NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

2008 PROCEEDINGS

Section 6:
Future Trends in Monitoring
Innovative Approaches
Performance Approach

Washington DC
August 10 – 16, 2008

ILI
INDEPENDENT LABORATORIES INSTITUTE

ELAB

THE NELAC INSTITUTE

NEMC

NEMC 2008
SYMPOSIUM SPONSORS

NEMC 2008
PROGRAM COMMITTEE

CONFERENCE CHAIR

Lara Autry, USEPA Office of the Science Advisor

PROGRAM CHAIR

Earl Hansen, PhD., Independent Laboratories Institute

CONFERENCE ORGANIZER

Jerry Parr, The NELAC Institute

BOARD OF TRUSTEES

Robert Benz, NSI Solutions
H. M. (Skip) Kingston, PhD., Duquesne University
Matthew Sica, Maine Center for Disease Control and Prevention
David Speis, Accutest Laboratories
Jan Young, USEPA Office of Solid Waste

SESSION CHAIRS

Lara Autry, USEPA Office of Science Advisor
Robert Benz, NSI Solutions
Richard Burrows, PhD., TestAmerica
Charles Carter, PhD., TestAmerica
Nancie Copeland, Environmental Express
David Friedman, Friedman Consulting
Diane Gregg, USEPA Region 6
Zoe Grosser, PhD., PerkinElmer
Earl Hansen, PhD., Independent Laboratories Institute
H. M. (Skip) Kingston, PhD., Duquesne University
Douglas Later, PhD., Torion Technology
Gonzalo Manchego, Duquesne University
Particia McIsaac, TestAmerica
Marlene Moore, Advanced Systems
Stuart Nagourney, NJ Department of Environmental Protection
Nick Nigro, ECCS Nationwide Mobile Laboratories
Jerry Parr, Catalyst Information Resources
Joe Romano, Waters Corporation
Charles Sellers, USEPA Office of Solid Waste
David Speis, Accutest Laboratories
Shannon Sturgeon, USEPA Office of Solid Waste
Gary Ward, PhD., Columbia Analytical Services
Wayne Whipple, USEPA Region 5
Robert Wyeth, Columbia Analytical Services
Shen-yi Yang, USEPA Office of Solid Waste

NEMC 2008
CONFERENCE HIGHLIGHTS

The Environmental Measurement Symposium, a combined meeting of the National Environmental Monitoring Conference (NEMC) and The NELAC Institute (TNI) was held August 10 – 16, 2008 in Washington DC, just blocks from the nation's capitol. The conference was co-sponsored by the US Environmental Protection Agency, the Independent Laboratories Institute, and The NELAC Institute.

A total of 469 people attended the 2008 Forum, which was a 9% increase in attendance over 2007. The meeting included:

- 19 technical breakout sessions with 100 presentations;
- a 2-day poster program with 23 posters;
- 4 keynote presentations;
- 3 EPA general sessions with 13 presentations;
- 13 TNI committee meetings;
- an assessment forum;
- a laboratory mentoring session;
- an accreditation body forum;
- a meeting of the Environmental Laboratory Advisory Board;
- 5 training workshops; and
- a 3-day exhibit program with 43 exhibitors and sponsors.

Highlights of the week included the following keynote speakers:

- Dr. Jorg Feldman from the University of Aberdeen who spoke on elemental speciation in environmental monitoring;
- Dr. Heidelore Fielder from the UN Environmental Program who spoke on global monitoring of persistent organic pollutants;
- Dr. J. Clarence Davies from Resources for the Future who spoke on EPA and nanotechnology; and
- TNI's own Bob Wyeth who spoke on moving forward on national accreditation.

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

SECTION 6 TABLE OF CONTENTS

SECTION 6 TABLE OF CONTENTS cont.

2008 NEMC Proceedings

FUTURE TRENDS IN MONITORING

Future Trends in Sensor Technology

National Environmental Monitoring Conference

13 August 2008

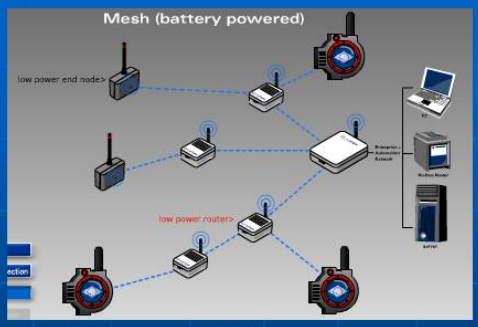
Michael Brody
- Environmental Protection Agency
- brody.michael@epa.gov

Stuart Nagourney
- New Jersey Department of Environmental Protection
- stu.nagourney@dep.state.nj.us

Marissa McInnis
- Environmental Protection Agency
- mcinnis.marissa@epa.gov

What is a Sensor Network?

Scientific American



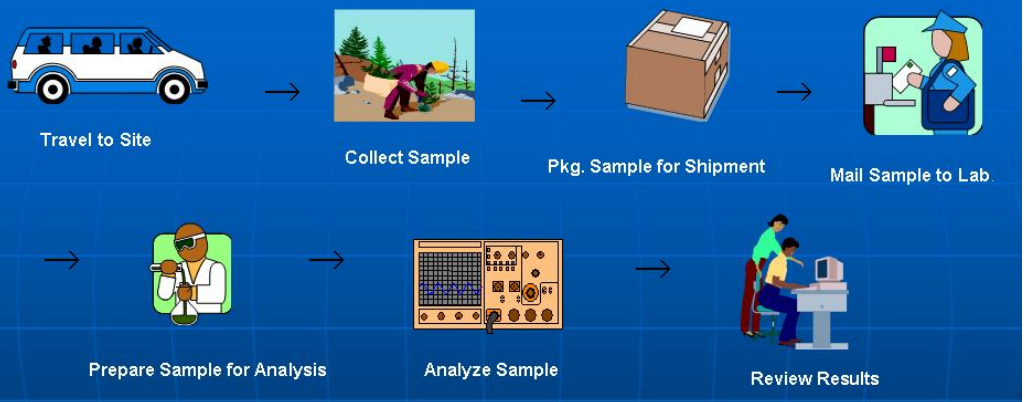
Courtesy of Crossbow Technology

"...a wireless network consisting of spatially distributed autonomous devices using sensors to cooperatively monitor physical or environmental conditions, such as temperature, sound, vibration, pressure, motion or pollutants, at different locations."

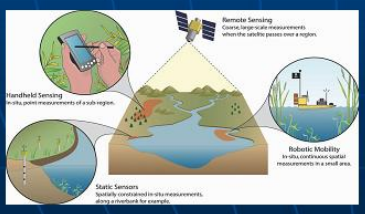
EPA Strategic Plan 2006-2011

- "Through distributed sensor networks, we could collect and transmit data faster and more frequently, improve data quality, enhance data integration, and improve data sharing…"
- "This technology could support our Report on the Environment, advance our foresight capabilities, and provide data that accurately portrays environmental conditions on a real-time basis."
- Advanced sensor technologies was the one emerging issue that arose most frequently during a series of futures/strategic planning workshops

Traditional Sampling



Sensors



Sensor Collects Data in Field; Without Discrete Sample - Transmits Info. Directly

Enable Dramatic Improvements

Performance Measurement, Program Management & Environmental Monitoring

- More easily understand dynamics
  - Spatial and temporal complexity
- Real-time data
  - Enable quick notification and response time to worsening conditions
- Smart sensors
  - Automate responses to threats to human health and the environment
- Reduce costs
  - Minimize traditional monitoring when sensors show that conditions are within acceptable tolerances
- Target sampling times and frequencies
  - Produce data best suited to achieve compliance

Sensors & Traditional Monitoring

- Traditional sampling and analysis methods
  - For now – perhaps more precision of individual measurement
  - But can be misleading about a site
- Sensors gather much more data
  - Useful information on temporal and spatial variations in contaminant levels
  - Real time data availability
  - Ability to evaluate trends
  - Sensors may cost more at first
    - Lower analytical costs over time

Sensor Data Issues

- Data Quality & Acceptability
  - Data comparability to traditional methods
  - Accuracy & precision
  - Management of larger volume of data
  - Regulatory acceptance will depend on these issues
- What is More Valuable
  - More significant digits or timeliness
  - System-level characterization of a site or ecosystem?
- Depends on the Decision to be Made

Moving Forward
Demonstration Projects Should

- Be a catalyst for change
  - Broad national interest
- Contribute to the adoption of advanced sensor technologies in a regulatory environment
- Existing monitoring efforts already underway for comparison purposes
- Sensor(s) chosen must be reliable and durable
- Demonstrate ability to capture spatial and/or temporal complexity

Potential Areas of Application
in Aquatic Ecosystems

- Septic Systems
- Non-Point Source Runoff
- Beach Water Quality
- Combined Sewer Overflows
- Concentrated Animal Feeding Operations
- Rapid tracking groundwater plumes

TYPES OF SENSORS

Sensor Category	Parameter	Cost ($)	Field-Readiness
Physical	Temperature	50-100	High
	Moisture, Content	100-500	High
	Flow Rate, Flow Velocity	1,000-10,000	High
	Pressure	500-1,000	High
	Light Transmission (Turbidity)	800 -2,000	High
Chemical	Dissolved Oxygen	800-2,000	High
	Electrical Conductivity	800-2,000	High
	pH	300-500	High
	ORP	300-500	Medium
	Major Ions (Cl^-, Na^+)	500-800	Low-Med
	Nutrients ($NO3^-$, $NH4^+$)	500-35,000	Low-Med
	Heavy Metals	NA	Low
	Small Organic Compounds	NA	Low
	Large Organic Compounds	NA	Low

Examples of environmental sensors: cost (NA=Not Available). (From: Distributed Sensing Systems for Water Quality Assessment and Management, WWC & UCLA/CENS; February 2007)

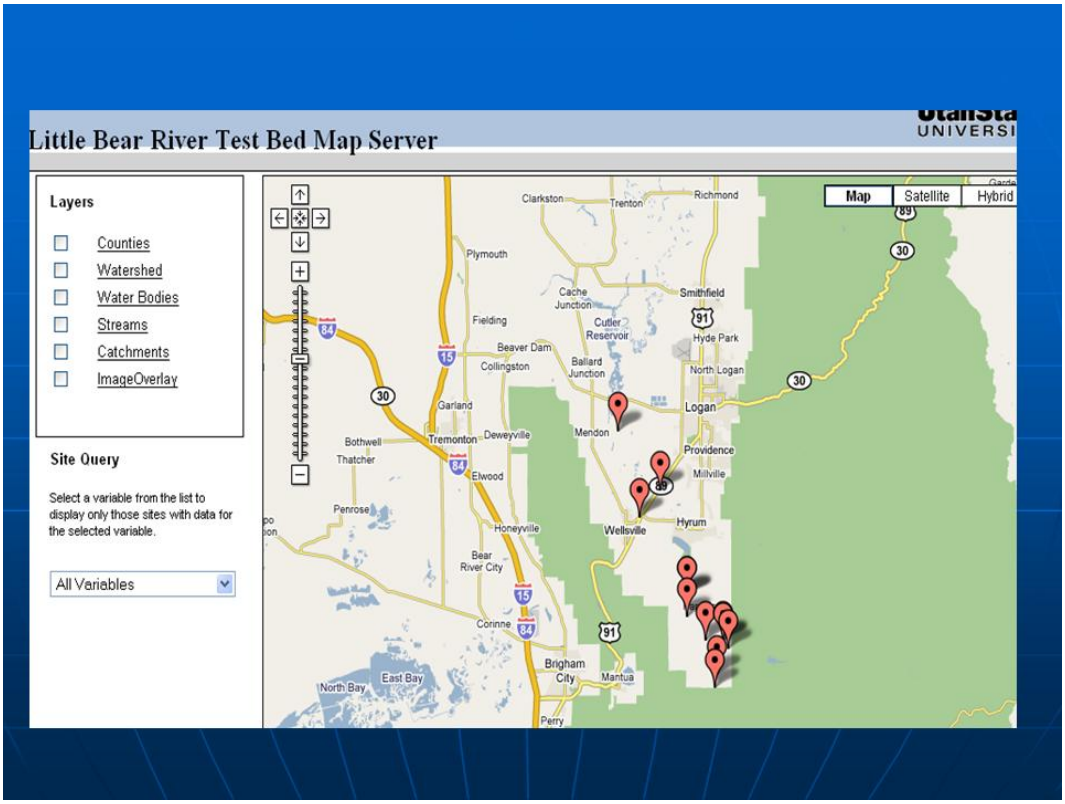
What's New in the World of Sensors?

- Some examples, websites and maybe some speculation

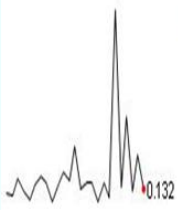
Utah State University

Little Bear River WATERS Test Bed Project

- Little Bear River Test Bed, near Logan, UT
  - http://water.usu.edu/littlebearriver
- One of 10 WATERS Network test bed projects in the US - funded by NSF
  - http://www.watersnet.org/wtbs/index.html
- Focus on sensors, deployment of sensor networks, development of new modeling tools, and cyberinfrastructure.

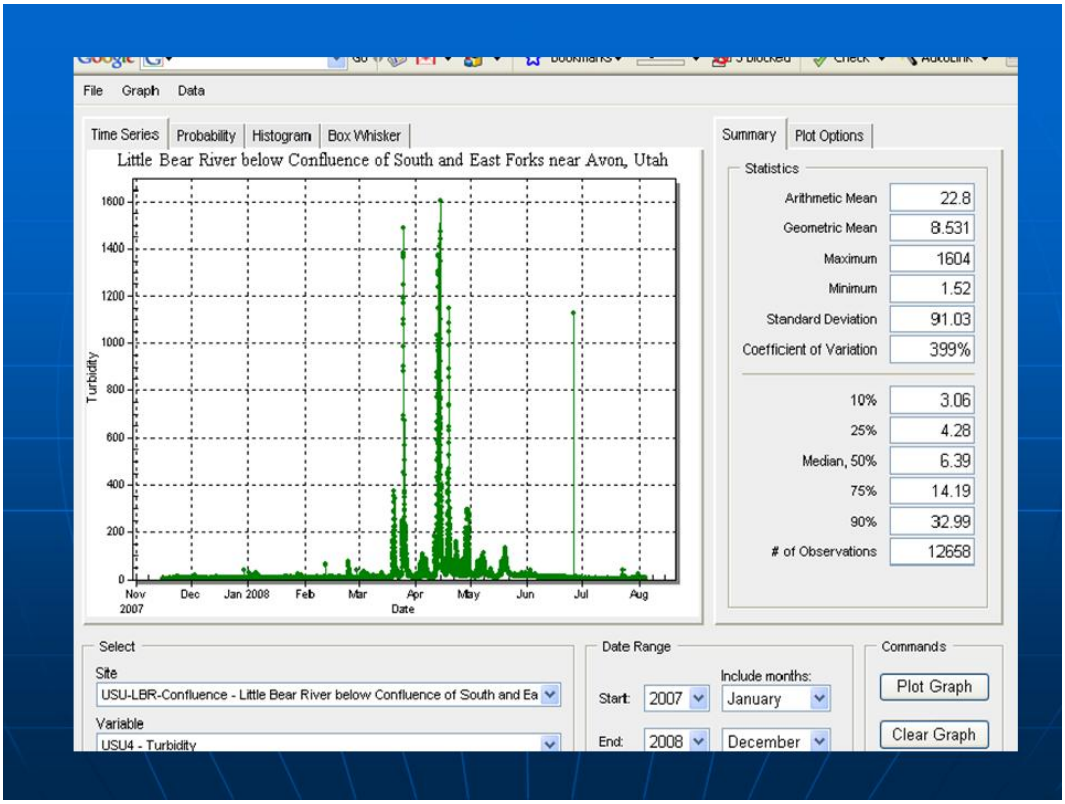


Example of Current Conditions at a Specific Sensor



USU5 - Turbidity 8/4/2008 12:00 PM 0.1322

- **VariableUnitsName:** nephelometric turbidity units
- **SampleMedium:** Surface Water
- **ValueType:** Field Observation
- **TimeSupport:** 5 second
- **DataType:** Variance
- **GeneralCategory:** Water Quality
- **QualityControlLevelID:** 0
- **MethodDescription:** Turbidity measured using a Forest Technology Systems DTS-12 turbidity sensor.



Contact Information

- David Stevens – Utah State
  - david.stevens@usu.edu
- Jeff Horsburgh – Utah State
  - jeff.horsburgh@usu.edu
- For Web Information:
  - CUAHSI Hydrologic Information System – provides web services
  - Consortium of Universities for the Advancement of Hydrologic Science, Inc.
  - http://his.cuahsi.org/index.html

Southern California Coastal Water Research Project

- Incorporation Of New And Rapid Measurement Methods Into Beach Water Quality Monitoring Programs

Background & Approach

- Beach water quality has been monitored the same way for decades
- Culture-based methods are slow; but
- Molecular methods are coming on line
  - measurement of organisms that are not easily cultured
- Allow measurements in about two hours
  - be field portable & adaptable to continuous automated operation

Neutral Testing Forum

- SCCWRP is California's independent testing organization
- Evaluated 6 classes of technology by 15 method developers
  - Common samples
  - Compared to traditional methods

Conclusions

- Acceptability based on:
  - Repeatability equal or better than current methods
  - False negatives no greater than current
  - False positives no higher than 20%
- New rapid methods are on the way
  - Principal obstacles are proper internal controls and training/certification
  - Rapid tests for some viruses may be available in 5 years

Southern California Coastal Water Research Project

Contact Information

- Stephen B. Weisberg
  - Executive Director
  - stevew@sccwrp.org
  - http://www.sccwrp.org/

Sensing & Decontamination

Grand Challenges

from Center of Advanced Materials for Purification of Water with Systems (WaterCAMPWS) - University of Illinois at Urbana-Champaign

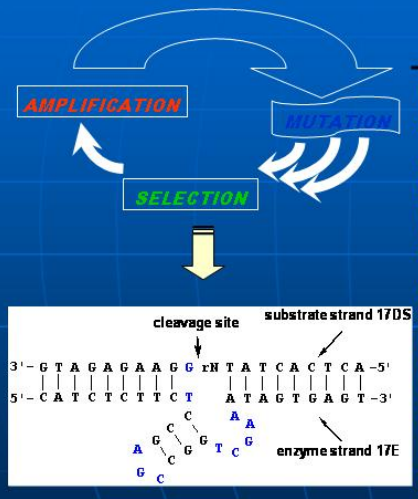
- Selective detection and removal of conventionally difficult to treat and emerging pollutants
- New detection methods directly linked to treatment methods

Decontamination: Targets, Relevance & Rationale

- Targets to date
  - Heavy Metals: Pb, Hg, As
  - Fuels And Fuel Additives: Mtbe
  - Oxyanions: Nitrate And Perchlorate
  - Halogenated Organics
  - Nitrosamines: NDMA
- Criteria for Candidate Contaminant List (NRC, 2001):
  - Common pollutant in drinking water resources
  - Often present at toxic concentrations
- Additional Criteria
  - Conventional sensing, adsorption or catalytic destruction technologies are expensive, incomplete, unreliable, or nonexistent

Molecules for Selective Binding

flexible backbone for detecting targeted contaminants including biological organisms
biologically-based manufacturing of detectors



Pb^{2+}-specific

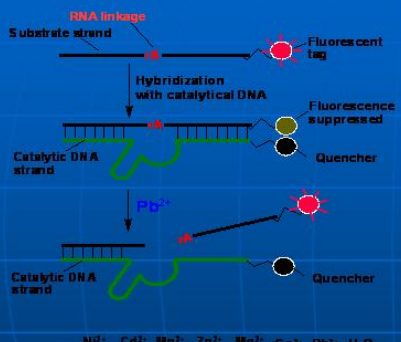
Partial list analytes recognized by selected DNA/RNA

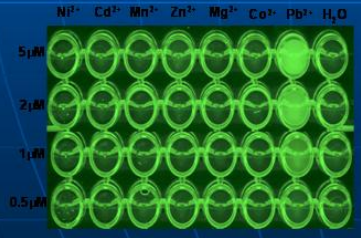
Metal ions (Mg(II), Ca(II), Pb(II), Zn(II))
Organic dyes (Cibacron blue, reactive green 19)
Amino acids (L-Valine, D-Tryptophan)
Nucleosides/nucleotides (Guanosine, ATP)
Nucleotide analogs (8-oxo-dG, 7-Me-guanosine)
Biological cofactors (NAD, FMN, porphyrins, Vitamin B_{12})
Aminoglycosides (Tobramycin, Neomycin)
Antibiotics (Streptomycin, Viomycin)
Peptides (Rev peptide)
Enzymes (Human Thrombin, HIV Rev Transcriptase)
Growth cofactors (Karatinocyte GF, Basic fibroblast GF)
Antibodies (human IgE)
Gene regulatory factors (elongation factor Tu)
Cell adhesion molecules (human CD4, selectin)
Intact viral particles (Rous sarcoma virus, Anthrax spores)

Biosensor Labeling for Rapid and Easy Detection

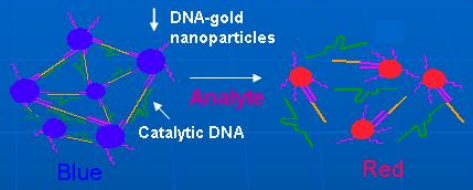
(already used for Pb sensing)

Fluorescent DNA Biosensors[1,2]





Colorimetric DNA Biosensors[3-6]



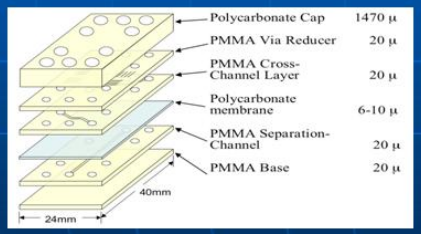
Detection limit: 2 ppb (ca. 100 ppb (CDC blood level) or 15 ppb (EPA drinking water)
Result in two issued patents and seven pending patents;
Technology transfer: **DzymeTech, Inc.**

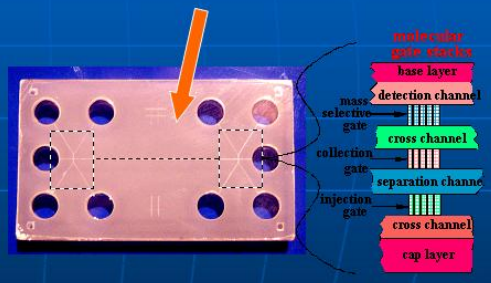
Next stage of development will be to immobilize the sensor on glass fiber paper - as simple as using Litmus Paper

Next Step – Continuous Monitoring

Lab on a Chip for Multiple Contaminants

Prototype has been built





Contact Information

- Richard Sustich
  - WaterCAMPWS
  - University of Illinois at Urbana-Champaign
- 847-438-4236
- sustich@illinois.edu

More Websites of Interest

- U Mass Boston
  - http://www.cesn.umb.edu/
- Boise State
  - http://ces.boisestate.edu/bsuinrasymposium.htm
- National Ecological Monitoring Network
  - http://www.neoninc.org/

More Websites

- UCLA
  - http://research.cens.ucla.edu/
  - *Distributed Sensing Systems for Water Quality Assessment and Management;* February 2007, [http://www.wilsoncenter.org/topics/docs/Sensor_whitepaper_lr.pdf]
  - Personal EIR http://peir.cens.ucla.edu/
  - CAFO and Nitrates study – southern California
- EPA - ORD
  - Multi-Analyte Nanoelectronic **Air Pollutant Sensors**
    - http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/6969/report/0

What Else is Coming?

- More Pilots
  - For example - CAFO in Oklahoma
- Sensing Linked To Environmental Process Control
  - Water Infrastructure – sensors detect contaminants and only then are purification processes turned on
  - Biological detection linked to nano-based contaminant removal?
- Analyses of Energy Savings
  - Replacement of traditional approaches with sensors & potential GHG reductions with sensor networks?
    - [College of New Jersey proposal]

EXES – An Advanced System for Environmental Data Assessment and Data Validation

Michael S. Johnson - USEPA Analytical Services Branch (ASB/OSRTI)

Nazy Abousaeedi, CSC

August 13, 2008

Benefits of Automated Data Review

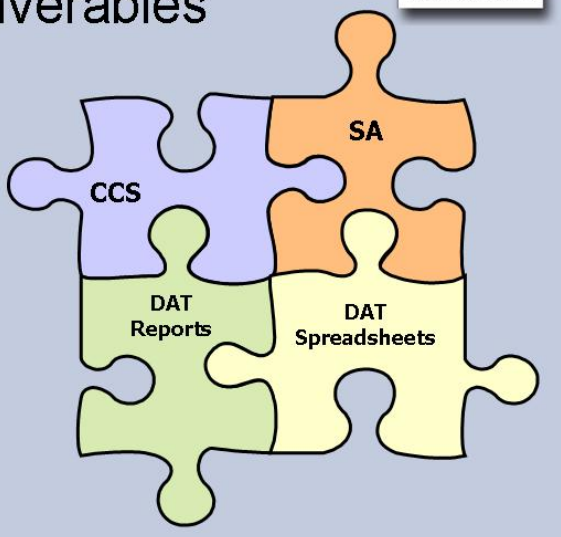
- Faster
- Reduces data validation resources
- Consistent verification/validation
- Expedites data processes and usage

Requirements for Automated Data Review

- Known analytical requirements
- Standard electronic data delivery format (i.e., SEDD)
- Well-defined QC criteria
- Data review applications providing:
  - defined verification/validation reports
  - customization to client's need

Electronic Data eXchange and Evaluation System (EXES) Processes and Deliverables

- Laboratory Self Assessment **(SA)**
- Contract Compliance Screening **(CCS)**
- Data Assessment Tool **(DAT)** Reports
- DAT Spreadsheets

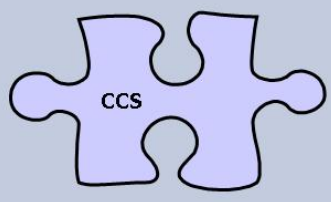


Laboratory Self Assessment

- Allows Laboratory to self-inspect data prior to delivery to clients
- Checks reporting and technical requirements
- Provides detailed reports to the Laboratory
- Aides Laboratories in providing better quality electronic deliverables

Contract Compliance Screening (CCS)

- Completeness and compliance check of the electronic data
- Based on Laboratory contract and method requirements
- Flexibility to accommodate variations to the analytical methods
- Detailed report provided to the Laboratory and summary report provided to the client



Data Assessment Tool (DAT)

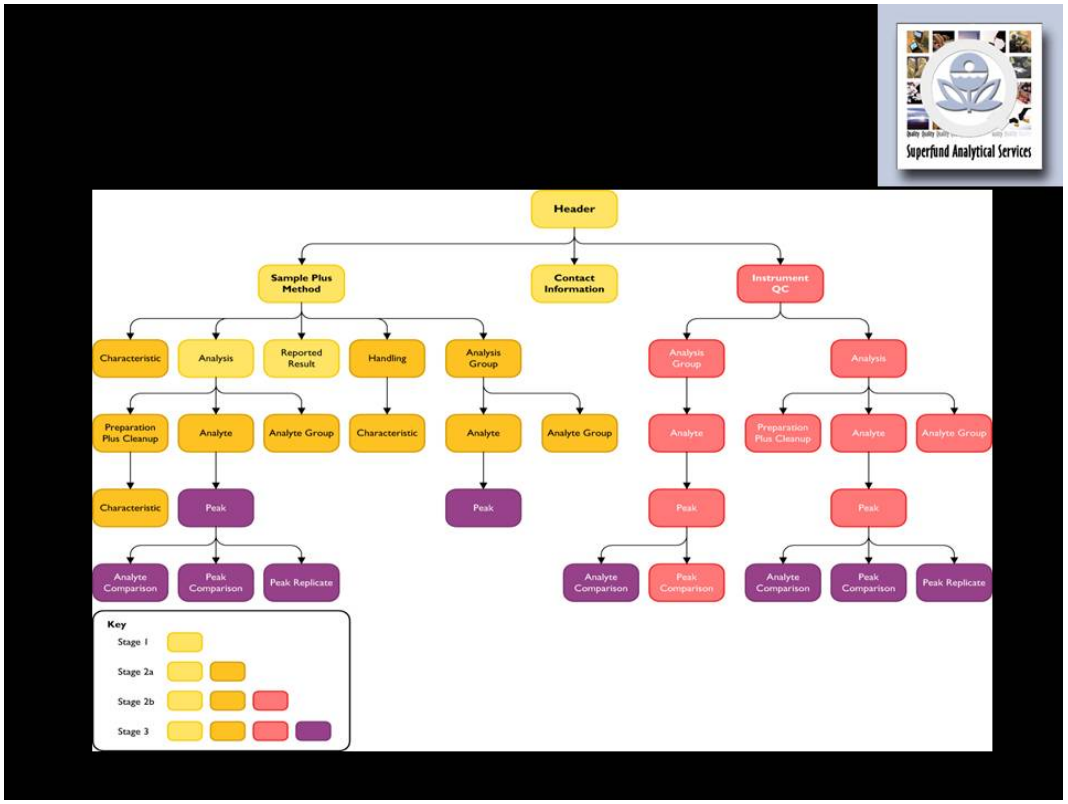
- Performs recalculation of information from raw data
- Performs data validation checks based on national or data user guidelines
- Can be customized based on client, project, or method variations
- Designed to assist data validation

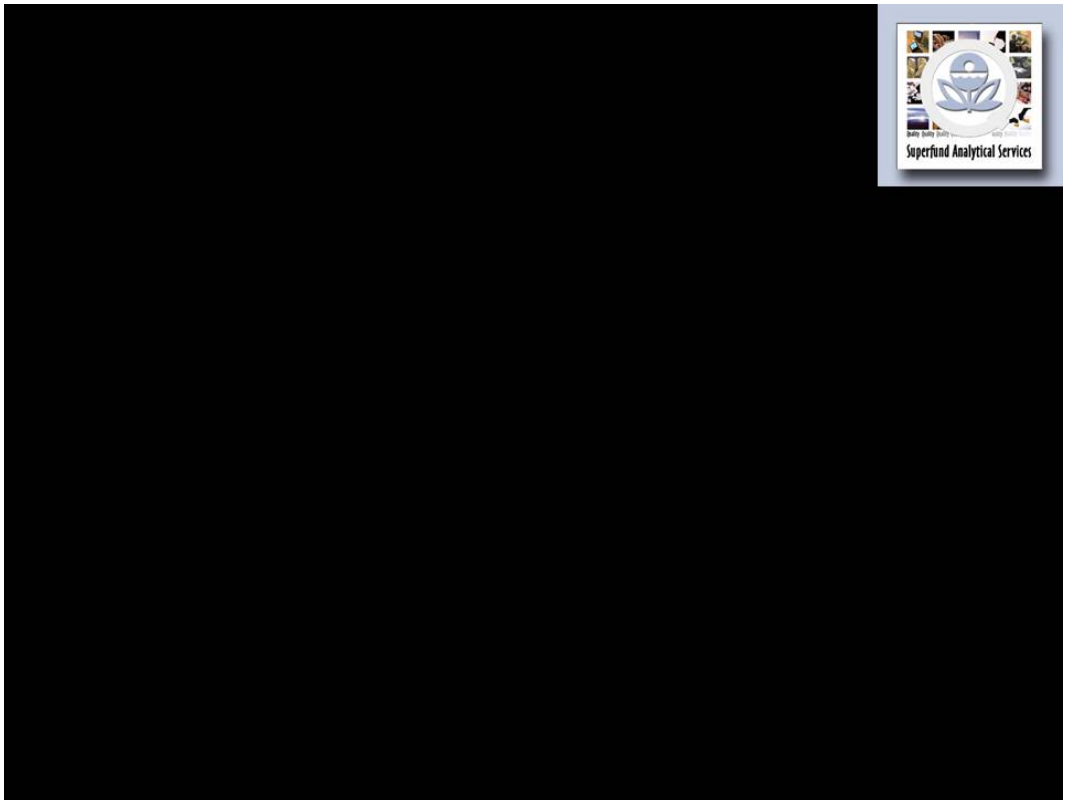
DAT Deliverable Reports

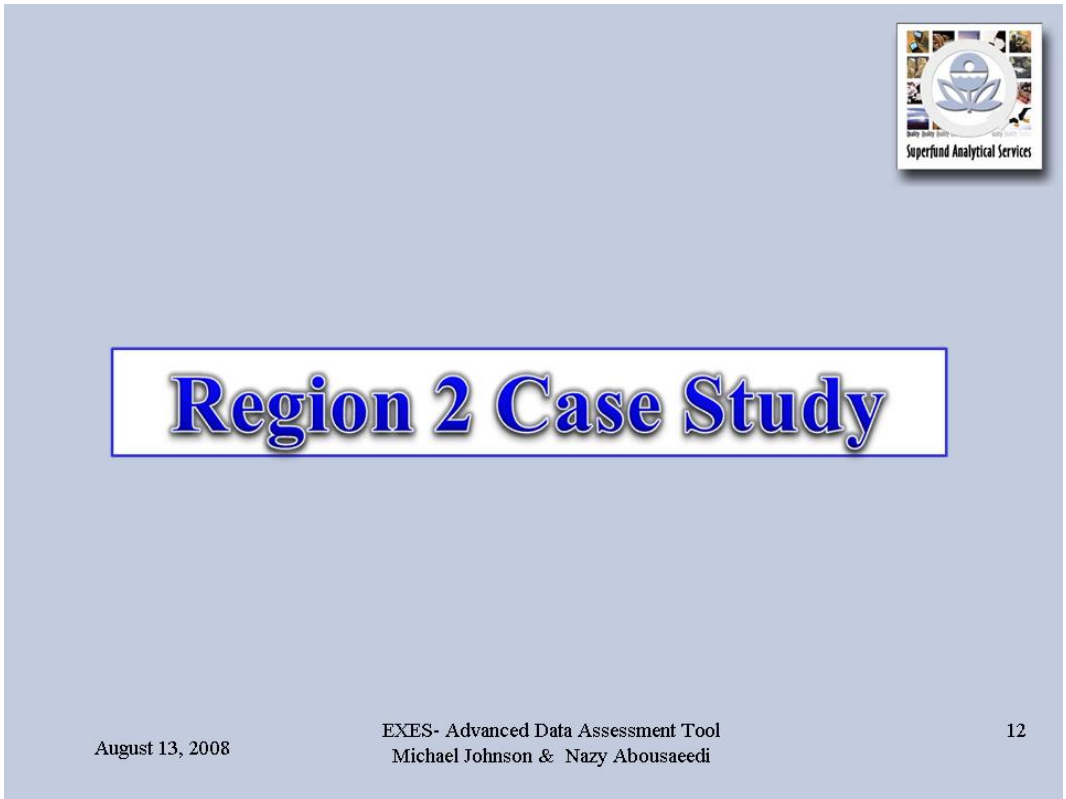
- Series of reports based on validation criteria
- Summary reports provide final results and validation flags
- Results based on data user's validation criteria
- Received within hours of data delivery from Laboratory

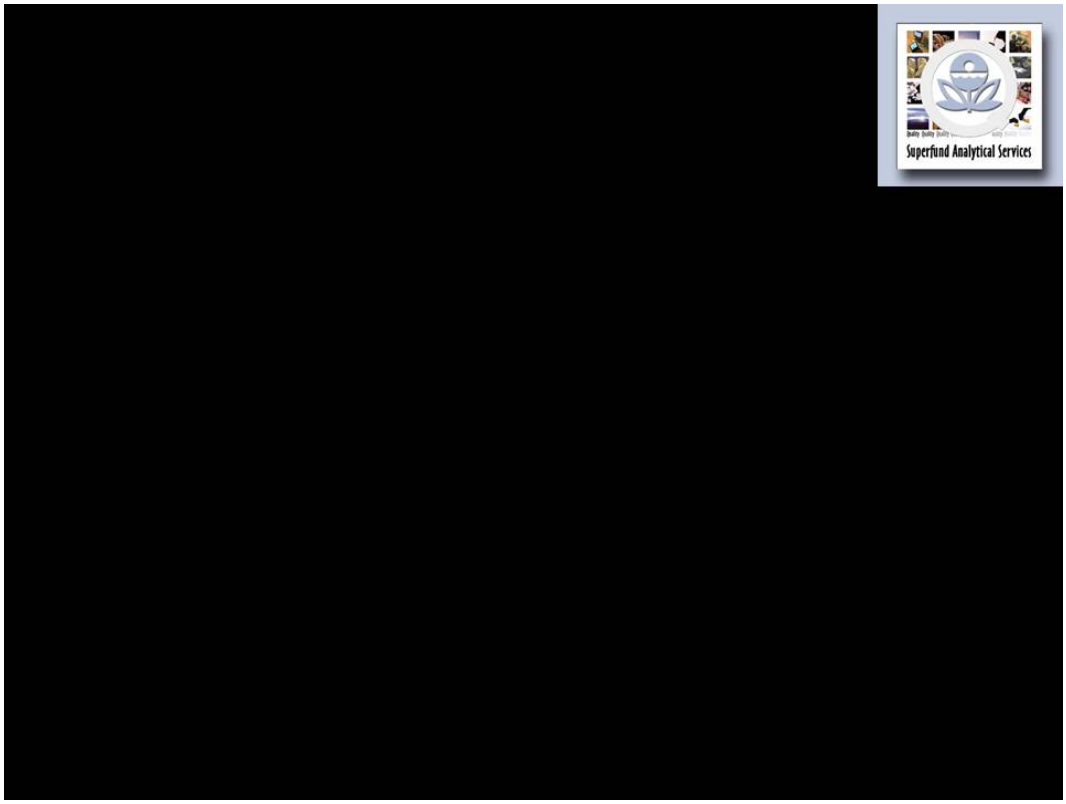
DAT Deliverable Spreadsheets

- Customized for each user or project
- Generally an Excel spreadsheet containing 60 to 70 Fields
- Amenable to loading into databases
- Combines Laboratory data, field data, and validation results






Region 2 Case Study
August 13, 2008
EXES- Advanced Data Assessment Tool
Michael Johnson & Nazy Abousaeedi
12



Overall Regional Approach

- Regional validation of all CLP data based on intended use
- Use CLP electronic reports and spreadsheets to streamline validation process
- Meet FASTAC turnaround objectives for data validation
- Meet customer needs for timely data of known quality

Use of Reports by the Regional Validators

- Region 2 used DAT validation reports to:
  - assist in identifying data issues
  - identify affected samples
  - qualify results
- Utilization of selected text in the DAT reports to generate final regional data validation report
- Allows validators to focus on areas requiring professional judgment and site-specific issues

Regional Efficiencies

- The DAT deliverables have reduced Regional validation times for organic data from approximately 2-3 hours/sample analysis in a full manual review to approximately .3-.75 hours/sample analysis for DAT assisted review.
- Inorganic review times have been reduced from approximately .4-.7 hours/sample analysis to approximately .3-.4 hours/sample analysis.

Regional Efficiencies (Cont.)

- Estimated FY07 savings for DAT-assisted CLP data validation was $958,700 (organic $870,400 and inorganic $88,300) when compared to fully manual data validation.
- These efficiencies do not include the savings realized by the ability to load fully validated data into site databases.

Contact Information

- Michael S. Johnson
  Phone: 703-603-0266
  Email: johnson.michaels@epa.gov
- Nazy Abousaeedi
  Phone: 703-818-4233
  Email: nazy@fedcsc.com

New Developments in Field Analytical Technologies

Field Analytics & a New Lab Business Model

Will You be Ready??

Deana Crumbling, EPA/OSRTI/TIFSD
crumbling.deana@epa.gov 703-603-0643
NEMC Conference Aug 13, 2008

Factors Complicating Interpretation of Soil Data

AND

What to Do about Them

(read, “opportunity”)

High analytical quality on small analytical subsamples has limited information value

True **sample** mean known to be **1920 ppb**

Subsample mass taken from a large partially homogenized soil **sample**	Range of results for 20 replicate **subsamples** (ppb)	Number of **subsamples** to average to get a result w/in 25% of true **sample** mean [1440 - 2400 ppb]
1 g (n = 20)	**1010 – 8000**	**39**
10 g (n = 20)	**1360 – 3430**	**5**
100 g (n = 20)	**1700 - 2300**	**1**

Adapted from DOE (1978) americium-241 study

Short-scale Heterogeneity Effects Usually Much Larger than Analytical Method Differences

> 95% of variability due to sample location

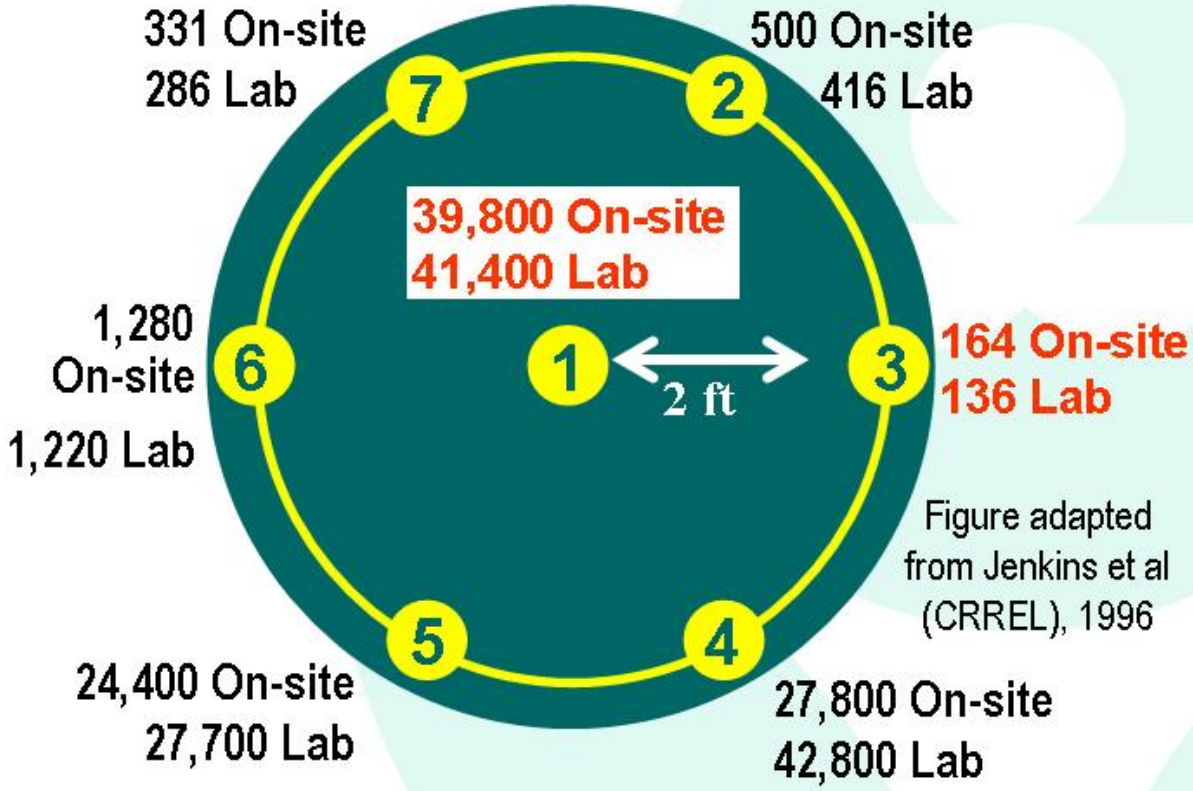
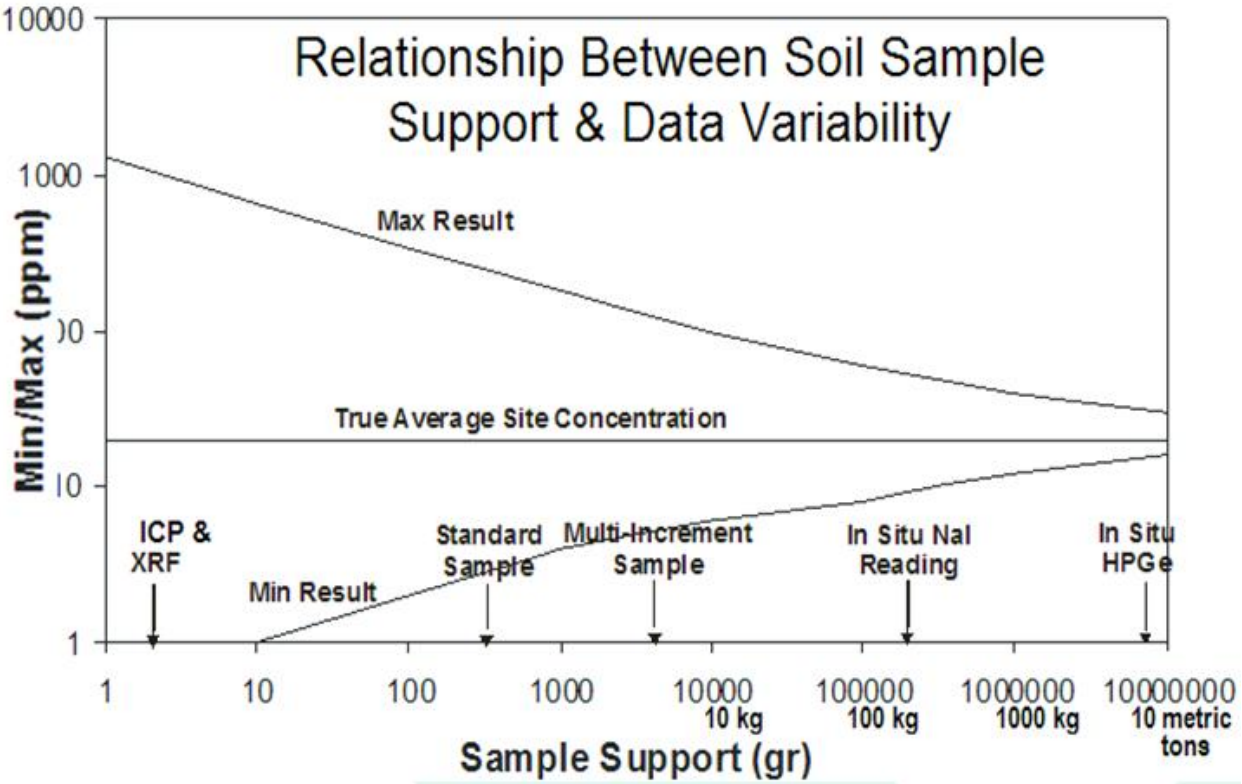


Figure adapted from Jenkins et al (CRREL), 1996

2008 NEMC - Wed

4

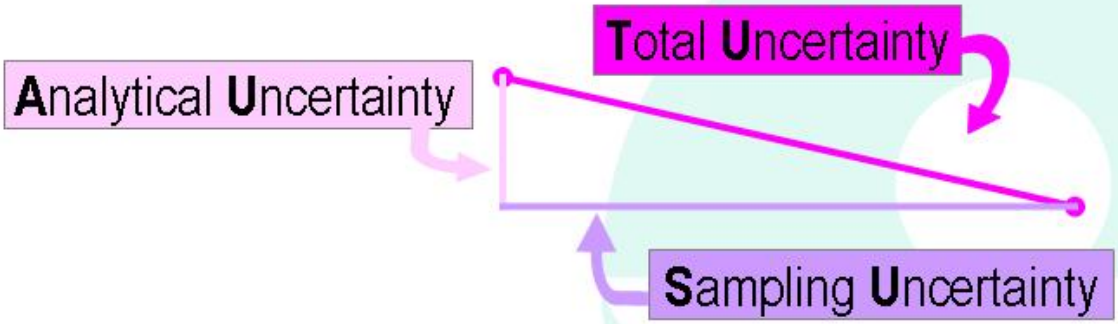
Current strategy of a few small grab samples, uncontrolled sample variability for high analytical quality analysis provides limited (& sometimes misleading) information value



2008 NEMC - Wed 5

Uncertainty Magnifies the Weakest Link in the Data Quality Chain

Uncertainties add according to $(a^2 + b^2 = c^2)$



Examples:

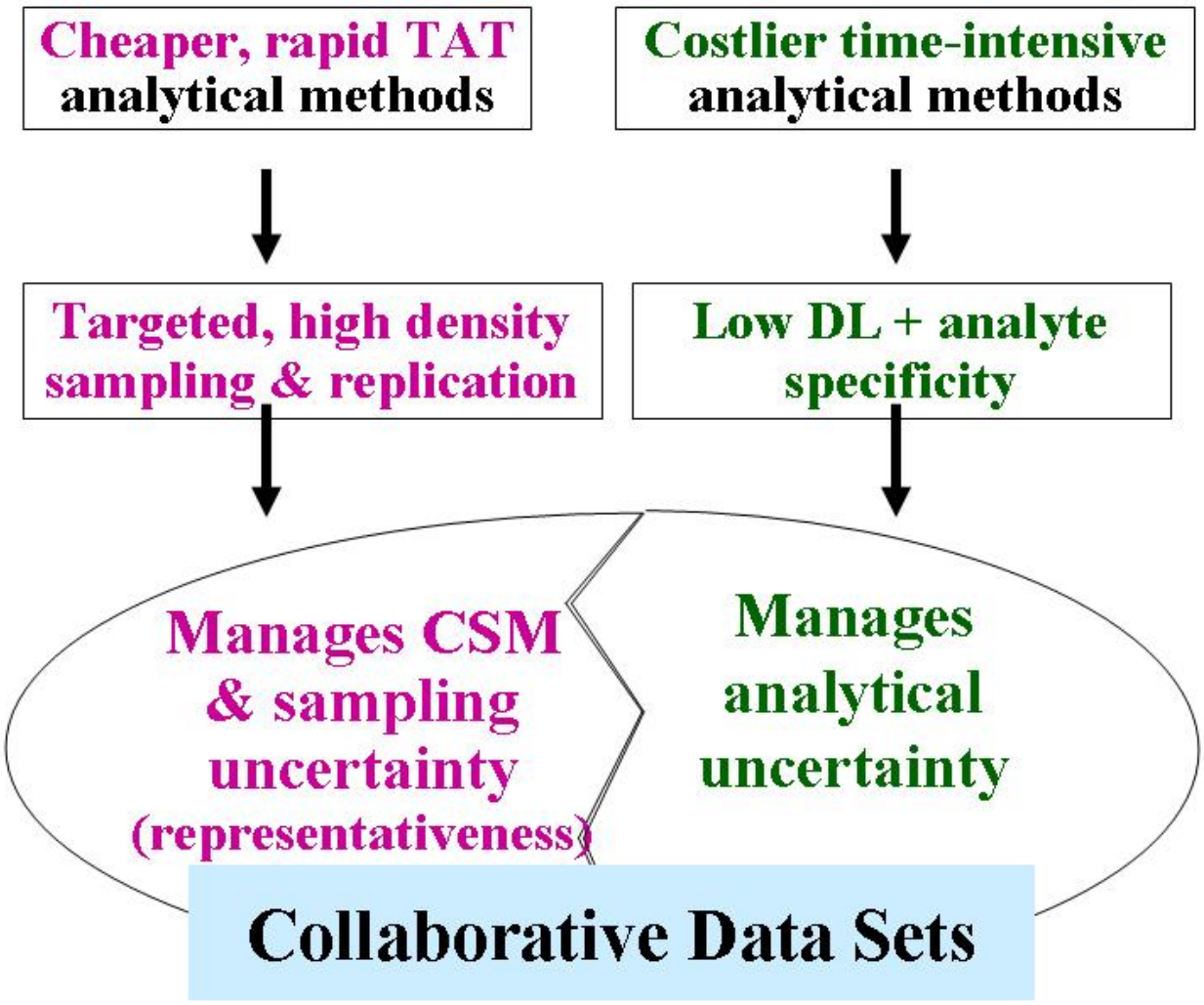
AU = 10 ppm, SU = 80 ppm: **TU = 81 ppm**

AU = 5 ppm, SU = 80 ppm: **TU = 80 ppm**

AU = 10 ppm, SU = 40 ppm: **TU = 41 ppm**

AU = 20 ppm, SU = 40 ppm: **TU = 45 ppm**

A Second-Generation Data Quality Model for Heterogeneous Matrices



Collaborative data sets complement each other so all sources of data uncertainty are managed. Either alone cannot produce reliable information.

Dysfunctionalities

- Poor control of within-sample heterogeneity → variable data → split & dup imprecision.
- Poor control of short-scale, between-sample heterogeneity → variability.
  - Risk assessment problems
  - Demonstrating compliance/exceedance
- Poor understanding of decision goals, representativeness & analytical science contribute to
  - Ineffectual sampling designs &
  - Inappropriate analytical test requests
- **Happen upstream of lab, but lab blamed when data not useful.**

What, Oh, What to Do ?!?

The future is not for faint of heart!

- Transform lab's role from "widget" provider to expert consultant
- Utilize experienced field & project practitioners
- Offer consulting services as a partner in the project planning team
- Yes…there are big, BIG barriers: engineering consultants & current mindset !!

♩ For the times, they are a-changin' ♩

- Current mindset slowly changing
- Old guard retiring; young not invested in the status quo
  - Schooled to be more appreciative of partnerships & specialized skills
- Hungry to understand what's been going wrong
  - Thrilled to have their concerns validated
- Fixed-price, PBCs for char. & cleanup, BF redevelopment & insurance cost
  - Fumble projects as usual…lose $/rep
  - Be efficient & get right 1st time…win big
- No more big bucks for cleanup

Interest in Something Better

- This year: 1st Triad conference ever, international attendance (~250 attend)
- Triad-based education proving need to use field tools defensibly
- ~ 10 classroom courses deliv'd so far
  - EPA can't accommodate the requests
  - Need private sector to pick up teaching
- 200 attending Web series of 8 2-hr XRF sessions teaching the why's & how-to's of using XRF definitively w/ QC, adaptive sampling & data analysis
  - Live & archived recordings
- To make Triad work, MUST use multi-disciplinary teams

Sorely Needed Project Skills that Labs Could Offer

- Creative, scientific thinking!
- Translate decision goals into data representativeness & data needs
- Select/design appropriate sampling & analytic SOPs
- Provide field analytic services w/ proper QC & data interpretation
- Design collaborative data sets
- Prepare project-specific, detailed, meaningful QAPPs
- Expertise in data mgt, interpretation
  - Databases & software for mapping, statistics & geostats
- Especially small firms

Sample Prep Expertise

- Gy-based sample handling
  - Representative subsampling of large volumes of solids
  - Learn more: articles & EPA guidance

Must use properly sized & shaped scoop

- Grinders & their appropriate use

2008 NEMC - Wed 13

Sampling Designs

- Building & refining a CSM
- Multi-increment averaging design
- Composite searching design
- Ranked set sampling
- Adaptive cluster sampling
- Use Visual Sample Plan (VSP) (free) PROPERLY
- GeoBayesian (free) sampling design
- Adaptive, dynamic decision trees for to guide sampling & analysis
- Stratified sampling design

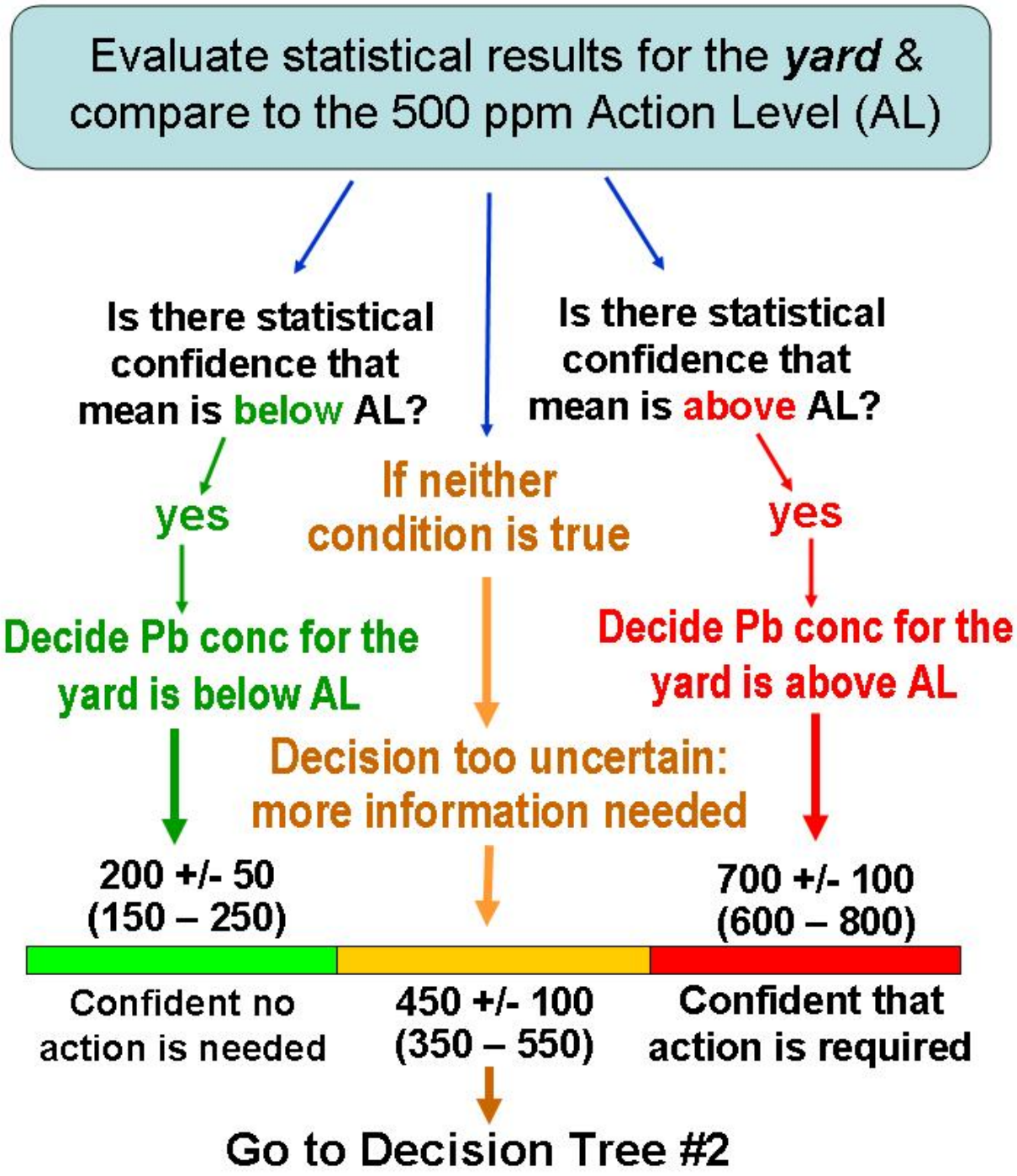
Data Uncertainty

- Great value in determining & managing uncertainty in real-time
- Navy uncertainty calculator (free)
- Set up spreadsheets

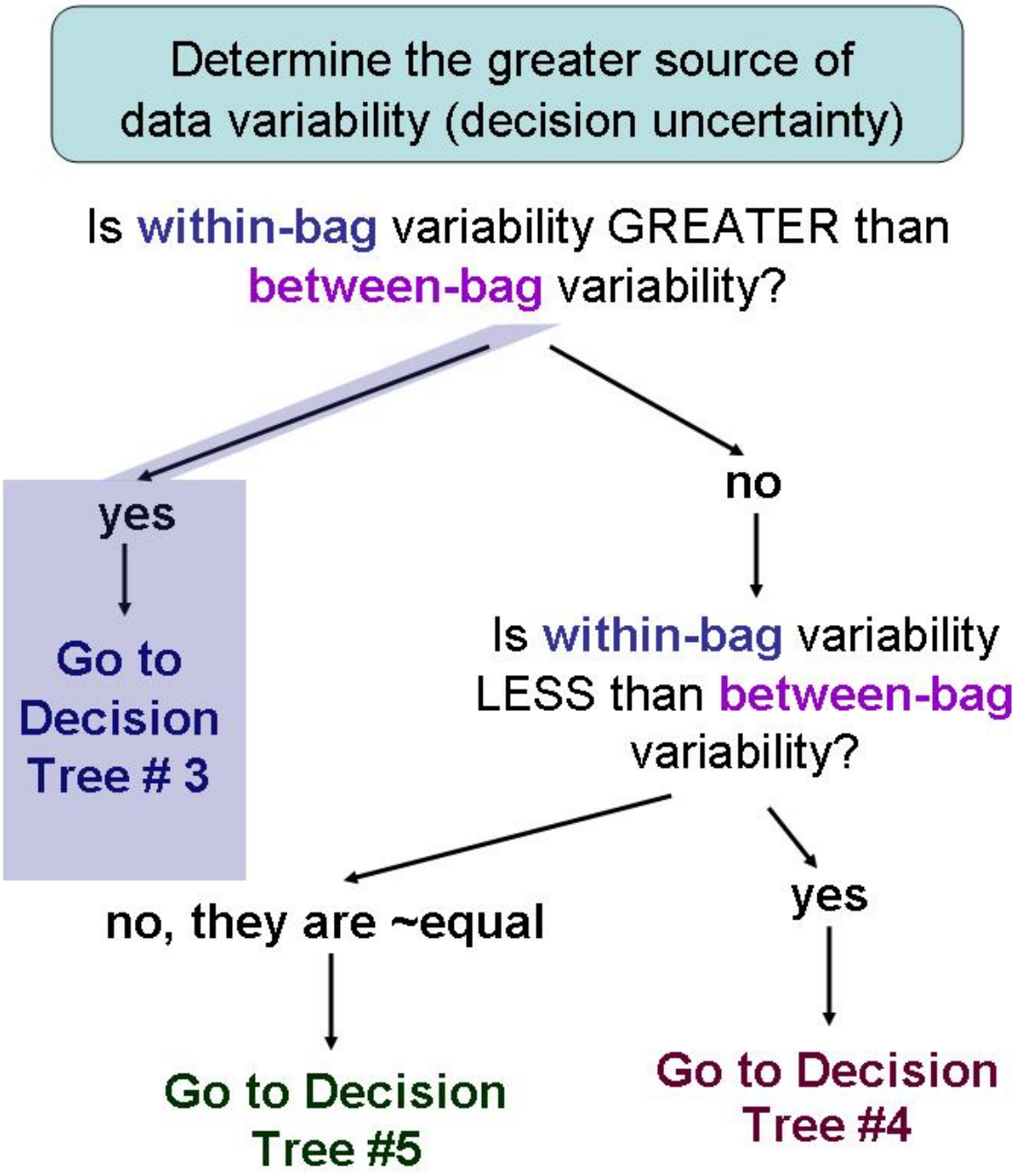
Improved Risk Assessment & Compliance Decisions via Uncertainty Mgt & a Stratified Sampling Design

Strategy	Mean	95UCL
uncontrolled micro-scale var. & traditional risk calculation	476	647
controlled micro-scale var. & traditional risk calculation		
stratified sampling & data analysis on preliminary CSM		
stratified sampling & data analysis on mature CSM		

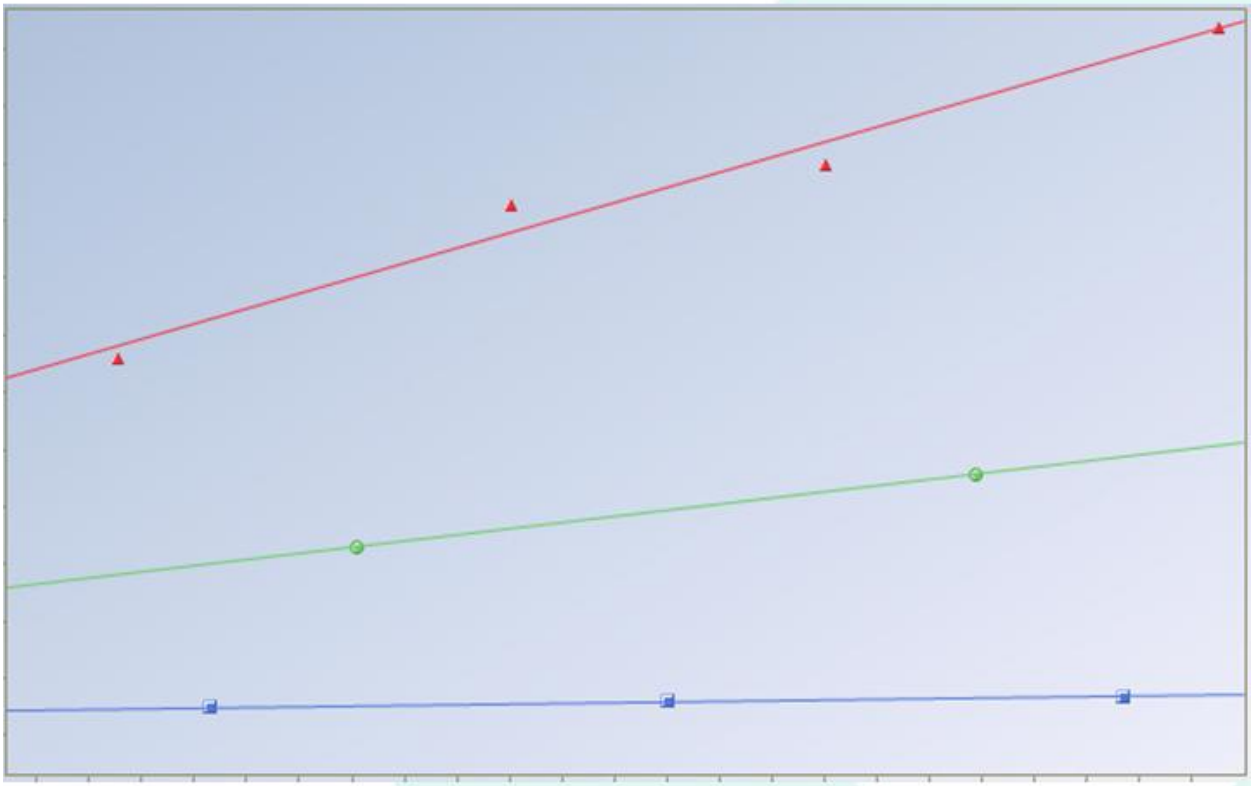
Data Uncertainty Managed Enough to Support Confident Decisions



Decision Tree #2



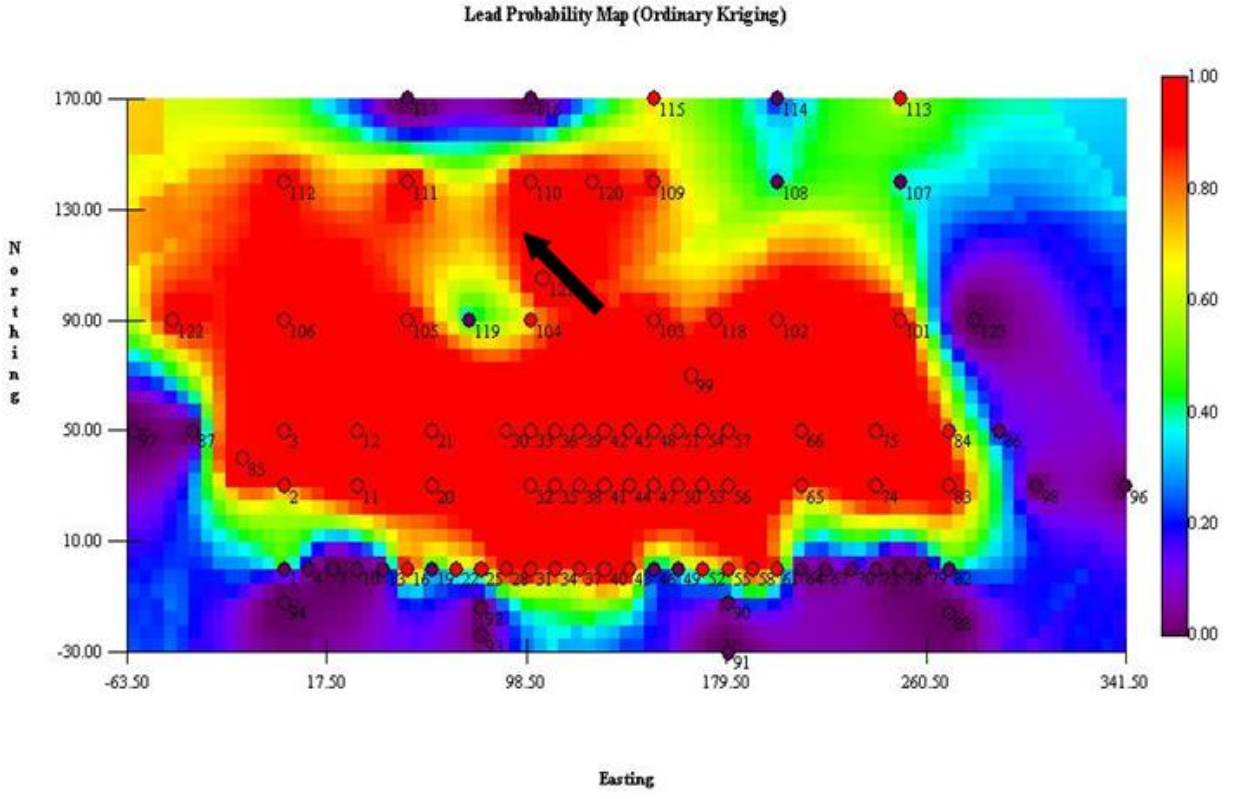
Data Analysis: Building a CSM & Stratifying Populations w/ ProUCL



2008 NEMC - Wed 19

Data Analysis: Communicating Uncertainty Using SADA software

Firing Range Berm, Plan View
Probability that 1-ft Deep Volumes > 250



2008 NEMC - Wed 20

Deana M. Crumbling, M.S.

