lessons Learned
Air drying when needed requires additional surface area and time to produce a dry flowable sample. However, the high initial water content of sediments with flowable characteristics makes particle size selection and particle size reduction without the air drying step more feasible than with sticky terrestrial soil samples. Subsampling using the two dimensional slabcake process on dried sediments works as well as it does for dried terrestrial soils. However, high water content sediments aren't easily subsampled using the square scoops commonly used in the dry sample two dimensional slabcake process. Subsampling high water content sediments is an area on on-going research.

(Related Session: Contaminated Sediments)

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Abstract

The Interstate Technology and Regulatory Council (ITRC) team on Incremental Sampling Methodology (ISM) spent three years developing guidance to improve the quality of site characterization. The ITRC ISM guidance document was publically released in February 2012, with internet based training given several times throughout 2012 and 2013. This original guidance addressed terrestrial surface and subsurface soil situations. The same principles can be applied to sediments. However, the actual processes need to be modified for this aquatic environment and the higher moisture content typical in sediments. The state of Hawaii has already begun adapting the ISM principles to the aquatic sediment environment.

Incremental Sampling Methodology (ISM) is a sampling and analysis protocol that is designed to reduce data variability and to increase sample representativeness. ISM helps to minimize the sampling errors associated with sampling by providing a systematic approach to project planning and field work, as well as an emphasis on quality assurance/quality control measures throughout the sampling effort and not just in the laboratory. Similar resources applied to an ISM project will often reduce uncertainty more than a project conducted using discrete sampling methods. This reduced uncertainty in some instances can reduce remediation or environmental liability insurance costs.

This poster will primarily focus on the modifications needed to accommodate the laboratory processing of ISM sediment samples. The topics include moisture management, particle size selection, particle size reduction and subsampling.

Air drying when needed requires additional surface area and time to produce a dry flowable sample. However, the high initial water content of sediments with flowable characteristics makes particle size selection and particle size reduction without the air drying step more feasible than with sticky terrestrial soil samples. Subsampling using the two dimensional slabcake process on dried sediments works as well as it does for dried terrestrial soils. However, high water content sediments aren't easily subsampled using the square scoops commonly used in the dry sample two dimensional slabcake process. Subsampling high water content sediments is an area on on-going research.

Background

Incremental Sampling Methodology (ISM) is an emerging tool for environmental stakeholders. It is designed to produce more representative site characterization data and thus facilitate better decisions with less uncertainty. This higher data quality has benefits for each stakeholder group. Responsible parties could see lower total remediation costs. Consultants could experience fewer late project contaminant discoveries. Communities could benefit from improved human and environmental health. Regulators could be more confident that all significant contamination has been found.

The Interstate Technology and Regulatory Council developed ISM guidance. It is designed for use by state and other government regulators, environmental consultants, responsible parties, laboratories and other community and environmental stakeholders.

ISM is a structured composite sample collection process followed by equally detailed sample processing and subsampling options at the laboratory. The goal is to produce an analytical subsample of a few grams that closely represents the many tons of soil or sediment represented by the decision unit. When the sample collection crew and laboratory analysts are successful, the final results more closely represent the actual conditions at the site. Knowing those conditions with less uncertainty enables the decision makers to determine where remediation is needed to protect human and environmental health without unnecessarily spending resources on areas that are near but below the action limits

The ITRC ISM guidance is available at www.itrcweb.org/ISM-1. The internet based training is available at www.clu-in.org/training.

\

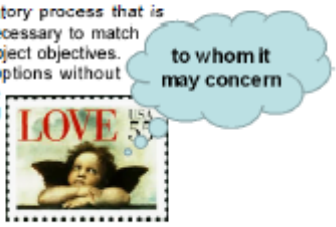
Applying Incremental Sampling

Mark Bruce, TestAmerica

Introduction to ISM Sample Processing

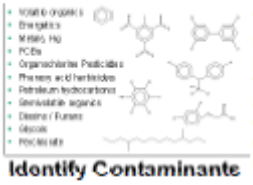
ISM sample processing involves four decisions. There are two fundamental decisions and two trade off decisions. The specific characteristics of sediments can change the decision making process relative to terrestrial soil and subsurface samples.

Since there is no universal laboratory process that is optimal for all ISM samples, it is necessary to match the ISM processes to the overall project objectives. Choosing laboratory processing options without knowing the project objectives is like writing a love letter and addressing it "to whom it may concern."



Fundamental decisions

The first fundamental decision is to identify the contaminants of concern. In addition to the analyte groups, each individual analyte must be listed because differences in physical and chemical properties influence which processes produce the best performance.



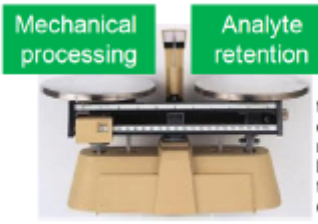
The second fundamental decision is to determine where to look for the analytes. Are there particles or objects in the sample container that should be removed prior to sample preparation and analysis? Are analytes on the exterior surfaces and pores the primary interest or should the interior of crystalline and hard particles or fibers be included as well?



If there are objects in the sample container that should be removed because they aren't part the sample, the process to remove them must be defined. For example, the use of a #10 sieve is a common choice. If analyte on the surfaces and exterior pores is the primary interest, then milling is not appropriate. Conversely if analytes that are currently contained in the interior of the hard particles should be included, then milling to reduce particle size and increase surface area can improve the recovery of these analytes. Milling is also useful to help manage the heterogeneity caused by the nugget effect. Nuggets are particles that have higher than average analyte concentrations and cause extreme small scale heterogeneity and lead to poor subsample representativeness if not managed properly.

Trade-off Decisions

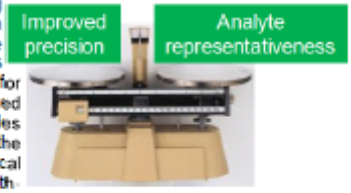
The first trade-off decision is determining whether or not air drying is appropriate. Air drying is a technically simple process to remove soil sample moisture and thus convert the sample into the crushable and flowable form. This dry sample can then be efficiently processed with mechanical means for the disaggregation, sieving, milling and splitting procedures. The currently available processing options for wet sticky soil and sediment are much more labor intensive. Thus, dry soil is usually much less expensive to process. However, the air drying process can result in the loss of lower boiling analytes that aren't strongly absorbed to the particles. Since samples for VOC testing are already handled through the large scale methanol extraction process, this primarily means that lower boiling SVOC analytes have the greatest loss potential during the air drying step.



Trade-off Decisions (continued)

The ITRC ISM-1 guidance has a table that semiquantitatively summarizes this loss potential based on work done by the US Army Corps of Engineers and TestAmerica. www.itrcweb.org/ISM-1/6_2_2_3_Sample_conditioning.html. When surface soil particles still have low boiling SVOCs present, they must be strongly retained with the particles. Thus, additional air drying at the laboratory is unlikely to result in the loss of additional analytes. This reasoning is not applicable to most sediments since air exposure in the field is minimal for most sediments.

The second trade off decision is whether or not to mill the soil or sediment sample. Milling is complete particle size reduction. These smaller particle size and more thoroughly mixed samples can be more reproducibly subsampled, thus the precision of the overall measurement process can be greatly improved compared to unmilled samples with significant small scale heterogeneity. However, milling introduces three potentially significant changes to the sample. The first is releasing the chemicals contained in the particle interiors into the measurement process. This has primarily been observed for metals. Metals that are locked up inside the coarse particles are generally not included in the measurement process by typical EPA sample preparation methods. Thus, releasing these metals into the measurement process through milling can add bias to the final results for some decision making options. The second potential change is accidental contamination of the sample by the materials used to make the mill. For example, a stainless steel puck mill is likely to add both iron and chromium to a milled soil sample. Elevated chromium results in particular could present an unacceptable high bias on sites with chromium as a contaminant of concern. Thus, the mill materials need to be selected with the specific analytes of concern in mind. The third potential change is the thermal degradation or loss of some organic analytes if the milling temperature gets too high. That is why the milling process described in EPA Method 8330B includes cool down steps to avoid degradation of some of the more temperature sensitive analytes.



Hawaii Department of Health

The Hawaii Department of Health (HI DOH) guidance covers planning, field implementation, laboratory sample processing and data interpretation. One example guidance document is EHA/HEER 2011-143-RB, "Technical Guidance Manual Notes: Decision Unit and Multi-Increment" Sample Investigations" at www.hawaiidoh.org/tgm-guidance/DU-MIS Notes (Final March 15 2011).pdf

The Hawaii DOH sediment sample processing guidance includes:

- Decant excess water from collected sediment sample by waiting several minutes and then carefully pouring excess water out of the container;
- Use a cellulose, paper filter to catch and replace fine sediment as needed; decontaminate filter holder between samples;
- For sediments that consist primarily of < 2 mm particles, consider subsampling samples in the lab for extraction and analysis without drying, in order to reduce sample preparation and analysis time (drying and sieving carried out primarily to remove large particles).
- Soil or sediment samples that consist entirely of < 2 mm material do not require drying and sieving to address fundamental error concerns, although some degree of drying may be desirable by the laboratory for sample processing or analysis purposes;
- If soil or sediment samples are not dried and sieved before subsampling, a separate subsample to determine moisture content should be taken so results can be reported on a dry weight basis;

Methodology to Sediments

Laboratories, Inc.

ISM Sediment Processing Adaptations

Moisture management
Sediment samples are rarely considered "surface soils" with significant air exposure prior to sample collection. Thus, potential analyte loss of low boiling analytes must be considered. If only high boiling organic or inorganic analytes are of interest then air drying can still be useful.

Air drying requires sufficient clean air flow to complete the drying process in a short enough time to meet holding time and analytical turn around time expectations. Some sediments have low enough water content that drying techniques used for soil samples are applicable. Other sediments with high water content must be spread in a thin layer. Once the surface moisture has evaporated, stirring occasionally will expose additional moist surfaces to the air to both speed drying and reduce the tendency to form "bricks" if the clay content is high. Once the sample is dry, then the ISM processing techniques applied to dry terrestrial soil samples can be used.



Sediment Air Drying

When analyte loss concerns or extended drying times dictate that the sediment sample be processed in its as-received wet condition, then the particle size selection, particle size reduction and subsampling techniques will need to be adapted.

Particle size selection
Many sediment samples have sufficient water to be flowable as-received. Thus, the sample can be placed on top of a sieve and shaken to achieve the needed particle size selection. This is most likely to be practical for sieve sizes 2 mm and larger. Smaller sieve sizes such as 0.25 mm are more likely to plug and produce an incomplete size separation.



Sediment Sieving

If the sediment sample isn't sufficiently liquid to be flowable and shouldn't be air dried, then it is possible to manually push the sediment through the sieve using a blunt wood spatula as has been used on sticky terrestrial soils. Care must be taken to avoid pushing too hard and damaging the sieve with larger sharp stones and rocks.

Air dried sediment samples can be disaggregated and sieved similar to dried soil samples.

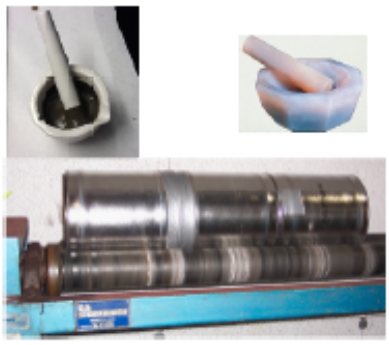


Dry Sediment Disaggregation and Sieving

Particle size reduction
When particle size reduction is appropriate there are several options each of which requires some degree of flowability either in dry or wet form. Dry flowable powdered sediments or liquid slurry sediments can use common milling equipment such as the manual mortar and pestle or ball mill. However, care must be taken to keep liquid sediment contents inside the milling apparatus.

Sediment Processing Adaptations

The mill materials must be taken into account and compared to the contaminants of concern. Common steel mills will contribute iron to the sample. Stainless steel mills will contribute chromium in addition to iron. Ceramic mills are made in part from aluminum oxides, so aluminum contribution to the sample should be considered. If both iron and aluminum must be avoided, then agate (high purity silicon oxides) is a possibility. The high cost of agate tends to limit the frequency of use.



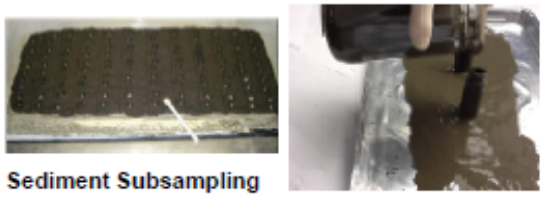
Sediment Milling

Subsampling
Dry or moist sediments can be subsampled using the 2D slabcake process. The 2D slabcake is a miniaturized version of what is often done in the field. The sample is spread in a thin layer and divided into a grid. A small increment is collected from each location and combined to produce the analytical subsample.

If the sediment moisture content is high the particles will tend to segregate quickly and reduce the analysts ability to collect a representative subsample. In some cases neither the stir and scoop or 2D slabcake techniques may be appropriate. A modification of the 1D slabcake process is under development.

With a dry powdered sample, it is initially contained in a jar and successively "sprinkled" back and forth in a line (or 1D slabcake). At least 20 passes are recommended to redistribute particles that might have segregated in the container. After distributing the sample in a line, a perpendicular cut with a rectangular scoop is made to select a sub sample.

Obviously a wet flowable sediment sample will not form an acceptable 1D slabcake. However, the principle can be adapted by pouring the runny sediment out of a jar back and forth in a line. Small containers (one for each subsample) can be positioned at different points along the planned lined. Each pass over the subsample container will deposit a small increment of sample. After a few back and forth passes, the sample in the container should be stirred to maintain its flowable characteristics.



Sediment Subsampling

Conclusion

The principles of incremental sampling methodology can be applied to sediment site characterization. The laboratory processing options can be adapted to properly address high water content.

Contact Mark Bruce - mark.bruce@testamericainc.com

©2013, TestAmerica Laboratories, Inc. All rights reserved. TestAmerica & Design™ are trademarks of TestAmerica Laboratories, Inc.

Combining Hyperspectral Imaging and LIDAR – New Chances in Environmental Monitoring

Toralf Meyer

Abstract

The Bureau of Economic Geology (BEG) has purchased a new imaging system, consisting of a combined full waveform lidar and a variety of camera systems, covering a range from 400 to 14000 nm. The unique combination of topographic and bathymetric lidar, color infrared and hyperspectral imaging significantly expands capabilities for environmental monitoring applications. While researchers at the BEG still focus on their traditional work of monitoring the Texas coastline and the quantification of hurricane damage, research has been extended into terrestrial and aquatic ecosystems throughout the US. The system has been successfully tested in Alaska, Louisiana, along the Texas coast and in the Texas savanna ecosystems.

The BEG sees substantial opportunities to expand its data collection and analysis, therefore providing services to the internal and external research community as well as Federal and State agencies. Future potential applications include (but are not limited to)

- Watershed modeling
- Assessment and monitoring of tectonic movements
- Vegetation assessments, incl. carbon storage, and aspects of biodiversity
- Land use land cover change assessments
- Management of natural or manmade disasters, e.g. oil spills, wildfire
- Mineral prospecting

The poster indicates the technical parameters of the system and presents examples from previous mission conducted with the combined lidar and hyperspectral system. Examples outlined in the presentation include carbon assessments on Freeman Ranch, Texas, topographic assessments along the North Slope of Alaska and a costal survey conducted on South Padre Island.

(Related Session: Modeling, Mapping, and Geospatial Tools)

Determination of 4-Nonylphenol in Biosolids and Biosolids-Applied Soil Using SpeedExtractor and GS/MS/MS

William Ickes

Abstract

4-nonylphenol (4-NP) is metabolite of nonylphenol polyethoxylates which are anthropogenicaly-produced substances utilized in many consumer products. Because of its close association with household products, large quantity of 4-NP, which is highly hydrophobic, can be quickly sorbed by the organic rich solid phase during wastewater treatment. Concentrations as high as several thousand mg/kg (ppm) have been detected for 4-NP in biosolids, making biosolids a possible major source for 4-NP in the environment. Land application of biosolids as soil amendment has been a cost-effective biosolids management option for many municipalities. Biosolids production in the United States reached 8.2 million dry ton/year in 2010, 70% of which was land applied. However, there is a strong concern over potential pollution of the environment with various biosolids-associated anthropogenic chemicals such as 4-NP. 4-NP can bind to estrogen receptors, making it a threat to various organisms in the environment. There is a need for fast, accurate, and sensitive detection of 4-NP in environmental samples.

Development of a State Wastewater Laboratory Certification Program

Franklin Hall

Abstract

Kentucky's Energy and Environment Cabinet is currently pursuing a Wastewater Laboratory Certification Program for all organizations performing analysis of Kentucky Pollutant Discharge Elimination System (KPDES) compliance data. A summary of the process will be provided. This summary will cover from the planning states through the development of the regulation and associated documents (laboratory manual and application). Significant activities include: review of current national and state certification programs, determination of the affected universe, stakeholders' involvement, determination of cost, drafting requirements and the technical review/editing process.

Abstract

Kentucky's Energy and Environment Cabinet is currently pursuing a Wastewater Laboratory Certification Program for all organizations performing analysis of Kentucky Pollutant Discharge Elimination System (KPDES) compliance data. A summary of the process will be provided. This summary will cover from the planning stages through the development of the regulation and associated documents (laboratory manual and application). Significant activities include: review of current national and state certification programs, determination of the affected universe, stakeholders' involvement, determination of cost, drafting requirements and the technical review/editing process.

What is Laboratory Certification?

Laboratory certification is a process that provides formal recognition to the managerial and technical competence of a laboratory performing specific analyses defined by a certifying body or environmental program.

Why Develop a Wastewater Laboratory Certification Program?

Kentucky received a Notice of Intent (NOI) from a consortium of environmental groups regarding coal industry Discharge Monitoring Report (DMR) data inconsistencies. As a result of the NOI, the State conducted Performance Audit Inspections (PAIs) that included twenty seven laboratories performing analyses to meet the requirements of KPDES permits. The State found poor documentation with little to no quality assurance/quality control (QA/QC) being performed. Overall, there was no uniform standard of quality for the data being produced and submitted to the State for compliance purposes.

Where to Start?

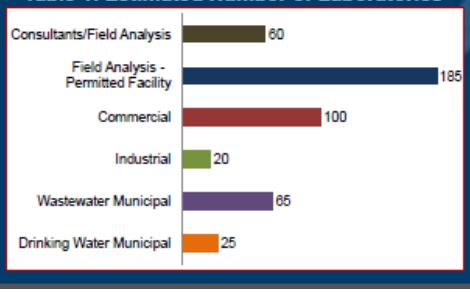
In order to begin this process, a survey of KPDES permitted facilities was conducted to see who was performing analyses and submitting results to the State for compliance. It is estimated that there are approximately 6,000 facilities in Kentucky submitting DMR data. For a breakdown in the number of laboratories performing analyses for the DMRs, see Table 1.

The State then performed a national survey to see what kinds of certification programs existed and which states had programs. See Figure 1.

While developing a Wastewater Laboratory Certification Program, the state created a stakeholder group to discuss the impacts the requirements of the program will have. These stakeholders met several times with the State as this program was being developed. See Figure 2.

With the input of the stakeholder group, the State developed a regulation and laboratory manual. Then the DOW began the legal process to move the draft regulation into effect. See Figure 3.

Table 1. Estimated Number of Laboratories



Program Goal

The State's goal is to create a Wastewater Laboratory Certification Program that is both achievable and legally defensible at a minimum cost.

Figure 1. States with Wastewater Certification Programs



States with only TNI certification: 11
States with only state-created program: 14
States with both TNI and state program: 3
TOTAL States with certification programs: 28

States with no certification program: 22

Kentucky would be 18th state with a state-created program.

Certification Fees Development

Fee schedules were developed by first surveying what other state programs charge and then by applying our estimated number of laboratories and our desired on-site audit frequency to the estimated number of personnel the State would require to implement this program. It is the State's goal that the majority of implementation costs for this program be covered by the certification fees collected.

The State estimates that certification will cost approximately $0.20 per analysis performed.

Average costs to a laboratory per year will be $2,000 - $2,500.

Range of costs to a laboratory per year will be $0 - $5,700.

Figure 2. Stakeholder Group Participants



Figure 3. The Legal Process to Create a Regulation



Where is the Program Now?

The Wastewater Laboratory Certification Program regulation (401 KAR 5:320) was taken up by the Administrative Regulation Review Subcommittee on July 9, 2013. The subcommittee voted on and accepted the amendments to the regulation and it has now been referred to the Interim Joint Committee on Natural Resources and Environment (step 8 in Figure 3, above). This regulation could become effective as early as September.

Summary of the Laboratory Certification Program

- Establishes a uniform standard for data quality.
- Establishes a tiered approach to certification.
- Establishes tiered fees for certification based on facility size and variety of analyses being performed.
- Establishes tools for application.
- Outlines what each laboratory must do in order to be compliant with the requirements established in 40 CFR 136.

Contact Information

Frank Hall
Frank.Hall@ky.gov
(502) 564-3410 extension 4959

Patrick Garrity
Patrick.Garrity@ky.gov
(502) 564-3410 extension 4968

Fully Automating Environmental Analyses Using Inline Autodilution

Paul Field

Abstract

The prepFAST is a completely integrated inline autodilution system for ICP-OES and ICP-MS instruments. Three of the most powerful, fully-automated functions of prepFAST include: 1) inline dilution of a single multi-element stock standard to generate calibration curves, 2) user defined inline dilution of samples, and 3) inline dilution Quality Control Over Range samples to eliminate QC failures. In environmental samples organic ligand concentration, complexation, pH and ionic strength, are major factors that control the partitioning of metals between the dissolved (< 0.45 mm) and particulate (>0.45 mm) phases in natural waters. As a result, most environmentally important metals have high affinity for particles and therefore exhibit low dissolved and high total metal concentrations. To cover the full range of natural variability, auto calibration curves generated from single multi-element stock standard solution with calibration coefficients greater than 0.9999. Accuracy of dissolved metal concentrations determined for NIST 1643e are in excellent agreement with certified values. Omaha tap water is used as the EPA 200.8 defined, Laboratory Fortified Matrix (LFM) and Quality Control Standard (QCS). The fully automated method for environmental samples illustrates, recovery of 95-105% and precision of less than +/- 3% greatly exceeding EPA requirements of 70-130% and +/- 10%, respectively.

High Throughput Analysis of Hydraulic Fracturing Waste Water

Michael Sgroi

Abstract

By-products of hydraulic fracturing (fracking) generate huge volumes of waste water at gas well sites. Both organic and inorganic contaminants are present in this water. All of this water must be properly analyzed to ensure that no harmful substances are released back into the ecosystem. Sensitive and more efficient methods are necessary to analyze the large number of waste water samples from these fracking locations, which grow in number each year. Accelerated plasma source spectroscopic techniques used to analyze the fracking waste water samples will be explored.

Background on Fracking

Technique and Analytical Challenges

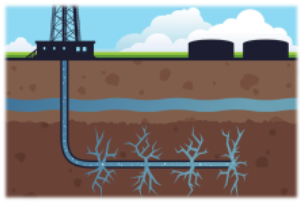


Fig.1: *Schematic diagram of the fracking process.*

- Hydraulic fracturing (fracking) is a relatively new method of extracting natural gas from dense shale deposits situated deep under low-permeable rock layers miles below the surface
- Huge volumes of hydraulic fluids need to be pumped into wells to fracture the shale deposit and free up the gas
- Although about 90% of this fluid is water, a variety of additives are used, including:
  - Propants like sand or bauxite
  - Gelling agents like cellulose polymers and cross-linkers
  - Foam additives
  - Scale inhibitors like ammonium chloride and phosphonates
  - Corrosion inhibitors like methyl and isopropyl alcohol
  - Biocides
  - Friction reducers like light crude oil distillates
  - Surfactants
  - Acids like HCl
- This process leads to environmental concerns about drinking water quality in the surrounding area and the tremendous amount of waste water produced
- Many samples are generated that need to be tested, e.g. towards the content of trace and ultra trace metals and metalloids

Political Background and Progress on Legal Framework

- Critics of fracking have pointed the finger at former Vice President Dick Cheney, who largely authored the 2005 Energy Bill (the so-called Halliburton Loophole), which explicitly exempted fracking from federal review under the Safe Drinking Water Act (SDWA)
- Under this provision, drilling companies are under no obligation to make public which chemicals they use, although many of them are recognized or suspected carcinogens
- The U.S. Environmental Protection Agency (USEPA) is currently investigating cases of suspected contamination in towns located near fracking activities
- This current state of legislation is sure to change as time moves forward and the political climate evolves

Conclusion

- Original method total analysis time: 4 min 27 s could be reduced to 2 min 45 s using the newly develop method → efficiency increase of 38.2% without changes to the original method (0 s plasma stabilization time, 0 s rinse time, only 20 s flush time)
- Combined with the total integration time a duty cycle of only 25.5% could be achieved without effecting the figures of merit more than sufficient for fracking samples

Introduction

There are important organic and inorganic components to the testing of fracking related samples. Besides EPA methods such as SW-84622 and 200.733, the focus here is the inorganic elemental analysis associated with fracking samples and how the volume of those samples that will surely rise in the coming years can be better and more efficiently be dealt with by using the ***CETAC ASXpress Plus*** rapid sample introduction system.

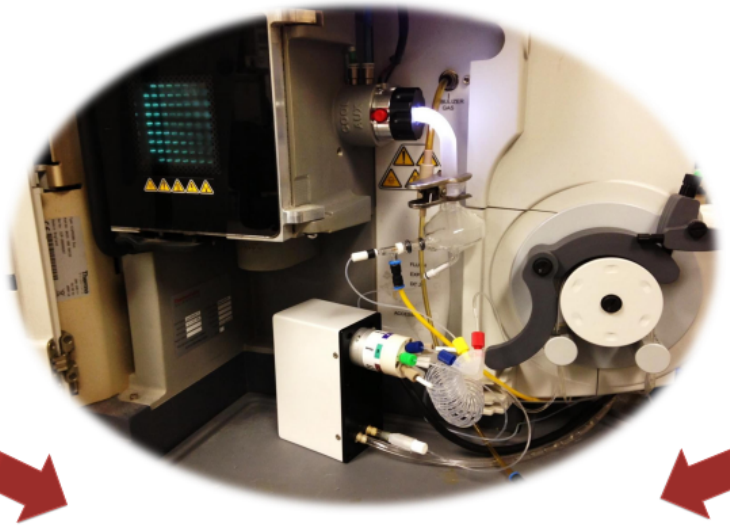


Fig.2: *CETAC's ASXpress Plus* rapid sample introduction system coupled to a *Thermo iCAP dual 6000 series* ICP-OES system.

Results

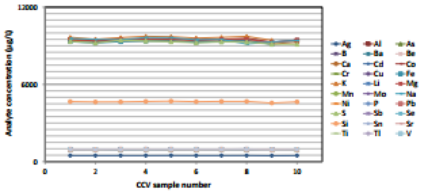


Fig.4: *Found concentrations in 10 CCV samples recorded during analysis of fracking waste water showing the figures of merit of the developed system and method.*

- Precision was less than 1% RSD and accuracy was within 5% across 10 measurements of the same CCV sample containing 32 elements of interest e.g. in fracking waste water samples
- Carryover was undetectable for most elements and those that could be measured were on the maximum of 5% or well below

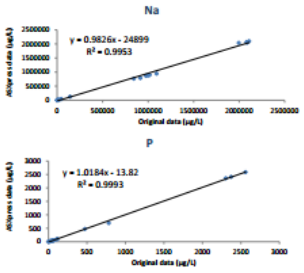


Fig.5: *Validation of the original and the ASXpress accelerated method for selected elements of interest.*

Introduction

There are important organic and inorganic components to the testing of fracking related samples. Besides EPA methods such as SW-84622 and 200.733, the focus here is the inorganic elemental analysis associated with fracking samples and how the volume of those samples that will surely rise in the coming years can be better and more efficiently be dealt with by using the *CETAC ASXpress Plus* rapid sample introduction system.

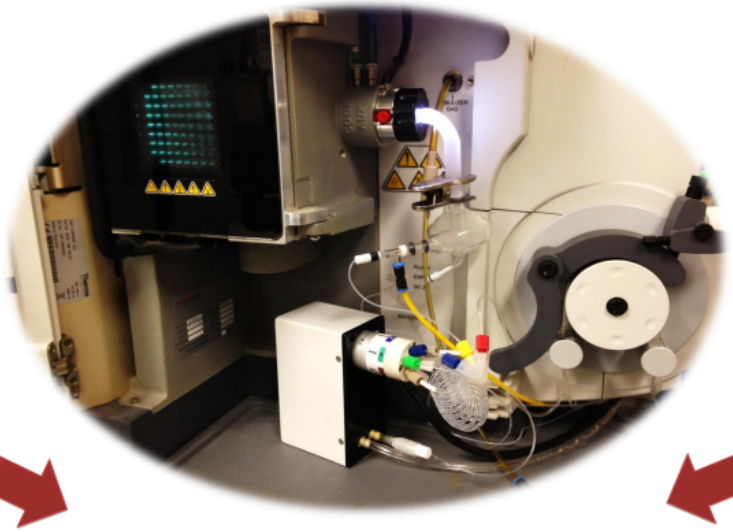


Fig.2: *CETAC's ASXpress Plus* rapid sample introduction system coupled to a *Thermo iCAP dual 6000 series* ICP-OES system.