U.S. EPA, Office of Superfund
Remediation & Technology Innovation

1200 Pennsylvania Ave., NW (5203P)
Washington, DC 20460

PH: (703) 603-0643
crumbling.deana@epa.gov

www.triadcentral.org

Flexible Approaches to Environmental Measurement – The Evolution of the Performance Approach

Lara Autry, US EPA
August 13, 2008

2008 Environmental Measurement Symposium

Overview

- Purpose/Scope of the Forum on Environmental Measurements (FEM)
- Introduction/History
- Recent Developments
- Implementation Status
  - Office of Air and Radiation (OAR)
  - Office of Pesticides and Prevention (OPP)
  - Office of Solid Waste (OSW)
  - Office of Water (OW)
- Summary

FEM Purpose/Scope

- Promote consistency and consensus within the Agency on measurement issues.
- Enhance Agency programs by recommending principles for:
  - Validating and disseminating methods for sample collection and analysis;
  - Developing scientifically rigorous, statistically sound and representative measurements; and
  - Employing a quality systems approach that ensures data gathered and used by the Agency are of known and documented quality.

FEM Purpose/Scope (cont.)

- Establish procedures and policies that provide consistent, yet flexible, measurement tools to support environmental decision-making.
- Provide EPA and the public with a central point for addressing measurement methodology issues with multi-program impact.

Action Agenda

- Improving the Quality of Agency Methods
- Implementation of the Performance Approach
- Technical Assistance
- Method Detection/Quantitation
- General Laboratory Competency
- Laboratory Accreditation
- National Environmental Monitoring Conference (NEMC)

Implementation of the Performance Approach

- Renewed commitment to what implementation means ten years from when it began.

Original Concept

- Performance approach to environmental measurement specifies the minimum quality of measurements rather than specifying the protocols and methods to be used
  - Agency or State would specify action level
  - Regulators determine and specify performance criteria
  - Laboratory select any validated method meeting specifications

History

- Initiated through the Environmental Monitoring Management Council (EMMC)
- EMMC recommended use of performance approach to Administrator
  - September 1997 – Letter of Intent
  - October 6, 1997 – Federal Register Notice of Intent
  - September 1998 – Implementation Plans Developed

Vision

- Reduce the cost of monitoring.
- Stimulate the development and use of new, more cost-effective monitoring technologies.
- Speed up the introduction of new methods or measurement approaches by eliminating the need for formal rulemaking.
- Improve data quality through the generation of performance data.
- Flexibility

Forces in the Performance Approach

FOR Performance Approach	AGAINST Performance Approach
Equipment Vendors →	← Regulated Entities
Science Policy Leaders →	← State Laboratories
Few Multi-Media Laboratories →	← Commercial Laboratories
Few "In the Know" Advisory Groups →	← State Regulators
ACIL (10% of Laboratories) →	
Regional Laboratories →	

Redefined Approach

- The EPA is introducing Flexible Approaches to Environmental Measurement – The Evolution of the Performance Approach.
- Key Goals:
  - Increased emphasis on flexibility in choosing sampling and analytical approaches to meet regulatory requirements for measurements;
  - Development of processes for validation that assure 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.

Flexible Requirements

- Identification of goals such as action levels, technology performance, and mandates or limitations of the program or project.
- Goals are translated into measurement requirements.
- Making measurement quality requirements more flexible.

Measurements Meet Requirements

- Validation
  - Phase 1 – evidence on general performance on a range of materials that define a matrix class.
  - Phase 2 – users demonstrate requirements for a specific use are met.
- Process will allow for appropriate choice of specificity.

Increase Collaboration

- Development of validation processes for applications of new technology that will require collaboration with stakeholders.
- Agency must continue to play a key role in development.

Rapid Assessment

- Agency is committed to rapid assessment of proposed alternatives to these requirements and to timely approval of these alternatives.

OAR

- Stationary Source Program
  - New methods and monitoring specifications are performance based
  - Existing measurement requirements being revised to incorporate performance approach as resources allow
  - Nimble alternative test methods approval process

OAR (cont.)

- Ambient Air Monitoring Program
  - New Federal Reference Methods (FRM) are performance based where possible and performance criteria are directly linked to data quality objectives (e.g., FRM for PM-10)
  - Extensive collaboration with stakeholders (State/Local/Tribal agencies) to validate data quality and assess new technologies

OAR (cont.)

- Transportation and Air Quality
  - Measurement requirements for sulfur in diesel and non-diesel fuels are now performance-based
  - In the process of streamlining and adding flexibility to vehicle and engine testing requirements for certification.

OPP

- Adopted and fully supported the Performance Approach for submission of pesticide analytical methods by registrants.
- Antimicrobial Testing Program results can potentially be used for enforcement. Historically, this required analysis using the registrant's submitted method. OPP has been evaluating new processes for analysis:
  - OPP and OECA have agreed that OPP and State partner laboratories can use established broadly accepted methods for the analysis of antimicrobial products containing Quaternary Ammonium active ingredients.
  - OPP is in the process of arranging a collaborative study, involving State laboratories, to evaluate methods for the analysis of antimicrobial products containing the phenolic active ingredients.

OPP (cont.)

- Adopt quantitative methodologies for evaluating the efficacy of antimicrobial products.
  - A pre-collaborative study comparing two quantitative test methodologies for determining the efficacy of sporicides was conducted.
- Modify existing methodology to take advantage of emerging new technologies
  - Modify existing pesticide multiresidue methods so they are able to measure newly registered pesticides
  - Participate in two international intercalibration programs
- Evaluate "universal" quantitative method for utility in determining the efficacy of antimicrobials against a wide range of microorganisms including viruses.
  - OPP will be participating in an OECD sponsored method validation exercise with the new method.

OSW

- Performance approach used since summer of 1997 and has met the goals of becoming totally performance based.
- Data quality and performance requirements for Resource Conservation and Recovery Act (RCRA)
- Federal regulatory barriers removed by promulgation of the Methods Innovation Rule in 2005.

OW

- Method Update Rule, effecting changes to 40 CFR 136.6, provides added flexibility for wastewater methods.
- OW typically develops/approves multiple technologies and methods for monitoring a particular contaminant.
- Drinking water program builds flexibility into methods based on individual-procedure-based performance model.
- OW continues to build transparency into method development by including more information in the method itself and in related journal articles and reports, as appropriate.

OW (cont.)

- OW continues to operate an Alternate Test Procedures (ATP) program to address new and modified methods that go beyond the flexibility identified in approved methods. Program improvements incorporated based on lessons learned.
- Drinking water program instituting an Expedited Methods Approval approach to speed approval of newly developed or modified methods based on SDWA authority.
- OW actively pursuing partnerships for methods development to bring new technologies into use faster.

Next Steps

- Marketing and outreach
- New Notice of Intent
- Form partnerships and pilot projects
- Strategy sessions
- Training
- Timeline

Contact Us

- FEM Website:
  - www.epa.gov/osa/fem
- Executive Director:
  - Lara Autry
    autry.lara@epa.gov
    919-541-5544

2008 NEMC Proceedings

INNOVATIVE APPROACHES

Emerging Contaminants in Raw and Finished Drinking Waters

Yongtao (Bruce) Li, Joshua S. Whitaker, and Christina L. McCarty; Underwriters Laboratories, Inc., 110 South Hill Street, South Bend, IN 46617; 574-472-5562; yongtao.li@us.ul.com

ABSTRACT

Emerging contaminants in waters are a current topic in source water protection and remediation, drinking water quality control, and wastewater reclamation. A list of 74 emerging contaminants including endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) were analyzed using highly sensitive and specific chromatographic and mass spectrometric techniques. The analytes were analyzed through screening a number of source water and finished drinking water samples. The obtained results are important for the future studies of EDCs and PPCPs on the occurrence levels and fate in raw and finished drinking water, the control and removal, the human health effects, and the impacts on ecological systems.

INTRODUCTION

Endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) are two classes of emerging contaminants that have received public concern. EDCs have been found to potentially endanger and threaten aquatic species and public health by affecting the endocrine and reproductive functions. Endocrine disruption is linked to reproductive abnormalities in wildlife, increased breast cancer rates, birth defects, etc. EDCs of interest include: 1) human sex hormones and estrogenic pharmaceuticals used for anti-nausea, premature labor prevention, ovalation inhibition, and hormone replacement therapy; 2) alkylphenols in the environment resulting from the microbial degradation of nonionic surfactant alkylphenol ethoxylates in wastewater and sewage treatment plants and 3) other potential endocrine-mediated active phenols, such as bisphenol. A used in the synthesis of epoxy resins and polycarbonate plastics. EDCs have contaminated drinking water sources through the discharge of wastewater, sewage waste disposal and overflows, and the use of treated sewage sludge as a fertilizer in agriculture. The occurrence of these EDCs in drinking water, surface water and groundwater was largely dependent on the location. High concentrations of EDCs were commonly present in the effluents of wastewater and sewage treatment plants.

The PPCPs of interest include prescription and over-the-counter drugs, drugs used in hospitals, veterinary drugs, drugs used for farm animal feed (cattle, poultry, swine, etc.), drugs used for fish hatcheries, and antimicrobials used in personal care products. A variety of PPCPs were reported in wastewater treatment plant (WWTP) effluents, surface water, and groundwater as well as in finished drinking water. The concentration levels of selected PPCPs in water supplies and drinking water varied. PPCPs primarily originate from wastewater, sewage waste, and septic tanks as well as other sources including farm animal feed (cattle, poultry, swine, etc.), fish hatcheries, and landfill runoff. Although no known adverse human health effects are associated with the detected PPCPs, the contamination from PPCPs is of great concern due to potential long-term health effects.

The main challenges in analyzing human hormone/estrogen EDCs and PPCPs are sensitivity and accuracy. First, they are typically present at sub- to low part-per-trillion levels in waters, which require highly sensitive and specific analytical techniques. Secondly, they may have a wide range of different properties and stabilities, which require multiple methods. Thirdly, they mainly originate from wastewater and sewage waste. The sample matrices often severely interfere with the analytical performance. Therefore, analytical methods must be robust and reliable to deal with varied matrices and concentration levels.

In this report, the authors selected and screened 74 EDCs and PPCPs, which frequently appeared in a number of published papers and research project reports. The water samples were analyzed by using state-of-the-art chromatographic and mass spectrometric techniques. The obtained results from finished drinking water and surface water samples were summarized.

EXPERIMENTAL

The reversed-phase liquid chromatography/electrospray ionization/mass spectrometry and tandem mass spectrometry (LC/ESI/MS and MS/MS) were carried out by using Waters Acquity UPLC and TQD, Alliance 2695 Separation Module and Quattro micro API, and Alliance 2690 Separation Module and ZMD. The gas chromatography/mass spectrometry (GC/MS) was carried out by using Varian CP 3800 and Saturn 2200 GC/MS.

For all the analytical methods, water samples were prepared by using solid phase extraction (SPE) techniques, and internal standard calibrations were used in the quantitation of emerging contaminants. Hormone/estrogen EDCs and PPCPs were analyzed by LC/ESI/MS/MS. Phenolic EDCs were analyzed by LC/ESI/MS. GC/MS was used to analyze fragrances.

RESULTS AND DISCUSSION

The minimum reporting levels (MRLs) of the selected analytical methods are listed in Tables 1 to 8. Tables 1 to 4 summarize the results from the finished drinking water samples. Tables 5 to 8 summarize the results from the surface water samples. The results were qualitatively summarized into four categories, based on the frequency of the samples detected positively. These categories included: (1) the most frequently detected EDCs and PPCPs, which were detected in over 20% of the samples; (2) frequently detected EDCs and PPCPs, which were detected in 5-20% of the samples; (3) the least frequently detected EDCs and PPCPs, which were detected in less than 5% of the samples; and (4) non-detected EDCs and PPCPs.

As shown in Tables 1-8, the results obtained from the finished drinking water samples were generally consistent with those obtained from the surface water samples in terms of the frequency of the samples detected positively. First, over 50% of the studied EDCs and PPCPs were not detected or detected in less than 5% of the surface water and finished drinking water samples. 50% or less of the studied EDCs and PPCPs were detected in 5% or more of the surface water and finished drinking water samples. Although the studied surface waters might not be directly related to the finished drinking waters, the positive results indicate that the current drinking water treatment systems are not very effective for the removal of a number of EDCs and PPCPs. Secondly, more analytes were detected in the surface water samples in the category of the most frequently detected EDCs and PPCPs. In the thirteen EDCs and PPCPs most frequently detected in the surface water samples, most of them were also detected in over 20% of the

finished drinking water samples. Thirdly, the detected concentrations were generally higher in the surface water samples than those in the finished drinking water samples. Finally, clofibric acid, diethylstilbestrol (DES), prednisone, and 2,4,6-trichlorophenol were not detected in the surface water samples but were detected in the finished drinking water samples.

Table 1. Most frequently detected EDCs and PPCPs in the finished drinking water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Caffeine	50	122	25	50-639
Carbamazepine	1.0	122	51	1.0-296
Cotinine	1.0	122	74	1.2-17.9
DEET	5.0	122	47	5.0-445
Estrone	0.5	205	42	0.5-38.7
Gemfibrozil	0.5	150	41	0.5-13.4
Galaxolide	10	77	44	10.1-1,926
Nicotine	5.0	122	43	5.0-95.8
Paraxanthine	5.0	122	30	5.8-114

Table 2. Frequently detected EDCs and PPCPs in the finished drinking water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Acetaminophen	5.0	122	19	5.0-23.9
Aspirin	50	144	10	57.2-105
Dilantin	2.0	150	16	2.0-188
Diltiazem	1.0	122	14	1.5-52.3
17β-Estradiol	0.5	205	15	0.6-1.5
Lincomycin	0.1	122	15	0.1-8.5
Monensin	0.1	116	17	0.1-56.0
Naproxen	2.0	150	12	2.9-23.8
Progesterone	0.1	205	28	0.1-1.7
Sulfamethoxazole	2.0	150	17	2.2-152
Theobromine	50	122	15	50.8-315
Theophylline	5.0	150	12	5.2-50.2
Tonalid	10	77	13	10.0-232
Trimethoprim	1.0	122	15	1.0-15.4

Table 3. Least frequently detected EDCs and PPCPs in the finished drinking water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Azithromycin	1.0	122	3	25.5-108
Bezafibrate	0.5	150	1	0.8
Bisphenol A	100	156	3	131-515
Chloramphenicol	5.0	150	2	5.8-6.9
Clofibric acid	0.5	150	2	0.7-0.8
Diclofenac	0.5	150	2	1.6-1.8
Diethylstilbestrol (DES)	0.5	205	1	1.1
17α-Estradiol	0.5	205	2	0.5-1.9
17α-Ethynylestradiol	0.5	205	7	0.6-1.4
Fluoxetine	1.0	122	5	1.2-19.9
Ibuprofen	50	150	7	128-178
Nonylphenol	500	156	5	509-2,525
Phenylphenol	100	156	3	107-111
Prednisone	2.0	150	1	2.3
Sulfadimethoxine	0.1	122	4	0.2-1.5
Sulfamethazine	1.0	122	3	1.0-1.5
Sulfamethizole	5.0	150	4	6.8-8.7
cis-Testosterone	0.1	205	2	0.6-2.0
trans-Testosterone	0.1	205	8	0.1-0.8
2,4,6-Trichlorophenol	100	155	3	169-389

Table 4. Non-detected EDCs and PPCPs in the finished drinking water samples

Analyte	MRL ng/L	Analyte	MRL ng/L
Estriol	0.5	Narasin	0.1
4-n-Octylphenol	500	Oleandomycin	1.0
4-tert-Octylphenol	500	Oxytetracycline	500
Pentachlorophenol	100	Penicillin G	2.0
Tetrabromobisphenol A	100	Penicillin V	2.0
Amoxicillin	50	Roxithromycin	1.0
Antipyrine	1.0	Salinomycin	0.1
Bacitracin	500	Simvastatin	1.0
Carbadox	50	Sulfachloropyridazine	5.0
Chlorotetracycline	50	Sulfadiazine	5.0
Ciprofloxacin	50	Sulfamerazine	5.0
Doxycycline	50	Sulfathiazole	5.0
Enrofloxacin	500	Triclosan	5.0
Erythromycin	1.0	Tylosin	1.0
Lasalocid	1.0	Virginiamycin M1	1.0
Levothyroxine	2.0		

Table 5. Most frequently detected EDCs and PPCPs in the surface water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Acetaminophen	5.0	63	15	5.0-78.4
Caffeine	50	63	29	50-1,516
Carbamazepine	1.0	63	44	1.0-522
Cotinine	1.0	63	53	1.0-23.3
DEET	5.0	63	45	5.0-400
Diltiazem	1.0	63	14	1.0-210
Gemfibrozil	0.5	52	29	0.5-1,530
Galaxolide	10	40	39	10.5-3,811
Lincomycin	0.1	63	19	0.1-1.9
Nicotine	5.0	63	40	5.3-199
Paraxanthine	5.0	63	34	5.8-547
Sulfamethoxazole	2.0	63	31	5.1-680
Trimethoprim	1.0	63	15	1.0-406

Table 6. Frequently detected EDCs and PPCPs in the surface water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Aspirin	50	52	6	58.6-339
Bisphenol A	100	82	5	110-500
Dilantin	2.0	63	7	200-813
17β-Estradiol	0.5	67	5	0.5-14.5
Estrone	0.5	67	9	0.5-192
Fluoxetine	1.0	63	6	1.1-37.8
Monensin	0.1	59	3	0.8-4.6
Naproxen	2.0	52	8	2.1-263
Nonylphenol	500	82	9	504-3,305
Progesterone	0.1	67	8	0.1-0.7
Sulfadimethoxine	0.1	63	8	0.1-1.3
trans-Testosterone	0.1	67	8	0.1-0.6
Theobromine	50	63	4	68.4-406
Theophylline	5.0	52	3	5.9-20.9
Tonalid	10	40	3	10.1-367

Table 7. Least frequently detected EDCs and PPCPs in the surface water samples

Analyte	MRL ng/L	Total Sample	Positive Sample	Conc. ng/L
Azithromycin	1.0	63	2	115-221
Bezafibrate	0.5	52	1	1.8
Chloramphenicol	5.0	52	1	8.0
Diclofenac	0.5	52	2	15.7-34.2
17α-Estradiol	0.5	67	3	0.7-10.7
17α-Ethynylestradiol	0.5	67	2	0.6-7.2
Ibuprofen	50	52	2	57.0-220
Lasalocid	1.0	63	2	4.9-12.1
Levothyroxine	2.0	62	1	8.3
4-n-Octylphenol	500	82	1	1,300
4-tert-Octylphenol	500	82	1	253
Phenylphenol	100	82	4	101-218
Simvastatin	1.0	63	1	2.8
Sulfamethazine	1.0	63	3	1.3-4.0
Sulfamethizole	5.0	63	1	8.2-177
cis-Testosterone	0.1	67	3	0.2

Table 8. Non-detected EDCs and PPCPs in the surface water samples

Analyte	MRL ng/L	Analyte	MRL ng/L
Estriol	0.5	Oleandomycin	2.0
Pentachlorophenol	100	Oxytetracycline	2.0
Tetrabromobisphenol A	100	Penicillin G	1.0
Amoxicillin	50	Penicillin V	0.1
Antipyrine	1.0	Prednisone	2.0
Bacitracin	500	Roxithromycin	1.0
Carbadox	50	Salinomycin	5.0
Chlorotetracycline	50	Sulfachloropyridazine	5.0
Ciprofloxacin	50	Sulfadiazine	5.0
Clofibric acid	0.5	Sulfamerazine	2.0
Diethylstilbestrol (DES)	0.5	Sulfathiazole	5.0
Doxycycline	50	Triclosan	5.0
Enrofloxacin	500	Tylosin	1.0
Erythromycin	1.0	Virginiamycin M1	1.0
Narasin	500	2,4,6-Trichlorophenol	100

CONCLUSIONS

This paper reported the screening results of 74 EDCs and PPCPs in surface water and finished drinking water samples. The most frequently and frequently detected EDCs and PPCPs provided useful information for developing a representative and meaningful list of EDCs and PPCPs for future studies, which may include: assessment and fate of EDCs and PPCPs in raw and finished drinking water, control and removal of EDCs and PPCPs, human health effects and ecological impacts of EDCs and PPCPs, and inter-laboratory study on method performance evaluation.

REFERENCES

Dana W. Kolpin, Edward T. Furlong, Michael T. Meyer, E. Michael Thurman, Steven D. Zaugg, Larry B. Barber, and Herbert T. Buxton, Environ. Sci. Technol. 36 96), 1202-1211, 2002.

Eva M. Golet, Alfredo C. Alder, and Walter Giger, Environ. Sci. Technol. 36 (17), 3645-3651, 2002.

C. G. Daughton, J. Am. Soc. Mass Spectrom. 12, 1067-1076, 2001.

Michele E. Lindsey, Michael Meyer, and E. M. Thurman, Anal. Chem. 73 (19), 4640-4646, 2001.

Niina M. Vieno, Tuula Tuhkanen, and Leif Kronberg, Environ. Sci. Technol. 39 (21), 8220-8226, 2005.

David L. Sedlak, Karen Pinkston, and Ching-Hua Huang, Occurrence Survey of Pharaceutically Active Compounds, Research Project Completion Report, Project No. 91051; American Water Works Association Research Foundation; 2005.

Paul Westerhoff, Yeomin Yoon, Shane Snyder, and Eric Wert, Environ. Sci. Technol. 39 (17), 6649-6663, 2005.

Brett J. Vanderford, and Shane A. Snyder, Environ. Sci. Technol. 40 (23), 7312-7320, 2006.

Brett J. Vanderford, Rebecca A. Pearson, David J. Rexing, and Shane A. Snyder Anal. Chem. 75 (22), 6265-6274, 2003.

C. Desbrow, E. J. Routledge, G. C. Brighty, J. P. Sumpter, and M. Waldock, Environ. Sci. Technol. 32 (11), 1549-1558, 1998.

Holger M. Kuch and Karlheinz Ballschmiter, Environ. Sci. Technol. 35 (15), 3201-3206, 2001.

Tom Benijts, Willy Lambert, and André De Leenheer, Anal. Chem. 76 (3), 704-711, 2004.

Kei O. Isobe, Mitsunori Tarao, Mohamad P. Zakaria, Nguyen H. Chiem, Le Y. Minh, and Hideshige Takada, Environ. Sci. Technol. 36 (21), 4497-4507, 2002.

Maria J. López de Alda, Damià Barceló, J. Chromatogr. A, 892, 391-406, 2000.

P. Lee Ferguson, Charles R. Iden, Anne E. McElroy, and Bruce J. Brownawell, Anal. Chem. 73 (16), 3890-3895, 2001.

Chiara Baronti, Roberta Gurini, Giuseppe D'Ascenzo, Antonio Di Corcia, Alessandra Gentill, and Roberto Samperi, Environ. Sci. Technol. 34 (24), 5059-5066, 2000.

Xiu-Sheng Miao and Chris D. Metcalfe, Anal. Chem. 75 (15), 3731-3738, 2003.

Sebastian Zuehlke, Uwe Duennbier, and Thomas Heberer, Anal. Chem. 76 (22), 6548-6554, 2004.

Paul D. Anderson, Vincent J. D. D'Aco, Peter Shanahan, Steven C. Chapra, Mary E. Buzby, Virginia L. Cunningham, Beth M. DuPlessie, Eileen P. Hays, Frank J. Mastrocco, Neil J. Parke, John C. Rader, John H. Samuelian, and Bradley W. Schwab, Environ. Sci. Technol. 38 (3), 838-849, 2004.

Gregory A. Loraine and Mark E. Pettigrove, Environ. Sci. Technol. 40 93), 687-695, 2006.

José B. Quintana and Thorsten Reemtsma, Rapid Commun. Mass Spectrom. 18, 765-774, 2004.

Hong Chang, Jianying Hu, and Bing Shao, Environ. Sci. Technol. 41 (10), 3462-3468, 2007.

Mark. J. Benotti and Bruce J. Brownawell, Environ. Sci. Technol. 41 (16), 5795-5802, 2007.

the standard in safety

Emerging Contaminants in Raw and Finished Drinking Waters

Yongtao B. Li, Joshua S. Whitaker, and
Christina L. McCarty
Underwriters Laboratories

NEMC, August 14, 2008

Presentation Outline

- Emerging Contaminants in waters
- Analytical Methodologies
- Analytical Results
- Conclusions

Underwriters Laboratories

What are Emerging Contaminants?

- Perfluorochemicals/Perfluorosurfactants (PFCs)
  - Perfluoro-n-octanoic acid (C8, PFOA), perfluoro-1-octanesulfonate (PFOS), perfluoro-n-butanoic acid (C4, PFBA), etc.
- Blue-Green Algal/Cyanobacterial Toxins
  - Microcystins, cylindrospermopsin, saxitoxins, etc.
- Flame Retardants
  - Brominated flame retardants: Polybrominated diphenyl ethers (PBDEs), polybrominated bisphenol A (PBBs), polybrominated phenols, etc.
  - Phopshate flame retardants: Tris(2-chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP), tris(2,3-dibromopropyl) phosphate (TDBPP), etc.

Underwriters Laboratories

What are Emerging Contaminants?

- Endocrine Disrupting Chemicals (EDCs)
- Pharmaceuticals and Personal Care Products (PPCPs)/Pharmaceutically Active Compounds (PhACs)

Underwriters Laboratories

What are EDCs?

- Human hormones
- Estrogenic pharmaceuticals
  - Used for anti-nausea, premature labor prevention, ovalation inhibition, and hormone replacement therapy.
- Nonylphenols and octylphenols
  - Microbial degradates of nonionic surfactant alkylphenol ethoxylates
- Bisphenol A
  - Used in the synthesis of epoxy resins and polycarbonate plastics.
- Other potential endocrine-mediated active phenols
- Pesticides and herbicides

Underwriters Laboratories

What are PPCPs?

- Prescription and non-prescription human drugs and antibiotics
- Drugs used in hospitals
- Veterinary drugs and antibiotics
- Drugs and antibiotics used for animal feeds and fish hatcheries
- Antimicrobials and fragrances used in personal care products (PCPs)

Underwriters Laboratories

Sources of EDCs and PPCPs

- Industrial and municipal wastewater discharge, raw sewage waste disposal and overflow, and septic tanks.
  - Excretion, bathing, disposal of medications, cleaning, etc.
- Treated sewage sludge used as fertilizers
- PPCPs also originate from other sources.
  - Farm animal feed (cattle, poultry, swine, etc.), fish hatcheries, landfill runoff, etc.
- EDCs also originate from pesticide applications

Underwriters Laboratories

Why do we analyze EDCs and PPCPs?

- EDCs and PPCPs have been detected in a variety of water matrices.
- The removal efficiency of EDCs and PPCPs is largely unknown.
  - Sewage and drinking water treatment systems are not well engineered or equipped for the removal of EDCs and PPCPs.
- The fate of EDCs and PPCPs in the environment is poorly understood.
  - PPCPs tend to dissolve easily in water and do not evaporate at normal temperature of pressure.

Underwriters Laboratories

Why do we analyze EDCs and PPCPs?

- The side effects on human health are poorly understood.
  - Steroidal estrogens are known to be human carcinogens.
  - Estrogens cause developmental/reproductive problems in humans.
- The impacts on ecological systems are largely unknown.
  - Estrogens cause reproductive abnormalities in wildlife.
- Drug-resistant bacteria - Superbugs
  - Streptococcus pneumoniae bacteria
  - Golden Staph bacteria
  - VRE bacteria

Underwriters Laboratories

A Screening List of EDCs and PPCPs

- 17 EDCs and 57 PPCPs were selected.
- The list was based on:
  - EDCs and PPCPs from the research reports of USGS
  - EDCs and PPCPs studied by other research groups
  - EDCs and PPCPs frequently detected in various waters
  - EDCs and PPCPs requested by clients
  - Availability of standards
  - Analytical performance issues

Underwriters Laboratories

Analytical Methodologies

- L200 for phenolic EDCs
  - SPE sample preparation
  - LC/ESI/MS in negative ion mode
  - Internal standard calibrations
- L211 for hormone/estrogen EDCs
  - SPE sample preparation
  - LC/ESI/MS/MS in positive and negative switching ion modes
  - Internal standard calibrations

Underwriters Laboratories

Analytical Methodologies

- L220 for PPCPs
  - SPE sample preparation
  - LC/ESI/MS/MS in positive ion mode
  - Internal standard calibrations
- L221 for PPCPs
  - SPE sample preparation
  - LC/ESI/MS/MS in negative ion mode
  - Internal standard calibrations
- S170 for fragrances (galaxolide and tonalid)
  - SPE sample preparation
  - GC/MS and internal standard calibrations

Underwriters Laboratories

Analytical Results

- Most frequently detected EDCs and PPCPs
  - Detected in over 20% of the samples
- Frequently detected EDCs and PPCPs
  - Detected in 5-20% of the samples
- Least frequently detected EDCs and PPCPs
  - Detected in less than 5% of the samples
- Non-detected EDCs and PPCPs

Underwriters Laboratories

Most frequently detected EDCs and PPCPs in finished drinking water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Caffeine	50	122	25	50-639
Carbamazepine	1.0	122	51	1.0-296
Cotinine	1.0	122	74	1.2-18
DEET	5.0	122	47	5.0-445
Estrone	0.5	205	42	0.5-39
Gemfibrozil	0.5	150	41	0.5-13
Galaxolide	10	77	44	10-1,926
Nicotine	5.0	122	43	5.0-96
Paraxanthine	5.0	122	30	5.8-114

Underwriters Laboratories

Frequently detected EDCs and PPCPs in finished drinking water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Acetaminophen	5.0	122	19	5.0-24
Aspirin	50	144	10	57-105
Dilantin	2.0	150	16	2.0-188
Diltiazem	1.0	122	14	1.0-52
17β-Estradiol	0.5	205	15	0.6-1.5
Lincomycin	0.1	122	15	0.1-8.5
Monensin	0.1	116	17	0.1-56
Naproxen	2.0	150	12	2.9-24
Progesterone	0.1	205	28	0.1-1.7
Sulfamethoxazole	2.0	150	17	2.2-152
Theobromine	50	122	15	51-315
Theophylline	5.0	150	12	5.2-50
Tonalid	10	77	13	10-232
Trimethoprim	1.0	122	15	1.0-15

Underwriters Laboratories

Least frequently detected EDCs and PPCPs in finished drinking water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Azithromycin	1.0	122	3	26-108
Bezafibrate	0.5	150	1	0.8
Bisphenol A	100	156	3	131-515
Chloramphenicol	5.0	150	2	5.8-6.9
Clofibric acid	0.5	150	2	0.7-0.8
Diclofenac	0.5	150	2	1.6-1.8
Diethylstilbestrol (DES)	0.5	205	1	1.1
17α-Estradiol	0.5	205	2	0.5-1.9
17α-Ethynylestradiol	0.5	205	7	0.6-1.4
Fluoxetine	1.0	122	5	1.2-20
Ibuprofen	50	150	7	128-178

Underwriters Laboratories

Least frequently detected EDCs and PPCPs in finished drinking water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Nonylphenol	500	156	5	509-2,525
Phenylphenol	100	156	3	107-111
Prednisone	2.0	150	1	2.3
Sulfadimethoxine	0.1	122	4	0.2-1.5
Sulfamethazine	1.0	122	3	1.0-1.5
Sulfamethizole	5.0	150	4	6.8-8.7
cis-Testosterone	0.1	205	2	0.6-2.0
trans-Testosterone	0.1	205	8	0.1-0.8
2,4,6-Trichlorophenol	100	150	3	169-389

Underwriters Laboratories

Non-detected EDCs and PPCPs in finished drinking water

Analyte	MRL (ng/L)	Analyte	MRL (ng/L)
Estriol	0.5	Narasin	0.1
4-n-Octylphenol	500	Oleandomycin	1.0
4-tert-Octylphenol	500	Oxytetracycline	500
Pentachlorophenol	100	Penicillin G	2.0
Tetrabromobisphenol A	100	Penicillin V	2.0
Amoxicillin	50	Roxithromycin	1.0
Antipyrine	1.0	Salinomycin	0.1
Bacitracin	500	Simvastatin	1.0
Carbadox	50	Sulfachloropyridazine	5.0
Chlorotetracycline	50	Sulfadiazine	5.0
Ciprofloxacin	50	Sulfamerazine	5.0
Doxycycline	50	Sulfathiazole	5.0
Enrofloxacin	500	Triclosan	5.0
Erythromycin	1.0	Tylosin	1.0
Lasalocid	1.0	Virginiamycin M1	1.0
Levothyroxine	1.0		

Underwriters Laboratories

Most frequently detected EDCs and PPCPs in surface water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Acetaminophen	5.0	63	15	5.0-78
Caffeine	50	63	29	50-1,516
Carbamazepine	1.0	63	44	1.0-522
Cotinine	1.0	63	53	1.0-23
DEET	5.0	63	45	5.0-400
Diltiazem	1.0	63	14	1.0-210
Gemfibrozil	0.5	52	29	0.5-1,530
Galaxolide	10	40	39	10-3,811
Lincomycin	0.1	63	19	0.1-1.9
Nicotine	5.0	63	40	5.3-199
Paraxanthine	5.0	63	34	5.8-547
Sulfamethoxazole	2.0	63	31	5.1-680
Trimethoprim	1.0	63	15	1.0-406

Underwriters Laboratories

Frequently detected EDCs and PPCPs in surface water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Aspirin	50	52	6	59-339
Bisphenol A	100	82	5	110-500
Dilantin	2.0	63	7	200-813
17β-Estradiol	0.5	67	5	0.5-14
Estrone	0.5	67	9	0.5-192
Fluoxetine	1.0	63	6	1.1-38
Monensin	0.1	59	3	0.8-4.6
Naproxen	2.0	52	8	2.1-263
Nonylphenol	500	82	9	504-3,305
Progesterone	0.1	67	8	0.1-0.7
Sulfadimethoxine	0.1	63	8	0.1-1.3
trans-Testosterone	0.1	67	8	0.1-0.6
Theobromine	50	63	4	68-406
Theophylline	5.0	52	3	5.9-21
Tonalid	10	40	3	10-367

Underwriters Laboratories

Least frequently detected EDCs and PPCPs in surface water

Analyte	MRL (ng/L)	Total Sample	Positive Sample	Conc. (ng/L)
Azithromycin	1.0	63	2	115-221
Bezafibrate	0.5	52	1	1.8
Chloramphenicol	5.0	52	1	8.0
Diclofenac	0.5	52	2	16-34
17α-Estradiol	0.5	67	3	0.7-11
17α-Ethynylestradiol	0.5	67	2	0.6-7.2
Ibuprofen	50	52	2	57-220
Lasalocid	1.0	63	2	4.9-12
Levothyroxine	2.0	62	1	8.3
4-n-Octylphenol	500	82	1	1,300
4-tert-Octylphenol	500	82	1	253
Phenylphenol	100	82	4	101-218
Simvastatin	1.0	63	1	2.8
Sulfamethazine	1.0	63	3	1.3-4.0
Sulfamethizole	5.0	63	1	8.2
cis-Testosterone	0.1	67	3	0.2

Underwriters Laboratories

Non-detected EDCs and PPCPs in surface water

Analyte	MRL (ng/L)	Analyte	MRL (ng/L)
Estriol	0.5	Oleandomycin	2.0
Pentachlorophenol	100	Oxytetracycline	2.0
Tetrabromobisphenol A	100	Penicillin G	1.0
Amoxicillin	50	Penicillin V	0.1
Antipyrine	1.0	Prednisone	2.0
Bacitracin	500	Roxithromycin	1.0
Carbadox	50	Salinomycin	5.0
Chlorotetracycline	50	Sulfachloropyridazine	5.0
Ciprofloxacin	50	Sulfadiazine	5.0
Clofibric acid	0.5	Sulfamerazine	2.0
Diethylstilbestrol (DES)	0.5	Sulfathiazole	5.0
Doxycycline	50	Triclosan	5.0
Enrofloxacin	500	Tylosin	1.0
Erythromycin	1.0	Virginiamycin M1	1.0
Narasin	500	2,4,6-Trichlorophenol	100

Underwriters Laboratories

Conclusions

- The results obtained from the finished drinking water samples were generally consistent with those obtained from the surface water samples in terms of the frequency of the samples detected positively.
- The detected PPCPs and their concentration levels are generally consistent with the results from other reports.
- 50% or less of the studied EDCs and PPCPs were detected in 5% or more of the surface water and finished drinking water samples.

Underwriters Laboratories

Conclusions

- More analytes were detected in the surface waters in the category of the most frequently detected EDCs and PPCPs. Most of them were also detected in over 20% of the finished drinking waters.
- The detected concentrations were generally higher in the surface waters than those in the finished drinking waters.
- The positive results indicate that the current drinking water treatment systems are not very effective for the removal of a number of EDCs and PPCPs.

Underwriters Laboratories

Conclusions

- The most frequently and frequently detected EDCs and PPCPs provided useful information for developing a representative and meaningful list of EDCs and PPCPs for future studies.
  - Occurrence assessment and fate of EDCs and PPCPs in raw and finished drinking water
  - Control, removal, and modeling of EDCs and PPCPs
  - Human health effects and ecological impacts of EDCs and PPCPs
  - Inter-laboratory study on method performance evaluation.

Underwriters Laboratories

the standard in safety

Contact

Dr. Yongtao B. Li

Yongtao.Li@us.ul.com

574-472-5562

Underwriters Laboratories

Analysis of Emerging Contaminants in Drinking Water Using ON-line SPE/LC/MS/MS

Claude Mallet
Waters Corporation
34 Maple St.
Milford, MA 01757-3696
508-482-3045
claude_mallet@waters.com

ABSTRACT

The analysis of "emerging contaminants" (ECs) has shown a considerable interest in the field of environmental research. This increase of interest was sparked by two factors: first, new analytical tools (GC/MSMS or LC/MS/MS) with sub-ppb detection capability and second, concerns about adverse effect on human health and wildlife. ECs comprise a large selection of chemicals such as pharmaceuticals, veterinary drugs, nanomaterials, personal care products and household chemicals. As it can be seen those chemicals differ from the familiar pollutants such as pesticides, dioxins, heavy metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCB's). In the early 90's, European scientists identified trace amount of pharmaceutical drugs in surface and ground waters. This prompted national wide surveys in Europe and America. The results showed over 100 such contaminants at un-expected ppb levels. ECs are defined as pollutants that are not currently registered in a routine monitoring program. The selection of candidates for future regulation will depend on toxicity research, potential health issues, their persistence in the environment and last, public awareness.

The main disadvantage with current drinking water methods is the amount of manual labor (several hours to days) needed to produce an ideal sample for LC/MS/MS. It often requires to process large volume of sample between 1 and 20 liters to ensure a high enrichment ratio for trace level analysis (sub-ppb). As an example, a typical extraction method usually starts with a 500 mL of sample and ending up with a final volume of a 100 uL (5 000: 1 enrichment ratio). If higher sensitivity is required, the only alternative left is to process larger sample volume, but will require an increase in manual labor. With an automated platform, small injection volumes (< 20 mL) are injected onto an extraction column (reversed-phase polymer sorbent, 30 um) with a high aqueous flow rate. Weak interferences are removed from the extraction column with a mild organic wash. The automated analysis is continued with the elution of the trapped analytes on the extraction column toward a focusing column (reversed-phase hybrid silica, 3.5 um) using a back flush method and detection by MS/MS.

This presentation will discuss the performance of ON-line SPE/LC/MS/MS for the analysis of emerging contaminants such as, pharmaceuticals, veterinary drugs and personal care products, in drinking water. One major advantage is the reduction of sample volume from 1 liter to a 20 mL sample. With a 1 000:1 enrichment factor, the limit of detection (LOD) was measured at 10 ppt. In practical terms, manual labor required to process one sample was limited to simply filling a 20 mL vial. Overall, the extraction protocol was reduced from 3-5 hours to less than 5 minutes. The analysis time is typically less than 20 minutes.

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Analysis of Emerging Contaminants In Drinking Water using ON-line SPE/LC/MS/MS

C.R. Mallet
Waters Corporation

NEMC 2008
Washington, DC, USA

Drinking Water – Few Facts

Safe Drinking Water Act (1974)

UNITED STATES • ENVIRONMENTAL PROTECTION AGENCY •

Contaminants
-Disinfectant
-Inorganic chemical
-Organic chemical *
-Disinfectant byproduct
-Microorganism
-Radionuclides

Organochlorine
Organophosphorous
Organonitrogen
Carbamates
Triazines
Phenoxyacetic acids
…. etc

CCL1 – March 1998
CCL2 – February 2005
CCL3 – February 2008

Emerging Contaminants

"Emerging contaminants (ECs) are chemicals that recently have been shown to occur widely in water resources and identified as being a potential environmental or public health risk"

December 2007
US EPA Method 1694
Pharmaceucticals and personal care Products in water, soil, sediment and Biosolids by HPLC/MS/MS

Emerging Contaminants

- **Human Pharmaceuticals**
  - Painkiller
  - Antibiotics
  - Antibacterials
  - Antidiabetics
  - B-Blockers
  - Contraceptives
  - Illicit drugs
  - Antidepressants
  - Impotence drugs
  - Lipid regulators
  - Barbiturates
  - Tranquilizers
  - Opioids
  - Antiepileptics
  - Over-the-counter drugs
- **Hormones**
  - Estrogen
- **Veterinary Pharmaceuticals**
  - Antibiotics
  - Antibacterials
- **Personal Care Product**
  - Sunscreen
  - Cosmetics
  - Skin lotion
  - Beauty cream
  - Hair spray
  - Hair dyes
  - Shampoos
- **Benzotriazoles**
  - Anticorrosive agents
  - Engine coolants
  - Aircrafts deicers
  - Antifreeze liquids
- **Algal toxins**
  - Microcystins

Drinking Water Analysis How It's Done Currently

Sample Preparation → **Chromatography** → **Mass Spectrometry**

Raw sample:
- Caco-2, microsomes, P450, hepatocytes … etc
- Tissue, CSF, plasma, serum urine, tears … etc
- water, sediment, food … etc

Extracted sample For LC/MS/MS

Ideally, the final sample should be as clean as a non-extracted standard.

Polarity:
Silica- C_{18}, C_8, C_4, C_2
Hybrid- C_{18}, C_8, C_4, C_2
Polymer- C_{18}, C_8, C_4, C_2
Embedded polar group
Cyano, Phenyl
Particle size:
1.8, 2.5, 3.5, 5 or 8 µm
Internal diameter:
4.6, 3.9, 2.1, 1.0, 0.32 mm and 75 µm
Length:
150, 100, 50, 30, 20 mm

Source:
ESI
APcI
Nano-ESI
Mass analyzers:
magnetic sectors
electric sectors
time of flight
quadrupole
ion trap
FT-ICR

Drinking Water Analysis How It's Done Currently

Collection → **Sample Preparation** → **Analysis** → **Results**

1L to 20 L

- Sample container
- Shipping container

- Shipping cost

- Filtration
- Extraction
- Clean up
- Concentration
- Derivatization

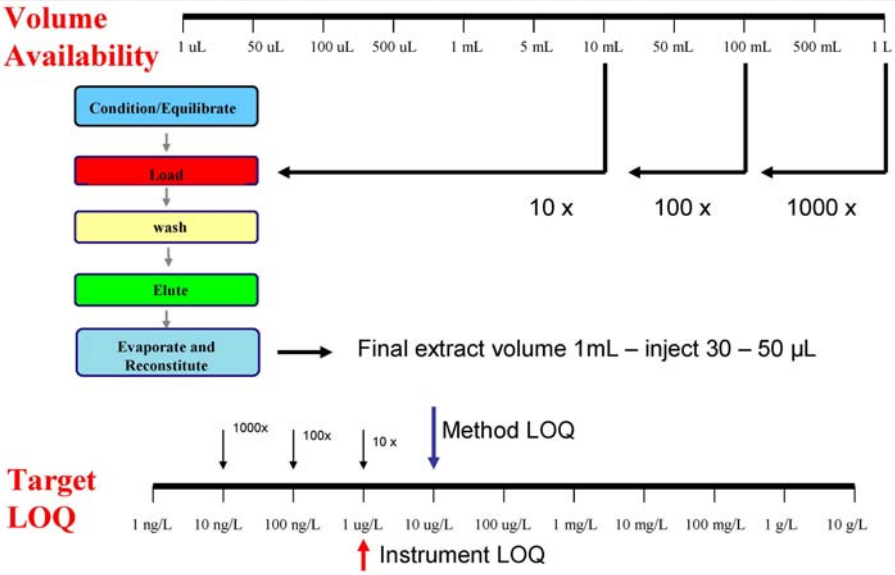
- Manual Work
- Hours to days
- Consumable – Disposable
- Sample storage
- Lab space
- Additional Equipment:
  - Glass ware
  - Manifold
  - Evaporator

LC/MS
GC/MS
LC/MS/MS
GC/MS/MS

Automated System

Qualitative
Quantitative
RSD's > 15 % +

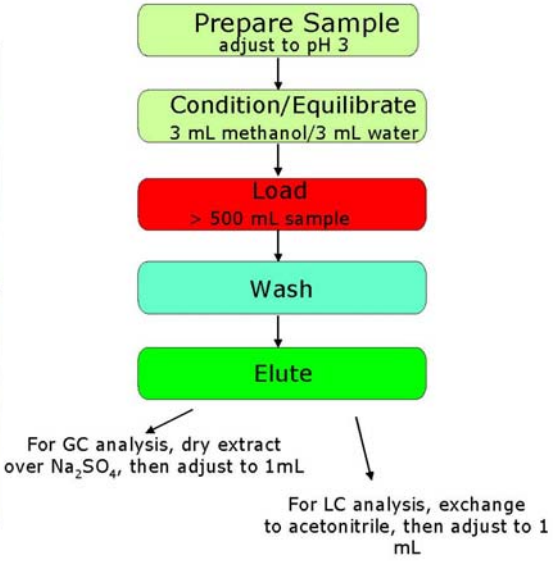
Off Line SPE Protocol



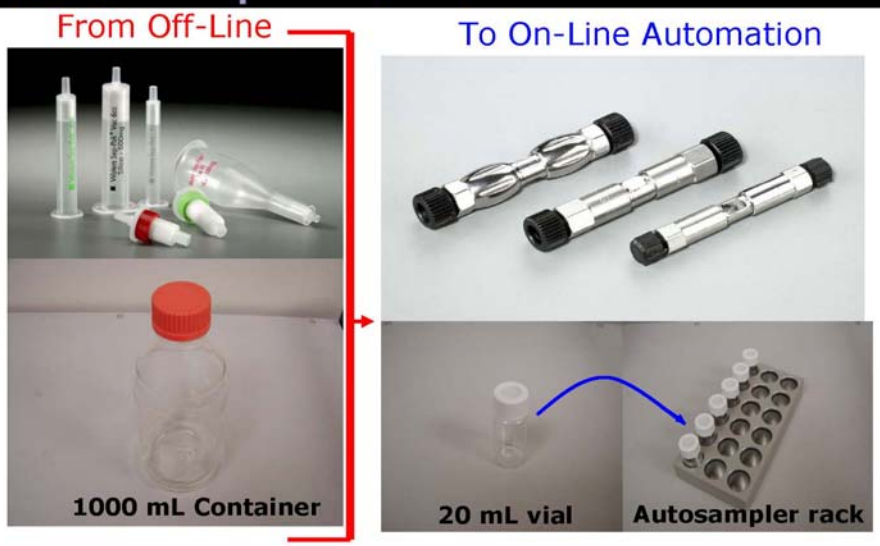
Off Line Sample Preparation Extraction Protocol

Barrels or Syringe

OFF-line SPE Extraction Manifold



ON Line vs OFF line



ON line SPE
Volume Equivalency

Volume Availability

1 uL | 50 uL | 100 uL | 500 uL | 1 mL | 5 mL | 10 mL | 50 mL | 100 mL | 500 mL | 1 L

Condition/Equilibrate → Load → wash → Elute →

Final extract volume is 0 (mL, µL, nL ... ?)
Analytes are trapped on Extraction Column
Direct elution to HPLC Column

Off Line SPE Extraction

500 mL (starting volume) → **1 mL final** (elution volume)

500:1 enrichment

LC/MS Analysis

30 - 50 µL (injection volume)

30 µL – 1/33th of original volume – 15.0 mL
50 µL – 1/20th of original volume – 25.0 mL

Drinking Water Analysis
Going Forward: AquaAnalysis System

Collection → **Sample Preparation** → **Analysis** → **Results**

20 mL

- Sample container
- Shipping container

- Shipping cost

ON-line SPE/LC/MS/MS

Integrated System

- Fully Automated – no manual work
- Results in minutes instead of hours/days
- Reusable chemistries – longer cycle time
- Reduction of sample storage space
- Minimum lab space required
- No additional equipment needed
- Reduction of analytical costs

Qualitative
Quantitative
RSD's < 15 %

ON-line SPE Classification

Two Step Protocols (TiSP)

A- Sequential SPE (1-1, 1-0)
B- Parallel SPE (2-1)
C- Parallel LC (1-2)
D- Parallel SPE/LC (2-2)
E- Staggered sequential SPE/LC (4-4) or (8-8)

Overview:

- Load & shoot protocols only
- Limited selection of chemistries
- High matrix effects
- Limited to simple matrix
- Low column life expectancy

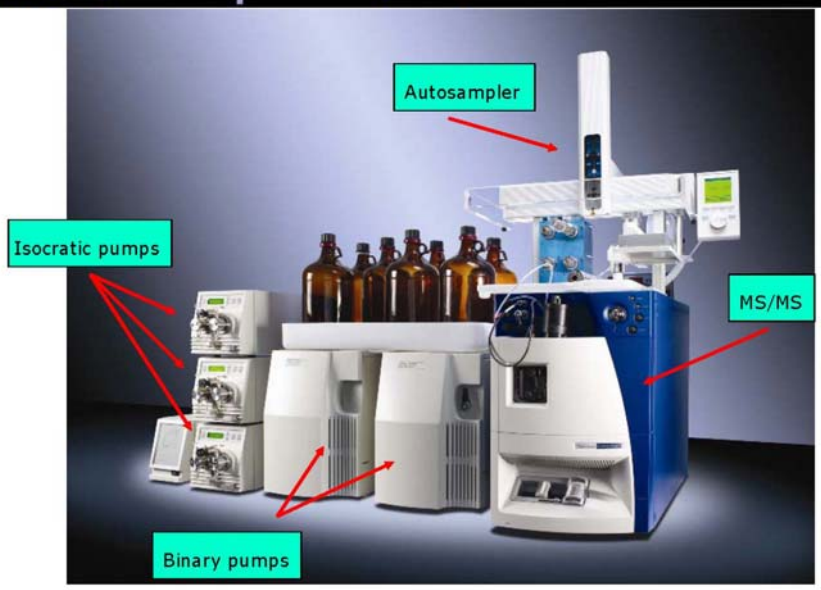
Multiple Step Protocol (N > 2) (MiSP)

A- Sequential^{N} SPE (1-1)
B- Parallel^{N} SPE (2-1)
C- Parallel^{N} LC (1-2)
D- Parallel^{N} SPE/LC (2-2)
E- Staggered^{N} sequential SPE (4-4) or (8-8)
F- Parallel^{N} SPE (6-1)
G- Parallel^{N} SPE/LC (6-2)

Overview:

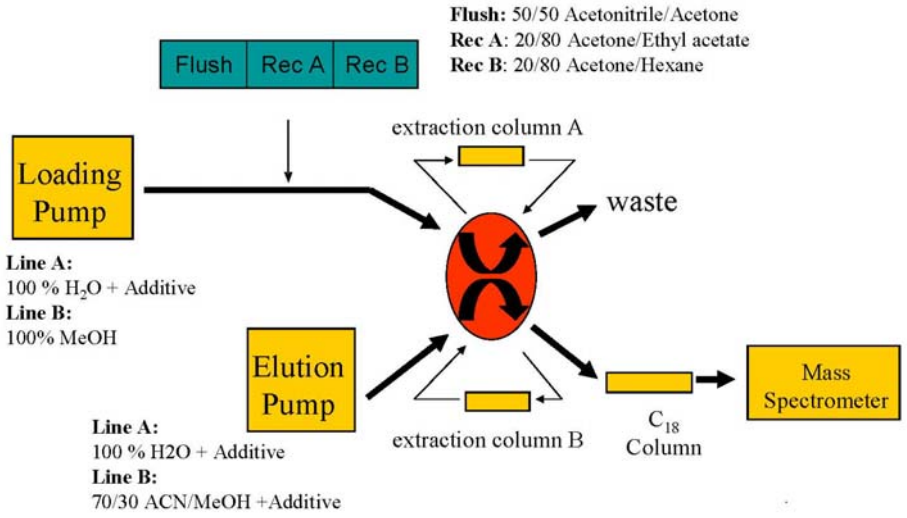
- High effenciency extraction protocols
- Pre-elution wash steps
- Post extraction re-conditioning
- Low matrix effects
- High column life expectancy
- Lower detection limits

ON-Line SPE/LC/MS/MS System

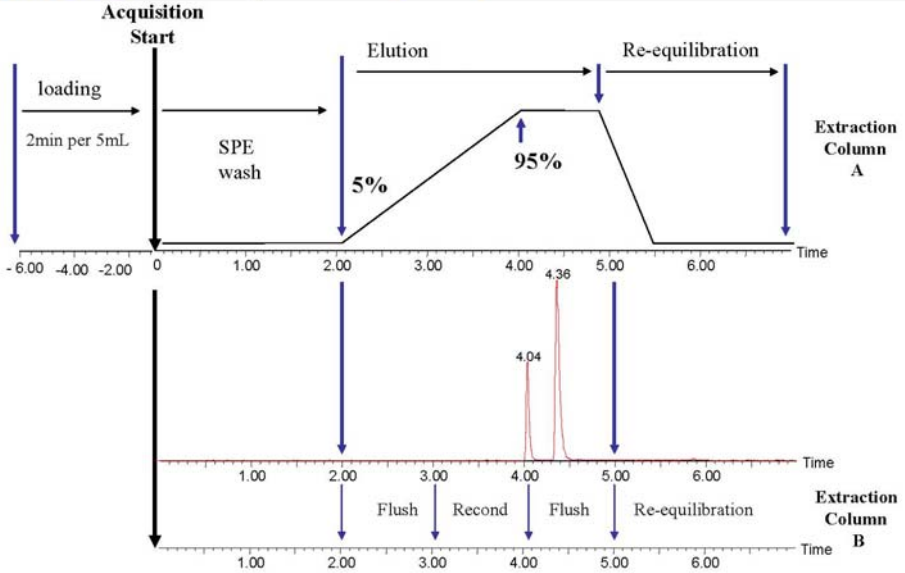


ON-line SPE 2-1 configuration

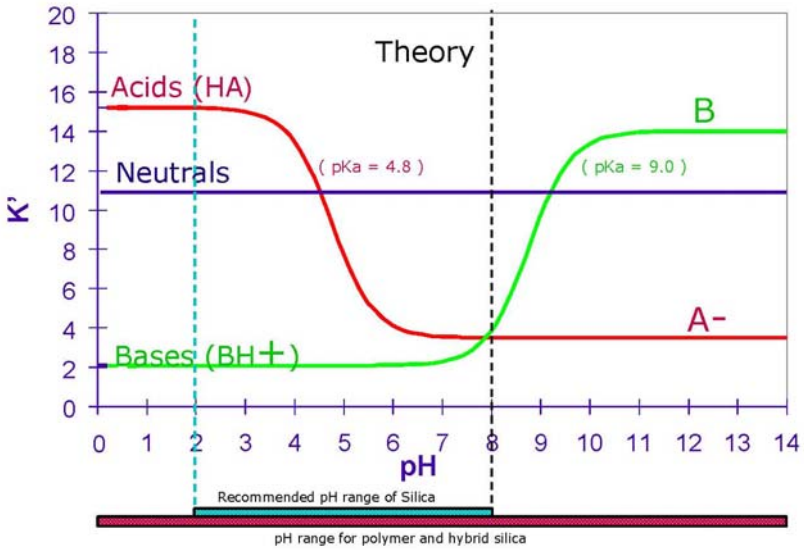
Parallel^N extraction (2-1) configuration



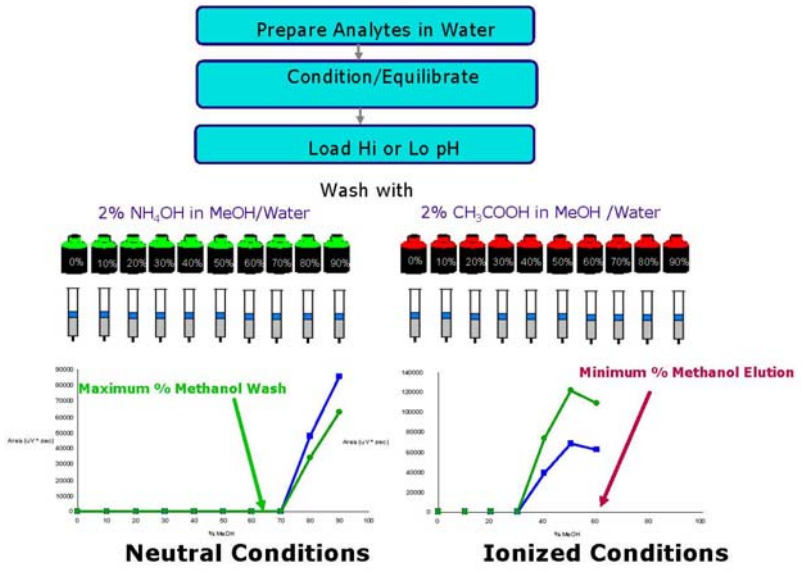
ON-line SPE 2-1 configuration Sequential and Parallel Events



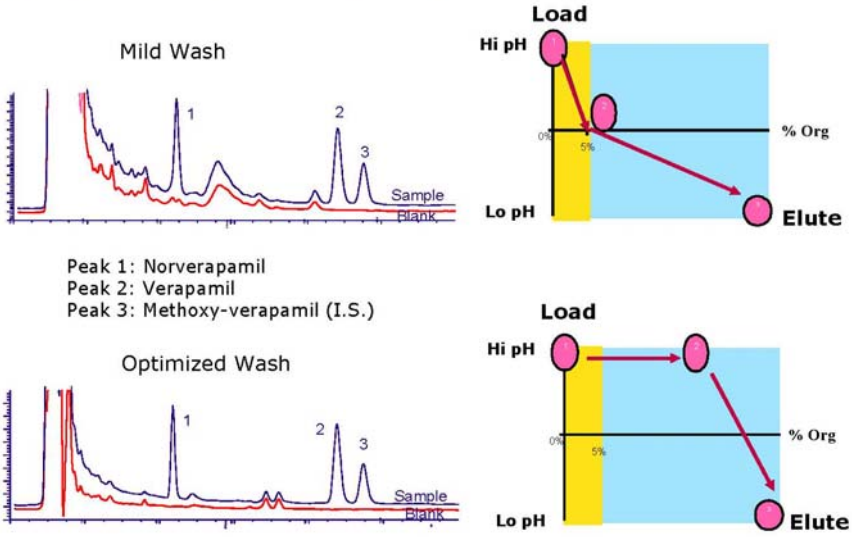
Loading and Elution Conditions



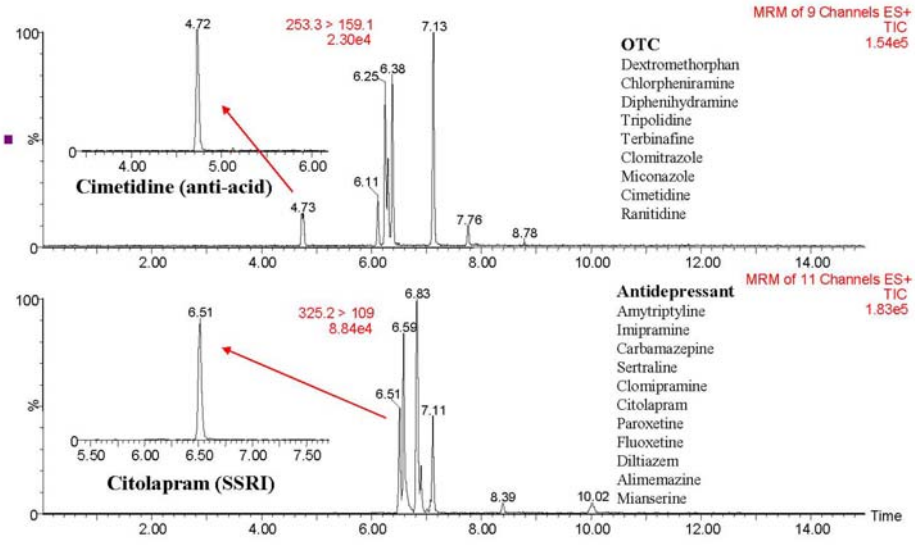
SPE Washing Conditions



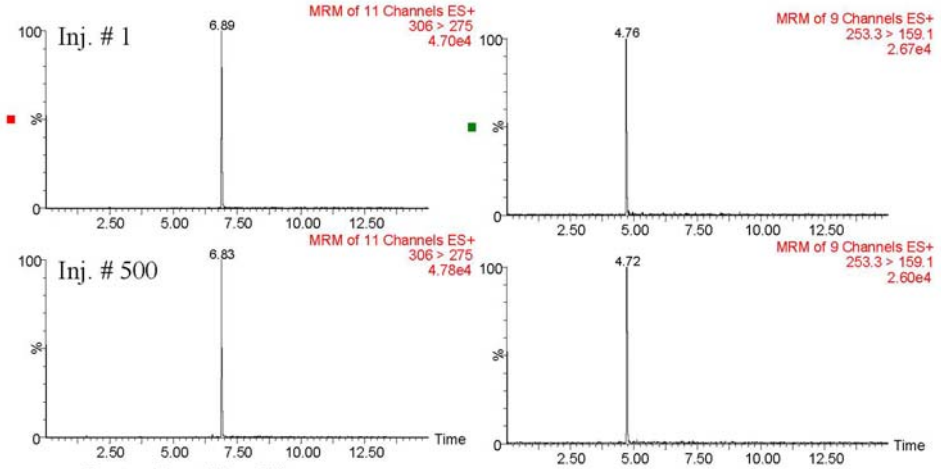
Washing Conditions



Emerging Contaminants
15 mL water spike injection at 10 ppt



Reproducibility & Column Lifetime
15 mL water spike injection at 10 ppt



Sertraline (N = 10)

Rt	**6.86**	**0.17%**
Area	**2037**	**10.2%**

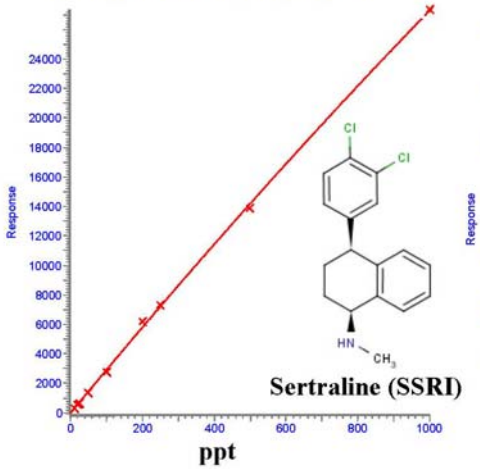
Cimetidine (N = 10)

Rt	**4.74**	**0.5%**
Area	**2074**	**8.6%**

Linearity
1 to 1000 ppt

Antidepressant

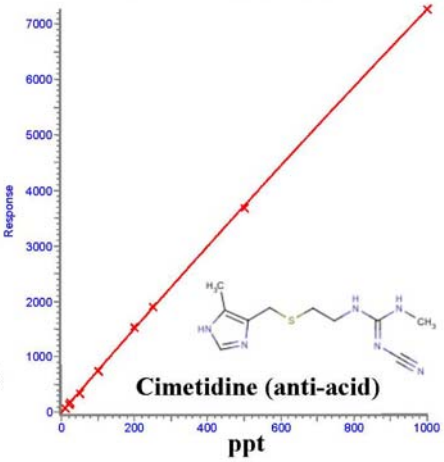
Coefficient of Determination: R^2 = 0.998657
Curve type: 2nd Order, Weighting: 1/x



Sertraline (SSRI)

OTC

Coefficient of Determination: R^2 = 0.999660
Curve type: 2nd Order, weighting: 1/x

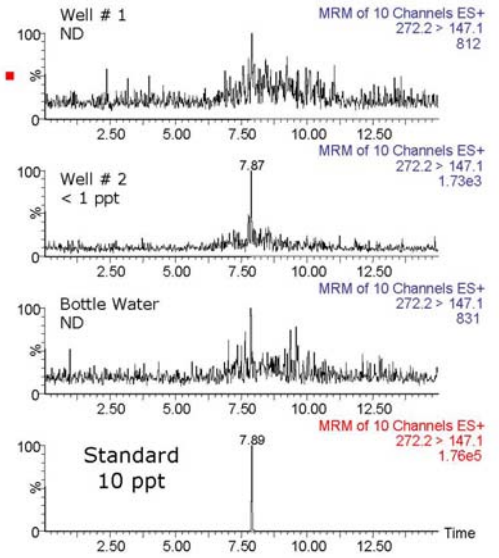


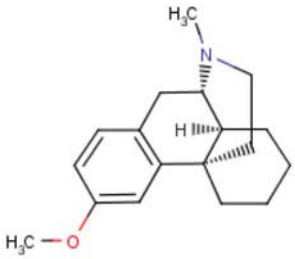
Cimetidine (anti-acid)

Analysis of Over-The-Counter Drugs & Antidepressant in Potable Water

- Study was conducted with 10 sources of potable water from surrounding areas:
  - Town
  - Well
  - Bottled

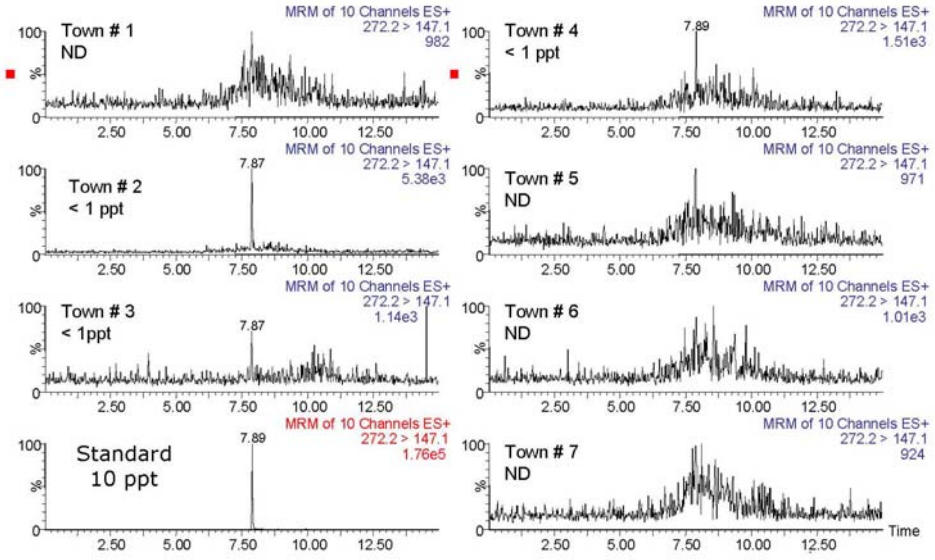
Antitussive In Potable Water



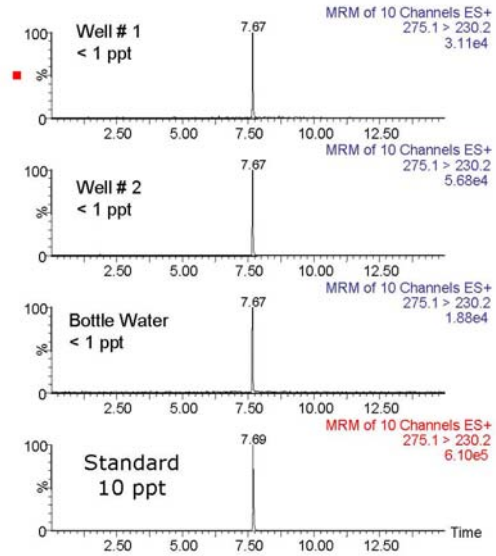


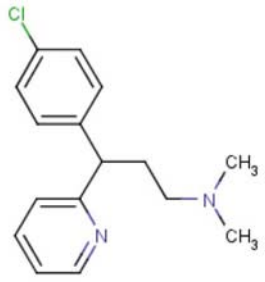
Dextromethorphan
(Cough suppressant)

Antitussive In Potable Water



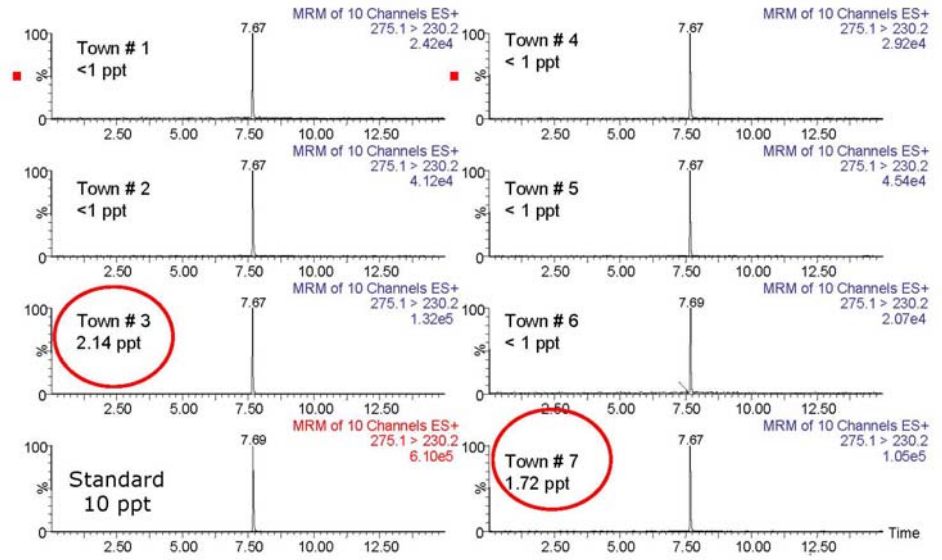
Anti-histamine in Potable Water



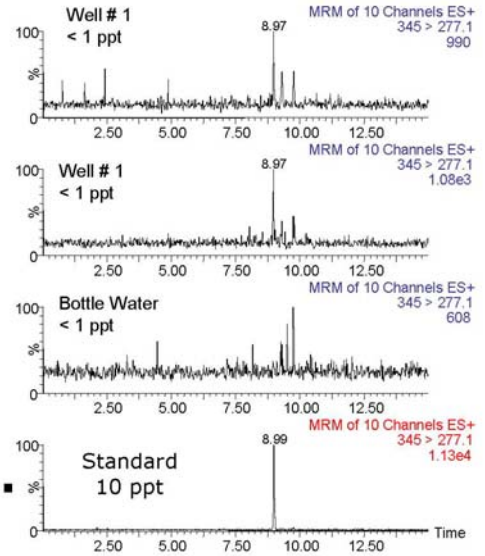


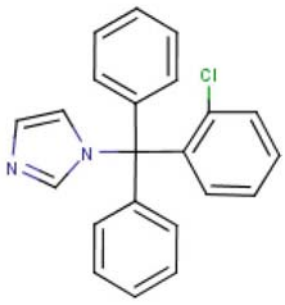
Chlorpheniramine
(allergies)

Anti-histamine in Potable Water



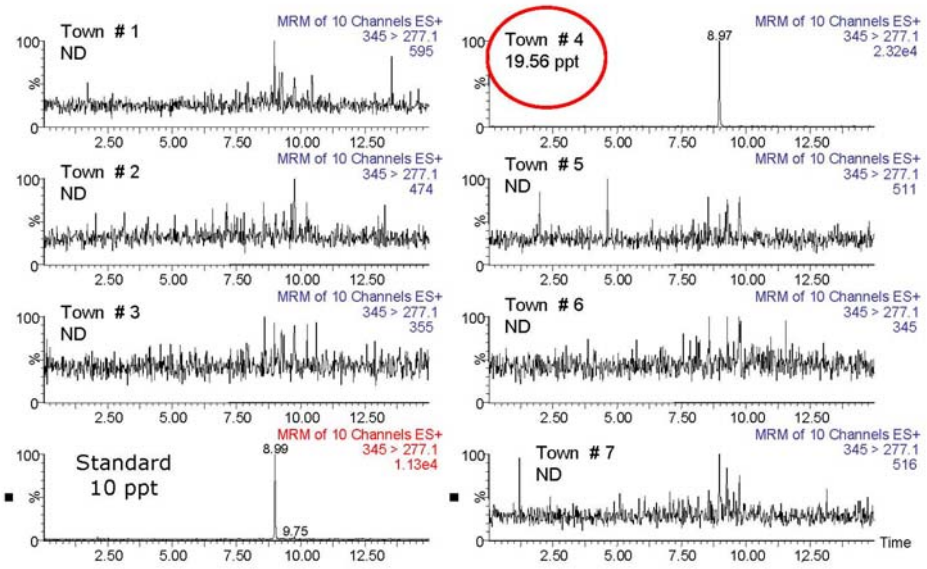
Anti-fungal in Potable Water





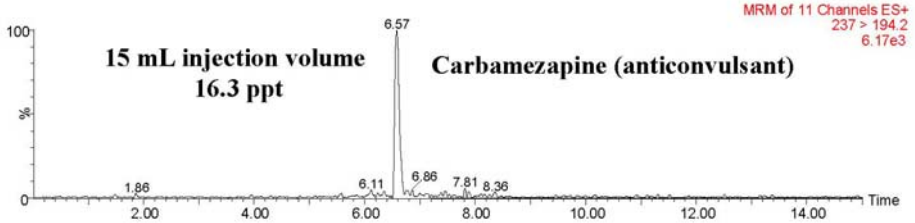
Clotrimazole
(Antifungal)

Anti-fungal in Potable Water



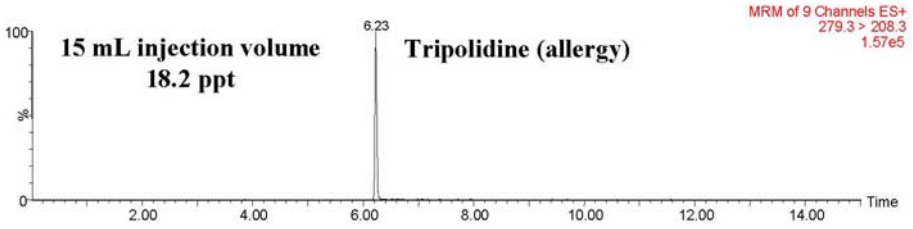
Town Water

Antidepressant	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Amytriptyline	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Imipramine	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	ND	ND	ND	ND
Carbamezapine	ND	ND	ND	ND	ND	ND	ND	ND	16.3	5.3
Sertraline	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Clomipramine	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	ND	ND	ND
Citolapram	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Paroxetine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoxetine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diltiazem	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Alimemazine	1.55	< 1.0	< 1.0	ND	ND	ND	ND	ND	ND	ND
Mianserine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND



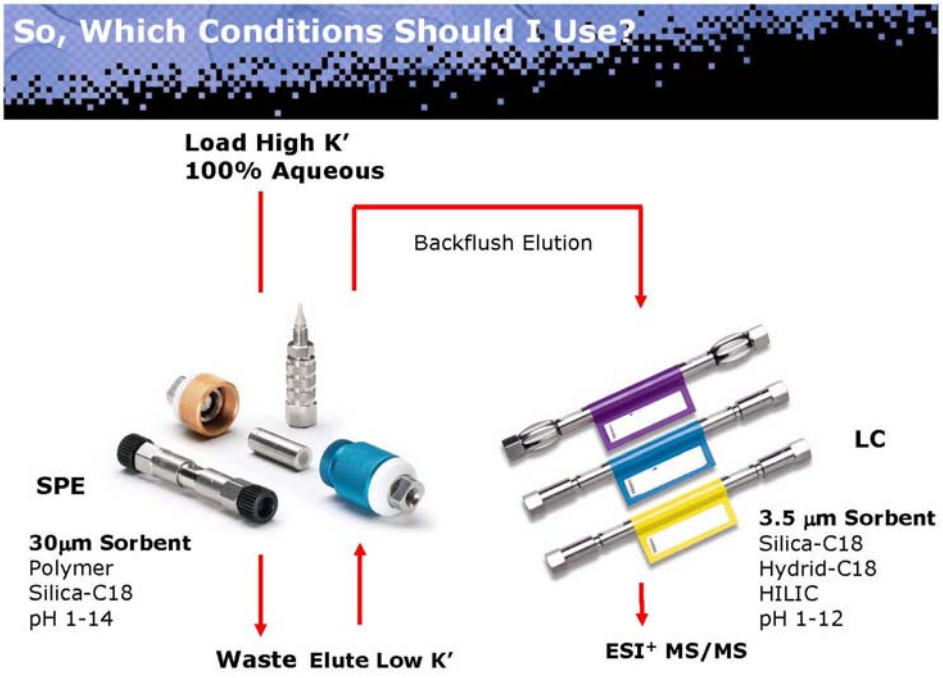
Town Water

OTC	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Dextromethorphan	ND	ND	< 1.0	ND	ND	< 1.0	ND	ND	ND	ND
Chlorpheniramine	1.1	7.2	8.0	12.2	3.9	6.6	ND	< 1.0	< 1.0	ND
Diphenihydramine	< 1.0	< 1.0	< 1.0	< 1.0	1.18	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Tripolidine	< 1.0	10.2	11.6	18.2	2.3	7.4	< 1.0	< 1.0	ND	ND
Terbinafine	ND	< 1.0	< 1.0	< 1.0	ND	ND	< 1.0	< 1.0	ND	ND
Clomitrazole	ND	ND	ND	ND	ND	ND	ND	4.6	< 1.0	< 1.0
Miconazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cimetidine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ranitidine	ND	ND	ND	ND	ND	1.1	< 1.0	ND	ND	ND



Conclusions

- Fully automated
- Trace level detection (ppt)
- Minimum sample preparation (6 min)
- High reduction of manual labor (80%)
- Wide pH range SPE & LC sorbents
- Wide selection of chemistries available
- High level of reproducibility and robustness


So, Which Conditions Should I Use?
Load High K'
100% Aqueous
Backflush Elution
SPE
30µm Sorbent
Polymer
Silica-C18
pH 1-14
Waste
Elute Low K'
LC
3.5 µm Sorbent
Silica-C18
Hydrid-C18
HILIC
pH 1-12
ESI+ MS/MS

Emerging Organic Pollutants by LC/ESI-MS-MS

Chunyan Hao
Ontario Ministry of the Environment
125 Resources Road
Etobicoke, ON Canada M9P 3V6
416-235-6033
chunyan.hao@ontario.ca

ABSTRACT

The study on emerging organic pollutants (EOPs) in the environment has drawn more and more attention since last decade. Liquid chromatography with electrospray tandem mass spectrometry (LC/ESI-MS-MS) technique is demonstrated to be a powerful tool for the determination of these EOPs. However, due to the complex nature of environmental samples, matrix effects are a common issue in the analysis that is impossible to completely eliminate. In this study, using an Applied Biosystems/MDS Sciex 4000Qtrap mass spectrometer coupled with an Agilent 1100 liquid chromatograph with electrospray ionization interface, we explored matrix effects during LC/ESI-MS-MS analysis of EOPs in detail and demonstrated the best approach to compensate for these effects. Our experimental results showed matrix effects existed in the form of signal (electrospray ionization efficiency) suppression or enhancement, and the level of suppression or enhancement of certain EOPs was affected by sample type, volume, pH, sample extract storage time, and the ionization mode employed. Also demonstrated was the use of isotope-labeled analogues provided the best tool to offset matrix effect for native EOPs. With more and more isotope-labeled analogues available, the new labor and time-saving strategy is to use isotope-labeled surrogates to correct for matrix effects and obtain accurate, high-quality analytical data.

Matrix Effects in Liquid Chromatography Electrospray Tandem Mass Spectrometry Analysis of Emerging Organic Pollutants

NEMC 2008
Washington DC, USA

Chunyan Hao, Xiaoming Zhao and Paul Yang

Laboratory Services Branch
Ontario Ministry of the Environment
Toronto, Canada

Protecting our environment. Ontario

Laboratory Services Branch
Ontario Ministry of the Environment

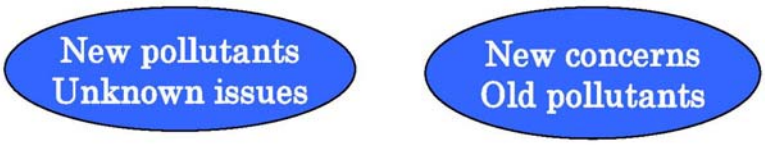
The mission of the Laboratory Services Branch is to be a respected scientific leader and provider of analytical science and services to support environmental programs and regulations for the purpose of protecting the people and environment of Ontario.

2

Protecting our environment. Ontario

Emerging Organic Pollutants (EOPs)

- Occur in the environment as a result of human activities
- Minimal knowledge of their background levels and effects in the environment and no Ontario guidelines/regulations are set
- Anticipated risks for environment and human health – alone or synergistically



❖ Efficient, reliable analytical methods are critically needed to address the occurrence, concentration and fate of these compounds in the environment

3

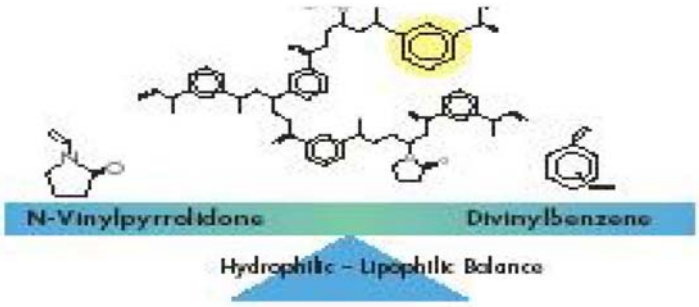
Typical EOPs Detected in the Environment

- **PPCPs (Pharmaceuticals and Personal Care Products):**
  - Defined by chemical classes
  - Human & veterinary drugs, diagnostic agents, biologics, nutraceuticals, fragrances, sun-screen agents, etc.
- **EDCs (Endocrine Disrupting Chemicals):**
  - Defined by biological effects or mechanisms
  - Substances that can act like natural hormones
- **Surfactants:**
  - Perfluorinated surfactants
  - Nonylphenol and its ethoxylate isomers

One multi-residual method detects all?

4

Solid Phase Extraction (SPE)
– HLB (Hydrophilic-Lipophilic Balance) Cartridges



- Exhibit both hydrophilic and lipophilic retention characteristics
- Can retain both polar and non-polar compounds
- Suitable for acidic, basic and neutral compounds

5

Instrument

HPLC: Agilent HP1100
chromatographic separation

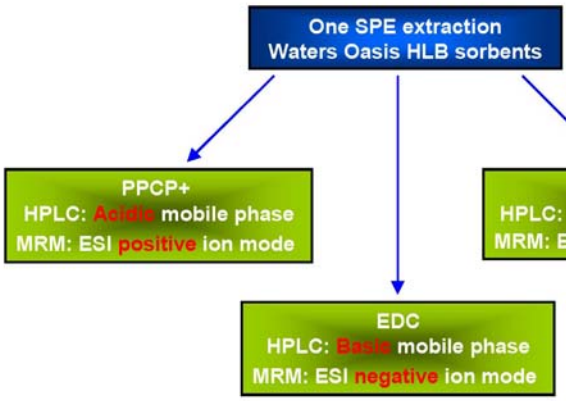
HPLC: high performance liquid chromatography

MS/MS: MDS Sciex 4000
QTRAP MS detection

MS: mass spectrometry

6

MOE Method E3454

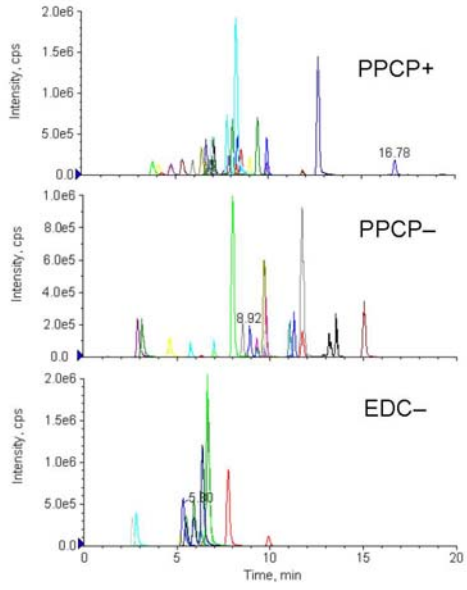


Hypersil Gold column (100 x 2.1 mm, 3 um), flow rate 0.2 mL/min, gradient elutions

MRM: multiple reaction monitoring; ESI: electrospray ionization

7

Protecting our environment. Ontario



LC/ESI-MS-MS Chromatogram

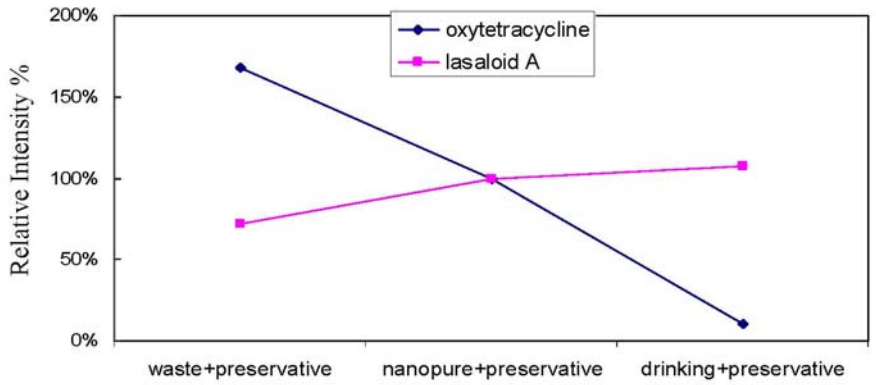
51 EOPs analyzed

- 38 PPCPs
- 10 EDCs
- 3 surfactants

8

Protecting our environment. Ontario

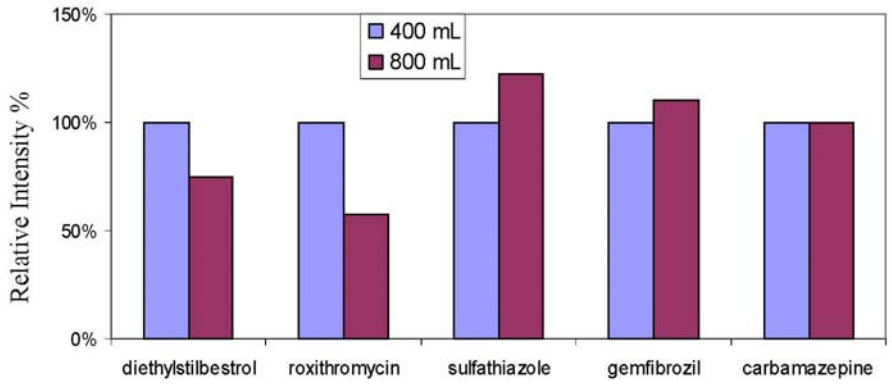
Phenomenon 1: Sample Type Effect



9

Protecting our environment. Ontario

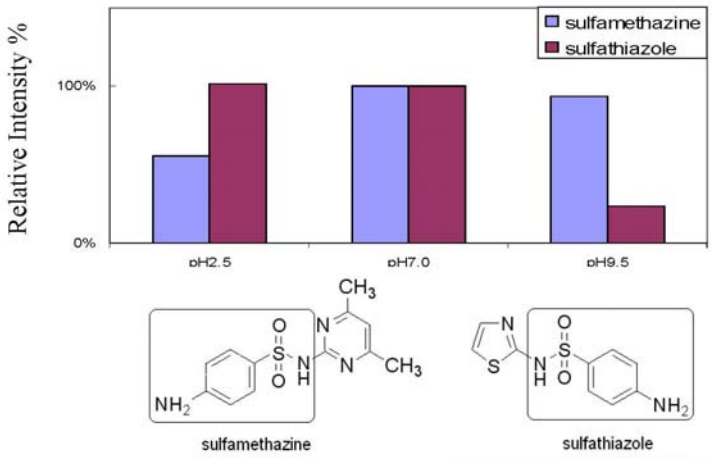
Phenomenon 2: Sample Volume Effect



10

Protecting our environment. Ontario

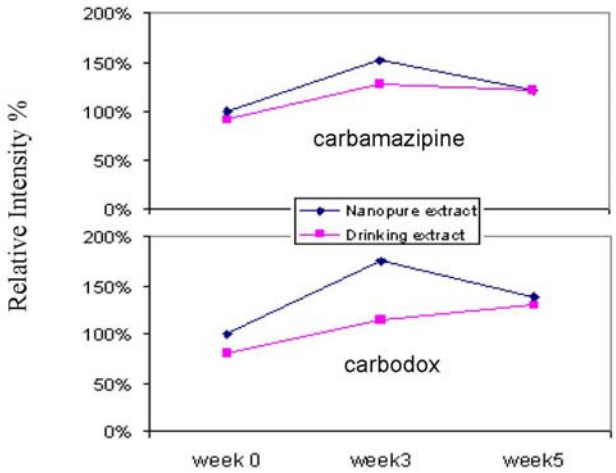
Phenomenon 3: Sample pH Effect



11

Protecting our environment. Ontario

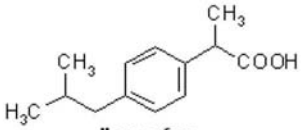
Phenomenon 4: Sample Extract Storage



12

Protecting our environment. Ontario

Phenomenon 5: Ionization Mode

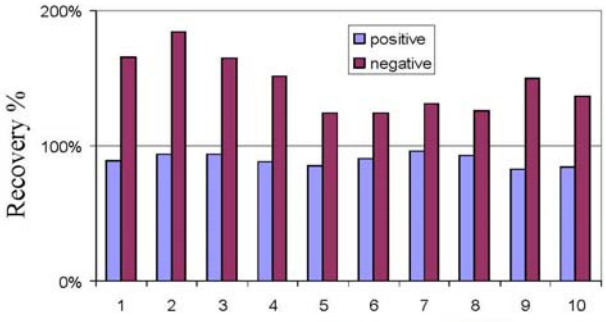


Ibuprofen
MW 206.29

205/161 $[M–H]^-$/ $[M–H–COO]^-$

207/161 $[M+H]^+$/ $[M+H–HCOOH]^+$

Ibuprofen data
Sept–Dec 2005

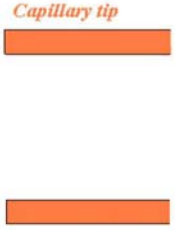


13

Protecting our environment. Ontario

Electrospray Ionization

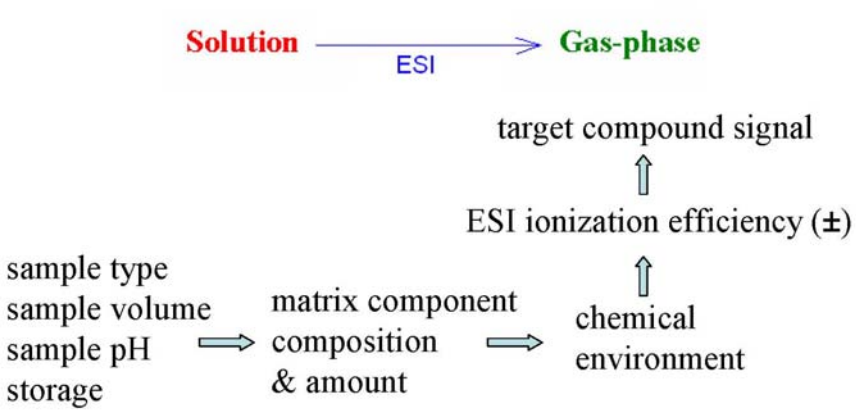
- Soft ionization: transfer ions from solution to gas phase;
- Charged droplets formed under the effect of a high potential; droplets shrink: solvent evaporation and uneven fission; generation of gas phase ions: charge residue or ion evaporation mode;
- Ionization efficiency affected by voltage & chemical environment, eg. pH, solvent, chemical composition, etc.



14

Protecting our environment. Ontario

Matrix Effects



15

Protecting our environment. Ontario

Eliminate Matrix Effects during ESI

- Sample clean-up
- Better separation
- Standard addition: standards under same effects

All need extra work, except

- Isotope dilution: isotope-labelled (^{15}N, ^{13}C & ^{2}H) standards to compensate for matrix effects

16

Protecting our environment. Ontario

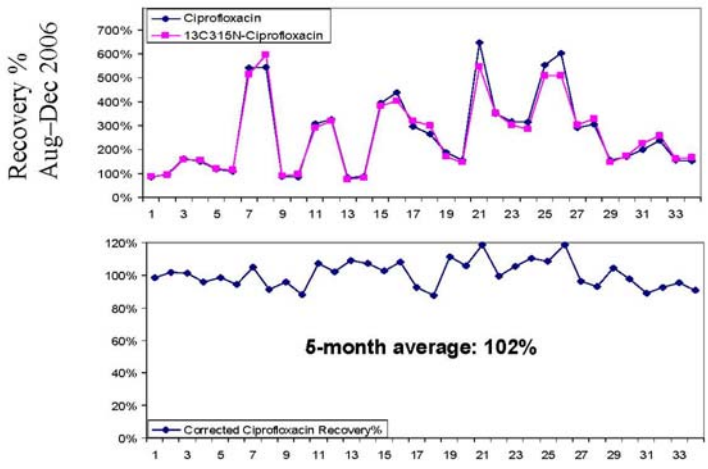
Isotope-labelled (^{15}N, ^{13}C & ^{2}H) Standards

- Same chemical nature as native compounds, but different mass
- Same retention time, different MRM channel

$^{2}H_{10}$-carbamazepine, $^{13}C_3{}^{15}N$-ciprofloxacin, $^{13}C_3$-ibuprofen, $^{2}H_3$-ibuprofen, $^{13}C^{2}H$-naproxen, $^{2}H_9$-progesterone, $^{13}C_6$-sulfamethazine, $^{13}C_6$-sulfamethoxazole, $^{2}H_4$-acetaminophen, $^{2}H_4$-clofibric acid, $^{2}H_4$-diclofenac, $^{2}H_6$-gemfibrozil, $^{2}H_4$-indomethacin, $^{2}H_{16}$-bisphenol A, $^{2}H_4$-equilin, $^{2}H_4$-estrone

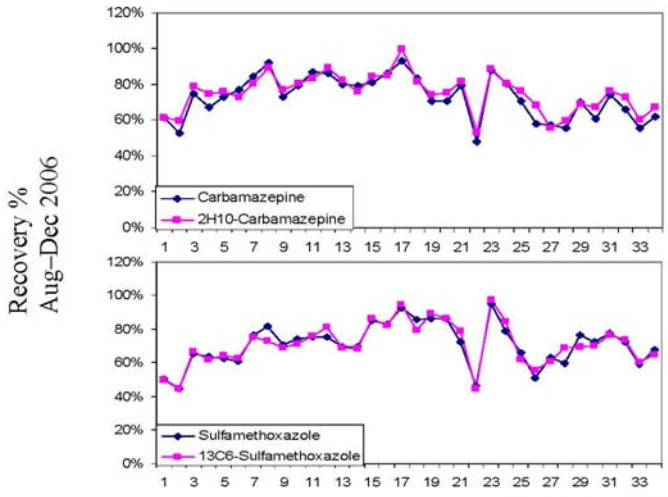
17

Isotope Dilution Correction



18

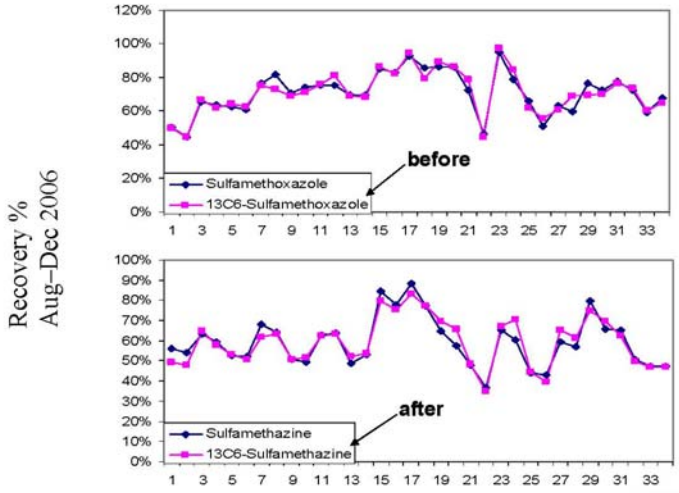
^{13}C or ^{2}H?



19

Protecting our environment. Ontario

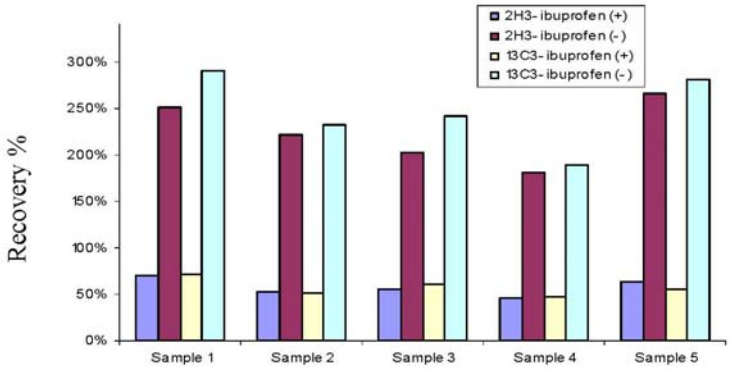
Before or After Extraction



20

Protecting our environment. Ontario

Before or After & Positive or Negative

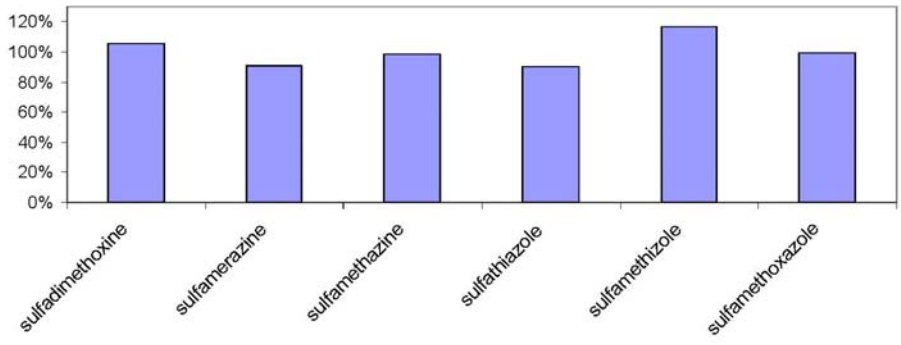


$^{2}H_{3}$ ibuprofen added before extraction
$^{13}C_{3}$ ibuprofen added after extraction

21

Same or Similar Structure

Recovery corrected by $^{13}C_{6}$-sulfamethazine



22

Conclusion

- LC/ESI-MS-MS is a powerful tool for monitoring emerging organic pollutants
- Isotope-labelled standards can effectively compensate for matrix effects during ESI
- ^{13}C & ^{2}H-labelled standards behave similarly, ^{2}H-labelled standards are economical choice
- In a multi-residue method, isotope-labelled standards can be used to provide more precise and accurate results for compounds with similar structure
- Added before or after extraction, isotope-labelled compounds always help to increase data quality

23

24

Contamination Reduction for Quantifying Trace Levels of Perfluorinated Compounds

Peter J. Lee
Waters Corporation
34 Maple Street
Milford, MA 01757
508-482-2827
peter_lee@waters.com

ABSTRACT

Perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used for over 50 years in various applications including surfactants, fire fighting foam, surface treatments, and as a polymerization aid in making polytetrafluoroethylene (PTFE) and other fluoropolymers. PFCs are extremely stable and not prone to environmental degradation. Long chain PFCs such as PFOA and PFOS bioaccumulate in animals causing tumors and disturbing reproductive development. Trace levels of PFCs have been measured in ground-water, wastewater treatment plants, lake water, the marine environment, and even in the Arctic. In recent toxicological studies, PFOA, PFOS and other PFCs have been detected at parts per billion levels in wildlife tissues and human serum. Consequently, worldwide interest in analyzing the potential impact of PFCs on human health and the environment has increased greatly.

One of the most difficult problems in quantifying trace levels of PFCs in samples is background PFC contamination. Since PFCs are present in many PTFE components used in the separation system, trace levels of PFCs can leach out. In addition, PFCs are also detected in common HPLC solvents and lab water. Because background PFC contaminants interfere with quantification, the PFC contaminants must be removed in order to accurately quantify trace levels of PFCs.

In this presentation, the sample preparation and instrument setup for UPLC-MS/MS determination of PFCs in groundwater, surface water and drinking water will be discussed. Moreover, the reduction of background PFC contamination to eliminate interference and allow accurate quantification of trace level of PFCs will be addressed. This approach can facilitate workflow for analyzing PFCs in environmental and biological samples and is easy to be implemented in contract analytical labs, government agencies, clinical and medical research institutions to satisfy legislation concerns and protect public health.

Contamination Reduction for Quantifying Trace Levels of Perfluorinated Compounds

NEMC 2008, Washington, DC

Peter J. Lee, Joe Romano, Jeremy Shia, Michael Young, Alice J. Di Gioia

Water Corporation

August 14, 2008

Outline

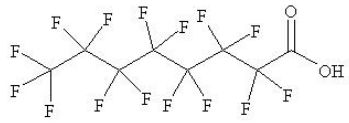
- Needs for perfluorinated compound (PFC) analysis
- Analytical detection method
  - Eliminating the interference of PFC contaminants
    - Improving quantification accuracy
- System solution
  - SPE for sample preparation
  - UPLC/TQD
    - Analysis of PFC in bottled water
      - Water cooler

Perfluorinated Compounds (PFCs)

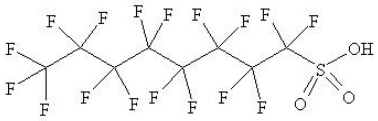
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Widespread applications
  - Surface treatments, surfactants, firefighting foam
  - Polymerization aid in making polytetrafluoroethylene (PTFE) and other fluoropolymers etc.
- Stable and persistent in the environment (POP)
  - Bio-accumulative
- Identified in environmental samples worldwide
  - Found in arctic polar bears
  - Many Americans have ~5 ppb of PFOA in their blood!
- Worldwide interest in PFC analysis



PFOA



PFOS

Sources of PFC Background Contaminants

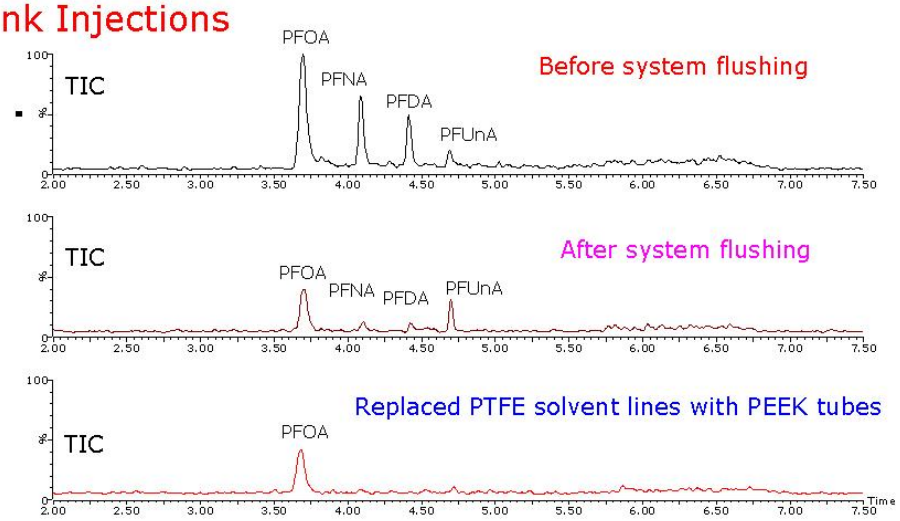
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Mobile Phases
  - Water
  - Organic solvent
    - Methanol
- PTFE components of LC instrument
  - Mostly pre-injector
    - Solvent lines
    - Degasser
    - Pump seals

PFC Contaminant Peaks in Gradient Separation

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Blank Injections

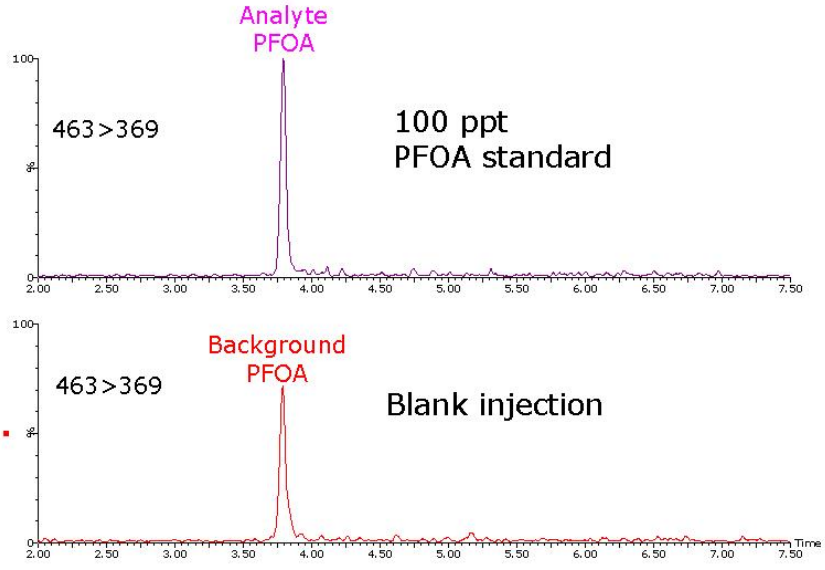


TIC chromatograms of 10 MRM channels of blank diluent
(with a 2.1x50mm UPLC BEH C18 column)

 5

PFC Contaminants: Interference with Quantification

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

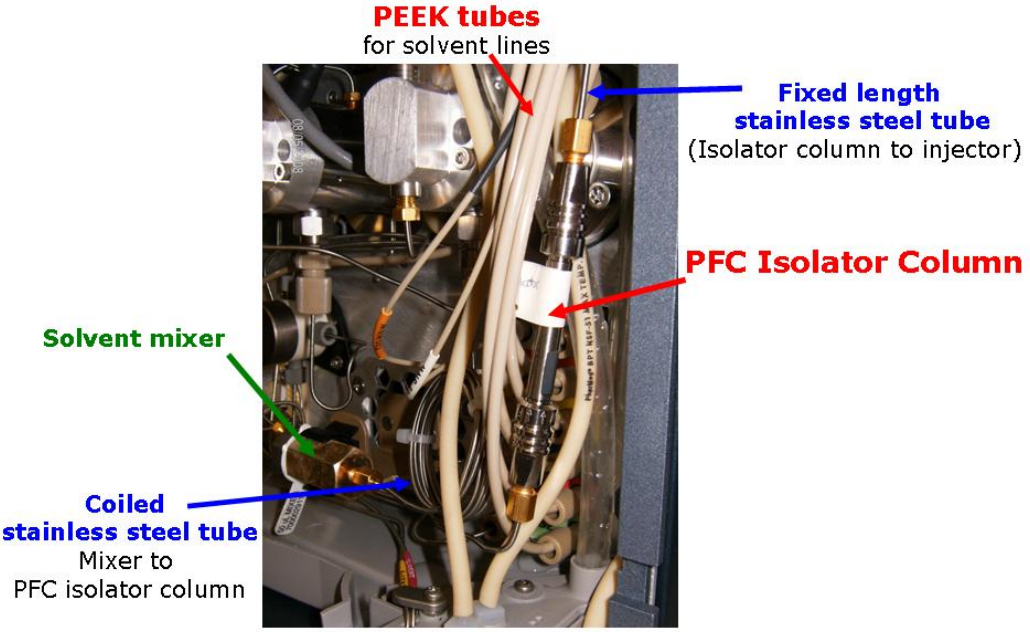


MRM (463>369) chromatograms

 6

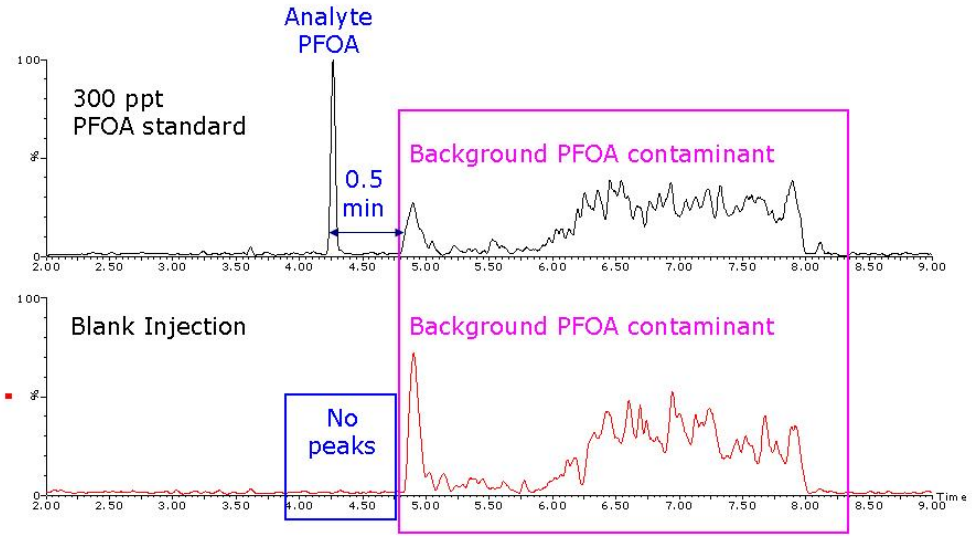
PFC Isolator kit: Eliminate Background PFC Interference

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



MRM Chromatograms of PFOA: Isolator Column In-line

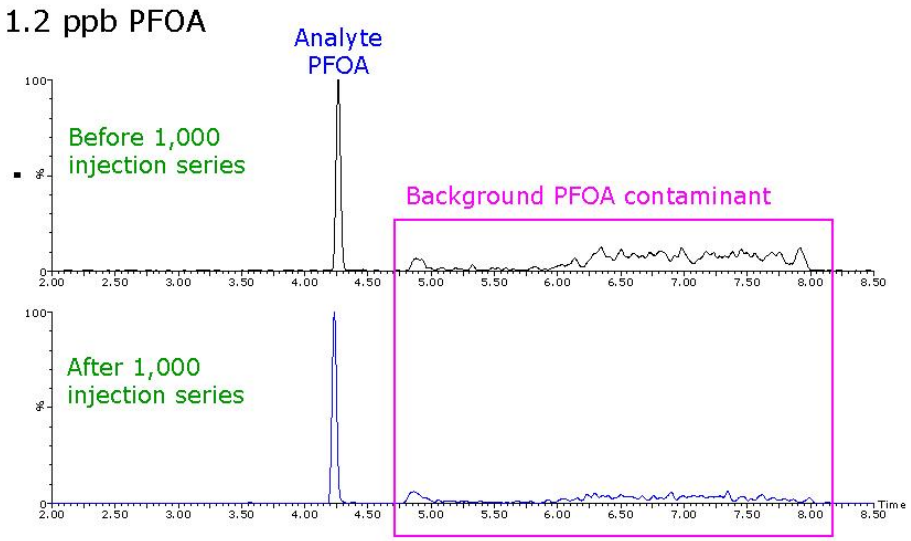
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



MRM chromatograms of 463>369 channel

Reproducibility and Stability

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

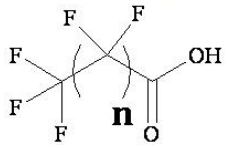


MRM chromatograms of 463>369 channel

 9

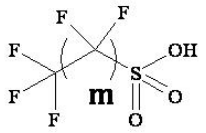
10 PFCs of Interest

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



Carboxylated PFCs

n = 4, PFHxA
n = 5, PFHpA
n = 6, PFOA
n = 7, PFNA
n = 8, PFDA
n = 9, PFUnA
n = 10, PFDoA



Sulfonated PFCs

m = 3, PFBuS
m = 5, PFHxS
m = 7, PFOS

- Mix 1mL of MeOH solution containing 100 ppb of 10 PFC standards with 3mL of H2O to make a 25ppb working solution.
- Dilute the 25ppb solution with MeOH/H2O (25:75) to make a series of diluted PFC standard solutions for UPLC/MS/MS analysis.

 10

Rapid PFC Analysis Using UPLC/TQD

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- UPLC-TQD tandem quadrupole mass spectrometer

  - UPLC
    - Speed, resolution, sensitivity
  - TQD
    - Fast scan rate
      - Compatible with UPLC high speed separation
    - IntelliStart technology
      - Automatic tuning and optimization of MS parameters
      - Easy to operate and maintain
  - Small footprint
    - Save laboratory bench space

 11

UPLC/TQD Conditions

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- System: ACQUITY UPLC®/TQD with Isolator column
- Analytical column: ACQUITY UPLC BEH C18 2.1x 50 mm
- Mobile Phase A: 2mM ammonium acetate in water/MeOH [95:5]
- Mobile Phase B: MeOH
- Column Temp: 50 °C
- Injection volume: 10 µL (full loop)
- Gradient table:

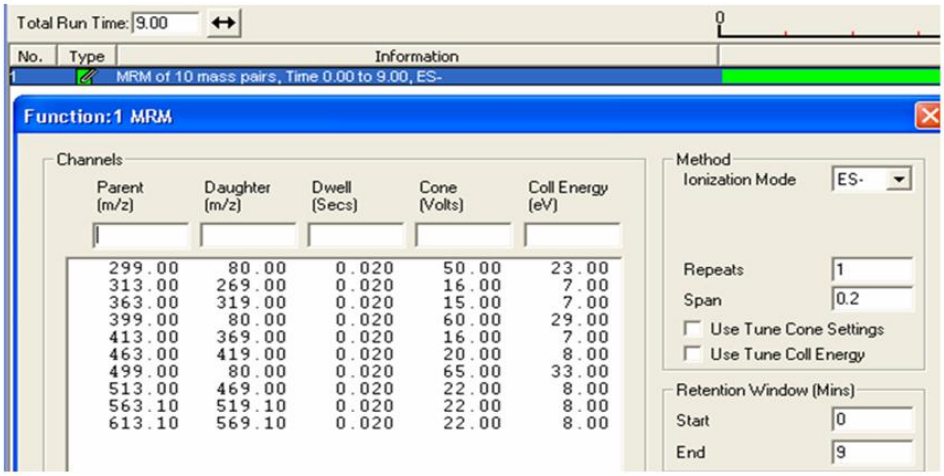
Time (min)	Flow (mL/min)	%B	Curve
0.0	**0.40**	**25**	
0.5	**0.40**	**25**	**6**
5.0	**0.40**	**85**	**6**
5.1	**0.40**	**100**	**6**
5.6	**0.40**	**100**	**6**
7.0	**0.55**	**100**	**1**
9.0	**0.40**	**25**	**1**

 12

UPLC/TQD Conditions

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

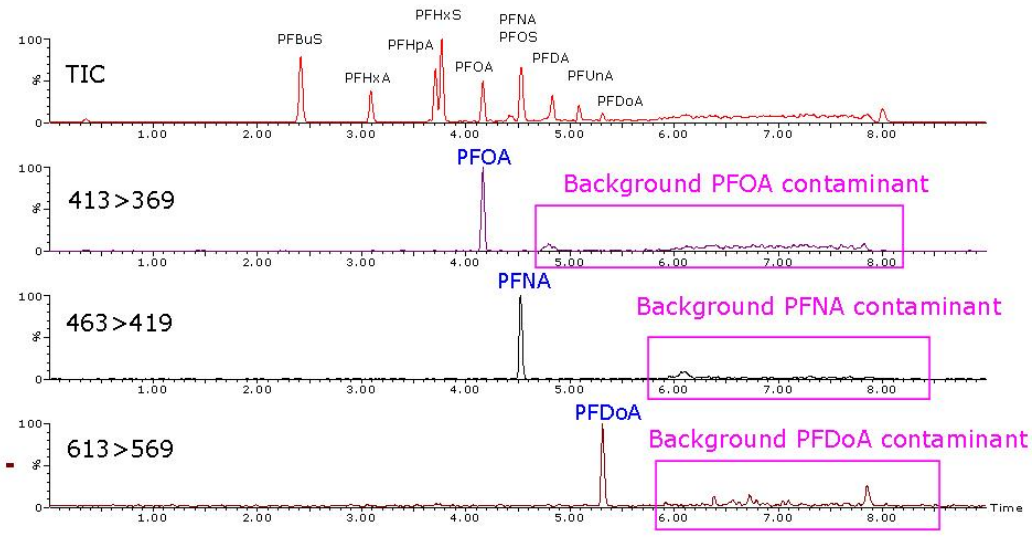
- MS method setting
  - Ionization Mode: ES-
  - Single MRM time window with 10 Channels



 13

Separation of 10 PFCs

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

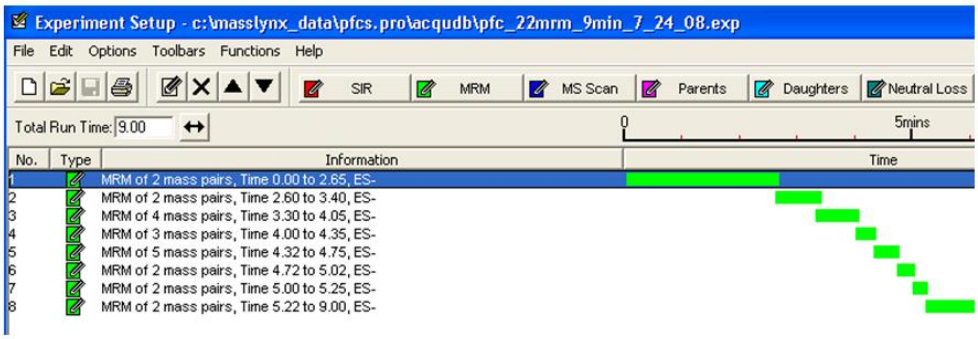


TIC and MRM chromatograms of a mixture of 10 PFC standards (1.2 ppb)

 14

Refined MS Method: with Multiple MRM Time Windows

Waters
THE SCIENCE OF WHAT'S POSSIBLE.



- 22 MRM transitions arranged into 8 time windows
  - Allow more time to scan target MRM transitions at the PFC peak
    - Give better signal to noise (S/N) ratio of detection
    - Ensure >15 data points per PFC peak
      - Provide better peak detection for quantification

 15

MRM Parameters for PFCs

Waters
THE SCIENCE OF WHAT'S POSSIBLE.

Function	PFC	RT (min)	MRM Transitions	Dwell time (s)	Cone Voltage (V)	Collision Energy (eV)
1	PFBuS	2.41	299 > 80 299 > 99	0.060	50	23 23
2	PFHxA	3.09	313 > 269 313 > 119	0.065	15	8 22
3	PFHpA	3.71	363 > 319 363 > 169	0.035	15	7 18
3	PFHxS	3.77	399 > 80 399 > 99	0.035	55	29 29
4	PFOA	4.17	413 > 369 413 > 169	0.040	16	8 19
4	MPFOA	4.17	417 > 372	0.040	16	8

- Optimized MRM transition, CV and CE
  - Obtained automatically using IntelliStart technology

 16

MRM Parameters for PFCs

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Function	PFC	RT (min)	MRM Transitions	Dwell time (s)	Cone Voltage (V)	Collision Energy (eV)
5	PFNA	4.53	463 > 419 463 > 169	0.030	20	10 20
5	PFOS	4.55	499 > 80 499 > 99	0.030	60	35 35
5	MPFOS	4.55	503 > 80	0.030	60	35
6	PFDA	4.84	513 > 469 513 > 219	0.060	20	10 18
7	PFUnA	5.11	563 > 519 563 > 319	0.060	18	10 18
8	PFDoA	5.32	613 > 569 613 > 169	0.060	18	10 24

- Primary MRM transition for quantification
- Secondary one for ion ratio confirmation (eliminate false positive)

 17

SPE Method for PFC Analysis

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Oasis® HLB
PFC Method

Condition
5 mL methanol/10 mL water

Load
500 mL water sample

Purge
with N_2 for 20 min
To remove water

Elute
2 mL methanol

Evaporate
to 500 µL

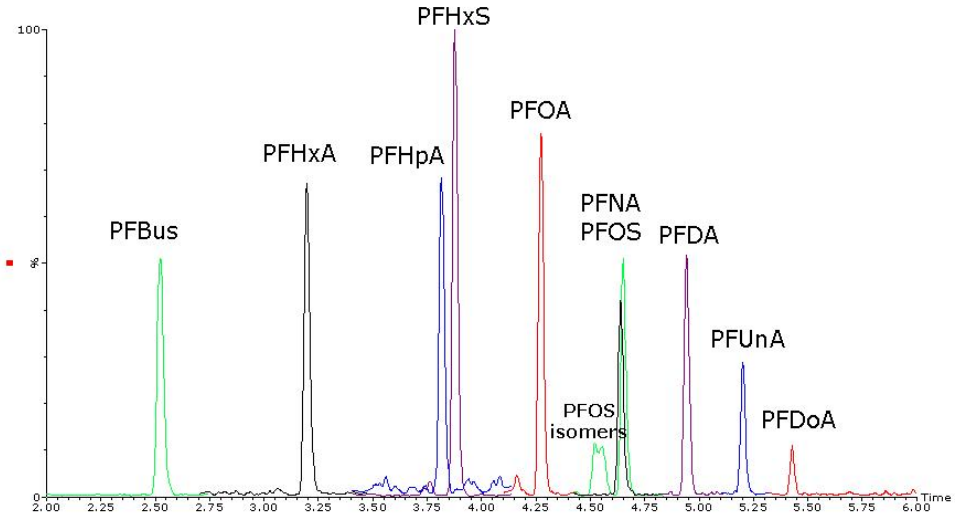
Dilute
with D.I. water (1:3 ratio)
for UPLC analysis

Waters OASIS® SAMPLE EXTRACTION PRODUCTS

 18

PFCs Spiked Bottled Water Sample (1ppt)

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

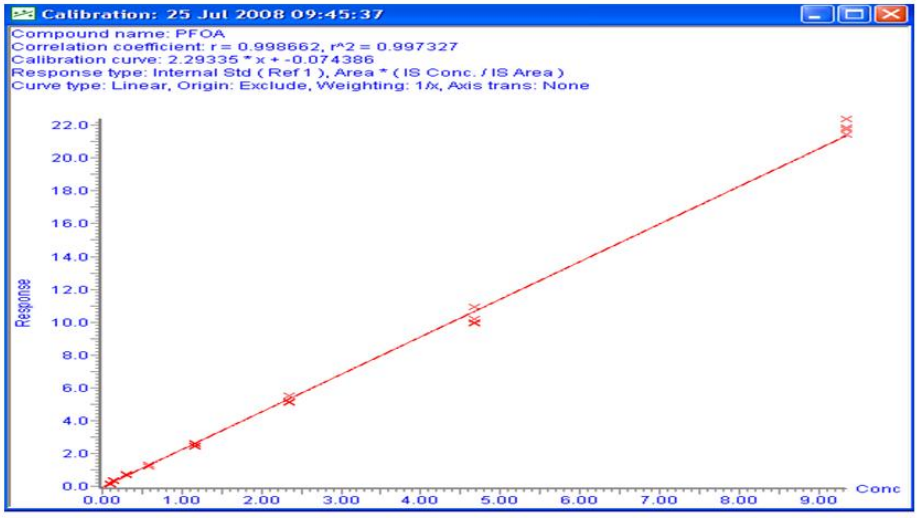


Overlay chromatogram of the 10 primary MRM transitions
SPE enrichment factor (250)

 19

Typical Calibration Curve

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



PFOA calibration curve (0.09 ppb to 9.4 ppb); correlation coefficient, $r^2 > 0.997$

 20

SPE Method Recovery

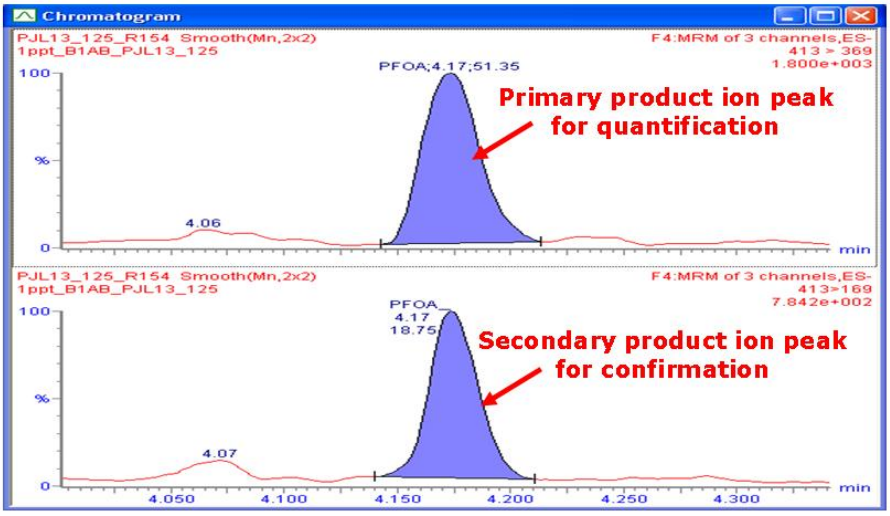
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Target 10 PFCs	1 ppt spiked water (n=6)	
	Recovery (%)	RSD (%)
PFBuS	105	6
PFHxA	112	11
PFHpA	124	15
PFHxS	103	5
PFOA	122	17
PFNA	107	9
PFOS	104	6
PFDA	109	8
PFUnA	100	9
PFDoA	105	12

 21

PFOA Detected in Bottled Water

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



Primary and secondary transition MRM chromatograms of PFOA
(SPE Enriched Bottled Water Sample)

 22

Method Precision and Accuracy

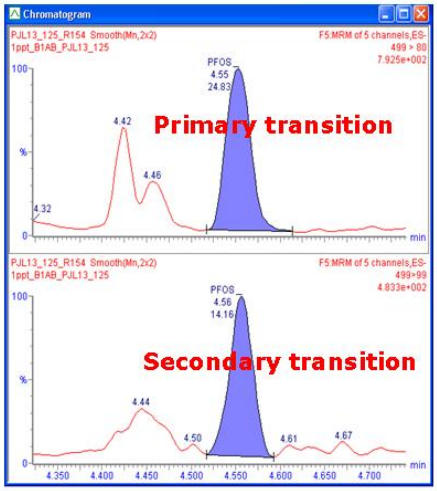
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

PFOA detected in the bottled water				
Injection	sample 1	Sample 2	sample 3	sample 4
1	0.43	0.50	0.52	0.50
2	0.51	0.50	0.54	0.50
3	0.44	0.52	0.53	0.52
4	0.46	0.50	0.61	0.50
5	0.47	0.53	0.52	0.53
6	0.52	0.54	0.52	0.54
Average (ppt)	**0.47**	**0.52**	**0.54**	**0.52**
RSD (%)	**7.6**	**3.8**	**6.6**	**3.8**
Mean = **0.51 ppt**				

Instrument LOQ <25ppt; SPE enrichment factor =250; Method LOQ <0.1ppt

PFOS Detected in Bottled Water

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™



MRM chromatograms of PFOS
(SPE Enriched Bottled Water Sample)

PFOS in the bottled water				
Injection	sample 1	Sample 2	sample 3	sample 4
1	0.42	0.39	0.44	0.29
2	0.37	0.44	0.43	0.35
3	0.48	0.52	0.39	0.35
4	0.48	0.46	0.39	0.38
5	0.44	0.52	0.42	0.35
6	0.36	0.43	0.36	0.36
Average (ppt)	**0.42**	**0.46**	**0.40**	**0.35**
RSD (%)	**12.7**	**11.1**	**7.7**	**8.1**
Mean = **0.41 ppt**				

Instrument LOQ <25ppt; SPE enrichment factor =250; Method LOQ <0.1ppt

Summary

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Issues of PFC analysis
- System solution for analyzing trace levels of PFCs
  - PFC isolator kit for accurate quantification
    - eliminating interference of background PFC contamination
  - SPE method
    - enriching and isolating PFCs from sample matrices
      - High recovery
  - UPLC-TQD
    - rapid, sensitive, and selective method
      - quantifying 10 PFCs in 9 minutes
- Detection of 0.5 ppt of PFOA and 0.4 ppt of PFOS
  - Water cooler drinking water samples
    - great precision and accuracy

 25

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Thank You

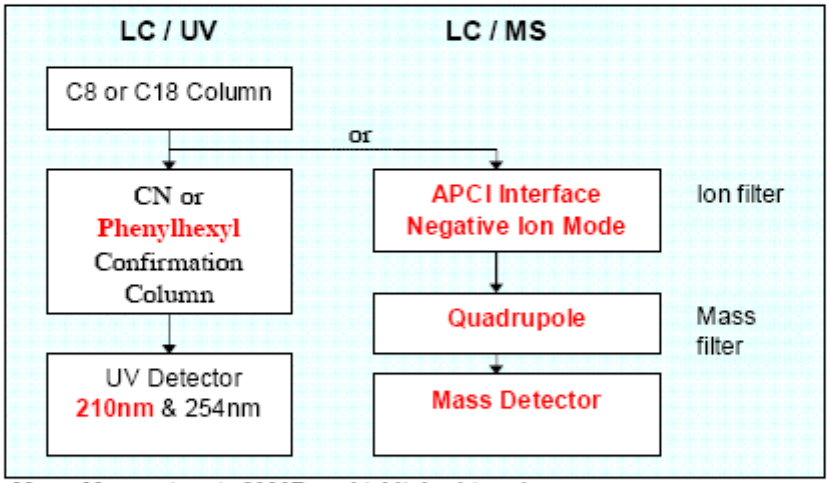
LC/MS and the New Energetics Method EPA 8330B

Larry Penfold; TestAmerica, Inc., 4955 Yarrow St., Arvada, CO 80439; 303-736-0119; larry.penfold@testamericainc.com
Alan Hewitt (USACE/CRREL); TestAmerica
8330B Workgroup members: Richard Burrows, Brad Chirgwin, Susan Decker, Karen Kuoppala, Patrick Rainey, and Pammela Schemmer

INTRODUCTION

Method 8330B describes the analysis of trace concentrations of energetic residues by high performance liquid chromatography (HPLC). It was developed at the U.S. Army ERDC CRREL laboratory. Although the method is written primarily for the use of an ultraviolet (UV) detector, it also includes an option for the use of a mass spectrometric (MS) detection. In fact, 8330B is the first EPA method to mention the use of HPLC/MS specifically for the analysis of nitroaromatic, nitramine, and nitro ester compounds.

Figure 1: Instrument Options in 8330B



Note: New options in 8330B are highlighted in red.

In the study presented here, soil samples were collected and analyzed at the CRREL laboratory using LC/UV. Ground soils and extracts were sent to the TestAmerica Denver laboratory for analysis by LC/MS. CRREL's results were not available to TestAmerica at the time of analysis.

Sensitivity data are also presented. Of particular interest for LC/MS analysis, the U.S. Department of Defense (DOD) MERIT emerging contaminant list includes 2,4-dinitrotoluene and 2,6-dinitrotoluene (DNTs). Risk-based action levels for the DNTs in groundwater and tap water have been lowered in some states, and the new action levels may be adopted in other jurisdictions in the near future. These new DNT action levels are at or below the detection limits for the conventional LC/UV analysis by EPA Method 8330B.

Finally, results from a recent series of LC/UV and LC/MS analyses of an environmental water sample are presented as an example of a typical situation where differences in sensitivity and selectivity were important.

LC/MS has been widely used in forensic and military applications for analysis of energetic residues because of its improved sensitivity and high degree of specificity. Although TestAmerica has been using LC/MS for environmental studies for more than ten years, there is scarcity of published data demonstrating the performance of LC/MS for the analysis of environmental samples. The purpose of this presentation is to compare the performance characteristics of the two detector systems. The relative performance characteristics suggest the optimal use of the two detector systems in different environmental investigative or remedial situations.

CRREL/TESTAMERICA LC/UV VERSUS LC/MS COMPARABILITY STUDY

Contaminated soils from military training ranges were collected by ERDC-CRREL personnel. These included five samples from a mortar firing point and five samples from an impact range where the 120 mm mortar rounds filled with Comp B were subject to low order detonations. Mortar propellant is primarily nitroglycerin. Composition B consists of 60% military grade RDX (also contains approximately 10% HMX) and 39% military grade TNT (also contains ~1% other nitrotoluenes). Each sample was comprised of 100 increments. A 40 x 40 meter grid was used to cover most of the open area at the firing point, and a 20 x 20 meter grid was used to collect soil from the impact range. The bulk sample processing was done at the ERDC-CRREL laboratory:

- Entire sample air dried,
- Sieved to < 2mm,
- Puck mill, five 60 second grinds with 2 minute cooling between grinds
- 10 gram subsamples taken using 30 random increments

The LC/UV analysis was performed at ERDC-CRREL laboratory. The LC/MS analysis was performed at the TestAmerica Denver laboratory, using one set of acetonitrile extracts prepared by ERDC-CRREL and a replicate set extracts prepared by TestAmerica. The same solvent extraction process was used at both labs:

- 10 g sample + 20 mL of acetonitrile
- Low temperature sonication for 18 hours
- Filter extract

A straight alkyl chain reverse phase separation column with an isocratic water/methanol mobile phase was used for the LC separation in all analyses at both laboratories. The LC/MS analysis was conducted using an atmospheric pressure chemical ionization (APCI) interface operated in the negative ion mode. Three isotopically labeled internal standards

RDX 13C-3
1,3-DNB-d4
2,4-DNT-d3

and one isotopically labeled surrogate (nitrobenzene-d5) were used for the LC/MS analysis. The LC/UV instrumental analysis was conducted as described in Method 8330B. Results are shown in Table 1.