ASXpress Plus – Function Principle

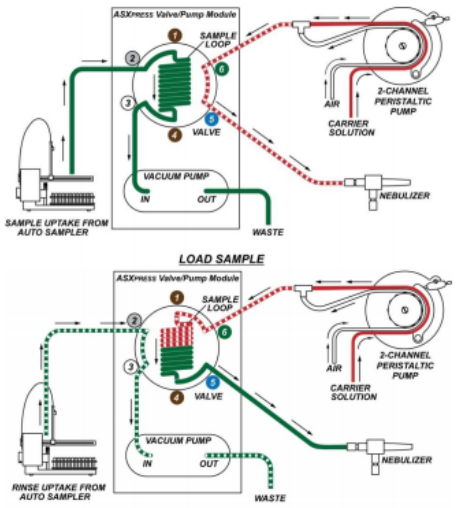


Fig.3: *Function principle of the ASXpress Plus system and connections for sample load (upper part) and sample injection and simultaneous rinsing (lower part).*

Advantages and Features

- Robust coupling to any ICP-OES or ICP-MS system due universal setup and GUI controlled software running without any need for an user intervention after installation
- Increased efficiency due to shortened sample uptake / stabilization time
- Minimized carryover and memory effects due to air bubble wash step and no exposition of the sample to peristaltic pump tubing
- Constant flow to nebulizer (no fast uptake) to ensure plasma stability and easy in-line addition of internal standards

Results

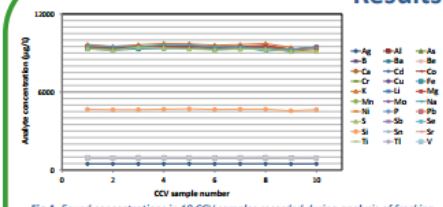


Fig.4: *Found concentrations in 10 CCV samples recorded during analysis of fracking waste water showing the figures of merit of the developed system and method.*

- Precision was less than 1% RSD and accuracy was within 5% across 10 measurements of the same CCV sample containing 32 elements of interest e.g. in fracking waste water samples
- Carryover was undetectable for most elements and those that could be measured were on the maximum of 5% or well below

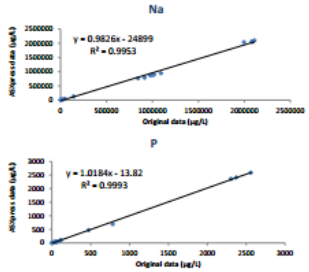


Fig.5: *Validation of the original and the ASXpress accelerated method for selected elements of interest.*

Analytical Method

ICP-OES Conditions:

- RF Power: 1150 W
- Nebulizer Gas Flow: 0.7 L/min
- Purge gas mode: Boost, pump rate: 45 rpm
- Humidified argon supply and *GE SeaSpray* nebulizer for high TDS matrices

Sample Matrix:

- 5 mL HCl + 2 mL HNO3 for 50 mL sample
- ISTDs: Y @ 1.000 mg/L and In @ 10.000 mg/L
- CCB & CCV every 10 samples
- USEPA 6010B / 200.7 / fracking combined

ASXpress Plus Configuration:

- 5 mL 2 mm I.D. aqueous loop and 1.5 mm I.D. port sized aqueous valve
- Extra loop rinse:
  - Loop rinse delay: 4.0 s
  - Loop evacuation delay: 3.0 s
- Loop load: 10 s
- Equalization time: 2.0 s
- Time to evacuate probe: 2.0 s
- Rinse station fill: 11 s
- Pump timeout: 60 s
- ASXpress Firmware: 2.50

How Much Can a 15m X 0.25mm X 0.10µm GC Column Be Trimmed for Maintenance Before the BDE 49 and 71 Resolution Requirements Are No Longer Met for EPA Method 1614

Christopher Rattray, Restek

Abstract

Polybrominated diphenyl ethers (PBDEs) have been found to be persistent and bioaccumulative in the environment. The technical mixtures containing penta and octa congeners were voluntarily withdrawn in the United States in 2005 and the last remaining PBDE mixture, decaBDE, should be completely phased out by the end of 2013. While these mixtures have been phased out of production and use, the concentrations in the environment have not been declining and are currently still widely monitored.

The analysis of PBDEs is challenging due to structural isomers that need to be chromatographically separated and thermally label compounds of interest that may breakdown during gas chromatography. PBDEs included in EPA Method 1614 are well resolved on a 15m x 0.25mm x 0.10µm Rtx-1614 GC column, a 5% diphenyl, 95% dimethyl polysiloxane type phase that was specifically designed to meet method resolution requirements. Using a short, thin film column also allows the elution of decabromodiphenyl ether (BDE-209) without on-column thermal degradation.

Monitoring efforts of the levels of PBDEs include a wide array of biota and environmental matrices. Non-volatile material may still persist even in cleaned-up final extracts, requiring GC column and inlet maintenance to be performed. Using a 15m x 0.25mm x 0.10µm column, how many loops of the GC column can one clip for maintenance before the Method 1614 resolution requirements of BDE 49 and BDE 71 can no longer be met? The resolution between BDE 49 and 71 must be less than 40% valley height to meet method criteria.

Kentucky's Approach to Defining EPA's "Most Sensitive Method" for NPDES Permits

Patrick Garrity

Abstract

Laboratories reporting NPDES compliance sample results to Kentucky's Pollutant Discharge Elimination System (KPDES) have had difficulty understanding permit language that includes "most sensitive method" statement. The questions that arise are what is "most sensitive" and what is "sensitive enough". This most often occurs with metals (total and recoverable) and other contaminants with low Kentucky KPDES reporting limit requirements. Kentucky has established a Demonstration of Capability (DOC) that allows for a technical review of the laboratory's capability in achieving the required reporting limits. The DOC includes an Initial and Ongoing Demonstration of Capability; Method Detection Limit Study; and Reporting Limit Standard verification at the required reporting limit.

Introduction

- EPA boiler plate language for NPDES permits includes "most sensitive method"
- Most sensitive method often times defined as "newest technology"
- Laboratories are limited to one test method (e.g. EPA 200.8 – ICP/MS for metals
- In 2011, Kentucky chose to further define "sensitive enough" analytical method
- Demonstration of Capability (DOC) proposed to verify laboratory capability
- DOC effective as of July 2011.

Objective

- Permits specify certain parameters with low required reporting limits (RRL)
- RRL is based on 70% of the Kentucky Water Quality Standard (WQS)
- Many EPA approved methods are capable of low reporting limits
- There is no "one size fits all" method to parameter categories (e.g. metals)
- Establish a procedure to better demonstrate laboratory/method capability
- Opportunity for laboratories to demonstrate the sensitivity of any EPA approved method

Derived RRL from WQS

- 401 KAR 10:031 Surface Water Standards
- Water Quality criteria or WQS based on human health, and warm water aquatic habitat
- Warm water aquatic habitat subdivided into Acute and Chronic criteria
- Some metals acute and chronic WQS criteria based on hardness concentration
- DOW's RRL based on 70% of the WQS criteria
- The RRLs are more stringent for certain pollutants like cadmium, free cyanide, selenium, etc.
- See table below for examples:

Parameter	Units	WQS	RRL
Free Cyanide	µg/L	5.2	3.64
Thallium	µg/L	0.24	0.168
Cadmium[1]	µg/L	0.27	0.19
Lead[1]	µg/L	3.18	2.23
Mercury	µg/L	0.051	0.036

[1] The WQS is dependent on an exponential equation that uses a hardness value of 100 mg/L.

DOC Procedure Overview

IDC

- Analyze four (4) mid-range concentration laboratory fortified blanks (LFB)
- Can be same day or different day
- Calculate the Percent Recovery for each

MDL

- As described in 40 CFR 136 Appendix B
- Analyze seven (7) LFBs over two (2) to three (3) non-consecutive days
- LFBs spiked at 3 to 5 times the expected minimum reporting limit
- Calculate the variance (S^2) and standard deviation (S) of the replicate measurements
- Compute the MDL using the following equation: MDL = 3.143 * S

RLS

- Analyze a known standard at or below the required reporting limit
- Analyzed as either the lowest concentration calibration standard OR as a stand alone verification standard
- If the RLS is used as the lowest concentration calibration standard it must also be used to determine the acceptance of the calibration curve and cannot be ignored or not considered during any future verification of the calibration curve

Requirements, Acceptance Criteria and Frequency

- Criteria required for laboratories to demonstrate that methods are "sensitive enough" for their intended use.
- See table below for summary:

Demonstration	Parameter	Requirement	Frequency
IDC	IDC Replicates (4 mid-range LCS)	• Each must be within 80 to 120% of the mean value; • %RSD must be ≤15%.	Initial and Annual
MDL	7 Replicates	• Replicates analyzed over 2 to 3 non-consecutive days; • Calculated MDL must be less than the RRL; • Spike concentration must be less than 10 times the calculated MDL.	Initial and Annual
RLS	Lowest Standard of Initial Calibration Curve	• Must be used with the calibration, cannot be dropped from use; • Must be ±30% of the expected value (e.g. 70-130% Recovery); • Concentration must be ≤ RRL.	Initial and performed each day that samples are analyzed
RLS	Verification Standard	• Must be ±30% of the expected value (e.g. 70-130% Recovery); • Concentration must be ≤ RRL.	Performed each day that samples are analyzed

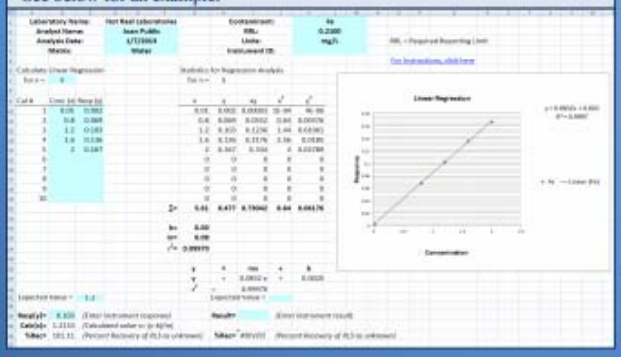
MDL Worksheet for Laboratories

- Worksheet provides laboratories with calculated MDL based on 40 CFR 136 Appendix B. Designed for seven replicates. Also verifies that calculated MDL is within 10[1] of spike concentration.
- See below for an example:



RLS Worksheet for Laboratories

- Worksheet provides laboratories with linear regression (best fit) statistics based on y=mx+b. Will also calculate percentage recovery of RLS (calculated as an unknown using the new calibration).
- See below for an example:



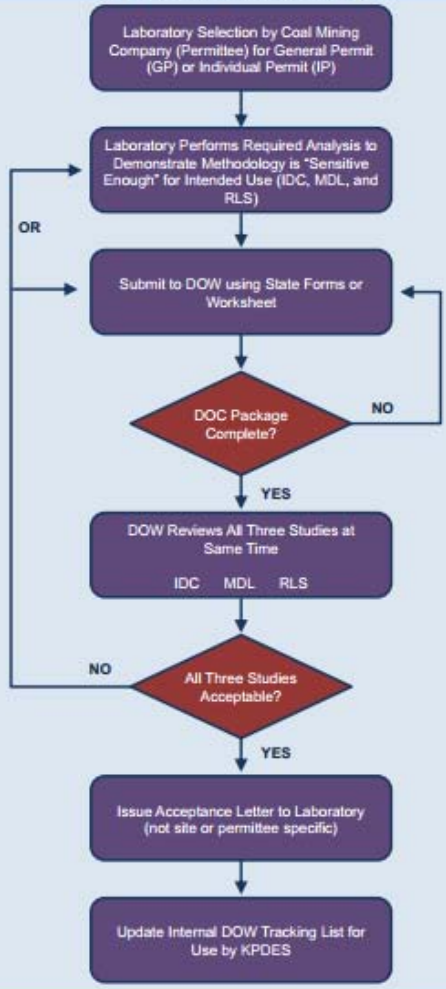
Data User Needs

- Receive DOC submission from the wastewater laboratories
- Review and approval of DOC documents
- Approval letter sent to the laboratory for the parameters approved
- Receive Reasonable Potential Analysis (RPA) and in-stream monitoring data
- MRL or PQL of the submitted parameters checked with the submitted DOCs
- Run RPA on the accepted data for imposing limits or monitoring requirements on the parameters
- Perform trend analysis on the submitted in-stream chemistry data for specific parameters of concern

Technical Assistance

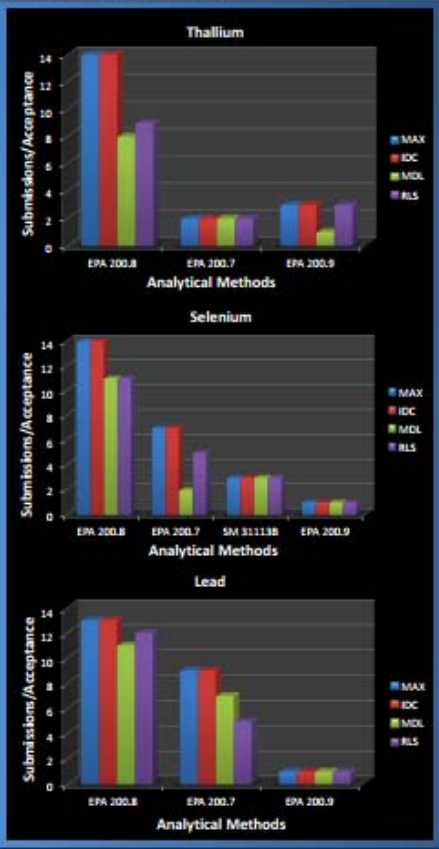
- DOC Procedure, Worksheet, State Reporting Forms
- After review of laboratory DOC submission – email deviations
- Phone/email assistance to further explain DOC errors
- Review re-submission by laboratory
- May require additional assistance

DOC Process for Coal Mining Operations For Pre-Application Outfall Analysis



Laboratory Participation and Overall Success

- The graphs below show the DOC acceptance numbers for Thallium, Selenium, and Lead by different analytical methods



Conclusions

- DOC provides a realistic report card for laboratory capability/performance
- DOC is a stepping stone for laboratories planning to apply for wastewater certification
- Technical assistance training and user tools have been crafted due to DOC process
- DOC will greatly improve the quality of data submitted for pre-mining and issued permit applications
- DOC approval of laboratories will reduce the time and improve the effectiveness of the technical review of submitted data
- DOC approval of laboratories will promote confidence measure between the client and the laboratory with regards to the quality of the data

Future Developments

- Development of a web user-interface for the submission of future DOC documents
- Development of a DOC approval database with web user-interface features
- Annual issuance of DOC approval certificates to concerned laboratories

Contact Information

Patrick Garrity
Patrick.Garrity@ky.gov
(502) 564-3410 extension 4968

Frank Hall
Frank.Hall@ky.gov
(502) 564-3410 extension 4959

Quantitative and Qualitative Extraction and Determination of Cyanide in Soils and Sediments

William Lipps, OI Analytical

Abstract

The toxicity and mobility of cyanide in soil is governed by its chemical form. Simple cyanide, or the cyanide ion (CN-), can be weakly adsorbed onto soil particles at pH >9.2. Weak metal-cyanide complexes ([M(CN)4]-2 and strong metal – cyanide complexes ([M(CN)6]-3 or [M(CN)6]-3) have an affinity for metal oxides and organic matter that decreases with increasing pH, however, other salts in solution tend to inhibit adsorption. Simple cyanide, weak metal-cyanide complexes, and strong-metal cyanide complexes are readily soluble in water. Metal – Metal cyanide complexes, such as Prussian Blue (Fe4[Fe(CN)6)3), are insoluble in water and are the most common forms of cyanide found in sediment and soil.

A common practice for the extraction of cyanide in soil and sediment is acid distillation. This approach is valid for all cyanide forms except the metal-metal cyanide complexes that are most likely to be present. The quality control practice of spiking a soil sample with simple cyanides, or strong metal-cyanide complexes to validate acid distillation is misleading because these cyanide complexes are readily soluble. Acid distillation of cyanide in soil results in low and irreproducible recoveries for the metal-metal cyanide complexes most likely to be present. Acid distillation of cyanide in soil is ineffective and does not accurately measure “total” cyanide nor does it estimate cyanide toxicity.

This will present an extraction and analysis scheme that selectively extracts and determines the various forms of cyanide that could be present in a soil or sediment sample. Analytical results demonstrating differentiation of potentially toxic simple and weak metal-cyanide complexes as well as non-toxic cyanides, strong metal-cyanide, and metal-metal cyanide complexes will be reported.

(Related Session: EPA Approval of Innovative Approaches to Monitoring)

Introduction

The toxicity and mobility of cyanide in soil is governed by its chemical form. Simple cyanide, or the cyanide ion (CN^-), can be weakly adsorbed onto soil particles at pH>9.2. Weak metal-cyanide complexes ($[M(CN_4)]^{-2}$) and strong metal – cyanide complexes ($[M(CN)_5]^{-3}$ or $[M(CN)_6]^{-3}$) have an affinity for metal oxides and organic matter that decreases with increasing pH, however, other salts in solution tend to inhibit adsorption. Simple cyanide, weak metal-cyanide complexes, and strong-metal cyanide complexes are readily soluble in water. Metal – Metal cyanide complexes, such as Prussian Blue ($Fe_4[Fe(CN)_6]^3$), are insoluble in water and are the most common forms of cyanide found in sediment and soil. Metal-metal cyanide complexes are insoluble in acid solution, and solubility increases with pH.

A common practice for the extraction of cyanide in soil and sediment is acid distillation. This approach is valid for all cyanide forms except the metal-metal cyanide complexes that are most likely to be present. Acid distillation of cyanide in soil does not accurately measure "total" cyanide, and it fails to estimate cyanide toxicity.

This poster presents an extraction and analysis protocol that selectively extracts and determines the various forms of cyanide that could be present in soil.

Experimental

There are currently no USEPA methods for total cyanide that were written specifically for soil. SW-846 9013 Extraction Procedure for Solids and Oils (Appendix to Method 9010)[1] is the closest to a total cyanide procedure for solid and soil samples. This method states it analyzes "soluble cyanide" without defining what soluble cyanide is.

An extraction and analysis scheme that selectively extracts and determines the various forms of cyanide present in a soil sample was developed. Analytical results demonstrate differentiation of potentially toxic simple and weak metal-cyanide complexes from relatively non toxic cyanides, strong metal-cyanide, and metal-metal cyanide complexes.

ASTM D 6888, ASTM D 7284, and ASTM D 7511 determine available and total cyanide respectively. Available cyanide includes the cyanide ion and metal-cyanide complexes that liberate cyanide as HCN upon acidification. Total cyanide includes available cyanide plus strong metal-cyanide complexes particularly those of iron. Iron cyanide complexes do not liberate cyanide upon acidification and require either boiling and reflux (acid distillation) or UV irradiation to dissociate the cyanide into a measurable form. ASTM D 7284[2], D 6888[3] and D 7511[4] are flow injection gas diffusion amperometric methods. An aqueous sample is injected into an acidic stream where cyanide in the sample converts to HCN. The HCN diffuses across a membrane into a basic stream and is converted back into the cyanide ion. The cyanide ion contacts a silver electrode oxidizing the silver and generating electrons. The electrons generated are proportional to the cyanide concentration. ASTM D 7284 and D 6888 employ acidification alone and measure available cyanide. ASTM D 7284 determines total cyanide following a preliminary manual acid distillation.

Experimental

ASTM D 7511 employs a UV irradiation step to dissociate cyanide from the strong metal-cyanide complexes, such as iron cyanides, eliminating the need for a preliminary distillation. After UV irradiation, the sample stream is treated identically to ASTM D 6888 and measures the iron complexes and all available cyanide.

ASTM D 6888 and D 7511 gas diffusion amperometry methods are unique in that they don't require acid distillation to separate cyanide from the sample matrix; un-distilled extracts can be determined by direct injection. These methods make it possible to "speciate" available from total cyanide by extraction, followed by direct injection into the analyzer.

Results and Discussion

Extraction and Analysis of Chemical Forms of Cyanide from Soil and Solid Waste

Insoluble cyanide complexes, such as Prussian Blue, are bound to particulate matter or soil particles and are not quantitatively recovered by distillation procedures. A sodium hydroxide extraction followed by a total cyanide analysis using ASTM D 7511, completely recovers all cyanides. A commercial cyanide in soil quality control (QC) sample[5] and laboratory prepared sand fortified with Prussian Blue were extracted in buffered extraction solutions ranging from pH 2 to pH 14. Once extracted, samples were immediately filtered and analyzed for total cyanide by ASTM D 7511 (data is presented in Figure 1). At pH 9.2 almost all of the cyanide from the QC sample is recovered but very little of the Prussian Blue. At pH 14, the Prussian Blue is completely recovered. Thus it is possible to extract and analyze the different forms of cyanide complexes. A pH 14 extraction solution can be analyzed for available cyanide by ASTM D 6888 and "true total" cyanide by ASTM D 7511 simultaneously as described previously[4].

The following extraction protocol was developed for analysis of available and total cyanide in soil and solid waste. This simple extraction followed by analysis by gas diffusion amperometry methods on the CNSolution™ 3100 provide a rapid and accurate assessment of cyanide species and relative concentrations in soil. With these data, cyanide mobility and toxicity can be estimated.

Extraction Procedure for Available and "True Total" Cyanide

1. Weigh 1.00 gram sample into a 25 mL centrifuge vial and add 10 mL of 1 N NaOH.
2. Shake for 10 minutes, centrifuge, and immediately filter into a 200 mL volumetric flask.
3. Dilute to the mark with reagent water and mix. Protect from light.
4. Determine available and "true total" cyanide by ASTM D 6888 and ASTM D 7511.

Figure 2 compares the total cyanide recovered from a commercially available quality control standard by distillation and analysis by ASTM D 7284 to the total cyanide recovered by pH 14 extraction and analysis by ASTM D 7511.

Figure 1. Total Cyanide Recovery from Extraction Solutions of (pH 2 to 14) Soil QC Samples and Prussian Blue Fortified Sand Samples

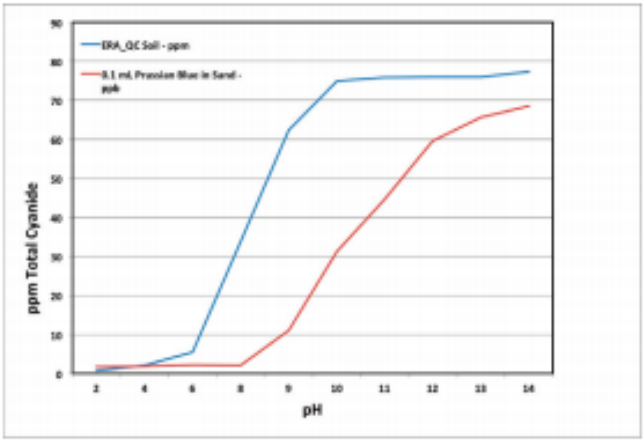
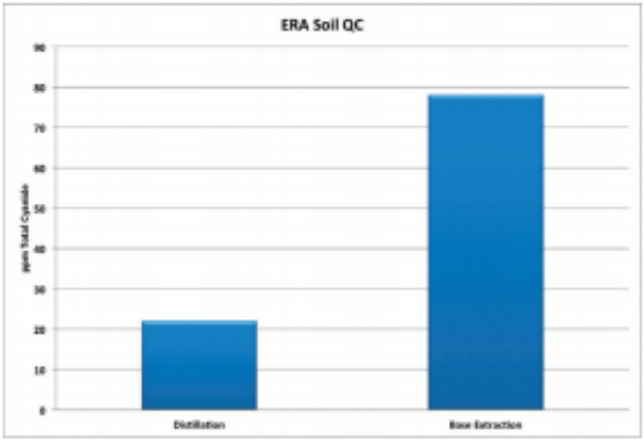


Figure 2. Comparison of Total Cyanide Recovered by Acid Distillation and Alkaline Extraction



Results and Discussion

Figure 3. Comparison of Total Cyanide Recoveries from Prussian Blue Spiked Sand Obtained by Acid Distillation and Alkaline Extraction

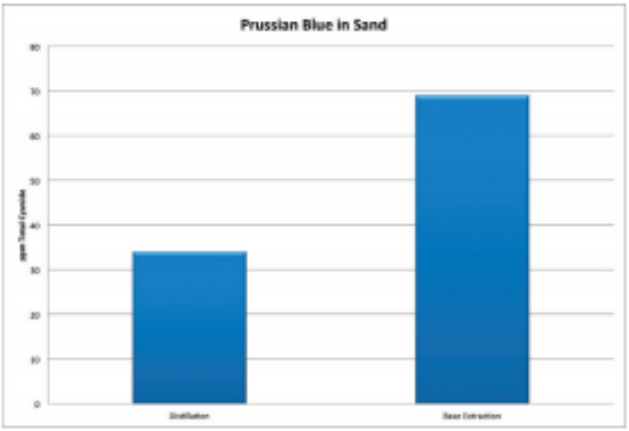


Figure 4. Recovery of Prussian Blue Cyanide in Various Soil Matrices by Extraction at pH 14

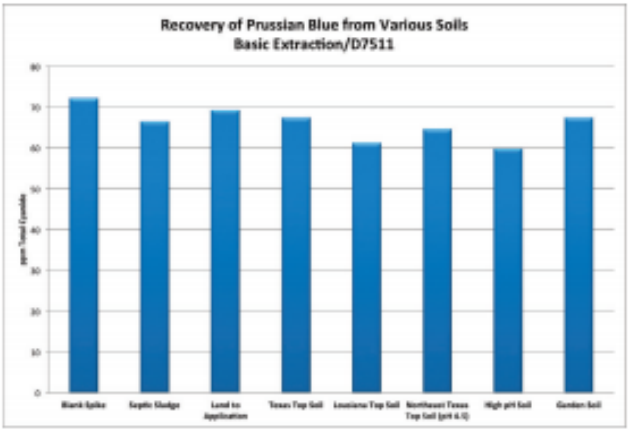


Figure 3 compares the recovery of a Prussian Blue fortified reagent sand by distillation and analysis by ASTM D 7284 to total cyanide recovered by a pH 14 extraction and analysis by ASTM D 7511. Approximately 3-4 times more cyanide was recovered from the soil using alkaline extraction versus acid distillation.

To demonstrate applicability of the pH 14 extraction, seven soils from various locations were characterized then fortified with a known concentration of Prussian Blue. The data is summarized in Figure 4.

Summary & Conclusions

Acid distillation procedures commonly used for determination of total cyanide in soil are inaccurate. Acid distillation only partially recovers insoluble metal-metal cyanide complexes. Extraction with a basic solution quantitatively recovers cyanide. Extraction at high pH followed by analysis with gas diffusion amperometry methods quantitatively recovers all cyanide and enables "speciation" of the various cyanide forms present in a soil or solid waste sample.

References

1. U.S. EPA Method 9013A Cyanide Extraction Procedure for Solids and Oils, U.S. EPA Office of Solid Waste SW-846 Manual, Nov. 2004.
2. ASTM D 7284-08 Standard Test Method for Total Cyanide in Water by Midi or Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection, ASTM International, West Conshohocken, PA, www.astm.org.
3. ASTM D 6888-09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection, West Conshohocken, PA, www.astm.org.
4. ASTM D 7511-12 Determination of Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection, ASTM International, West Conshohocken, PA, www.astm.org.
5. Environmental Resource Associates, Cyanide in Soil lot# D077-541, ww.eraqc.com
6. OI Analytical Application Note #3793, Simultaneous Analysis of Available and Total Cyanide by Gas Diffusion Amperometry Methods USEPA OIA-1677 and ASTM D 7511-12.