Linear regression plots of LC/UV results compared to LC/MS results are shown in the adjoining Figure 2. If results were perfectly correlated with no bias, the correlation coefficient would be r = 1.00 and the slope = 1.0.

The correlation was close to 1.00 for all four of the major constituents in the firing range samples indicating consistent results between LC/UV and LC/MS.

The slope was close to 1.0 for all compounds, except HMX where the 0.755 slope indicates a 25% low bias for the LC/MS results. This was investigated and attributed to ionization suppression. C-13 labeled HMX was purchased, and incorporated as an internal standard for all subsequent analyses. The bias was proven to be eliminated in a series of later analyses.

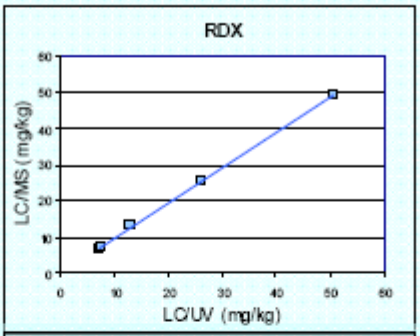
The precision results for the three measurements for each sample shown in Figure 1 were as follows:
RDX mean RSD = 3.2%
TNT mean RSD = 4.9%
HMX mean RSD = 11.8%
NG mean RSD = 10.1%

With the soil samples ground to a fine powder, the results from the two detector systems at the two laboratories was well within the instrument calibration error, which has a control limit of 15% RSD in Method 8330B.

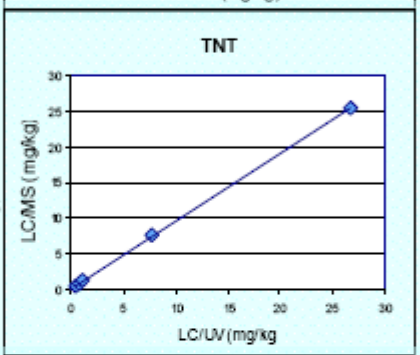
This demonstrated that at the concentrations studied the two detector systems produced comparable results for the major contaminants found at DoD firing ranges.

Figure 2 - Regression Plots
LC/UV vs. LC/MS

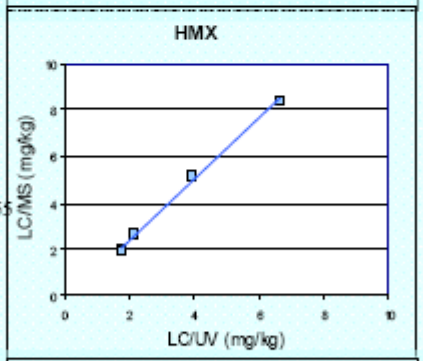
r = 0.9998
slope = 1.02



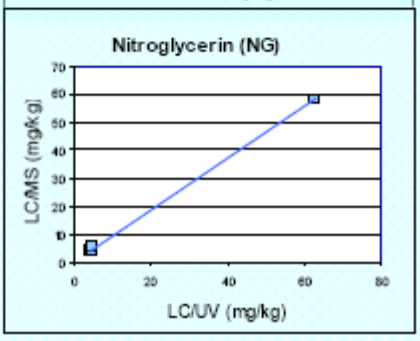
r = 1.000
slope = 1.05



r = 0.9980
slope = 0.755



r = 0.9996
slope =



LC/UV VERSUS LC/MS SENSITIVITY

The samples in the study had to be tested using a range of extract dilutions due to the relatively high concentrations of the major contaminants. The results shown in Table 1 do not provide a direct comparison of detection limits because the two labs used different dilution levels. Still, the greater sensitivity of the LC/MS method for soil samples was indicated by the detection of the amino-dinitrotoluenes that were not detected by LC/UV.

LC/MS detection limits are 2-3 times lower than the LC/UV detection limits. If LC/MS/MS is used, then detection limits are approximately 5 times lower than LC/UV. There has been little demand for lower detection limits for the 8330 compounds, and as a result reporting limits provided by laboratories using LC/MS have generally been higher than the instrument is capable of producing. However, new risk levels for the DNTs may drive the need for lower reporting limits:

USEPA IRIS $1x10^{-6}$ risk level	= 0.05 ug/L each isomer
2008 Wisconsin GW PAL	= 0.05 ug/L each isomer
Region IX Tap Water PRG	= 0.099 ug/L as $\sum$ of isomers
1 risk WI study	= 0.03 ug/L as $\sum$ of isomers

The LC/UV detection limit for the DNTs is approximately 0.04 ug/L. By comparison, the lowest LC/MS calibration point for is 0.04 ug/L, and the detection limits are 0.02 ug/L for LC/MS and 0.01 ug/L for LC/MS/MS. If action levels are set based on these risk values, then quantitatively reliable results will be needed at these concentrations, and LC/MS will be a necessity.

LC/UV VERSUS LC/MS SELECTIVITY

TestAmerica's experience is that water samples are frequently more difficult to analyze than soil samples. Elevated baselines and interfering peaks due to extracted unidentified compounds are more common with LC/UV. It is readily apparent to analysts that the MS detection system shown in Figure 1 is more selective. A recent example follows. Earlier this year we were asked to test storm water runoff from an army ammunition plant in the Midwest. This was a permit requirement for the cleanup work being performed there. The LC/UV analysis produced the chromatogram shown in Figure 4.

Figure 4 – Runoff Sample by LC/UV

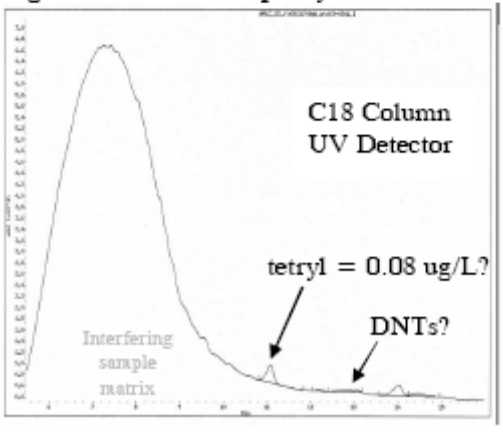
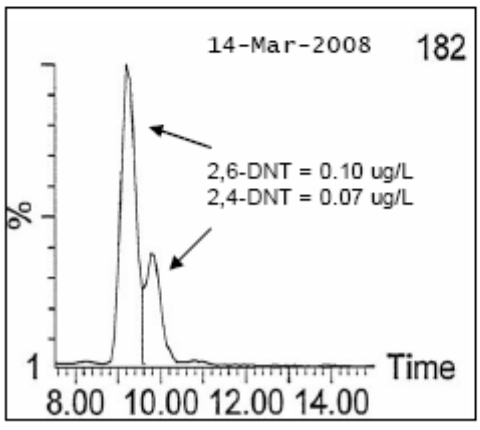


Figure 5 – Runoff Sample by LC/MS



A peak was found on the C18 primary column at the retention time for tetryl, 11.1 minutes. A much smaller peak was also found on the phenylhexyl confirmation column at the tetryl retention time. Although tetryl was identified by the data system on both columns, it was unlikely that tetryl was present in the sample because the pH of the water was 7.7. Tetryl would be expected to hydrolyze under these conditions. The sample was analyzed by LC/MS, and tetryl was not detected with a detection limit of 0.02 ug/L. The tetryl by LC/UV was shown to be a false positive result. TestAmerica and other labs have periodically encountered false positive tetryl results by LC/UV. When the U.S. Army HTRW QA lab program was operating, ground water samples were sometimes sent to TestAmerica to disprove the presence of tetryl. What might cause the misidentification? Samples with matrix interferences can cause retention time (RT) shifts, and 3,5-dinitroaniline has a similar RT and so might be misidentified as tetryl. Another possibility suggested by Dr. Thomas Jenkins (formerly with ERDC CRREL), is 2,4,6-trinitrobenzaldehyde. Both compounds are degradates of TNT.

A second concern with the runoff sample was the lack of DNT detections, which were expected given the site history. The LC/UV data system did not identify peaks for either 2,4-DNT or 2,6-DNT. The sample was analyzed by LC/MS, and both DNTs were readily detected, as shown in Figure 5, at concentrations approximately two times higher than the reagent water LC/UV detection limits (0.04 ug/L). Interferents in the sample had elevated the baseline in the UV chromatogram such that false negative results were reported. As with tetryl, this is not an isolated example. Complex samples can contain many substances that readily extract in acetonitrile and that produce a UV response. These substances have the potential of either false positive or false negative results at low concentrations, and in this case both types of errors were observed in one sample, and the discrepant results were resolved by LC/MS.

CONCLUSION

Dual column LC/UV analysis for explosive residues has proven to be a very reliable method over the last 20 years. This study served to demonstrate that with an appropriately prepared sample LC/MS results are highly comparable to results from LC/UV. The two methods performed at two laboratories produced results well within the precision errors of the instruments. For samples, such as the firing range soils in the CRREL/TestAmerica study, the concentrations of the primary contaminants are relatively high and the sample matrix did not present analytical problems. LC/UV is a simpler technology, it is more readily available at a large number of laboratories, and it is less expensive. For all of these reasons, LC/UV should be the method of choice in such situations.

However, LC/MS has been demonstrated to be the better analytical tool when lower detection limits are needed or when testing for low concentrations of explosive compounds in difficult sample matrices, which can include surface waters, ground waters, vegetation, and biota. It is a more sensitive and more selective technique. LC/MS will be needed to meet the demands of lowering risk levels. LC/MS is actively used for the USACE/MMRP program and has been included in the AFCEE QAPP since February 2005. It is the method of choice for definitive forensics analysis. Despite well established applications in a wide range of media, there still is not an adequate EPA SW-846 method for either LC/MS or LC/MS/MS analysis of explosive residues. Method 8330B includes LC/MS, but no instrument conditions are given, the optimal ions for analysis are not listed, and interferences unique to LC/MS are not discussed. We suggest that a new SW-846 method is needed for explosive residues by LC/MS.

Table 1: LC/UV LC/MS Comparison, Firing Range Samples

(all results in mg/kg)

Sample		Soil Sample Separate Preparation at Each Lab CRREL LC-UV	TAL LC/MS	Extract Prepared by CRREL TAL LC/MS
Impact Range		(n=3)		
LO#3 MI#5	HMX	2.16±0.06	2.65	2.68
Soil	RDX	13.0±0.36	13.4	13.0
	TNT	1.14±0.04	1.1	1.11
	2AmDNT	<0.04	<0.045	<0.045
	4AmDNT	<0.04	0.061	0.086
Impact Range		(n=3)		
LO#3 MI#10	HMX	6.67±0.09	7.7	9.07
Soil	RDX	50.6±0.20	49.4	49.2
	TNT	25.5±0.12	27.7	25.8
	2AmDNT	0.079±0.003	0.062j	<0.045
	4AmDNT	0.115±0.008	0.198	0.246
Impact Range		(n=1)		
LO#3 MI#2	HMX	1.78	1.79	2.00
Soil	RDX	7.28	6.36	7.13
	TNT	0.55	0.454	0.454
	2AmDNT	<0.04	<0.02	<0.045
	4AmDNT	<0.04	0.043j	0.057j
Impact Range		(n=1)		
LO#3 MI#6	HMX	1.76	1.81	2.09
Soil	RDX	7.68	7.27	7.56
	TNT	0.8	0.871	0.800
	2AmDNT	<0.04	0.021j	<0.045
	4AmDNT	<0.04	0.040j	0.056j
Impact Range		(n=1)		
LO#3 MI#3	HMX	3.92	4.89	5.37
Soil	RDX	26.2	24.9	26.0
	TNT	7.52	7.65	7.80
	2AmDNT	0.098	0.091j	0.150
	4AmDNT	0.118	0.176	0.292
Firing Point		(n=3)		
LO#3 MI#5 Soil	NG	62.8±2.16	57.3	60.00
Firing Point		(n=3)		
LO#3 MI#10 Soil	NG	4.99±0.16	4.42	3.10
Firing Point		(n=1)		
LO#3 MI#6 Soil	NG	3.98	3.98	4.60
Firing Point		(n=1)		
LO#3 MI#V1C Vegetation	NG	5.08	5.04	5.68
Firing Point		(n=1)		
LO#3 MI#2 Soil	NG	4.94	4.81	5.51

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

LC/MS and The New Energetics Method EPA 8330B

Larry Penfold
Federal Program QA Manager

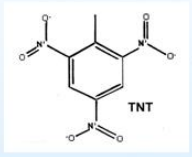
July 2008

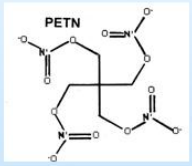
TestAmerica

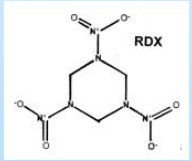
THE LEADER IN ENVIRONMENTAL TESTING

Classes of Compounds

- Nitroaromatics - TNT, DNT, TNB, DNB, NB, & Tetryl
- Nitro esters - PETN, nitroglycerin
- Cyclic nitramines - RDX & HMX







GC or LC methods can be used

LC is more reliable

2

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

8330 - Primary Method for Explosive Residue Analysis

- EPA Method 8330 - high pressure liquid chromatography with a ultraviolet detector (HPLC/UV)
- Developed by USACE CRREL laboratory in late 1980's
- Updated to 8330B in November 2006

3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

8330B Changes

- 5 changes related to multi-incremental sampling (MIS)
- 8 changes related to extraction and analysis

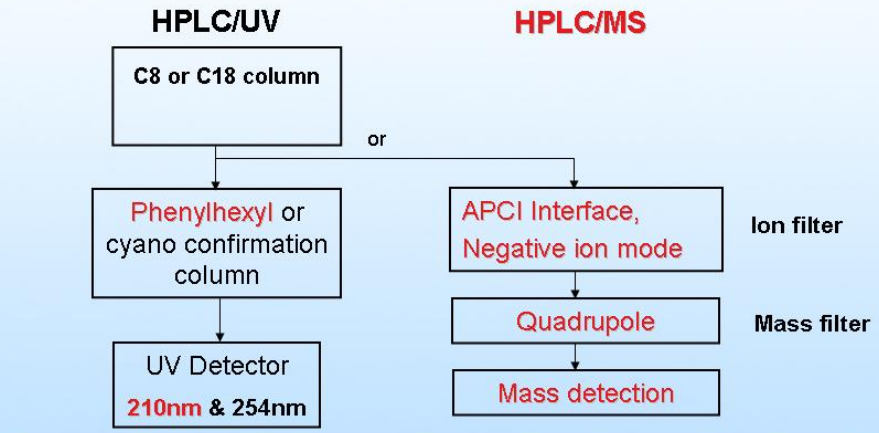
One more change not often discussed

8330B is first EPA method to mention use of a mass spectrometric detector for energetic residues

4

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

New Instrumental Analysis Options



Study conducted to compare performance of 2 systems

APCI = Atmospheric Pressure Chemical Ionization

5

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Precision and Bias

6

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Two Sets of Firing Range Samples Collected by CRREL

1) 5 soils from firing point for 120mm mortar

40 x 40 meter grid
100 increments per sample
5 samples

Mortar propellant is primarily nitroglycerin

Defense NewsLink public website photo

7

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Collection (continued)

2) 4 soil + 1 vegetation sample from impact range
mortar round filled with Comp B was subject to low order detonation, 20 x 20 m grid,
100 increments per sample

Particles and chunks of unexploded Comp B scattered throughout area

Photo courtesy of Alan Hewitt, ERDC-CRREL

Composition B:
60% Military grade RDX (also contains about 10% HMX)
39% Military grade 246TNT (also ~1% other TNT isomers & DNTs)

8

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Physical Processing

Air Dry → Sieve < 2mm → Puck Mill Grinding → MIS Subsampling

Photos courtesy of Alan Hewitt, ERDC-CRREL

9

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Same Extraction at Both Labs

CRREL provided TestAmerica

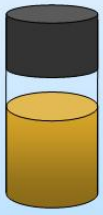
5 acetonitrile extracts,

4 ground soils, extracted by TAL

1 ground vegetation, " " "

Extraction Procedure:

1. 10 g sample (soil or vegetation) + 20 mL of acetonitrile
2. Low temperature sonication for 18 hours
3. Filter extract
4. TestAmerica only: dilute 1:1 with acidified CaCl2 solution



10

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Instrumental Analysis

- LC/UV analysis performed at CRREL per 8330B
- LC/MS analysis performed at TestAmerica

RDX 13C-3
1,3-DNB-d4
2,4-DNT-d3 } Internal Standards

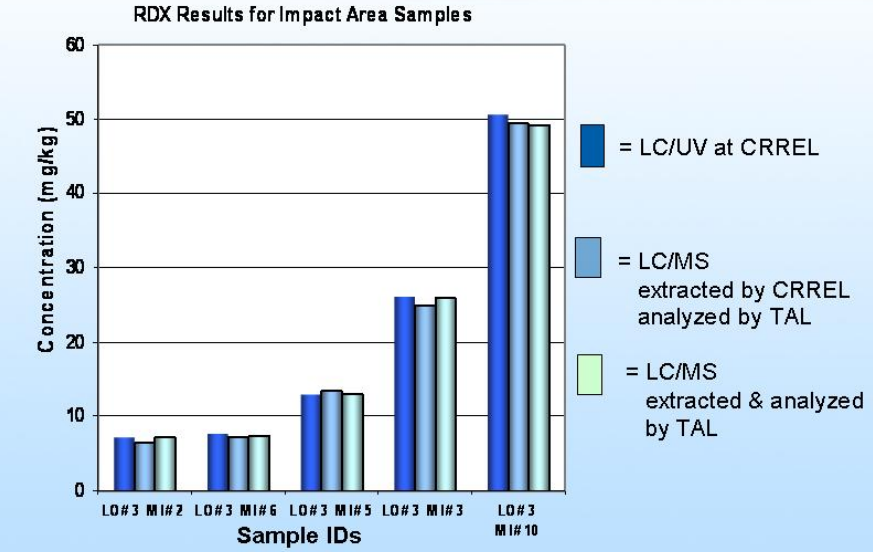
Nitrobenzene-d5 } Surrogate Standard

CRREL's results unknown to TestAmerica at time of analysis

11

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

RDX Results



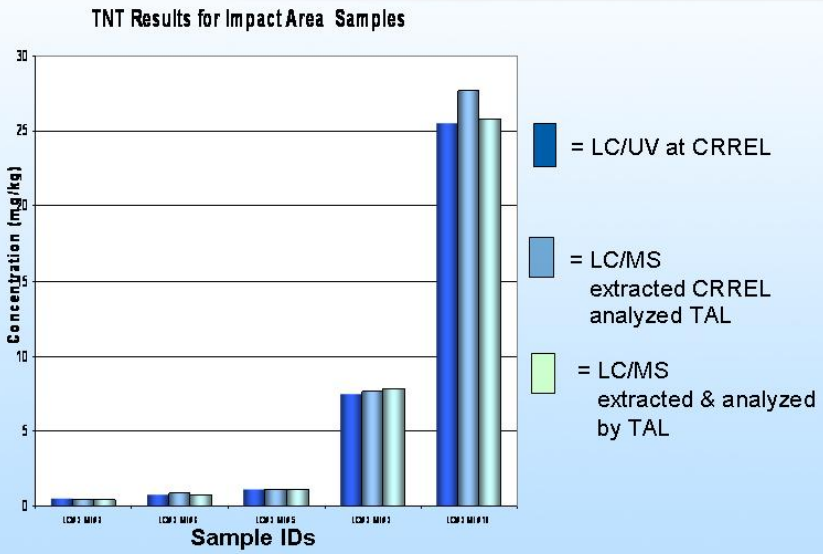
RSD = 7.1% 2.8% 1.8% 2.7% 1.5%

Mean RSD = 3.2%

12

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TNT Results



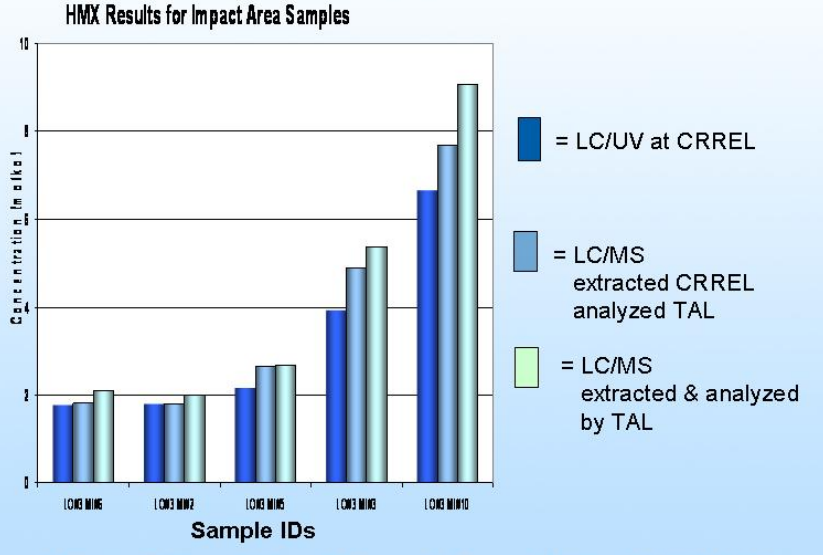
RSD = 11.4% 5.0% 1.9% 1.8% 4.5%

Mean RSD = 4.9%

13

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

HMX Results



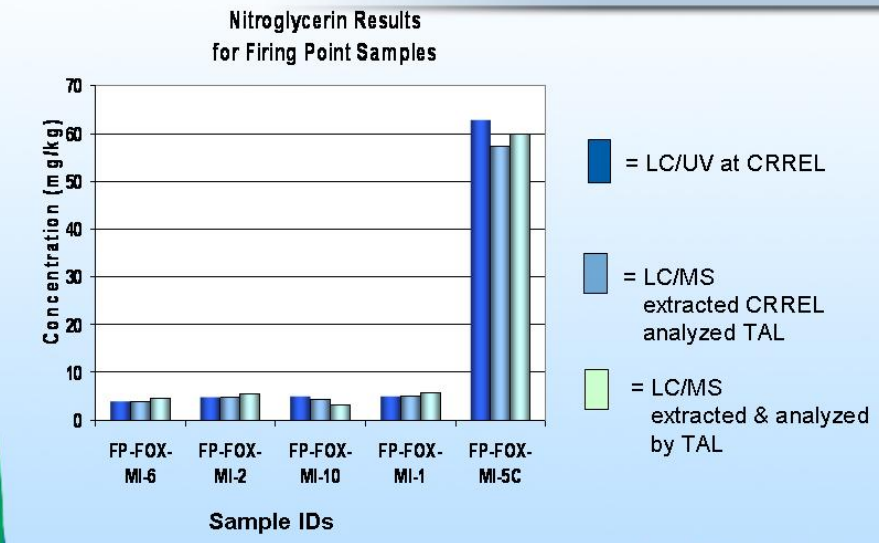
RSD = 8.5% 7.3% 23.% 6.8% 4.6%

Mean RSD = 11.8%

14

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nitroglycerin Results



RSD =	8.5%	7.3%	23.%	6.8%	4.6%

Mean RSD = 10.1%

15

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

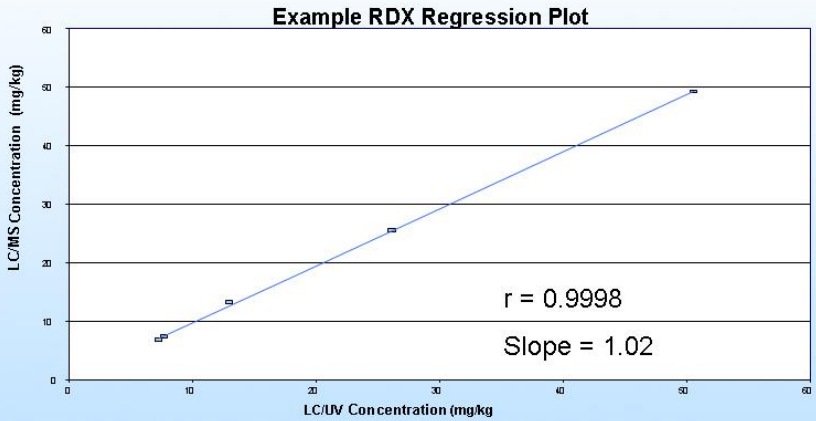
With Proper Sample Preparation

Overall precision between
labs and instruments
equivalent to calibration control limits
for a single instrument

16

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Another Way to Compare Results, LC/UV versus LC/MS



Ideally correlation coefficient, r = 1.0, indicating consistency and slope = 1.0, indicating lack of bias

17

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Regression Statistics LC/UV versus LC/MS

	Correlation Coefficient	Slope
RDX	0.9998	1.02
TNT	1.0000	1.05
Nitroglycerin	0.9996	1.07
HMX	0.9980	0.775

HMX slope = 0.755 indicates LC/MS results biased 25% low

HMX bias investigated

18

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Lesson Learned for HMX

- Bias attributed to ionization suppression at APCI interface
- Purchased HMX 13C4 labeled compound
- Used as internal standard
- Subsequent analysis showed bias eliminated
- Labeled HMX now routine internal standard

19

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sensitivity

20

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Results for Amino-dinitrotoluenes

- More detections for amino-dinitrotoluenes by LC/MS as compared to LC/UV
- LC/MS detection limits 2-3 x lower than LC/UV
- LC/MS/MS ~ 5 x lower than LC/UV

Note: CRREL samples had high concentrations, required dilutions, as a result differences in sensitivity not so obvious as in examples to follow

Is difference in sensitivity important?

21

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

DNTs as Emerging Contaminants

USEPA IRIS $1x10^{6}$ = 0.05 ug/L each isomer

2008 Wisconsin GW PAL = 0.05 ug/L each isomer

Region IX Tap Water PRG = 0.099 ug/L as $\sum$ of isomers

1 risk study = 0.03 ug/L as $\sum$ of isomers

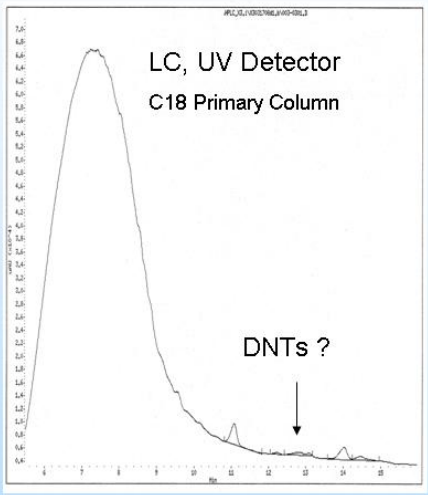
At these concentrations LC/MS needed

Actual DNT example to follow

22

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

DNTs in Storm Water Runoff Explosives Manufacturing Site



DNTs not detected on phenylhexyl confirmation column

MDLs = 0.06 ug/L

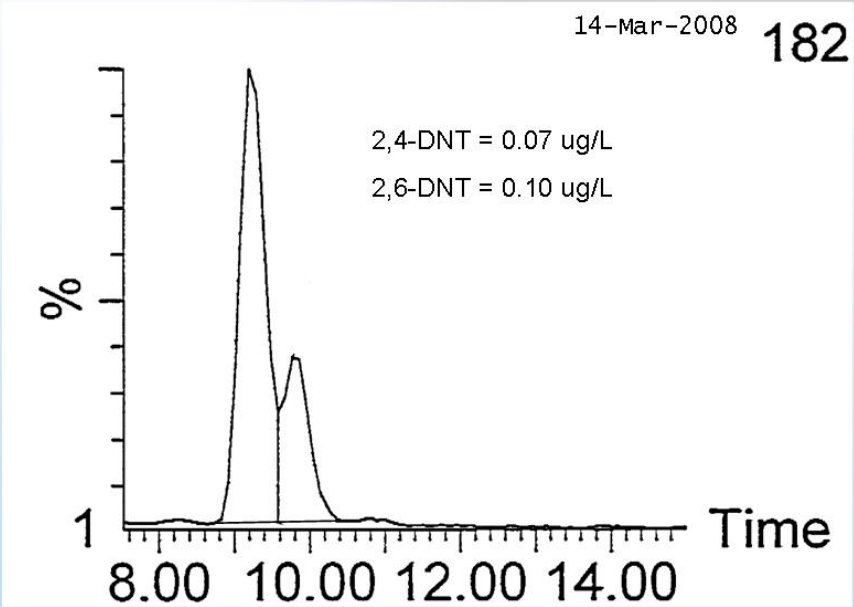
Could 2,4- and 2,6-DNT be in sample?

Site history suggests they could be present

23

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

DNTs in Runoff Water by LC/MS



24

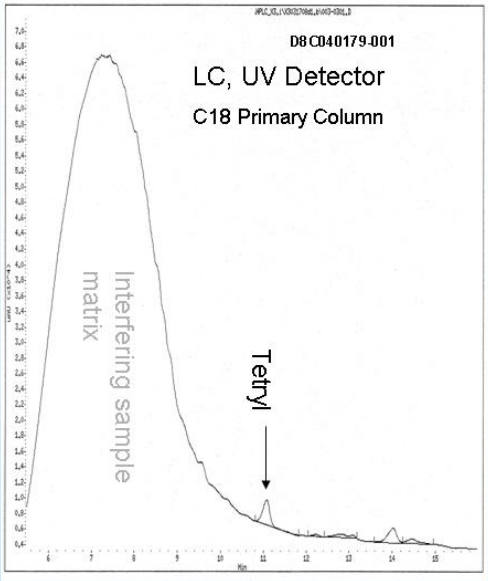
TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Selectivity

25

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Same Storm Water Runoff Sample



Small tetryl peak found phenylhexyl confirmation column

Is tetryl really in sample?

pH water = 7.7

Not likely

26

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Tetryl in Runoff Water by LC/MS

Tetryl not detected

- LC/MS detection limit = 0.02 ug/L,
  (2-3 times lower than LC/UV)
- TestAmerica frequently disproved suspect tetryl results in water using LC/MS
- Similar tetryl results at other LC/MS labs

Note: Occasionally false positives by LC/UV for other compounds, Only at low concentrations in difficult samples

27

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What Might Cause False Positive Results for Tetryl

- Sample matrix can cause RT shifts
- 3,5-dinitroaniline has similar RT as tetryl
- 2,4,6-trinitrobenzaldehyde has caused confusion – Thomas Jenkins

28

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Summary

- LC/UV analysis for explosive residues proven very reliable analytical tool over last 20 years

- There is a place for LC/MS too
  - Results highly comparable to LC/UV
  - Greater sensitivity
  - Greater selectivity

29

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Place for LC/MS

LC/MS should be analytical tool of choice when

- Lower detection limits needed
- Need accurate results in difficult sample matrix (e.g., waters and biota)

30

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Conclusion

- LC/MS is a useful and needed analytical technology
- Well established applications in wide range of media
  - Method of choice for forensics analysis
  - Actively used by DOD

31

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

DOD Guide for Implementing EPA 8330B

"Due to the potential increase in matrix interference resulting from Method 8330B sample preparation protocol and the need for definitive data, **project teams should consider using mass spectrometry as the primary detector when using Method 8330B.** Mass spectrometry provides both selectivity and sensitivity and is best suited to handle these analytical issues."

June 2008

32

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

We have an urgent problem

33

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Conclusion

Method 8330B includes LC/MS, but instrument conditions are not included

New SW-846 methods are needed for explosive residues by LC/MS and LC/MS/MS

34

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Acknowledgments

- USACE CRREL: Alan Hewitt
- TestAmerica: Mark Bruce, Richard Burrows, Brad Chirgwin, Susan Decker, Karen Kuoppala, Andrew Meyer, Patrick Rainey, Pammela Schemmer

35

What's Wrong with Forensic Environmental Methods?

Albert Robbat, Jr., Christian Ziegler, and Kevin MacNamara; Tufts University Chemistry Department, 62 Talbot Ave., Medford, MA 02155; 617-627-3474; arobbat@tufts.edu
Irish Distillers – Pernod Ricard, Midleton Distillery, Midleton, Cork, Ireland

ABSTRACT

Forensic environmental investigations rely on quantitative measurements of specific chemicals or groups of chemically related compounds. Using single ion selected ion monitoring (SIM) or extraction (SIE) will result in overestimation of compound abundance due to common ion interferences from the matrix. Use of a single fragmentation pattern to quantify an entire homologous group of compounds will underestimate compound presence. We built a library of C_1 to C_4 alkylated PAH fragmentation patterns from automated sequential 2D GC-GC/MS analysis of a diesel fuel using the Ion Signature mass spectral deconvolution software. Based on the patterns obtained, the results of a 1D GC/MS analysis as would be performed by SIM or SIE was compared against the approach of using multiple patterns per homolog. Significant overestimation occurs for C_4-naphthalene, C_1-fluorene, and C_1- to C_3- dibenzothiophene. On the other hand, marked underestimation occurs for C_2-naphthalene, C_2-fluorene, C_3-phenanthrene, and C_1-dibenzothiophene when one fragmentation pattern is used to identify all isomers in a homolog.

INTRODUCTION

Fossil-fuel contaminated environmental samples can contain thousands of different chemicals. Information regarding selected components of these samples can determine source(s) of a contamination as well as elucidate degradation, evaporation, photo-oxidation, transport, or washing effects on a contaminant.[1, 2] For fossil fuels, benzene[2, 3], benzothiophene[4], polycyclic aromatic hydrocarbons (PAHs))[5], and their alkylated analogs (C_1- to C_4- saturates), as well as n-alkanes, diamondoids[6], hopanes[7], steranes[8], terpanes[9], and their derivatives are all of interest to analysts performing forensic investigations. This information is used to assign liability for a release, determine risk to human health and the environment, and to direct efforts towards remediation.[10]

Forensic environmental investigations most frequently use gas chromatography (GC) due to the high separation power afforded by modern capillary columns. When GC is hyphenated to a universal detector such as an FID, identification of key components of the sample is compromised. Furthermore, unresolved complex mixture (UCM) chromatograms result from the coelution of many components, further compounding the ability to identify oftentimes low-concentration compounds. Selective detectors somewhat ameliorate this problem but have found limited use due to the small number of relevant compounds that are amenable to this technique.

Mass spectrometry (MS) is the most powerful detection scheme in widespread use. Positive identification is possible using the match of retention times and mass spectra, which are stored in a library such as NIST or Wiley for comparative purposes. Unfortunately, mass spectra from a GC/MS analysis are often complicated by coelution, rendering standard spectral searching algorithms ineffective at identification. Selected ion monitoring (of the base or molecular ion

m/z value) is often used to "look past" the matrix for components of interest.[2, 11-15] This can be done by programming the mass spectrometer to only acquire one or two ions per compound or group, or by allowing the instrument to perform full scan mass spectra and then use off-line data processing to extract ion current.

The inherent assumption of SIM is that the ions chosen for analysis are specific for only that group of compounds. In a very complex matrix, this may not be the case. Furthermore, when a single confirming ion is used for identification, identification is complicated by the change in ratios for various isomers in a given family of homologs. For example, base and largest confirmation ion for 2,3,6-trimethylnaphthalene and 2-(1-methylethyl)naphthalene are 170 and 155 (60%) *and* 155 and 170 (30%), respectively. Both C_3 isomers may be identified because ion chromatograms co-maximize, or alternatively, because relative abundances used for identification only match one isomer, the other is ignored. When both isomers are considered to be present, the same response factor for both is used, which may result in over or underestimation of true C_3-naphthalene concentration. When one compound is deemed present, C_3-naphthalene concentration is underestimated.

This paper addresses fundamental shortcomings in forensic environmental analyses employing GC/MS such as Nordtest [16], ASTM [17], or EPA methods. The 2005 NIST mass spectral library and automated sequential 2D GC-GC/MS with Ion Signature spectral deconvolution software were used to build libraries of fragmentation patterns for C_1- to C_4- naphthalene, fluorene, phenanthrene, and dibenzothiophene analogs. Using the resolving power of GC-GC/MS and deconvolution algorithms in the Ion Signature software, previously unpublished fragmentation patterns were found in diesel fuel. Once the libraries of patterns were assembled, spectral deconvolution allows the analyst to then find the same patterns in 1D GC/MS data, and therefore, the task of assembling libraries using the long GC-GC/MS runtimes needs only to be performed once per sample type. After building the libraries, we compare the results of an analysis of 1D GC/MS data using single ion SIM or SIE *and* use of a single fragmentation pattern per homolog versus using multiple patterns per homolog.

EXPERIMENTAL

Standards and Reagents

Diesel fuel #2 standard was purchased from Restek (Bellefonte, PA), and used as received. Naphthalene, 1,2-dimethylnaphthalene, 2,3-dimethylnaphthalene, and 1-ethylnaphthalene were obtained from Sigma-Aldrich (St. Louis, MO) and diluted with HPLC, GC/MS grade dichloromethane (Fischer, Fair Lawn, NJ) to make 5, 10, 50, 100, and 250 ppm standards, which were used to calculate response factors. Naphthalene-d8 and acenaphthene-d10 were purchased from Restek and used as received as internal standards at 50ppm in each calibration standard mixture.

Gas Chromatography/Mass Spectrometry

The MS was scanned from 35 to 550 m/z, with a 150 threshold count and 1.00 min solvent delay for all 1D and 2D GC/MS analyses. The quadrupole and ion source were held at 150 ^{0}C and 230 ^{0}C, respectively. Deconvolution algorithms were developed at Tufts University (Medford, MA) and are incorporated into a quantitative data analysis software program by Ion Signature Technology (North Smithfield, RI), which was used throughout this investigation. The NIST

(Gaithersburg, MD) Mass Spectral Search Program v2.0 was used for spectral searching and as a basis for fragmentation libraries.

An Agilent (Little Falls, DE) model 6890/5975 GC/MS instrument was generously loaned to our lab for this work. A CIS-4 temperature programmable injector made by Gerstel Inc. (Baltimore, MD) was used for injections. To obtain response factors, a Restek Rxi-5ms 15m x 0.25mm i.d., with 0.25µm film thickness capillary GC column, encased in a MACH oven (RVM Scientific, Santa Barbara, CA) was used. The GC oven was kept at 280 ^{0}C and acted as a heated transfer line from the injector to the MACH column and from the MACH to the MS. The GC temperature program was isothermal, 60 ^{0}C, for 1 min and then 10 ^{0}C/min to 300 ^{0}C, and held for 10 min. The column head pressure was 10.13psi. The CIS-4 temperature programmable injector and MACH oven were controlled by Maestro software (Gerstel), which was integrated into Agilent's Chemstation software. A 30 m Agilent HP-5ms column in the conventional 6890 oven was used for the 1D GC/MS diesel fuel analysis. The oven was ramped from 60 ^{0}C (1 min) to 300 ^{0}C (5 min) at 5 ^{0}C/min under 4.35 psi constant pressure. Splitless injections of 1µL were made.

For automated sequential 2D GC/MS analyses, the following conditions were used. Column 1 was 30m x 0.25mm, 0.25µm film thickness DB-1701ms (Agilent) capillary column. This was connected on one end to the CIS-4 inlet in the first oven and connected on the other end to a column flow switching device (Gerstel) in a separate, adjacent oven. The second column was the 30m HP-5MS column described above housed in the second oven. This column was threaded through a Gerstel CTS-2 cryotrap to freeze effluent from the first column. Rapid heating of the CTS-2 cryotrap was performed to thermally desorb the heartcut for separation on the second column. A MCS2 mass flow controller (Gerstel) in a separate pneumatics module provided a constant cross-flow of 10mL/min while a proportional valve with sensor received and moderated the outlet flow. An MCS autosampler (Gerstel) was used to make 1µL splitless injections. The CIS-4 inlet was ramped at 10 ^{0}C/sec from 60 ^{0}C to 300 ^{0}C. The inlet pressure at the head of the DB-1701ms column was held at 17.69psi for 2-min and then ramped to 30.75 psi at 0.537 psi/min, where it was held isobaric for 10 min. The oven housing column 1 was held for 2 min at 60^{0}C and then temperature programmed to 300 ^{0}C at 10 ^{0}C/min where it was held for 15 min. One minute long cuts were made after the fourth minute by turning the countercurrent flow across the crosspiece off, forcing eluates to the cryotrap, where it was frozen at -100 ^{0}C. The CTS-2 cold trap was heated at 25 ^{0}C/sec to 300 ^{0}C to start the second chromatographic run. The oven temperature programming conditions for the second column was identical to the 1D conditions described above. Sample injection, heart cutting, freeze trap, thermal desorption, and external pneumatics module were all controlled by the Maestro software.

Quantitative Analysis of Alkylated PAH

Elution times of components were converted into retention indexes using naphthalene at 100.00, phenanthrene at 200.00, and pyrene at 352.77 index units.[18] Retention times for the first and last eluting compound in a homolog were used to determine experimentally obtained retention windows. Reported windows in Table 2 were generated by subtracting or adding 0.5 min to the leading or tailing edge of the first and last homolog peaks, respectively. This was performed because slight retention time shifts were observed between the 1D GC/MS and the 2D GC-GC/MS data. Table 1 gives the alkylated PAH patterns used to determine retention indices as reported in Table 2.

The Ion Signature software is a quantitative GC/MS analysis software package that uses *.D files obtained from Agilent equipment. The extracted base ion signal for the homolog was used to determine area count, denoted $Area_{SIE}$. The peak area for only those peaks where the criteria for positive compound identification were met was summed and denoted $Area_{Deconvolution}$. To determine the percent difference between areas obtained by SIM or selected ion extraction (SIE) methods versus using full scan MS data, deconvolved using multiple patterns per compound, the following equation was used:

$$\frac{Area_{SIE} - Area_{Deconvolution}}{Area_{Deconvolution}} \times 100\%$$

RESULTS AND DISCUSSION

Forensic methods widely used in the industry typically employ single ion SIM/SIE, two ion monitoring (i.e. comaximization of the base and one confirmation ion) or, at best, a single pattern per homolog (two or more ions and their relative abundances) to quantify all alkylated PAH homologs in complex samples. Except for methyl isomers of alkylated PAH, all of these methods will result in erroneous quantification of homolog abundance. In contrast, the methodology we employ in this work and suggest for future analyses employs multiple fragmentation patterns per homolog. Using the Ion Signature deconvolution algorithms, peak area is only quantified when main and all confirmation ions match the relative error criteria within the program. Further, the algorithms will adjust the signal of the quantitation ion if the matrix adds signal, thus reducing overestimation due to the common ion effect. In this work, we demonstrate the utility of automated sequential 2D GC-GC/MS and the Ion Signature software for building libraries of compounds. Once these libraries are built, patterns are grouped according to similarity within a homolog and used to quantify alkylated PAH abundance in 1D GC/MS.

Figure 1 shows the FID trace for the diesel fuel on a DB-1701ms column. As is typical for diesel fuels, a large unresolved complex mixture (UCM) hump is present. The blue lines on the figure denote the location of heart cuts made to the second, HP-5ms column. In the heartcut, an UCM hump is still present, but alkylated PAH were generally separated from the polar and aliphatic compounds which make up the UCM[19]. Cut 14 contains C_1- to C_4-naphthalenes, well separated from each other and the UCM. In this example, it is a trivial exercise to identify all the C_1 and C_2 isomers in the software by performing a spectral search for the peaks, as these isomers are all present in NIST and/or Wiley. In contrast, however, not all of the C_3- and C_4- isomers are in the databases. While some peaks corresponding to unknown C_3- and C_4-naphthalene isomers may have a relatively good quality match with known patterns, others do not, as their fragmentation pattern is markedly different from any known isomer.

The extracted ion current profile for the molecular ion for C_4 naphthalene at m/z 184 is shown in Figure 2a. Analysts employing SIM or SIE with a single ion to quantify alkylated PAH would attribute all of the peak area in Figure 2a to C_4-naphthalene, overestimating compound abundance. The percent overestimation that would result from use of a single ion to quantify all alkylated PAH homologs is reported in Table 2 as a percent of correct peak area. If the criterion of co-maximation of any of the confirmation ions shown in Figure 2b (1D GC/MS) is used, abundance may differ from analyst to analyst depending on the specific confirmation ion chosen. If a single fragmentation pattern (i.e. the four ions in the figure plus their relative abundances, in

this case the pattern is for 1,2,3,4-tetramethylnaphthalene) is chosen, only the peaks labeled 'C' would be attributed to C_4-naphthalene. This is partially because interference from a common matrix ion distorts ion traces. Figure 2c shows heartcuts 14 and 15, in which C_4-naphthalenes were found to elute. Using 1,2,3,4-tetramethylnaphthalene again as a surrogate for identification, three additional peaks are identified. It should be clear from this example already that peak area will be missed for other peaks where three confirmation ions comaximize with the molecular ion, but in different ratios. The amount of underestimation of correct peak area by using a single fragmentation pattern to identify all isomers is also reported in Table 2 as a percentage of correct peak area. For the purposes of this study, we chose mono-, di-, tri-, or tetramethyl PAH isomers as surrogates for each homolog. Table 1 lists and denotes patterns that were used for this quantitative analysis. Clearly, though, quantification of alkylated PAH or any compound or groups of compounds by GC-GC is too time intensive for the high throughput and fast turnaround times demanded by industry.

We found that even using as many unique patterns we could obtain from NIST or the literature, peaks where several homolog-specific ions comaximized but in differing intensity from known patterns still were missed. Therefore, we used the automated sequential 2D GC/MS data to develop a library of fragmentation patterns for each of the alkylated PAH homologs. Fragmentation patterns of the 12 C_2-naphthalenes can be found in NIST. Only five unique fragmentation patterns are needed to identify the 12 isomers, as some isomers are very similar in their fragmentation. From these five patterns, there are only 8 unique ions common to all patterns as one of the five most abundant ions. Likewise, if the five most abundant ions for the C_4-naphthalenes we could find in NIST or the literature are tallied, only 16 ions are found. The aromatic structure of the parent PAH limits fragmentation of the alkylated homolog. Only differences in type of functional group and its location determine the ions for a given isomer. Further, the molecular ion is always present as one of the largest 5 ions in all alkylated PAH fragmentation patterns. To find new patterns, selected ion extraction of all ions was performed in the heartcuts. Where several ions co-maximized with the molecular ion, a pattern was found. In some cases, these patterns were markedly different from those in the literature or NIST. These new patterns were put into the Ion Signature deconvolution software to determine the scan-to-scan variance of the ions in a more quantitative fashion. Where the relative error criterion was met (typically, using a RE of 7), the pattern was confirmed as an alkylated PAH pattern and put into the library.

As an example, Figure 3 shows a set of five C_4-naphthalene peaks. The three peaks in the middle are a good match for pattern C_4-N A, which is similar to 1-methyl-7-(1-methylethyl)naphthalene. However, the two outside peaks are not a good match for C_4-N A. In contrast, pattern C_4-N D is a good match for these peaks. The Ion Signature software plots each ion at each scan as a bar, normalized to the main ion (typically, the base ion is made as the main ion in a method). Where each set of bars is of the same height, actual and expected relative abundances for the ions are identical. Where bars are markedly different in height, the actual abundance for that ion is greatly different than the expected abundance. The software only displays bars when the scan-to-scan variance of the relative abundance of the ions is less than a value chosen by the analyst. This eliminates any peaks where ions do not comaximize, and will also eliminate peaks where ion ratios are very far different than expected. In Figure 3, the relative error was set at 30 in order to illustrate the mismatch of expected and actual ion abundance.

Figure 2d shows a composite picture of all the C_4-naphthalenes we identified in diesel. Five patterns (A-E) were used to account for the more than 20 peaks obtained. Of these patterns, two were novel patterns developed by the combinatorial approach discussed above. A list of patterns for all alkylated PAH is found in Table 1. Diesel fuels from other sources, different petroleum distillates, or coal tar may require additional patterns to the ones reported here. Work is in progress towards automated sequential 2D GC-GC/MS analysis of crude oil and coal tar to further expand the library of alkylated PAH.

Response factors for 1,2-dimethylnaphthalene, 2,3-dimethylnaphthalene, and 1-ethylnaphthalene were also generated in this study and are reported in Table 3. We found that response factors could be significantly different (by a factor of more than 2) depending on the isomer and ion used to quantify the peak. These response factors can be expected to be different, as the base ion for the three isomers are not all the same. Clearly, the same response factor for one alkylated PAH cannot be used for all isomers in that homolog, and further, response factor of the parent PAH should not be used for higher order analogs.

CONCLUSION:

In this study we demonstrated a method for finding fragmentation patterns in complex matrices for compounds of interest. In doing so, we show why single ion SIM or SIE, single ion with confirmation ion analysis, or use of a single fragmentation pattern will result in over or underestimation of alkylated PAH abundance. Finally, we showed a brief example of markedly different response factors obtained for three alkylated PAH isomers, demonstrating that a single response factor is insufficient to quantify all homologs. Our results indicate that diagnostic ratios of alkylated PAH, which are used to determine source and weathering of an oil spill, may lead to erroneous conclusions when single ion SIM or SIE is used to determine ratios.

ACKNOWLEDGEMENTS

The Authors wish to thank Agilent Technologies, Gerstel GmbH, RVM scientific, and Ion Signature Technology for their generous donation or loan of equipment, supplies, and software. Their support made this work possible.

Table 1: Patterns used to identify alkylated PAH.

Isomers Represented	Fragmentation Pattern	Quant Ion (%RA)	Confirmation Ions (%RA)			
C_1 Naphthalenes						
1-methyl	C_1 N A*#	142 (100)	141 (80)	115 (30)	143 (12)	
2-methyl	C_1 N B	142 (100)	141 (51)	115 (16)	143 (12)	
C_2 Naphthalenes						
1; and 2-ethyl	C_2 N A*	141 (100)	156 (55)	115 (18)	142 (12)	
1,7; and 2,6-dimethyl	C_2 N B*	156 (100)	141 (85)	155 (30)	115 (15)	
2,3-dimethyl	C_2 N C*#	141 (100)	156 (98)	155 (30)	115 (23)	128 (16)
1,2; 1,3; and 1,4-dimethyl	C_2 N D	156 (100)	141 (75)	155 (18)	157 (13)	115 (13)
1,5; 1,6; 1,8; and 2,7-dimethyl	C_2 N E	156 (100)	141 (55)	155 (30)	115 (12)	

C_3 Naphthalenes						
1-propyl	C_3 N A*	141 (100)	170 (26)	115 (18)	142 (12)	
2-(1-methylethyl)	C_3 N B*	155 (100)	170 (30)	153 (18)	128 (17)	156 (14)
1-methyl-8-ethyl	C_3 N C*	155 (100)	170 (65)	77 (20)	153 (19)	115 (14)
Unknown isomer	C_3 N D*	155 (100)	170 (55)	153 (28)	128 (20)	156 (13)
Unknown isomer	C_3 N E*	170 (100)	155 (91)	153 (21)	169 (18)	171 (14)
1,4,5; and 1,4,6-trimethyl	C_3 N F*#	155 (100)	170 (75)	153 (30)	152 (25)	128 (20)
Unknown isomer	C_3 N G	141 (100)	115 (70)	170 (30)	142 (12)	
1,6,7-trimethyl	C_3 N H	170 (100)	155 (75)	169 (17)	153 (16)	171 (14)
2,3,6-trimethyl	C_3 N I	170 (100)	155 (58)	169 (17)	171 (14)	153 (11)
1-(1-methylethyl)	C_3 N J	155 (100)	128 (62)	170 (40)	115 (32)	127 (27)
Unknown isomer	C_3 N K	155 (100)	170 (92)	153 (21)	169 (19)	152 (18)
C_4 Naphthalenes						
1-methyl-7-(1-methylethyl)	C_4 N A*	169 (100)	184 (50)	154 (20)	170 (15)	
1,4,5,8-tetramethyl	C_4 N B*	184 (100)	169 (68)	185 (15)	153 (12)	
1,2,3,4-tetramethyl	C_4 N C*#	169 (100)	184 (80)	170 (14)	141 (14)	
Unknown isomer	C_4 N D*	184 (100)	169 (92)	153 (21)	141 (15)	
Unknown isomer	C_4 N E*	169 (100)	184 (95)	153 (25)	**165 (25)**	170 (15)
2-methyl-1-propyl	C_4 N F	155 (100)	184 (30)	156 (14)	153 (12)	
1-butyl	C_4 N G	141 (100)	142 (50)	184 (40)	115 (25)	
2-butyl	C_4 N H	141 (100)	142 (72)	184 (30)	115 (23)	
1-(2-methylpropyl)	C_4 N I	141 (100)	184 (30)	142 (20)	115 (10)	
2-(1,1-dimethylethyl)	C_4 N J	169 (100)	141 (46)	184 (30)	128 (17)	129 (16)
1-(1,1-dimethylethyl)	C_4 N K	169 (100)	141 (30)	184 (30)	129 (15)	128 (15)
C_1 Fluorenes						
1; and 2-methyl	C_4 F A*#	165 (100)	180 (75)	178 (25)	179 (25)	
4; and 3-methyl	C_4 F B	165 (100)	180 (94)	178 (25)	179 (25)	166 (15)
9-methyl	C_4 F C	180 (100)	165 (93)	179 (22)	178 (20)	181 (15)
C_2 Fluorenes						
Unknown Isomer	C_2 F A*#	194 (100)	179 (91)	89 (17)	180 (16)	
2-ethyl and 2,3-dimethyl	C_2 F B*	179 (100)	194 (80)	89 (20)	180 (17)	
Unknown Isomer	C_2 F C*	179 (100)	194 (65)	178 (51)	89 (25)	180 (21)
Unknown Isomer	C_2 F D*	165 (100)	166 (35)	194 (25)	180 (25)	
9,9; and 1,9-dimethyl	C_2 F E	179 (100)	194 (40)	180 (14)	89 (10)	
9-ethyl	C_2 F F	165 (100)	194 (38)	166 (16)		
C_1 Dibenzothiophenes						
Unknown isomer	C_1 D A*	198 (100)	197 (70)	199 (19)		
3-methyl and 4-methyl	C_1 D B#	198 (100)	197 (50)	199 (17)	99 (10)	
C_2 Dibenzothiophenes						
dimethyl isomers except 1,2; 1,3; 2,3	C_2 D A*#	212 (100)	211 (45)	197 (20)	213 (17)	
1,2; 1,3; 2,3-dimethyl	C_2 D B*	212 (100)	197 (55)	211 (37)	213 (25)	

ethyl isomers	C_2 D C	197 (100)	212 (52)	184 (31)		
C_3 Dibenzothiophenes						
4-ethyl-6-methyl	C_3 D A*	211 (100)	226 (78)	212 (17)	227 (13)	
1,4,8; 1,4,6; 1,2,4; 2,4,6; 2,6,7; and 3,4,6;-trimethyl	C_3 D B*#	226 (100)	211 (45)	227 (20)	212 (10)	
Unknown isomer	C_3 D C	226 (100)	211 (82)	227 (25)	212 (20)	
C_1 Phenanthrenes						
1; and 4-methyl	C_1 P A*#	192 (100)	191 (55)	189 (30)	193 (17)	190 (15)
2; 3; and 9-methyl	C_1 P B	192 (100)	191 (39)	189 (20)	193 (15)	190 (10)
C_2 Phenanthrenes						
2; and 9-ethyl	C_2 P A*	191 (100)	206 (70)	189 (20)	192 (20)	
9,10-dimethyl	C_2 P B*	206 (100)	191 (85)	189 (16)	89 (15)	
Unknown isomer	C_2 P C*	206 (100)	191 (35)	189 (29)	205 (25)	
2,5-dimethyl	C_2 P D*#	206 (100)	191 (51)	189 (27)	205 (20)	
3,6; 1,7; and 2,7-dimethyl	C_2 P E	206 (100)	191 (20)	205 (20)	189 (17)	
2,3; and 3,5-dimethyl	C_2 P F	206 (100)	191 (40)	189 (18)	205 (16)	
C_3 Phenanthrenes						
Unknown isomer	C_3 P A*	205 (100)	220 (85)	189 (45)	206 (30)	204 (10)
2,3,5-trimethyl	C_3 P B*#	220 (100)	205 (58)	189 (21)	221 (18)	101 (18)
1-ethyl-2-methyl	C_3 P C	205 (100)	220 (60)	206 (21)	189 (20)	204 (12)

* indicates pattern found in the diesel fuel.
# indicates pattern used to calculate peak area and percent underestimated, see Table 2.

Table 2: Comparison of alkylated PAH peak areas by SIM and full scan mass spectrometry using one fragmentation pattern per homolog versus spectral deconvolution of full scan data.

PAH Homolog	Experimental Retention Indices		% Overestimation (SIM)	% Underestimation (Single Pattern)
	From	To		
C_1 Naphthalene	216.73	227.87	0	0
C_2 Naphthalene	235.29	255.53	1	54
C_3 Naphthalene	250.47	279.15	4	12
C_4 Naphthalene	270.72	299.39	20	16
C_1 Fluorene	285.90	297.71	32	0
C_2 Fluorene	299.39	319.44	3	72
C_1 Phenanthrene	316.88	329.67	4	2
C_2 Phenanthrene	330.77	350.50	2	15
C_3 Phenanthrene	345.39	373.16	7	72
C_1 Dibenzothiophene	310.31	322.00	251	100
C_2 Dibenzothiophene	324.92	343.20	30	27
C_3 Dibenzothiophene	338.81	357.81	29	14

Notes:
1. The SIM signal is based on the molecular ion for each homolog.
2. The full scan signal is based on one fragmentation pattern per homolog as shown in Table 1.
3. The SIM and full scan data are compared against the peak areas obtained by the deconvolution software using the fragmentation patterns listed in Table 1 for each homolog.
4. The retention index range is used to calculate peak area differences.

Table 3: Response factors of C_0 and three C_2-naphthalenes using various extracted ions for area integration.

Compound	Response factor for ion		% RSD
	Actual Base Ion	m/z 156	
Naphthalene	0.918	-	5.000
1-ethylnaphthalene	1.434	0.645	6.667
1,2-dimethylnaphthalene	1.073	0.950	7.667
2,3-dimethylnaphthalene	1.477	1.477	7.333

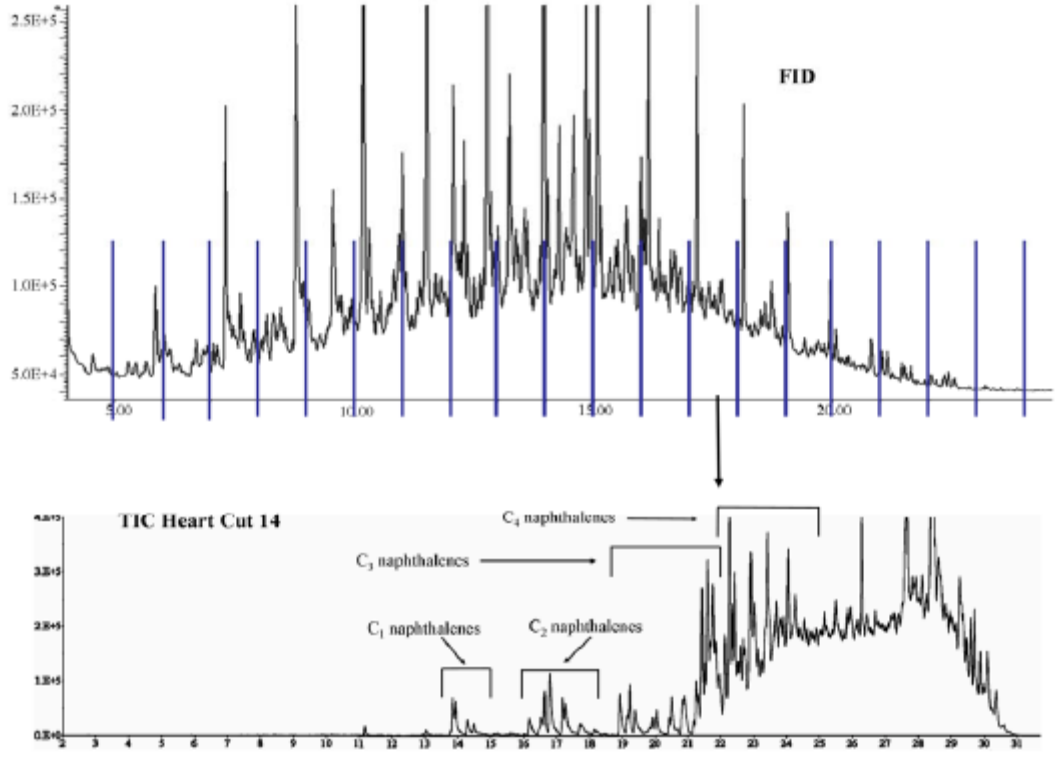


Figure 1: FID trace of neat diesel on DB-1701ms column and TIC of Heart Cut 14. Elution windows for C_1 to C_4 naphthalenes are indicated.

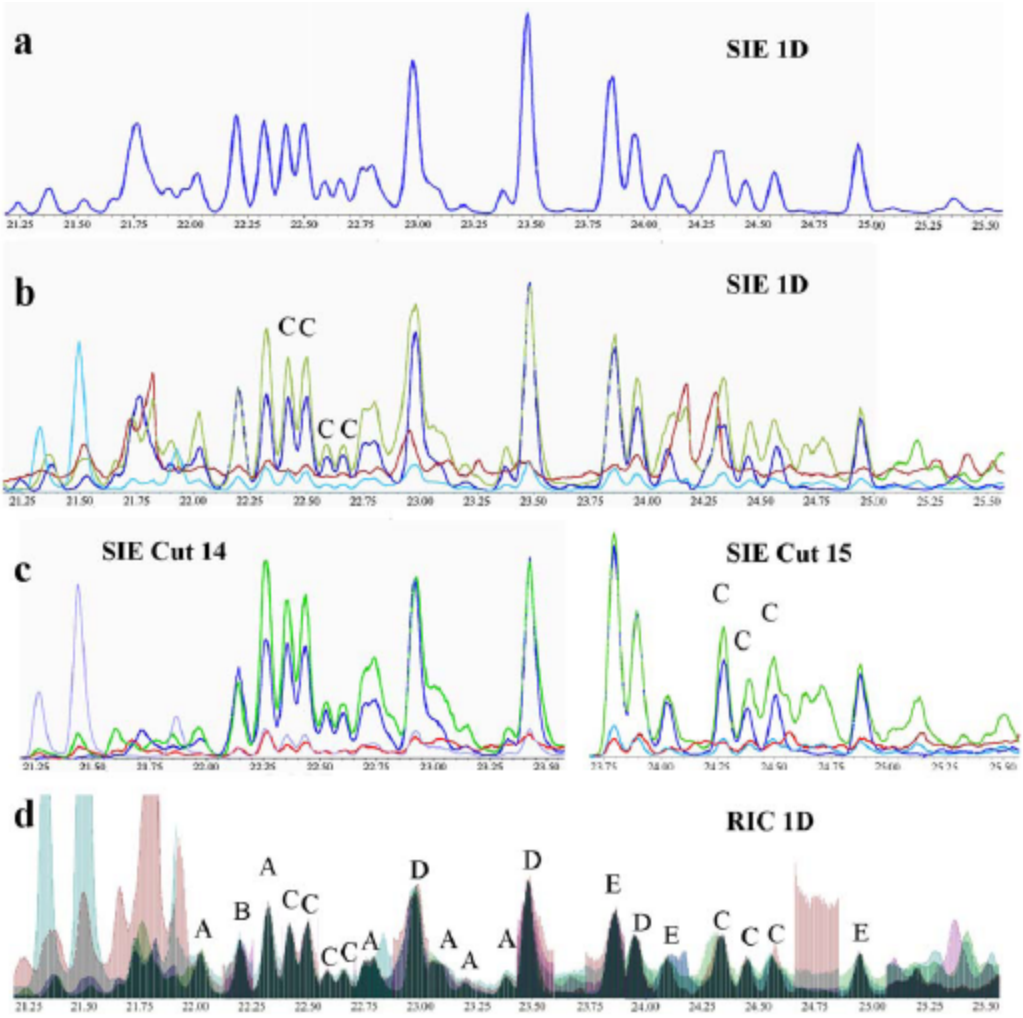


Figure 2: (a) Extracted ion profile for the molecular ion for C_4-naphthalene at m/z 184 from a 1D GC/MS analysis. (b) Extracted ion profiles for m/z 184 (blue), 169 (light green), 170 (red), and 141 (light blue) from a 1D GC/MS analysis. Ion chromatograms from 21.25 to 22.00 min and 24.00 to 24.75 min do not co maximize. (c) The same ions, extracted from heart cuts 14 and 15. Evident is the fact that ion profiles are much "cleaner." Also evident is the fact that peak profiles from the windows indicated above are either cleaner or ion current is dramatically reduced. (d) A composite view of 1D-data as visualized in the Ion Signature software. Peaks are indicated with a letter coinciding with a pattern from Table 1 optimized to match the peak profile. Note that between 20 and 21.8 min and at 24.75 min, no literature or found patterns match the peak profile ion current, in agreement with results seen in heartcuts 14 and 15.

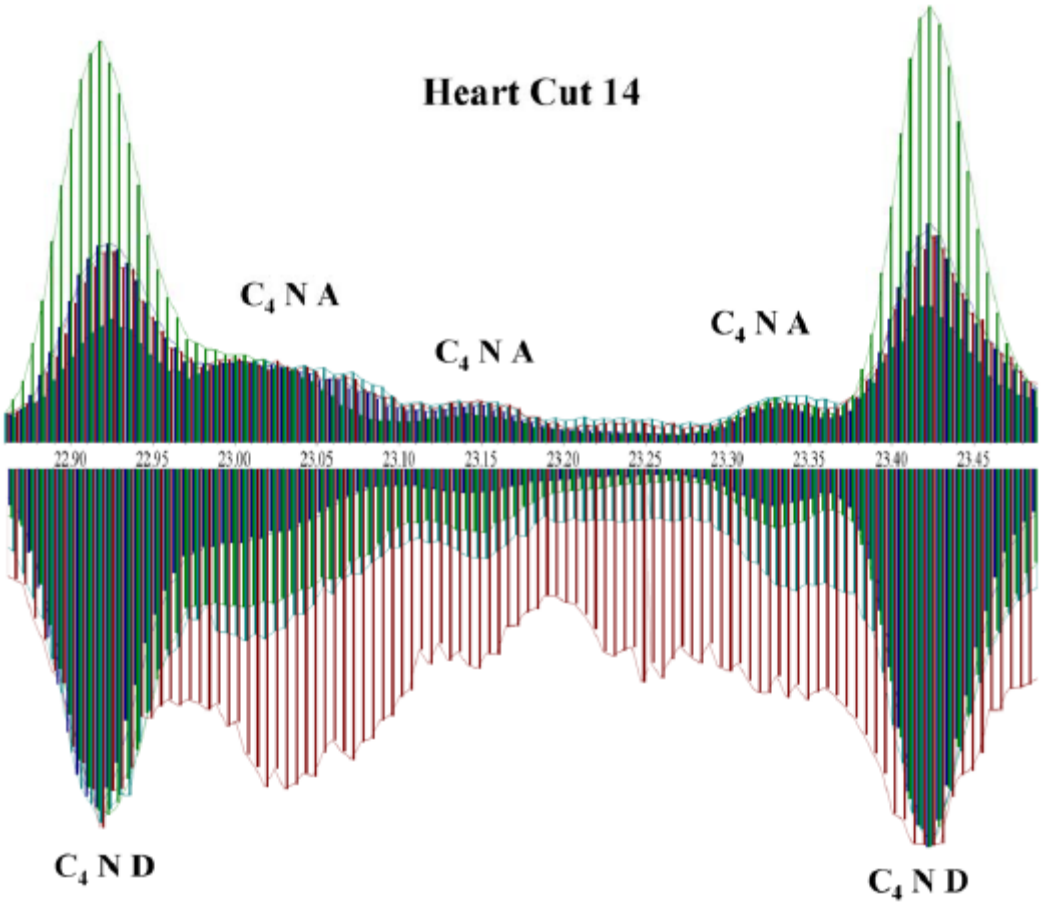


Figure 3: Mirror image reflection of data as visualized in the IFD software. Top portion of the figure shows that three peaks are a good match for C_4 N A, while the two outside peaks are not. The bottom portion of the figure is an inverted view of the same peaks as visualized when using pattern C_4 N D. Now evident is the fact that the two outside peaks are a good match for C_4 N D but not the three inside peaks.

REFERENCES

1. Stout, S. A.; Uhler, A. D.; McCarthy, K. J., A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environmental Forensics* **2001,** 2, (1), 87-98.
2. Wang, Z. D.; Fingas, M. F., Development of oil hydrocarbon fingerprinting and identification techniques. *Marine pollution bulletin* **2003,** 47, (9-12), 423-452.
3. Alimi, H.; Ertel, T.; Schug, B., Fingerprinting of Hydrocarbon Fuel Contaminants: Literature Review. *Environmental Forensics* **2003,** 4, (1), 25-38.
4. Wang, Z.; Fingas, M., Use of Methyldibenzothiophenes as Markers for Differentiation and Source Identification of Crude and Weathered Oils. *Environmental science & technology* **1995,** 29, (11), 2842-2849.

5. Wang, Z.; Li, K.; Fingas, M.; Sigouin, L.; Menard, L., Characterization and source identification of hydrocarbons in water samples using multiple analytical techniques. *Journal of Chromatography A* **2002,** 971, (1-2), 173-184.

6. Wang, Z.; Yang, C.; Hollebone, B.; Fingas, M., Forensic Fingerprinting of Diamondoids for Correlation and Differentiation of Spilled Oil and Petroleum Products. *Environmental Science & Technology* **2006,** 40, (18), 5636-5646.

7. Prince, R. C.; Elmendorf, D. L.; Lute, J. R.; Hsu, C. S.; Haith, C. E.; Senius, J. D.; Dechert, G. J.; Douglas, G. S.; Butler, E. L., 17-Alpha(h),21-Beta(h)-Hopane as a Conserved Internal Marker for Estimating the Biodegradation of Crude-Oil. *Environmental science & technology* **1994,** 28, (1), 142-145.

8. Wang, Z. D.; Stout, S. A.; Fingas, M., Forensic fingerprinting of biomarkers for oil spill characterization and source identification. *Environmental Forensics* **2006,** 7, (2), 105-146.

9. Stout, S. A.; Uhler, A. D.; McCarthy, K. J., Middle distillate fuel fingerprinting using drimane-based bicyclic sesquiterpanes. *Environmental Forensics* **2005,** 6, (3), 241-251.

10. Stout, S. A.; Uhler, A. D.; Naymik, T. G.; McCarthy, K. J., Environmental Forensics Unraveling Site Liability. *Environmental science & technology* **1998,** 32, (11), 260A-264A.

11. Abraham, B. M.; Liu, T. Y.; Robbat, A., Data Comparison Study between Field and Laboratory Detection of Polychlorinated-Biphenyls and Polycyclic Aromatic-Hydrocarbons at Superfund Sites. *Hazardous Waste & Hazardous Materials* **1993,** 10, (4), 461-473.

12. See, for example, section 7.5.5 of EPA method 8270c.

13. Stout, S. A.; Magar, V. S.; Uhler, R. M.; Ickes, J.; Abbott, J.; Brenner, R., Characterization of naturally-occurring and anthropogenic PAHs in urban sediments - Wycoff. *Environmental Forensics* **2001,** 2, (4), 287-300.

14. Wang, Z. D.; Fingas, M., Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography. *Journal of Chromatography A* **1997,** 774, (1-2), 51-78.

15. Gaines, R. B.; Hall, G. J.; Frysinger, G. S.; Gronlund, W. R.; Juaire, K. L., Chemometric Determination of Target Compounds Used to Fingerprint Unweathered Diesel Fuels. *Environmental Forensics* **2006,** 7, 77-87.

16. Daling, P. S.; Faksness, L.-G.; Hansen, A. B.; Stout, S. A., Improved and Standardized Methodology for Oil Spill Fingerprinting. *Environmental Forensics* **2002,** 3, (3), 263 - 278.

17. ASTM, Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography. **2000**.

18. Vassilaros, D. L.; Kong, R. C.; Later, D. W.; Lee, M. L., Linear Retention Index System for Polycyclic Aromatic Compounds: Critical Evaluation and Additional Indices. *Journal of Chromatography* **1982,** 252, 1-20.

19. Frysinger, G. S.; Gaines, R. B.; Xu, L.; Reddy, C. M., Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental science & technology* **2003,** 37, (8), 1653-1662.

2008 National Environmental Monitoring Conference

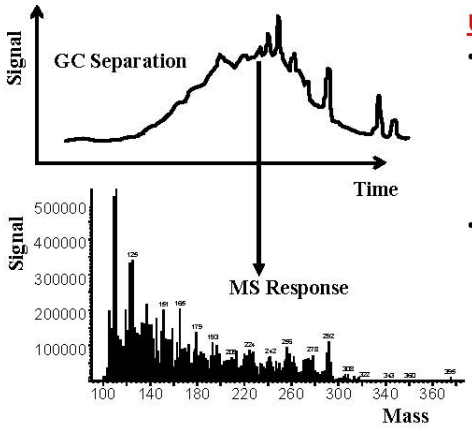
What's Wrong with Forensic Environmental Methods?

Christian Zeigler* and Albert Robbat, Jr.

The Approach

- Quantitative analysis by GC/MS of selected components and families
  - PAH and Alkylated PAH
  - Use ratios: e.g.…
- Delineate weathering (water washing, evaporation, degradation)
- Determine source
- Direct remedial efforts and assign blame

The Problem



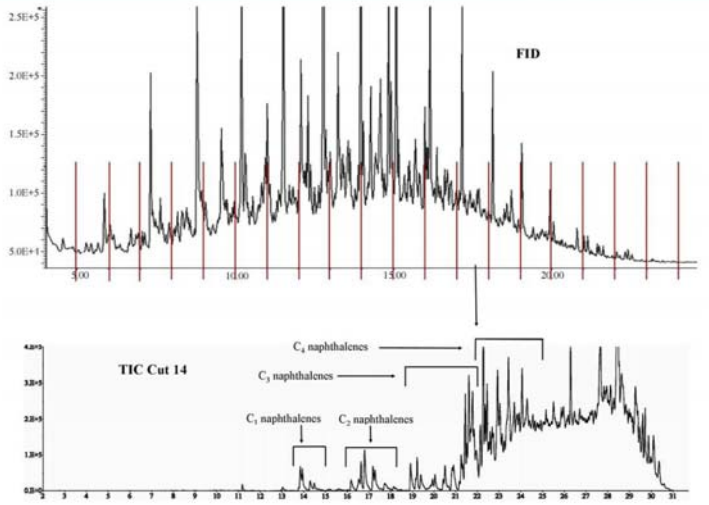
Unresolved Chromatograms Mean

- Dramatic increases in
  - false positives/negatives
  - sample preparation
  - sample reanalysis rates
- Dramatic decreases in
  - precision and accuracy
  - sensitivity
  - robustness

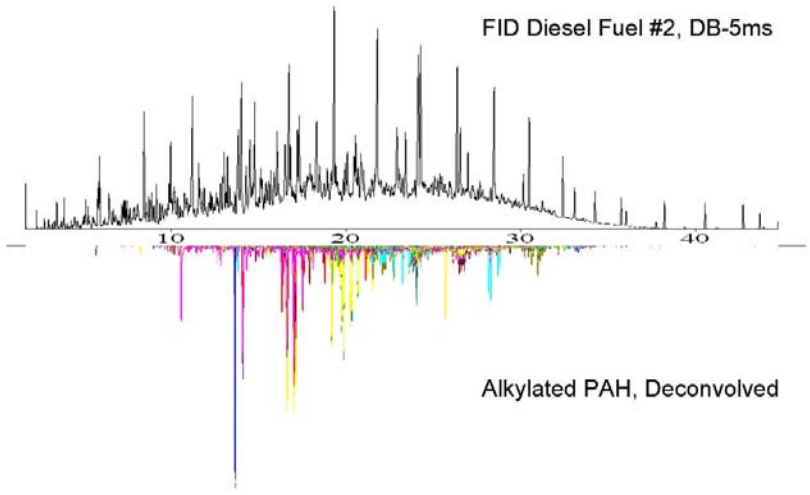
Current Methodology: Selected Ion Monitoring

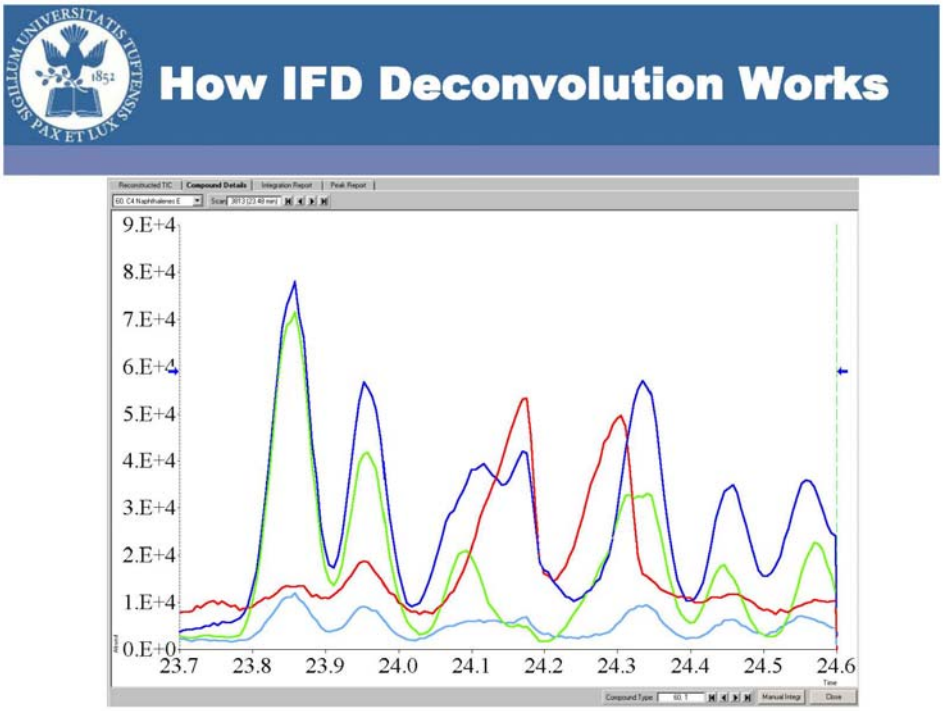
- One or two m/z values per compound *or family*
  - Higher sensitivity *(but only if..)
  - Identification based on retention time
    - Little advantage over FID
  - At best co-maximization of confirming ion with molecular
  - Assumes all ion current due to compounds of interest and all are similarly fragmenting
    - Response factors

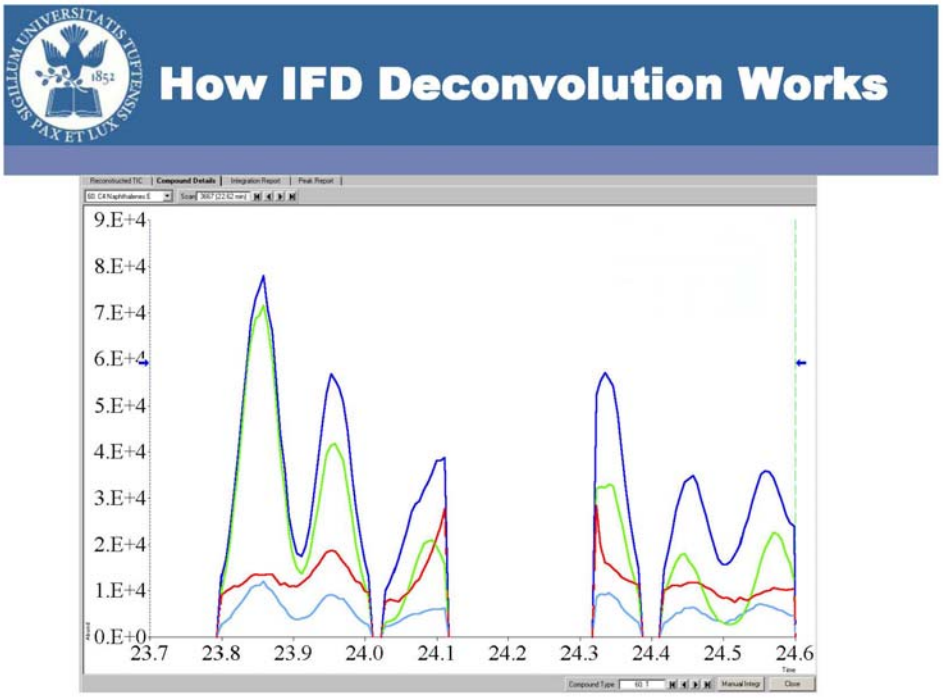
Automated Sequential GC-GC/MS of Diesel #2



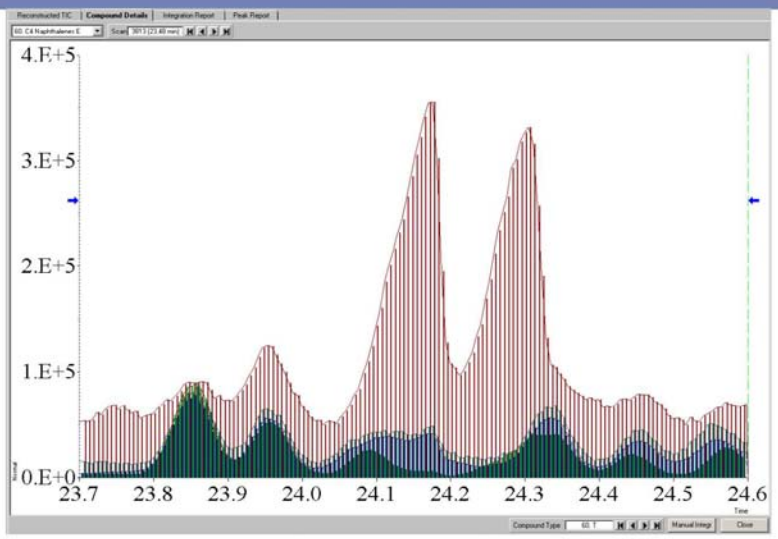
Mass Spectral Deconvolution



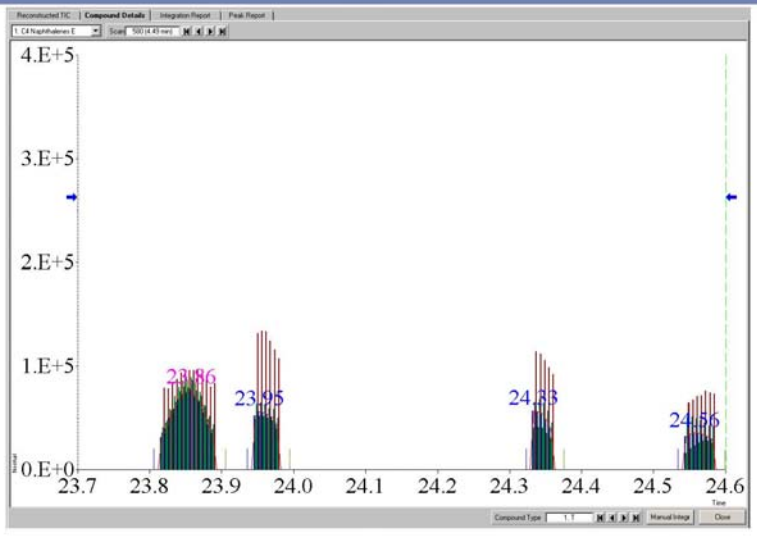

How IFD Deconvolution Works
9.E+4
8.E+4
7.E+4
6.E+4
5.E+4
4.E+4
3.E+4
2.E+4
1.E+4
0.E+0
23.7
23.8
23.9
24.0
24.1
24.2
24.3
24.4
24.5
24.6


How IFD Deconvolution Works
9.E+4
8.E+4
7.E+4
6.E+4
5.E+4
4.E+4
3.E+4
2.E+4
1.E+4
0.E+0
23.7
23.8
23.9
24.0
24.1
24.2
24.3
24.4
24.5
24.6

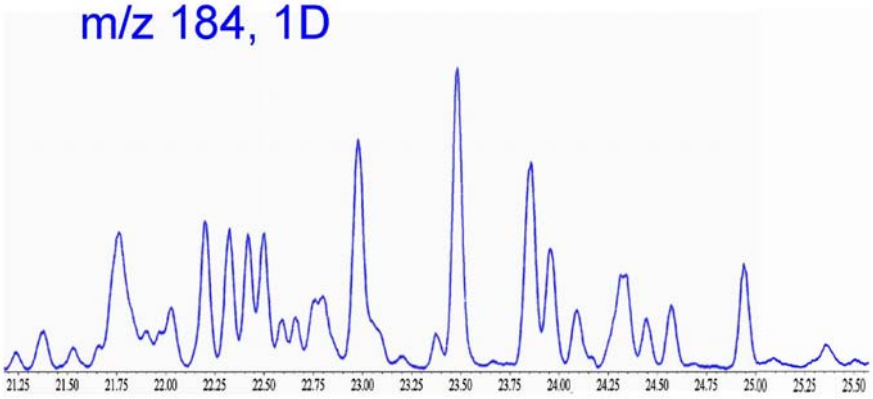
How IFD Deconvolution Works



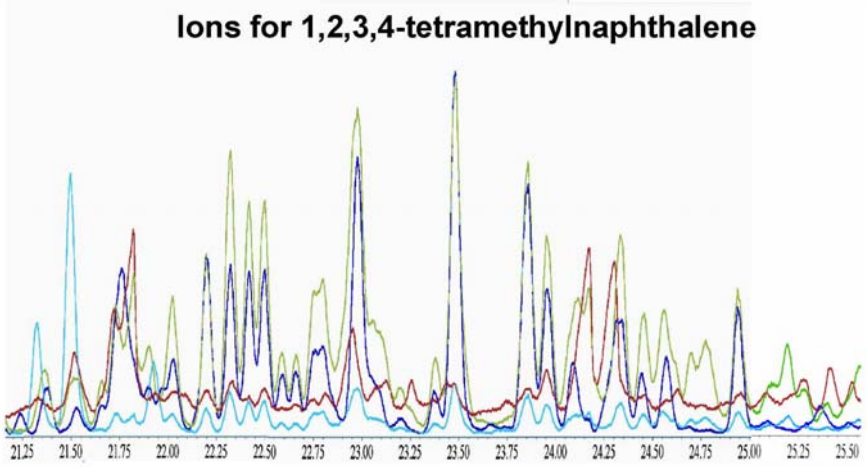
How IFD Deconvolution Works



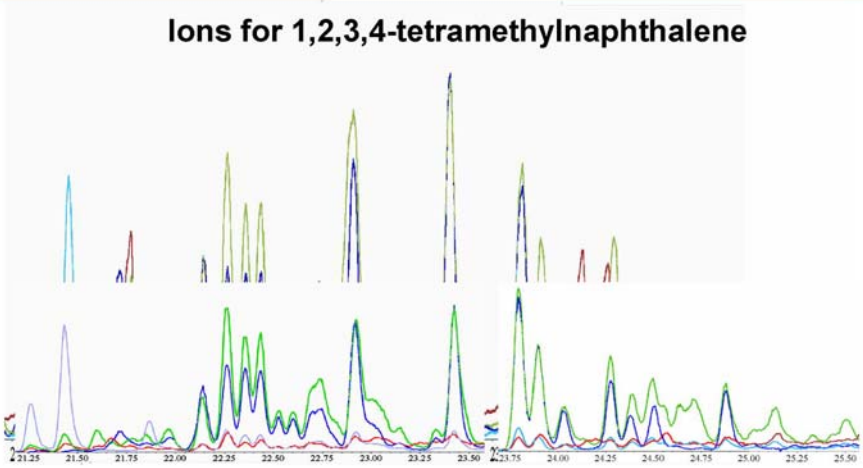
C_4-Naphthalenes - SIM



C_4-Naphthalenes – 1D



C_4-Naphthalenes – Heart Cuts

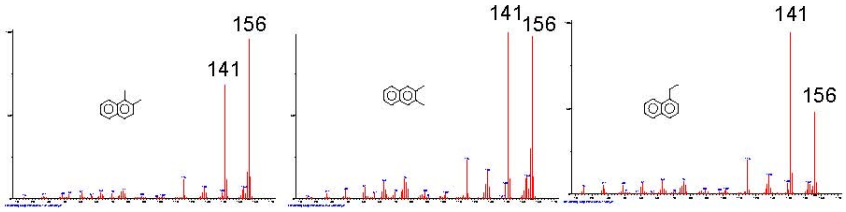


Results: Over and Underestimation

PAH Homolog	Experimental Retention Indices		% Overestimation (SIM)	% Underestimation (Single Pattern)
	From	To		
C_1 Naphthalene	216.73	227.87	0	0
C_2 Naphthalene	235.29	255.53	1	54
C_3 Naphthalene	250.47	279.15	4	12
C_4 Naphthalene	270.72	299.39	20	16
C_1 Fluorene	285.90	297.71	32	0
C_2 Fluorene	299.39	319.44	3	72
C_1 Phenanthrene	316.88	329.67	4	2
C_2 Phenanthrene	330.77	350.50	2	15
C_3 Phenanthrene	345.39	373.16	7	72
C_1 Dibenzothiophene	310.31	322.00	251	100
C_2 Dibenzothiophene	324.92	343.20	30	27
C_3 Dibenzothiophene	338.81	357.81	29	14

Response Factors

- Relates signal to concentration
- Based on fragmentation



Response Factor Results

Compound	Response factor for ion		% RSD
	Actual Base Ion	m/z 156	
Naphthalene	0.918	-	5.000
1-ethylnaphthalene	1.434	0.645	6.667
1,2-dimethylnaphthalene	1.073	0.950	7.667
2,3-dimethylnaphthalene	1.477	1.477	7.333

- Significant differences
- Limited number of isomers

Conclusion

- Single ion SIM will lead to overestimation
- Single pattern to quantify all homologs will underestimate
  - Must use multiple patterns
  - GC-GC/MS good method for library building
- Response factors are fragmentation specific
  - Manufacture necessary for accurate quantiation

Acknowledgements

The U.S. Environmental Protection Agency (ORD and Regions)
The U.S. Department of Defense (Army and Air Force)
State Department's of Environmental Protection

- Florida
- Massachusetts
- New Jersey
- North Carolina
- Illinois
- Tennessee

The Electric Power Research Institute
Agilent Technologies
Ion Signature Technology
Gerstel
RVM Scientific
Irish Distillers
Tufts University

Real-Time Measurement of EPA Regulated Volatile and Semivolatile Contaminants in the Field Using a New Toroidal Ion Trap GC-TMS

Douglas Later
Torion Technologies, Inc.
796 E. Utah Valley Drive, Ste 200
American Fork, UT 84003
801-705-6601
doug.later@torion.com

ABSTRACT

A wide variety of environmental sample matrices, including liquids and solids are routinely sampled and transported to a central laboratory where they are processed using laboratory instrumentation. Detecting target environmental analytes in real-time at the sampling site using a hand-portable miniaturized gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS) can reduce sampling costs, increase sample throughput, and provide time-effective data, even with complex matrix samples.

Environmental compound mixtures are introduced to the GC-TMS system using a solid phase microextraction (SPME) fiber with a 65 µm polydimethylsiloxane-divinylbenzene (PDMS/DVB; Supelco, Bellefonte, PA) coating that is exposed to the sample for ~5-60 seconds. Separation occurs on a resistively heated low thermal mass (LTM) capillary GC (MTX-5, 5 m x 0.1 mm, 0.4 µm df) coupled directly to the TMS. Most compounds of environmental concern can be detected using this GC-TMS that demonstrates unit mass resolution or better over a mass range of 50-500 Daltons. Embedded peak deconvolution algorithms are used to deconvolve co-eluting peaks and confirm the identification of environmental target analytes by comparison with a user-defined, pre-loaded compound library. Detection limits in the low picogram range are possible.

Examples of the instruments performance with volatile and semivolatile organic compounds will be highlighted in this presentation. For example, a mixture of U.S. Environmental Protection Agency's (EPA) 624 volatile halocarbon organic compounds was spiked into culinary tap water. After exposure of the PDMS/DVB SPME fiber to the spiked water sample for ~ 10 seconds and injection into the GC-TMS, 24 of 26 compounds were chromatographically resolved in less than 65 seconds with positive identification of all 26 target analytes achieved using the deconvolution software. Other toxic industrial compounds (TICs), including dimethyldisulfide, pentafluorotribenzyl-phosphate, pyridine, 4-chloroacetophenone, hexachlorobenzene, dinitrotoluene, 2-4 ring neutral polycyclic aromatic hydrocarbons (PAH) and diethylphthalate, as well as several chemical warfare agents and their precursors and simulants, have also been analyzed and included in the GC-TMS library. Selected examples of such semivolatile analytes will also be presented and discussed to illustrate the functionality and application of this new innovative technology for contaminant measurement in real time during field sampling.

TORION

Environmental Measurement Symposium

Real-Time Measurement of EPA Regulated Volatile and Semivolatile Contaminants in the Field Using a New Toroidal Ion Trap GC-TMS

Douglas W. Later, Christopher R. Bowerbank, Tiffany C. Wirth,
Joseph L. Oliphant, and Edgar D. Lee
Torion Technologies, Inc., American Fork, Utah

Innovative Approaches to Analyzing Conventional and Emerging Pollutants
NEMC 2008

Presentation Outline

- Analytical Field Measurements: Criteria & Trends
- Why GC-TMS
- Instrumentation:
  - SPME Sampling and Injection
  - Capillary Gas Chromatography
  - Toroidal Ion Trap Mass Spectrometer
- Examples of Environment Analyses
  - Volatiles
  - Trihalomethanes
  - Semivolatiles

TORION™

Criteria of Field Measurement

Analyte to be detected	Determination of agents most likely to be encountered
Sensitivity	Lowest concentration of target analyte that results in positive response; ideally, lower than levels necessary for injury to personnel
Resistance to interference	Factors such as smoke, moisture, or other chemicals that prevent the device from accurately providing a response
Response time	Time to collect, analyze, and provide feedback
Start-up time	Time to assemble and deploy the device
Detection status	Vapor, liquid, and/or aerosols
Alarm capability	Audible, visual, or both
Portability	Ease of transport, which encompasses weight and dimensions
Power capabilities	Battery versus alternating current
Battery needs	Quantity and type of batteries
Operational environment	Extremes of conditions under which the device operates
Durability	Amount of abuse the device withstands
Procurement costs	Cost per device needed
Operator skill level	Skill involved in using the device
Training requirements	Number of hours and type of educational background required for operation

TORION™

Field Analytical Measurement Trends

- *Faster and faster analysis methods*
- *Increase measurement sensitivity*
- *Increase measurement selectivity*
- *Reliable operation in harsh environments*
- *Increase productivity*
- *Increase data delivery efficiency: quantity +time*
- *Reduce analytical costs*

4 TORION™

Why Mass Spectrometry?

- GC-MS is the legal and laboratory standard for chemical identification
- High sensitivity and high selectivity (especially using GC inlet)
  - High Sensitivity ⇨ Low false negative rates
  - High Selectivity ⇨ Low false positive rates
  - Much higher selectivity than spectroscopic techniques or ion mobility spectrometry (i.e., molecular weight, fragment ions, relative intensities vs. one ion mobility value)

TORION™

Why Ion Trap MS?

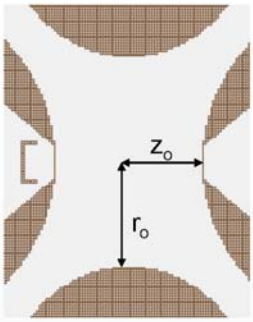
- Simple, rugged design (no critical alignment of ion optics)
- Less stringent vacuum requirements (requires 1 mtorr operating pressure)
- High duty cycle ⇨ High sensitivity
- Low power (especially with small ion trap mass analyzers)

TORION™

Mitigating Factors of Ion Trap MS

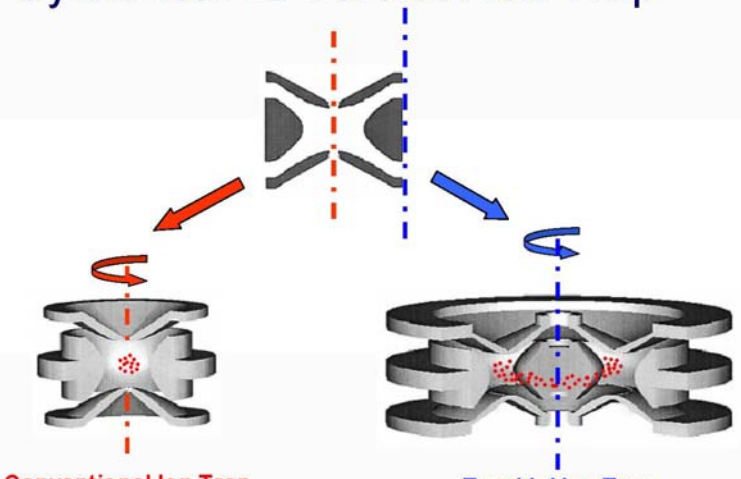
- Barriers to miniaturization
  - 3-D ion trap is an "ion bottle" with somewhat fixed relative dimensions (r_o vs. z_o)
  - Ion-ion repulsion (space charge)
- Commercial traps optimized at r_o = 1 cm, ~16 kV_{p-p}
- Decrease of r_o yields lower rf power (by the square of the reduction), but will lead to earlier onset of space charge

$$q = \frac{-8eV}{m(r_0^2 + 2z_0^2)\Omega^2}$$



TORION™

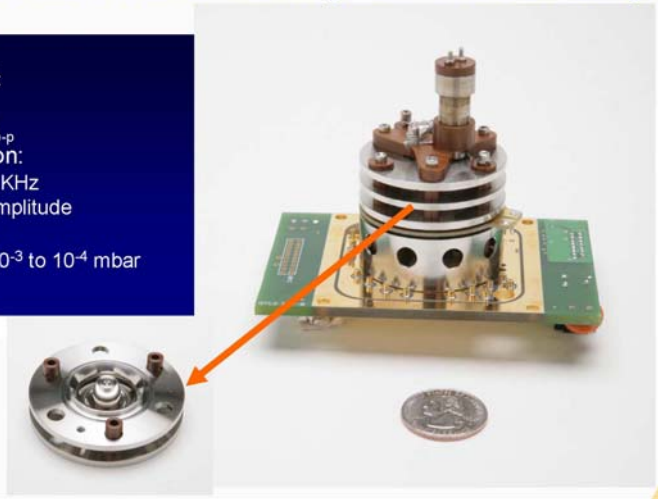
Cylindrical vs Toroidal Ion Trap



TORION™

TMS Electrodes and Analyzer Assembly

- RF Trapping Field:
  - ~ 4 MHz
  - ~ 1200 (max) V_{p-p}
- Resonance Ejection:
  - ~1.6 MHz - 110 KHz
  - ~3.5 to -1.5 V amplitude
- Pressures:
  - He buffer gas: 10^{-3} to 10^{-4} mbar
- CEM Detector



TORION™

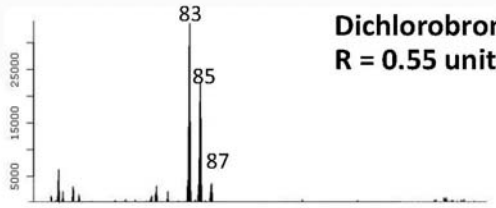
GUARDION ™ -7 GC-TMS

Specifications

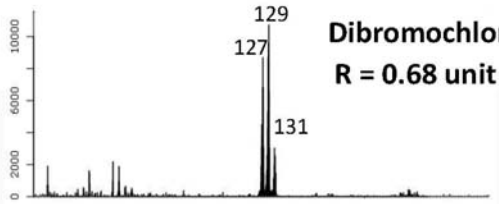
- **Dimensions:** 47 cm x 36 cm x 18 cm
- **Weight:** <13 kg or 28 lbs (including batteries)
- **Peak Power**: ~ 80 W
- **Sample Introduction**: SPME
- **GC**: RTX-5, 5 m x 0.1 mm x 0.4 µm
- **TMS:** Toroidal Ion Trap
- **Mass Range**: 45 to >500 Daltons
- **Resolution**: < Unit mass
- **Vacuum**: turbo molecular and roughing pumps
- **~50 Analyses**: battery power
- **~100 Analyses**: cartridge He gas supply

TORION™

TMS Resolution > Unit Mass



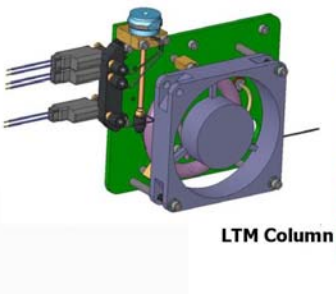
Dichlorobromomethane
R = 0.55 unit



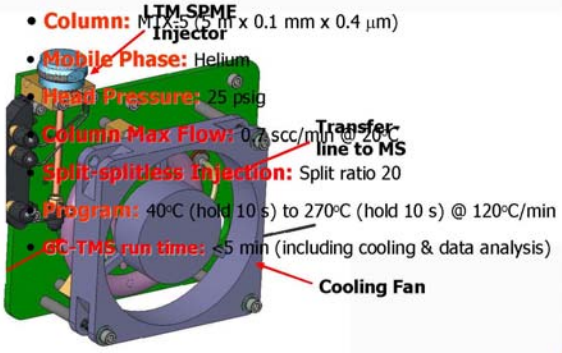
Dibromochloromethane
R = 0.68 unit

TORION™

LTM Capillary Gas Chromatograph



- **Column:** MTX-5 (5 m x 0.1 mm x 0.4 μm)
- **Mobile Phase:** Helium
- **Head Pressure:** 25 psig
- **Column Max Flow:** 0.7 scc/min @ 20°C
- **Split-splitless Injection:** Split ratio 20
- **Program:** 40°C (hold 10 s) to 270°C (hold 10 s) @ 120°C/min
- **GC-TMS run time:** <5 min (including cooling & data analysis)



TORION™

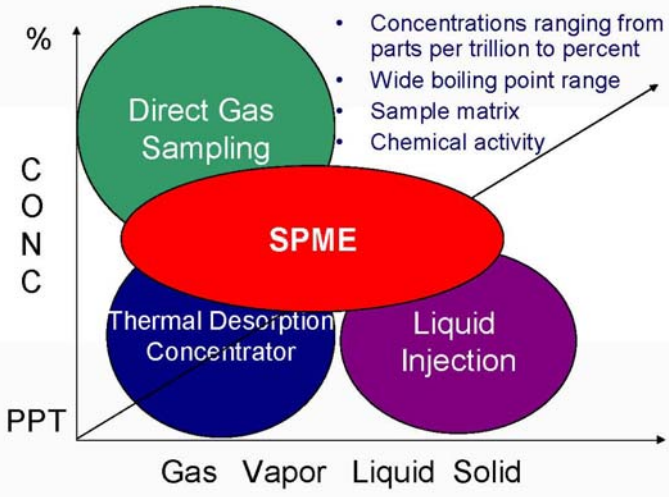
SPME Sample Collection-Injection

Sampling Techniques

- Head Space
- Direct Immersion
- Direct Contact

TORION™

The Challenge of a Universal Sampler



- Concentrations ranging from parts per trillion to percent
- Wide boiling point range
- Sample matrix
- Chemical activity

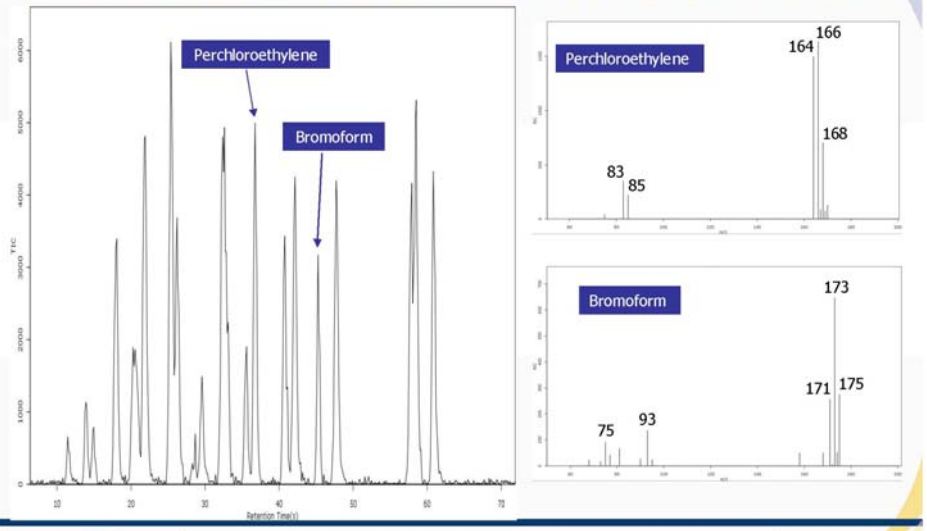
TORION™

Examples of Environmental Applications

- EPA 624 Volatile Halocarbons
  - Spiked into Drinking Water
  - Detected in a Soil SRM
- Trihalomethanes (THMs) in Drinking Water
- EPA 8270 Semivolatiles in Water
  - Different SPME Phase

TORION™

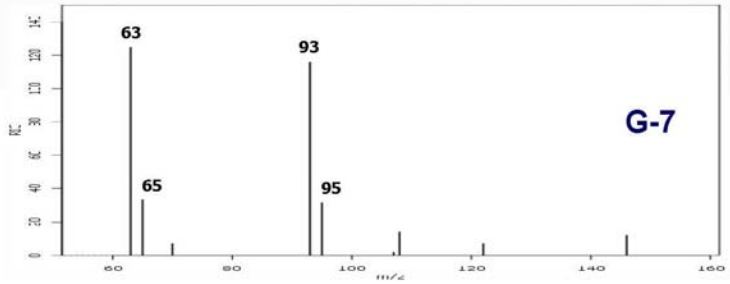
EPA Method 624 Volatile Halocarbons

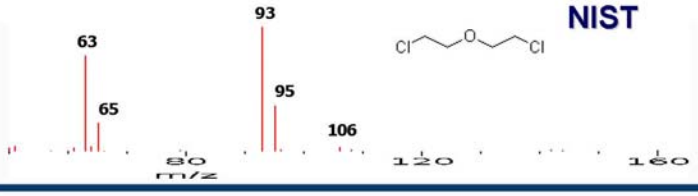


TORION™

Spiked into Drinking Water: 1-10 ppm

Mass Spectra: Bis(2-chloroethyl)ether

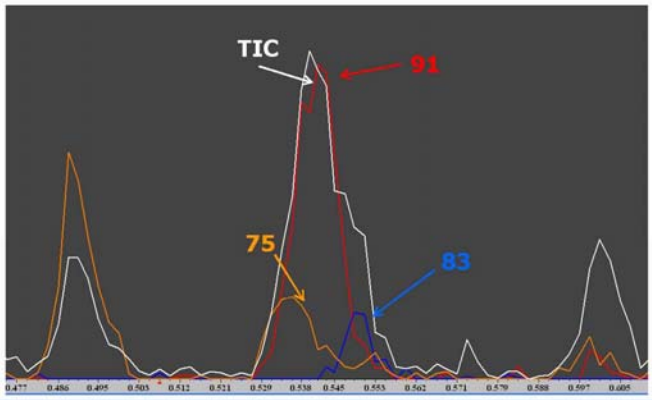




TORION™

Peak Deconvolution and Identification

- Original mass spectral data effectively resolved into components
- Extract accurate individual mass spectra for each analyte
- Accurately distribute the signal from masses shared by several components



TORION™

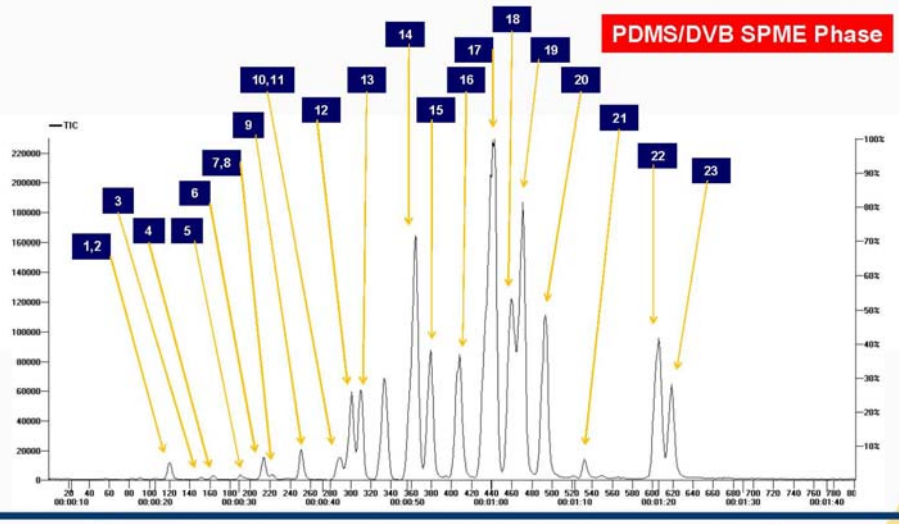
Sampling Procedure
VOCs in Soil

- 1g of Soil SRM into 3mL H_2O
- Initial Column Temperature: 40 ºC
- Extraction: Shook sample for 10 seconds, then sampled headspace with SPME for 50 seconds, repeated 5 times at room temperature
- SPME: PDMS/DVB phase—direct exposure

TORION™

VOCs in Soil (23 of 42 compounds identified)

PDMS/DVB SPME Phase



TORION™

Soil Standard Reference Material

VOCs in Soil

(23 of 42 compounds identified)

1	carbon tetrachloride	13	xylene
2	benzene	14	isopropylbenzene
3	trichloroethene	15	bromobenzene
4	bromodichloromethane	16	1,3,5-trimethylbenzene
5	cis-1,3-dichloropropene	17	1,2,4-trimethylbenzene
6	toluene	18	1,3-dichlorobenzene
7	trans-1,3-dichloropropene	19	1,4-dichlorobenzene
8	1,1,2-trichloroethane	20	1,2-dichlorobenzene
9	tetrachloroethene	21	1,2-dibromo-3-chloropropane
10	chlorobenzene	22	1,2,4-trichlorobenzene
11	1,1,1,2-tetrachloroethane	23	naphthalene
12	ethylbenzene		

TORION™

VOCs in Soil

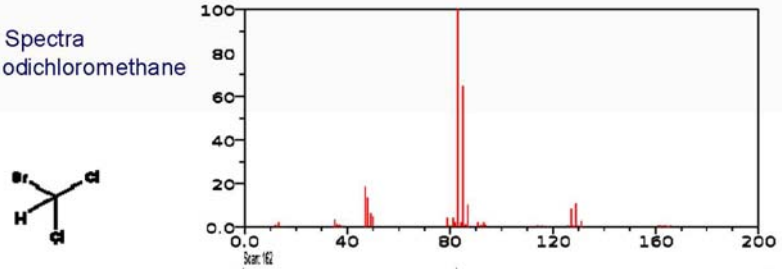
(19 of 42 compounds not identified)

1	1,1,1-Trichloroethane	11	bromomethane
2	1,1,2,2-Tetrachloroethane	12	chloroethane
3	1,1-dichloroethylene	13	chloroform
4	1,2,3-trichloropropane	14	chloromethane
5	1,2-dichloroethane	15	cis-1,2-dichloroethylene
6	2-butanone	16	MTBE
7	2-hexanone	17	methylene chloride
8	4-methyl-2-pentanone	18	Styrene
9	acetone	19	Trichlorofluoromethane
10	bromoform		

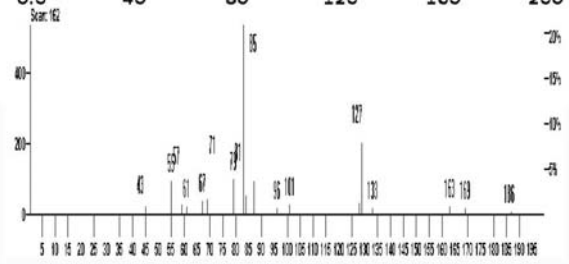
TORION™

Bromodichloromethane

NIST Spectra
Bromodichloromethane



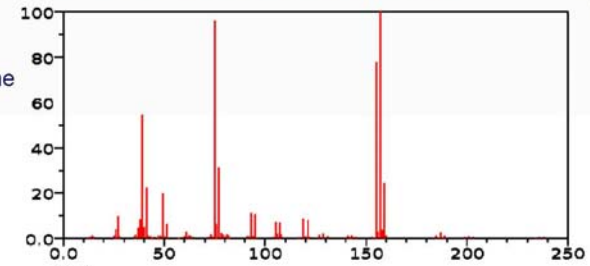
GUARDION-7 Spectra
Bromodichloromethane

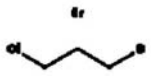


TORION™

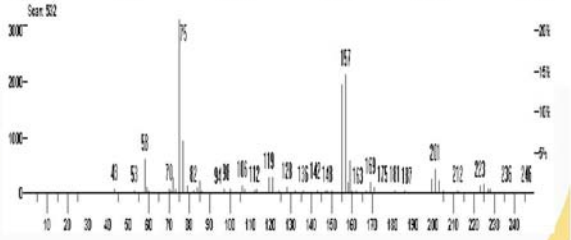
1,2-Dibromo-3-chloropropane

NIST Spectra
1,2-Dibromo-3-chloropropane





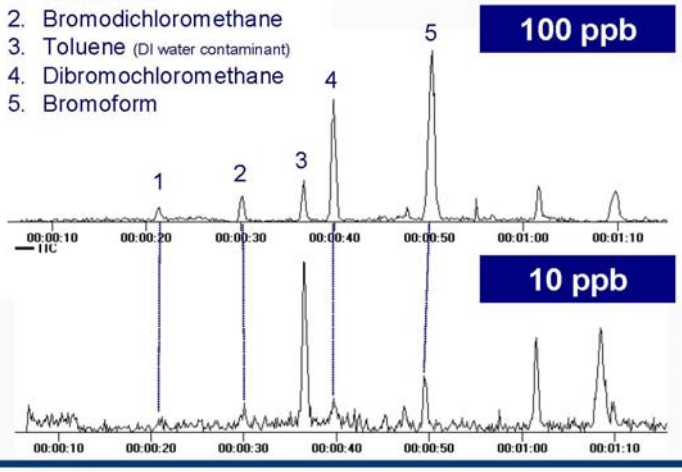
GUARDION-7 Spectra
1,2-Dibromo-3-chloropropane



TORION™

SPME Analysis of Trihalomethanes

1. Chloroform
2. Bromodichloromethane
3. Toluene (DI water contaminant)
4. Dibromochloromethane
5. Bromoform



TORION™

Spiked into Drinking Water: 0.01-0.10 ppm

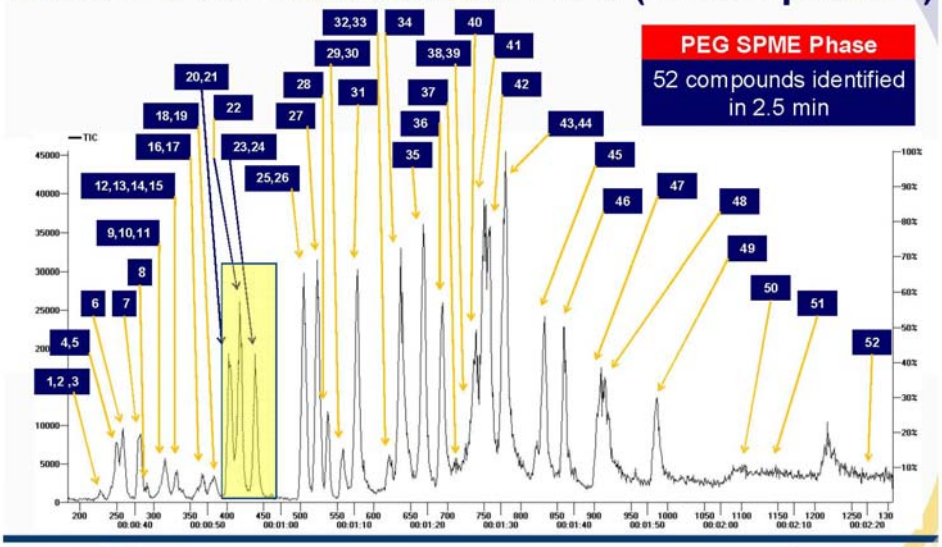
Sampling Procedure

8270 Semivolatiles in Water

- 20µL of 8270 Megamix into 10mL H_2O
- Initial Column Temperature: 80 ºC
- Extraction: Immersion of SPME fiber for 5 seconds in sample for sample collection
- SPME: 3 phases used:
  - PDMS/DVB/CAR
  - PEG
  - PDMS/DVB

TORION™

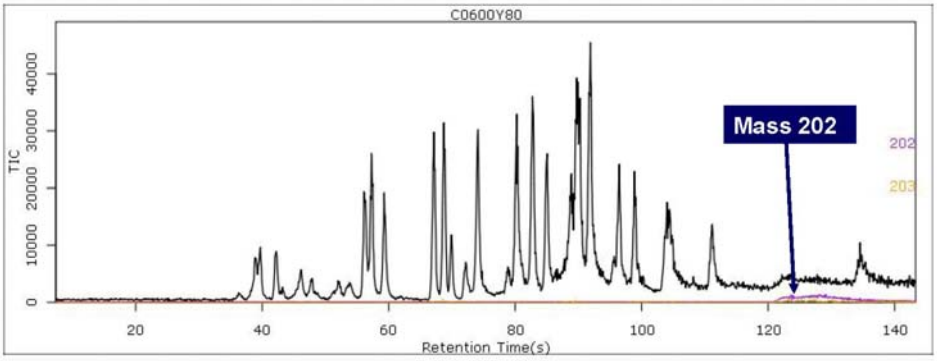
EPA 8270 Semivolatiles Standard (76 compounds)



TORION™

Spiked into Tap Water: 1-10 ppm each

Fluoranthene and Pyrene Elution



TORION™

8270 Semivolatile Compounds in Water

(52 of 76 compounds identified)

1	Aniline	19	2,4-Dimethylphenol	37	2,4-Dinitrotoluene
2	Phenol	20	2,4-Dichlorophenol	38	2,3,4,6-Tetrachlorophenol
3	Bis(2-chloroethyl)ether	21	1,2,4-Trichlorobenzene	39	2,3,5,6-Tetrachlorophenol
4	2-Chlorophenol	22	Naphthalene	40	Diethylphthalate
5	1,3-Dichlorobenzene	23	4-Chloroaniline	41	4-Chlorophenyl phenyl ether
6	1,4-Dichlorobenzene	24	Hexachlorobutadiene	42	Fluorene
7	1,2-Dichlorobenzene	25	4-Chloro-3-methylphenol	43	Diphenylamine
8	Bis(2-chloroisopropyl)ether	26	2-Methylnaphthalene	44	Azobenzene
9	Benzyl alcohol	27	1-Methylnaphthalene	45	4-Bromophenyl phenyl ether
10	N-Nitroso-di-n-propylamine	28	Hexachlorocyclopentadiene	46	Hexachlorobenzene
11	Hexachloroethane	29	2,4,6-Trichlorophenol	47	Phenanthrene
12	2-Methylphenol	30	2,4,5-Trichlorophenol	48	Anthracene
13	4-Methylphenol	31	2-Chloronaphthalene	49	Di-n-butylphthalate
14	3-Methylphenol	32	2-Nitroaniline	50	Fluoranthene
15	Nitrobenzene	33	Dimethylphthalate	51	Pyrene
16	Isophorone	34	Acenaphthylene	52	Benzyl butyl phthalate
17	2-Nitrophenol	35	Acenaphthene		
18	Bis(2-chloroethoxy)methane	36	Dibenzofuran		

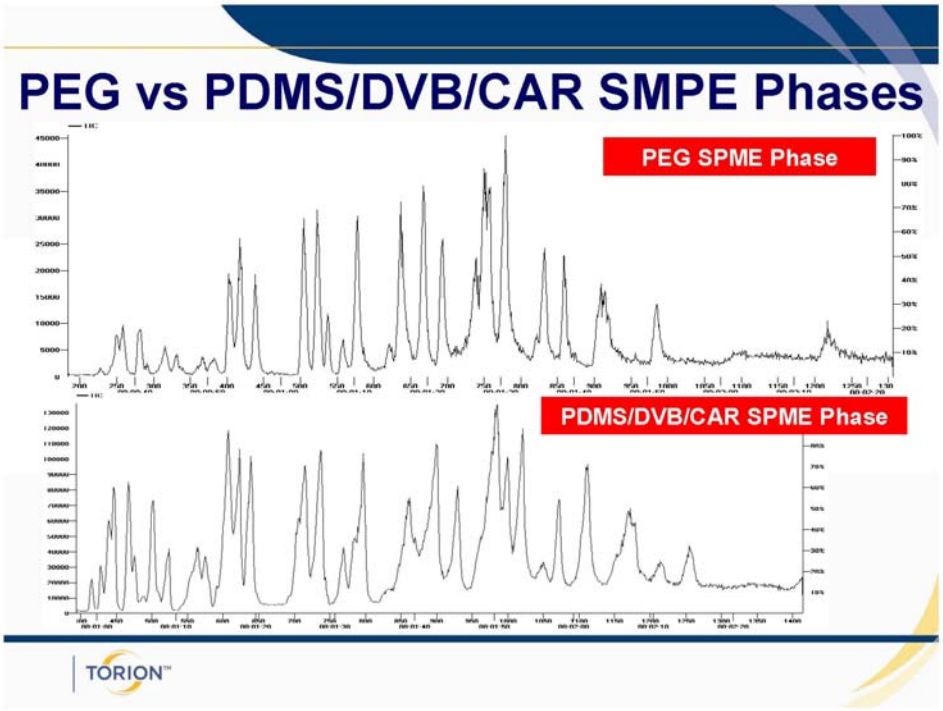
TORION™

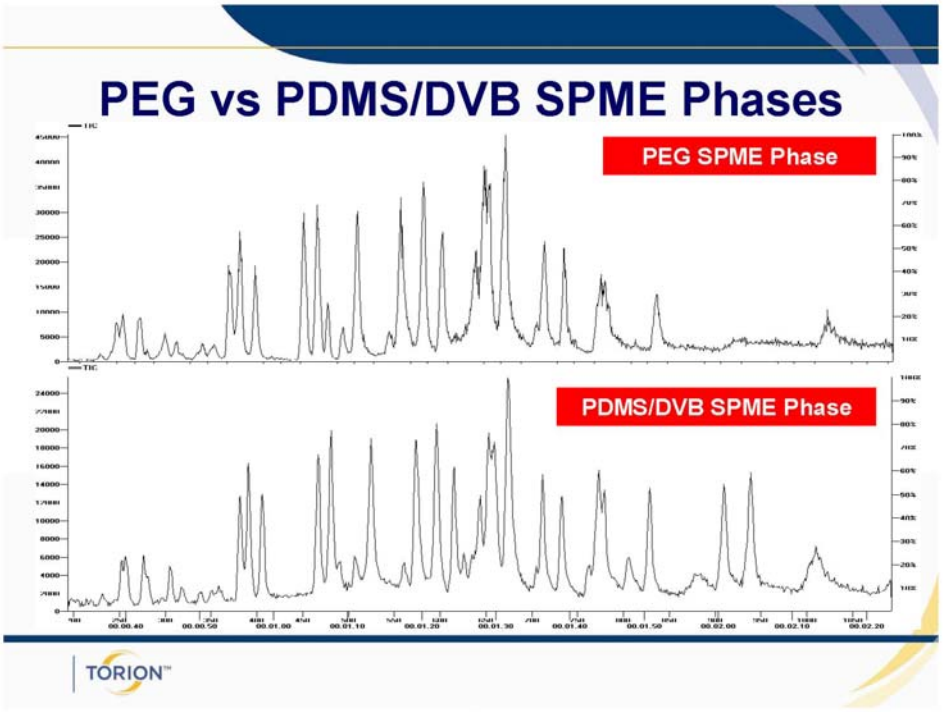
8270 Semivolatile Compounds in Water

(24 of 76 compounds not identified)

1	Nitrosodimethylamine	13	carbazole
2	Pyridine	14	bis(2-ethylhexyl)adipate
3	1,4-dinitrobenzene	15	benz(a)anthracene
4	1,3-dinitrobenzene	16	chrysene
5	2,6-dinitrotoluene	17	bis(2-ethylhexyl)phthalate(dioctyl)
6	1,2-dinitrobenzene	18	di-n-octyl phthalate
7	3-nitroaniline	19	benzo(b)fluoranthene
8	2,4-dinitrophenol	20	benzo(k)fluoranthene
9	4-nitrophenol	21	benzo(a)pyrene
10	4-nitroaniline	22	indeno(1,2,3-cd)pyrene
11	4,6-dinitro-2-methylphenol	23	dibenz(a,h)anthracene
12	pentachlorophenol	24	benzo(g,h,i)perylene

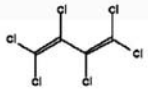
TORION™

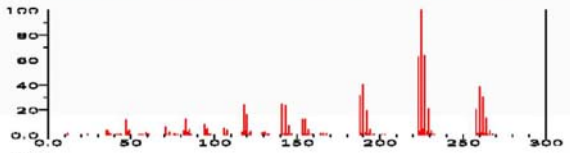

PEG vs PDMS/DVB/CAR SMPE Phases
PEG SPME Phase
PDMS/DVB/CAR SPME Phase
TORION


PEG vs PDMS/DVB SPME Phases
PEG SPME Phase
PDMS/DVB SPME Phase
TORION

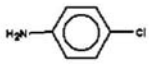
Hexachlorobutadiene & 4-Chloroaniline

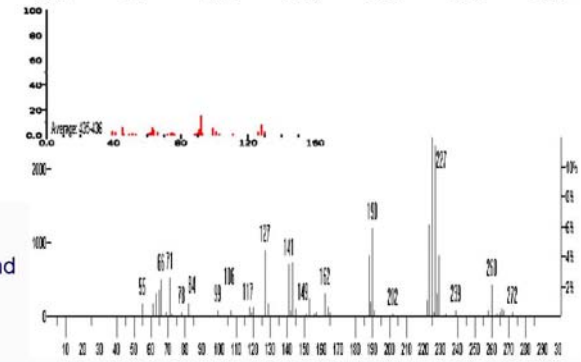
NIST Spectra
Hexachlorobutadiene





NIST Spectra
4-Chloroaniline



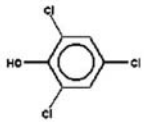


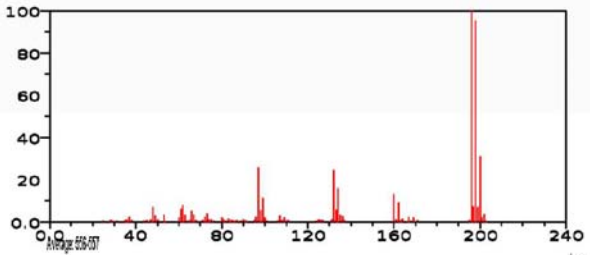
GUARDION-7 Spectra
Hexachlorobutadiene and
4-Chloroaniline

TORION™

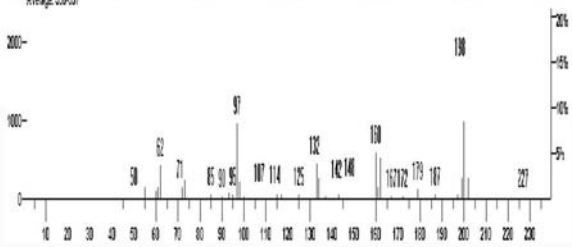
2,4,6-Trichlorophenol

NIST Spectra
2,4,6-Trichlorophenol





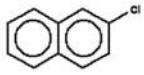
GUARDION-7
Spectra
2,4,6-Trichlorophenol

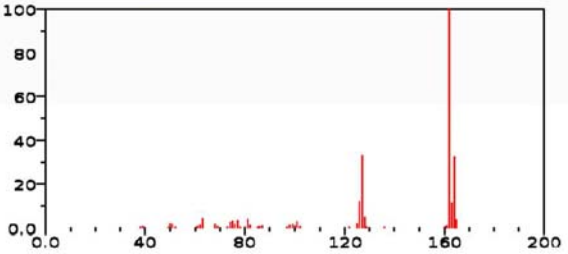


TORION™

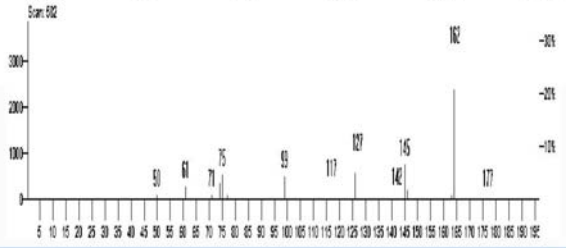
2-Chloronaphthalene

NIST Spectra
2-Chloronaphthalene





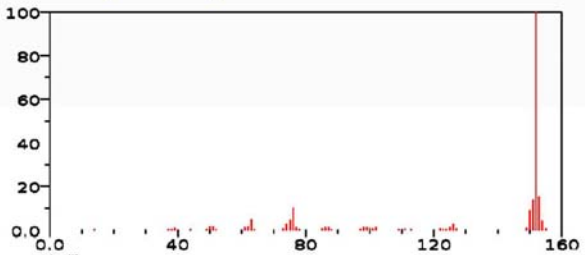
GUARDION-7 Spectra
2-Chloronaphthalene



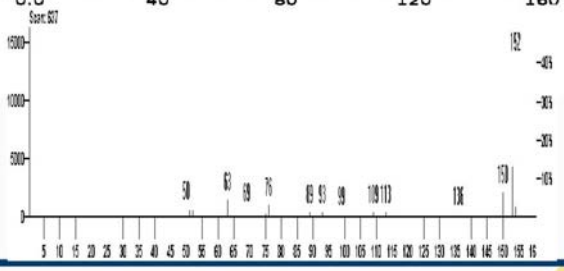
TORION™

Acenaphthylene

NIST Spectra
Acenaphthylene



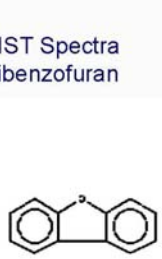
GUARDION-7 Spectra
Acenaphthylene

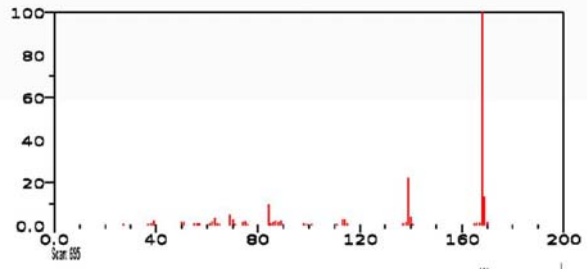


TORION™

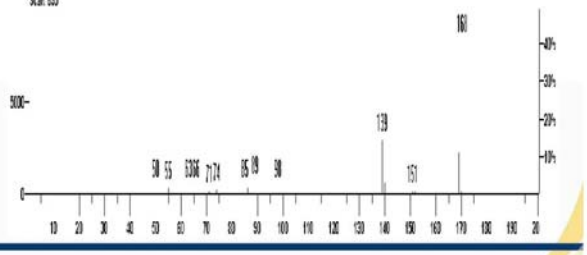
Dibenzofuran

NIST Spectra
Dibenzofuran





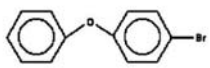
GUARDION-7 Spectra
Dibenzofuran

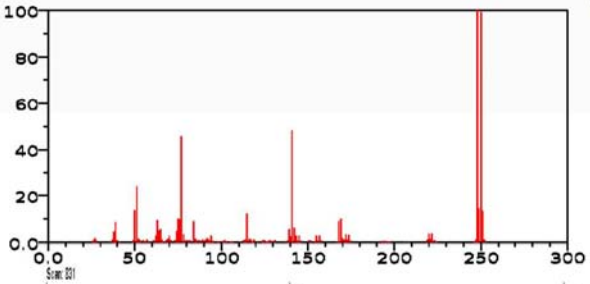


TORION™

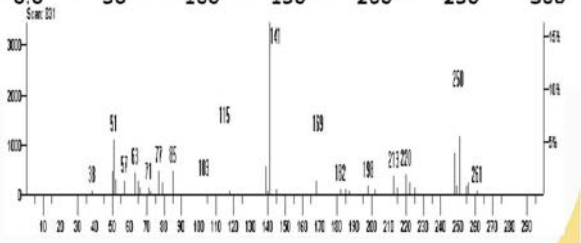
4-Bromophenyl phenyl ether

NIST Spectra
4-Bromophenyl phenyl ether





GUARDION-7 Spectra
4-Bromophenyl phenyl ether



TORION™


Thank You for Participating Today
TORION TECHNOLOGIES INC.
Solid Science— Creative Ideas— Innovative Products
TORION™

Hydrazine - A New Analytical Approach

Ali Haghani, Dr. Andrew Eaton, and Dr. Jim Wan; MWH Laboratories, 750 Royal Oaks #100, Monrovia, CA 91016; 626-386-1138; ali.haghani@mwhglobal.com

ABSTRACT

Hydrazine has been used extensively for the past half of the century. Annually 260 tons are manufactured and used in many applications including in defense, Pharmaceuticals, power and in aerospace industries. In addition to manufacturing, two studies one by Shank and Whitaker (1998) and the other one by Najm et al (2005) demonstrated that hydrazine can be potentially formed during chloramination as disinfection byproduct (DBP) under high free ammonia and/or high pH in drinking water.

Hydrazine is classified by the U.S. Environmental Protection Agency (EPA) as a "probable human carcinogen" with a 10-6 cancer risk level of 10 ppt (ng/L) in drinking water. Same level of toxicity seen in NDMA another DBP associated with use of chloramination during water treatment. In 2008 EPA published their CCL3 (Contamination Candidate List3) for potential future collection of nationwide occurrence data through UCMR3 (Unregulated Contaminant Monitoring Rule 3) and hydrazine was included in the list.

In this context, high-performance analytical method is of essential importance for the precise and accurate monitoring of trace level of hydrazine in aqueous environment. Currently there is no EPA approved method for performing this analysis. The most current and sensitive method that has been published for this compound uses an off-line extraction followed by derivatization and analysis using Gas Chromatography Mass Spectroscopy in tandem in Chemical Ionization mode. With a 250 concentration step one can achieve detections close to the 5 ppt (ng/L) levels.

MWH laboratories have developed a new simplified method for analysis of hydrazine that does not require an off-line enrichment step and it only requires less than 10 ml of sample collection to reach equal or lower than 1 ppt of detection.

The authors will discuss the method approach, the limitation of the method, and provide data on precision and accuracy of the method under routine conditions, and provide data on the Lowest Concentration Minimum Reporting Limit (LCMRL) achievable with this method.

Hydrazine Analysis a New Approach

Ali Haghani
Andrew Eaton, Ph.D.
Jim Wan, Ph.D.