O·I·Analytical
a xylem brand
www.oico.com

Sinkhole Hazard Assessment Based on In-Situ Monitoring Soil Strain Using BOTDR, TDR, and GPR Techniques

Yongli Gao

Abstract

Sinkholes are closed depressions on land surface and serve as direct links between the surface and the underlying aquifers. Soil void can form abruptly and then expand progressively until a sinkhole develops. The goal of this research is to develop a cost-effective and efficient method to monitor the soil void formation and propagation, which would potentially prevent and greatly reduce damages caused by future sinkhole collapses. Recent monitoring methods include Ground Penetrating Radar (GPR), inclinometers, Interferometric Synthetic Aperture Radar (InSAR), real-time water pressure monitoring in karst opening, the Brillouin Optical Time Domain Reflectometry (BOTDR), and Time Domain Reflectometry (TDR). The unique features of the BOTDR and TDR techniques such as distributed measurement, long distance range, high resolution, and remote monitoring make them more effective to monitor soil voids and sinkhole development. An experimental study of monitoring the process of sinkhole collapse using BOTDR technology demonstrates that in-situ measurements of strains in different soil layers are good indicators of vertical disturbance in soil. Time series of optical fiber strain analysis exhibit the progress of horizontal disturbance in soil. GPR and In-situ monitoring of soil strain using TDR technique were applied in several karst areas in China. These two methods are more cost effective. GPR can also be used to detect near surface soil voids in a more effective and timely manner.

(Related Session: Academic Research Topics in Environmental Measurement and Monitoring)

Summer Surface Albedo Evolution of Arctic Sea Ice –A Case Study from Ice Stations during 4th CHINARE in 2010

Wentao Xia

Abstract

Assessing Arctic snow/ice surface albedo change is essential to understand local energy budget and ice/albedo feedback under global warming scenario. In-situ measured albedo data played essential role for large scale remote sensing monitoring of albedo change by providing ground truth reference. The direct analysis can also give substantial information for the spectral albedo change variation by time location and object been observed. The case study for the in-situ albedo measurement during the long term ice station of 4th Chinese Arctic Research Expedition (CHINARE) with two portable spectroradiometers collecting data for snow and melt pond objects in 7 low latitude short term ice stations and 1 high latitude ice station.

Results showed the changes of surface albedo for various ground objects in different latitude, and the rapid reduction of albedo in the summer melt season. The snow albedo tend to be 0.65~0.69 in the low latitude and marginal ice zone, and reduces from 0.86 to 0.67 in one week during the high latitude long-term ice station. The melt pond object tend to be various, there are water, refrozen ice surface, and sometimes-snow covering the melt pond. The melt pond snow are only seen in the long term ice station, which have albedo of 0.75 to 0.55 in one week. The melt pond ice object tend to have a 0.38 to 0.61 albedo, which varies greatly in different latitudes. The melt pond water tend to have a higher albedo of 0.27, versus the sea water albedo of 0.18. Such rapid decreasing of sea albedo in polar region and marginal ice zone contribute much to the surface ice/albedo feedback and could significantly contribute to the rapid shrinking summer sea ice extent in Arctic.

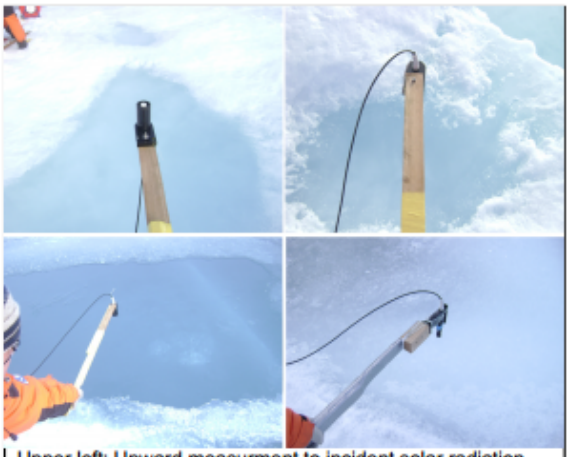
(Related Session: Academic Research Topics in Environmental Measurement and Monitoring)

Abstract

The case study for the in-situ albedo measurements during the 4th Chinese Arctic Research Expedition (CHINARE) with two portable spectroradiometers collecting data for snow and melt pond objects in 7 short term ice stations and 1 high-latitude long term ice station, to observe the changes of surface albedo for various ground objects in different latitude, and the rapid reduction of albedo in the summer melt season.

Results show that the snow albedo tends to be 0.65~0.69 in the low latitude and marginal ice zone, and reduces from 0.86 to 0.67 in one week during the high latitude long-term ice station. The melt pond objects are water, refrozen ice surface, and snow cover on ice. The melt pond snow was only seen in the long term ice station, with albedo reduced from 0.75 to 0.55 in one week. The melt pond ice had albedo 0.38 to 0.61 and varied greatly in different latitudes. The melt pond water had albedo of 0.27, lager than the 0.18 of sea water albedo.

Such rapid decreasing of sea ice ice albedo and evident difference in polar region and marginal ice zone contribute much to the surface ice/albedo feedback and rapid shrinking summer sea ice extent in Arctic.



Upper left: Upward measurment to incident solar radiation
Upper right: Downward measurment to exitance radiation
Down left: Melt pond with deep water
Down right: Refrozen melt pond with thick ice

Background

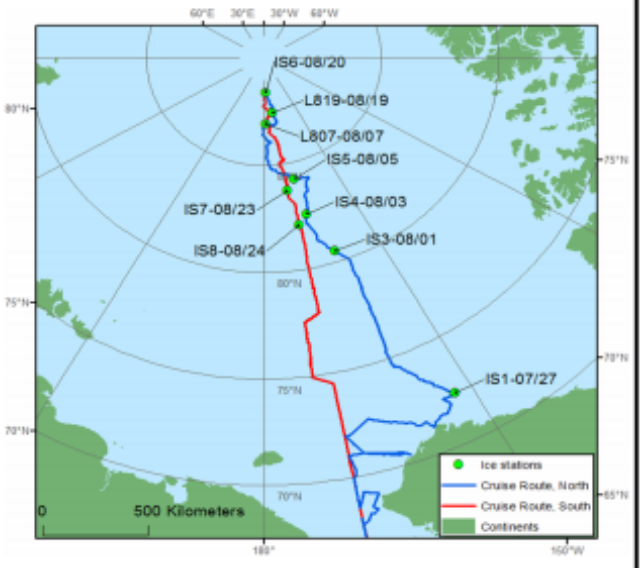
In Arctic summer, highly-scattering, snow-covered sea surface ice turns into a combination of wet snow, decomposed-granular ice, bare ice, melt ponds and leads. Such melting process significantly lowers surface albedo, which is generally defined as the ratio of solar energy directed upward over energy incident upon the same surface. Such reduction of surface albedo plays one major role in the local heat budget, causing areal and thickness regression of Arctic sea ice cover, and amplifies the well-defined ice/albedo feedback.

As a case study, in-situ observations of the 7 short-term ice stations and 1 long term ice station of CHINARE 2010 located from marginal ice zone with the latitude of 72°N, toward the North Pole around latitude of 87°N. These measurements provide opportunity to observe the rapid changing sea ice albedo across distinctly different area of Arctic ice pack. As the measurements spanning across the Pacific sector of Arctic, they would provide ground truth data to be up-scaled to and referenced by satellite imagery.

Fieldworks

With two Analytical Spectral Devices' (ASD) Field Spec® 3 portable spectroradiometer devices. The short term ice stations are denoted by time sequence, from IS-1 to IS-8. The long term ice station was conducted from Aug 09 to Aug 19, and is denoted by date as L809 (Aug 9), L811 (Aug 11), etc.

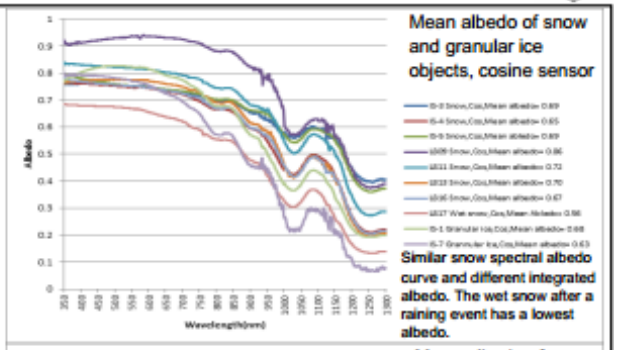
Three types of sensors were used to collect radiation energy. The sensors with 180 degree (cosine) and 5 degree field of view (FOV) saw most application during the radiometric measurements, and the one with 25 degree FOV was mainly used in the IS-1 for comparison. Spectral radiance/reflectance was measured at the 350nm - 2500nm spectra with the spectral resolution of 1nm. The device can be set to measure the radiance or measure the spectral reflectance by calibrating with white reference. Most radiometric measurements were conducted for melt ponds profiles and surrounding snow/granular ice, which were mainly conducted with hand held measurement, by holding a pole attached with the sensor, walking along a profile. The incident solar radiation was measured by upward-looking measurement to the sky, or by measuring the white reference. Objects measured were the regular snow cover, decomposed granular ice (formed by surface layer of bare sea ice decomposed by melted snow cover), sea ice (specifically refers to the bare ice exposed by snow pits), sea water, snow cover on melt pond ice, ice on melt pond water, water in melt pond.



Ice Stations (IS)	Denoted as	Measurements Start		Measurements End		Geographic Coordinate	
		Date	Time(UTC)	Date	Time(UTC)	Longitude	Latitude
1st Short term IS	IS-1	07/27	01:00	07/27	05:00	152°34'W	72°18'N
3rd Short term IS	IS-3	08/01	21:54	08/01	22:11	161°14'W	80°29'N
4th Short term IS	IS-4	08/03	21:18	08/03	22:17	165°32'W	82°36'N
5th Short term IS	IS-5	08/05	02:35	08/05	03:09	167°08'W	84°10'N
Long term IS, 2nd day	L809	08/09	07:13	08/09	08:44		
Long term IS, 5th day	L811	08/11	21:51	08/11	22:29		
Long term IS, 6th day	L812	08/12	21:14	08/12	22:57	Continuously drifting, from	
Long term IS, 7th day	L813	08/13	21:10	08/14	03:26	170°22'W, 86°48'N (L807) to	
Long term IS, 10th day	L816	08/16	21:51	08/17	01:05	172°16'W, 87°20'N (L819).	
Long term IS, 11th day	L817	08/17	21:08	08/18	04:20		
Long term IS, 12th day	L818	08/18	21:34	08/18	22:34		
6th Short term IS	IS-6	08/20	03:20	08/20	03:57	177°09'W	88°22'N
7th Short term IS	IS-7	08/23	07:33	08/23	09:08	170°38'W	83°45'N
8th Short term IS	IS-8	08/24	01:54	08/24	03:28	169°31'W	81°57'N

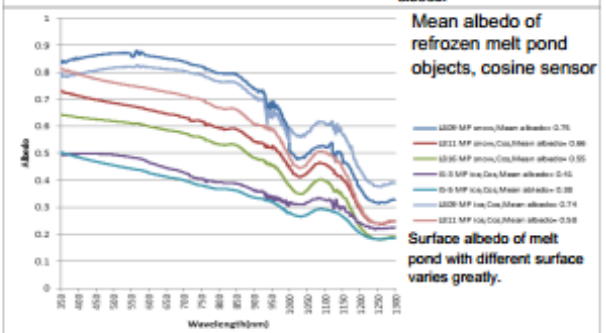
The spectral albedo of a particular wavelength (λ) is defined as Eqn (1)
The wavelength-integrated albedo in this study is defined as Eqn (2):
Where F↑(λ) and F↓(λ) is the exitance and incident irradiation.

$$\alpha(\lambda) = \frac{F\uparrow(\lambda)}{F\downarrow(\lambda)} \quad (1) \qquad \alpha(\lambda)_t = \frac{\int_{350}^{1300} F\uparrow(\lambda)d\lambda}{\int_{350}^{1300} F\downarrow(\lambda)d\lambda} \quad (2)$$



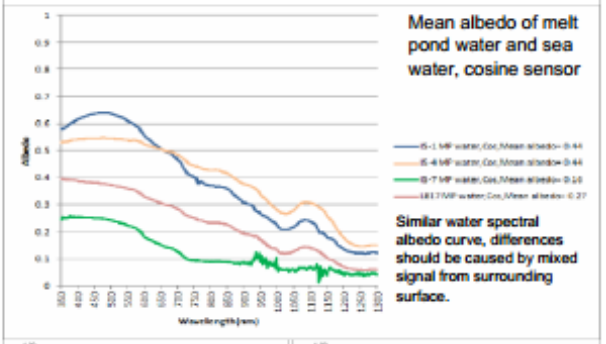
Mean albedo of snow and granular ice objects, cosine sensor

Similar snow spectral albedo curve and different integrated albedo. The wet snow after a raining event has a lowest albedo.



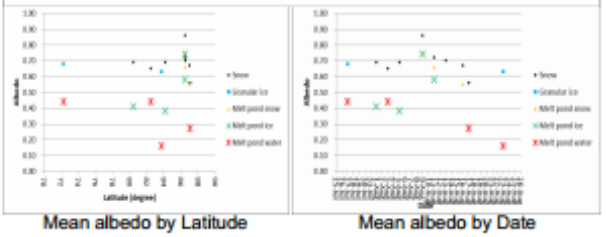
Mean albedo of refrozen melt pond objects, cosine sensor

Surface albedo of melt pond with different surface varies greatly.



Mean albedo of melt pond water and sea water, cosine sensor

Similar water spectral albedo curve, differences should be caused by mixed signal from surrounding surface.



Mean albedo by Latitude

Mean albedo by Date

Summary and Conclusion

1. Main sources of error are incompatibility of different sensor FOV (directional scattering and mixed signal), inconsistency of referencing incident solar radiation measurements, and systematically instrument error.

2. The albedo changes of melt pond tend to be more complicated, due to different types of objects related to melt ponds, such as refrozen surface ice and snow on ice, melting pond surface with thin water layer, and deep melt pond water.

3. Surface albedo of snow/granular ice surface and melt pond rapidly decreases with time in both visible and NIR bands. The difference of albedo is also significant on various latitudes which located in rapid melting marginal ice zone and first-year ice.

4. Highly varied albedo of similar surface objects proposed much challenge to remote sensing up-scaling and model parameterization.

SW-846: What You Need to Know

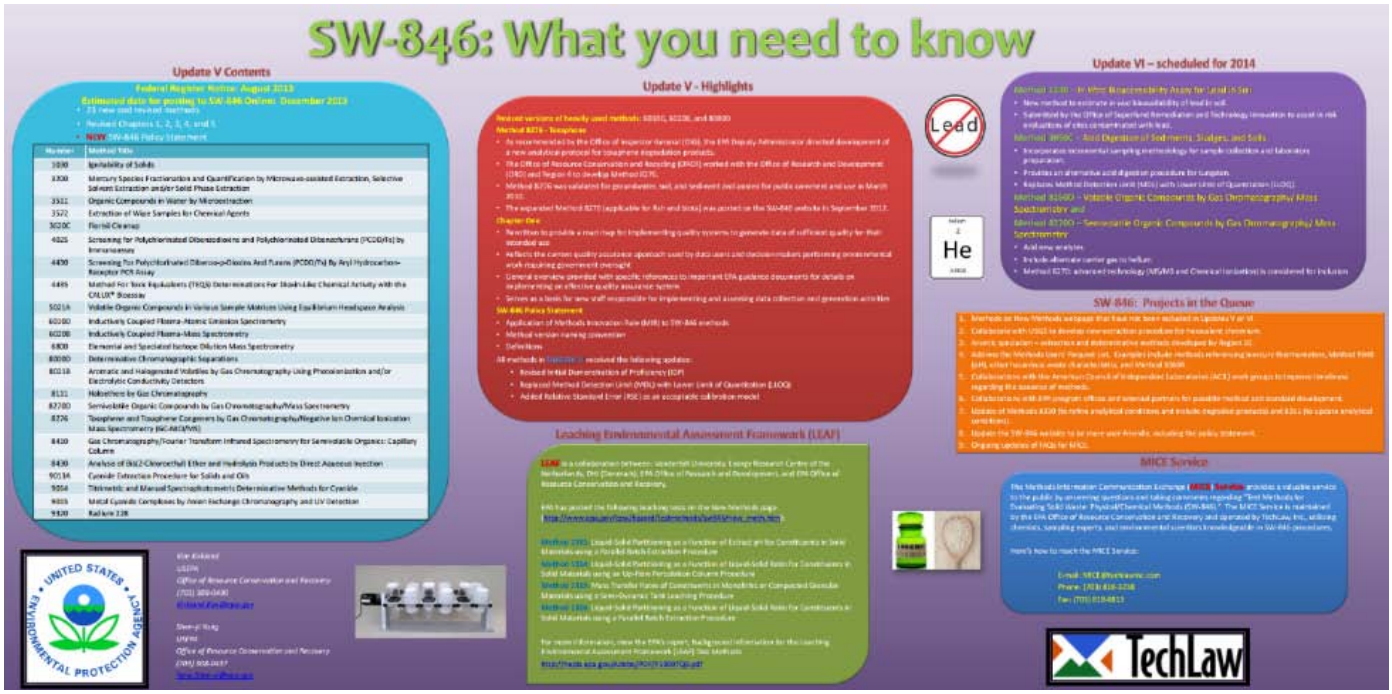
Amy Dahl

Abstract

The purpose of this poster is to provide the public with current information regarding "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," also known as SW-846, published by EPA's Office of Resource Conservation and Recovery (ORCR). Topics to be covered will include:

- Final Update V for SW-846 – highlights of important changes to methods and chapters, including 8000, 5021, 6010, 6020, and Chapters 1 and 2
- Update VI – target list
- New lead bioaccessibility Method 1340
- Helium shortage and its impact on SW-846
- Hexavalent chromium method development
- Updated toxaphene Method 8276 to include fish tissue
- Leaching Environmental Assessment Framework – summary of latest SW-846 methods 1313, 1314, 1315, and 1316 for characterizing leaching behaviors of waste materials developed in collaboration with Vanderbilt University
- Methods Information Communication Exchange (MICE) Service – updated frequently asked questions (FAQs) online

(Related Session: EPA Approval of Innovative Approaches to Monitoring)


SW-846: What you need to know
Update V Contents
Update V - Highlights
Update VI – scheduled for 2014
SW-846: Projects in the Queue
Leaching Environmental Assessment Framework (LEAF)
MICE Service
Lead
He
TechLaw

Performance of Method 8270 Using Hydrogen Carrier Gas on Bruker SCION GC-MS

Ed George, Bruker Corporation

Abstract

USEPA Method 8270 for semi volatiles is used by laboratories to measure a mixture of acids, bases, and neutrals in a wide variety of matrices. Sample extracts can range from clean water to sludge coming from superfund clean-up sites. The complexity of these extracts combined with the increased sensitivity of newer GC/MS systems (lower reporting limits) demand a robust instrument that is easy to operate and maintain.
Adding to method complexity is the uncertainty in both cost and supply of helium, forcing some laboratories to consider hydrogen as carrier gas. Hydrogen is not an inert gas- it is reactive and can be an explosion hazard if allowed to build up in either the GC oven or manifold of a mass spectrometer. The Bruker SCION GC-MS Hydrogen Carrier Package will ensure safe routine operation, with little or no performance change for EPA Method 8270. A unique axial ion source design provides excellent robust operation and minimizes unwanted protonation and spectral distortions. In addition, the Gas Chromatograph with Bruker Split/Splitless (SSL) injector and inert pathway prevent compound degradation and reactions with hydrogen.

Analysis of PCB Arochlors Utilizing GC Tandem Mass Spectrometry

Dale Walker, Agilent Technologies

Abstract

The poster demonstrates the applicability of GC tandem mass spectrometry to monitor exposure to PCB Arochlors in matrix. The same methodology is also applied to matrices such as gas-phase air, particulate phase air, sediment and sediment pore water. Human health studies concluded that PCB Arochlors are probable carcinogens and exposure can also result in deleterious effects on the immune, reproductive and endocrine systems.

Traditionally the analysis for PCB Arochlors is done by GC Electron Capture Detector (ECD) methodology. Historically a traditional single stage GCMS system has lacked the ability to achieve the detection limits of an ECD due to matrix interferences.

In this study we employed the use of a GC-tandem mass spectrometry (GC-MS/MS) The GC-MS/MS not only achieved but surpassed the required detection limits of the traditional GC ECD detector. In addition to achieving the detection limits the system also offers confirmation of the compound by using the individual Congener groups to positively identify the compounds by utilizing both the GC retention times and the MRM transition for the Arochlor. Comparing the data with that obtained via GC-ECD suggests that GC-MS/MS is an appropriate tool and offers a confirmatory technique. Labs may now expand GC-MS/MS for the analysis of PCB Arochlors in matrix.

(Related Session: Operational and Advocacy Issues Impacting the Environmental Laboratory Industry)

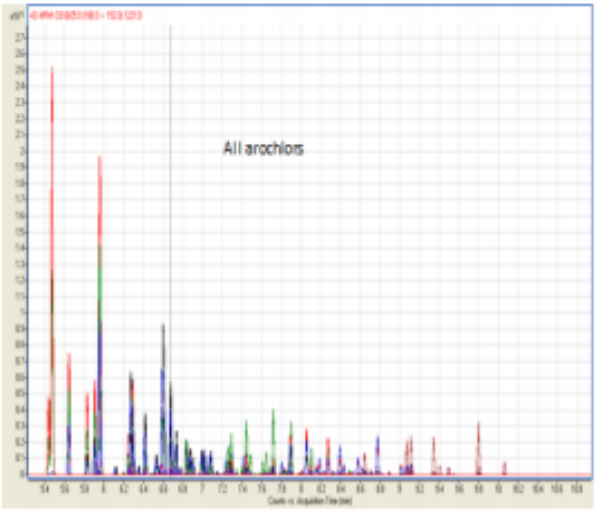
Introduction

Poly chlorinated biphenyls or PCB Aroclors are ubiquitous synthetic entities not known to naturally occur in the environment. These compounds were synthesized primarily for use as coolants and insulating fluids in electrical equipment. Initially PCB Aroclors were valued for their chemical stability however, the fact that they are so stable resulted in environmental persistence and ultimately, a ban on PCB production

Aroclors are PCB mixtures that were produced from approximately 1930 to 1979. Aroclor is one of the most commonly known trade names for PCB mixtures. There are many types of Aroclors and each has a distinguishing suffix number that indicates the degree of chlorination. The numbering standard for the different Aroclors is as follows:
The first two digits generally refer to the number of carbon atoms in the phenyl rings (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture. For example, the name Aroclor 1254 means that the mixture contains approximately 54% chlorine by weight.

Herein is a presentation of Data collected on Agilent's GC-tandem mass spectrometer GCMS/MS 7000B which offers both superior sensitivity and selectivity for the analysis of PCB Aroclors in matrices The purpose of the analysis is to quantitatively identify the amount of PCB Aroclors present in the matrix

.



Instrument Parameters

Deca	497.7	Wide	427.7	Wide	20	25
Nona	461.7	Wide	391.8	Wide	20	25
Octa	427.8	Wide	357.8	Wide	20	25
Hepta	393.8	Wide	323.9	Wide	20	25
Hexa	359.8	Wide	289.9	Wide	20	25
Penta	325.9	Wide	255.9	Wide	20	25
Tetra	291.9	Wide	222	Wide	20	25
Tri	258	Wide	186	Wide	20	25
Di	222	Wide	152	Wide	20	25
Mono	188	Wide	152	Wide	20	25
Acenaphtene D10	164	Wide	160	Wide	20	50
Acenaphtene D10	164	Wide	82	Wide	20	50

:

GC-MS/MS Conditions
MMI Inlet (He)
Injection Volume: 1 µL
Mode: splitless injection
Injector split/splitless: 250 °C

Column #1
HP5MSUI (30 m x 250 µm x 0.25 µm)
Constant Flow: 0.72 mL/min

Oven Program:
70 °C for 1.5 min
16 °C/min to 200 °C for 1. 5 min

MS Transfer Line: 280 °C

EI Mode, Source: 280 °C

Run Time: 10.125 min

Results and Discussion

Analytical Method

A Multi point calibration curve was used for unknown's analysis and quantification. The PCB Aroclor calibration concentrations are as follows:
5ng/ml, 10ng/ml, 20ng/ml, 40ng/ml, 50ng/ml

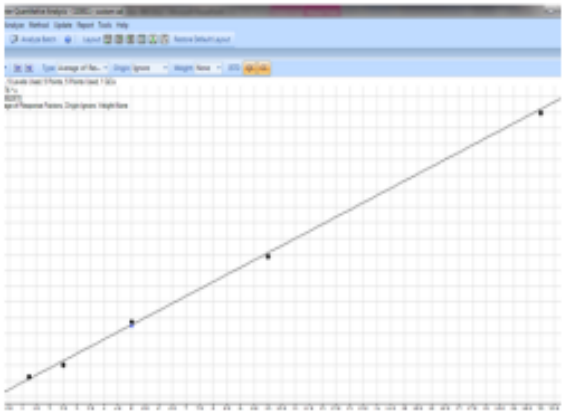
A single time segment was used to monitor the Mono through Nona transitions.

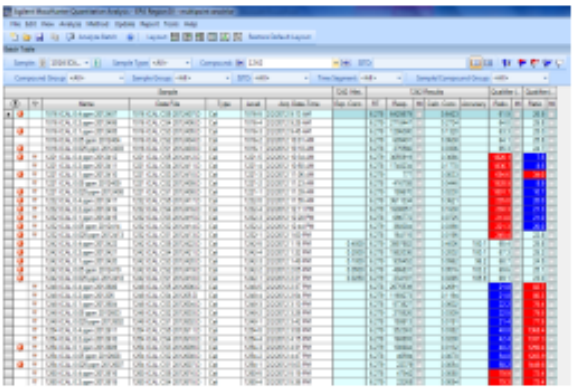
For Mass Quantification the Relative Response Factor (RRF) method was used to determine the amount of each Aroclor present in the sample. Mass quantification was on the sum of all relevant transitions for the particular Aroclor

Quantification is based on the following:
(Formula based on injection and quantification of a known mass of Internal Standard (IS) and a calibration standard containing individual Aroclors of interest, an RRF was calculated for each Aroclor.

All individual Aroclors were then combined into a single calibration curve Table which is used in the analysis of unknowns) the assumption used is that the RRF stays the same between the calibration standard and sample. Example RRF calculations are as follows:

From the calibration standard data:
RRF Aroclor 1260 = (mass 1260 in calibration standard/area 1260 in calibration standard) /(mass IS in calibration standard/area IS in calibration standard)
From the sample, data rearranging the RRF equation to solve for Aroclor mass and plugging in the RRF calculated above: Mass Aroclor 1260 = (RRF Aroclor 1260)x(area Aroclor1260 in sample)x(mass IS in sample/area IS in sample





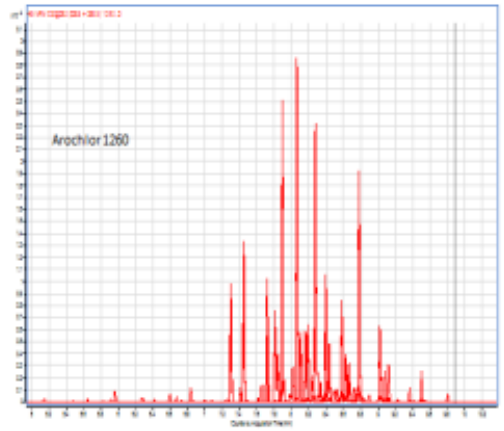
9 unique Aroclor standards were used for acquiring the calibration curves. When analyzing unknown samples there is often co-eluting Aroclors. In these instances a subset of the Aroclors total areas is used to isolate and identify the Aroclor from other Aroclors.

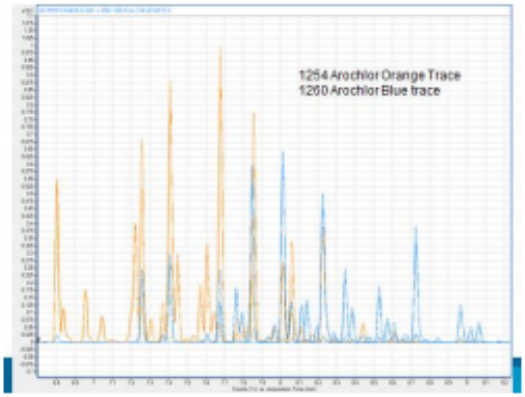
In these instances it is necessary to use both the Quantitative and Qualitative program in Mass Hunter to make the appropriate determination as to what co-elution's exist and the effect that it has on the concentration of a particular Aroclor.

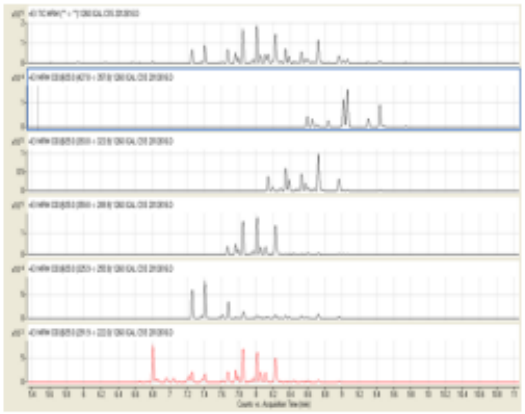
Based on previous work by Dr. Frame[1] the following table shows the predicted ratios of 5 individual Aroclors.