MWH Laboratories
Monrovia, CA 91016
www.mwhlabs.com

Why interest in Hydrazine

- 260 tons annually used.
- (EPA) as a "probable human carcinogen" with a 10^{-6} cancer risk level of 10 ppt (ng/L) in drinking water.
- Another Disinfection byproduct (DBP) associated with chloramination, similar to NDMA.
- Hydrazine is included in Contaminant Candidate List 3 (CCL 3) released in 2008 for possible national monitoring for UCMR 3.
- Developing a method for a pilot study

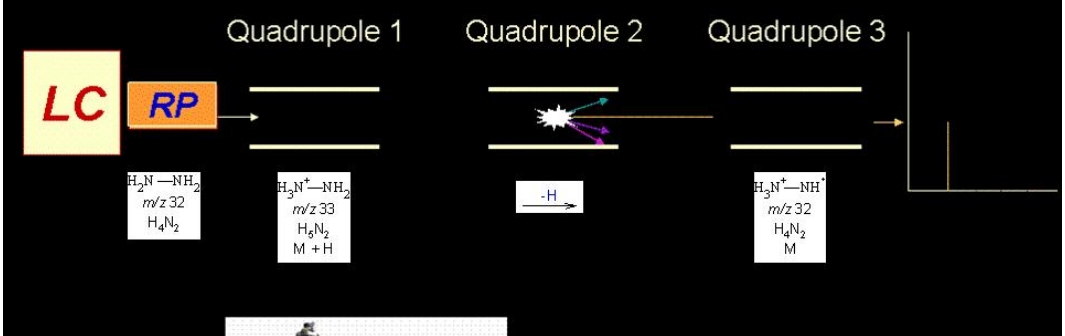
Agenda

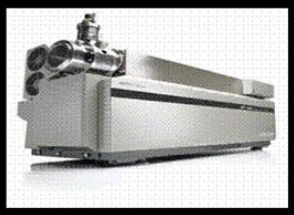
- To demonstrate a brand new method for analysis of hydrazine in aqueous matrices at ppt levels.
- To demonstrate the set up and discuss few analytical challenges encountered and how they were resolved.
- To assess precision and accuracy of the method in real world type matrices.

Currently available methods

- Photometric
- UV
- Fluorescence
- GC
- GCMS, CI

The set up HPLC-SPE-MS/MS : First challenge





MS/ MS scans:
Precursor Ion
Product Ion

The challenges of using LC-MS-MS for hydrazine

- Hydrazine with formula weight of 32 amu is too small to give a reliable fragment:

$H_2N—NH_2$ ***m/z* 32** H_4N_2 **M** → $H_2N—NH_2$ ***m/z* 32** H_4N_2 **M** → $H_3N^+—NH_2$ ***m/z* 33** H_5N_2 **M + H** —(-H)→ $H_3N^+—NH^•$ ***m/z* 32** H_4N_2 **M**

$H_2N—NH_2$ *m/z* 32 H_4N_2 M —(-H)→ $HN^-—NH_2$ *m/z* 31 H_3N_2 M + H - H_2

Octanol-water Partition coefficient poses: The Second challenge

Calculated LogP: -1.19+/- 0.44

LogP for water: -1.38+/- 0.21

LogP for methanol: -0.72+/- 0.18

LogP for Chloromethane: 0.97+/- 0.20

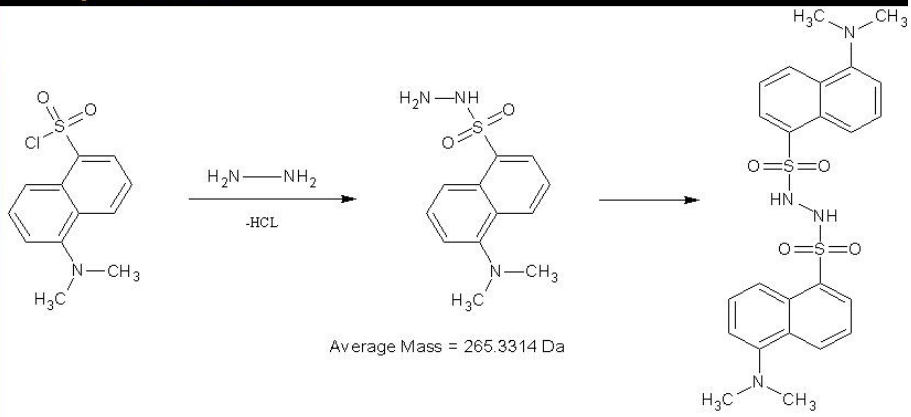
RP technology will not work.

Solution to both challenges was derivatization approach

- Ortho-phthaldehyde (OPA)
- Dansyl chloride
- 9-fluorenylmethoxycarbonyl chloride (FMOC-Cl)
- 2,3-anthracene dicarboxaldehyde (ADA)
- 2,3-naphtalene dicarboxaldehyde (NDA)

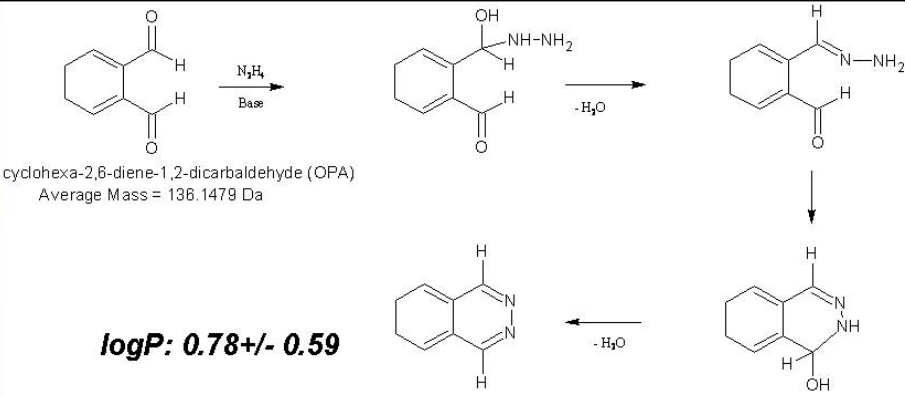
Dansyl-Cl and FMOC-Cl ruled out

- There are more than one possible product:



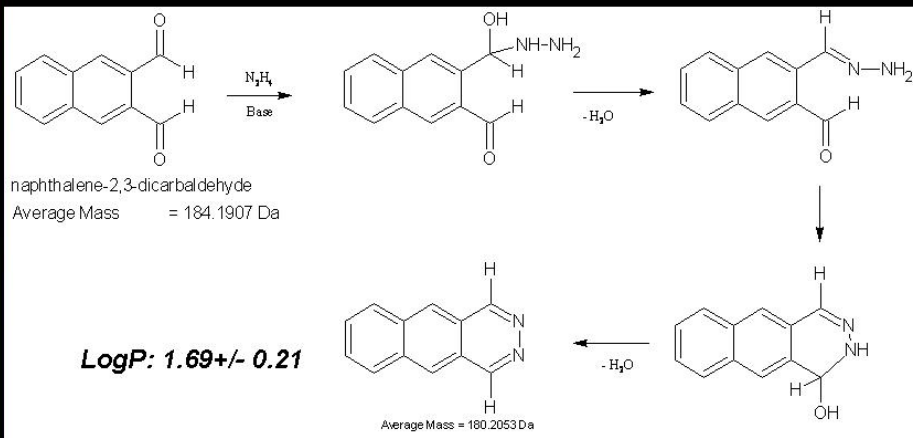
OPA

- Producing one stable derivative



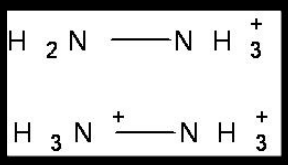
NDA as the derivatization agent

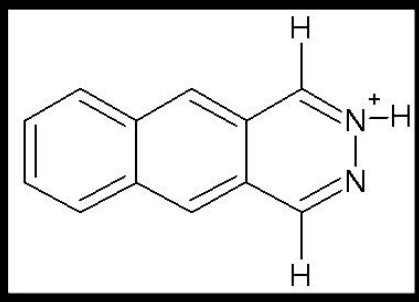
- Generates one stable derivative



Fluorescence tech. done in acidic conditions

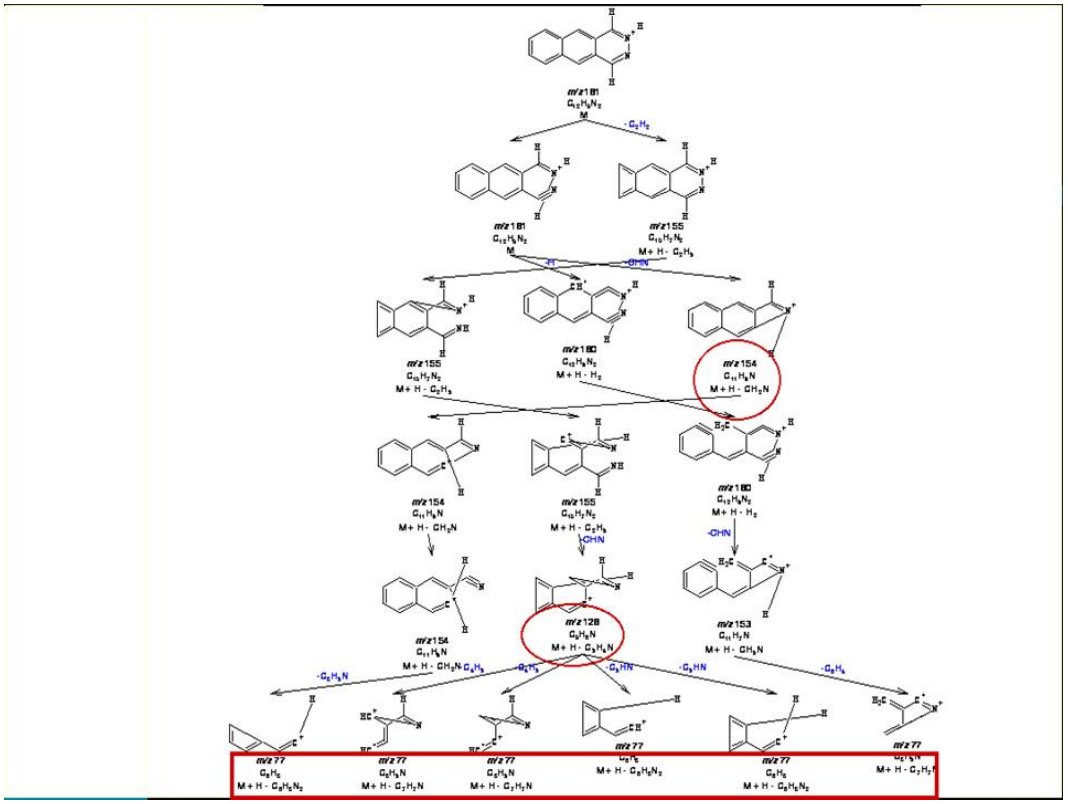
- hydrazine is a base and in acidic environment 99% of hydrazine are in protonated stage which will suppress the nucleophilc reaction.
- In Base the lone pairs are free to react.





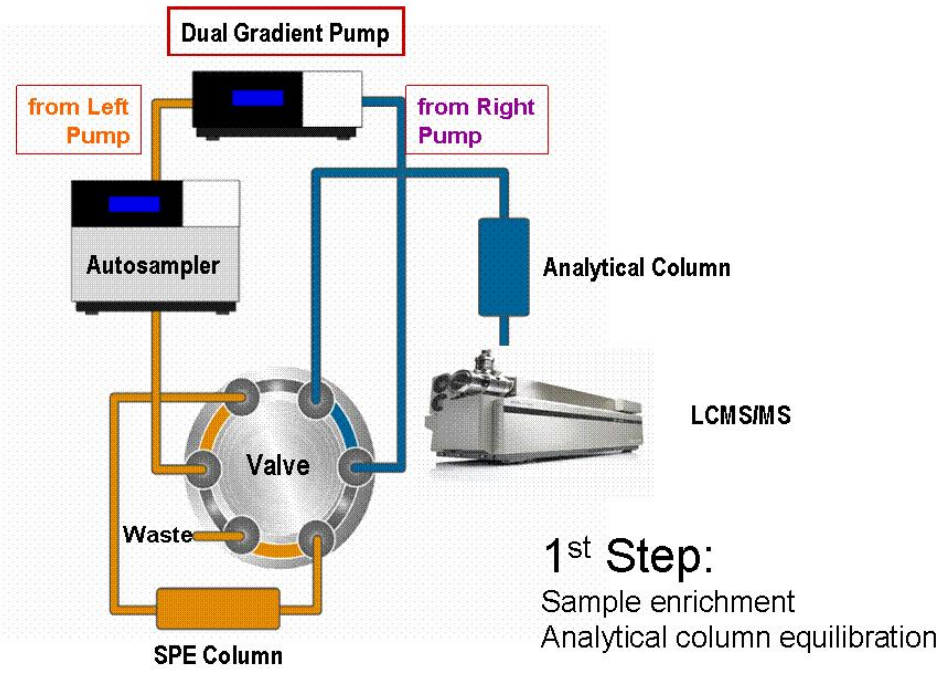
Derivatization optimum conditions

- Due to the lone pairs on the Nitrogen of hydrozine the more basic conditions favors the rate and completion of the reaction.
- In acidic conditions only when pH dropped down to <3, we saw product formations.
- Room ambient temperature worked better than >30C.
- Rate of the reaction was faster than could be measured <1min.

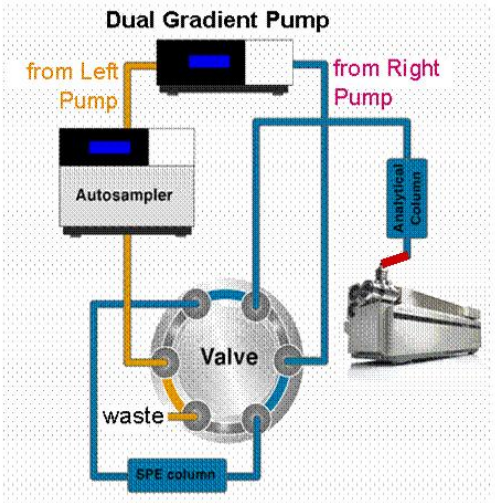


MS/MS Optimization

Compound	Q1	Q3	DP	CE	CXP
Hydrazine	181	154.1	86	33	10
Confirm-1	181	127.1	86	43	8
Confirm-2	181	77	86	69	10
IS-N ^{15}	183	155.1	86	33	10



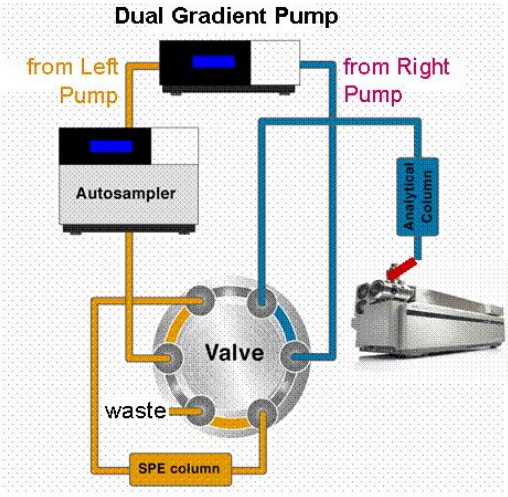
1st Step:
Sample enrichment
Analytical column equilibration



2nd Step:

Transfer to analytical column

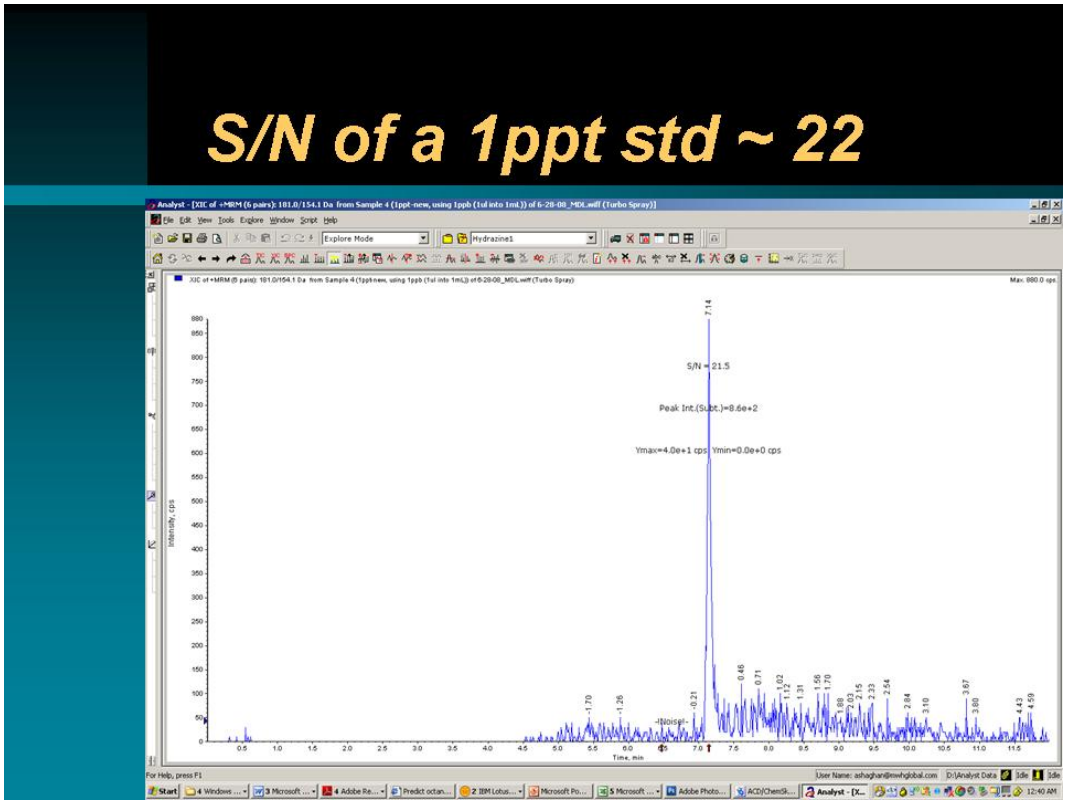
Wash of autosampler

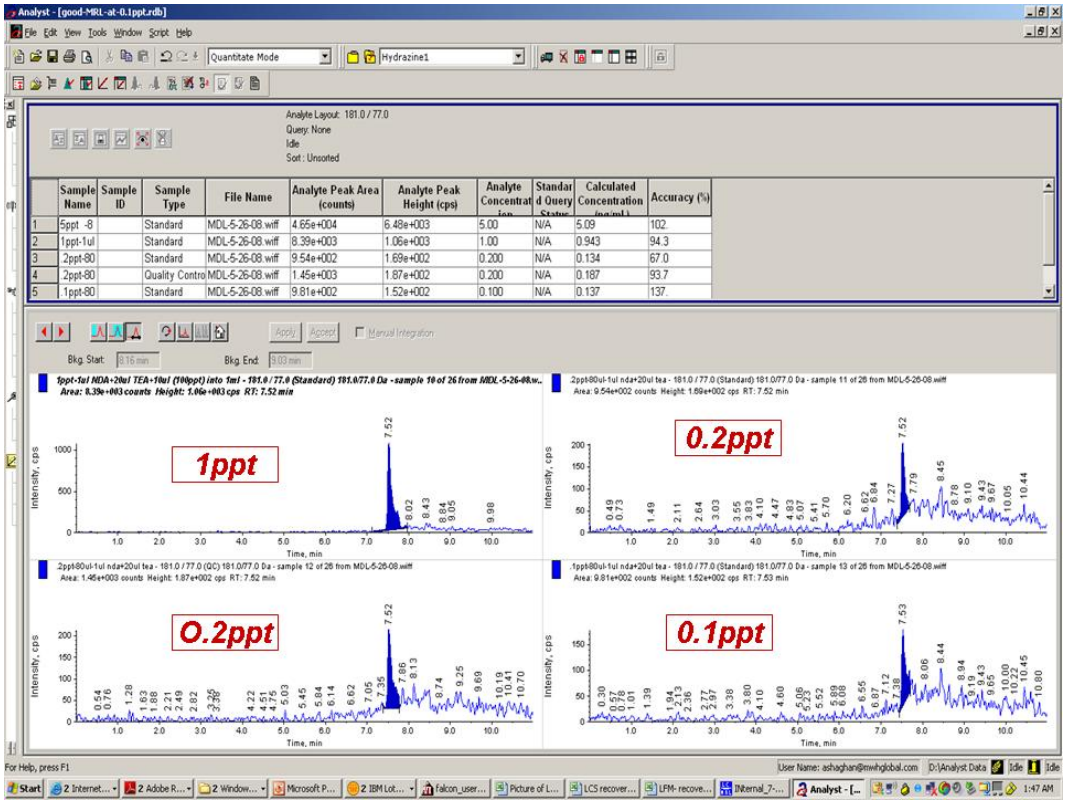


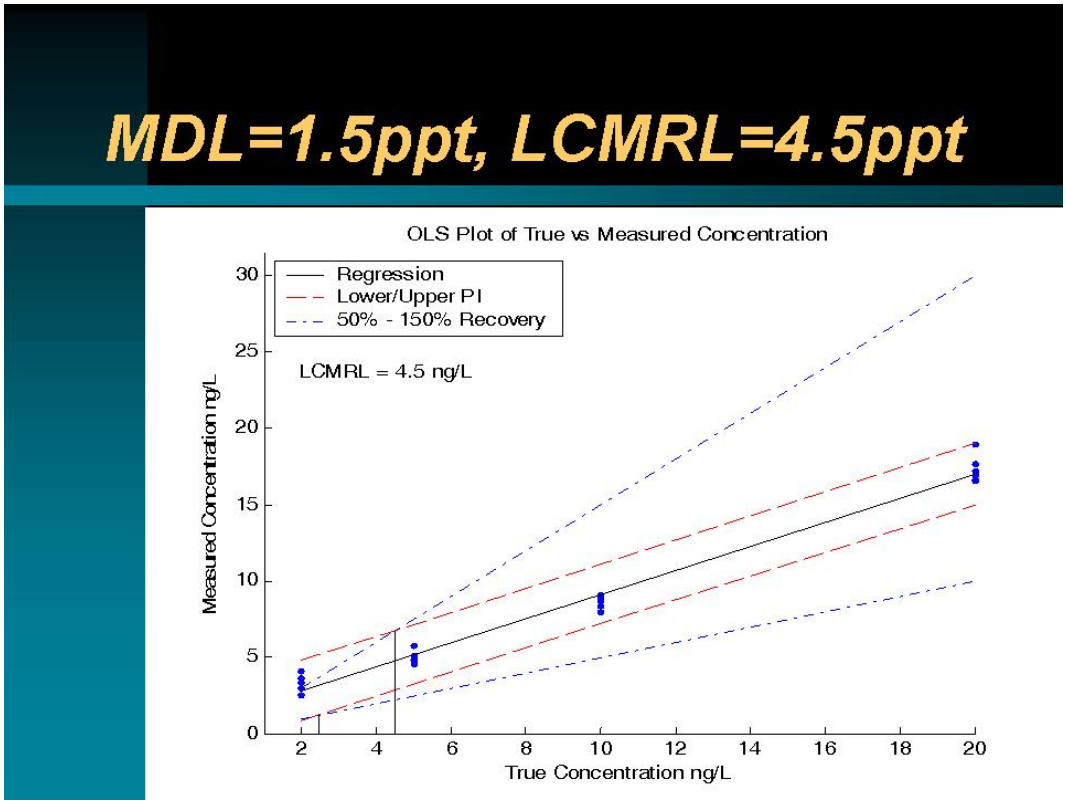
3rd Step:

Analytical separation and detection

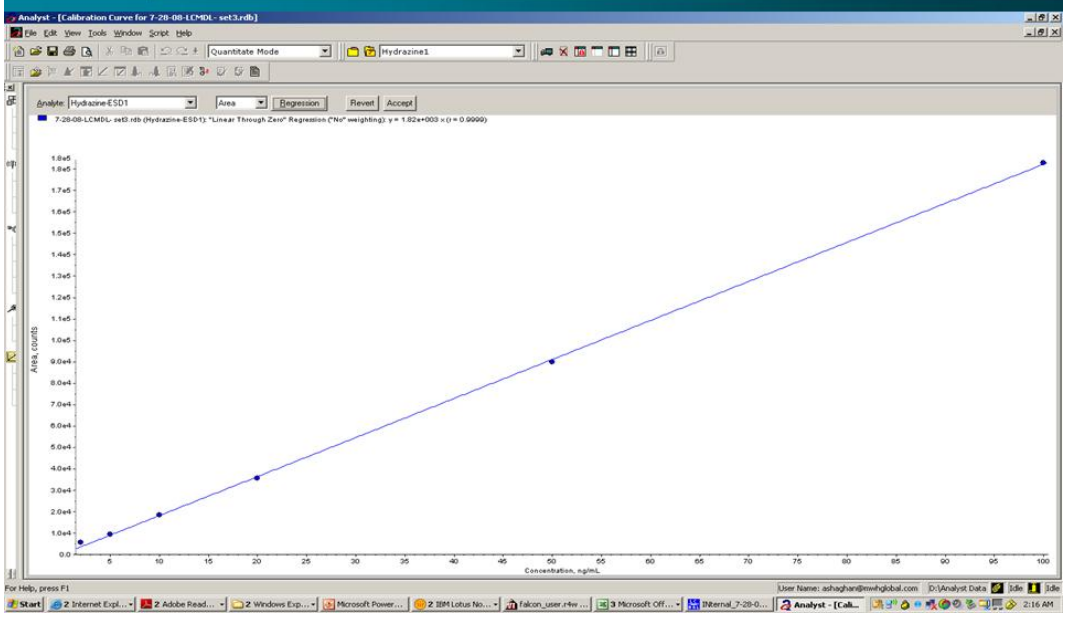
Wash/re-equilibration of SPE column




Analyst - [good-MRL-at-0.1ppt.rdb]
Quantitate Mode
Hydrazine1
Analyte Layout: 181.0 / 77.0
Query: None
Idle
Sort: Unsorted
Sample Name | Sample ID | Sample Type | File Name | Analyte Peak Area (counts) | Analyte Peak Height (cps) | Analyte Concentration | Standard Query Status | Calculated Concentration (ng/mL) | Accuracy (%)
1 | 5ppt -8 | | Standard | MDL-5-26-08.wiff | 4.65e+004 | 6.48e+003 | 5.00 | N/A | 5.09 | 102
2 | 1ppt-1ul | | Standard | MDL-5-26-08.wiff | 8.39e+003 | 1.06e+003 | 1.00 | N/A | 0.943 | 94.3
3 | 2ppt-80 | | Standard | MDL-5-26-08.wiff | 9.54e+002 | 1.69e+002 | 0.200 | N/A | 0.134 | 67.0
4 | 2ppt-80 | | Quality Contro | MDL-5-26-08.wiff | 1.45e+003 | 1.87e+002 | 0.200 | N/A | 0.187 | 93.7
5 | 1ppt-80 | | Standard | MDL-5-26-08.wiff | 9.81e+002 | 1.52e+002 | 0.100 | N/A | 0.137 | 137
Bkg. Start:
Bkg. End:
1ppt
0.2ppt
O.2ppt
0.1ppt
Intensity, cps
Time, min
For Help, press F1
User Name: ashaghan@mwhglobal.com
D:\Analyst Data
Idle
1:47 AM


MDL=1.5ppt, LCMRL=4.5ppt
OLS Plot of True vs Measured Concentration
Regression
Lower/Upper PI
50% - 150% Recovery
LCMRL = 4.5 ng/L
Measured Concentration ng/L
True Concentration ng/L
0
5
10
15
20
25
30
2
4
6
8
10
12
14
16
18
20

Linear through zero
R=0.9999



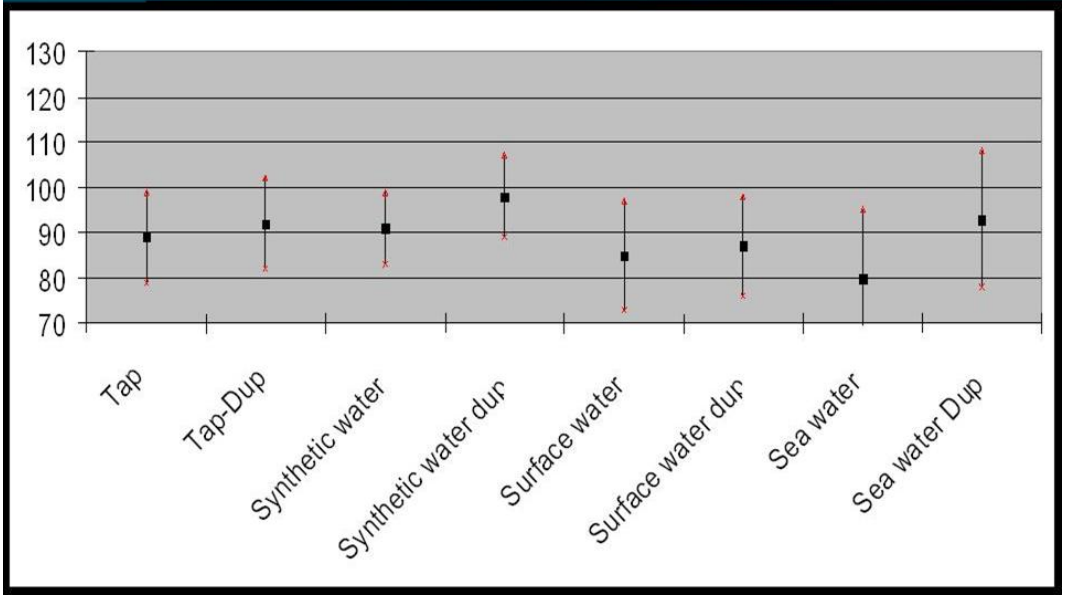
Spike at 5ppt/Hydrazine-D4
Calibrated with Hydrazine
Internal Std Hydrazine-N^{15}

Transition		181->154			181->127			181->77
	IS - based	IS - based	ES - based	IS - based	IS - based	ES - based		ES - based
IS transition	183->155	183->127		183->155	183->127			
Ics1	5.12	5.03	4.13	4.82	4.88	3.85		4.75
Ics2	5.27	5.01	3.68	5.51	4.92	3.84		3.95
Avg Recovery	**3.91**	**5.02**	**3.91**	**5.17**	**4.90**	**3.85**		**4.35**
Ave Recovery %	**78.10**	**100.40**	**78.10**	**103.30**	**98.00**	**76.90**		**87.00**

Cont. 50ppt std

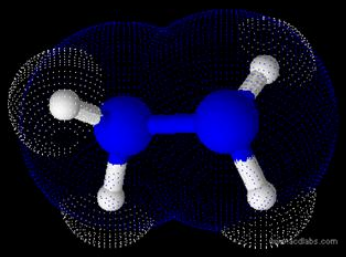
Transition		181->154			181->127			181->77
	IS -based	IS -based	ES -based	IS -based	IS -based	ES -based	ES -based
IS transition	183->155	183->127		183->155	183->127		
Ics1	43.10	45.20	47.90	42.50	45.00	47.20	47.60
Ics2	46.00	46.50	51.40	44.80	45.00	50.10	48.60
Ics3	41.70	44.90	47.40	40.70	43.80	46.30	47.40
Ics4	42.50	43.00	46.30	44.40	44.60	48.50	47.10
Ics5	42.40	43.00	47.70	42.70	43.10	48.00	49.90
Ics6	39.80	43.90	48.10	39.80	44.20	48.20	50.30
Ics7	44.40	43.40	49.30	43.30	42.90	48.10	49.90
Avg Recovery	**42.84**	**44.27**	**48.30**	**42.60**	**44.09**	**48.06**	**48.69**
Ave Recovery%	**85.69**	**88.54**	**96.60**	**85.20**	**88.17**	**96.11**	**97.37**
% RSD	**5%**	**3%**	**3%**	**4%**	**2%**	**2%**	**3%**

MS spiked at 10ppt in triplicates



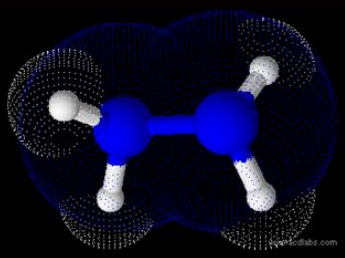
Conclusion

- A new approach for Hydrazine analysis is demonstrated
- This technique can be used for pilot studies



Thank you for your attention

Questions?



Contact:

Ali.Haghani@mwhglobal.com

Andrew.Eaton@mwhglobal.com

Improving Accuracy and Sensitivity for 1,4-Dioxane Analysis

Mark Bruce
TestAmerica, Inc.
4101 Shuffel St. NW
North Canton, OH 44720
330-966-7267
mark.bruce@testamericainc.com

ABSTRACT

Groundwater contamination with 1,4-dioxane has become a common problem since this chemical has been used both as a fuel oxygenate and industrial solvent. Analysis down to the low parts per billion level is needed to support many risk based cleanup or decision thresholds. A variety of analytical techniques have been used over the past 20 years to determine 1,4-dioxane in water samples. Initially sensitivity was limited to parts per million levels using direct aqueous injection into a GC with flame ionization detector. Purge & trap GC/MS volatiles analysis initially produced reporting limits (RL) of about 500 ug/L. The addition of azeotropic distillation sample preparation to the GC-FID improved the reporting limits to about 50 ug/L. Over the years improvements in purge & trap GC/MS technology have improved full scan reporting limits to 100 - 200 ug/L for volatiles analysis. Alternatively liquid-liquid extraction with full scan semivolatile GC/MS analysis produced 10 ug/L reporting limits. Recent sensitivity improvements in semivolatile GC/MS instrumentation have improved reporting limits to 1 ug/L. However, typical 1,4-dioxane recoveries are 30-60% with the semivolatile analysis option.

Recent mass spectrometer instrumentation developments now allow both full scan and selected ion monitoring (SIM) during the same analytical run. This facilitates using SIM for 1,4-dioxane along with a standard volatiles analysis. This advancement has reduced reporting limits to 5 ug/L for the volatiles analysis as well. In addition, calculated analyte recovery generally falls between 80 and 120%. Addition optimizations in the purge and trap system have further reduced the RL to 1 ug/L. Adding a deuterated 1,4-dioxane internal standard at the beginning of the sample preparation process for either the volatile or semi-volatile analysis options improves calculated analyte recovery even further. The choice as to which method is best will depend on a variety of factors including; sensitivity, accuracy, other analytes of interest, turn around time and cost.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Improving Accuracy and Sensitivity for 1,4-Dioxane Analysis

Mark Bruce Ph.D.
Thomas Stiller
Marcel Mol

National Environmental Monitoring Conference
Washington D.C.

August 14, 2008

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

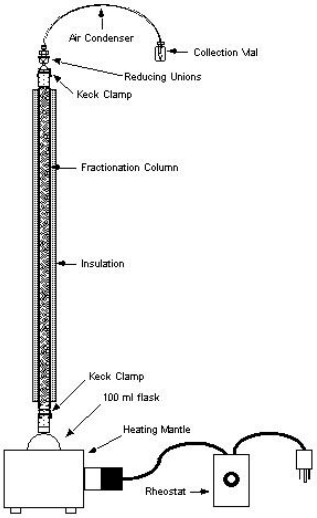
Why look for 1,4-Dioxane?

- Common ground water contaminant
- Uses
  - ~ Fuel oxygenate
  - ~ Solvent
  - ~ Solvent stabilizer
- Byproduct in consumer products
- EPA classification:
  - ~ Group B2, probable human carcinogen
    - One-in-a-million increased cancer risk at 3 ug/L
    - http://www.epa.gov/ttn/atw/hlthef/dioxane.html

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What methods were used?

- Direct aqueous injection, GC-FID (Method 8015)
  - ~ Reporting limit: 1000 ug/L
- Azeotropic distillation, GC-FID (Methods 5031 & 8015)
  - ~ Reporting limit: 40 ug/L



3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What methods were used?

- Liquid / liquid extraction, GC/MS (Method 3520 & 8270)
  - ~ Original reporting limits: 10 ug/L
  - ~ Recent improvements reduced reporting limits:1 ug/L
  - ~ Low biased results

4

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What methods were used?

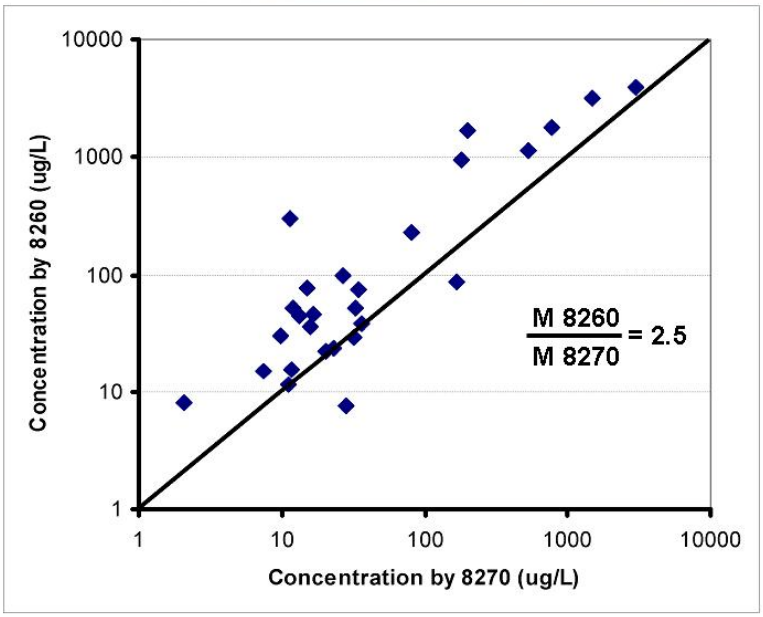
- Purge & Trap, GC/MS (Method 5030 & 8260)
  - ~ Full scan reporting limits: 50 - 200 ug/L
  - ~ Poor purging efficiency

5

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Compare 8260 & 8270 Results

- Method 8260 calibration through sample prep corrects for low absolute recovery



6

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Add Selected Ion Monitoring

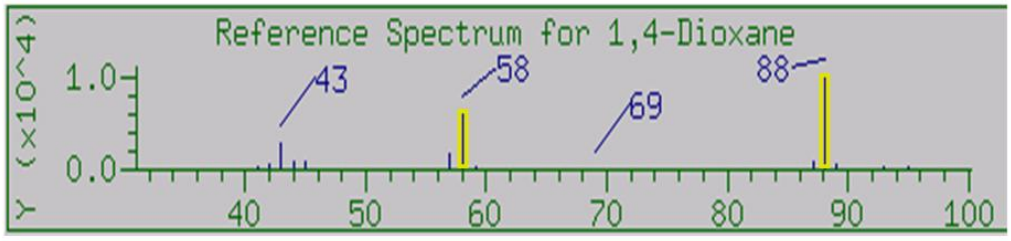
- Purge & Trap, GC/MS (Method 5030 & 8260)
  - ~ SIM reporting limits: <= 5 ug/L
  - ~ Optimized P&T conditions
  - ~ 1,4-dioxane-d8 internal standard
  - ~ Not compromise other VOC analytes
  - ~ Utilize simultaneous Full scan & SIM GC/MS

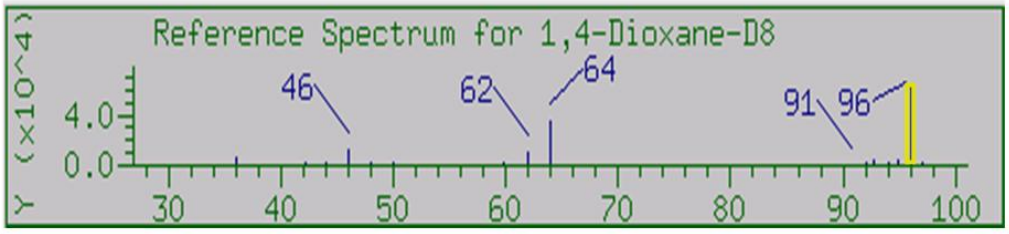
7

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

1,4-Dioxane Spectra

- Ions for selected ion monitoring highlighted in yellow



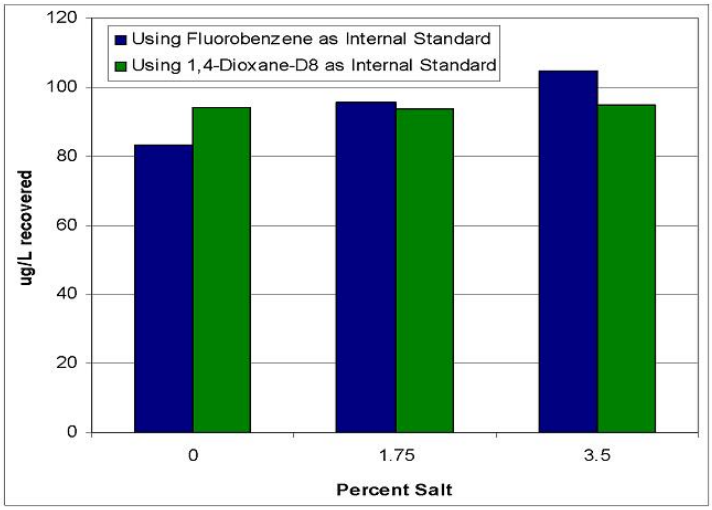


8

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

1,4-Dioxane-d8 is better I.S.

- Deuterated 1,4-dioxane internal standard compensates for matrix effects better



9

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Limited by Carryover

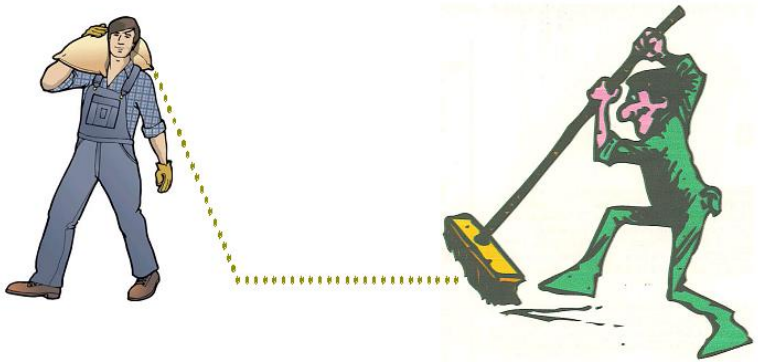
- Low purging efficiency leaves much analyte behind in water
- Analyte carryover into subsequent analyses
  - ~0.5 to 5%
- Longer bake time
- More rinses

10

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Limited by Carryover

- Leads to longer cycle time, reduced productivity, increased cost per run
- Instrument can produce 1 ug/L RL, but carryover limits the practical RL to 5 ug/L
- Investigating claims of reduced carryover P&T systems



11

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Method 8261 Vacuum Distillation

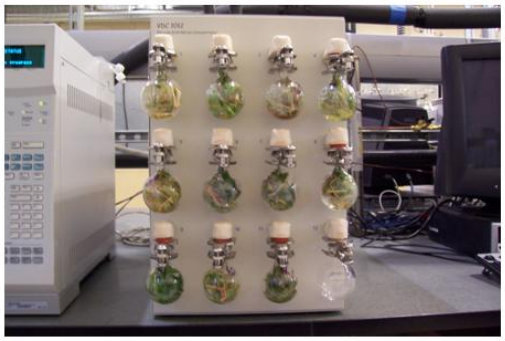
- Vacuum Distillation apparatus
  - ~ Agilent 6890/5973 GC/MS System
- Wide Variety of Matrices
- RLs similar to 8260
- 1,4 Dioxane to 5 ug/L

12

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Method 8261 Calibration

- Routine Calibration Range 5 -200 ug/L
- 1,4-Dioxane
  - ~ + Large Suite of monitored analytes
- Wide variety of matrices
  - ~ 5g aliquots typical
- Full scan spectra



13

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

1,4-Dioxane by Method 8261

- Calibration Curve

Analyte	Cal1 25ng*	Cal2 50ng*	Cal3 250ng*	Cal4 500ng*	Cal5 1000ng*	MEAN	%RSD
1,4-Dioxane	415.51	436.09	371.52	358.11	338.72	383.99	10.6

* mass per 5 mL Reagent water

- 10.6 %RSD over five point calibration spanning 25-1000ng
- Many different & challenging matrices
  - ~ Waters, soils, tissues
  - ~ Single Calibration
  - ~ Low reporting limits

14

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

1,4-Dioxane MDL by 8261

- Performed by spiking 12.5 ng of 1,4-Dioxane into 5 mL of reagent water (2.5 ug/L)
- MDL = 1.345 ug/L
- Mean recovery = 3.084 ug/L
- Mean percent recovery 123%R

REP1	REP2	REP3	REP4	REP5	REP6	REP7
3.55	2.65	2.85	3.8	2.98	3.01	2.75

15

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Compare Current Methods

- Method 8270
  - ~ Reporting Limit
    - ° 1 ug/L
  - ~ Strengths
    - ° Lower RL than 8260 full scan
    - ° No extra cost if 8270 analytes already needed
  - ~ Limitation
    - ° Results can have low bias (50-75%)

16

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Compare Current Methods

- Method 8260 full scan
  - ~ Reporting Limit
    - ° 50 ug/L
  - ~ Strengths
    - ° No extra cost if 8260 analytes already needed
    - ° No modifications to "normal" instrument parameters
    - ° Limited carryover problems
  - ~ Limitations
    - ° Higher reporting limit
    - ° Low relative response factor

17

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Compare Current Methods

- Method 8260 SIM with 1,4-dioxane-d8 internal standard
  - ~ Reporting Limit
    - ° 1-5 ug/L
  - ~ Strengths
    - ° Lower reporting limit than 8260 full scan
    - ° Fewer bulk matrix effects than 8260 due to purging efficiency differences
    - ° Better accuracy than 8270
    - ° Relative response factor near 1
  - ~ Limitations
    - ° Operating parameter optimizations reduce productivity
    - ° More frequent carryover problems
    - ° More sensitive to spectral interference from coelutions

18

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Compare Current Methods

- Method 8261 full scan
  - ~ Reporting Limit
    - ° 5 ug/L
  - ~ Strengths
    - ° Full scan spectra
    - ° Applicable to many matrices
    - ° Better accuracy than 8270
  - ~ Limitations
    - ° Smaller autosampler capacity
    - ° More setup labor

19

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Which method to use?

- The right choice will depend on:
  - ~ Matrix
  - ~ Reporting limit
    - ° 1, 5, 50 ug/L
  - ~ Accuracy
    - ° +/- 25%, -75-10%
  - ~ Historical trend data
    - ° What was used before
  - ~ Other analytes
    - ° Add into 8260, 8261 or 8270
  - ~ Turn around time
    - ° 8260 or 8260 SIM usually shorter TAT
  - ~ Cost

20

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Acknowledgements

- Bryce Stearns (Burlington)

21

A New SW-846 Method for the Analysis of Toxaphene and Toxaphene Congeners Using Gas Chromatography/ Negative Ion Mass Spectrometry.

Scott Sivertsen
USEPA
980 College Station Road
Athens, GA 30605
706-355-8869
sivertsen.scott@epa.gov

ABSTRACT

US EPA SW-846 methods have typically relied on dual column gas chromatography coupled with electron capture detection (GC-ECD) for analysis of low concentrations of organochlorine pesticides, including toxaphene, in environmental samples. Toxaphene is one of the most widely applied pesticides in the world and is a complex mixture of predominately polychlorinated camphenes estimated at 800-plus congeners. Once in the environment, toxaphene degradation begins. Weathered residues in environmental samples may not match laboratory standards. Adding to this complexity, degradation can result in metabolites not present in laboratory standards. To tackle the complexity of GC-ECD toxaphene analysis, the US EPA is investigating an alternate determinative technique. The Agency is presently validating a method utilizing gas chromatography coupled with detection by low resolution methane negative ion mass spectrometry (GC-NIMS) which uses scan or selected ion monitoring (SIM). Initial target analytes in the method are environmentally relevant toxaphene congeners as well as technical toxaphene. Using SIM, we were able to obtain congener limits of detection ranging from 0.00020-0.0026 µg/L for water and 0.0070-0.047 µg/kg for soils. This method is performance-based and allows for inclusion of other toxaphene congeners in extracts from solid and liquid matrices plus organochlorine pesticides routinely analyzed by Method 8081A.

INTRODUCTION

Toxaphene is a broad-spectrum insecticide introduced in 1945 by Hercules and has been used and produced globally under a variety of names. It is the most widely-used pesticide ever produced and global production is estimated at 0.45–1.33 X 10^6 tons. Because of its broad usage and volatility, toxaphene is an ubiquitous contaminant which experiences atmospheric transport and has been detected in the Arctic and Antarctic environments [1,2].

Toxaphene is a complex mixture of chlorinated camphene derivatives, primarily bornanes and bornenes containing 6 - 10 chlorines with potential for 32,768 theoretical isomers in the technical mixture. Steric hindrance prevents most synthetic pathways from successful completion, resulting in a mixture which is currently estimated at 800-plus congeners. Once introduced into the environment, selective weathering, degradation and bioaccumulation begin.

The determination of toxaphene has typically been performed using GC-ECD. While GC-ECD is quite sensitive to electron-capturing species, it is also non-specific in its response, resulting in

potential matrix interference. When toxaphene is analyzed, qualitative identification of residues is based on matching chromatographic profiles of analytical standards to those found in environmental samples. When a weathered toxaphene sample is encountered and the potential for matrix interference is introduced, the sample might not match an analytical toxaphene standard. Additionally, degradation products would be excluded, due to their chromatographic elution prior to any congeners found in toxaphene. Ultimately, proper identification of toxaphene as an incurred residue is dependent on the subjective judgment of the analyst when GC-ECD is used.

Mass spectrometry is a technique which has experienced broad acceptance in environmental analysis. The analysis of toxaphene, like most organochlorine pesticides found in method 8081A can be performed by gas chromatography with electron ionization (EI). These pesticides, however, are not detected well due to severe fragmentation in the EI mode. Chemical ionization mass spectrometry provides a much "softer" ionization, resulting in less fragmentation. The mass spectrometer is a highly sensitive detector when operated in the negative ion SIM mode, with methane introduced as the moderating gas. GC-NIMS is also less prone to matrix interference than GC-ECD analysis. On-column detection limits in the femtogram range can be obtained while providing mass spectral confirmation of target analytes.

As advances in toxaphene congener-specific analysis are made, regulators can receive more specific information on sample composition without the potential for under-reporting toxaphene residues as a result of matrix interference or weathering.

MATERIALS AND METHODS

Chemicals

Table 1: Toxaphene Congeners Evaluated

Common name	IUPAC name	CAS Registry #
Hx-Sed	2-exo,3-endo,6-exo,8,9,10-Hexachlorobornane	57981-29-0
Hp-Sed	2-endo,3-exo,5-endo,6-exo,8,9,10-Heptachlorobornane	70649-42-2
Parlar 26	2-endo,3-exo,5-endo,6-exo,8,8,10,10-Octachlorobornane	142534-71-2
Parlar 40	2-endo,3-exo,5-endo,6-exo,8,9,10,10-Octachlorobornane	166021-27-8
Parlar 41	2-exo,3-endo,5-exo,8,9,9,10,10-Octachlorobornane	165820-16-6
Parlar 44	2-exo,5,5,8,9,9,10,10-Octachlorobornane	165820-17-7
Parlar 50	2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-Nonachlorobornane	66860-80-8
Parlar 62	2,2,5,5,8,9,9,10,10-Nonachlorobornane	154159-06-5

Mixed-congener standards (DE-TOX 483 and DE-TOX 484) were obtained from LGC Promochem (Teddington, UK) at a concentration of 5 ng/µL and combined for use as calibration and spiking solutions. Surrogate compounds decachlorobiphenyl (DCB) and tetrachloro-*meta*-xylene (TCMX) were obtained from Ultra Scientific (N. Kingstown, RI) and added to all samples prior to preparation to monitor extraction efficiency. PCB #204 from o2si Smart Solutions (Charleston, SC) was added to calibration standards and all extracted samples prior to analysis for use as an internal standard.

Laboratory pure organic-free water was produced at the time of use by a Barnstead NanoPure purification system (Dubuque, IA).

Organic solvents (dichloromethane, hexane, acetone, iso-octane) were pesticide-grade or equivalent and purchased from Mallinckrodt Baker (Phillipsburg, NJ).

Equipment

Water samples were processed by continuous liquid-liquid extraction using a Corning Accelerated One-Step Extractor/Concentrator (Lowell, MA). Solid samples were extracted by pressurized fluid extraction (PFE) using a model 200 Dionex Accelerated Solvent Extractor (Sunnyvale, CA). Gel permeation cleanup of the solid samples was performed on a J2 Scientific AccuPrep GPC system (Columbia, MO) utilizing a 25 mm x 700 mm low pressure glass column packed with 70 g of Bio-Rad Laboratories SX-3 Biobeads (Hercules, CA). Dichloromethane was used as the mobile phase at a flow of 5 mL/minute. GC-NIMS analysis was performed with an Agilent 5973 GC-MS system (Santa Clara, CA) operated in the negative ion mode using a chemical ionization (CI) source. The moderating gas was research-grade methane from National Specialty Gases (Charlotte, NC). An Agilent 30 m x 0.25 mm x 0.25 µm DB-XLB column was used to perform the analytical separations. UHP grade helium from Airgas (Radnor, PA) was the carrier gas.

Sample Preparation

Water and Solid Samples

Replicate laboratory control samples (LCS) were spiked with toxaphene congeners at 3 different concentrations to evaluate method performance. Each batch consisted of 8 limit-of-detection (LOD) extracts, 3 mid-level and 3 high-level spikes. A procedural blank was carried through the process as a negative control. Surrogates (500 ng TCMX, 50 ng DCB) were spiked into all extracts. Extracts were reduced to a final volume of 1 mL in hexane.

Water Extraction

Eight 1-L aliquots of organic-free water were spiked at the LOD level with toxaphene congeners at 0.0020 µg/L and with Parlar 62 at 0.010 µg/L. Three 1-L samples were spiked at 0.25 µg/L and three at 0.40 µg/L. All samples were extracted with 100 mL of dichloromethane for 6 hours using EPA SW-846 Method 3520C [3].

Solid Extraction and Cleanup

Eight 30 g aliquots of Hydromatrix® were spiked at the LOD level with toxaphene congeners at 0.067 µg/kg and with Parlar 62 at 0.33 µg/kg. Three 30-g samples were spiked at 8.3 µg/kg and three at 13 µg/kg to create the mid-level and high-level spikes.

The samples were extracted using EPA SW-846 Method 3545A [4]. PFE extraction conditions were 100°C under 1500 psi for 5 minutes per static cycle using 1:4 acetone:dichloromethane. Each sample was extracted with two static cycles and a 70% flush volume. Purge time was 150 seconds.

Following extraction and concentration to a 5-mL volume, solid sample extracts were subjected to size exclusion chromatography, followed by sulfuric acid cleanup (EPA SW 846 Methods 3640A and 3665A, respectively) [5, 6].

GC-NIMS Analysis

Instrument Conditions

Selected toxaphene congeners (Table 1) were analyzed by GC-NIMS. Methane at a 40% flow of 2 mL/min was used as the moderating gas with the CI source. One-µL injections were made at 250°C in the splitless mode with the purge valve activated at 0.6 minutes. The initial oven temperature was 60°C for 1 minute. Then, the first oven ramp was programmed to 150°C at 10°C/minute, followed by a 3°C/minute increase to 260°C. Finally, the temperature was increased from 260°C to 320°C with a 5-minute hold. Carrier gas was set at a constant flow of 1.0 mL/minute. The capillary-direct interface was 280°C. The source and quadrupole were 160°C and 150°C, respectively.

Mass Analyzer Tuning

The mass analyzer was tuned prior to calibration using the CI autotune function and criteria with 2H-perfluoro-5,8-dimethyl-3,6,9-trixadodecane (PFDTD). The tuning file was saved with an electron multiplier increase of 175 V above the autotune value for enhanced sensitivity resulting in an increased signal-to-noise ratio. Additionally, a SIM mass defect experiment was performed to verify mass calibration. This generally resulted in selected ions that were 0.1 mass unit lower than theoretical values. (This process assures that the apex of the mass peak is monitored.) Table 2 summarizes the selected ions monitored and the elution time of the analytes. Table 3 shows the dwell times. A SIM group was used having a total dwell time of 510 milliseconds.

Table 2: Characteristic Ions for Toxaphene Congeners, Surrogates and Internal Standards

Compound	RT (min)	Primary Ion	Secondary Ion(s)
TCMX	18.05	242.8	240.8
Hx-Sed	33.93	308.7	306.7, 310.7
Hp-Sed	34.57	342.7	340.7, 344.7
Parlar 26	35.04	376.7	378.7, 380.7
Parlar 41	39.41	376.7	378.7, 380.7
Parlar 40	39.73	376.7	378.7, 380.7
Parlar 44	40.11	376.7	378.7, 380.7
Parlar 50	40.64	412.7	410.7, 414.7
PCB #204	42.21	429.7	410.7, 427.7
Parlar 62	44.74	376.7	378.7, 380.7
DCB	49.54	497.7	499.7

Table 3: SIM Ions and Dwell Times (milliseconds)

m/z	Dwell	m/z	Dwell	m/z	Dwell
240.80	50	242.80	50	324.70	25
326.70	25	306.70	25	308.70	25
310.70	25	340.70	25	342.70	25
344.70	25	376.70	25	378.70	25
380.70	25	410.70	25	412.70	25
414.70	25	427.70	25	429.70	25
497.70	5	499.70	5		

Internal Standard Criteria

PCB #204 (not present in Aroclor mixtures) was added to all calibration solutions as an internal standard (ISTD) at 400 pg/µL. The PCB congener was also used to evaluate the system for the presence of oxygen. Based on limited studies to date, the oxygen reaction observed with PCBs that produces ions potentially interfering with toxaphene determination is completely eliminated in modern instruments under appropriate conditions. PCB #204 serves to monitor this situation by the absence of the $(M\text{-}Cl+O)^-$ ion (m/z 410.7) when no oxygen is present. No significant oxygen reaction was observed in this study.

Initial and Continuing Calibration

An initial calibration (ICAL) was performed using an 8-point curve with concentrations at 0.5, 1, 2, 5, 25, 125, 250 and 500 pg/µL. Parlar 62, which has been reported to be thermally labile, was calibrated from 5-500 pg/µL because of its lower response than other congeners. Average response factors were used, except when 20% relative standard deviation (RSD) was exceeded. In those cases, a first-order linear regression (non-forced origin) calibration model was utilized resulting in coefficients of determination ≥ 0.99.

Continuing calibration verification (CCV) check standards were analyzed every 12 hours or less. Congeners and surrogates were evaluated against a criterion of ±20% difference. The CCV evaluation criteria for the ISTD required the response be within a factor of two (-50% to +100%) relative to the ICAL. Sample ISTD responses were compared to the CCV, also with the requirement that the response be within a factor of two compared to the CCV. No CCV excursions were observed during this study.

RESULTS AND DISCUSSION

Data for the 3 spiking levels was evaluated with respect to bias and precision. US EPA SW-846 Method 8000B provides guidance of 70-130% recovery. A benchmark of 20% RSD was used to evaluate precision.

Solid Samples

Tables 4-6 present data from solid extractions which represent soils. Masses in Tables 4 and 5 are 400 and 250 pg on-column, respectively. On-column masses in Table 6 are 2 pg with the exception of Parlar 62, which was 10 pg. Table 7 presents the calculated LODs for the PFE-extracted spikes.

The data from all PFE extracts was determined to be within precision and bias control limits. Additionally, LOD values appear realistic given instrument sensitivity and extraction efficiency.

Table 4: Percent Recovery and Precision in High Level Solid Extracts (13.3 µg/kg)

	High Spike 1	High Spike 2	High Spike 3	Mean	Std Dev	%RSD
Hx-Sed	75.2	79.1	76.5	76.9	2.0	2.6
Hp-Sed	75.9	79.5	77.0	77.5	1.8	2.4
Parlar 26	80.7	85.6	82.2	82.8	2.5	3.1
Parlar 41	81.8	87.7	84.5	84.7	2.9	3.5
Parlar 40	80.3	85.6	82.9	83.0	2.7	3.2
Parlar 44	89.6	97.3	94.3	93.7	3.9	4.1
Parlar 50	83.9	89.2	86.8	86.6	2.6	3.0
Parlar 62	87.8	92.4	92.2	90.8	2.6	2.9

Table 5: Percent Recovery and Precision in Mid-Level Solid Extracts (8.33 µg/kg)

	Mid-Range 1	Mid-Range 2	Mid-Range 3	Mean	Std Dev	%RSD
Hx-Sed	81.1	84.9	81.5	82.5	2.1	2.6
Hp-Sed	81.8	85.8	81.7	83.1	2.3	2.8
Parlar 26	84.4	89.5	84.9	86.2	2.8	3.2
Parlar 41	86.7	92.3	87.3	88.8	3.1	3.5
Parlar 40	86.0	90.6	87.2	87.9	2.4	2.7
Parlar 44	93.9	100	94.6	96.2	3.4	3.5
Parlar 50	90.1	94.9	90.1	91.7	2.8	3.1
Parlar 62	92.7	96.4	90.4	93.2	3.1	3.3

Table 6: Bias and Precision of Low Level Solid Extracts (0.0667 µg/kg)

	LOD 1	LOD 2	LOD 3	LOD 4	LOD 5	LOD 6	LOD 7	LOD 8	Mean	Std Dev	%RSD
Hx-Sed	81.5	78.5	74.5	85.0	82.5	86.0	82.0	87.5	82.2	4.2	5.1
Hp-Sed	81.5	78.5	74.0	75.5	76.5	83.0	79.0	83.5	78.9	3.5	4.4
Parlar 26	82.5	84.0	80.5	79.5	79.0	87.5	84.5	91.0	83.6	4.1	4.9
Parlar 41	86.0	88.5	77.0	77.0	79.0	86.5	84.0	88.5	83.3	4.9	5.9
Parlar 40	84.0	88.0	75.5	81.5	81.0	91.0	81.0	90.5	84.1	5.4	6.4
Parlar 44	91.5	97.5	84.5	84.5	87.5	89.5	83.0	87.0	88.1	4.7	5.3
Parlar 50	87.0	93.0	80.5	81.5	87.5	93.0	88.0	94.0	88.1	5.2	5.8
Parlar 62	79.7	78.0	74.4	76.8	75.4	87.3	71.5	77.4	77.6	4.7	6.0

Table 7: Calculated Solid LOD Results (µg/kg), (n=8, Student t=2.998, 99% confidence interval)

	Mean	Std Dev	LOD
Hx-Sed	0.0548	0.0028	0.00841
Hp-Sed	0.0526	0.0023	0.00701
Parlar 26	0.0557	0.0028	0.00827
Parlar 41	0.0555	0.0033	0.00985
Parlar 40	0.0560	0.0036	0.0108
Parlar 44	0.0588	0.0031	0.00942
Parlar 50	0.0587	0.0034	0.0103
Parlar 62	0.259	0.016	0.0465

Water Samples

Tables 8-10 present data from water extractions. On-column masses are the same as those presented in Tables 4-6 (soil data).

As was the case with the PFE data, all water extracts were determined to be within precision and bias control limits. Because the calculated LOD for Hp-Sed in the water spikes was less than one-tenth the value spiked, the LOD of 0.00013 µg/L was elevated to the reporting limit of 0.00020 µg/L. LOD values are realistic concentrations which can be detected, given instrument sensitivity and extraction efficiency.

Table 8: Percent Recovery and Precision in High Level Water Extracts (0.400 µg/L)

	High Spike 1	High Spike 2	High Spike 3	Mean	Std Dev	%RSD
Hx-Sed	93.3	105	88.9	95.8	8.4	8.8
Hp-Sed	93.8	105	86.9	95.3	9.3	9.8
Parlar 26	94.2	105	84.9	94.8	10.3	10.8
Parlar 41	92.9	104	83.5	93.4	10.2	10.9
Parlar 40	94.9	107	87.2	96.5	10.1	10.5
Parlar 44	105	120	94.8	106	12.5	11.7
Parlar 50	96.4	106	85.1	95.9	10.6	11.0
Parlar 62	113	125	107	115	9.2	8.0

Table 9: Percent Recovery and Precision in Mid-Level Water Extracts (0.250 µg/L)

	Mid-Range 1	Mid-Range 2	Mid-Range 3	Mean	Std Dev	%RSD
Hx-Sed	101	104	101	102	1.8	1.8
Hp-Sed	100	103	101	102	1.5	1.5
Parlar 26	98.5	101	99.8	99.7	1.2	1.2
Parlar 41	96.5	99.6	96.4	97.5	1.8	1.9
Parlar 40	100	105	102	103	2.5	2.4
Parlar 44	108	112	109	110	2.0	1.8
Parlar 50	99.2	103	100	101	1.8	1.8
Parlar 62	118	124	121	121	3.2	2.6

Table 10: Bias and Precision of Low Level Water Extracts (0.00200 µg/L)

	LOD 1	LOD 2	LOD 3	LOD 4	LOD 5	LOD 6	LOD 7	LOD 8	Mean	Std Dev	%RSD
Hx-Sed	107	106	101	98.5	106	104	108	101	104	3.5	3.4
Hp-Sed	101	106	102	101	102	104	106	101	103	2.1	2.1
Parlar 26	102	101	96.0	95.5	101	94.0	96.0	86.5	96.4	4.9	5.1
Parlar 41	99.5	96.5	94.0	90.0	99.5	100	93.0	89.5	95.3	4.3	4.5
Parlar 40	105	102	91.5	106	108	99.5	106	99.0	102	5.3	5.2
Parlar 44	107	118	104	101	125	107	113	94.5	109	9.7	9.0
Parlar 50	102	98.0	90.5	93.0	99.0	98.5	94.5	89.0	95.5	4.4	4.6
Parlar 62	108	92.5	102	85.0	96.4	107	97.4	85.3	96.6	8.7	9.0

Table 11: Water LOD Results (µg/L), (n=8, Student t=2.998, 99% confidence interval)

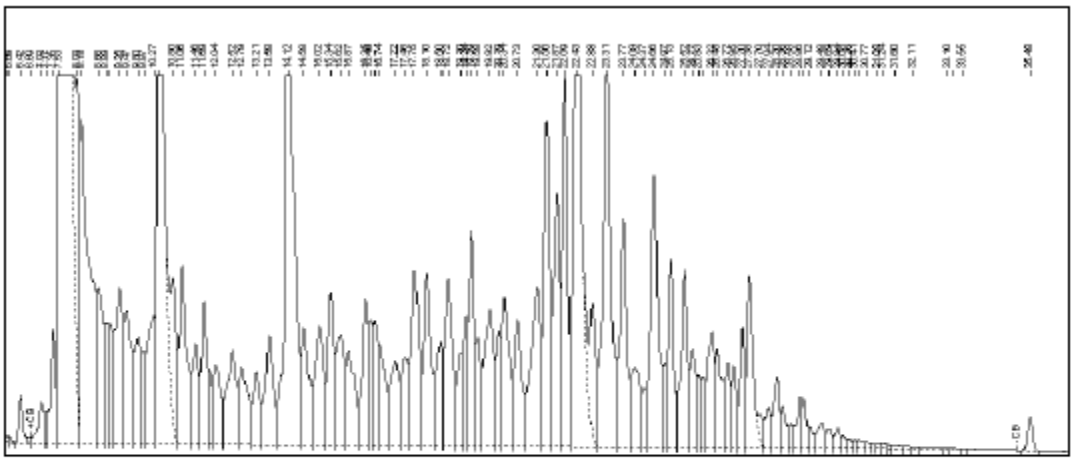
	Mean	Std Dev	LOD
Hx-Sed	0.00208	0.000071	0.00021
Hp-Sed	0.00205	0.000043	0.00020
Parlar 26	0.00193	0.000098	0.00029
Parlar 41	0.00191	0.000085	0.00026
Parlar 40	0.00204	0.000106	0.00032
Parlar 44	0.00217	0.000195	0.00058
Parlar 50	0.00191	0.000089	0.00027
Parlar 62	0.00966	0.000871	0.0026

Application to Samples Having Naturally Incurred Residues

A request for GC-NIMS congener analysis as well as GC-ECD analysis for technical toxaphene was received by us for multiple water samples from monitoring wells at a Superfund site. Drinking water MCL levels of 3 µg/L were requested for technical toxaphene.

As a result of matrix interference, the requested minimum reporting limit (MRL) of 3 µg/L was unobtainable for all but several of the samples using GC-ECD. In order to analyze most of the extracts, a 200:1 dilution was required. GC-MS in the EI scan mode and library searching revealed the possible presence of multiple chlorinated phenols, camphenes, bornanes and also DDD, DDT and BHC isomers.

Figure 1: GC-ECD Chromatogram of Sample 09 at 200:1 Dilution



No clear toxaphene pattern was observed in the above chromatogram and an MRL of 77 µg/L was reported. The sample required a dilution of 200:1 for GC/ECD due to severe matrix interference.