Table 3. Typical PCB Homologue Composition (% wt) of Five PCB Aroclors PCB Homologue	Aroclor 1016 (%)	Aroclor 1242 (%)	Aroclor 1248 (%)	Aroclor 1254 (%)	Aroclor 1260 (%)
Mono-CB	0.7	0.8	0	0	0
Di-CB	17.8	18.0	0.4	0.2	0.1
Tri-CB	54.7	44.9	22.0	1.3	0.2
Tetra-CB	26.8	32.8	56.6	18.4	0.9
Penta-CB	0.5	3.4	19.6	53.0	8.6
Hexa-CB	0	0.3	2.0	26.8	43.4
Hepta-CB	0	0	0.6	0.7	36.6
Octa-CB	0	0	0	0	8.3
Nona-CB	0	0	0	0	0.7
Deca-CB	0	0	0	0	0
Percentage	12.00	81.79	8.79	19.73	10.81

Results and Discussion







PCB Aroclors are persistent environmental pollutants. In the United States and other countries around the world, PCBs were widely used as dielectric fluids in transformers and capacitors and also used as coolants. In 1979, PCB production was banned in the late twentieth century.

The work presented herein demonstrates the applicability of GC tandem mass spectrometry to monitor exposure to PCB Aroclors in matrix. The same methodology is also applied to matrices such as gas-phase air, particulate phase air, sediment and sediment pore water. Human health studies concluded that PCB Aroclors are probable carcinogens and exposure can also result in deleterious effects on the immune, reproductive and endocrine systems.

Traditionally the analysis for PCB Aroclors is done by GC Electron Capture Detector (ECD) methodology. Historically a traditional single stage GCMS system has lacked the ability to achieve the detection limits of an ECD due to matrix interferences.

In this study we employed the use of a GC-tandem mass spectrometry (GC-MS/MS) The GC-MS/MS not only achieved but surpassed the required detection limits of the traditional GC ECD detector. In addition to achieving the detection limits the system also offers confirmation of the compound by using the individual Congener groups to positively identify the compounds by utilizing both the GC retention times and the MRM transition for the Aroclor. Comparing the data with that obtained via GC-ECD suggests that GC-MS/MS is an appropriate tool and offers a confirmatory technique. Labs may now expand GC-MS/MS for the analysis of PCB Aroclors in matrix.

Bibliography

1. Frame et al. (1996) has reported on the detailed analyses of the PCB congener distributions present in Aroclors 1016, 1242, 1248, and 1254. Because of variation to the chlorination process during chemical synthesis, no two batches of the same Aroclor had identical PCB congener distributions. In fact, substantial differences in congener profiles between batches of the same Aroclor could lead to significant differences in biological effects (Kodavanti et al., 2001).
ons

Comparison of US EPA 245.7 to ISO 17852 and ISO 12846 Using CVAAS and CVAFS

David Clarke

Abstract

The methods governing the quantification of Hg in drinking, surface, ground, and waste water are promulgated by the US EPA and based on cold vapor sample introduction. Similar methods can be found in the EU; however, these methods are published by the International Standards Organization. In this study two separate comparisons are made between US EPA and similar ISO methods. The first comparison is made between US EPA 245.7 and ISO 17852 using cold vapor atomic fluorescence. The second comparison is made between US EPA 245.7 and ISO 12846 using cold vapor atomic absorption. The objective of this study is to highlight advantages and disadvantages of each of these methods to both atomic absorption and atomic fluorescence mercury analyzers. Several sample preparation differences are highlighted and optimized. A groundwater standard reference material (ERM-CA615) was used as a matrix standard.

(Related Session: Topics in Drinking Water)

Complete Determination of Acids, Bases, and Neutrals in Water Using Mixed-Mode Solid Phase Extraction for EPA Method 8270

Xiaoyan Wang

Abstract

An accurate, precise, and cost-effective method has been developed for EPA Method 8270 water analysis using mixed-mode solid phase extraction and GC/MS detection. Compared to liquid-liquid extraction which requires multiple extractions at two pH values and the consumption of a large amount of organic solvents, this newly developed method needs only one extraction at one pH. The overall average recovery and relative standard deviation was found to be 94.7% and 3.1% for 137 target analytes and 6 surrogates analyzed in this study. Method detection limits ranged within 0.26-3.08 ppb based on seven replicate extractions of 500 mL fortified reagent water samples. This innovative approach has also been applied to lake water samples with acceptable recoveries and relative percentage differences. High throughout can be achieved by extracting multiple samples simultaneously using SPE manifold with multiple positions.

(Related Session: Advances in Sample Preparation and Clean-up)

Data Quality Screening Using Trend Charts

Roseanne Sakamoto

Abstract

While data validation and quarterly reports are necessary deliverables for long-term project review, they may be of limited use in helping a project manager quickly track the quality of work performed under a Quality Assurance Project Plan (QAPP) in near real time. Trend charts are being piloted in Region 9. They are a visual method for tracking QAPP implementation and the quality of data produced under the QAPP. Trend charts may cover field sampling QC results, analytical laboratory QC and sample results, number of field and laboratory audit findings, and percentage of data validation performed.

Trend charts graphically present what is communicated in data validation reports for specific contaminants of concern. The charts provide information on laboratory performance in calibration, continuing calibration, laboratory control sample, laboratory control sample duplicate, matrix spike, matrix spike duplicate (or deuterated compound recoveries), and blank results. Field sampling performance in duplicate and blank sample collection are also being charted and monitored. Cumulative information on the percent of data validated, audits conducted may also be included. Field and Laboratory QA/QC criteria are based on QAPP and Field Sampling Plan (the +/- 15% or 20% precision and accuracy) established criteria.

By reading the trend charts, anyone, with or without chemistry expertise, may easily, transparently determine whether the project is in conformance with the plans and whether data quality objectives are being met. It is recommended, however, that a chemist be consulted when making a critical decision based on the data provided in the trend charts.

A paper discussing its use may be accessed at: http://www.epa.gov/region09/qa/pdfs/TrendCharting.pdf
-- The opinions expressed in the paper and poster presentation are those of the authors and do not necessarily reflect the view of the US EPA, unless stated otherwise (e.g., requirements, regulatory citation). Mention of any trade names or commercial products does not constitute endorsement or recommendations for use. --

Abstract

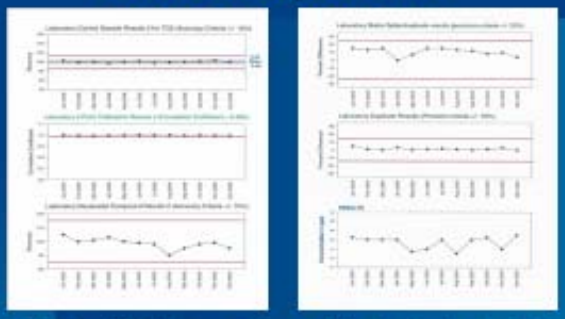
While data validation and quarterly reports are necessary deliverables for long-term project review, they may be of limited use in helping a project manager quickly track the quality of work performed under a Quality Assurance Project Plan (QAPP) in near real time. Trend charts are being piloted in Region 9. They are used as a visual method for tracking QAPP implementation and the quality of data produced under the QAPP. Trend charts cover field sampling, laboratory analysis, number of audit findings, and percentage of data validated.

Trend charts quantitatively, graphically present what is communicated in validation reports for specific contaminants of concern. The charts provide information on laboratory performance in calibration, continuing calibration, laboratory control sample, laboratory control sample duplicates, matrix spike/matrix spike duplicates (or deuterated compound recoveries), and blank results. Field sampling performance in duplicate and blank sample collection are also being charted and monitored. Cumulative information on the percent of data validated, audits conducted also may be included. The QA/QC criteria for all charts are based on the QAPP or Field Sampling Plan (the +/- 15% or 20% precision, accuracy criteria). By reading the trend charts, anyone, with or without chemistry expertise, may easily determine whether the project is in conformance with the plans and whether data quality objectives are being met. It is recommended, however, that a chemist be consulted when making an critical decision based on the data provided in trend charts.

Data Quality Screening and QAPP Oversight Using Trend Charts

- Quick Oversight Tool for Project Managers, QA Officers, Field Samplers, Laboratory Managers
- Verify, Evaluate QAPP Implementation
  - Field Sampling
  - Laboratory Analysis
    - Performance Evaluation Samples
  - Data Validation
  - Audits in Field and Laboratory

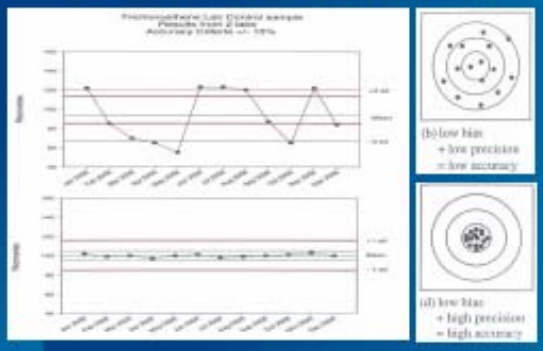
Or a Summary of Core QA/QC Results that Spans a Year:



Results from these QC checks show good performance (within red error bars) or above calibration criteria of >0.995 correlation coefficient (for second chart on left). Review and potentially corrective action should be performed on points that fall outside of error bars or below .995. No corrective action needed for above charts.

Demonstration of Trend Chart Use on Laboratory Control Sample

Corrective Action Needed for Chart on Top



PRP Laboratory QC Results for TCE

(consider validating excursions – highlighted boxes in yellow)



Value of Trend Charts

- Quick visual for use in QAPP implementation oversight; easy to assimilate;
- Self monitoring and tracking performance (short- and long-term trends) of QA/QC conducted by laboratory and field staff, and whether there were excursions from QAPP criteria (e.g., +/- 15%);
- Sources of error, whether field, lab or matrix can easily be determined by aligning charts by date;
- Implement corrective action in lab and field;
- Improved control of data quality;
- Single out of control events fade into background of long-term positive trend – keeps things in perspective;
- Potentially Responsible Party vice-president sold by this feature; stated he never had time to read QTRLY reports or understand them;
- Potential usefulness at public meetings to show overall positive trend where there is concern over an anomalous result.

Trend Charts Convey a Thousand Words...

What are they?

- Plot to present Laboratory QA/QC results graphically as opposed to narrative or tabulated information provided in quarterly reports
- They are a tool for monitoring excursions from control criteria. For our purposes they are generally composed of "limit" lines that shouldn't be crossed over. These lines are based on laboratory and field precision and accuracy criteria established in QA Project Plan.
- Points on the trend charts are obtained from laboratory control charts or validation reports.

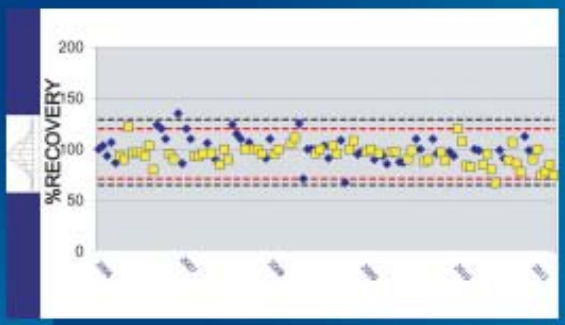
What Would You Prefer to Review?

A 100-page annual report like this that's difficult to assimilate...



Performance Evaluation Sample Results Over 5 Years for Two Laboratories

(see some trending for both)

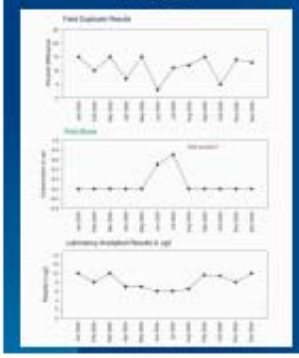


Field QC Samples

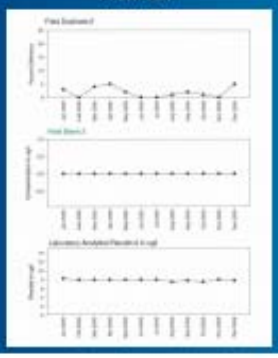
Split Sample Results from Two Samplers

Trainers performance shows much less variability, error introduction.

Novice



Trainer



Other Advantages

- Improved use of resources; focus validation on contaminants of concern, or those instances where conditions are out of control;
- Allows QA Office to spot check sites – offer assistance to Project Manager.

LIMITATIONS

- An effective broad brush tool for identifying sources of error in the field, laboratory or matrix, fine tuned oversight still necessary to determine cause of out of control situations.
- Check with project chemist on the validity of your assumptions before using the data to make decisions.

Response thus Far

- Well received by regulators at site meetings; sought expansion for use at other sites due to ease of over-sight with quarterly reporting;
- Potentially Responsible Party supported use due to ease in interpretation and communication of information; able to target corrective action;
- Contract Laboratory Program (CLP) is finding utility for use in lab oversight;
- Minimal or no added cost to obtain QC information to prepare charts as information is already available in LIMS and through the CLP.

Evaluation of a Device for Preparing Calibrated Air Sampling Tubes That Mimics Real Air Sampling Conditions

Katherine Stenerson

Abstract

Spiking calibration standards onto air sampling tubes in order to generate calibration curves and conduct desorption efficiency and breakthrough studies can be a difficult task. One approach is to inject a liquid standard directly onto sample media using a micro-syringe. However, this technique has a major drawback; the compounds in the calibration standard are dispensed in the liquid form, which does not realistically mimic how the real air samples are taken. For example, in a multi-bed thermal desorption tube if spiking is done directly onto the first adsorbent bed (which is the weakest), some of the compounds in the calibration standard will never be exposed to the later beds, which contain the stronger adsorbents. In a real situation, some compounds always move from the first bed into subsequent beds while sampling is taking place.

Ideally, when preparing calibration standards, the spiking technique used should mimic conditions in which the air sample was taken in the field. A sample prep device, known as ATIS which stands for "adsorbent tube injection system" was specifically designed for the task of spiking air sampling tubes. It incorporates the technique of “flash vaporization” to completely vaporize a liquid calibration standard and transfer it to sampling media, mimicking the behavior of real air samples. The device consists of injection glassware housed in an aluminum block that heats to vaporize the calibration standard. A stream of gas flowing through the injection glassware carries the vaporized compounds onto an adsorbent tube which is attached to the device. The research presented will demonstrate the use of the ATIS, compare the reproducibility of different spiking techniques, and illustrate the different factors that can affect accuracy and precision.

(Related Session: Air Methods/Monitoring)

Evaluation of an Automated Air Sampling System: LESS™

Kyle Hunt, Signature Science LLC

Abstract

Manually collecting SUMMA® canisters or sorbent tubes during vapor intrusion (VI) monitoring typically employs a single device to collect single samples with limited duplicates or distributive pairs. Such labor and equipment intensive sampling provides limits spatial and temporal data while also limiting the capability to record flow rates and sample durations real-time. Signature Science developed LESS™, a fully programmable, constant flow air sampler with an integrated micro-controller and data acquisition system that can collect up to 28 discrete air samples including simultaneous duplicates using a common manifold. Flow rates range from 5-750 mL/min.
To validate this new collection system against traditional technologies, comparison thermal desorption tubes were collected using LESS™ and a manual air sampling pump in a controlled laboratory test against 109 compounds (nC2 – nC12). Individual, duplicate, or distributive volume pair samples were collected to determine recoveries, false-positives, and false-negatives at safe sampling volumes.

Fifty-four (54) of 109 targets were quantified by a third-party NELAC accredited laboratory using EPA's Method TO-17. Remaining analytes were reported as TICs yielding total detections of 103 analytes: the exception being the most volatile hydrocarbons (acetylene, ethylene, ethane, and propane), 1-butanol, and methanol (spiking solvent). False-negatives were observed for 3 compounds at the 1 ppb-v concentration: 2-hexanone (31%), naphthalene (6%), and acetone (3%). Blank samples reported false-positives for acetone, hexachlorobutadiene, 1,2,3 - and 1,2,4-trichlorobenzene, with levels at or near the analytical reporting limit.
At all test concentrations and collection volumes, LESS™ recovered the target analytes at similar precision and accuracy as the traditional manual pump. Recoveries for both were between 80% and 180% with correlations at or above 0.90.

In the spring of 2012, LESS™ was employed in a VI study at Hill AFB in Utah. The study was a long-term characterization of VI over diurnal sampling events across a year to estimate the changes in contamination levels over time. Typically, sampling methods for VI collect infrequent samples using SUMMA® canisters over a 24-hour time period. This approach produces limited sample data that may not accurately assess VI occurrence or the magnitude. Using a LESS™ manifold based sampler, continuous collection (at 4-hour intervals) over a five-week period showed the utility of dense sampling and the results demonstrated periods of vapors associated with VI in February and March, with less frequency episodes toward the end of sampling period.
For each collection event described above, this poster will present the data and summarize the findings.

(Related Session: Air Methods/Monitoring)

Extraction Methods Versus Phenol Recoveries in a Single-Blind Performance Evaluation Study

Amanda Cover, Environmental Standards

Abstract

Twelve commercial laboratories participated in an annual single-blind performance evaluation (PE) study as required under an industrial client's corporate laboratory program. The PE study was performed to determine the accuracy of the laboratory reported results when compared to known values and to ensure compliance with client analytical and reporting quality assurance requirements. A review of the semi volatile organic compound (SVOC) results performed by SW-846 Methods 8270C and 8270D exhibited a large discrepancy in the reported results for phenol. Upon, further review, it was discovered that the laboratories that prepared the SVOC PE sample using Method SW-846 3520C had higher phenol recoveries and higher recoveries for surrogate compound phenol-d5 than the laboratories that utilized SW-846 Method 3510C.

This presentation will focus on the SVOC preparation methods SW-846 Methods 3510C and 3520C and their impact on phenol and substituted phenol recoveries in the single-blind performance evaluation (PE) Study. (Related Session: Advances in Sample Preparation and Clean-up)

Abstract

Twelve commercial laboratories participated in an annual single-blind performance evaluation (PE) study as required under an industrial client's corporate laboratory program. The PE study was performed to determine the accuracy of the laboratory reported results when compared to known values and to ensure compliance with client analytical and reporting quality assurance requirements. A review of the semivolatile organic compound (SVOC) results performed by SW-846 Methods 8270C and 8270D exhibited a large discrepancy in the reported results for phenol. Upon, further review, it was discovered that the laboratories that prepared the SVOC PE sample using Method SW-846 3520C had higher phenol recoveries and higher recoveries for surrogate compound phenol-d_5 than the laboratories that utilized SW-846 Method 3510C.

This poster will focus on the SVOC preparation methods SW-846 Methods 3510C and 3520C and their impact on phenol and substituted phenol recoveries in the single-blind performance evaluation (PE) Study.

Introduction

- PE samples are test samples that are prepared by spiking known concentrations of select analytes into a well-characterized matrix. Single-blind PE samples are submitted for analysis to participating laboratories who are aware that the samples are PE samples, but do not know the PE samples' analytes or true concentrations. In this study, the PE samples submitted to the laboratories were analyzed for volatile organic compounds (VOCs), SVOCs, polychlorinated biphenyls (PCBs), metals, mercury, and cyanide.

- In the SVOC fraction of this PE study, SW-846 Method 3520C, the continuous liquid-liquid extraction procedure, was observed to have better recoveries for the three laboratories that prepared the SVOC PE sample using this method. Table 1 summarizes the phenol, substituted phenol, and surrogate compound phenol-d_5 percent recoveries for all participating laboratories.

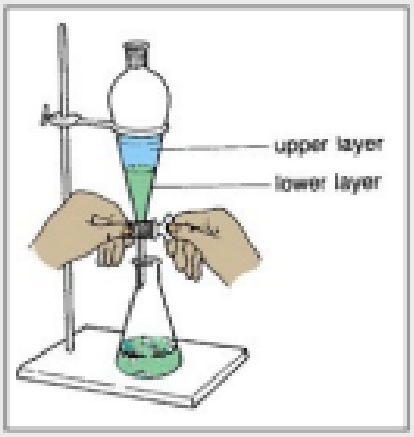
Table 1. PE Study Recoveries and and Associated Preparation Methods

Laboratory	Prep Method	Phenol %Rec in PE	2-chlorophenol %Rec	4-chloro-3-methylphenol %Rec	2-methylphenol %Rec	Phenol -d_5 %Rec
SepFun 1	3510C	36%	78%	101%	68%	36%
SepFun 2	3510C	22%	69%	84%	54%	21%
SepFun 3	3510C	30%	74%	81%	61%	32%
SepFun 4	3510C	28%	62%	70%	55%	25%
SepFun 5	3510C	32%	85%	101%	74%	33%
SepFun6	3510C	28%	78%	84%	68%	26%
SepFun 7	3510C	32%	78%	101%	68%	33%
SepFun 8	3510C	34%	66%	91%	65%	39%
SepFun 9	3510C	14%	48%	64%	38%	13%
L/L 1	3520C	71%	60%	85%	82%	86%
L/L 2	3520C	76%	76%	91%	75%	74%
L/L 3	3520C	101%	102%	113%	102%	110%

SepFun = Separatory Funnel Extraction
L/L = Liquid-Liquid Extraction

SVOC Preparation Methods Overview

- **SW-846 Method 3510C – Separatory Funnel Extraction Method**
  - This preparation method utilizes shaking, venting, and settling to extract organic compounds in the sample to the solvent layer. The sample pH is adjusted to pH < 2 and serially extracted three times with methylene chloride using a separatory funnel. The sample pH is then adjusted to pH > 11, and the serial extraction process is repeated. The Kuderna-Danish Technique is used to concentrate the samples to the required final extract volume. This extraction process takes 30 - 45 minutes to complete.



Above: Separatory Funnel
Below: Continuous Liquid-Liquid Extractor

- **SW-846 Method 3520C – Continuous Liquid-Liquid Extraction Method**
  - This preparation method utilizes heat and condensation to extract organic compounds in the sample to the solvent in the boiling flask. The sample pH is adjusted to pH < 2 and is transferred to the extractor. The boiling flask contains methylene chloride. The sample is extracted for 18 - 24 hours allowing more contact time between solvent and sample. The pH of the sample is adjusted to pH > 11, and the extraction process is repeated. The Kuderna-Danish Technique is used to concentrate the samples to the required final extract volume. Table 2 provides sample preparation information, where provided, for all laboratories.

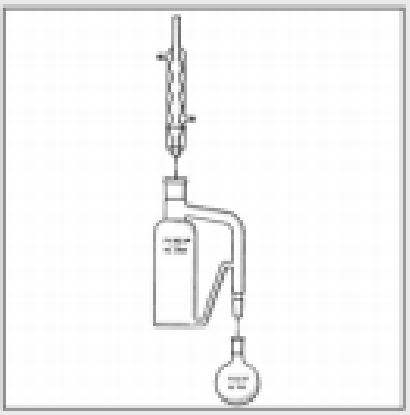


Table 2. PE Sample Preparation and Analysis Details for All Laboratories

Laboratory	Prep Method	Analysis Method	pH adjustment	Solvent	Concentration Temp	Initial Volume	Final Volume	Extraction Time	Column type
SepFun 1	3510C	8270D	pH < 2; pH > 11	$MeCl_2$		1050mL	1mL		Phenomenex ZB-5
SepFun 2	3510C	8270D	pH < 2; pH > 11	$MeCl_2$		1000mL	1mL		Phenomenex ZB-5MSi
SepFun 3	3510C	8270C	pH < 2; pH > 11	$MeCl_2$	70° C	1000mL	1mL		Phenomenex ZB-semivolatiles
SepFun 4	3510C	8270D	pH < 2; pH > 11	$MeCl_2$	71° C	1040mL	1mL		Trace Gold TG-5MS
SepFun 5	3510C	8270C	pH < 2; pH > 11	$MeCl_2$	88° C	1003mL	1mL		Agilent J&W DB-5MS
SepFun6	3510C	8270C	pH < 2; pH > 11	$MeCl_2$		1010mL	1mL		Agilent DB-5MS
SepFun 7	3510C	8270C	pH < 2; pH > 11	$MeCl_2$		1000mL	1mL		Restek RXI-5Sil MS
SepFun 8	3510C	8270C	pH < 2; pH > 11	$MeCl_2$	70° C	1000mL	1mL		Restek XTI-5
SepFun 9	3510C	8270C	pH < 2; pH > 11	$MeCl_2$		990mL	1mL		Agilent DB-5MS
LiL 1	3520C	8270C	pH < 2; pH > 11	$MeCl_2$		1000mL	1mL	6 hrs	Agilent VF-5MS
LiL 2	3520C	8270C	pH <2	$MeCl_2$	91° C	1000mL	1mL	18 hrs	Agilent DB-5MS
LiL 3	3520C	8270D	pH < 2; pH > 11	$MeCl_2$		996mL	5mL		Agilent HP-35MS

Phenol and Substituted Phenol Recoveries

- Figures 1 through 4 illustrates the difference in percent recoveries between the two preparation methods for each phenolic compound. Figure 1 shows that there is clear improvement in phenol recoveries when Method 3520C is used whereas the recoveries for 2-chlorophenol, 4-chloro-3-methylphenol, and 2-methylphenol are comparable between the two preparation methods.

Figure 1: Phenol Recoveries

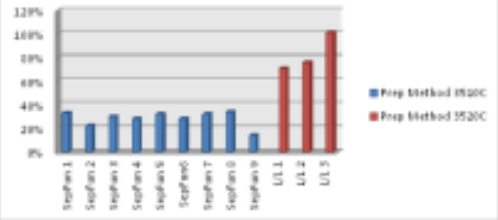


Figure 2: 2-Chlorophenol Recoveries

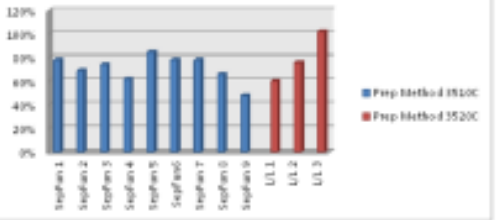


Figure 3: 4-Chloro-3-Methylphenol Recoveries

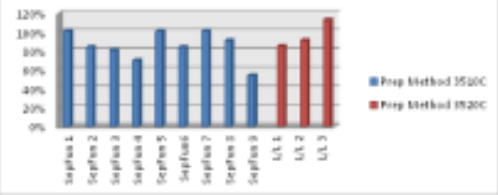
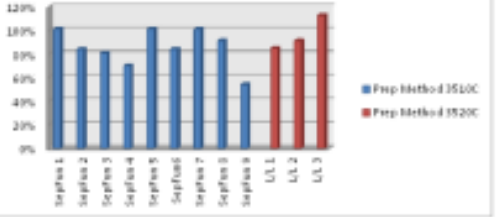


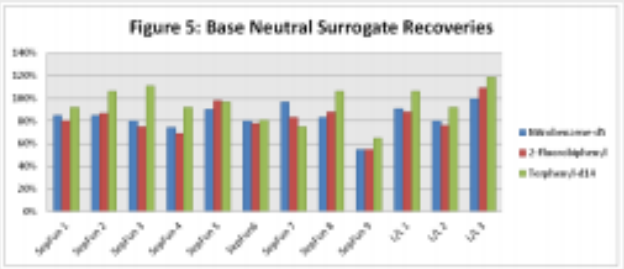
Figure 4: 2-Methylphenol Recoveries



Base/Neutral and Acid Surrogate Recoveries

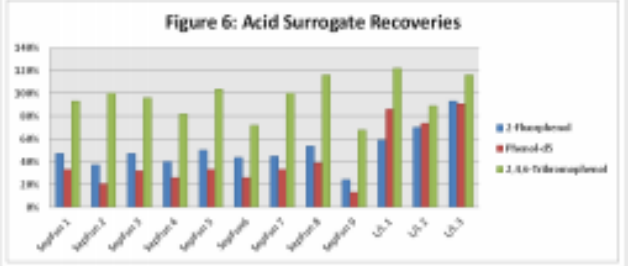
- Base/Neutral surrogate recoveries, summarized in Figure 5, are comparable regardless of which preparation method was used.

Figure 5: Base Neutral Surrogate Recoveries



- Figure 6 shows that the recoveries for phenol-d_5 and 2-flurophenol improved markedly when Method 3520C was used for sample extraction. The recoveries for phenol-d_5 and 2-fluorophenol ranged from 13% - 39% and 24% - 54%, respectively, when Method 3510C was used by the laboratories whereas the recoveries for phenol-d_5 and 2-fluorophenol ranged from 74% - 91% and 59% - 93%, respectively when Method 3520C was used. There was less of an impact on the recoveries for 2,4,6-Tribromophenol, the more substituted phenol compound, across all laboratories and both preparation methods.