Sample 09 was analyzed at 2 dilutions by GC-NIMS to ensure that all parameters were inside the established linearity range. In addition to being analyzed at 50:1 (Figure 2 below), it was analyzed undiluted. Matrix interference was non-existent in both analyses when integrating extracted ion profiles. The 6 toxaphene congeners included in this study were readily quantified, as well as Hx-Sed and Hp-Sed, degradation products and indicators of weathered toxaphene.

The GC-NIMS analyses clearly show the advantage of this methodology. If the analyst had only GC-ECD technology, the sample would have been reported with an MRL of 77 and no clear indication as to whether toxaphene was present in the sample.

Analytical results using GC-NIMS methodology are presented in Table 12. Summing the toxaphene congeners and ignoring the degradation products results in a value of 5.0 µg/L. While one cannot directly correlate this to a technical toxaphene value, the result is indicative of chlorinated bornanes present at a level above the 3 ug/L MCL for technical toxaphene.

Figure 2: GC-NIMS Chromatogram of Sample 09 at 50:1 Dilution

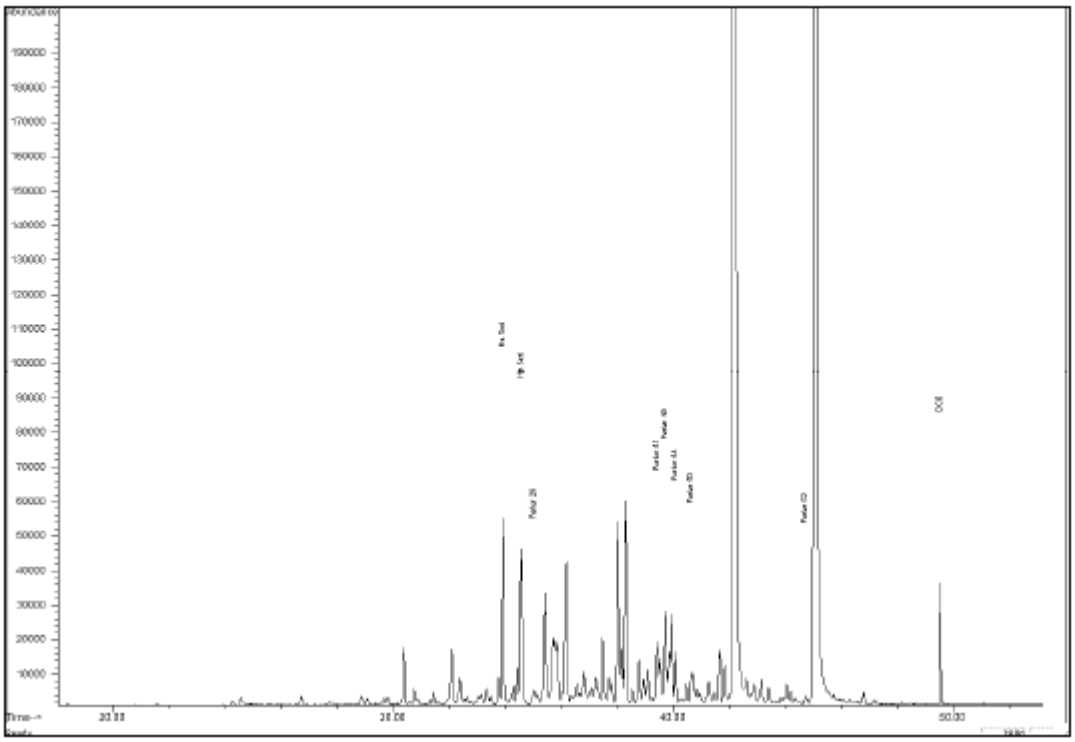


Table 12: Congeners Determined in Sample 09 Using GC-NIMS (µg/L)

Hx-Sed	1.3
Hp-Sed	1.6
Parlar 26	0.47
Parlar 41	0.58
Parlar 40	1.6
Parlar 44	0.30
Parlar 50	0.68
Parlar 62	1.4

Future Work

Although performance data are presented only for toxaphene congeners, technical toxaphene and additional target analytes (e.g., from US EPA SW-846 Method 8081A) may be added if acceptable performance can be demonstrated. The chemical and chromatographic behaviors of these additional compounds may result in co-elution of some target analytes. Additional cleanup/fractionation schemes may be required.

The US EPA is beginning multiple laboratory validation studies to document method performance. Phase I will consist of determinations made on spiked standards. Phase II will include materials having incurred residues. It is hoped that proposed SW-846 Method 8276 will be promulgated by December 2009.

ACKNOWLEDGEMENTS

Special thanks must go to numerous people without whom this work could not have been completed. Thanks to Sallie Hale, Bill Brumley, Shen-yi Yang and Ray Anderson for technical support, discussions and editorial suggestions. Thanks to Diana Burdette, Mike Brady, Rashe Malcolm and Matt Beecher for sample preparation.

NOTICE

Although the research described in this paper has been funded wholly by the US EPA, it has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. Agency for Toxic Substances and Disease Registry (ATSDR), August 1996. *Toxicology Profile for Toxaphene*. U.S. Department of Health and Human Services, Public Health Service.

2. The Handbook of Environmental Chemistry, Vol. 3, Part K. *New Types of Persistent Halogenated Compounds* (ed. by J. Paasivirta) Springer-Verlag, Berlin, Heidelberg 2000.

3. U.S Environmental Protection Agency, December 1996. *Method 3520C Continuous Liquid-Liquid Extraction*. US EPA Office of Solid Waste.

4. U.S Environmental Protection Agency, February 2007. *Method 3545A Pressurized Fluid Extraction (PFE)*. US EPA Office of Solid Waste.

5. U.S Environmental Protection Agency, September 1994. *Method 3640A Gel-Permeation Cleanup*. US EPA Office of Solid Waste.

6. U.S Environmental Protection Agency, December 1996. *Method 3665A Sulfuric Acid/Permanganate Cleanup*. US EPA Office of Solid Waste.

A New SW-846 Method for the Analysis of Toxaphene and Toxaphene Congeners Using Gas Chromatography/Negative Ion Mass Spectrometry

Scott K. Sivertsen
US EPA Region 4
Science and Ecosystem Support Division
Analytical Support Branch
Athens, GA

Toxaphene Background

- What's in a name???
  - Toxaphene (Hercules), Melipax (GDR), camphechlor, chlorobornanes, chlorinated monoterpenes, terpenes…
- Timeline
  - 1945 Introduced by Hercules
  - 1982 Use restricted in USA
  - 1986 Distribution of remaining stock ends
  - 1990 All registered applications cancelled
  - 2001 Dirty Dozen: Stockholm Convention on POPs

Toxaphene Background

- Broad Spectrum Pesticide - Wide Usage
  - Mid-1970s: Most widely applied pesticide in USA and other countries
  - Cotton, soybeans, cattle dip/spray (exoparasites)
  - 1960s: Piscicide - elimination of undesired lake fish
  - Global production 0.45 – 1.33 X 10^6 tons
- Global Transport – Arctic/Antarctic Contaminant
- EPA IRIS: B2 - Probable Human Carcinogen
- Produced by the Chlorination of α-pinene
  - Pine tree stumps → turpentine → pinene → toxaphene (mainly hexa - nonachloro bornanes)

Hercules Brunswick Site

Estuarine Site: Terry/Dupree Creeks

Hercules Brunswick Site

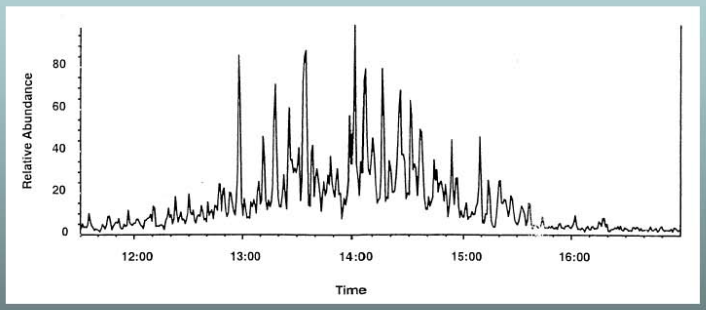
- 1948 – 80s: Active Toxaphene Production
- 1984: 009 Landfill (WW sludge) → NPL Site
- Terry Creek Dredged by USACE since 1938
- 1966: 250-300 Pounds Discharged Daily
- 1997: Terry/Dupree Spoil + Outfall → Candidate NPL Site

Analytical History

- DDT and PCB More Widely Studied
- Toxaphene Analysis Lags by ~ 2 Decades
  - Less well understood as a result
- Complex Mixture
  - 32,768 theoretical congeners (steric hindrance)
  - 177 – 675 congeners estimated by ^{1}H-NMR
  - Estimated by some to be 800 congeners
- 1993: Congeners Become Available

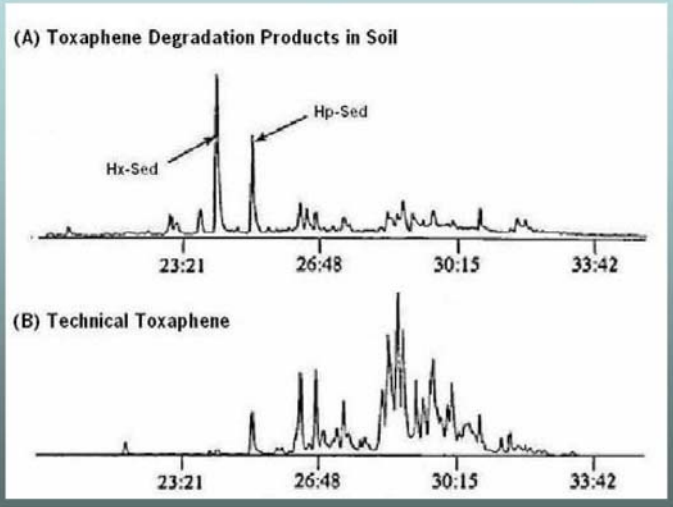
Analysis of Toxaphene

- GC-ECD/EPA Method 8081A



Technical Toxaphene Standard
Qualitative pattern matching. Standard = Sample.
3 – 7 Peaks typically used.

Problem: Toxaphene Degrades



- GC-ECD Qualitative ID Difficult – Metabolites Missed

EPA OIG Addresses Concerns

- 2002: Citizen Concerns of Underestimation
- Site Visits/Literature Review by OIG
- 2005: OIG Recommends EPA
  - Perform additional toxicity testing
  - Develop GC-NICI-MS methodology
    (Best available science)
- Toxaphene Submitted to IRIS for Review
- 2007: NICI-MS Method Development Begins at R4

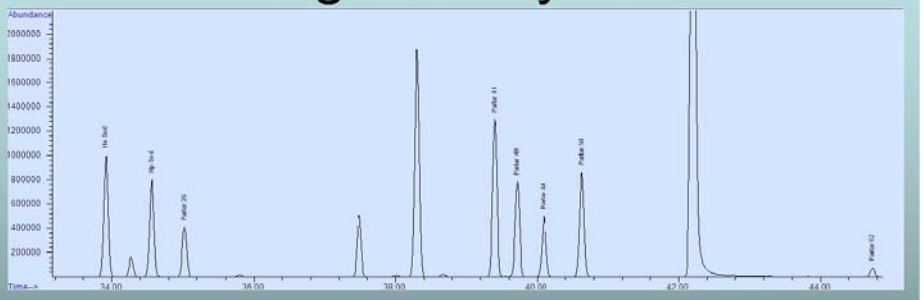
Why Congener Analysis?

- Weathered Residue ≠ Technical Standard
  - Metabolism, selective volatility of congeners
  - Persistence & toxicity varies with congener
  - Minor constituents → bioaccumulated (marine mammals)
  - 5 Congeners = 95% of residue (human serum)
    - Parlars 40, 41, 44, 26, 50
  - Fate varies with congener and environment
- Better Quantitation/Less Subjective
  - Better agreement in measurements
  - Focused on environmentally significant congeners

Nomenclature

- IUPAC
  - 2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-Nonachlorobornane
- CAS Registry
  - 66860-80-8
- Parlar – DB-5 Elution Order (50.1?)
  - Parlar #50
- Structure Related
  - Andrews and Vetter (AV codes) B9-1025
    - Computer generated based on IUPAC
  - Nikiforov NCB-4925
  - Wester B [12012]-(212)
- Parlar and AV Codes Most Commonly Used

Congeners by NICI



NICI TIC of Select Congeners: 500 pg On-Column

- NICI-MS methane
- DE-TOX 483 + 484 (LGC Standards)
- SIM - 25ms dwell time : 3 ions/congener: 25 scans across peak
- Hot splitless (250°C)
- DB-XLB 30 m x 0.25 mm x 0.25 µm
- 55 Minute run-time

NICI Method Performance

- Dynamic Range
  - 500 fg – 500 pg on-column
    - Average RF <20% RSD
    - COD ≥ 0.99
  - Parlar 62 (5 – 500 pg) thermally labile?
- Chromatographic Separation

Analyte	Retention Time
Hx-Sed	33.92
Hp-Sed	34.56
Parlar 26	35.02
Parlar 41	39.40
Parlar 40	39.72
Parlar 44	40.10
Parlar 50	40.64
Parlar 62	44.73
PCB # 204	42.20

R4 Initial Test Method Evaluation

- Soil and Water Methods
- 3 Levels – Multiple Replicates
  - Near-low calibration standard
  - Mid-calibration range
  - 80% of upper calibration standard

Soil Low – Clean Matrix

LOD % Recovery											
	LOD 1	LOD 2	LOD 3	LOD 4	LOD 5	LOD 6	LOD 7	LOD 8	Mean	Std Dev	%RSD
Hx-Sed	81.5	78.5	74.5	85.0	82.5	86.0	82.0	87.5	82.2	4.2	5.1
Hp-Sed	81.5	78.5	74.0	75.5	76.5	83.0	79.0	83.5	78.9	3.5	4.4
Parlar 26	82.5	84.0	80.5	79.5	79.0	87.5	84.5	91.0	83.6	4.1	4.9
Parlar 41	86.0	88.5	77.0	77.0	79.0	86.5	84.0	88.5	83.3	4.9	5.9
Parlar 40	84.0	88.0	75.5	81.5	81.0	91.0	81.0	90.5	84.1	5.4	6.4
Parlar 44	91.5	97.5	84.5	84.5	87.5	89.5	83.0	87.0	88.1	4.7	5.3
Parlar 50	87.0	93.0	80.5	81.5	87.5	93.0	88.0	94.0	88.1	5.2	5.8
Parlar 62	79.7	78.0	74.4	76.8	75.4	87.3	71.5	77.4	77.6	4.7	6.0

PFE Extraction/GPC/H_2SO_4 Cleanup

0.0667 µg kg^{-1} (ppb) spike level

2 pg on-column (10 pg Parlar 62)

Soil Mid – Clean Matrix

Mid Range % Recovery							
	Mid Range 1	Mid Range 2	Mid Range 3	Mean	Std Dev	%RSD
Hx-Sed	81.1	84.9	81.5	82.5	2.1	2.6
Hp-Sed	81.8	85.8	81.7	83.1	2.3	2.8
Parlar 26	84.4	89.5	84.9	86.2	2.8	3.2
Parlar 41	86.7	92.3	87.3	88.8	3.1	3.5
Parlar 40	86.0	90.6	87.2	87.9	2.4	2.7
Parlar 44	93.9	100	94.6	96.2	3.4	3.5
Parlar 50	90.1	94.9	90.1	91.7	2.8	3.1
Parlar 62	92.7	96.4	90.4	93.2	3.1	3.3

PFE Extraction/GPC/H_2SO_4 Cleanup

8.33 µg kg^{-1} (ppb) spike level

250 pg on-column

Soil High – Clean Matrix

High Range % Recovery							
		High Range 1	High Range 2	High Range 3	Mean	Std Dev	%RSD
Hx-Sed		75.2	79.1	76.5	76.9	2.0	2.6
Hp-Sed		75.9	79.5	77.0	77.5	1.8	2.4
Parlar 26		80.7	85.6	82.2	82.8	2.5	3.1
Parlar 41		81.8	87.7	84.5	84.7	2.9	3.5
Parlar 40		80.3	85.6	82.9	83.0	2.7	3.2
Parlar 44		89.6	97.3	94.3	93.7	3.9	4.1
Parlar 50		83.9	89.2	86.8	86.6	2.6	3.0
Parlar 62		87.8	92.4	92.2	90.8	2.6	2.9

PFE Extraction/GPC/H_2SO_4 Cleanup

13.3 µg kg^{-1} (ppb) spike level

400 pg on-column

Water Low – Clean Matrix

LOD % Recovery											
	LOD 1	LOD 2	LOD 3	LOD 4	LOD 5	LOD 6	LOD 7	LOD 8	Mean	Std Dev	%RSD
Hx-Sed	107	106	101	98.5	106	104	108	101	104	3.5	3.4
Hp-Sed	101	106	102	101	102	104	106	101	103	2.1	2.1
Parlar 26	102	101	96.0	95.5	101	94.0	96.0	86.5	96.4	4.9	5.1
Parlar 41	99.5	96.5	94.0	90.0	99.5	100	93.0	89.5	95.3	4.3	4.5
Parlar 40	105	102	91.5	106	108	99.5	106	99.0	102	5.3	5.2
Parlar 44	107	118	104	101	125	107	113	94.5	109	9.7	9.0
Parlar 50	102	98.0	90.5	93.0	99.0	98.5	94.5	89.0	95.5	4.4	4.6
Parlar 62	108	92.5	102	85.0	96.4	107	97.4	85.3	96.6	8.7	9.0

Continuous Liquid-Liquid Extraction

0.0020 µg L^{-1} (ppb) spike level

2 pg on-column (10 pg Parlar 62)

Water Mid – Clean Matrix

Mid-Range % Recovery							
	Mid Range 1	Mid Range 2	Mid Range 3		Mean	Std Dev	%RSD
Hx-Sed	101	104	101		102	1.8	1.8
Hp-Sed	100	103	101		102	1.5	1.5
Parlar 26	98.5	101	99.8		99.7	1.2	1.2
Parlar 41	96.5	99.6	96.4		97.5	1.8	1.9
Parlar 40	100	105	102		103	2.5	2.4
Parlar 44	108	112	109		110	2.0	1.8
Parlar 50	99.2	103	100		101	1.8	1.8
Parlar 62	118	124	121		121	3.2	2.6

Continuous Liquid-Liquid Extraction

0.25 µg L^{-1} (ppb) spike level

250 pg on-column

Water High – Clean Matrix

High Range % Recovery							
	High Range 1	High Range 2	High Range 3		Mean	Std Dev	%RSD
Hx-Sed	93.3	105	88.9		95.8	8.4	8.8
Hp-Sed	93.8	105	86.9		95.3	9.3	9.8
Parlar 26	94.2	105	84.9		94.8	10.3	10.8
Parlar 41	92.9	104	83.5		93.4	10.2	10.9
Parlar 40	94.9	107	87.2		96.5	10.1	10.5
Parlar 44	105	120	94.8		106	12.5	11.7
Parlar 50	96.4	106	85.1		95.9	10.6	11.0
Parlar 62	113	125	107		115	9.2	8.0

Continuous Liquid-Liquid Extraction

0.40 µg L^{-1} (ppb) spike level

400 pg on-column

Calculated LOD

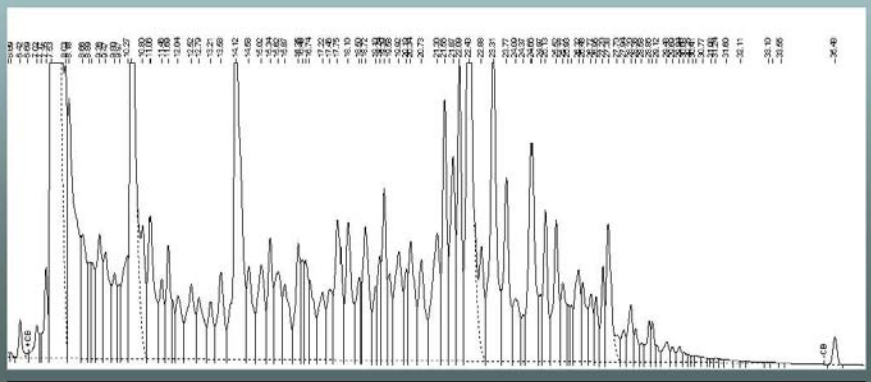
Statistical LOD (ppb)		
	Soil	Water
Hx-Sed	0.0084	0.00021
Hp-Sed	0.0070	0.00020
Parlar 26	0.0083	0.00029
Parlar 41	0.0098	0.00026
Parlar 40	0.011	0.00032
Parlar 44	0.0094	0.00058
Parlar 50	0.010	0.00027
Parlar 62	0.047	0.0026

MRLs - Soil 0.033 µg kg^{-1}, Water 0.0010 µg L^{-1} / P62 5x greater

n = 8, 99% CI, Student t = 2.998

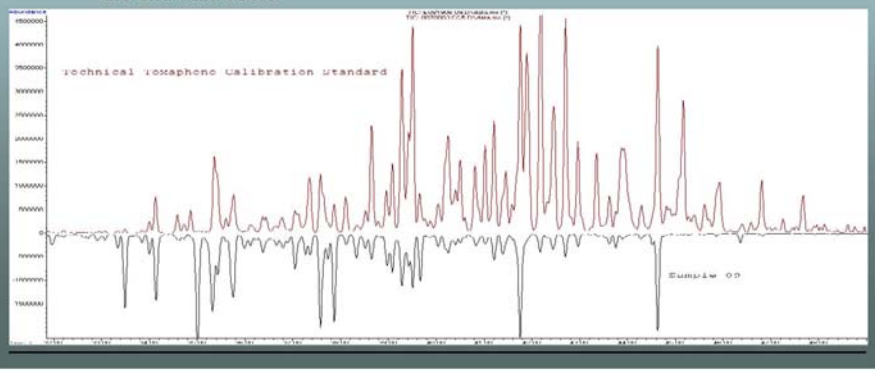
Method Application to Incurred Residues

- NICI Congener & GC-ECD Technical Toxaphene Request
- Superfund Site - Former Pesticide Formulation Facility
  - Historical toxaphene reporting at site (1980s to present)
- Most ECD Analyses Reported as <MRL (200:1 Dilution)
- GC-ECD Results Inconclusive for Toxaphene (Matrix Interference)



Method Application

- **Kitchen-Sink Samples**
- **GC-EI/MS TICs - Hydrocarbons, DDTs, BHCs, Chlorophenols, Chlorinated camphenes, etc.**
- **Initial NICI Analyses Showed Congeners Present**
- **Further NICI Analysis Confirmed Technical Toxaphene**
  - Technical toxaphene confirmed, congeners & degradation products detected
  - Provided us with the ability to report technical toxaphene as well as congeners to the end-data users



Future Work

- Inter-laboratory Initial Demonstration of Proficiency (in progress)
- Publish as a SW-846 Determinative Method
- Acquire Performance Data for Addition of 8081A Organochlorine Pesticides

Works Cited

- Agency for Toxic Substances and Disease Registry (ATSDR), August 1996. Toxicology Profile for Toxaphene. U.S. Department of Health and Human Services, Public Health Service
- Appropriate Testing and Timely Reporting Are Needed at the Hercules 009 Landfill Superfund Site, Brunswick, Georgia, EPA OIG Report 2005-P-00022
- The Handbook of Environmental Chemistry, Vol. 3, Part K, New Types of Persistent Halogenated Compounds (ed. by J. Paasivirta) Springer-Verlag, Berlin, Heidelberg 2000
- http://www.atsdr.cdc.gov/hac/PHA/terrycreek/tcd_p1.html
- http://www.epa.gov/superfund/sites/npl/nar437.htm
- http://www.epa.gov/superfund/sites/npl/nar1488.htm

Acknowledgements

- Sallie Hale, Bill Brumley, Shen-yi Yang and Ray Anderson for technical support, discussions and editorial suggestions
- Diana Burdette, Mike Brady, Rashe Malcolm and Matt Beecher for sample preparation

Remote Sensing Techniques to Detect Surface Water Quality Constituents in Coastal and Inland Water Bodies from Point or Non-Point Pollution Sources

Alfonso Blanco, P.E.; USEPA Office of Wastewater Management, Washington, D.C.
William Roper; weroper@verizon.net

INTRODUCTION

Point and Non-Point Sources (NPS) typically contains high concentrations of nutrients, which degrade water supplies and aquatic ecosystems. Identifying and characterizing these discharges and receiving streams can be difficult, time consuming, and costly because these contaminated discharges originate from numerous sources with restricted access due to few roads, steep terrain, and private ownership. A remote sensing technique for locating and characterizing the chemical quality of these discharges and affected streams could provide an efficient and cost-effective means of obtaining data on the sources and their effects in a watershed from a desktop.

GOALS AND OBJECTIVES

The purpose of this presentation is to demonstrate remote sensing techniques that use spectral reflectance technology for identifying and characterizing surface waters affected by point or non-point sources. These methods are used to extract surface reflectance for the identification and characterization of water quality constituents such as Chlorophyll a. Water quality samples at each of the sites can be collected concurrently with the spectral data and the orbit cycles or flyover from the satellites or airborne sensors. The ground truth data can be used to verify that spectral reflectance is capable of differentiating the different water column constituents. Specific objectives are:

(1) To correlate aerial surface spectral reflectance imaging data with ground spectral reflectance data to verify that the images observed from the air are comparable to those recorded on the ground;

(2) To quantify the relation between key water quality measurements collected in the water and the over head collected spectral reflectance data; and

(3) To demonstrate the cost effectiveness of analyzing water quality constituents remotely.

Identifying and characterizing the chemistry of these water bodies can be difficult, time consuming, and costly because can be originated from numerous areas and sources. The present technology requires field sampling in areas having few roads, steep terrain, and limited access because of private ownership or high security. A remote sensing technique for locating and characterizing the chemical quality of discharges and affected streams could provide an efficient and cost-effective means of obtaining data on the sources and effects in a watershed.

Remote Sensing Techniques to detect Surface Water Quality Constituents in Coastal and Inland Water Bodies from Point or Non Point Pollution Sources

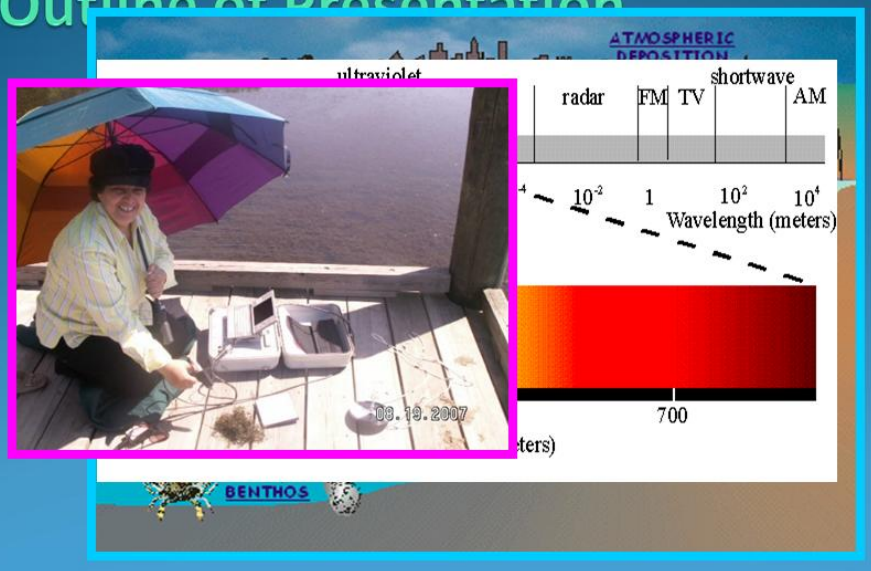
Presented by

Alfonso Blanco and William Roper

US Environmental Protection Agency

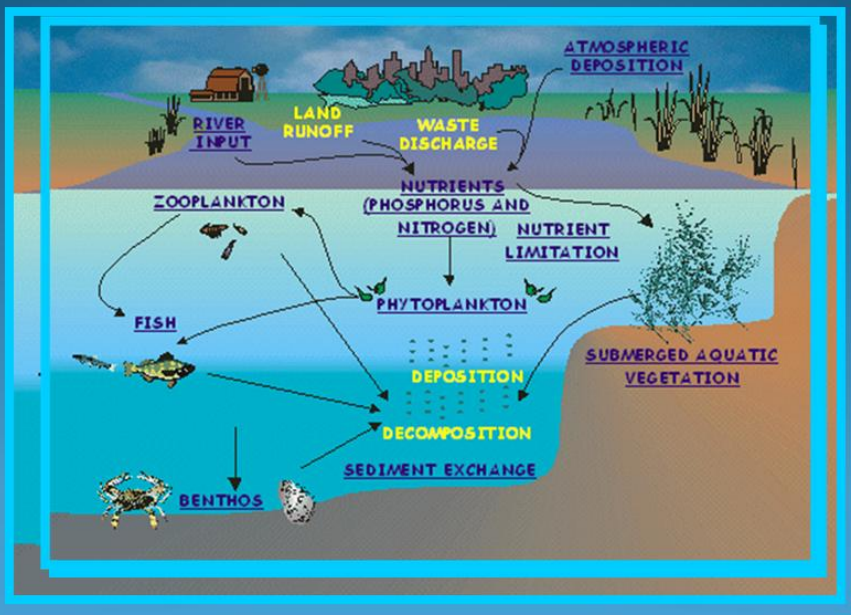
George Mason University

Outline of Presentation

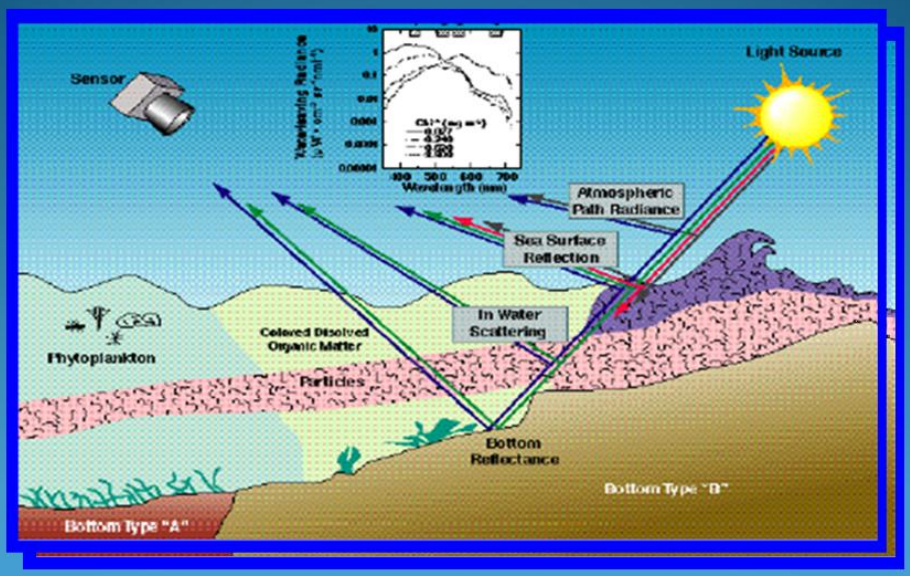


Test Site Location at Carroll Island

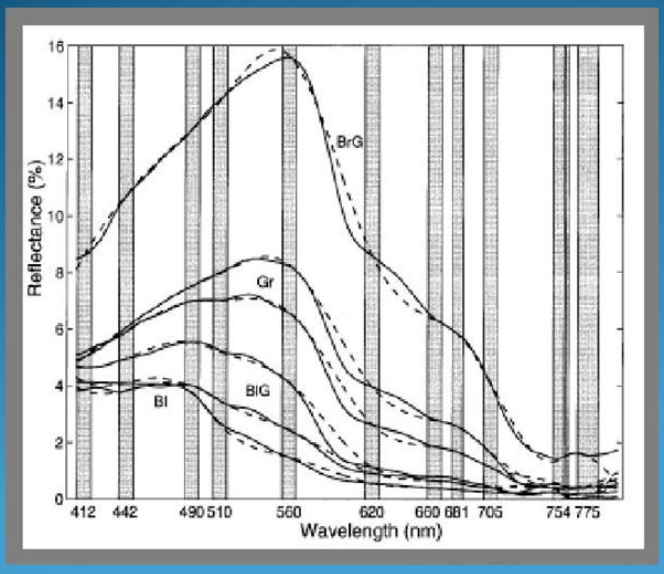
Components of the Chesapeake Bay Ecosystem



Reflectance Componets



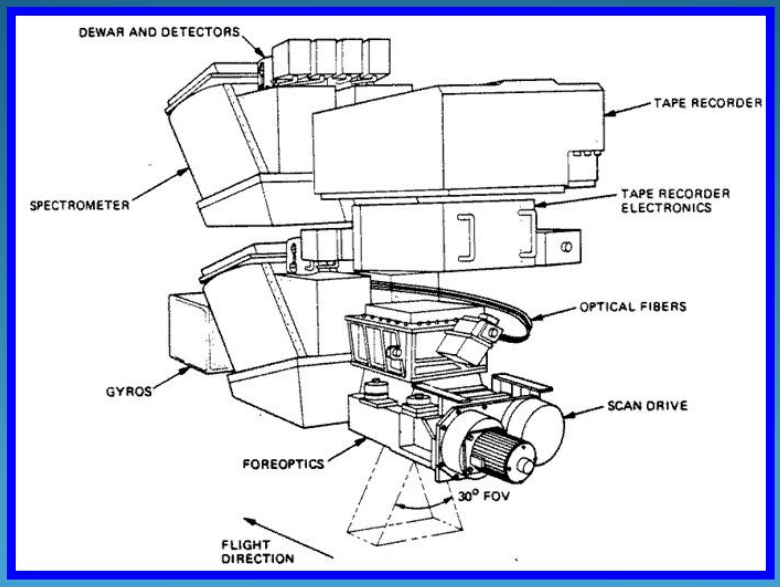
Typical Spectral Signature of Coastal Waters

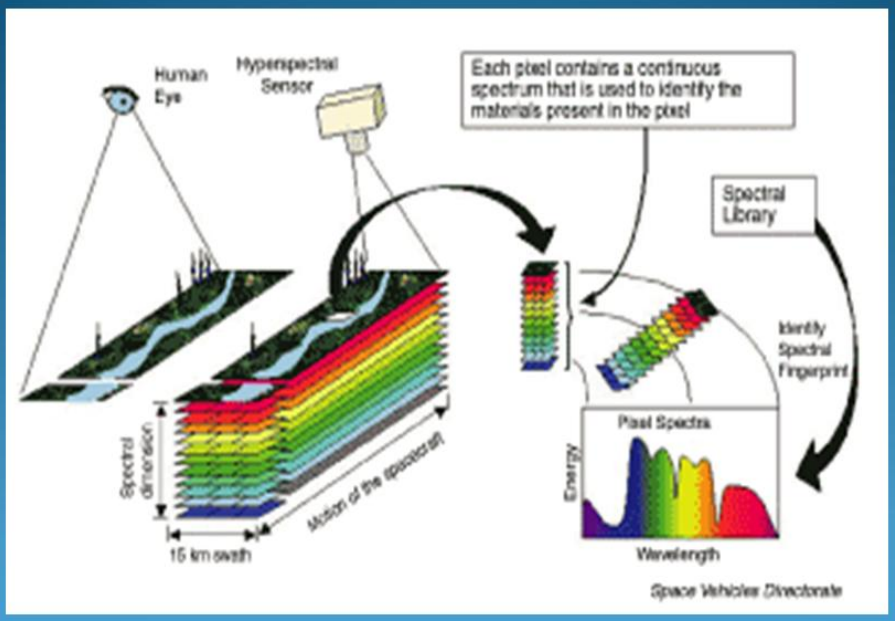


B1 – Clear blue water
GR – Green water
BIG – Blue-Green water
BrG – Brownish-Green water

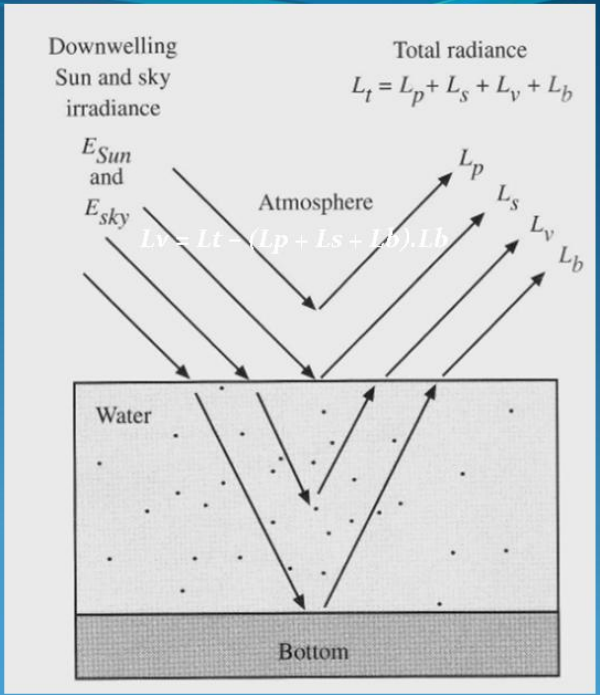
Arial View of Carroll Island

AVIRIS Sensor System

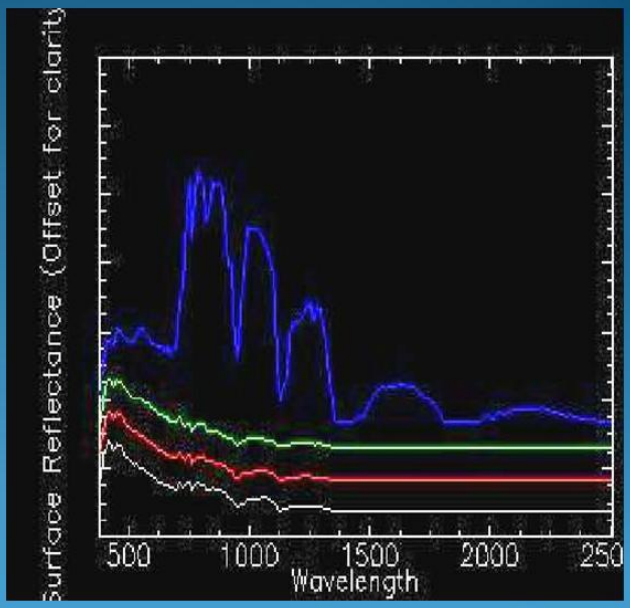




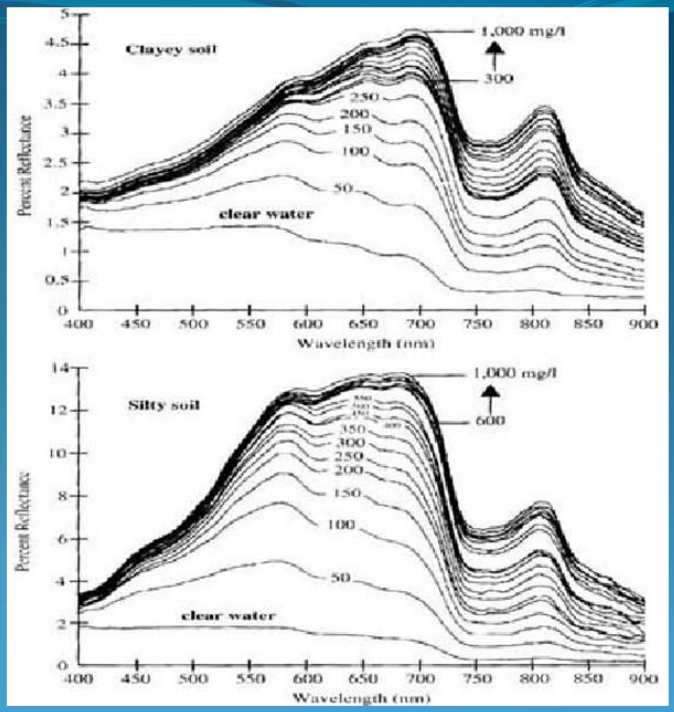
Radiance Relationships



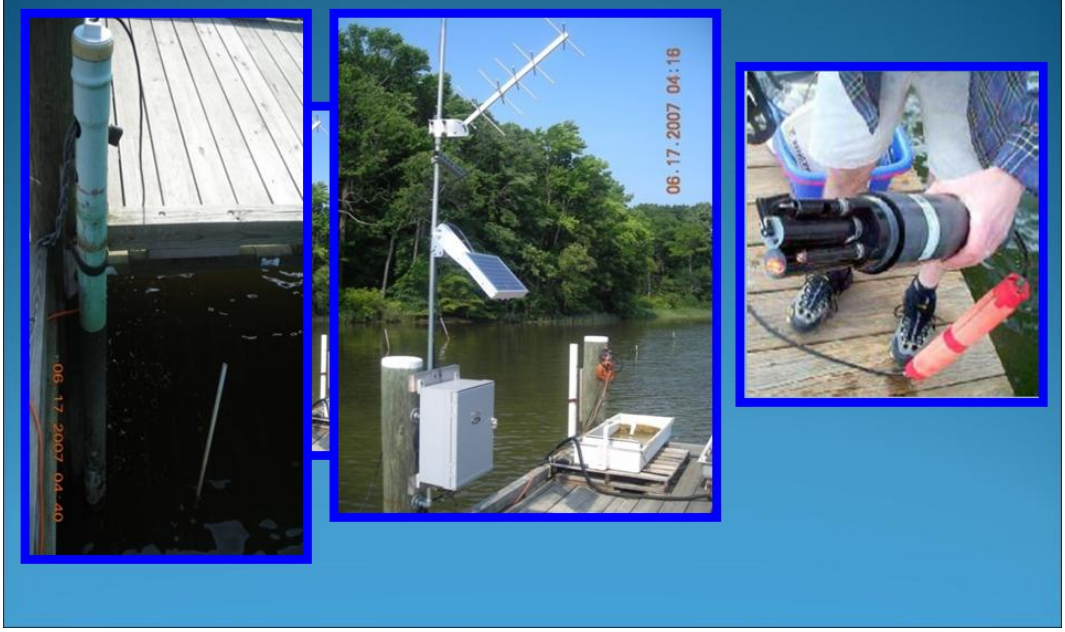
Chlorophyll-a signature using ENVI



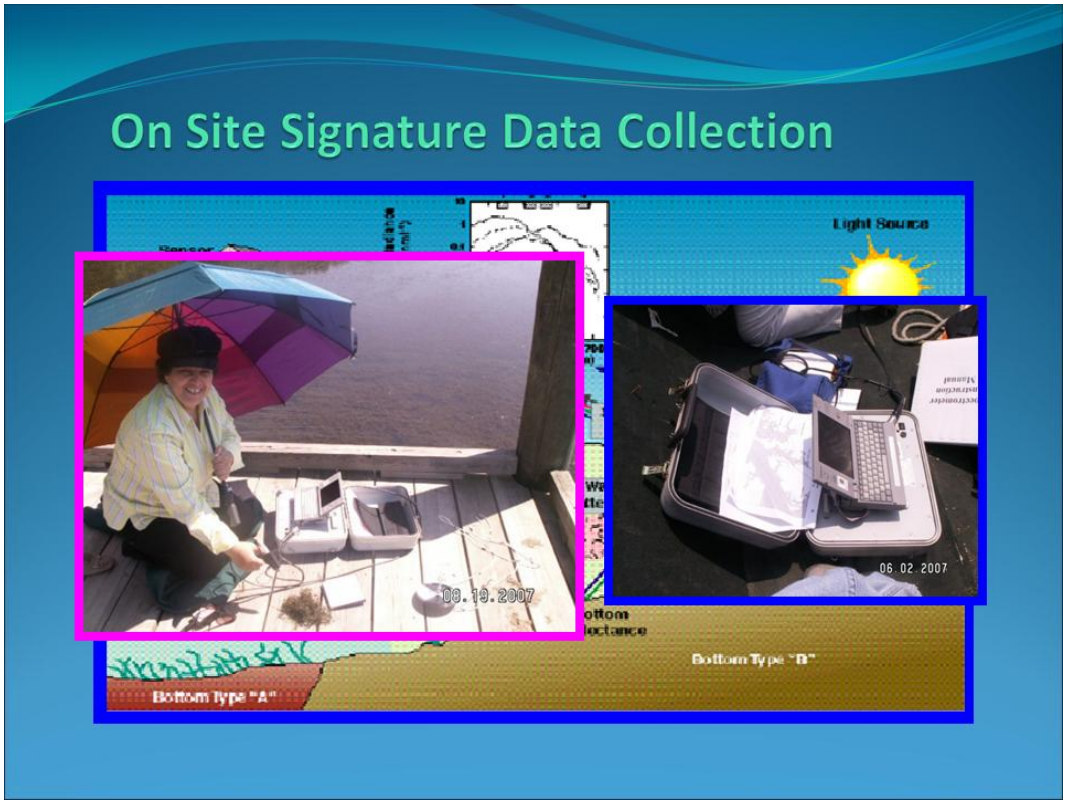
Typical Reflectance Spectral signature of clear and algae laden water

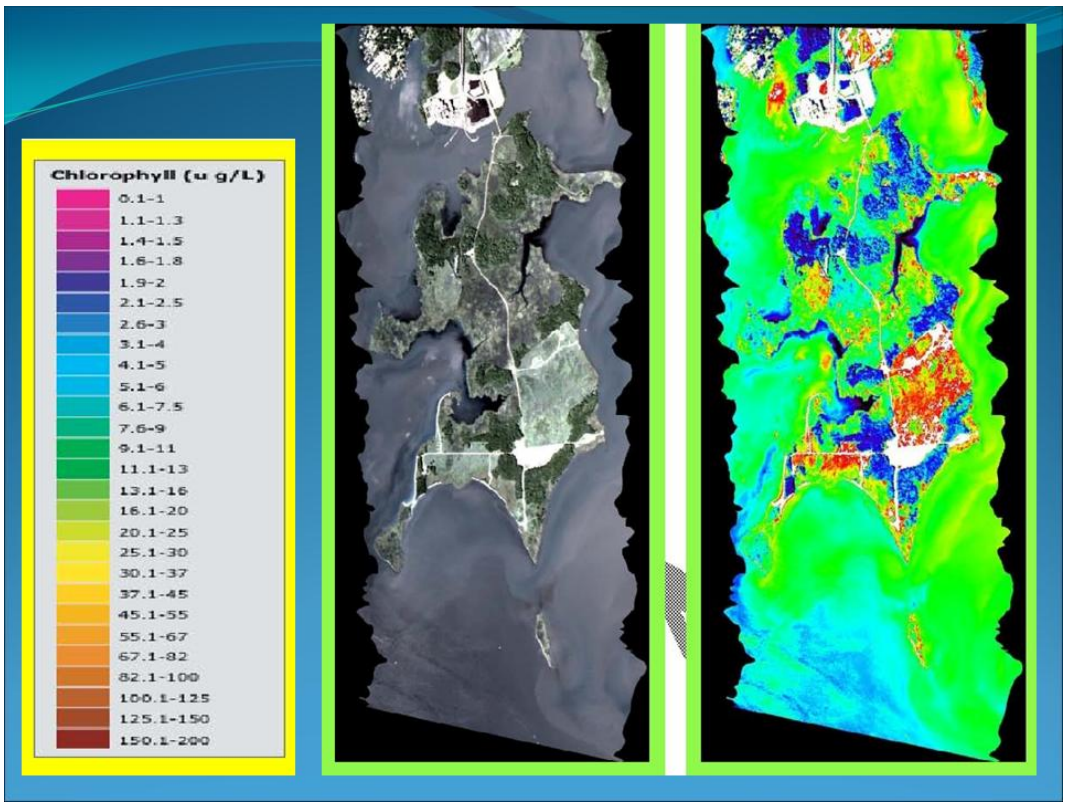


Maryland Water Quality Monitoring Site



On Site Signature Data Collection


On Site Signature Data Collection
Light Source
08.19.2007
06.02.2007
Bottom Type "A"
Bottom Type "B"


Chlorophyll (u g/L)
0.1-1
1.1-1.3
1.4-1.5
1.6-1.8
1.9-2
2.1-2.5
2.6-3
3.1-4
4.1-5
5.1-6
6.1-7.5
7.6-9
9.1-11
11.1-13
13.1-16
16.1-20
20.1-25
25.1-30
30.1-37
37.1-45
45.1-55
55.1-67
67.1-82
82.1-100
100.1-125
125.1-150
150.1-200

Conclusions

- Chlorophyll-a is a reasonable surrogate for phytoplankton characterization
- Dissolved organic matter is related to phytoplankton production
- Water quality monitoring based on spectral algorithm analysis can be used to map several water quality parameters using multi-spectral and/or hyper-spectral data

Conclusions (continued)

- Algae concentrations, location, distribution, and amount of photosynthesis. Can be identified and mapped and analyzed using satellite data and GIS
- AVIRIS due to higher spatial resolution is better for smaller area applications
- The AVIRIS air borne systems has more limitations regarding cost and availability than MODIS


08.19.2007
Each pixel contains a continuous spectrum that is used to identify the materials present in the pixel
Spectral Library
Identify Spectral Fingerprint
Pixel Spectra
Energy
Wavelength
Space Vehicles Directorate

2008 NEMC Proceedings

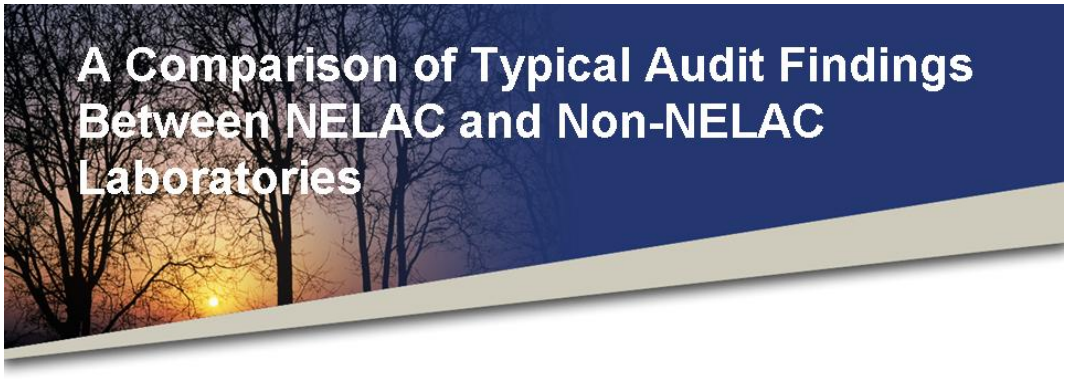
PERFORMANCE APPROACH

A Comparison of Typical Audit Findings between NELAC and Non-NELAC Labs: A Case for Uniform Quality System Standards for all Environmental Labs

Patrick Conlon
Environmental Standard
1140 Valley Forge Road
Valley Forge, PA 08050
610-935-5577
pconlon@envstd.com

ABSTRACT

With Daubert vs Merrill Dow in 1993, the door was opened toward more regulatory flexibility in the technical requirements of analytical methods. Moving away from the prescribed recipes of standardized and published instructions on what constitutes "commonly accepted practices" toward as technical standard of "does it do what it purports to do" had profound implications. This shift is directly responsible for the broadening of the flexibility allowances incorporated in SW-846 starting with update III, the broadening in the flexibility allowances in the Federal programs including CLP, DOD and in TRIAD, and the broadening in the flexibility allowances in the CWA program as incorporated in the MUR and later USEPA Memos. This shift also is directly responsible for the shift toward more focus on comprehensive Quality System Standards, because where data does not rely on common acceptable practice for defensibility the underlying documentation supporting the data, showing that "it does what it purports to do" is even more important. These two changes, i.e. a move toward greater flexibility and a move toward greater definition in appropriate quality system requirements are complementary, because the quality system requirements provide guidelines for a) maintaining documented control over a flexible system and b) documentary requirements to establish that a method is "doing what it purports to do". The shift toward greater emphasis on Quality System Standards is reflected in the NELAC standard and in the EPA's own standards for work performed for Federal programs. There are not, however, clear and uniform requirements for quality systems for work performed outside of the EPA programs and the NELAC program. Environmental Standards in the course of their auditing and consulting activities has opportunity to see a wide variety of both NELAC and Non-NELAC laboratories, including commercial, industrial and municipal. This presentation will compare and contrast common practices that may be found in NELAC vs. Non-NELAC laboratories. The theme of the presentation is that there is a need for greater definition of uniform quality system standard across all laboratories.



A Case for Uniform Quality System Standards for all Environmental Laboratories

Patrick A. Conlon
Environmental Standards

ENVIRONMENTAL STANDARDS

- Historical perspective on method flexibility expansion of quality system requirements
- Environmental Standards
- Quality System areas used for comparison
- Scorecards and comments
- Observed trends
- Features and benefits of NELAC

ENVIRONMENTAL STANDARDS

Method Flexibility & Quality System

Origins:

- Frye vs. the United States (1923)
  - "*Standard Acceptable Practice*"
- Daubert vs. Merrell Dow (1993)
  - Federal Rules of Evidence and Technical Support of an Argument
  - "*Does it do what it purports to do*"
- Direct effect on US EPA policy and methods

ENVIRONMENTAL STANDARDS

US EPA Streamlining Initiatives

- Regulatory Reform Act of 1995
- US EPA Streamlining Initiatives
  - Method Flexibility
  - Fast Track for Adoption of Method Innovation
  - US EPA Shift to Performance Based Approach
  - Focus on Quality System that supports data rather than on prescriptive methodologies
  - ISO-17025 International Guidelines

ENVIRONMENTAL STANDARDS

Environmental Standards

- Performs ~ 75 laboratory audits a year.
- Broad cross-section of industrial, municipal, and commercial laboratories.
- NELAC and Non-NELAC.
- Serves as consultant for Industrials and Municipalities.
- Writes Quality Assurance Plans and Technical Requirements.
- Scope of audits include technical issues, data usability, customer service, and client needs.

ENVIRONMENTAL STANDARDS

Quality System Areas Evaluated

Part 1

1. Management's knowledge of, participation in, and responsibility for data quality.
2. Analyst technical proficiency.
3. Appropriate quality controls.
4. Non-conformance and corrective action processes and documentation.
5. Ethics.

ENVIRONMENTAL STANDARDS

Quality System Areas Evaluated
Part 2

6. Sample handling and integrity issues.
7. Method validation elements.
8. Document control.
9. Documentation sufficient to reconstruct events.
10. Standards, reagents, and consumables - suitability and traceability.

ENVIRONMENTAL STANDARDS

Scorecard Legend by Size and Sector

SI – Small Industrial (2-10)
LI – Large Industrial (10-25)
SM – Small Municipal (2-10)
LM – Large Municipal (10-30)
C – Commercial Non-NELAC
SN – Small NELAC (5-25)
LN – Large NELAC (25-100)

ENVIRONMENTAL STANDARDS

Management System

- Knowledge and Responsibility for Laboratory.
- Management approval of internal policies and procedures.
- Internal Supervision, Review, and Audits.
- Management review of Systems and Effectiveness of Processes.

S I	L I	S M	L M	C	S N	L N
2	8	3	7	5	6	9

ENVIRONMENTAL STANDARDS

Analyst Technical Proficiency

- Documented Training
- Sign-offs of “read and understood” forms acknowledging personal responsibility.
- Technical Oversight & Review.
- PT and internal performance may prompt additional training.

S I	L I	S M	L M	C	S N	L N
2	7	2	6	4	5	9

ENVIRONMENTAL STANDARDS

Quality Controls

- Can the laboratory report actual laboratory performance?
- Quality Controls appropriate for the method and data reported?
- Appropriate Acceptance Criteria for the methods and data reported?
- PT Performance.

SI	LI	SM	LM	C	SN	LN
2	8	4	8	5	6	9

ENVIRONMENTAL STANDARDS

Non-conformance and Corrective Action System

- Clearly defined and appropriate corrective actions for deficiencies.
- Clearly identified acceptance criteria for reported data.
- Clear standards of acceptance for reportability.
- Overall system for identification and correction of deficiencies.

SI	LI	SM	LM	C	SN	LN
1	6	1	6	4	5	8

ENVIRONMENTAL STANDARDS

Ethics and Analytical Integrity

- Well-defined guidelines – including all data manipulation.
- Documented training and sign-off on individual responsibility.
- Verification - Are the data accurately processed?

SI	LI	SM	LM	C	SN	LN
1	6	1	5	5	5	8

ENVIRONMENTAL STANDARDS

Sample Integrity Issues

- Facility storage and handling practices.
- Sample preservation and holding times.
- COC and access security.
- Unique identification of samples.

SI	LI	SM	LM	C	SN	LN
5	7	5	8	5	6	8

ENVIRONMENTAL STANDARDS

Method Validation

- Valid method detection limits (MDLs).
- In-house Performance Measures.
- Demonstrations of Capability.
- Generally Accepted Reporting Practices.

SI	LI	SM	LM	C	SN	LN
2	7	2	6	4	5	7

ENVIRONMENTAL STANDARDS

Document Control

- Laboratory Manuals and SOPs.
- Form and Instructions.
- Reports.
- Data Archive.

SI	LI	SM	LM	C	SN	LN
2	8	3	7	5	6	9

ENVIRONMENTAL STANDARDS

Standards, Reagents, Consumables Suitability and Traceability

- Certificates requested and maintained.
- Standard and reagents source and preparation fully documented.
- Storage of standards, reagents, samples.
- Traceable recording of all lots and materials as used.

S I	L I	S M	L M	C	S N	L N
3	8	4	7	5	7	9

ENVIRONMENTAL STANDARDS

Scorecard Tally as Percent

#	S I	L I	S M	L M	C NN	S N	L N
Mgt Sys	2	8	3	7	5	6	9
Proficiency	2	7	2	6	4	5	9
QC	2	8	4	8	5	6	9
NCS	1	6	1	6	4	5	8
Ethics	1	6	1	5	5	5	8
Sample	5	7	5	8	5	6	8
Validation	2	8	2	6	4	5	8
Doc Ctrl	2	8	3	7	5	6	9
Records	3	7	2	7	5	6	8
Std R & C	3	8	4	7	5	7	9
TOTAL	23%	73%	27%	67%	47%	57%	85%

ENVIRONMENTAL STANDARDS

Observed Trends

- Networking is synergistic with consensus.
- Large vs. Small. NELAC vs. Non-NELAC.
- Large utilities and industries driven by risk.
- All are driven by cost !
- Traditions: Any practice that has been done routinely for more than six months is a norm.
- No News is Good News?
- We have not had a serious problem since…; therefore, we must be doing enough.

ENVIRONMENTAL STANDARDS

Features and Benefits of NELAC

- Uniform quality system standard that complements method flexibility and the Method Update Rule.
- Networking, dialog, and connection to resources.
- Consensus building replaces the comforts of “tradition.”
- Data of known and documented quality replaces “no news is good news.”

ENVIRONMENTAL STANDARDS

Raise the Bar – Lower the Bar ?

- Since 1995, the US EPA has moved far forward in the implementation of method flexibility in both SW-846 and more recently in the Methods Update Rule.
- Method flexibility requires and assumes an underlying quality system to support that data.
- The USEPA needs to consider raising the bar on minimum quality system requirements for all environmental analysis.

ENVIRONMENTAL STANDARDS

Thank You

"Setting the Standards for Innovative Environmental Solutions"

Environmental Standards, Inc.
1140 Valley Forge Road
P.O. Box 810
Valley Forge, PA 19482
610.935.5577
solutions@envstd.com
www.envstd.com

ENVIRONMENTAL STANDARDS

Performance Testing Calculus – An Absolute View

Stephen J. Arpie, M.S.
Absolute Standards, Inc.
P.O. Box 5585
Hamden, CT 06518
203-281-2917
stephenarpie@absolutestandards.com

ABSTRACT

The calculations used for PT evaluations range from fixed limits to study means. In this presentation, we will explore the pros and cons of the present and proposed NELAC/TNI scoring scheme, the resulting impact on laboratory accreditation and the scientific justification. Questions will be raised as to the accuracy and appropriateness of using study means as compared to performance based-fixed limits. Ultimately, we will look for best practice approaches currently structured within USEPA methods for the analysis of drinking water, wastewater and solid waste and see if they can shape the direction of future calculations within the USEPA PT program scoring criteria.

INTRODUCTION

Environmental laboratory accreditation within the U.S. has several components that include proficiency testing when available. Due to the nature of performance testing, laboratories, accreditation bodies (ABs) and manufacturers are especially critical of the scoring criteria used for evaluation. Prior to 1998, the USEPA offered a no-charge PT program for its drinking water program (WS-SDWA), and wastewater program (WP-CWA) categories. They did not offer a PT for "solid waste – soil matrix" for the RCRA program. The criteria used for these liquid PTs were fixed limits with only a few examples of study mean scoring, for example Total Residual Chlorine. This scheme was similar in scope to the publication authored by the USEPA entitled, "1998 Criteria Document". This 1998 document formed the basis for value assignment and scoring under the new privatized version of the PT program audited by the National Institute of Standards and Technology (NIST-NVLAP). This is how the NIST-NVALP accredited providers were expected to score participating laboratories.

While the PT scope did not include more challenging matrices such as soil, or air, it did demonstrate that well-behaved liquid PTs, having both homogeneous and stable properties, could be used to profile a laboratory's analytical capability. By 2002, NELAC had published an analyte list for soil and corresponding scoring criteria that was based upon study means. These tables are commonly referred to as fields of proficiency tests (FoPTs). Many accreditation bodies were increasing their scope to include solid matrices such as sand, soil, and sludge. Several AB's already had soil PTs as a requirement and were aligning their state programs with the national approach presented by the NELAC FoPTs. In additional, several non-NELAC states were requiring soil PTs for accreditation, such as Connecticut and Massachusetts.

Soil PTs are traditionally viewed as a greater production challenge for the PT provider and a greater analytical challenge for the laboratory. Consequently, the acceptance limits are frequently more generous for soil PTs than that of the same compound in a water matrix PT. The assigned value is derived from the participants under test, and it is usually several percentage points lower than the true gravimetric value due to low recovery. From 2003 to 2006, the NELAC FoPT subcommittee re-evaluated the selection of analytes and scoring criteria specifically for solid matrix. A procedure was written and modified to look at historical data from several PT soil studies. While there was significant discussion within the PT subcommittee membership as to the application of the SOP, the general intent was to include only the data points that appeared to be in control. Where data for a particular analyte did not linearly conform, an equation as a function of study mean was set as the requirement to determine the assigned value. If it was possible to set a fixed limit or regression equation, then it was considered but this was rarely the case. Additionally, due to the complexity of the fields of proficiency testing (FoPT), and the limitations of analytical chemistry, it was necessary to write in special conditions to the final release, such as, a laboratory must see at least 10% of the assigned value. For clarity, with all of the notes associated with the release, the reader is encouraged to browse the final 2006 record, which became effective July 1, 2007. The final standard included more analytes, more linear scoring for the WP-CWA list, and revised formulation ranges for both WP-CWA and RCRA lists.

PHILOSOPHY

While the 2006 edition of the standard, included edits to WP-CWA PT, we are mainly concerned with the RCRA-Solids portion and the use of study means as the basis of setting assigned values, and ultimately their scoring ranges. It is this table that has the most assigned values as a function of study means and not a function of production formulation. Currently, many soil PTs such as Trace Metals, Semi-Volatiles, Chlorinated Pesticides, Herbicides, Petroleum Hydrocarbons, and Low Level PAHs have assigned values derived from the participants under test. It follows that the acceptance criteria are bound to the study mean, whether the range of acceptance equals plus or minus 3 times the standard deviation (Range = Study Mean + -3SD), or it is modified by the c and d cofactors as depicted in Table 1A & B. The default mindset is the use of study means as opposed to formulation values for the assigned value and the associated scoring criteria.

Table 1A. FoPT Metals (partial list).

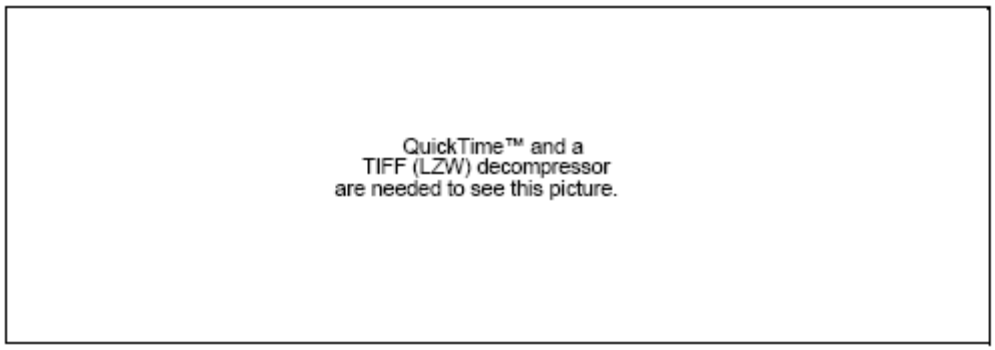
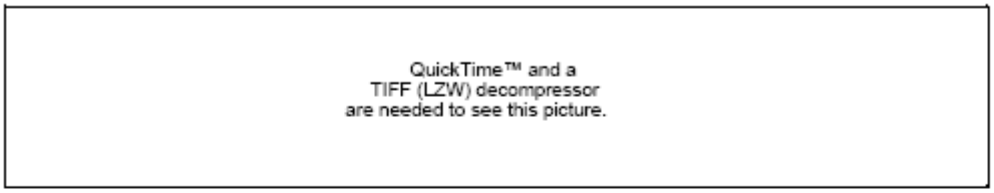


Table 1B. FoPT Base/Neutrals (partial list).



In Table 1A and 1B, we can see that the assigned value is dependent upon the study mean from the participants and not the formulation value in production. As a requirement of participation, laboratories under test are required to treat the PT sample as if it is a routine sample and thus multiple assays are typically not permitted. Because of this, it is unlikely that any individual laboratory can demonstrate any statistical weight on their reported measurement. These single points are combined from other participants' single points, to generate an assigned value and a standard deviation to yield the acceptance limits. Further, laboratories are not required to report uncertainties with their answers and thus are not performing a metrological function.

To assure that all laboratories are accredited at all times, in a fair and consistent manner, it becomes critical to use assigned values based on gravimetric formulation and scored with fixed limits or regression equations. "Study mean calculus", which generates PT Provider specific criteria, is in conflict with this assurance. In fact, each study from the same provider generates a specific set of scoring ranges. In effect, there are no set criteria. Only the initial formulation design is fixed, and every point after is allowed to vary. The initial design and formulation is fixed metrologically, yet, every calculation after production is allowed to vary based on participants reported values.

Let's think about what this really "means" in practice. The PT provider is required to generate a PT sample with known and documented quality. Next, the laboratory generates a calibration curve with know and documented quality. However, when the PT provider generates the assigned value and associated scoring criteria, the FoPTs require a technique that disconnects from quality and critical traceability. If we refer to ISO/IEC CD 17043, "Conformity assessment – general requirements for proficiency Testing", published 03/14/2008, we see in Annex B,

B.1 Determination of the assigned value and its uncertainty

B.1.1 There are various procedures available for the establishment of assigned values. The most common procedures are listed below in an order that, in most cases, will result in increasing uncertainty for the assigned value. These procedures involve the use of:

a) **known** values – with results determined by specific proficiency test item formulation (e.g. manufacture or dilution);

b) **certified** reference values – as determined by definitive test or measurement methods (for quantitative tests);

c) **reference** values– as determined by analysis, measurement or comparison of the proficiency test item alongside a reference material or standard, traceable to a national or international standard;

d) **consensus** values from expert laboratories – expert laboratories should have demonstrable competence in the determination of the measurand(s) under test, using validated methods known to be highly accurate and comparable to methods in general use. The laboratories may, in some situations, be reference laboratories; and

e) **consensus** values from participant laboratories – using statistical methods described in ISO 13528 and with consideration of the effects of outliers.