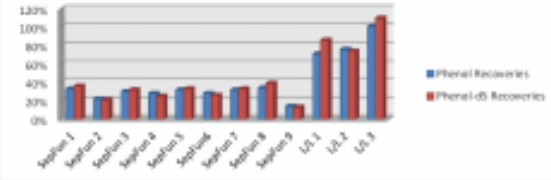
Figure 6: Acid Surrogate Recoveries



Phenol and Surrogate Correction

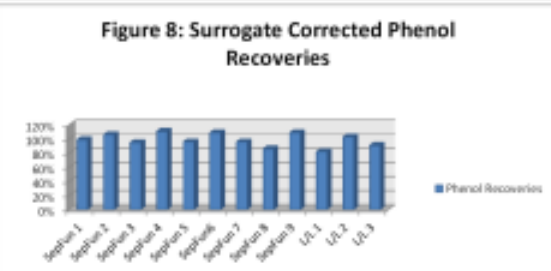
- A further look at phenol recoveries compared to phenol-d_5 recoveries in Figure 7 shows that the phenol recovery is near identical to its associated phenol-d_5 recovery. This trend between the target compound and surrogate recoveries indicates that it's difficult to achieve an adequate recovery for phenol; therefore, the results may not be the best measurement of phenol's true concentration.

Figure 7: Phenol Recoveries vs. Phenol-d5 Recoveries



- When target compound recoveries are low or erratic, surrogate correction is a technique which provides a better estimate of a target compound's true concentration. Figure 8 shows what the phenol recoveries in this PE study would have been had the results been surrogate corrected with phenol-d_5. The corrected recoveries range between 82% - 111%. It is important to note that while the recovery for laboratory L/L 3 decreased slightly, all results are comparable to each other regardless of preparation method.

Figure 8: Surrogate Corrected Phenol Recoveries



Conclusion

- Continuous liquid-liquid extraction provides better results for phenol and acid surrogates whereas no difference in results was observed for the substituted phenolic compounds and base/neutral surrogates between the preparation methods.
- If phenol is a compound of interest at a site, it is recommended that laboratories utilize the continuous liquid-liquid technique for sample extraction.
- Due to the strong relationship between phenol recoveries and phenol-d_5 recoveries, surrogate correction allows for a better estimate of phenol's true concentration.
- Laboratory L/L 3 reported the best recovery for phenol. This laboratory used a final volume of 5 mL rather than 1 mL, which provided improved recovery for phenol (see Table 2).
- Similar phenol results were observed in another PE Study managed by Environmental Standards, Inc.

ENVIRONMENTAL STANDARDS
www.envstd.com

Contact
Amanda Cover
Senior Quality Assurance Chemist
Environmental Standards, Inc.
acover@envstd.com or 610.935.5577

ISO 17025 Accreditation of U.S. National Guard Weapons of Mass Destruction—Civil Support Team Mobile Laboratories

Molly Isbell

Abstract

In the United States, responsibility for managing the consequences of the release of a Weapon of Mass Destruction (WMD) involving chemical, biological, radiological, nuclear, or high-yield explosive (CBRNE) falls to the civil emergency management structure. In 1999, the U.S. Congress established dedicated response teams within the National Guard to aid civil authorities in the event of a domestic terrorist event involving WMD. Currently, there are 57 full-time National Guard WMD-Civil Support Team (WMD-CST) units, with one in every state and U.S. Territory (and two in New York, California, and Florida). These quick-response units are designed and trained to support the response to a CBRNE event by identifying agents and other substances, advising on response measures, and assisting with requests for additional military support.

Each WMD-CST unit consists of 22 highly-trained, full-time National Guardsmen operating under federally approved CBRNE response doctrine. In addition to other specialized response capabilities, each team has a fully autonomous mobile analytical laboratory designed for field identification of chemical and biological agents, as well as toxic industrial chemicals/toxic industrial materials (TICs/TIMs) and radionuclides.

In an effort to standardize analytical practices and procedures across the CST community and bolster the technical credibility and defensibility of analytical data generated by the CST laboratories, the National Guard began an initiative in 2007 to achieve ISO/IEC 17025 accreditation for all of the CST mobile laboratories. To support this effort, Signature Science developed and assisted with the implementation of an over-arching quality management system to meet the requirements of the ISO 17025 standard in the context of the CSTs' unique mission and capabilities. Today, 24 of the 57 teams, plus the National Guard Bureau CST Program Office have achieved ISO 17025 accreditation.

This poster provides information about the unique approach and challenges associated with this accreditation effort. For example, development of the quality program required addressing the complexity of a joint state and federal military command structure along with uniquely military procurement, training, and methods development efforts. In addition, the quality management system needed to take into account the CST mission of qualitative identification of threat agents for purposes of response action, as opposed to a more traditional environmental paradigm of quantitative analysis in support of regulatory decision making. The system that has been developed and implemented meets ISO/IEC 17025 requirements as well as the needs of the CST mission, where quantitation is of little importance, while false positive and false negative errors potentially have life and death consequences. Finally, a comprehensive proficiency testing program has been established that fully covers a wide range of analytical methods involving identification of biological pathogens, select toxins, chemical warfare agent-related chemicals, TICs/TIMs, and explosives, in environmental matrices, on various collection media, and in samples of powders, liquids, soils, sludges, and vegetation, and for microscopical characterization of unknown samples.

(Related Session: Laboratory Accreditation)

Reduced Volume Technology: Modernization of Collection & Preparation Techniques in Extractable Organic Analyses

Judith Morgan

Abstract

The Environmental Protection Agency (EPA) requires the use of approved methods to analyze samples for compliance purposes. For semi-volatile organic analyses, the current traditional methods typically require a sample volume of 1000mLs for sample preparation, followed by Gas Chromatography, Gas Chromatography/Mass Spectrometry, or High Performance Liquid Chromatography. This technique requires a substantial use of the toxic solvent Methylene Chloride. The preparation time, sample handling, sample collection time and solvent use can be significantly reduced by the use of new and innovative micro extraction techniques. The information presented will be centered on innovations in sample preparation techniques combined with Large Volume Injection Technology that provides options to reduce the use and exposure to solvent and results in significant benefits to the client sample collection process, environment, and laboratory analytical process.

New methods in SW-846 and the flexibility of existing methods has allowed for technology that provides advancements that are reshaping the focus of the analytical industry. While there is no replacement chemical for the widely used extraction solvent (methylene chloride) that is required in the current suite of approved EPA methods, there are ways to reduce its use and with no sacrifice to quality. ESC has enhanced and retooled traditional organic sample preparation with validation of two new choices that result in reduced sample collection volume and subsequent decreased solvent volume. In order to preserve detection levels, Large Volume Injection technology on traditional GC and GC/MS instrumentation is necessary. Method 3511 brings the required volume of 180mLs solvent, in traditional liquid-liquid extractions, to a mere 2mLs, which is a 98.9% reduction in solvent. The enhanced version of Method 3510 reduces the solvent volume by 90%. In addition, the sample size is reduced to 40mL for 3511 and 100mL for the enhanced 3510.

Aside from the obvious benefits, there are some hidden savings that are notable. The smaller container is easier to handle and pack, thus reducing breakage and bulkiness of field supplies, not to mention the additional benefit where a low purge well exists. In addition, the overall individual container weight is reduced by ~95%, making cooler size smaller and lighter, resulting in less fuel to transport and finally less waste for disposal. The analytical data shows that both techniques are equal to or superior to their traditional larger volume counterparts.

(Related Session: Advances in Sample Preparation and Clean-up)

Study of Snow Cover Dynamics in Upstream Area of Heihe River Using Time Series MODIS Data (2002–2012)

Yunbo Bi

Abstract

Snow cover is an important water source of major Asian rivers and greatly influences water availability in the downstream areas. In this study, snow cover dynamics of the upstream areas of Heihe River in the northwestern China during hydrological years 2002–2012 (September through August) are examined using the flexible multiday combined MODIS snow cover products. The time series of multiday, seasonal, and annual snow covered area (SCA), snow covered days (SCD), peaks of maximum SCA, and snow cover index (SCI) for each hydrological year (HY) are examined. Results show that the HY2008 had the greatest snow cover distribution and HY2003 had the smallest. Temperature data from A'rou freeze/thaw observation station is used to represent the low valley temperature and temperature data from Yeniugou cold region hydrological station are used to represent the high mountains temperature in upstream area of Heihe River. The deseasonal temperature data and snow cover data showed high correlation ($r=0.89$, $p<0.01$) with the SCA data in a 76 days lag. To investigate the influence of the snow cover dynamics, we will further examine the interrelation between SCA and runoff in the region.

(Related Session: Academic Research Topics in Environmental Measurement and Monitoring)

Using Automated Sample Prep to Streamline Laboratory Accreditation

Philip Bassignani

Abstract

The presentation will cover the usage of FMS automated Pressurized Liquid Extraction and Solid Phase Extraction coupled with Power Prep multi column clean-up procedures to rapidly develop method validation for POPs analysis accreditation with minimal staff. The focus being to provide a successful and proven blue print for startup labs to follow resulting in accreditation.

Analytes covered will include Dioxins/Difurans, PBDEs, PCBs and PAHs analyzed by a variety of analytical platforms from Single Quadrapole MS, Triple Quadrapole MS and HRMS.

The presentation will cover sample extraction of Tissue, Serum, soil/sediment and Aqueous samples and their respective extract clean-ups, as well as the respective analysis. Data included will be performance recoveries, RMs and CRMs, and PT samples.

Conclusions show that using the FMS total prep platform can result in multi-component accreditation in the absolute shortest time duration. Further, the accreditation blue print provided can be easily transferred to start up lab seeking accreditation for the fore mentioned analytes.

(Related Session: Advances in Sample Preparation and Clean-up)

Volatiles in Air: Active vs Passive

Elizabeth Winger, Calscience Environmental Laboratories, Inc.

Abstract

Elizabeth Winger is the Air Program Director for Calscience Environmental Laboratories, Inc., located in Garden Grove California. Elizabeth has a wealth of practical experience and knowledge, having more than twenty five years of experience in environmental laboratory testing services. She has been the Air Program Director at Calscience for the last two years, previous to that she served for twelve years as the Laboratory Director for the air testing services division of a national laboratory network. Previous to that Elizabeth was employed by an oil company. Elizabeth attended the University of California at Santa Barbara where she earned a degree in Biological Sciences with a minor in Chemistry.

SECTION 24

BIOGRAPHIES

Abousaeedi, Nazy

Ms. Abousaeedi has been working for CSC for over 20 years supporting EPA Analytical Services Branch (ASB) in their effort to provide analytical data of known and documented quality to its customers in a cost-effective and efficient manner. Ms. Abousaeedi leads and manages CSC's Monitoring Program Management Offering (DatAssess).

DatAssess is CSC's proven turn-key solution for managing the entire cradle-to-grave lifecycle of environmental and public health monitoring program activities and providing data monitoring, scheduling, tracking, automated data compliance, validation/usability, reporting and data management support.

Education and professional degrees:

- MS in Chemistry
- Certified Project Manager Professional (PMP)

Contact Information: nazy@fedcsc.com; 703-818-4233

Aneja, Viney

Viney Aneja is a Professor in the Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University. He obtained his B. Tech. degree in Chemical Engineering from the Indian Institute of Technology, Kanpur, India; and MS and Ph.D. degrees from the Department of Chemical Engineering, N. C. State University, Raleigh, N.C. Before joining the faculty of the Department of Marine, Earth, and Atmospheric Sciences at N. C. State in 1987, he conducted and supervised research at Corporate Research and Development, General Electric Company, New York, and Northrop Service, in Research Triangle Park in the areas of environmental science and engineering and separations technology. In 2001 he was also appointed Professor of Environmental Technology, Department of Forestry and Environmental Resources. In addition, he has been a visiting professor at the University of Uppsala, Sweden in 1979; at Jawahar Lal Nehru University in New Delhi, India in 1980; and at the Arrhenius Laboratory in Stockholm, Sweden in 1985. The U.S. Secretary of Agriculture appointed him as a member of the U.S. Agricultural Air Quality Task Force. He was a member of the US Environmental Protection Agency's Science Advisory Board Environmental Engineering Committee; and is also a member of the US EPA's SAB Integrated Nitrogen Committee, and EPA's Science Advisory Board (SAB) Estimating Air Emissions from Animal Feeding Operations Panel. He is a Member Representative of the University Corporation for Atmospheric Research, Boulder, CO.

Dr. Aneja's industrial and academic research contributions have been extensively recognized. He won the Noryl Division Proprietary Innovation Award from General Electric in 1983, the Air Pollution Control Association Award for Distinguished Service in 1984, the General Electric Managerial Award in 1986, and at North Carolina State University he received the 1991-92 Outstanding Extension Service Award. In 1998 the Air and Waste Management Association gave him its Frank A. Chambers Award, the Association's highest scientific honor; in 1999 he became a Fellow of the Association; in 2001 he received the Association's Lyman A. Ripperton Award for distinguished achievement as an educator. He is the recipient of the 2007 North Carolina Award in Science, the highest award a civilian can receive from the Governor of North Carolina. In 2009 he received the Senior National Research Council (NRC) Research Associateship. In 2010 he received Distinguished Alumnus Award from the Indian Institute of Technology Kanpur, India. In 2010 he was invited by the U.S. White House Council on Environmental Quality to assist in the BP Gulf Spill.

At North Carolina State University Dr. Aneja has developed one of the nation's leading agricultural air-quality research programs (http://www.meas.ncsu.edu/airquality). He has published over 150 scientific papers, 120 book chapters and conference proceedings scientific papers, 45 technical reports, 5 US patents, and two books on his research. Dr. Aneja has directed 7 post-doctoral fellows, 13 doctoral dissertations, and 37 masters' theses.

Much of his work has focused on the science needed to make important decisions on environmental, bio-resource, and climate policies in North Carolina and the nation. He has conducted research on natural and anthropogenic emissions of nitric oxide, ammonia, and sulfur compounds and demonstrated the important roles of these substances in ozone formation and gas-to-particle conversion. His research on atmospheric photochemical oxidants in the North Carolina mountains has clarified the role of long range transport of pollutants and impact of these compounds on the formation of acid rain and on the damage to trees at high elevation. His most recent research has concentrated on the critical issue of the contribution of animal feeding operations to air quality; quantifying the emissions, transformation, transport and fate of pollutants in the environment, and climate. His contributions have been featured on CNN, ABC, CBS, NBC, National Public Radio, Public Broadcasting Service, The New York Times, Associated Press, Environmental Manager, and Fortune magazine. Dr. Aneja's research has enjoyed support from a broad base of public and private sources. While conducting his extensive research, Dr. Aneja has maintained a heavy teaching load. He teaches a large and popular introductory courses (Introduction to Weather and Climate), an two upper division air quality course (Fundamentals of Air Pollution; and Fundamentals of Air Quality and Climate Change), and graduate courses, and has also given numerous short courses to public and private sector audiences.

Dr. Aneja has a long and distinguished record of public service, and he has been frequently sought as a lecturer and consultant to the Federal and State governments, professional societies, international organizations, and the private sector on issues related to environmental science and public policy. He was invited to visit the University of Munich, Germany in 1988 to discuss the problem of forest decline; to Berlin, Germany, during 1992 to discuss environmental issues in Eastern Europe; the Ministry of International Trade and Industry, Japan, in 1994 to discuss urban and rural air quality; to the University of Sydney, Australia, and Hebrew University, Jerusalem, Israel in 1996 to discuss environmental issues; and the Ministry of Agriculture, Rome, Italy, in 1999 to discuss the role of intensively managed agriculture on the environment; and New Delhi, India in 2011 to discuss air quality, sustainability, and climate change. In 2000 he was a member of the North Carolina Delegation to the Netherlands on Agricultural Air Quality, and in 2001 he was leader of the U.S. Department of State Delegation to France on Environment Science and Technology. In 1990 Dr. Aneja served on the NASA panel for the selection of NASA Specialized Centers for Research and Training; and from 1994 to 2000 he served on the Exam Advisory Committee of the Institute of Professional Environmental Practice. From 1987-90 he served as the Site Director for the Mountain Cloud Chemistry Program. In 1990 he was appointed the Mission Scientist for the "Southern Oxidant Study"; in 1994 he was appointed Program Scientist for the U.S. EPA and NSF funded Project "NOVA"; in 1996 he was appointed the Science Team Leader for the North Carolina Department of Environment and Natural Resources Program on "Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, Deposition, and Assessment," and in 2001 he was appointed Program Scientist and Principal Investigator for the Animal and Poultry Waste Management Center/ Smithfield Foods funded Program OPEN (Odor, Pathogens, and Emissions of Nitrogen). He served as a member of the Technical Advisory Committee on North Carolina Environmental Defense Fund, a member of the North Carolina Progress Board; and serves as a Director of the Air and Waste Management Association, and Chair of the Association's Education Council. He has served on the editorial boards of the journals Environmental Pollution, Chemosphere, Journal of the Air and Waste Management Association, and Environmental Manager; and currently serves as Editorial Board Member of the international journal Atmospheric and Climate Science; and Atmospheres; and Associate Editor for International Journal of Air Quality, Atmosphere, and Health; International Journal of Physical Review & Research International; International Journal of Applied Environmental Sciences; International Journal of Atmospheric Pollution Research; The Open Environmental & Biological Monitoring Journal; Journal of Marine Science: Research & Development; Journal of Environmental Research and Management; and the Scientific Journals International; and on the Reader Advisory Panel of Nature.

Contact Information: vpaneja@ncsu.edu; 919-515-7808

Anumol, Tarun

Tarun Anumol is a fourth year PhD student in the Department of Chemical & Environmental Engineering working with Dr. Shane Snyder at the University of Arizona. He earned his bachelors in Engineering in India and a M.S. in Civil & Environmental Engineering from Carnegie Mellon University in Pittsburgh. His research revolves around occurrence, fate and attenuation of trace organic contaminants in water with a focus on advanced treatment technologies like ozone and granular activated carbon. He is also responsible for developing analytical methods for the trace level detection of emerging organic contaminants including pharmaceuticals, pesticides, endocrine-disrupting compounds (EDCs) and disinfection by-products in environmental matrices at the Snyder Research Lab. He has extensive experience using liquid chromatography, mass spectrometry and is currently working on time of flight instrumentation.

Contact Information: tanumol@email.arizona.edu; 412-656-0490

Askren, Daniel

Dan Askren is the operation's manager of EPA's radiation monitoring network at the National Analytical and Radiation Environmental Laboratory in Montgomery, Alabama. He received his bachelor's degree from Beloit College in Wisconsin and his masters and Ph.D. from the University of Georgia. Prior to joining EPA in 2006, he was a professor of geology for 14 years at Georgia Southwestern State University.

Contact Information: askren.dan@epa.gov; 334-270-3422

Baer, Travis

Travis Baer is an Engineering Specialist at the San Antonio District Office, Field Operations, Oil & Gas Division of the Railroad Commission of Texas. Baer's expertise includes well construction, design and plugging, oil and gas waste management, Railroad Commission oil and gas rules and regulations and reservoir modeling. His three years of well-rounded experience at the Railroad Commission include evaluation of completion and plugging proposals as they pertain to statewide rules and regulations, technical application review and permit writing for oil and gas waste management facilities and activities and participation in rulemaking for well casing, cementing, drilling and well control. His primary focus and duties have been on oil and gas well drilling, completion and production operations in the Eagle Ford Shale and south-central Texas region. Baer earned an Outstanding Service award by the RRC in Fiscal Year 2012 for his role in providing technical assistance and training to new employees in Surface Waste Management while taking on his new duties in the Field Operations. Baer is a member of the Society of Petroleum Engineers and is the Commission representative for the Environmentally Friendly Drilling program run by Texas A & M University and the Houston Advanced Research Center. He graduated in December 2008 with a BS in Petroleum Engineering from the University of Texas at Austin.

Contact Information: Travis.Baer@rrc.state.tx.us; 210-227-4822

Bagawandoss, Kesavalu

Education:

- J.D. Southern University Law Center
- Licensed to practice Law in Louisiana
- Senior Associate Editor, Southern University Law Review
- Ph.D., Engineering (Environmental Science), University of Oklahoma
- M.S., Chemistry, Wichita State University
- B.S., Chemistry, Loyola College, University of Madras, Madras, India

Professional Experience:

- Currently serves as a Corporate Technical Director for Accutest Laboratories
- Served as a Laboratory Director for Environmental and the AIHA program
- For 6 years, performed Data Validation & Laboratory audits; Provided Litigation Support Services and served as an Expert witness; Involved in data management using TerraBase software with ArcGIS; Provided advice and witnessed sample collection; Provided Analytical Services for the US EPA, Superfund Program for various analytical protocols for 20 years.

Contact Information: drdoss@accutest.com; 713-271-4700

Bensigner, Marlin

Owner of Chromtec, LLC

Education:

- BS Chem. Engineering, Univ. of Michigan
- BS Chemistry and Physics, Western Mich. Univ.
- MS Analytical Chemistry, Western Mich. Univ.
- MS Physical Metallurgy, Western Mich. Univ.

Jobs:

- Sealed Power Corp – QC Manager of 3 Cast Iron Foundries; Member of Metallurgy Department Product and Process Development Dept.
- Kalamazoo Spice Extraction Co., QC Manager; Process Development Manager; Analytical Method
- Development Manager
- Parke Davis (Warner Lambert) – Analytical Method Development Dept. and Process Development Dept.
- On Jan 1, 1980 Bensinger formed Chromtec

Chromtec, LLC was conceived as a Process Development consulting company to assist spice extraction companies in India, Africa, South America and Mexico. Production techniques Bensinger utilized ranged from Liquid-Solid Extraction to Super Critical Extraction; Solvent Removal and Purification; Natural Product Purification and accompanying analytical techniques to control these processes in the areas that these plants were located.

The most memorable contribution to pushing back the “frontier of science” for Bensinger was the determination of the pungencies of the 5 major capsaicinoids in hot peppers. This took a team of skilled researchers under his direction at Kalamazoo Spice Extraction Co. from 1971 to 1974. This work still stands today and is used as the measure to determine pungency by instrumental means (ASTA 21.3 and AOAC 995.03).

Contact Information: chromtec@bellsouth.net; 575-521-4281

Boyd, JoAnn

JoAnn Boyd, BS/MBA, is the quality assurance manager for Southwest Research Institute Chemistry & Chemical Engineering Division. She is the management representative for the ISO 9001:2000 Quality System, chairs the Division Quality Council, and is the division representative for the SwRI Quality Council. Ms. Boyd has Lead Auditor training for ISO 9001:2000, ISO 17025, and NQA-1 requirements. Ms. Boyd has extensive experience in establishing and coordinating quality programs such as ISO 9001:2000, ISO Guide 17025 and 17020, Good Laboratory Practice (GLP), Current Good Manufacturing Practices (cGMP) in support of pharmaceuticals, and a number of government regulatory quality programs. She served as Chairman of the Accreditation Process Committee for Institute for National Environmental Laboratory Accreditation (INELA) in support of NELAP. She is currently on the Consensus Standards Board, Field Monitory, Policy, and Laboratory Standards Accreditation Committees with The NELAC Institute. Ms. Boyd is currently Chairman of the Beyond Compliance Specialty Section committee for the Society of Quality Assurance (SQA). Ms Boyd has extensive knowledge and experience in establishing quality programs, data validation, laboratory and field audits and surveillances, and developing and performing training programs.

Contact Information: jboyd@swri.org; 210-522-2169

Burnett, David

David Burnett is the Director of Technology for the Global Petroleum Research Institute (GPRI) and is the Research Project Coordinator for the Department of Petroleum Engineering. He currently serves as the one of the Managing Partners of the U.S. RPSEA Environmentally Friendly Drilling System Technology Integration Program representing a $5 million joint partnership among university/industry and government organizations dedicated to reducing the impact of O&G operations in environmentally sensitive areas. In addition through GPRI, he leads a research team developing advanced membrane filtration technology to reduce waste water volumes at rig sites, including flow back fracturing fluids. He received the 2006 Hearst Energy Award for Technology in the oil industry and his research team recently received Gulf Publishing's 2008 World Oil Awards (environmental, health and safety).

Prior to coming to Texas A&M, Burnett was a Program Manager for BP's Westport Technology Center (Houston) developing and managing research programs for oil and gas joint ventures. He has a B. S. and M.S. in Chemistry from Sam Houston State University and an MBA from Pepperdine University, Los Angeles California.

Contact Information: burnett@pe.tamu.edu; 979-845-2274

Burrows, Richard

Dr. Burrows is the Director of Technical Services at TestAmerica. He has 27 years experience in environmental analysis and a Ph.D in analytical chemistry from the University of Bristol.
He is currently Chair of the TNI Chemistry Expert Committee.

Contact Information: richard.burrows@testamericainc.com; 303-393-1351

Cahill, Ed

Vice President Asbestos Division

Cahill has 18 years with EMSL and 30 years in the industry. Prior to his current position, he worked at Testwell Craig Laboratories, NorthEastern Analytical, and Children's Hospital of Philadelphia. He has a Bachelor's in Biology from University of Buffalo. He is a member of ASTM's Asbestos and Nanotechnology committees. He is a member of the Environmental Information Association.

Contact Information: ecahill@emsl.com; 856-303-2565

Capri, Julie

Julia Capri is a Senior Program Manager at CSS-Dynamac Corporation. She has over 25 years of experience in U.S. EPA emergency response and laboratory operation programs, and possesses a B.S. and M.S. in Chemistry from Xavier University. She is the Program Manager for the PHILIS Operations and Maintenance Support Contract. PHILIS is a NELAP accredited emergency response mobile laboratory program for the U.S. EPA Office of Emergency Management's CBRN Consequence Management Advisory Team (CMAT), and is a member of the Emergency Response laboratory Network (ERLN). PHILIS Mobile laboratories provide on-site organic analyses to support consequence management during national emergency and Superfund site cleanup response actions.

Contact Information: Kaelin.Lawrence@epa.gov; 732-321-6625

Cardona, Dwain

Dwain Cardona is currently a Senior Applications Scientist for Thermo Fisher Scientific GC- GC/MS supporting both single quadrupole and triple quadrupole technology product line development. His experience includes analytical method development for contract pharmaceutical research and development labs with 9 years experience in chromatography and mass spectrometry. In recent years, Dwain has been collaborating with industry experts to develop a diverse range of applications on advanced mass spectrometry systems including the areas of forensic toxicology, metabolomics and environmental sample analysis with specific emphasis on migration from helium to hydrogen carrier gas in GC/MS. Dwain hopes to provide GC/MS users with a trusted resource for analytical challenges in their laboratories.

Thermo Fisher Scientific
Senior Applications Scientist
3 Years
Texas State University - San Marcos
BA: Biology Minor: Biochemistry

Contact Information: dwain.cardona@thermofisher.com; 512-251-1597 ext 1463

Chakraborti, Sayan

Mr. Chakraborti is a Senior Program Manager with MRIGlobal in their Kansas City office for the past 2 years leading the Energy and Environment group. He has more than 20 years of experience in supporting US government and industrial clients in hazardous and radioactive waste management, and in soil and groundwater remediation. He has bachelors and masters degrees in chemical engineering and an MBA.

Prior to joining MRIGlobal, Mr. Chakraborti was with Weston Solutions where he provided project management support for a variety of projects in India, China, and the Middle East in Weston's Global Division.

Contact Information: schakraborti@mriglobal.org; 816-753-7600

Chambers, Laura

Laura Chambers is the Product Manager for the GCMS product line at Shimadzu Scientific Instruments (SSI) in Columbia, MD. A 20-year resident of Texas, Laura has worked in the field of analytical instrument development and product management for over 15 years, and took on the role of Product Manager at Shimadzu approximately one year ago. She holds a degree in analytical chemistry, and has over 25 years direct laboratory experience in commercial, academic, and research & development laboratories.

Contact Information: lachambers@shimadzu.com; 410-381-1227

Citriglia, Mark

Mark Citriglia is currently the Manager of Analytical Services for the Northeast Ohio Regional Sewer District. Mark has a Bachelor's of Science from Cleveland State University with a Major in Biology and a Minor in Chemistry. He has worked for the Northeast Ohio Regional Sewer District (NEORSD) for 23 years. He started at NEORSD in the Analytical Services department (laboratory) as a Wastewater Analyst, and has successfully gained the skills and knowledge to become the Manager of Analytical Service. Mark is a member of the Water Environment Federation, The NELAC Institute, and the Lab Safety Institute. Mark was the recipient of the 2007-2008 Northeast Section Ohio Water Environment Association "Lab Analyst Award", 2009 Ohio Water Environment Association "Lab Analyst Award", and the 2010 Water Environment Federation Laboratory Excellence Award.