It is important to note that "e) consensus values from participant laboratories" offer the highest degree of uncertainty and thus are the least desirable. Interestingly, many of the soil PTs that are currently on the fields of test are study mean determinations. The assigned values are derived from the laboratories under test and the acceptance ranges are bound to that value.

There are other highly respected publications that we can refer to. In "The International Harmonized Protocol for The Proficiency Testing of Analytical Chemistry Laboratories", pages 145-196, we can see a similar discussion. A stable and homogenous formulation process better represents the assessment of the assigned value when it is compared to the consensus participation assignment process.

Quoting from 3.2.5 Formulation we see:

"Formulation comprises the addition of a known amount or concentration of analyte (or a material containing the analyte) to a base material containing none. The following circumstances have to be considered.

- The base material must be effectively free of the analyte, or its concentration must be accurately known.
- It may be difficult to obtain sufficient homogeneity (see Section 3.11) when a trace analyte is added to a solid base material.
- Even when the speciation is appropriate, the added analyte may be more loosely bonded to the matrix than the analyte native in typical test materials, and hence the recovery of the added analyte may be unrealistically high.

Providing that these problems can be overcome, the assigned value is determined simply from the proportions of the materials used and the known concentrations (or purity if a pure analyte is added). Its uncertainty is normally estimated from the uncertainties in purity or analyte concentrations of the materials used and gravimetric and volumetric uncertainties, though issues such as moisture content and other changes during mixing must also be taken into account if significant. The method is relatively easy to execute when the proficiency testing material is a homogeneous liquid and the analyte is in true solution. However, it may be unsuitable for solid natural materials where the analyte is already present ("native" or "incurred").

It is important to note that soil PTs can be made homogenous and stable and thus the assigned value should be based upon known values and not robust study means. It follows that the performance limits can also be based upon a fixed or regression equation. Fixed limits in particular can be determined by reasonable performance of the least accurate method. This will allow all participants to be scored against the same criteria no matter the matrix, method or PT provider. The next consideration is: What do we do with analytes that are difficult to stabilize or homogenize? These tests can be posted to the experimental table where the study mean is the basis for the assigned value. It can also be recommended that no FoPT item that is based upon a study mean should be on accreditation table. These tests are best for the experimental. One can look at the study mean types as samples that are still in the design or research and development phase. They are suitable for testing and gathering data, but not appropriate for accreditation purposes.

The current TNI Draft Interim Standard, June 15, 2007, Volume 3 Proficiency Testing (PT) Provider Requirements, Section 7.1.2 reads "PT providers shall analytically verify the assigned value by direct analysis against a calibration standard made from, or traceable to, a primary reference material (e.g. National Institute of Standards Technology (NIST), United States Pharmacopoeia (USP), etc) if available". What is the purpose of 7.1.2 if the FoPT is based upon study means? It is evident that 7.1.2 is impotent, since it has no weight in the value assignment process and the basis for the scoring scheme. Let us now look at the Homogeneity and Stability sections 7.2 – 7.3. A quick read of this language requires the PT to be both homogenous and stable in order to be fit for use. Therefore, the assigned value can be set by the manufacturer at time of formulation, and not derived from the data coming back from the participants. The scoring can be bound to the gravimetric value, and documents such as: USEPA SW846, and "State Of Connecticut Department of Environmental Protection Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements Semivolatile Organics by Method 8270, SW-846, Version 2.0 July 2006", can be used as guidance. We recognize that there are many other documents that can offer expert guidance in this area. But in all cases, the discussion should be centered on using production values, rather than participant reported values.

SUMMARY

To organize where the reader can take this discussion forward, the following is presented.

The Case for Assigned Values via Formulation and Fixed Limit Scoring Criteria:

A. The designs are required to be homogenous and stable.

B. Calculations are more easily understood by:
   1. Laboratory participants;
   2. Accreditation Bodies (ABs);
   3. Can be explained to any other users of the data.

C. It will be easier to modify the Fields of Proficiency Testing if we align with performance based methods and not dodgy statistics.

D. Is necessary if accreditation is to be compared on a national level and not on a provider study level.

E. Study means and standards deviations can still be calculated but they will not be used for PT study value assignment, setting scoring ranges, or accreditation evaluation. They will be merely a statistical monitor for a particular study or during the R&D, fit for use, and design phases.

F. Is necessary if long term evaluations of how well a laboratory is doing for a particular analyte is more readily determined.

G. PTOB/PTPA can better evaluate a providers program.

H. The PT Provider process of evaluation is greatly reduced, as they do not have to use robust statistical treatments, or multi-modal distributions to account for sample preparation or overall analytical determination. The job of the PT provider is to make a homogeneous, stable PT that measures a labs capability to recover, detect and report an accurate result.

I. The USEPA Methods 8260, 8270 and others show expected recoveries for classes of analytes. From this and other sources, performance based PT criteria can be established. Essentially, the procedure should include looking at published methods, and data, that speaks to typical recoveries and then using this information to assign fixed limits or regression equations as acceptance criteria.

J. A laboratory's accreditation is based upon their analytical capability, competence, training, and technology, rather than other participants' results.

K. Others.

The Case for Assigned Values via Study Means and Associated Scoring Criteria:

A. Exploratory process used in the preliminary designs of PTs.

B. Exploratory process in fitness for use determinations.

C. Appropriate if no traceable assigned value is required.

D. Appropriate if no fixed limit can be agreed upon, and the laboratories under test fully understand the scoring mechanism.

E. Appropriate if a regression equation cannot be determined. (Typically due to wide scatter of data points.)

F. Appropriate if the PT design is not stable due to many factors including reactivity, volatility, packaging, transport or inherent formulation design incompatibilities.

G. Appropriate if laboratory side sample prep and technology are deficient in recovery and detection.

H. Others.

Comments and suggestions are encouraged. However, it is imperative that we focus on adhering to credible standards emphasizing the chemical principles that are internationally recognized. The key documents are ISO17043 and IUPAC's Harmonized Protocol as referenced. Performance-based methods (PBM's) need to include performance-based tests (PBTs). It is with known values that performance can be accurately measured.

REFERENCES

1. ISO/IEC CD 17043, "*Conformity Assessment – General Requirements for Proficiency Testing"*, published 03/14/2008, Annex B.

2. IUPAC Technical Report, "*The International Harmonized Protocol for The Proficiency Testing of Analytical Chemistry Laboratories*", Pure Appl. Chem., Vol. 78, No. 1, published 2006, pages 145-196.

3. National Standards For Water Proficiency Testing Studies Criteria Document, U.S. Environmental Protection Agency, Published August 1998.

4. The NELAC Institute Draft Interim Standard, "Proficiency Testing (PT) Provider Requirements", Published June 15, 2007.

5. NELAC PT for Accreditation, Fields of Proficiency Testing with PTRLs, Solid and Chemical Materials, Effective July 1, 2007, Experimental Tables and Accreditation Tables.

Conducting a Demonstration of Method Applicability

Deana Crumbling, S. Dyment; USEPA, 1200 Pennsylvania Ave. NW (5203P); Washington, DC 20460; 703-603-9903; crumbling.deana@epa.gov
R Johnson; Argonne National Lab

ABSTRACT

The DMA is critical in evaluating and understanding the utility of any real time measurement technology or novel approach at a site. In accordance with Triad's goal of managing decision uncertainty, a DMA provides an initial look at any technology or strategy performance in terms of its ability to meet project decision criteria and guide dynamic work strategies.

The DMA can take many forms such as a comparison of a field based analytical method to a more established laboratory method or an evaluation of whether a particular tool or approach will work at a specific site. The format of a DMA is dictated by site characteristics and the intended use of the data. The resulting efforts provide many project benefits including: strategies to deal with matrix heterogeneity, testing a preliminary CSM to refine sampling protocols, development of field based action levels, designing appropriate QA/QC requirements, using collaborative data sets, improving data management, determining contingencies, and evaluating sample throughput/project staffing or other logistics.

This presentation will include an overview of the DMA process and provide examples of how DMA's have been structured under Triad projects. Examples are expected to highlight the multitude of activities than can be considered for a DMA while demystifying the process and providing a platform to design a DMA for your next project.

Quality Control Strategies for Field Portable XRF Applications in Soil

Deana M. Crumbling, M.S.
Office of Superfund Remediation and Technology Innovation
U.S. Environmental Protection Agency, Washington, D.C.
(703) 603-0643, crumbling.deana@epa.gov
NEMC, Washington, DC August 11, 2008

Managing Decision Uncertainty Affordably and Transparently

1

"Data of Known Quality"

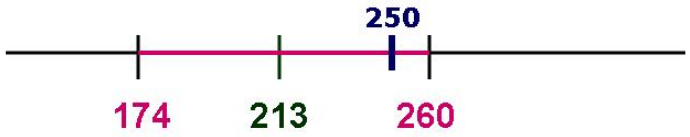
- Critical to support defensible decision-making
- "Known quality" means that the uncertainty of the data results are understood
- Good science
- QC evaluates the "error" or uncertainty in a measurement system
- QC is just as important for field analysis as for lab analysis

2

QC, Data Uncertainty & Decision-Making

Soil result = 213

assume **± 20% RPD** is acceptable QC limit for dup precision



Cannot claim the measurement system can distinguish values between 174 & 260.

If AL = 250, and you get 213, can the decision-maker be confident that the result is below the AL? **No**

(it is within the range of data uncertainty)

3

What can be done to control data imprecision caused by matrix variability?

- Add'l replicates allow statistical confidence
  - "Error" estimation is needed to produce "definitive data"
    "For the data to be definitive, either analytical or total measurement error must be determined."
    --"DQOs for Superfund" guidance (1993) (p. 43)
- Adapt sample processing to reduce heterogeneity

These are nearly impossible to implement under traditional laboratory mechanisms! But easily done using real-time, adaptive S&A & tools like XRF (1 leg of Triad)

4

Real-time Data-Decision Uncertainty Management

- Real-time availability of results
  - instantly recognize data-decision uncertainty
  - adaptively increase replicates to calculate "error"
  - adapt sample processing & analysis to improve reduce data error
  - document statistical decision confidence
- XRF field project example

5

Field Portable X-Ray Fluorescence (XRF) Instrumentation

- Increasingly common field-operated instrument
- Often operated by sample-collection technicians
- Vendor training NOT equate to knowing how to generate data of known quality
- Common excuse: "data just used for screening"
- If "screening data" not known quality, shouldn't trust any decisions
  - Might as well flip a coin

Operator Needs to Detect & Control Potential XRF Problems

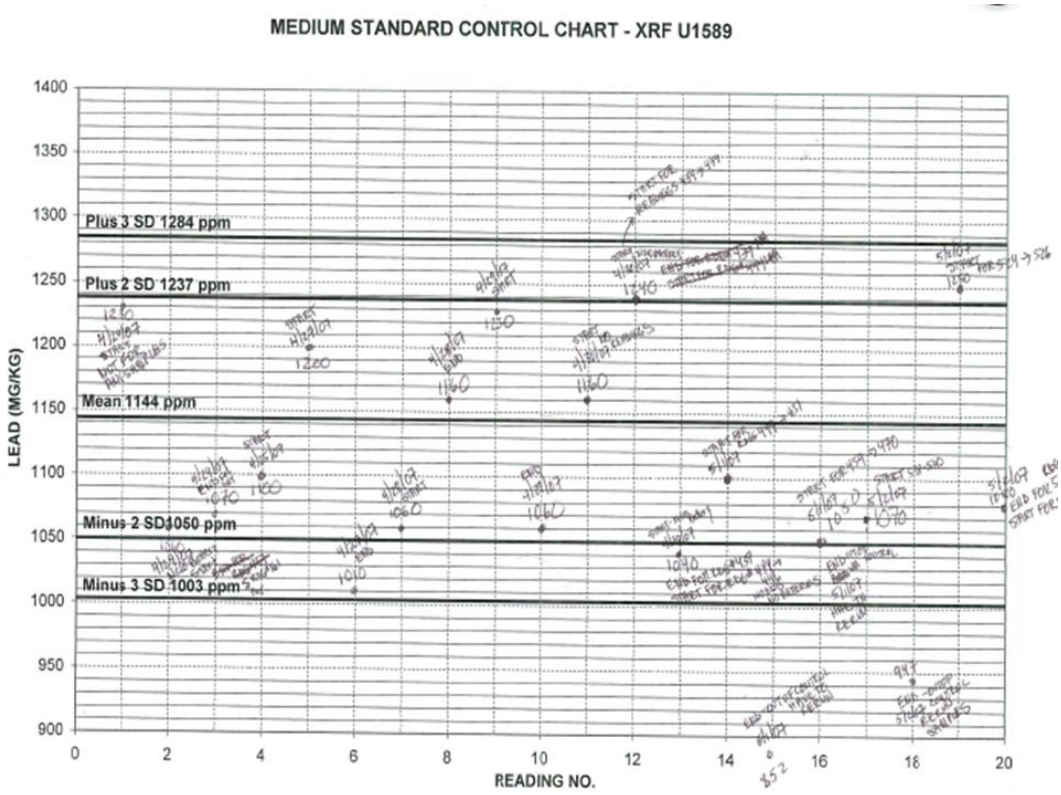
- Understand QC practice, interpretation & CA
  - Initial calibration (generally done at factory)
  - Instrument drift
  - Window contamination
  - Element spectral interference effects
  - Matrix effects (water, matrix minerals absorb X-rays,…)
  - Unacceptable detection limits
  - Matrix heterogeneity effects (particle size/conc effects)
  - Operator errors (window not “square” on matrix)

7

Example: XRF LCS & Corrective Action in Real-time

- Annotated control charts for NIST control
  - Set-up before field project
  - Controls run in field at least 4 times per day
  - Reported results were bracketed by in-control QC (see example next slide)
- Charts detect inadequate instrument performance for investigation & QA-corrective action
  - Check battery power; CA = replace battery
  - Check for instrument cross-contamination; CA = clean
  - Re-standardize instrument—rerun controls & samples
  - Call expert user or vendor support

8



Other XRF QC that Can be Performed

- Instrument & sampling replicates
  - Determine sources of data error
  - Analytical side or matrix sampling side
- Split samples w/ ICP for comparison to XRF results
  - **Avoid random 10% selection**
  - Be selective: Get enough of the right conc so have comparison data points where needed most to build decision confidence
  - ***Valid ICP-XRF comparisons require control over sample heterogeneity***

10

Measuring Heterogeneity Effects

- Duplicates are a way to assess heterogeneity's impact on data repeatability
- 4 of 6 lab dups were out-of-control (lab's QC limit was 35% RPD)
- Action level = 500 ppm

Sample ID	Original ICP result	Lab duplicate ICP result	%RPD
NW10-B-0-2	**453**	**666**	**38**
NW14-C-0-2	**1040**	**688**	**41**
NW16-A-2-10	**760**	**1038**	**31**
SWNW2-D-0-2	**874**	**2187**	**86**
SWNW4-A-0-2	**996**	**874**	**13**
SWNW5-B-2-10	**689**	**987**	**36**

11

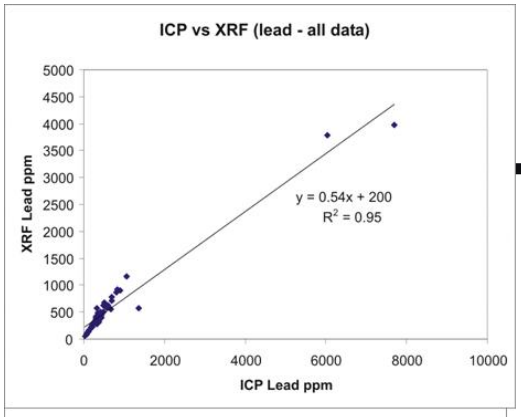
Comparing XRF & ICP Data

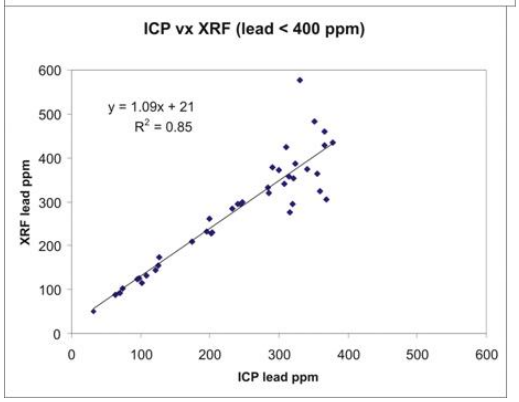
You can't expect XRF to match ICP any better than ICP matches itself!

Data Comparability
Between Field & Lab Methods
(the term "confirmation" is misleading)

First, a word about regression…

12

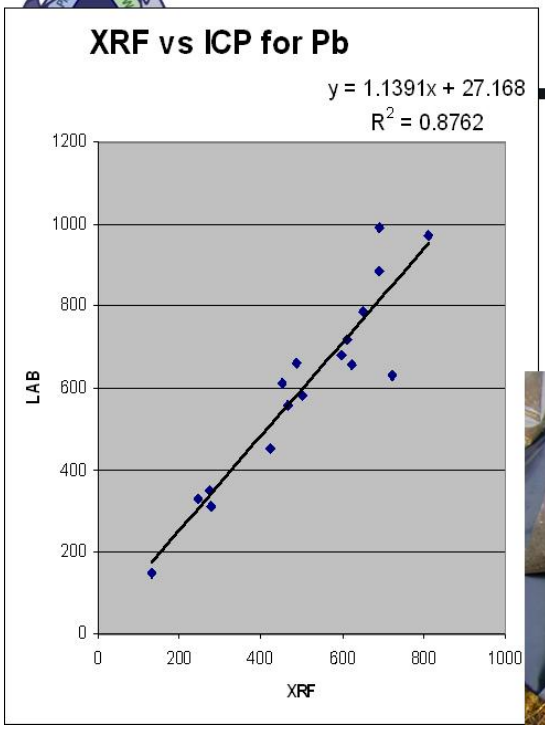




Don't be Fooled by "Stealth" Regressions!

- Poor regressions often fly under the radar.
- Common error is using 1 or 2 very high results
- Falsely improves R^2
- Over-dependence on R^2 (such as in SW-846!)
- Often neglect slope & intercept! (More important than $R^{2)}$

13



Bagged Samples

- Take ~300 – 1 kg soil in plastic bag
- Shoot several times over bag for XRF result
- Send to ICP lab for subsampling & analysis

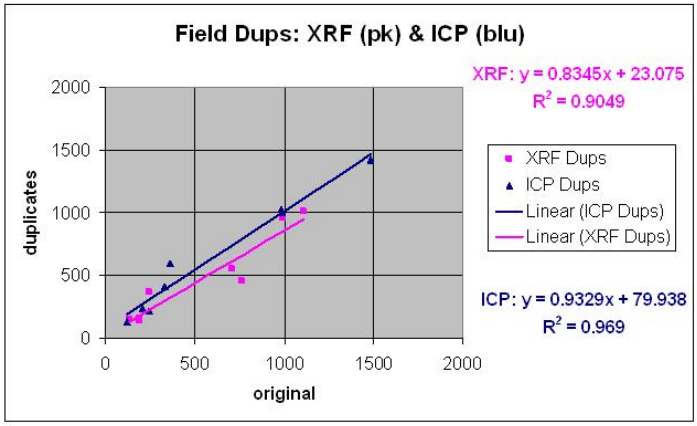
Confidence in Bag Pb Results, Didn't get the Same Info w/ ICP Data

Sample ID	Date Sampled	Date Analyzed	Time	XRF Reading No.	Run Time (30 sec minimum)	Uncorrected Result	
NW10-B-0-2	24-Apr	27-Apr	1054	219	33	330	
NW10-B-0-2	24-Apr	27-Apr	1058	220	30	404	
NW10-B-0-2	24-Apr	27-Apr	1101	221	30	505	
NW10-B-0-2	24-Apr	27-Apr	1105	222	30	473	
					AVERAGE	428	
					STANDARD DEVIATION OF RESULTS	78	
					95th UCL on the Mean	**519**	
					IS 95th UCL less than 500??	YES	NO X
					If no, are at least 2 readings below 500? If yes, then proceed to below	YES X	NO
NW10-B-0-2	24-Apr	27-Apr	1110	223	30	363	
NW10-B-0-2	24-Apr	27-Apr	1113	224	30	377	
NW10-B-0-2	24-Apr	27-Apr	1117	225	30	403	
NW10-B-0-2	24-Apr	27-Apr	1121	226	30	418	
NW10-B-0-2	24-Apr	27-Apr	1125	227	30	528	
NW10-B-0-2	24-Apr	27-Apr	1131	228	38	416	
					AVERAGE	422	
					STANDARD DEVIATION OF RESULTS	63	
					95th UCL on the Mean	**458**	
					Is 95th UCL less than 500?? If no, rehomogenize and repeat	YES X	NO

15

Plot XRF's Dups & ICP's Dups

1 set of samples had both XRF & ICP dups (2 XRF results & 2 ICP results on same bagged sample). Plot the ICP lab original/duplicate sets & the XRF original/ duplicate sets & then place both plots on the same graph.



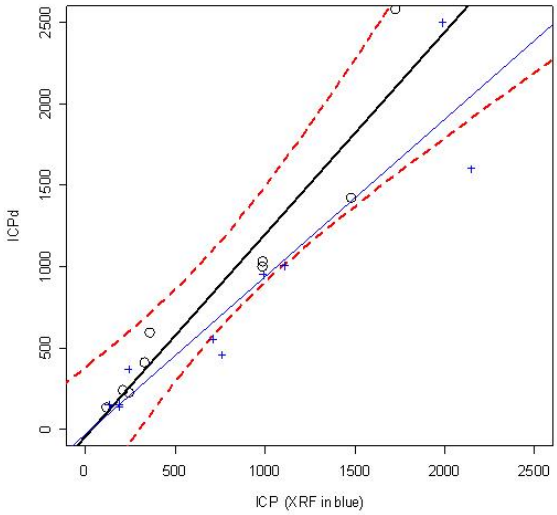
They are pretty close, but are they the "same"?

I.e., given the noise in both data sets, is the XRF data numerically comparable to the ICP data?

16

No "Correction" Required

When "noise" is taken into account, the XRF & ICP data are equivalent (XRF line falls w/in uncertainty of ICP line).



The ICP & XRF data sets are comparable (at least up to 2500 ppm).

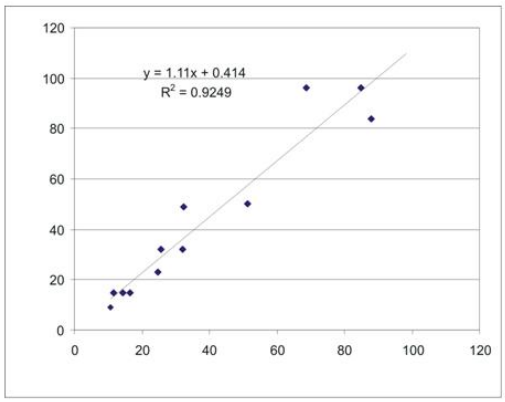
Lab = 1.1391(XRF) + 27.168
R^2 = 0.8762

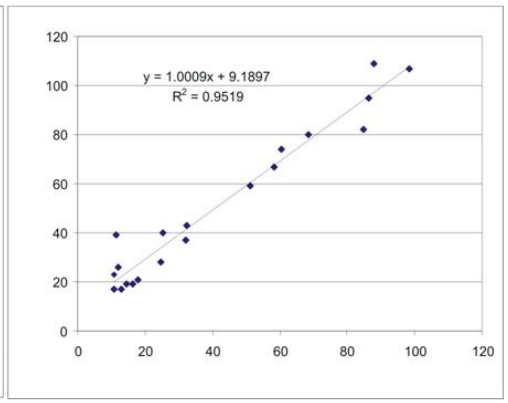
If you did the same statistical analysis for splits between 2 ICP labs, would you correct one for the other?

17

Which is Which?

These scatter plots show the results of soil arsenic analyses. One is a plot of splits between two different ICP labs; the other plots XRF vs ICP splits. Samples were crushed & sieved before splitting.





18

It Is Not Fair...

…to hold XRF data to a higher standard than lab analysis.

And <u>then</u> call all XRF data "screening" & all lab data "definitive".

19

Technology-Specific Performance Assessment

Yves Tondeur, Ph.D. & Jerry Hart
Analytical Perspectives
2714 Exchange Drive
Wilmington, NC 28405
yt@ultratrace.com

ABSTRACT

The moment we stop asking questions about the functionality of our controls, we drive ourselves into a situation whereby our methodologies offer misinformation on the actual performance. A case in point is comprehensive and stable isotope-dilution high-resolution mass spectrometry (ID-HRMS) or tandem MS/MS, which are the underlying technologies for methods measuring minute quantities of PCDD/Fs, PCBs, PAHs, pesticides, PPCPs and PBDPEs.

Tradition determinism—i.e., perpetuating old habits by continuing to rely on old ways to assess performance—is a sure way to lock ourselves into the past and limit improvements for the future. It is essential we realize that not all technologies are created equal. Furthermore, the perception that one quality mold fits all is an obstacle to quality gains. In the small amount of time allocated, we will attempt to show why it is important to rethink the quality system framework so that we can transform the way QC is carried out by focusing more on the decisive procedural steps and replacing obsolete practices. The object is to keep ID–HRMS and ID-MS/MS honest by making the related methods more transparent and accountable. This has ramifications on how future ID-based methods should be written, however, this paper will discuss the more immediate need of how to align the NELAC Quality System standards with the ID technology specific needs.

Technology - Specific Performance Assessment

24th National Environmental Monitoring Conference

Yves Tondeur, Ph.D.
Jerry Hart
Analytical Perspectives

August 11-15, 2008
Washington, D.C.

14-Nov-08

Objectives

Develop Awareness

ALL TECHNOLOGIES NOT CREATED EQUAL

Correct Perceptions

ONE QUALITY MOLD FITS ALL

Keep Isotope Dilution Honest

MORE TRANSPARENT
METHODS ACCOUNTABLE
NO MORE DECISIVE ERRORS ALLOWED TO GO UNNOTICED
RETHINK QUALITY FRAMEWORK
TRANSFORM THE WAY QC IS CARRIED OUT
REVISED QA/QC APPROACHES REPLACING OBSOLETE PRACTICES

Analytical Perspectives

14-Nov-08

TECHNOLOGY

COMPREHENSIVE & STABLE

ISOTOPE - DILUTION

HIGH - RESOLUTION

OR

TANDEM

MASS SPECTROMETRY

TECHNOLOGY

ULTRATRACE

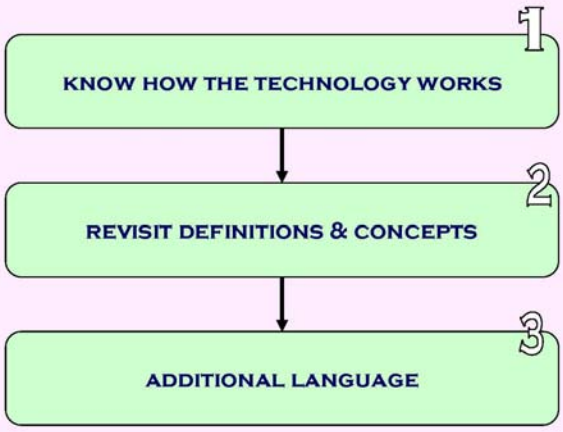
ISOTOPE DILUTION – BASED

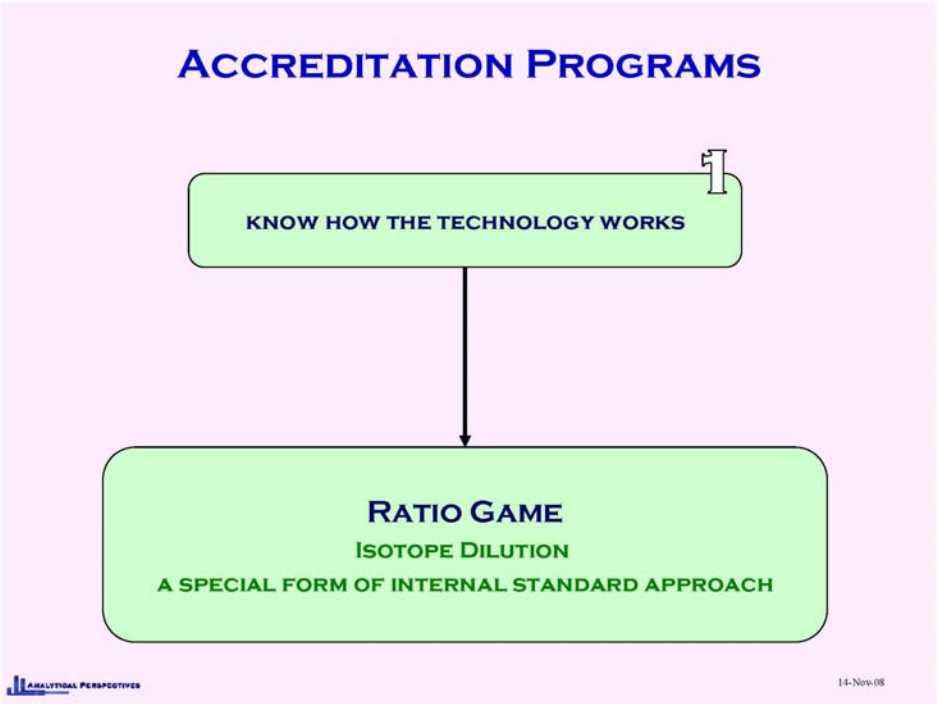
US METHODS

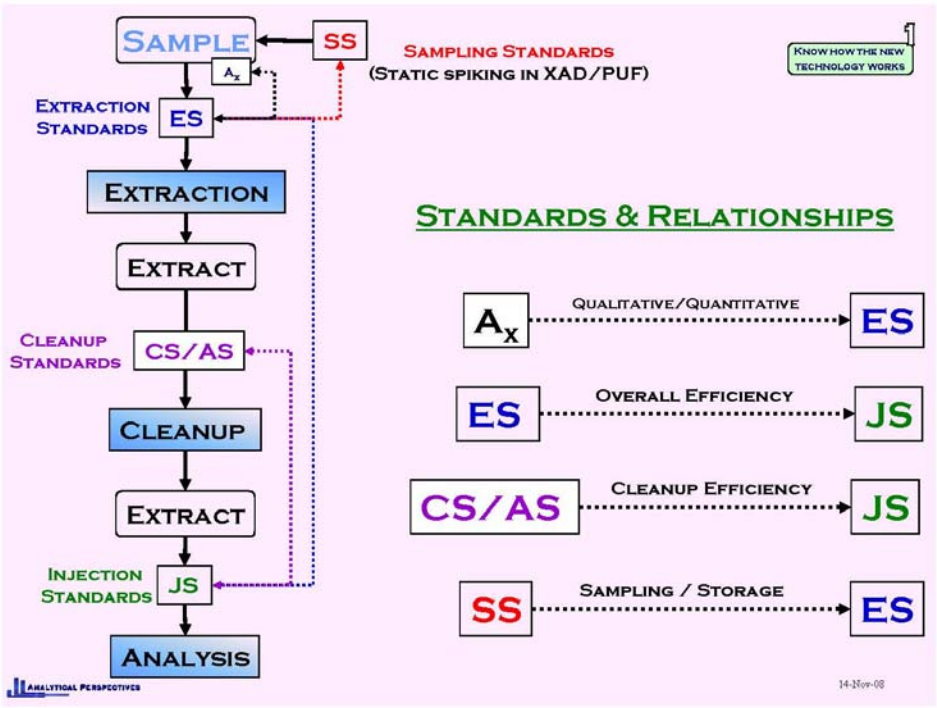
8290
23
0023A
TO9A
428
429
1613
1668A
1614
1694
1698
1699

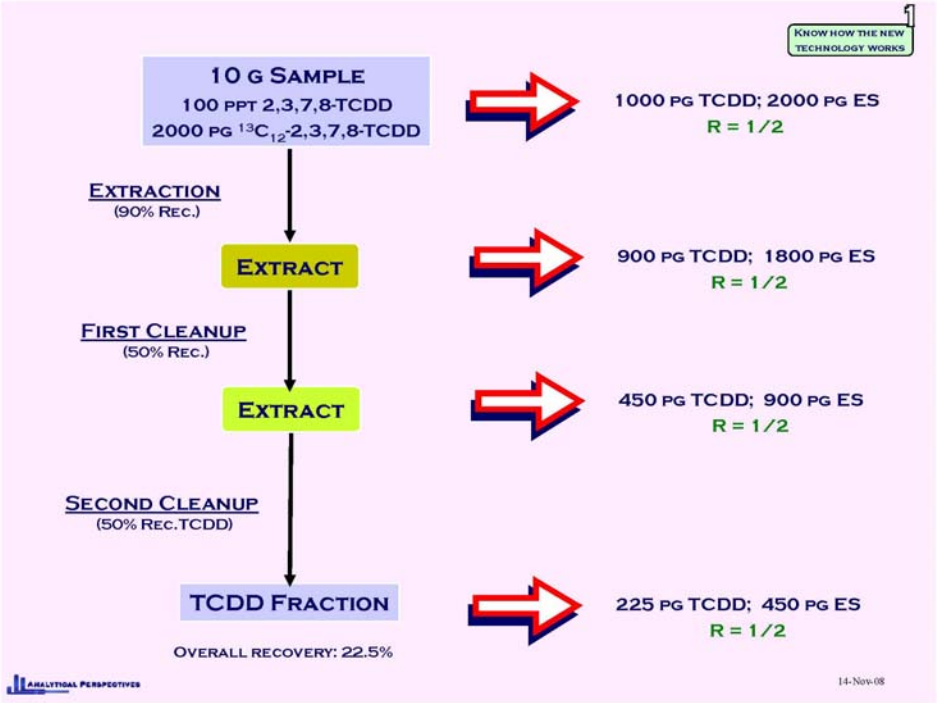
1. METHODS
2. EDUCATION
3. ACCREDITATION PROGRAMS

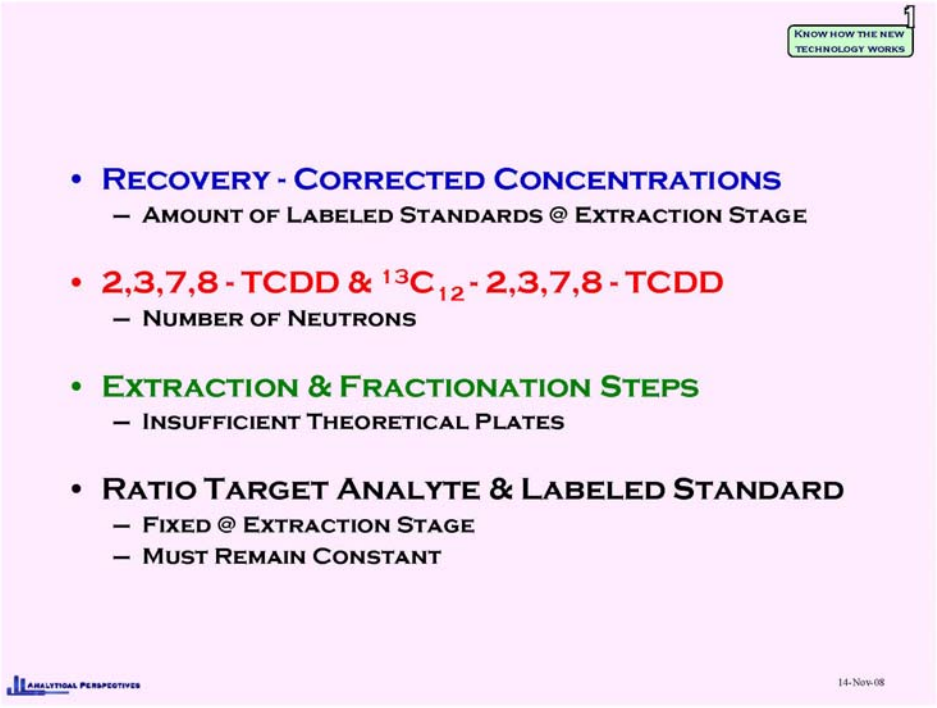
ACCREDITATION PROGRAMS




ACCREDITATION PROGRAMS
1
KNOW HOW THE TECHNOLOGY WORKS
RATIO GAME
ISOTOPE DILUTION
A SPECIAL FORM OF INTERNAL STANDARD APPROACH
ANALYTICAL PERSPECTIVES
14-Nov-08


SAMPLE
SS
A_x
SAMPLING STANDARDS
(STATIC SPIKING IN XAD/PUF)
KNOW HOW THE NEW TECHNOLOGY WORKS
EXTRACTION STANDARDS
ES
EXTRACTION
EXTRACT
CLEANUP STANDARDS
CS/AS
CLEANUP
EXTRACT
INJECTION STANDARDS
JS
ANALYSIS
STANDARDS & RELATIONSHIPS
A_x
QUALITATIVE/QUANTITATIVE
ES
ES
OVERALL EFFICIENCY
JS
CS/AS
CLEANUP EFFICIENCY
JS
SS
SAMPLING / STORAGE
ES
ANALYTICAL PERSPECTIVES
14-Nov-08


KNOW HOW THE NEW TECHNOLOGY WORKS
10 G SAMPLE
100 PPT 2,3,7,8-TCDD
2000 PG $^{13}C_{12}$-2,3,7,8-TCDD
1000 PG TCDD; 2000 PG ES
R = 1/2
EXTRACTION
(90% REC.)
EXTRACT
900 PG TCDD; 1800 PG ES
R = 1/2
FIRST CLEANUP
(50% REC.)
EXTRACT
450 PG TCDD; 900 PG ES
R = 1/2
SECOND CLEANUP
(50% REC.TCDD)
TCDD FRACTION
225 PG TCDD; 450 PG ES
R = 1/2
OVERALL RECOVERY: 22.5%
ANALYTICAL PERSPECTIVES
14-Nov-08


KNOW HOW THE NEW TECHNOLOGY WORKS
• RECOVERY - CORRECTED CONCENTRATIONS
– AMOUNT OF LABELED STANDARDS @ EXTRACTION STAGE
• 2,3,7,8 - TCDD & $^{13}C_{12}$ - 2,3,7,8 - TCDD
– NUMBER OF NEUTRONS
• EXTRACTION & FRACTIONATION STEPS
– INSUFFICIENT THEORETICAL PLATES
• RATIO TARGET ANALYTE & LABELED STANDARD
– FIXED @ EXTRACTION STAGE
– MUST REMAIN CONSTANT
ANALYTICAL PERSPECTIVES
14-Nov-08

KNOW HOW THE NEW TECHNOLOGY WORKS

ACCREDITATION PROGRAMS

MOST DECISIVE STEP

SPIKING

ANALYTICAL PERSPECTIVES 14-Nov-08

KNOW HOW THE NEW TECHNOLOGY WORKS

SPIKING

THREE CRITICAL ASPECTS

NOT ADDRESSED IN METHODS

TO ENSURE PERFORMANCE

1. INTEGRATION
2. DELIVERY TECHNIQUE
3. SOLUTIONS RELIABILITY

ANALYTICAL PERSPECTIVES 14-Nov-08

SPIKING

KNOW HOW THE NEW TECHNOLOGY WORKS

ISOTOPE DILUTION
EXTREMELY FORGIVING

DISTINCTION BETWEEN
ACHIEVING A 25 PERCENT RECOVERY
&
UNKNOWINGLY SPIKING
1/4TH OF THE LABELED STANDARDS

SPIKING

KNOW HOW THE NEW TECHNOLOGY WORKS

ISOTOPE DILUTION
EXTREMELY FORGIVING

25 PERCENT RECOVERY = ACCURATE RESULTS

1/4TH LABELED STANDARDS = FACTOR OF 4 ERROR

100 PERCENT RECOVERY = INACCURATE RESULTS

ISOTOPE DILUTION

TRADITIONAL QC SAMPLES

SYMBOLS OF OLD - NOT ADAPTED

THINKING

PERPETUATING PERCEPTION

ALL TECHNOLOGY ARE CREATED EQUAL

ONE QUALITY MOLD FITS ALL

ENEMY WITHIN OUR QUALITY SYSTEMS

TROJAN HORSE ?

ACCREDITATION PROGRAMS

2

REVISIT NELAC DEFINITIONS & CONCEPTS

CELL/PROFICIENCY TESTING
PBMS
MDL
CALIBRATION
OPR / LCS / MS
UNCERTAINTY

ACCREDITATION PROGRAMS

WHY WE NEED A BETTER SYSTEM
RE – ESTABLISHING THE LINK BETWEEN

QC SAMPLE
&
PERFORMANCE ASSESSMENT

WHERE & WHEN
IT IS NEEDED
(SITUATIONAL)

2
REVISIT NELAC
DEFINITIONS & CONCEPTS

ACCREDITATION PROGRAMS

LCS

APPENDIX D: ESSENTIAL QC REQUIREMENTS

D.1.1.2.1 LABORATORY CONTROL SAMPLE

APPENDIX C: DEMONSTRATION OF CAPABILITY

C.3 INITIAL TEST METHOD EVALUATION

C.3.3 EVALUATION OF PRECISION & BIAS (EQUIVALENT TO 4 LCS)

NOTE: MDL IS EQUIVALENT TO 7 LCS

LCS

D.1.1.2.1 Laboratory Control Spike (NELAC 2003)

Purpose:

The LCS is used to evaluate the **performance** of the **total** analytical system, including all **preparation** and **analysis** steps. Results of the LCS are compared to **established criteria** and, if found to be outside of these criteria, indicates that the analytical system is "out of control".

LCS

2
Revisit NELAC Definitions & Concepts

D.1.1.2.1 Laboratory Control Spike (NELAC 2003)

Purpose:

The LCS is used to evaluate the **performance** of the **total** analytical system, including all **preparation** and analysis steps. Results of the LCS are compared to **established criteria** and, if found to be outside of these criteria, indicates that the analytical system is "out of control".

How do we go about doing this in a *correct* manner?

Too vague! Incomplete description because …

How are they established?

…because "*preparation*" includes the most critical and decisive step without being made explicit.

Analytical Perspectives
14-Nov-08

What if…

- The process that was followed to **establish** the criteria failed to recognize the "Trojan horse" nature of the LCS / OPR in the context of isotope-dilution HRMS or MS/MS ?

- The approach followed had an inherent bias due to the study's design?

relying on flawed approaches is not beneficial to NELAC's efforts of building quality systems

OPR & LCS

(1613)

Laboratory Control Sample (LCS)—See ongoing precision and recovery standard (OPR).

OPR—**Ongoing precision** and recovery standard (OPR); a ***laboratory blank*** spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its **purpose** is to assure that the results produced by the laboratory remain within the limits specified in this method for ***precision*** and ***recovery***.

Tacitly implies "*accuracy*" when A_x is the target.

Where are the precision DQOs in Table 6 of Method 1613B?

REVISIT NELAC DEFINITIONS & CONCEPTS 2

OPR & LCS

Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121

" Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for **precision** and recovery. "

ANALYTICAL PERSPECTIVES 14-Nov-08

REVISIT NELAC DEFINITIONS & CONCEPTS 2

OPR & LCS

Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121

There is no clear target precision information in this table.

" Its purpose is to assure that the results produced by the laboratory remain within the ***limits specified*** in this method for ***precision*** and recovery. "

Let's translate these limits into something we can relate to better.

ANALYTICAL PERSPECTIVES 14-Nov-08

OPR & LCS

Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	[redacted]	7.8–12.9
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121

One way of reading this table is to say that on one day we can achieve 6.7 and 15.8 on the next.

" Its purpose is to assure that the results produced by the laboratory remain within the ***limits specified*** in this method for ***precision*** and recovery. "

This effectively means that we have a tolerated percent difference as high as *91 percent* for 2,3,7,8-TCDD in a matrix presenting no challenges !

OPR & LCS

2
REVISIT NELAC DEFINITIONS & CONCEPTS

Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	[redacted]	82–121

This effectively means that we have a tolerated percent difference as high as *155 percent* on the Extraction Standard recovery!

" Its purpose is to assure that the results produced by the laboratory remain within the ***limits specified*** in this method for ***precision*** and recovery. "

ANALYTICAL PERSPECTIVES
14-Nov-08

Let's consider the congener that can constitute as much as 40 to 60 percent of the TEQ in certain matrices:

2,3,4,7,8-PeCDF

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED[1]

CDD/CDF	Test Conc. (ng/mL)	IPR[2] s (ng/mL)	IPR[2] X (ng/mL)	[redacted]	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
2,3,7,8-TCDF	10	2.0	8.7–13.7	7.5–15.8	8.4–12.0
1,2,3,7,8-PeCDD	50	7.5	38–66	35–71	39–65
1,2,3,7,8-PeCDF	50	7.5	43–62	40–67	41–60
2,3,4,7,8-PeCDF	50	8.6	36–75	34–80	41–61
1,2,3,4,7,8-HxCDD	50	9.4	39–76	35–82	39–64
1,2,3,6,7,8-HxCDD	50	7.7	42–62	38–67	39–64
1,2,3,7,8,9-HxCDD	50	11.1	37–71	32–81	41–61
1,2,3,4,7,8-HxCDF	50	8.7	41–59	36–67	45–56
1,2,3,6,7,8-HxCDF	50	6.7	46–60	42–65	44–57
1,2,3,7,8,9-HxCDF	50	6.4	42–61	39–65	45–56
2,3,4,6,7,8-HxCDF	50	7.4	37–74	35–78	44–57
1,2,3,4,6,7,8-HpCDD	50	7.7	38–65	35–70	43–58
1,2,3,4,6,7,8-HpCDF	50	6.3	45–56	41–61	45–55
1,2,3,4,7,8,9-HpCDF	50	8.1	43–63	39–69	43–58
OCDD	100	19	89–127	78–144	79–126
OCDF	100	27	74–146	63–170	63–159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31–113	22–152	71–140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27–184	21–227	62–160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27–156	21–192	72–134
[redacted]	100	38	16–279	[redacted]	77–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29–147	21–193	85–117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34–122	25–163	85–118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27–152	19–202	76–131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30–122	21–159	70–143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24–157	17–205	74–135
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	37	29–136	22–176	73–137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34–129	26–166	72–138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32–110	21–158	78–129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28–141	20–186	77–129
$^{13}C_{12}$-OCDD	200	95	41–276	26–397	96–415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9–15.4	3.1–19.1	7.9–12.7

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

2
REVISIT NELAC DEFINITIONS & CONCEPTS
ANALYTICAL PERSPECTIVES
14-Nov-08

2

REVISIT NELAC DEFINITIONS & CONCEPTS

OPR & LCS

Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16–279		77–130

For 2,3,4,7,8-PeCDF, i.e., one significant contributing congener to the TEQ, the tolerated "*precision*" is 315 percent !

Is this the kind of DQOs we really want ?

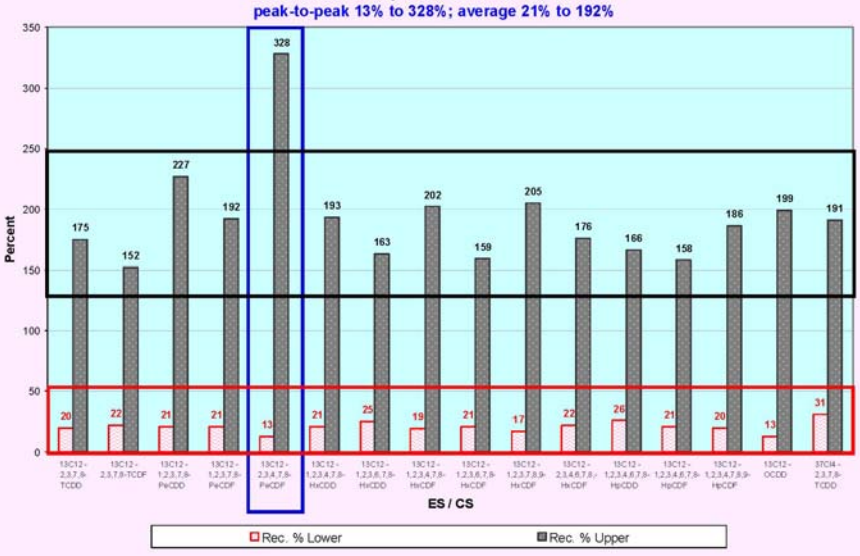
" Its purpose is to assure that the results produced by the laboratory remain within the ***limits specified*** in this method for precision and recovery. "

ANALYTICAL PERSPECTIVES

14-Nov-08

2

REVISIT NELAC DEFINITIONS & CONCEPTS



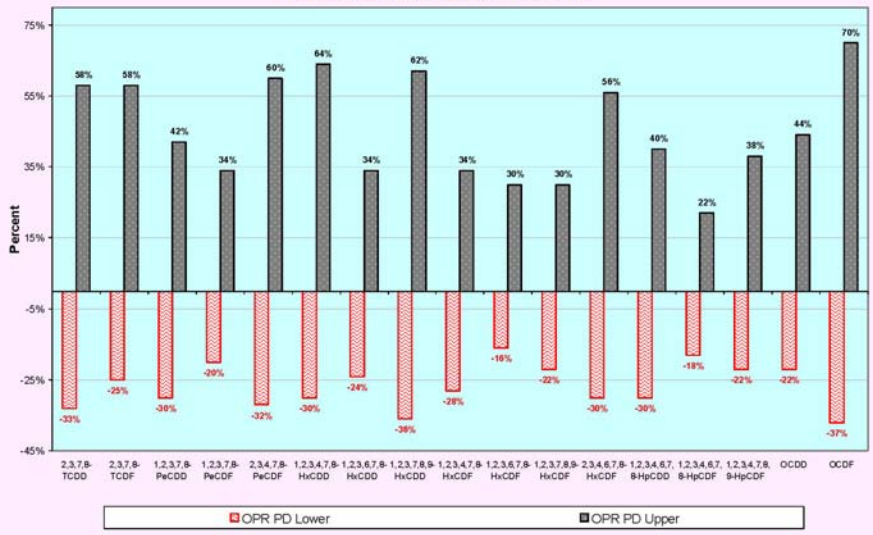
ANALYTICAL PERSPECTIVES

14-Nov-08

2

REVISIT NELAC DEFINITIONS & CONCEPTS

OPR Percent Difference Ranges (measured vs. expected)
Method 1613B Acceptance Criteria for Performance
peak-to-peak 107%; average -27% to 46%



ANALYTICAL PERSPECTIVES

14-Nov-08

2

REVISIT NELAC DEFINITIONS & CONCEPTS

OPR & LCS

NORMAL CASE

SPIKING A "NEUTRAL" MATRIX WITH

A_x
ES

A_x	=	2,3,7,8-TCDD	200 PG
ES	=	$^{13}C_{12}$-2,3,7,8-TCDD	2,000 PG

→ FINAL VOLUME: 20 µL
CORRECT ANSWER: 10 PG/µL (A_x)

ANALYTICAL PERSPECTIVES

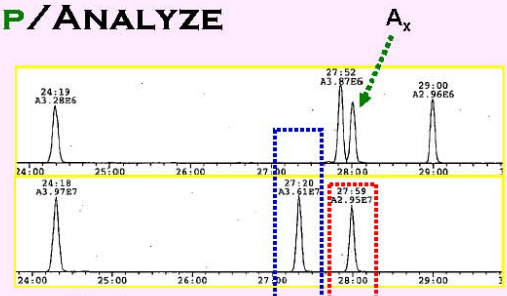
14-Nov-08

OPR & LCS

NORMAL CASE

EXTRACT/CLEANUP/ANALYZE

EXTRACTION
CLEANUP STANDARDS (CS)
FRACTIONATION
INJECTION STANDARDS (JS)
ANALYSIS



FINAL VOLUME: 20 µL
MEASURED CONCENTRATION: 10 PG/µL FOR A_x
CORRECT ANSWER: 10 PG/µL FOR A_x

$$C = \frac{A_{ax} \times 2000\ pg}{A_{es} \times RRF \times 20\ \mu L} = 9.2\ pg/\mu L\ (ng/mL)$$

OPR (ng/mL)
6.7–15.8

14-Nov-08

REVISIT NELAC DEFINITIONS & CONCEPTS 2

OPR & LCS

CASE 1

FACTOR OF 2 SPIKING ERROR (TECHNIQUE)

- SPIKING A "NEUTRAL" MATRIX WITH
  - 100 PG 2,3,7,8-TCDD (A_x)
  - 1000 PG $^{13}C_{12}$-2,3,7,8-TCDD (ES)
- EXTRACT/CLEANUP/ANALYZE
  - MEASURED ANSWER IN OPR/LCS IS 10 PG/µL FOR A_x
  - THUS, MEASURED BIAS IS 0%
  - BUT, SAMPLE RESULTS ARE REPORTED 2 TIMES HIGHER

14-Nov-08

CASE 1

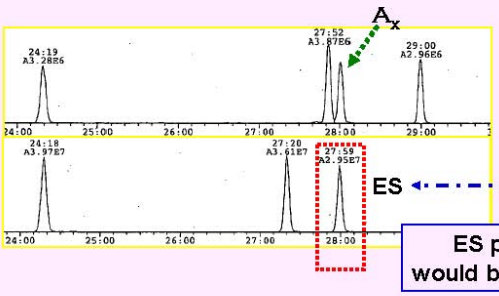
100% SPIKING ERROR (TECHNIQUE)

A_x = 2,3,7,8-TCDD 100 PG

ES = $^{13}C_{12}$-2,3,7,8-TCDD 1,000 PG

IF THE ACTUAL ES RECOVERY IS 100%, AND THE TECHNIQUE ERROR DOES NOT APPLY TO THE INJECTION STANDARDS

THE MEASURED RECOVERY IS 50%



ES peak would be ½ size

ANALYTICAL PERSPECTIVES 14-Nov-08

REVISIT NELAC DEFINITIONS & CONCEPTS 2

OPR & LCS

CASE 2

10 - FOLD SPIKING ERROR (TECHNIQUE)

- SPIKING A "NEUTRAL" MATRIX WITH
  - 2000 PG 2,3,7,8-TCDD (A_x)
  - 20,000 PG $^{13}C_{12}$-2,3,7,8-TCDD (ES)
- EXTRACT/CLEANUP/ANALYZE
  - MEASURED ANSWER IN OPR/LCS IS 10 PG/µL FOR A_x
  - THUS, MEASURED BIAS IS 0%
  - BUT, SAMPLE RESULTS ARE REPORTED 10 TIMES LOWER

ANALYTICAL PERSPECTIVES 14-Nov-08

SCENARIO	1	2	3	4
OPR / LCS	V	V	X	X
SAMPLE	V	X	V	X

V = PASSING
X = FAILED

Disconnect between conventional QC sample and performance assessment

Results of the LCS are compared to established criteria and, if found to be outside of these criteria,…

…indicates that the *analytical* system is "out of control" ?

ANALYTICAL PERSPECTIVES 14-Nov-08

ACCREDITATION PROGRAMS

3

ADDITIONAL LANGUAGE

ANALYTICAL PERSPECTIVES 14-Nov-08

ADDITIONAL LANGUAGE

D.1.1.2.1 Laboratory Control Spike (NELAC 2003)

Purpose: lacks functional value

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps.

ISOTOPE - DILUTION

ANALYTICAL PERSPECTIVES 14-Nov-08

ADDITIONAL LANGUAGE

D.1.1.2.1 Laboratory Control Spike (NELAC 2003)

Purpose:

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps.

→ FOCUS ON IMPORTANT & DECISIVE STEPS

…indicates that the analytical system is "out of control".

ANALYTICAL PERSPECTIVES 14-Nov-08

ADDITIONAL LANGUAGE

D.1.1.2.1 Laboratory Control Spike (NELAC 2003)

Purpose:

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps.

LCS = SPIKED BLANK + "STOP THE TROJAN HORSE"

…indicates that the analytical system is "out of control".

ANALYTICAL PERSPECTIVES 14-Nov-08

If you cannot detect,
you cannot correct !

TECHNOLOGY - SPECIFIC PERFORMANCE ASSESSMENT

14-Nov-08

Laboratory Support for Multi-Increment Sampling

Mark Bruce
TestAmerica
4101 Shuffel St. NW
North Canton, OH 44720
330-966-7267
mark.bruce@testamericainc.com

ABSTRACT

The US Army Corp of Engineers has adapted sample collection techniques from the mining and agricultural fields for use on military training ranges with heterogeneous distributions of energetic contaminants. These multi-increment sampling procedures have also been applied to both metals and organics. Large samples in the 1 to 5 kg range are typically sent to the lab for processing and subsampling prior to analysis. The laboratory process for energetics is described in SW-845 Method 8330B. The same principles have also been adapted for other analyte groups. This paper will summarize the various laboratory processing options for multi-increment samples and cover the advantages and limitations of each. These processing options include drying, sieving, chopping, grinding, wet and dry mixing. Subsampling techniques such as multi-increment and line & scoop will also be covered.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Laboratory Support for Multi-Increment Sampling

Mark Bruce Ph.D
Larry Penfold

National Environmental Monitoring Conference
Washington D.C.

August 11, 2008

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Audience survey

- Monitoring data users

- Monitoring data producers

2

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Chasing Error Sources

- Instrumental analysis

- Sample preparation

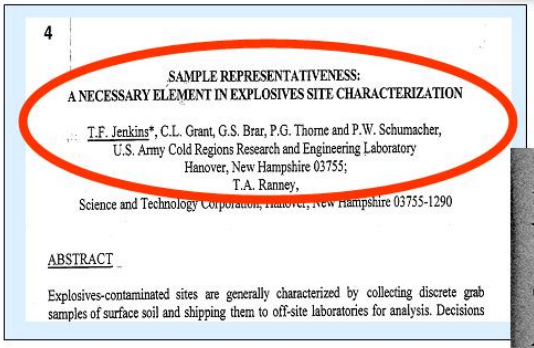
- Laboratory sub-sampling

- Field sample collection

3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sample collection is old news for some.



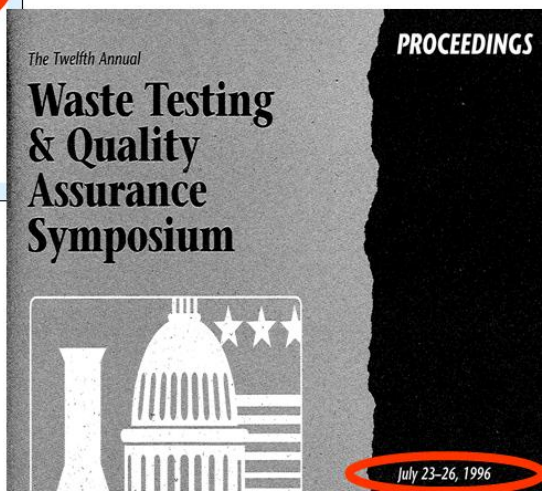
4

SAMPLE REPRESENTATIVENESS:
A NECESSARY ELEMENT IN EXPLOSIVES SITE CHARACTERIZATION

T.F. Jenkins*, C.L. Grant, G.S. Brar, P.G. Thorne and P.W. Schumacher,
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, New Hampshire 03755;
T.A. Ranney,
Science and Technology Corporation, Hanover, New Hampshire 03755-1290

ABSTRACT

Explosives-contaminated sites are generally characterized by collecting discrete grab samples of surface soil and shipping them to off-site laboratories for analysis. Decisions



4

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Multi-Increment Grid

5

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Produces Large Samples

6

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Air Dry

7

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sieve to Remove > 2 mm

8

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Puck Mill Grind

9

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Multi-Increment Subsample

10

Picture from USACE-Alan Hewitt

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Formalized and Expanded to Other Energetics in 8330B

METHOD 8330B

NITROAROMATICS, NITRAMINES, AND NITRATE ESTERS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

SW-846 is not intended to be a
procedures are written based on the
formally trained in at least the basic
technology.

In addition, SW-846 methods,
of method-defined parameters, are i
information on how to perform an ar
as a basic starting point for generati
either for its own general use or for a
included in this method are for guida
not be used as absolute QC accepta

1.0 SCOPE AND APPLICATION

1.1 This method is intende
residues by high performance liquid
detector. The following RCRA comp
determined by this method:

June 2008

DoD Environmental Data Quality Workgroup

Guide for Implementing EPA SW-846 Method 8330B

Introduction:

In November of 2006 the Environmental Protection Agency (EPA) published method 8330B.[1] The method provides instruction for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC). The method includes an appendix (A), which describes sampling methodologies for collecting and processing representative samples for analysis.

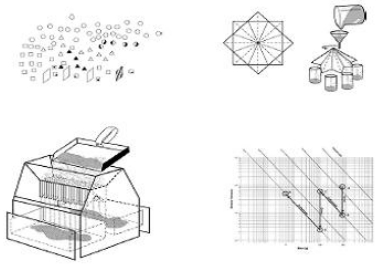
11

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

EPA Subsampling Guidance

Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples

Nov 2003



United States Environmental Protection Agency | Solid Waste and Emergency Response (5305W) | EPA530-R-99-015 July 1999 www.epa.gov/osw

Office of Solid Waste

EPA

RCRA Waste Sampling Draft Technical Guidance SW-846 Chapter Nine

Planning, Implementation, and Assessment

12

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

One Good Idea Grows

13

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

And Spreads Rapidly

14

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Look close at the options

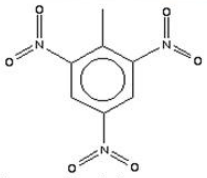
- Analytes
- Sample conditioning
  - ~ Dry - As is
- Sieve (exclude non-sample)
- Grind / disaggregate
- Sieve (max particle size)
- Mixing
  - ~ Dry – Wet - As is
- Sub sample
- Strengths & limitations

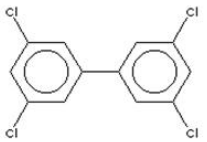
15

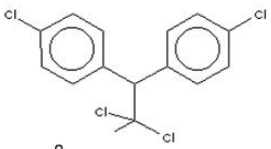
TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

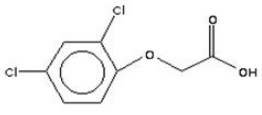
Choose your analytes

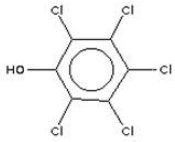
- Energetics
- Metals, Hg
- PCBs
- Organochlorine Pescticides
- Phenoxy acid herbicides
- Petroleum hydrocarbons
- Semivolatile organics
- Volatile organics

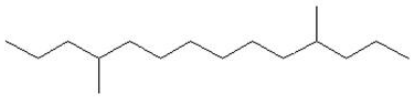












16

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sample – Not sample

- Sample jars often contain non-sample components
  - ~ Decantable water
  - ~ Sticks
  - ~ Leaves
  - ~ Rocks
- Specify particle size to remove

17

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Modifying moisture content

- Air dry
  - ~ Al foil or paper liner
  - ~ Ventilation hood
  - ~ Strength – easy to crush sample
  - ~ Limitation – volatile analyte loss

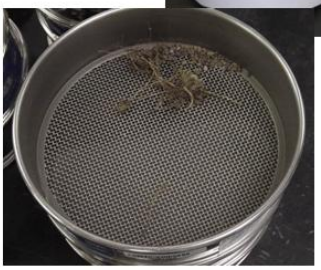
- Add water
  - ~ Make paste
  - ~ Strength – retains low boiling analytes
  - ~ Limitation – hinders extraction
- As is
  - ~ Strength – least analyte loss
  - ~ Limitation – hard to mix & grind

18

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sieve to separate sample from non-sample

- Disaggregate soil clumps
  - ~ Pestle, hammer
  - ~ Coffee chopper
  - ~ Blender
- Most common sieves
  - ~ #4 (6 mm), #10 (2 mm)
    - ° Also #1, #30, #36, #100
- Strength – reproducible size exclusion
- Limitation – requires dry sample



19

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

To grind or not to grind

- Yes
  - ~ Crystalline particles, fibrous threads
  - ~ Energetics, metals
  - ~ Strengths - facilitates mixing, improves precision, reduces sub-sampling error
- No
  - ~ Volatile, thermally labile, increased "availability"
  - ~ Low boiling PCBs, OCPs, TPHs, SVOCs, metals
  - ~ Strengths - better analyte retention, "accurate" metals risk assessment

20

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

How best to grind

- Puck mill or ring and puck mill
  - ~ "stable" energetics
- Ball mill
- Mortar and pestle
- Consider
  - ~ Analytes
  - ~ concentration of interest
  - ~ grinder materials
  - ~ Particle size needed

21

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

How fine is the grind?

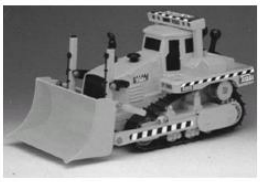
- What is the target particle size?
- How to determine completeness
  - ~ Visual inspection
  - ~ Pinch of "flour"
  - ~ Sieve #200 (~75 um)

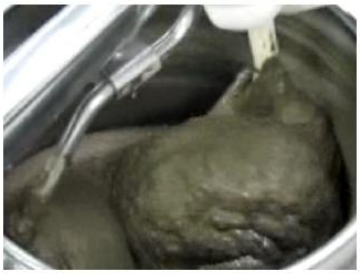
22

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Mixing to reduce heterogeneity

- Tumble in container
- Benchtop bulldozers
- "Bread dough" mixer
- Grinders
- High "G" mixer



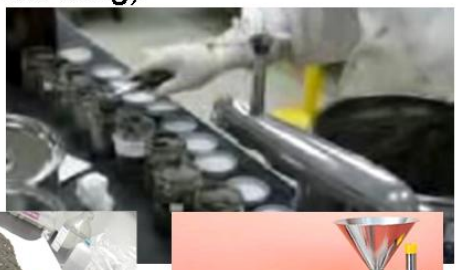


23

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sub-sampling Options

- Sequential scoops (fractional shoveling)
- Rotary Sectorial splitter
- Line & scoop
- Mix & dig-a-spot
- MIS pancake (8330B)

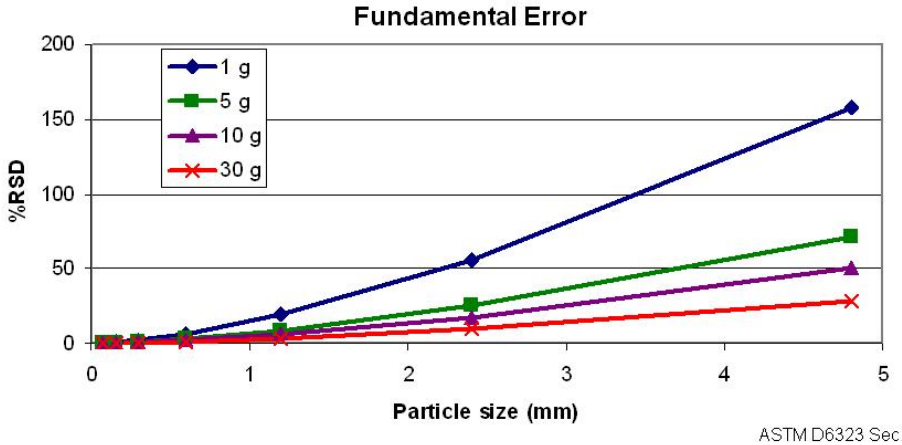


24

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Using large subsamples

- Larger particles
  - ~ Produce larger errors or require larger subsamples



25

ASTM D6323 Sec. A1.1

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

How to choose?

- Talk with your laboratory
- Specify the performance wanted/needed to make the decision
  - ~ List all Analytes
  - ~ Sample mass range
  - ~ Particle size to include/exclude
  - ~ Analyte accuracy - %R
  - ~ Analyte precision - %RSD
  - ~ Pebbles, crystalline material
    - ° Grind or not
      - – If yes to what max particle size

26

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Acknowledgements

- Alan Hewitt, Tom Jenkins

- Brad Chirgwin (Burlington),
  Mustahsan Farooqui (Portland),
  Ben Hicks (St. Louis),
  Karen Kuoppala (Denver),
  Brian Nagy (Honolulu),
  Patrick Rainey (W. Sacramento),
  Chris Rigell (Knoxville)

27

AUTHOR INDEX

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

AUTHOR INDEX