Mark is a certified State of Ohio Wastewater Class III Operator and a Class IV Certified Wastewater Analyst.

Contact Information: citrigliam@neorsd.org; 216-641-6000

Cocanour, Scot

Scot has been the CEO of Promium since 1998 when he and a partner founded the company. Since that time Promium has become the leader in providing laboratory information management systems (LIMS) to laboratories involved in environmental testing. Scot is trained as a chemist (Northern Arizona University) and previously owned and operated the largest laboratories in the Pacific Northwest until the company was sold to TestAmerica where Scot became an Executive Vice President.

Contact Information: scocanour@promium.com; 425-286-9200

Cook, Robin

Mrs. Cook is the Regulatory Compliance Officer for the City of Daytona Beach. Her tenure includes 5+ years with the City, serving her first two years as Chemist, supervising the lab. Mrs. Cook earned a Bachelors' Degree in Microbiology from the University of Florida. She currently holds the Treasurer position for Florida Society of Environmental Analysts (FSEA) and sits on the Microbiology committee for TNI. Her 17 years of experience in the industry include a position as laboratory analyst with a private utility company, Florida Water Services and then several years as a senior analyst in the Environmental Lab Division of Harbor Branch Oceanographic Institute along with volunteer positions on the TNI Quality systems committee.

Contact Information: cookr@codb.us; 407-314-5743

Cowherd, Chatten

Principal Advisor for Environmental Engineering MRIGlobal (formerly Midwest Research Institute). Headquartered in Kansas City, Missouri. More than 30 years of experience in field characterization of open sources with an emphasis on fugitive dust emissions and controls.

Director of the Center for the Study of Open Source Emissions.
PhD in chemical engineering from the Johns Hopkins University.
35-year member of A&WMA with Fellow status.

Contact Information: ccowherd@mriglobal.org; 816-360-5346

Creed, Jack

Received a Ph.D. from the University of Cincinnati in 1989 under Dr. Caruso and he has been working as a research chemist at the U.S. Environmental Protection Agency in the Office of Research and Development for the last 24 years. The major emphasis of the research areas that he has been involved with at the EPA are arsenic exposure assessment, arsenic treatment technologies and arsenic metabolism.

Contact Information: creed.jack@epa.gov; 513-569-7833

Dorman, Frank

Frank Dorman is currently an Associate Professor at The Pennsylvania State University where he teaches and conducts research in Analytical Chemistry, Separations Science, and Forensic Chemistry. Frank has worked as a teacher, researcher and developer of gas chromatographic and liquid chromatographic instrumentation and applications for nearly 20 years. During this time, Frank has attained a global reputation in separations science, focusing on the fundamentals and applications of GC and HPLC techniques to solve complex analytical challenges. Frank has worked in organic and organometallic compound separations, as well as elemental analysis, sample preparation techniques, and is a highly-regarded teacher and presenter of complex techniques and concepts in separation science. Frank utilizes various chromatographic detection systems, including several types of mass spectrometers, and also is involved in the development and application of multidimensional chromatography (GCxGC). Frank has a B.S in Chemistry from Juniata College in Huntingdon, PA, and a Ph.D, in Analytical Chemistry from The University of Vermont. Frank has also worked in the environmental testing industry at ITS Environmental (1991-1996), then moving to Restek Corporation (1996-2010) as the Director of Technical Development. Frank also is an Adjunct Professor at Juniata College, where he has maintained various research projects and served as a part-time instructor since 2003.

Contact Information: fld3@psu.edu; 814-863-6805

Dupes, Lester

Mr. Dupes is a Senior Quality Assurance Chemist with Environmental Standards, Inc., of Valley Forge, PA. He earned a Bachelor of Science Degree in Chemistry from Juniata College and is a Certified Environmental Analytical Chemist. He has total of 25 years of environmental chemistry experience (20 years with Environmental Standards) including mobile laboratory analysis, field and laboratory auditing, data validation and quality assurance consulting.

Contact Information: ldupes@envstd.com; 610-935-5577

Duplan, Neno

Neno Duplan is the founder, President, and CEO of Locus Technologies, a Silicon Valley-based environmental software company founded in 1997. Locus has pioneered the application of an online, on-demand model for data management in the environmental industry.

Locus Technologies is in large part responsible for the creation of an emerging technical sector: the storage and management of environmental industry data using Cloud computing. These data include the mountain of complex information related to water quality, air emissions, energy consumption, greenhouse gasses, and other activities, which, in the past, had been stored in various distributed silo applications.

Dr. Duplan earned a B.S. and Ph.D. degrees, in civil engineering from the University of Zagreb, Croatia and M.S. degree in civil and environmental engineering from Carnegie Mellon University. He has taught classes and was guest lecturer at Stanford, Carnegie Mellon, and U.C. Berkeley. Dr. Duplan is the author of more than 50 technical papers on the use of technology in the environmental industry.

Contact Information: neno@locustec.com; 650-960-1640

Eaton, Andrew

Dr. Andy Eaton is the Technical Director and Vice President of Eurofins Eaton Analytical, the largest potable water focused laboratory in the United States and a division of Eurofins, the world's largest food, environmental, and pharmaceutical testing company. He has a PhD from Harvard in Geochemistry and did post-doctoral work at CalTech. He has been at Eurofins (formerly MWH Labs) for more than 30 years and has served on numerous state, federal and industry working groups dealing with drinking water analytical methods and trends in reporting limits and method options.

Contact Information: AndyEaton@eurofinsUS.com; 626-386-1125

Elam, David L. Jr.

David founded Summa Consultants, Inc. in 1999 after nearly 20 years in the technical consulting business. As a consulting scientist, David helps environmental science and engineering firms build successful enterprises through the practical application of project and quality management systems. His experience includes project management, business development, quality systems design and implementation, training, and consulting firm management. Before starting Summa, David was employed as a Vice President, Project Director, and Practice Leader for an Engineering News-Record (ENR) 25 Environmental Consulting and Engineering Firm.

David is a Certified Manager of Quality/Organizational Excellence (CMQ/OE), a Project Management Professional (PMP), a Certified Industrial Hygienist (CIH), a Qualified Source Testing Observer (QSTO I-IV), and member of the American Chemical Society (ACS), the American Society for Quality (ASQ), the Air and Waste Management Association (AWMA), the Carolina Air Pollution Control Association (CAPCA), the Project Management Institute (PMI), and the Source Evaluation Society (SES). He holds an MS degree in Chemistry and a BS degree in Microbiology, both from Auburn University.

Contact Information: delam@summaconsultants.com; 919-967-0500

Elnakat, Afamia

Dr. Afamia Elnakat is an associate professor of research at the UTSA Texas Sustainable Energy Research Institute. She is also faculty of Environmental Science and Engineering at the University of Texas at San Antonio. Afamia's research is dedicated to emphasizing living sustainably while alleviating environmental impacts. Utilizing her multidisciplinary knowledge and background in engineering, biology, geology, chemical fate and transport, and water resources, Afamia specializes in multidisciplinary approaches in assessing environmental policies and institutional barriers to facilitate cooperation between different entities.

As a Registered Environmental Manager and with her private industry background, and commitment to community initiatives, Afamia has gained experience in technical, political and socioeconomical aspects of resource management.

Contact Information: afamia.elnakat@utsa.edu; 210-458-5742

Evans, Jessica

Jessica Evans is the director of the standards development team at NSF International. She brings over 8 years of experience working and developing standards in the food, water, sustainability and health sciences areas. Jessica has a degree in Supply Chain Management from Michigan State University. Prior to joining NSF, she held a supply chain management role with a Fortune 500 company working in the aerospace, automotive and health care industries.

Contact Information: jevans@nsf.org; 734-913-5774

Farhat, Shahla

Shahla K. Farhat, Ph.D. is an Environmental Scientist at GSI. Dr. Farhat specializes in the assessment and remediation of local and regional groundwater aquifer systems, fate and transport modeling, computer assisted tomography, infrared remote sensing, and Fourier transform infrared spectroscopy. She received a Ph.D. in Environmental Sciences and Engineering from the University of North Carolina at Chapel Hill. Dr. Farhat is the primary author of the "SourceDK Remediation Timeframe Decision Support System " software and "Low Risk Site Closure" guidance document developed by GSI for the Air Force Civil Engineer Center, and the "Mass Flux Toolkit", "Matrix Diffusion Toolkit", and "Source Attenuation Tool" software tools developed by GSI for the Environmental Security Technology Certification Program (ESTCP).

Contact Information: skfarhat@gsi-net.com; 713-522-6300

Favela, Kristin

Dr. Kristin Favela is a Senior Research Scientist in the Environmental Engineering and Monitoring Section within the Chemistry and Chemical Engineering Division at Southwest Research Institute in San Antonio, Texas. She has been with Southwest Research Institute for 5 years, and was previously with Tate & Lyle where she led programs associated with the identification and quantification of trace substances in food products. Dr. Favela's main area of expertise is the application of specialized mass spectrometric methods to solve complex problems in the areas of forensics, environmental monitoring, food chemistry, and bio-analytical chemistry. She received her Ph.D. in Chemistry at University of Arizona in 2005 and her B.S. in Chemistry, from Creighton University in 2000.

Contact Information: kristin.favela@swri.org; 210-522-4209

Feyerherm, Fred

Fred Feyerherm works for Agilent Technologies as a GC/MS Applications Engineer. Fred specializes in GC and GC/MS Pesticides, Semi-volatiles, Volatiles, Petrochemical, and Forensic Applications. Fred has developed many methods for the environmental industry, many branches of the federal government including the military, and numerous private laboratories. Fred has a BS in Chemistry from University of Houston. Prior to joining HP (now Agilent) in 1981, Fred was an analytical chemist at Dow Chemical in Freeport, TX. Fred has a total of 43 years gas chromatography experience, and 39 years GC/MS experience.

Contact Information: Fred_Feyerherm@Agilent.com; 972-699-6424

Forman, Ruth

Principal Chemist at Environmental Standards, Inc. Ms. Forman has over 27 years of environmental analytical and chemistry quality assurance experience. Ms. Forman is a graduate of Franklin and Marshall College in Lancaster, Pennsylvania with a degree in chemistry, and she is a certified environmental analytical chemist and a Principal Chemist at Environmental Standards for more than 24 years. Ms. Forman serves on ELAB and on ASTM subcommittee on hydraulic fracturing. Ms. Forman has authored and peer-reviewed numerous published manuscripts relating to data validation and data usability, laboratory auditing, performance evaluation studies, and analytical data management.

Contact Information: rforman@envstd.com; 610-935-5577

Frans, Christina Mott

Christina Mott Frans is a senior project chemist with EcoChem, Inc., Seattle, WA. She received her B.A. from George Mason University. After starting her twenty-year career at Viar & Compnay working on the Sample Management Office contract for EPA's Contract Laboratory Program, she decided it was time for a change of scenery and moved to beautiful Golden, Colorado, where she began gaining experience working in almost every aspect of an environmental laboratory. She worked for several different laboratories including TestAmerica, Environmental Science & Engineering, Actlabs, and at the on-site laboratory at the Rocky Mountain Arsenal. Her experience covered all laboratory areas with an emphasis on quality assurance. She is now managing data validation projects, conducting laboratory audits, and providing QA support for natural resource damage assessment (NRDA) projects. She currently resides in Auburn with her husband Ben, two terrific step children and their three horses.

Contact Information: cmfrans@ecochem.net; 206-233-9332

Fricker, Colin

Professor Colin Fricker is managing director of CRF Consulting an international consulting firm specializing in microbiology of water, which based in the UK. Professor Fricker obtained his Ph.D. in microbiology from the University of Reading in 1987. In 1986, he was awarded the WH Pierce Prize for outstanding contributions to microbiology. He is an adjunct professor in the department of environmental sciences at Queens University, Kingston, Ontario, Canada. Professor Fricker has over thirty years experience in environmental microbiology, has edited five books, and published more than seventy peer reviewed publications.

Contact Information: colinfricker@aol.com; 774-029-2101

Friedman, David

2006 – Present Consultant
Serve as a consultant to laboratories and instrument manufacturers in areas of business development, method validation, and market development. Serve as Technical Advisor to American Council of Independent Laboratories (ACIL).

1985 - 2005 U.S. Environmental Protection Agency
Senior advisor to senior management on monitoring issues, prepare policy papers and recommendations, serve as Executive Director of Agency's Forum on Environmental Measurements (i.e., EPA's senior management measurement policy organizations), prepare speeches for senior management, conduct special studies and programs, manage technical program to convert former Soviet bioweapons laboratory to an environmental monitoring/commercial analytical services laboratory, serve as internationally recognized expert on environmental monitoring and measurements, oversee EPA effort to establish a national environmental laboratory accreditation program, initiate and oversee major public communication and outreach programs such a national conferences and workshops, and develop and present training courses needed to implement new Agency programs and initiatives.

1978 – 1985 U.S. Environmental Protection Agency
Scientist and Section Chief in the Office of Solid Waste. Accomplishments included: development of both Toxicity and Reactivity Characteristics and the internationally recognized monitoring methods manual (Test Methods for Evaluating Solid Waste, SW-846), and for founding and, for 18 years, managing the Waste Testing and Quality Assurance Conference which has become the National Environmental Monitoring Conference (NEMC). Responsibilities also included coordination of EPA's hazardous waste research program.

1973 - 1978 U.S. Food and Drug Administration
1972 - 1973 Webco Enterprises
1967 - 1972 Union Carbide Corporation

Contact Information: friedmanconsulting@cox.net; 703-691-3059

Friedman, Maria

Ms. Friedman is a Quality Assurance Manager with TestAmerica Laboratories, Inc., where she has worked for 19 years. Her areas of expertise include ambient air analytical methodologies and implementing quality systems. She has been an active participant in TNI since 2005, when she joined TNI's Information Technology Committee, and she is the chair of TNI's Stationary Source Audit Sample Expert Committee, formed in 2008 to create standards to support the privatization of EPA's audit sample program. Ms. Friedman holds an MBA degree from the University of California - Irvine and a Bachelor of Science degree in Chemical Engineering from MIT in the Philippines, and has undergone training as an internal auditor in ISO/IEC 17025.

Contact Information: Maria.Friedman@testamericainc.com; 949-261-1022

Gallagher, David

David Gallagher has been with Horizon Technology since 2009 as a Senior Applications and Technical Specialist, working with customers and products to develop solutions to extract and concentrate analytes of interest from aqueous samples using solid phase extraction. Prior to this, he worked as a GC Analyst for one of the top commercial environmental testing companies in the US for 4 years. He holds a BS in Engineering from Virginia Tech and a MS in Mathematics from the University of Massachusetts at Lowell.

Contact Information: dgallagher@horizontechinc.com; 603-386-3620

Gentry, J.D.

J.D. Gentry is the Technical Director for ESC Lab Sciences and has been part of their team for 12 years. J.D. supervises the quality assurance team and is involved in implementation of new methods, method updates, internal and external audits, safety, waste disposal, new technology research and instrument repair. He oversees day to day laboratory quality and accuracy concerns to ensure method requirements are met.
J.D. Gentry began working in the sample preparation lab, at ESC Lab Sciences, in 2001 during his final semester in college. Upon completion of his chemistry degree from Western Kentucky University he was hired as a full time chemist. Prior to becoming Technical Director, JD held several positions including chemist, senior chemist, air laboratory manager, night shift supervisor, and volatile organics manager. During this time, he planned and developed the air analysis laboratory at ESC and has extensive experience in numerous organic methods. New method development and analytical instrument repair has always been his primary interest and is the lab activity that he enjoys the most.

Contact Information: JGentry@esclabsciences.com; 615-773-9684

George, Ed

Ed George has BS in Chemistry from the University of Notre Dame with concentration in Environmental Science. He worked for 15 years in the environmental laboratory industry, holding positions of Lab Technician (2 yrs), Lab Manager (10 yrs), and R&D Manager (3 yrs), responsible for developing novel sample preparation and analysis methods for water by GC/MS and LC/MS. He participated in several collaborative method development projects with the USEPA. From 2005-2009, he worked for Varian, Inc. as Application Lab Manager, developing applications for pesticide residues in food on ion trap and triple quadrupole GC/MS/MS and LC/MS/MS systems. He is currently the Single Quadrupole Product Manager and GC/MS Applications Specialist at Bruker.

Contact Information: ed.george@bruker.com; 510-683-4315

Gerads, Russell

Mr. Gerads is currently the CEO/President of Applied Speciation and Consulting. Mr. Gerads' responsibilities encompass all business and scientific aspects associated with Applied Speciation and Consulting, LLC. Mr. Gerads is the primary liaison for all internal and external scientific investigations assisting in their formulation, management, and execution. Mr. Gerads holds a Bachelor's degree in Chemistry from the University of Washington and has managed thousands of research projects associated with trace element and trace element speciation analyses associated with environmental, pharmaceutical, nutraceutical, government, forensics, clinical, and chemical manufacturing markets for nearly all matrices.

By invitation, Mr. Gerads has presented to the New Jersey Department of Environmental Protection, National Environmental Monitoring Conference, the Society of Forensic Toxicologists, and the International Water Conference. Mr. Gerads has published a number of scientific articles and also provides workshops and presentations at various scientific conferences throughout the year associated with trace element and trace element speciation analyses.

Contact Information: russ@appliedspeciation.com; 425-483-3300

Gandhi, Jay

Dr. Gandhi brings 27+ years of proficiency with virtually all analytical instrumentation and the techniques of Environmental, Petrochemical and Pharmaceutical testing and research. In his distinguished career, here are few highlights of his achievements.

1992-1993 – He received highest award from DuPont Company as non-DuPont employee for completing Recycled Vinyl Acetate project from conception to completion in record 10 months. This saved DuPont $12 million per year.

1994-1998 – At Varian Inc., He received several awards as exemplary employee for outstanding customer service.

2001 – At NASA being a principal investigator for Mars Exploration project, received several awards for Recycling of Water in Space project and several safety awards.
Since 2002 – He has shepherded several ASTM and USEPA methods, most recently USEPA method 218.7 for "Analysis of Hexavalent Chromium in Drinking Water".

Contact Information: jgandhi@metrohmusa.com; 713-202-8363

Godfrey, Bruce

Dr. Bruce Godfrey is the Laboratory Director at Curtis and Tompkins a 135 year old testing laboratory with nearly 100 employees in Berkeley, CA. He holds BA and Ph.D. degrees in Biochemistry from the University of California. An analytical chemist with more than 30 years experience, Dr. Godfrey has worked on a wide variety of environmental investigation and remediation projects with commercial clients, the US Departments of Defense and Energy, US-EPA, and state and local governments. Dr. Godfrey is a three time recipient of the ACIL's Preston Millar award for outstanding service to the Nation's trade association for commercial scientific and technical organizations.

Contact Information: Bruce.Godfrey@ctberk.com; 510-204-2222

Gratson, David

David Gratson is a Senior Technical Chemist who has been with Environmental Standards, Inc. for 9 months. Mr. Gratson has over 25 years of field and analytical quality assurance experience. He got his Bachelor of Science degree from Allegheny College and his Master of Science degree from the Colorado School of Mines. Previously he was a Senior Chemist at Neptune and Company Inc., an Associate Scientist at National Renewable Energy Laboratory, and an Analyst at Rocky Mountain Analytical Laboratories (now TestAmerica) in Denver.

Contact Information: dgratson@envstd.com; 281-752-9782

Grimmett, Paul

Paul Grimmett is a research chemist at the U.S. Environmental Protection Agency's Office of Research and Development (ORD). He has spent the last six years in ORD, developing organic detection methodology for nationwide monitoring and regulation of drinking water. Honors include the EPA National Exposure Laboratory Meritorious Research Support Award, the EPA Science Achievement Award, and Scientific and Technological Achievement Awards. He was awarded a B.S. in 1997 and an M.S. in 2004, both from Marshall University.

Contact Information: grimmett.paul@epa.gov; 513-569-7663

Gunning, Chris

Christopher Gunning is currently a Senior Accreditation Officer with the American Association for Laboratory Accreditation (A2LA), where he joined in March of 2009. He supports the day-to-day operations of accreditation, by assisting clients in obtaining and maintaining accreditation. He facilitates the assessment process for new and renewal laboratories in the Biological, Chemical, Environmental, and Mechanical fields of testing. Mr. Gunning has successfully completed the 2009 A2LA ISO/IEC 17025 Assessor Orientation course. Mr. Gunning performs management system assessments, performs oversights of assessors, and represents A2LA at public meetings. He serves as the recording secretary of the Life Science Advisory Committee (LSAC). Mr. Gunning also provides training both internally and publicly.

Prior to joining A2LA, Mr. Gunning worked as a Senior Research Associate with GenVec Inc. located in Gaithersburg, MD. He was responsible for managing the production, purification, and testing of adenoviral vectors to be used in cancer therapeutics as well as vaccine candidates. He also trained new employees in all related SOPs and technical skills related to these processes.

Mr. Gunning has a B.A. degree in Biology that was obtained from Saint Mary's College of Maryland located in Saint Mary's City Maryland.

Contact Information: cgunning@A2LA.org; 240-575-7481

Hayes, Heidi

Heidi Hayes is the Technical Director and Vice President of R&D at Eurofins Air Toxics, Inc. She has a MS in Chemistry from the Colorado School of Mines in Golden, CO and 20 years in the environmental laboratory industry with experience in designing and testing new analytical methods and in analytical instrumentation. She has spent the last 17 years at Air Toxics and currently oversees the testing of new media, protocols, and technology related to air phase analysis. Her current area of research is soil gas and indoor air sampling and analytical protocols to support vapor intrusion investigations.

Contact Information: hhayes@airtoxics.com; 916-985-1000

Healy, David

Mr. Healy earned his M.S. in Urban Planning from the University of California, Los Angeles. He is GIS geek, environmental planner, policy analyst, and manager with 35+ years of experience. He has worked as a GIS consultant for the last fifteen years as the owner of his own business and partner in Stone Environmental, a 45-person firm based in Montpelier VT. He is considered a leading innovator in the use of GIS in solving complex analytical and technical problems. He was instrumental in setting up the Vermont Center for Geographic Information in the late '80s. Most recently has been working on a many diverse spatial analysis and web-GIS application projects. His earlier career positions include Operations Administrator for the Vermont Center for Geographic Information; Policy Analyst for the Office of the Governor in the State of Vermont; and started his career at the Environmental Protection Agency Region IX in 1972 where he worked on programs for achieving air quality standards in the region.

Contact Information: dhealy@stone-env.com; 802-229-1879

Heier, Shawn

Shawn Heier is the Director of the Ultra Trace and Air Toxics Group for Maxxam Analytics in Mississisauga, Ontario. Mr. Heier has recently returned to Maxxam Analytics after being involved with start-up companies in the renewable energy sector for eight (8) years. Prior to leaving the Environmental Laboratory sector, Mr. Heier was the President and CEO of PSC Analytical Services prior to its merger with Maxxam Analytics in 2004.

Contact Information: sheier@maxxam.ca; 905-817-5731

Hickman, Daniel

Dan Hickman is the database administrator for the TNI National Environmental Laboratory Accreditation Database. He works with Accreditation Bodies to upload laboratory demographics and fields of accreditation and he is responsible for database table maintenance. He is retired from State of Oregon Department of Environmental Quality Laboratory after nearly 35 years service. Mr Hickman was the Laboratory Operations Manager, in charge of Technical Services, and Laboratory Accreditation, and has been involved with NELAC and TNI since startup. He was chair of the TNI National Database Committee and involved in writing the Database Development Plan, and the IT QA Plan, resulting in the construction of TNI Laboratory Accreditation Management System (LAMS). He was also the first chair of the TNI NELAP Board.

Contact Information: Danthrax33@msn.com; 503-236-9422

Hiegel, Christina

Christina Hiegel is a registered Civil/Environmental Engineer with an Engineering Degree from the University of Wyoming. She has been with Trihydro Corporation for over 11 years. Her primary responsibilities include providing technical support for projects in data defensibility, data quality, and leading data quality for use in compliance monitoring, risk assessments, closures and other applications. Ms. Hiegel is proficient in laboratory data validation and has been involved in developing and maintaining the corporate Quality Assurance and Quality Control standards and procedures for overall data quality for sites. She also has organized and developed the company technical group for data quality issues and teaching of others in EPA Methods and data validation and data quality applications. She is proficient in her understanding of EPA Risk Assessment Guidance for Superfund (RAGS), EPA online risk assessment database [Integrated Risk Information System (IRIS)], Region 1, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses, and the EPA National Functional Guidelines for Organic and Inorganic Data. She has performed EPA Tiered data validation and state specific validation in support of remedys and risk assessments and has prepared sampling plans, quality assurance plans, risk assessment reports, remedy reports, and other milestone reports in the risk-based corrective action process.

Contact Information: chiegel@trihydro.com; 307-745-7474

Hird, Simon

- Head of LC-MS at the UK's Food and Environment Research Agency (Fera). Have worked for Fera and precursors since 1995.
- Environmental Science BSc. 1st Class (Hons) Plymouth Polytechnic
- PhD. in Organic Biogeochemistry University of Plymouth
- Member of the Royal Society of Chemistry and a Charted Chemist
- Member of the Britsh Mass Spectrometry Society

After studying at Plymouth for 7 years, Simon joined M-Scan in 1990, a comercial mass spectrometry consultancy in the UK and was responsible for environmental and petrolem areas of contract research and

testing, mainly where oil and the environment clashed! He joined a government agency, the Central Science Laboratory (precursor to Fera), in Aberdeen in 1995 with responsibilities for the determination of petrochemical residues in the environment, mainly using GC-MS and GC-HRMS. After a re-organisation of the laboratory, Simon relocated to York, in the North of England, where he was introduced to LC-MS. Apart from a brief experience with isotope ratio mass spectrometry, he has never left the technique. Since 2005, Simon has managed a team of 20 specialists working on 20 LC-MS/MS instruments involved with the determination of a various types of residues and contaminants in foodstuffs and the environment.

Contact Information: simon.hird@fera.gsi.gov.uk; +44 1904 462567

Huang, Ying

Dr. Ying Huang received her PhD in civil engineering, Missouri University of Science and Technology, Rolla. She currently is an assistant professor in Civil Engineering at North Dakota State University. Her current research interests include structural health monitoring of transportation infrastructure and environments, intelligent transportation infrastructure, and multi-hazards assessment and mitigation, etc.

Contact Information: ying.huang@ndsu.edu; 701-231-7651

Hunt, Kyle

Mr. Hunt is senior chemist with 22 years of diversified experience in the field of environmental and analytical chemistry. For the past 5 years he has served as a Staff Chemist/QA Specialist with the consulting firm Signature Science LLC; providing technical solutions for governmental and commercial clients.

Mr. Hunt earned his B.S. in Chemistry for Texas State University in San Marcos Texas and holds an accreditation as a certified quality auditor from the American Society for Quality.

Contact Information: KyleHunt@signaturescience.com; 512-583-2463

Hunt, Margo

Margo received a BA in botany major from Drew University, followed by a MS degree in microbiology from Pennsylvania State University. Merck, Sharpe & Dohme employed her as a research soil microbiologist and, while working full-time, she completed her PhD in ecology from Rutgers University.

She changed careers by teaching as an adjunct professor at a variety of colleges and universities in New York and New Jersey. The courses she taught ranged from general biology, anatomy and physiology, microbiology, clinical microbiology, and ecology.

A third career change came as she started to work for the US Environmental Protection Agency, first in Region 2 as a microbiologist and a quality assurance officer reviewing QA Project Plans, certifying state drinking water microbiology laboratories, inspecting waste water microbiology and bioassay testing labs, and setting up and running temporary microbiology laboratories in the Virgin Islands during summer field sampling runs and during hurricane disaster duty. After ten years, she transferred to Headquarters in Washington DC to work with the Quality Staff and became involved with the Quality System and laboratory assessments programs and TNI, and conducted training in quality assurance. She retired in 2008.

As a volunteer she has worked for the past 12 years as the Standard Methods for the Examination of Water and Waste Waters Part 9000 (Microbiology) Coordinator. She sets up workgroups and is responsible for reviewing and revising the information and sending it out for consensus voting.

Contact Information: snowball02h@yahoo.com; 240-683-1369

Inkenhaus, Nick

Mr. Inkenhaus has over 18 years of professional experience in water management, industrial wastewater treatment, and industrial chemical supply. His professional experience spans across a broad range of industries, including; oil and gas, alternative energy, and power industry among others. Over his career Mr. Inkenhaus has worked for such companies as Siemens Water Technologies, and Carmeuse North America where he co-authored many industry related articles relating to flue gas treatment. At Range Resources he is primarily focused on managing water resources from sourcing, transportation, treatment, storage, reuse, and disposal. He holds a BS in Chemical Engineering from Carnegie Mellon University (1994).

Contact Information: winkenhaus@rangeresources.com; 724-843-3242

Jack, Richard

Richard is the North American Environmental Marketing Manager for Thermo Fisher Scientific Corporation and has been involved with environmental applications for over 15 years. Working with many regulatory agencies, he assists these agencies in developing robust analytical methods that are eventually used for compliance monitoring by bringing customer problems to his company to develop new applications, hardware, software or column chemistries. Richard is a co-author for EPA 557 and has also drafted several methods through ASTM and a member of the D19 Waster committee's task force on hydraulic fracturing. Previously, Richard was a product manager for Dionex and Hitachi High Technologies were he designed analytical instrumentation including ion chromatography, HPLC systems, pumps, autosamplers and a variety of detectors. Prior to analytical instrumentation, Richard worked at Clontech laboratories in Palo Alto, CA. Richard did his post-doctoral work at Virginia Tech and was involved in vaccine development then worked as an environmental scientist involved in bioremediation of toxic compounds in soils. Richard received his Ph.D. in Biochemistry and Anaerobic Microbiology from Virginia Tech University in Blacksburg, VA and his Masters in Ecology from the University of Tennessee in Knoxville, TN.

Contact Information: richard.jack@thermofisher.com; 408-481-4227

Jackson, Cary

Director of Regulatory Affairs
Hach Company – 10 Years

Dr. Jackson is a nationally and internationally recognized expert with over 35 years experience in water sciences and regulatory government relations. As a principle consultant to the USEPA Office of Water, he has developed, co-developed, or managed the development of over 30 promulgated test methods (chemistry and microbiology) for use in regulatory compliance monitoring and reporting purposes. Currently with Hach Company, Dr. Jackson directs the regulatory affairs activities for EPA and consensus-based method approvals where he is a task chair for ASTM International D19 Water, a US delegate to ISO, and a Federal Advisor to EPA on detection and quantitation (past). Dr. Jackson holds a Bachelor of Arts degree in chemistry from University of Northern Colorado and a Doctorate of Philosophy degree in Soil and Water Chemistry from Colorado State University.

Contact Information: cjackson@hach.com; 970-669-3050

Jeffrey, Alan

Alan Jeffrey is Senior Geochemist at DPRA/Zymax Forensics in Escondido, California. Dr. Jeffrey has over 20 years of U.S. and international experience in environmental and petroleum geochemistry. Much of his work has focused on the use of geochemical and stable isotope techniques to solve environmental problems, including sources of spilled hydrocarbon fuels and chlorinated solvents, and fugitive methane seeps.

Dr. Jeffrey has published papers on topics ranging from chemical oceanography and petroleum geochemistry to environmental forensics. He has presented technical papers at conferences and symposia in North America, Europe, Southeast Asia, and Australia. He has given numerous workshops on environmental forensic techniques and case studies using these techniques, and reviews technical papers for Environmental Forensics journal. He has provided expert witness services in numerous legal cases, both civil and criminal, involving release and theft of petroleum products, and has defended his opinions in deposition and trial. He has also provided litigation support in environmental contamination cases for numerous private law firms.

Dr. Jeffrey has B.Sc. and M.Sc. degrees in Chemistry from Queen's University, Canada, and he received his PhD in Oceanography from Texas A&M University.

Contact Information: alanj@zymaxusa.com; 760-781-3338

Katsikis, Catherine

Ms Katsikis is a Senior Scientist and QA Manager with Laboratory Data Consultants FL, Inc. (LDCFL, Inc.) for the last 7 years. She has been actively participating in the environmental industry for over 23 years with particular emphasis in Management and Quality Control/Quality Assurance practices. Ms. Katsikis holds a Chemistry degree with emphasis on Laboratory Supervision from Teachers Training Institute, Athens Greece. She also holds multiple certifications including, Quality Management in the Lab from Clemson University, Fortunes Magazine's "Worldwide Lessons in Leadership Series from Florida Atlantic University, Good Laboratory Practices (GLP) from The Center for Professional Advancement and ISO 17025 Internal Auditor training from the Laboratory Accrediting Bureau/NACLA.

She currently conducts internal and external laboratory/field audits, training classes on Ethics/Data Integrity, Quality Assurance practices for the lab and field, 3rd party Data validation, Document Control, FLADaPT, and US Army Corps of Engineers ADR. Her expertise includes implementation of QA programs, SOPs/QAM/QAPP development, laboratory management, and she is a QA consultant for state and private organizations.
Ms. Katsikis has served and past Vice President for FSEA (Florida Society of Environmental Analysts) where she is currently a committee member of the Host and Programming Committee and she is the Chair of the Professional Relations Committee.

Prior to the environmental industry, Catherine was employed as a laboratory supervisor in the Plastics industry, working with PVC stabilizers, plasticizers, polymers and organometallic compounds in chemical and physical testing.

Contact Information: ckatsikis@ldcfl.com; 561-753-0483

Keith, Larry

Dr. Larry Keith began working at the SE Water Research Lab in the mid 1960s and continued there when it became one of the national research labs after EPA was created in 1970. His talk focuses on this period. After leaving EPA in 1977 he worked for over 20 years at Radian International in Austin, TX. Today he does private consulting and specializes as an expert witness involving pollutant analysis and QA/QC, typically defending companies where litigation involves data of unknown or uncertain quality.

Contact Information: larrykeith@earthlink.net; 770-267-3686

Kelly, Kory

Kory Kelly obtained his Masters in Science in Analytical Chemistry from New Mexico State University. The topic of his graduate work was the manufacture and characterization of coupling gas chromatography with ion mobility spectrometry.

Upon joining Phenomenex in 2002, Kory's focus was developing applications with the goals of increased productivity and ruggedness. Based on this work, he has provided valuable direction on new product development. He recently joined the PhenoLogix method support team as the Technical Manager for GC and Environmental Projects, finding comprehensive solutions for hot topics and growing trends in his applied markets. As a technical subject matter expert, Kory collaborates with chromatographers domestically and internationally through personalized method support, technical training, and on-site seminars for environmental and GC related fields.

Contact Information: koryk@phenomenex.com; 310-212-0555

Kennedy, David

David Kennedy is the Business Development Manager of Phenomenex, Inc., a major manufacturer of chromatography consumables located in Torrance, CA., a position he has held for about one year. He has a BS in Chemistry and a Ph.D. in Analytical Chemistry from Iowa State University and has been active in the field of environmental chemistry and analysis for over 40 years. He has had subsequent careers in:

- Industrial research and development
- Environmental engineering
- Environmental testing laboratories
- Analytical instrument manufacturing
- Management consulting

He has been active for many years in ACIL and other professional organizations and has over 140 publications.

Contact Information: davidk@phenomenex.com; 760-992-0655

Kiepper, Brian

Dr. Brian Kiepper has held the position of Assistant Professor and Extension Specialist in the Department of Poultry Science at the University of Georgia (UGA) since 2008. He also holds adjunct faculty status in the UGA College of Engineering. Prior to starting his faculty appointment in 2008, Dr. Kiepper spent 10 years as a research engineer within the Faculty of Engineering Outreach Service at UGA. Dr. Kiepper's teaching, research and extension program focuses on water (in the areas of consumption, conservation, and re-use), wastewater (in the areas of generation, assessment, and treatment), and waste minimization in commercial and industrial manufacturing plants. Dr. Kiepper received his BSA degree in animal science from Tennessee Tech University; and his MS in food science and PhD in poultry science from the University of Georgia.

Contact Information: bkiepper@uga.edu; 706-542-6776

Konschnik, Joseph

Market Research Manager, RESTEK Corporation, 11 years with RESTEK

Joe Konschnik earned his B.S. Degree in Public Health/Environmental Health from West Chester University in West Chester, Pennsylvania. He also completed graduate level courses at UC San Diego and UC Irvine while working full-time for environmental labs in southern California.

Mr. Konschnik worked in the environmental laboratory industry for nineteen years before joining RESTEK in 2001. During his laboratory career, Mr. Konschnik performed wet chemistry, metals, and GC/MS methods and held management roles as GC/MS supervisor and Organics Lab Manager. He also served in senior management positions with environmental laboratory services companies in various operational and technical management roles, including Advanced Technologies Business Director, Technical Director and Laboratory General Manager with some of the nation's largest testing laboratory companies. In his current role Mr. Konschnik represents the voice of the customer for the sample preparation, air monitoring and chemical standards product lines, for all market segments globally.

Contact Information: joe.konschnik@restek.com; 302-838-5796

Lipps, William

Water Analyzer Products Manager, OI Analytical

William joined OI Analytical in 2004 as a product specialist for the automated chemistry analyzer (ACA) product line and is currently manager of the OI TOC and automated wet chemistry product lines. William is on ASTM Committee D19.05, D19.06, and the Standard Methods Committee.

Contact Information: william.lipps@xyleminc.com; 979-690-5230

Lortie, Dominic

Dominic Lortie is a chemist at the Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ), a branch of the ministry of Sustainable Development, Environment, Wildlife and Parks of the province of Quebec, Canada. He holds a M.Sc. degree in analytical chemistry from Université Laval in Quebec City, Canada, and he is currently completing a Masters degree in Nuclear Engineering at École Polytechnique in Montreal, Canada. As part of the CEAEQ, Mr. Lortie specializes in emergency preparedness and response planning. He provides extensive training to the first responder community in relation to man-made and natural disasters, including accidental releases of radioactive and chemical substances in the environment.

Contact Information: dominic.lortie@mddefp.gouv.qc.ca; 450-664-1750

Lu, Jun

Dr. Lu held a Ph.D degree in geochemistry in Virginia Tech and is a California professional geologist, certified Hydrogeologist and certified Engineering Geologist. As he has been involved in various environmentally related disciplines over 27 years of his professional career, he is in a unique position to most effectively integrate the multiple key disciplines for site characterization and forensic investigation. He has provided technical support for legal teams for environmental liability related projects and also served as a "Subject Matter Expert" of groundwater hydrogeology for the State of California Board of Professional Engineers and Land Surveyors. For the past twelve years, he has been extensively involved with environmental site characterization and forensics projects at various sites including petroleum refineries, terminals and pipelines, underground storage tanks, oil fields, MGPs, chlorinated solvents and various other industrial facilities. He has been invited to give and to chair the presentations on forensics subjects at national and international conferences and published numerous papers and book chapters within disciplines of geology and environmental forensics. Currently he is a Sr. Technical Leader with AECOM, a global professional technical and management support service provider.

Contact Information: Jun.Lu@aecom.com; 562-420-2933

Magnuson, Matthew

Matthew Magnuson is a Research Chemist with the US Environmental Protection Agency's / Office of Research and Development / National Homeland Security Research Center. After receiving his PhD from the University of Oklahoma in 1994, he joined EPA and worked on state-of-the-art research directed towards a wide range of problems in environmental and analytical chemistry related to risk management research of chemical and microbial contaminants in watersheds and drinking water. He has been involved with Homeland Security activities since November 2001, developing new approaches to resolving problems in detection, decontamination, and control of chemical and biotoxin contaminants. This includes providing advice, training, and guidance, covering a broad range of activities in Homeland Security, on topics such as: contaminants of interest; chemical terrorism; field and lab analysis, environmental and physical chemistry; and environmental data analysis.

In addition to over 50 peer reviewed publications, he has developed, presented, and evaluated training and guidance materials, targeted at field personnel, lab workers, and emergency responders, for several high profile Homeland Security projects.

Contact Information: magnuson.matthew@epa.gov; 513-569-7321

Marotta, Lee

Lee Marotta has been employed by PerkinElmer LAS for 20 years as a GC, GC/MS Product/Application Specialist helping and supporting customers in the field. Recently, Lee has a national position with PerkinElmer as a Field Application Scientist for the environmental and petroleum markets.

Prior to PerkinElmer, Lee worked at Exxon Corporate Research and Hoffman-LaRoche as a method development chemist for gas chromatography.

Contact Information: lee.marotta@perkinelmer.com; 201-864-0852

McLeroy, Keith

Mr. McLeroy is a Technical Advisor with the Oilfield Water Management Group at M-I SWACO. He had previously been with Texas A&M University for 12 years as an Associate Training Specialist and Subject Matter Expert, and is a sought out specialist in water, wastewater and oil/gas produced water chemistries and biologies. He contributes to numerous research projects at A&M, and is an analytical advisor to the Global Petroleum Research Institute at A&M's Petroleum Engineering Department. McLeroy is a member of the EPA's Hydraulic Fracturing Chemical & Analytical Methods panel. McLeroy has an extensive range of experience in analyzing and developing laboratory methods for oil & gas produced waters. McLeroy studied Microbiology at Texas Tech University and holds several environmental and laboratory certifications.

Contact Information: lmcleroy@slb.com; 713-689-2084

Miao, Xin

Dr. Xin Miao is currently an associate professor in the Geo-Spatial Science Program in the Department of Geography, Geology & Planning at the Missouri State University. He received his Ph.D in Remote Sensing and M.A. in Statistics (double degree) from the University of California, Berkeley in 2005. His research and teaching interests focus on the hyperspectral image analysis, data mining/ machine learning, environmental modeling methods, and related applications. His peer-reviewed papers in invasive species detection, ecosystem classification and sinkhole detection have been mainly published in Remote Sensing of Environment, PE&RS, International Journal of remote sensing et al. Currently he is a visiting associate professor in University of Texas at San Antonio during the sabbatical.

Contact Information: xinmiao@missouristate.edu; 417-631-1855

Misselwitz, Michelle

Michelle Misselwitz has over five years of experience with environmental and food safety applications as an Innovations Chemist at Restek Corporation. She uses her experience with sample preparation and instrument platforms including GC, GC-MS and comprehensive two-dimensional GC, to develop application data with the goal of providing a total solution for customers. Misselwitz has presented over 30 oral presentations at a variety of technical conferences and workshops. Prior to Restek she received a Bachelor of Science degree in Chemistry from The Pennsylvania State University.

Contact Information: chris.rattray@restek.com; 814-353-1300

Moore, Marlene

Marlene Moore has managed and performed work for full service sampling and testing laboratories. She majored in chemistry at Moravian College in Bethlehem, PA and has attended and provided a variety of management, business and technical training courses.

Current work includes performing assessments, evaluations and providing training. Training includes quality management training for organizational and project management, relative to sampling, testing and data collection activities of chemical and biological applications. Laboratory and sampling organizations from the private sector and government operations have benefited from the experiences and training presented during classroom discussions.

Contact Information: mmoore@advancedsys.com; 302-368-1211

Mudambi, Anand

Anand R. Mudambi is a chemist and has been working for the U.S. EPA in Washington DC since 1998. In his current position at the Office of the Science Advisor (OSA), Dr. Mudambi is the team leader of the Science & Technology Policy Council (STPC) staff. The STPC staff assists senior EPA leadership as they identify critical environmental and public health priorities and is responsible for cross-agency coordination during development of environmental policies. Prior to joining OSA, he worked in EPA's Office of Water where he developed and tested plans for coordinating local, state, and federal laboratory responses to water contamination incidents. He has also worked in US EPA's Superfund program where he developed guidance documents for analytical data review and electronic reporting requirements for laboratory analytical data. Before joining EPA, he worked for the US Army Corps of Engineers as an auditor for their National Laboratory Validation program.

Dr. Mudambi has a Ph.D. in Environmental Analytical Chemistry from the State University of New York at Syracuse, and Master's in Organic Chemistry from the University of Mumbai, India.

Contact Information: mudambi.anand@epa.gov; 202-564-2817

Nagourney, Stuart

Stuart Nagourney is currently a Research Scientist with the New Jersey Department of Environment Protection in the Office of Quality Assurance. Mr. Nagourney has held positions as:

- Research Scientist for the US Department of Energy,
- Manager of Analytical Laboratories for the Argus Division of Witco Corporation, and
- Bureau Chief for Inorganic and Radiological Services for the NJDEP.

He holds a BS in Chemistry from Brooklyn College and a MS in Inorganic and Physical Chemistry from Indiana University, Bloomington. Mr. Nagourney has taught chemistry and environmental science at several community colleges and Princeton University, and currently is an adjunct Professor of Chemistry at The College of New Jersey. His professional activities include serving on several national committees reviewing analytical test methods and providing peer review for numerous chemistry journals. Mr. Nagourney's responsibilities in the area of quality assurance and technology implementation includes conducting certification audits of environmental testing laboratories focusing on ion chromatograpy and atomic spectroscopic methods, review of DEP programs for adherence to quality principles, implementation of innovative environmental technologies and the development of staff training courses. His research includes collaborations with the USEPA and NIST to develop new reference materials to insure test method validity. He has recently provided peer review for the State of California on the analysis of groundwater samples for hexavalent chromium.

Contact Information: stu.nagourney@dep.state.nj.us; 609-292-4945

Neslund, Charles

Manager, Method Development, Specialty Services Group and Volatiles in Air Eurofins Lancaster Laboratories
With Eurofins Lancaster Laboratories for over 25 years.

Mr. Neslund is responsible for the HRGC/HRMS laboratory, the LC and GC Triple Quad section and the Method Development section of the Environmental Division. His responsibilities include management of dioxin/furan and PCB congener analysis on water, soil and tissue samples. He oversees the development of methods that employ LC/MS/MS for the analysis of glycols, urea herbicides, hydrazines and various other organics in water, solids and tissues. He has lead development efforts for the application of GC/MS/MS towards the analysis of pesticides and extractable semivolatile organics. His responsibilities also include the development and validation of methods that are required to comply with ISO 17025, GLP and FIFRA data submission requirements.

Mr. Neslund also serves as lead technical contact for evaluation of RSK175 applications, implementation of discrete analyzer chemistries and application of alternative sample preparation/digestion technologies. In addition, Mr. Neslund manages our Volatiles in Air Group. He assists in coordinating daily prioritization of workload and monitors holding time and turnaround time status of samples. He responds to client questions regarding Volatiles in Air data and methods and communicates technical issues or concerns about samples to project managers for clarification or resolution with client.

Awards:

- Dawson/Grundmann Innovation Award (1995)

Memberships

- American Chemical Society (ACS)
- Chromatography Forum of Delaware Valley (CFDV)
- Air & Waste Management Association (AWMA)
- Sediment Management Workgroup

Contact Information: cneslund@lancasterlabs.com; 717-556-7231

Nichols, Tonya

Dr. Tonya Nichols is the Associate Division Director of the Threat and Consequence Assessment Division within EPA's National Homeland Security Research Center. During her nine years at EPA, her research efforts have been directed to methods and tools to characterize contamination for assessing risks of exposure to biothreat agents.

Contact Information: nichols.tonya@epa.gov; 202-564-2338

Nobles, John

John Nobles went to work as a chemist for Georgia Pacific shortly after graduating from college. After 13 years with GP, he left to join a joint venture with several others. After three years it became clear he was a good scientist, but not a very good businessman. He went to work for PerkinElmer when venture failed. He has since worked for 4 different LIMS vendors and has been back with PerkinElmer for 12+ years. Currently an Informatics Product Specialist in the QA/QC market space. John is married 40+ years with three grown daughters. He is based in the Atlanta area and covers North America for PerkinElmer Informatics.

Contact Information: jerry.lominac@perkinelmer.com; 843-237-3036

Ostaszewski, David

David Ostaszewski is a senior manager at O'Brien & Gere located in Syracuse, New York where he has been employed for over 10 years. David currently serves as the manager of the air monitoring group at O'Brien & Gere where he manages and oversees ambient air monitoring, source emission testing, air pollution control, and air regulatory and compliance projects. He graduated from the State University of New York at Buffalo in 1986 with a degree in Mechanical Engineering and he is a registered Professional Engineer in New York State.

Contact Information: david.ostaszewski@obg.com; 315-569-3497

Packingham, Ann

Ms. Ann Packingham with InnovaPrep, a manufacturer of biological sample collectors and concentrators was involved as a laboratory technician during the R&D stages of development for the recently commercialized Concentrating Pipette, an automated micro particle concentrator which utilizes a patented process for rapid sample delivery developed by the company.

Contact Information: apack@innovaPrep.com; 816-619-3375

Parr, Jerry

Jerry Parr is the Executive Director of The NELAC Institute. He also serves on the Advisory Board for the Environmental Laboratory Washington Report, and is the conference organizer for the National Environmental Monitoring Conference. He has a BS in Chemistry from the University of Texas and has over 30 years of experience in environmental analytical chemistry.

Mr. Parr previously served on EPA's Environmental Laboratory Advisory Board, on the Board of the Environmental Sciences Section of ACIL and on several committees in the National Environmental Laboratory Accreditation Conference.

Contact Information: jerry.parr@nelac-institute.org; 817-598-1624

Pawlisz, Andrew

Mr. Pawlisz is a Senior Toxicologist at CRA for past 5 years. Previously, he has been employed by environmental consulting agencies, non-profit organizations, and government. Has over 18 years of experience planning, executing, and managing projects dealing with human and ecological risk assessments, avian and mammalian toxicology, and providing expert opinion to internal and external clients.

Mr. Pawlisz has completed his undergraduate degree at University of Guelph, Canada and a graduate degree at McGill University, Montreal, Canada.

Mr. Pawlisz is an active member of Society of Environmental Toxicology and Chemistry (SETAC), Society for Risk Analysis (SRA), and Society of Toxicology (SOT). He is a Diplomate of the American Board of Toxicology (D.A.B.T.), an European Registered Toxicologist (E.R.T.), and has published, presented, and peer reviewed numerous articles at for various organizations.

Contact Information: apawlisz@craworld.com; 972-679-7872

Perez, Gregory

Gregory Perez is Senior Environmental Analyst at the City of Tacoma Environmental Services Laboratory, located at the Center for Urban Waters in Tacoma Washington. He has been with the City for eight years, managing the Organics section of the Laboratory. He previously worked at the Washington State Department of Ecology's Manchester Environmental Laboratory performing a variety of organic analyses. He has worked in analytical laboratories since 1979. He has a Bachelor's degree in Chemistry from the University of South Florida in Tampa Florida.

Contact Information: gregory.perez@cityoftacoma.org; 253-502-2135

Peters, Ben

Ben Peters received his bachelor's degree in chemistry from LaGrange College in LaGrange GA and master's degree in chemistry from the University of Virginia in Charlottesville VA. The focus of his graduate studies where the synthesis and characterization of organic ligands, organometallic complexes and metal centered star shaped polymers. He started his career at a contract lab where he specialized in custom analysis/method development and consulting using GC/MS, Pyrolysis GC/MS, Purge and Trap GC/MS, Thermal desorption GC/MS/FID, Whole Air GC/MS, GC/FID, GC/TCD, GC/ECD, HPLC, FTIR, ICP-OES, and SEM/EDX. After nine years in this position he changed companies where as a Research and Support Chemist his responsibilities included QA/QC, product R&D, liaison between production and management. Following this he was a consultant providing analysis and expert testimony for private industry, contract labs, and law firms. Currently he is an Applications Specialist for CDS Analytical where his focus is on both education of current methods and discovering new markets for CDS products.

Contact Information: bpeters@cdsanalytical.com; 610-932-3636

Phatak, Sumedh

After earning his Bachelor's degree in Chemical Engineering from the Institute of Chemical Technology (UDCT) in India, Sumedh Phatak came to the US to pursue his Masters degree in Chemistry from Syracuse University. There he worked as a Teaching Assistant and a Research Assistant while conducting research on polymer chemistry. He has been working with Milestone Inc. as the Applications Chemist for about a year. Based out of their US headquarters in Shelton Connecticut, Sumedh primarily works on method development for customer samples, troubleshooting, providing on-site and remote applications support, marketing support and he also presents Milestone's technology to prospective clients through demonstrations, trade shows and webinars.

Contact Information: s.phatak@milestonesci.com; 866-995-5100

Phelps, Lara

Lara P. Phelps is the Senior Advisor for Measurement, Modeling, Monitoring, and Laboratory Science Issues with the U.S. Environmental Protection Agency (EPA) in the Office of the Science Advisor (OSA). In over 18 years with the EPA, she has served in various positions and roles within the Office of Air and Radiation and the Office of Research and Development before joining the OSA staff. Over her years of government service, she has gained expertise in a wide range of areas from budgeting and program planning to innovative strategies and technologies. At present, she is not only an advisor for science issues, but is serving as the Director of the Forum on Environmental Measurements, Director for the Council on Regulatory Environmental Modeling, Designated Federal Official for the Environmental Laboratory Advisory Board, and Quality Assurance Manager for OSA. As a native of North Carolina, Lara elected to do her Bachelor's and Master's work in Statistics at North Carolina State University with a minor in Mathematics. She has received numerous honors including four bronze medals and service recognition in support of the Nation's response to the Deepwater Horizon Oil Spill. Lara is also involved in several professional organizations such as The NELC Institute (TNI), the Source Evaluation Society, and the Air and Waste Management Association to list a few.

Contact Information: phelps.lara@epa.gov; 919-541-5544

Philp, Paul

R. Paul Philp has been a Professor of Petroleum and Environmental Geochemistry at the University of Oklahoma since 1984. He has a Ph.D. and D.Sc. from the University of Sydeny, Australai and a B.Sc. degree from the University of Aberdeen Scotland.

His current interests in the environmental field involve the application and utilization of stable isotopes to various aspects of environmental forensics. This includes their use in groundwater studies and vapor intrusion studies.

Contact Information: Pphilp@ou.edu; 405-325-4469

Phillips, John

John Phillips is a Principle Environmental Engineer with the Ford Motor Company and has worked in the Environmental Quality Office at Ford managing their environmental laboratory program for the past 20 years. Mr. Phillips has currently serves on the board of the Michigan Environmental Laboratory Association, sits on the Environmental Laboratory Advisory Board and the TNI Chemistry Expert Committee. He received a Bachelor of Science degree from Central Michigan University and a Masters' degree in Environmental Chemsitry from Michigan State University. He has also participated in the graduate environmental engineering program at Drexel University in Philladelphia, Pennsylvania. Mr. Phillips spent 13 years as an Environmental Research Chemist at Air Products and Chemicals prior to joining Ford.

Contact Information: jphill12@ford.com; 313-845-1648

Rattray, Christopher

Chris has a Bachelor of Science in Chemistry from the University of California, Riverside, and substantial experience with GC, GC-MS, sample preparation, standards formulation, and instrument calibration. His years performing organic EPA analysis include extensive work with methods 8270, 8260, 8141, and 8081. Over the course of his tenure at Microbac Laboratories, Inc., he was an organic analyst, organic supervisor, and technical director of the lab. After coming on as Restek's Environmental Innovations Chemist in 2011, Chris has been concentrating on the optimization of existing environmental methods.

Contact Information: chris.rattray@restek.com; 814-353-1300

Rose, Bob

Bob Rose has worked for the US Environmental Protection Agency (EPA) since graduating with a Masters Degree in Engineering from the University of Maryland in 1990. He joined EPA prior to the final phase out of Chlorofluorocarbon (CFCs), chemicals largely responsible for atmospheric ozone deletion, which was the focus of his graduate school research.

After the phase out of Chlorofluorocarbons he worked for the ENERGY STAR program, where he designed and managed the nation's first and only benchmarking system for comparing the energy efficiency of commercial buildings based on actual energy consumption and statistical comparison. Over 25% of the nation's commercial square footage has voluntarily been benchmarked, with the best performing quartile eligible for recognition by ENERGY STAR.

Since joining Office of Water in 2005, his interests have included technologies and methods of expanding water quality monitoring, partially as it serves water quality trading in which low cost, off site pollution reductions can be credited to regulated point sources.

Contact Information: rose.bob@epa.gov; 202-564-0322

Rosnack, Kenneth

Ken Rosnack is a Business Development Manager in the Food & Environmental Business Operations group for Waters Corporation. He joined Waters as part of the mass spectrometry organization. Mr. Rosnack has been involved with Mass Spec for the past 25+ years. He spent the first 10 years post graduate in the Pharmaceutical Industry where he focused on small molecule characterization for five years and then Protein/Peptide analysis for the next five. Following his career in pharmaceutical research, he took a position within the mass spectrometry instrument manufacturers' field and in 2000 accepted a position with Waters Corporation. Mr. Rosnack obtained his Masters Degree in Analytical Chemistry under the guidance of Dr. David Hercules at the University of Pittsburgh.

Contact Information: ken_rosnack@waters.com; 508-482-4639

Sack, Chris

Chris received a B.A. in Chemistry from the University of Kansas in 1982 and began his career as a chemist at the US Food and Drug Administration in March 1983 where he has continued for over 30 years. In his current position of Residue Expert he provides oversight of FDA pesticide operations, both locally and nationally. He works closely with international experts to enhance and develop analytical capacities of foreign residue laboratories. He is a member of World Health Organizations' guidance committee for International Total Diet Studies that provides expert advice for the continuing development of national TDS programs and plans the International Total Diet Study Workshops.

Chris is the author of several publications, including the FDA procedure for the determination of pesticides by LC-MS/MS. He have given over 80 presentations to a wide variety of constituents, from high school science students to national and international scientists and regulatory bodies, in equally diverse forums, from radio talk shows to international assemblies. He is the recipient of over 70 awards and letters of commendation including the FDA ORA Outstanding Service Award.

Contact Information: chris.sack@fda.hhs.gov; 913-752-2182

Sebroski, John

John is a Senior Scientist in the Environmental Analytics laboratory for Bayer MaterialScience LLC, located in Pittsburgh, PA. John is a graduate of Duquense University where he received his Master's degree in Environmental Science and Management. John is currently the chair of the Spray Polyurethane Foam Emissions Workgroup at the Center for Polyurethanes Industry of the American Chemistry Council. He is also the chair of the Spray Polyurethane Foam Emissions task groups at ASTM Subcommittee D22.05 on Indoor Air Quality.

Contact Information: john.sebroski@bayer.com; 412-777-3420

Shock, Ray

Ray Shock is an analytical chemist at TestAmerica Labs in Canton, OH. He has worked for TestAmerica for the last eight years and is currently focused on methylmercury analysis. He earned his bachelors degree in chemistry from Hope College in Holland, MI.

Contact Information: ray.shock@testamericainc.com; 330-966-9396

Sica, Matthew

Matthew Sica is the Principal Scientist for Matthew Sica Consulting, a consulting company specializing in laboratory operations and quality systems. With over 20 years' experience, he has gained expertise in management and quality systems, laboratory accreditation and certification, monitoring and testing issues, proficiency testing, and regulatory issues. With this perspective, he now brings together the needs for data users, data generators and regulators.

He has managed laboratories and has experience working for environmental testing and petroleum laboratories in areas ranging from bench chemistry and microbiology, field sampling, environmental site work and waste disposal. Field sampling and testing included work in site remediation and drinking water and wastewater programs.

He earned a Bachelors of Science degree in Environmental Science, with a concentration on environmental chemistry, at Rutgers University in New Brunswick, New Jersey. He has attended and provided a variety of management and technical training courses.

He is an EPA recognized Laboratory Certification Officer for the EPA Safe Drinking Water Program for inorganic chemistry, organic chemistry, microbiology and Cryptosporidium.

Current work includes consulting, training, and assessing for environmental and food laboratories, reference material producers and proficiency test providers to applicable standards including ISO/IEC 17025, DOD ELAP, ISO Guide 34, and ISO/IEC 17043.

Contact Information: msica@anab-aclass.org; 207-624-1532

Simon, Charles

Dr. Simon earned a Master's Degree in Environmental Analytical Chemistry from the University of South Carolina in 1979, and a PhD in physical chemistry from the University of Florida. He's been Director of VOC Reporting since its inception in 2010. Prior to that he operated another Method 25 laboratory for 15 years while also working as a contractor with the US Department of Justice Environmental and Natural Resources Division and EPA's Office of Enforcement and Compliance Assurance. He was the technical lead on dozens of cases involving hundreds of facilities from 1994 to 2012. He's also worked with NASA to define the sub-micron particulate ambient in low earth orbit, and with the Defense Threats Response Agency to develop and field automated radioactive particle and gas air sampling systems in support of the United Nations' Comprehensive Test Ban Treaty.

Contact Information: cgsimon@gowebway.com; 352-472-2899

Slavin, JoAnn

Joann Slavin, Senior Vice President and Laboratory Director, is responsible for and directs all laboratory operations and activities. She maintains all records for laboratory operations, including reports, billing and purchasing, is responsible for all contract administration, and serves as liaison between lab and client. She directs more than 50 scientists and technicians and manages the programs necessary to conduct the organic, inorganic, and bacteriological services of the laboratory. She also reviews and supervises the methods, protocols, and guidelines for sample collection and analysis based on USEPA and state contract requirements and chain-of-custody procedures. Slavin is currently a member of the H2M Board of Directors and is an ESOP Trustee As the Laboratory's safety officer, OSHA representative, and trained toxicologist, Slavin supervises all aspects of occupational safety and health programs.

In addition to her professional responsibilities, Slavin is the Past- President of the Melville Rotary and serves on the Melville Rotary board of directors. She has also worked with The INN, Family and Children's Services, and on a project sending American physicians to train doctors in geriatrics in Bangalore, India. She was an Amityville Girl Scout leader for 13 years, received an outstanding volunteer award from Girl Scouts of Suffolk County. She has also worked with the Harlem Children's Society on a program offering summer internships in the laboratory for high school students.

Slavin is a member of the American Laboratory Managers Association; New York Association of Approved Environmental Laboratories; American Chemical Society; ACIL; American Society of Mass Spectroscopy; Rho Chi Pharmaceutical Honor Society; and the Society of Forensic Toxicologists. A graduate of St. John's University with a BS and MS in toxicology, she resides in Amityville, NY with her husband Thomas and two children, Melissa and Thomas.

Contact Information: jslavin@h2m.com; 631-694-3040

Smelko, John

Mr. John J. Smelko has been serving as the North Region Environmental and Regulatory Compliance Manager for Cabot Oil & Gas Corporation since February of 2010. He graduated from the University of Pittsburgh and has more than 25 years of professional experience in the environmental field. Mr. Smelko spent much of that time in environmental consulting, starting with a part-time entry level position and working into high-level management. He has developed a diversified background serving both public and private sectors, and has served various industries, including oil and gas and petrochemical. He has worked as a chemist in both analytical and treatability laboratories, performed work as a field and project chemist, worked as a sampling and remediation technician, performed oversight and leadership roles in the areas of EH&S and demolition, and held field, project, operations, and office management positions.

Contact Information: john.smelko@cabotog.com; 412-249-3854

Smith, Kathy

Kathy Smith is Senior Database Administrator and Project Manager at The Narragansett Bay Commission (NBC) in Providence, Rhode Island and has been an employee there for 10 years. Kathy's career in Information Technology has spanned more than 30 years, beginning as a Programmer and advancing through numerous roles within Digital Equipment, Compaq and Hewlett Packard. As her career progressed, Kathy found an affinity for Databases and became an expert in both the Networked and Relational disciplines. She remains instrumental in designing and developing leading edge technology and displays an ability to see beyond the obvious when proposing a new solution. Kathy has a BS in Business Administration with a minor in Computer Science.
Most recently, Kathy has worked closely with a vendor to bring a state of the art Laboratory Information Management System (LIMS) to NBC. Throughout the process, Kathy was a visionary, first in understanding the complexities of the implementation and then suggesting solutions to the process. One significant inroad was the Mobile Solution that she will discuss today.

Contact Information: Ksmith@Narrabay.com

Smith, Stan

- Product Specialist for 4 years with Perkin Elmer, Inc.
- B.S. in Chemistry from Rensselaer Polytechnic Institute

Mr. Smith has over 20 years of experience in the environmental field and 28 years in the analytical laboratory environment. He has held several positions in laboratory operations, quality assurance, technical development, environmental health and safety, and laboratory management with environmental firms including Environment/One Corporation and Safety-Kleen. With Perkin Elmer, Mr. Smith spends most of his time working on applications and method development for inorganic spectroscopic techniques for a wide variety of industries.

Contact Information: stan.smith@perkinelmer.com; 630-368-3481

Speis, David

CEO; President, Environmental Services Division; QC Laboratories

Mr. Speis is the CEO and President of the Environmental Services Division for QC Laboratories in Southampton, Pennsylvania, where he has been employed since 2012. Mr. Speis began his career in environmental chemistry in 1969. His experience in environmental chemistry includes eleven (11) years with USEPA Region II as a bench chemist conducting the analysis of organic pollutants using sophisticated instrumentation. Mr. Speis is a member of the USEPA's Environmental Laboratory Advisory Board (ELAB – a Federal advisory committee) and Past Chair, a Board member and Treasurer of The NELAC Institute TNI) and a member of the Executive Committee for ACIL's Environmental Sciences Section. He served on the Editorial Advisory Board of Environmental Testing and Analysis and on the board of the International Association of Environmental Testing Laboratories (IAETL). He assisted in developing the initial framework for National Environmental Laboratory Accreditation while a member of the IAETL board. He served as the secretary of the New Jersey Department of Environmental Protection's Environmental Laboratory Advisory Committee and as the Chairman of the Board of Directors of the Institute for National Environmental Laboratory Accreditation.

ASSOCIATIONS

- The NELAC Institute, Board of Directors; Treasurer, Past Vice Chair, Member Field Activities Committee.
- Executive Committee of the Environmental Services Section of the American Council of Independent Laboratories (ACIL)
- National Environmental Monitoring Conference (NEMC) Board of Trustees
- Environmental Laboratory Advisory Board (ELAB – Federal advisory committee to USEPA) Member; Past Board Chair

EDUCATION

- BS Science Education, Northeastern University, Boston, Massachusetts

RELATED EDUCATION AND EXPERIENCE

- Published numerous articles on various topics in environmental chemistry and business management of commercial laboratory operations and is a frequent presenter at national conferences and forums.

Contact Information: dspeis@qclaboratories.com; 215-355-3900

Steady, Scott

Scott Steady is the Product Manager for VOC Emissions Testing and Certification at UL Air Quality Sciences in Marietta, GA. He graduated from Louisiana State University (cum laude) with a bachelor's degree in Chemical Engineering in 2000. After graduating, he worked for Trinity Consultants for 3 years assisting manufacturers with industrial source permitting and Clean Air Act compliance. For over 10 years, Scott has been working with manufacturers in the building products, furniture, electronics, and consumer products industries to help them understand their products impact on indoor chemical exposure levels. He has participated in development of the GREENGUARD Certification Programs, the BIFMA M7.1 test method for measuring emissions from office furniture, and he actively participates on the ASTM D22 committee on Air Quality.

Contact Information: 734-913-5774

Stefkovich, Joseph

Joe Stefkovich is currently a Product Manager with Xenosep Technologies and has been with them now for approximately 10 years. Previously, Stefkovich worked for Whatman (now GE Healthcare) for over 17 years where he was first introduced to Oil and Grease Testing and EPA Method 1664 in the early 1990's and has kept abreast of new developments in SPE and modifications ever since.

Contact Information: joe.stefkovich@xenosep.com; 973-239-0247

Sueker, Julie

Dr. Sueker is a hydrologist with 23 years of professional experience in geochemistry, environmental forensics, physical hydrology, isotope hydrology, isotope geochemistry, and hydrogeology. She has considerable experience in designing, managing, and conducting environmental forensic investigations and is skilled in applying physical, chemical, isotopic, and statistical approaches to evaluate sources and fate of constituents of interest in soil, surface water, and groundwater. Dr. Sueker leads the Applied Isotope Geochemistry technical team for ARCADIS.

Contact Information: Julie.Sueker@arcadis-us.com; 303-231-9115

Sun, Helen

Helen Sun is currently working as a product marketing specialist for GC/LC triple quadrupole mass spectrometers of Bruker. She got her Ph.D degree in analytical chemistry from University of California, Riverside in 2011, and worked as a research fellow in buck institute in the bay area continuing her research in mass spectrometry analysis. She joined Bruker Chemical and Applied Markets in May, 2012, working on developing new applications using GC and LC-triple quadrupole mass spectrometers.

Contact Information: helen.sun@bruker.com; 510-683-4330

Sylvester, Guy

Guy Sylvester is the CEO of Absolute Resource Associates in Portsmouth, New Hampshire, which he purchased with his wife Susan in 2000. Sylvester has over 25 years of experience in Industrial Hygiene, Environmental Indoor Air Quality and Environmental Analytical Testing. He currently is the Chapter Director for the Manchester New Hampshire Indoor Air Quality Association. He serves on the New Hampshire and North East Board of Directors of the American Lung Association, and National Board of Directors for the American Council for Accredited Certifications (ACAC.). Sylvester is a practicing Industrial Hygienist, Board Certified Microbial Consultant, Board Certified Indoor Environmental Consultant and State Certified Asbestos Inspector. Sylvester is also the Author of the book "MOLD: Myth or Monster?", and is a past winner of the New Hampshire Business

Review Business Excellence Award. Sylvester received his Bachelors Degree at California State University, Fullerton, and completed Post Graduate Course Work at the University of California, Irvine. His Continuing Education Course Work has been ongoing throughout his career as he maintains the training, licenses and credentials necessary to run his business, and stay current with the ever changing technology, methods, laws and trends which affect the environmental industry.

Contact Information: guys@absoluteresourceassociates.com; 603-436-2001

Telliard, William

Mr. Telliard joined the U.S. Environmental Protection Agency Office of Water Enforcement and Permits in 1972. In 1976, he transferred into the Office of Water Effluent Guidelines Division as Chief of the Energy and Mining Branch. He later became Director of Analytical Methods Staff in the Engineering and Analysis Division in the Office of Science and Technology--where he served until his retirement in 2006.

He directed and coordinated analytical methods development, sampling, analysis, and quality control/quality assurance for the EPA Office of Water. He has been principally responsible for the development of the list of Priority Pollutants and EPA's Environmental Monitoring Methods Index (EMMI). He was responsible for the selection of gas chromatography/mass spectrometry (GC/MS) as EPA's technique of choice for the measurement of organic pollutants. He was actively involved in the development and promulgation of regulations for the control of industrial discharges to waters of the United States.

According to an EPA memo, more than 100 analytical methods were developed under Mr. Telliard's direction during his 34-years at EPA. Those methods were developed for use in detecting the presence of numerous contaminants, including mercury, dioxin, PCB congeners, and parasites such as Cryptosporidium and Giardia.

Contact Information: watelliard@comcast.net; 804-756-7515

Tondeur, Yves

Education

- MS Chemistry & Ph.D. Chemistry from Free University of Brussels
- Postdoctoral Fellow, National Institute of Environmental Health Sciences, Research Triangle Park, NC
- Postdoctoral Fellow, Florida State University

Experience

Dr. Tondeur has more than 34 years of experience in environmental method development and applications. At the end of 1999, he started Analytical Perspectives, and is currently president and CEO. For nearly a decade and until recently, he was responsible for the day-to-day operations, Technical Director, and Quality Assurance Officer roles. During that time period, to comply with the promulgated EPA Methods Innovation Rule, he developed a tangible PBMS approach for comprehensive stable isotope-dilution mass spectrometry methodologies. The innovative analytical tool is applicable to Methods 8290, 23, TO-9A, 1613, 1668 and CARB 429. It aligns these methods' infrastructures with one that is better suited for the true and sustained application of PBMS. Embedded in the methodology are new, additional, and more effective QA/QC raising the laboratory's performance to higher levels than ever before; thus, significantly enhancing the data reliability and ensuring the data is fit for purpose. Dr. Tondeur helped introduce isotopedilution high-resolution mass spectrometric methodologies to the commercial field, authoring the first version of Method 8290. In the late eighties and early nineties, while as a partner with Triangle Laboratories, Dr. Tondeur worked with the EPA Office of Water in the development of Method 1613, and with the Office of Air Quality and Planning Standards in the development of the analytical section of Method 23. He organized a series of Executive Seminars at Analytical Perspectives, and

has offered numerous training seminars; e.g., QA in Thailand for USAID, teaching at the College of Mechanical & Energy Engineering, Zhejiang University, China; USEPA RTP, NC Workshop, and Texas Commission on Environmental Quality Workshop. He has published nearly 100 peer-reviewed articles in the scientific literature, some of which are book chapters. Several invited plenary lectures were given by Dr. Tondeur at International Symposia. He holds a patent on a process for extracting 2,3,7,8-tetrachlorodibenzo-p-dioxin, and, in March 2012, he was inducted into the Source Evaluation Society's Hall of Fame.

In April 2012, SGS acquired the assets of Analytical Perspectives. Dr. Tondeur is currently VP at SGS Analytical Perspective

Contact Information: yves.tondeur@sgs.com; 910-794-1613

Villegas, Leah

Leah Fohl Villegas Ph.D. is a Scientist V for CB&I Federal Services, with more than ten years of experience in parasitology. She was awarded her Ph.D. from the University of Pennsylvania and has worked on a variety of protozoan and viral pathogens of economical, environmental, and biomedical importance. Dr. Villegas has spent the majority of her career developing assays and methods for everything thing from assessing levels of complex cyanide in water to monitoring the fitness of drug-resistant apicomplexan parasites. Her current work is focused on developing enhancements to EPA Method 1623 for the detection of Cryptosporidium and Giardia parasites in surface water. Dr. Villegas trains analysts to perform Method 1623 and developed the online course and training tools for certification officers to audit the Method.

Contact Information: Villegas.Leah@epa.gov; 513-569-7886

Vining, Bryan

Bryan earned his doctorate in chemistry at Florida State University, working with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry at the National High Magnetic Field Laboratory. After a postdoctoral stint at Yale University, he began working on a variety of quantitative and qualitative analytical approaches using mass spectrometry. He spent seven years working in the pharmaceutical industry and six years in the environmental testing field. His current position is Director, Technical and QA Officer at SGS Analytical Perspectives in Wilmington, NC, where he has been working since 2008.

Contact Information: bryan.vining@sgs.com; 910-794-1613

Walker, Dale

Dale Walker is employed by Agilent Technologies as a Gas Phase applications chemist. His duties include working with environmental laboratories within North America to optimize applications utilizing gas chromatography (GC) and gas chromatography mass spectrometry (GC/MS). With over 25 years working with environmental testing methods, Dale previously was employed by a large environmental testing laboratory.

Contact Information: Dale.Walker@agilent.com; 916-458-2940

Waller, Debra

Debra Waller has been a Lead Certification Officer and NELAP assessor for the New Jersey Department of Environmental Protection for more than 10 years. Debra is in charge of the microbiology auditing team and microbial regulatory concerns for the NJDEP. Debra is also developing the cryptosporidium and giardia assessment program for the NJDEP. She is the Quality Assurance Officer for the NJ BEACH and several ambient water monitoring projects including the Barnegat Bay Monitoring Project. Debra specializes in quality assurance and quality control for ambient, drinking, biosolids, wastewater and public recreational sample testing. A former

licensed sewage treatment plant operator, twenty year drinking/wastewater laboratory veteran and the recipient of the NJWEA's Laboratory Analyst Excellence Award, Debra also specializes in the chemical analysis of wastewater and ambient water and has been instrumental in the research and development of ambient water method certification and project specific laboratory approvals for the NJDEP.

Contact Information: debra.waller@dep.state.nj.us; 609-984-7732

Watson, Kim

Ms. Watson is the Quality Assurance Manager at Stone Environmental, Inc. in Montpelier, Vermont. She manages compliance with Good Laboratory Practices (GLP) Standards (40 CFR Part 160), the National Environmental Laboratory Accreditation Program (NELAC) quality system and 17025 Standards, and Corporate Quality sAssurance (QA) programs. Her responsibilities include tracking regulatory updates, supervising QA/QC internal procedures and in the field, acting as the Quality Assurance Unit (QAU) for EPA related studies. She is responsible for developing and implementing quality systems for company processes both project and non-project related. She supports investigations for soil, air groundwater and surface water studies, database management, and report and quality assurance project plan (QAPP) writing.

Ms. Watson has over 29 years of experience in all phases of production and laboratory procedures, quality control and quality assurance, QA management and project management in an environmental analytical laboratory encompassing the EPA regulated environments (GLP, RCRA and CERCLA). She has over fifteen years of experience in private quality assessment consulting, data and method validation, environmental project planning and coordination, field and laboratory audits, third party review, and single and double blind performance testing programs.

Contact Information: kwatson@stone-env.com; 802-229-2196

Wellman, Melissa

Melissa Wellman has earned both a Bachelors and Masters Degrees in Meteorology. She has been working with the Air Quality Measurements and Studies Group within AECOM's Chelmsford, MA office for five years. Her project experience includes: ambient air quality, meteorological monitoring networks, and fenceline monitoring programs. Melissa's Fenceline air monitoring experience is associated with various remediation type activities primarily measuring PM10 and VOCs plus integrated sampling for specific VOCs (BTEX), particulates, Lead, Arsenic, PCBs, PAHs, and Hexavalent Chromium. Ms. Wellman is currently the deputy project manager for a number of AECOM operated fenceline air monitoring programs in New York, Massachusetts, New Jersey, Wisconsin, Ohio, Georgia, Pennsylvania, and Connecticut. Her responsibilities include: managing onsite field technicians, troubleshooting with the field technicians and directing the technical support of engineering staff, state agency and client exceedance notifications, database management, and data reporting.

Contact Information: melissa.wellman@aecom.com; 978-905-2100

Whetzel, James

Jim Whetzel has a B.S. degree in Chemistry and is a Project Manager and Quality Manager for the Survey Products Group of W. L. Gore and Associates. He has been with Gore for over 15 years and has more than 25 years experience in the environmental field, working in laboratories in Maryland, North Carolina, and Minnesota. His primary areas of responsibility include project management and technical support for GORE® Surveys, quality assurance, and development of new product applications. Jim has presented at more than a dozen conferences on the topic of passive sampling in air, water, and soil gas. He is also a contributing author on several ASTM and ITRC documents focused on passive sampling.

Contact Information: whetzel@agisurveys.net; 410-506-4776

Wilbur, Steven

Steve Wilbur is the software product manager for ICP-MS products at Agilent Technologies. He joined HP/Agilent in 1989 as a GC/MS applications engineer, and moved to the ICP-MS group as an applications scientist in 1995 with the introduction of the HP-4500, the world's first benchtop ICPMS. He has a Master's degree in molecular biology from Humboldt State University.

Contact Information: steven.wilbur@agilent.com; 425-356-6333

Williamson, Bill

Bill Williamson is a Senior Research Scientist in the Environmental Engineering and Monitoring Section within the Chemistry and Chemical Engineering Division at Southwest Research Institute in San Antonio, Texas. He has been with Southwest Research Institute for 20 years, with 15 years focused on analytical analysis of chemical warfare agents. Mr. Williamson's main area of expertise is the development of analytical techniques for detecting trace chemical agents in difficult matrices. He received an MBA and a B.S. in Chemistry, from the University of Texas at San Antonio.

Contact Information: bwilliamson@swri.edu; 210-522-2187

Willison, Stuart

Dr. Stuart Willison received his Ph.D. from the University of Cincinnati in Chemistry. He began working for the National Homeland Security Research Center at the Environmental Protection Agency in 2008 as a research chemist. His work has focused on method development in various matrices of concern for hazardous chemicals during the remediation of public areas after an incident.

Contact Information: Willison.stuart@epa.gov; 513-569-7253

Winkler, Paul

Dr. Winkler received his undergraduate degree in chemistry from the University of Colorado Denver in 1978 and his Ph.D. in analytical chemistry from the Georgia Institute of Technology in 1986. He started his post graduate career at the Dow Chemical Company where he was the Western Region Director for mass spectrometry. After leaving Dow, Dr. Winkler worked for the Finnigan Corporation developing LC/MS techniques including particle beam, thermospray, electrospray and APCI. Dr. Winkler left Finnigan and began a 15 year career working in contract laboratories in the environmental and pharmaceutical industries where he worked on developing LC/MS/MS methods for a wide variety of compounds and matrices. Dr. Winkler has been a Senior Field Application Specialist for AB Sciex for the last two years.

Contact Information: paul.winkler@absciex.com; 303-882-0792

Wyeth, Robert

Senior General Manager; Pace Analytical Services, Inc.

Mr. Wyeth is a 40 year veteran of the commercial environmental testing industry. He has served as a member of and Chairman of the Environmental Laboratory Advisory Board, a federal advisory committee to EPA and as an expert to the EPA Office of the Inspector General (OIG). He has also served as the National Laboratory Practices Chairman of the Water Environment Federation, served as member of various NELAC committees, as well as the Board of Directors of TNI. He currently serves as the Chairperson of the Consensus Standard Development Executive Committee. Mr. Wyeth is a member and past Chairmen of the ACIL Environmental Sciences Section. As a commercial environmental testing laboratory representative, Mr. Wyeth has also been involved at the

Federal, State and local levels in support of the overall needs of laboratories within the environmental community. On the professional level, executive management positions in laboratory administration, operations, and technical/sales management and quality assurances are areas of responsibility currently and/or previously held by Mr. Wyeth. Mr. Wyeth holds BS degrees in Chemistry and Physics from Illinois State University, and an MS in Chemistry from the State University of New York, College at Buffalo.

Contact Information: rfwyeth@yahoo.com; 716-674-1731

Yakub, Gary

Mr. Yakub is employed at Environmental Standards, Inc. as a Senior Quality Assurance Chemist. He has worked at Environmental Standards for three years.

Mr. Yakub has over twenty-five years of experience in the environmental field, working first as a laboratory analyst, then as the laboratory's Quality Assurance Officer, and now as an environmental consultant specializing in corporate environmental liability issues.

As an analyst, Mr. Yakub has performed all phases of environmental analyses, including wet chemistry, metals and mercury digestion and analyses, volatile organic analyses, semi-volatile organic analyses, pesticide and PCB analyses, and microbiological analyses.

As Quality Control Officer, Mr. Yakub developed and instituted a complete Quality Assurance/Quality Control Program for the laboratory, including documentation, sample and data handling procedures, chain-of-custody, internal auditing, a performance evaluation program, ethics/data integrity, and data validation.

Mr. Yakub has published peer-reviewed, original research on a variety of topics in wastewater microbiology and written chapters for environmental microbiology textbooks.

As an environmental consultant serving the environmental community, Mr. Yakub currently provides laboratory accreditation assistance, laboratory compliance audits, environmental data validation, document preparation and review, and other services to the client.

Mr. Yakub received a Bachelor of Science Degree in Biology from Indiana University of Pennsylvania, Indiana, PA in 1984, and a Bachelor of Science Degree in Chemistry from Duquesne University, Pittsburgh, PA IN 1986.

Contact Information: gyakub@envstd.com; 610-935-5577

Yang, Shen-yi

Ms. Shen-yi Yang, the RCRA Methods Program Manager, has joined the EPA Office of Resource Conservation and Recovery (formerly the Office of Solid Waste) for 22 years. Prior to joining the RCRA Methods Team, she worked as an Environmental Protection Specialist for the hazardous waste listings and delistings programs, especially on issues associated with waste sampling and analysis.

Earlier in her career, Ms. Yang worked as a project chemist in environmental engineering firms located in Maryland and Florida in support of site remediation projects for federal facilities for the U.S. Air Force, Navy, and Army Corp of Engineering; as a QA chemist and project coordinator in environmental laboratories; and as a chemist for the North Carolina Department of Nature Resources and Food and Drug Administration. Ms.Yang received a M.S. in soil chemistry from the Southern Illinois University, Carbondale, IL., and a B.S. in soil science from the National Chung Hsing University, Taichung, Taiwan.

Contact Information: yang.shen-yi@epa.gov; 703-308-0437

Yost, Debby

Debby L. Yost serves as a Senior Environmental Specialist with Chesapeake Energy Corporation and works at Chesapeake's corporate headquarters in Oklahoma City. Yost has been part of the Environmental Health and Safety and Regulatory Affairs Department since 2007. Yost has worked on a variety of projects involving both regulatory affairs and compliance issues associated with oil and gas exploration and production. Yost has a Bachelor of Science in Microbiology and a Master of Science in Agronomy (emphasis on soil chemistry and fertility) from Oklahoma State University. Prior to joining Chesapeake she worked as the Quality Control/Quality Assurance Manager for The Benham Group (now SAIC) offices in Oklahoma, Texas, Arkansas and Missouri for almost 18 years. Before that Yost worked at Oklahoma State University running the Cooperative Extension Services Soil, Water and Forage Analytical Laboratory and overseeing soil fertility research projects for over 13 years. During her time at OSU she authored and co-authored a number of publications.

Yost has also been an active participant in the Marcellus Shale Coalition (MSC) and has been part of Environmental Stewardship Subcommittee since 2010. She has served as chair or co-chair of this subcommittee and has overseen the development and roll-out of Recommended Practices on pre-drill water surveys and stray gas investigations as well as development of a Sampling and Analysis Plan for pre-drill sample collection and related fact sheets. Debby also participated in a work group tasked with developing a database for housing pre-drill water test data for MSC operator members.

Contact Information: debby.yost@chk.com; 405-935-4179

Zeiner, Stephen

Mr. Zeiner received a Bachelor of Science Degree in Chemistry from Shippensburg University. Mr. Zeiner is a certified environmental analytical chemist. Mr. Zeiner spent several years in an independent environmental laboratory prior to joining Environmental Standards, Inc. Stephen has been with Environmental Standards, Inc. for 19 years. As a Senior Technical Chemist, Stephen specializes in environmental chemistry quality assurance consulting, indoor air quality investigations, industrial laboratory program development and support, laboratory auditing, and data validation. Stephen has recently been involved with a large multi-state investigation/cleanup and administers two nationwide laboratory programs.

Contact Information: szeiner@envstd.com; 610-935-5577