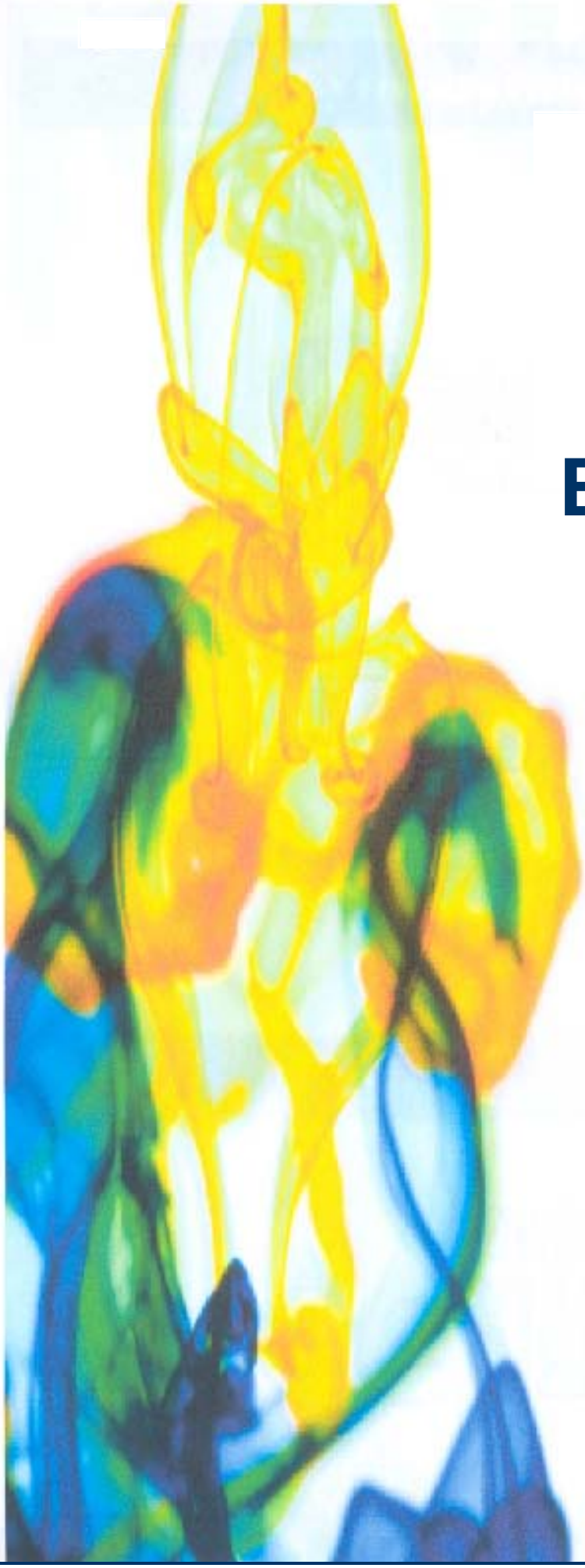

NEMC

National Environmental Monitoring Conference

Proceedings 2007

Cambridge, MA
August 19—25, 2007

NEMC 2007

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NEMC 2007

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NEMC 2007

CONFERENCE HIGHLIGHTS

The 23rd Annual National Environmental Monitoring Conference (NEMC) was held at the Hyatt Regency in Cambridge, Massachusetts from August 20 – 25, 2007. This was the first combined meeting of NEMC with the Forum on Laboratory Accreditation. The Conference was co-sponsored by the US Environmental Protection Agency, the Independent Laboratories Institute, and The NELAC Institute. Over 430 individuals attended. The 23rd meeting of NEMC had 127 technical presentations over 5 days:

- Seventeen technical breakout sessions with 94 presentations;
- Two-day poster program with 21 posters;
- Seven keynote presentations; and
- General session on detection and quantitation with 5 presentations.

Three training courses were offered in conjunction with NEMC 2007:

- Metal Speciation Analyses;
- Manual Integration – Introduction to Proper Techniques, Documentation and Optimal Settings; and
- Tools to Calculate and Evaluate Measurement Performance.

The exhibit program featured 42 exhibitors demonstrating the latest innovations in measurement technology, proficiency testing, laboratory automation, and related topics.

***

NEMC 2007

TABLE OF CONTENTS

KEYNOTE PRESENTATIONS

SPECIAL SESSION ON DETECTION AND QUANTITATION LIMITS

AIR METHODS

METALS SPECIATION

VAPOR INTRUSION

POSTER PRESENTATIONS

KEYNOTE PRESENTATIONS

DoD Emerging Contaminants Initiative

Paul Yaroschak
Office of the Secretary of Defense

ABSTRACT

Emerging Contaminants (ECs) are chemicals or materials of evolving regulatory interest. They have a real or perceived health threat. They have no existing peer-reviewed toxicity values or health standards or the existing standards are being re-evaluated. ECs usually have insufficient or limited health, science or technology information available. They may also become of interest because a new source, pathway or detection limit has been discovered. ECs in sediments can significantly affect response actions, including remediation, and thus significantly affect costs.

The Department of Defense developed an EC Initiative and created an ECs Directorate to deal with a host of EC issues. A three-tiered process has been developed for over-the-horizon scanning for ECs, conducting impact assessments in five DoD functional areas, and development of risk management options. The five functional areas are:

(1) Environmental, Safety and Health

(2) Mission/Readiness

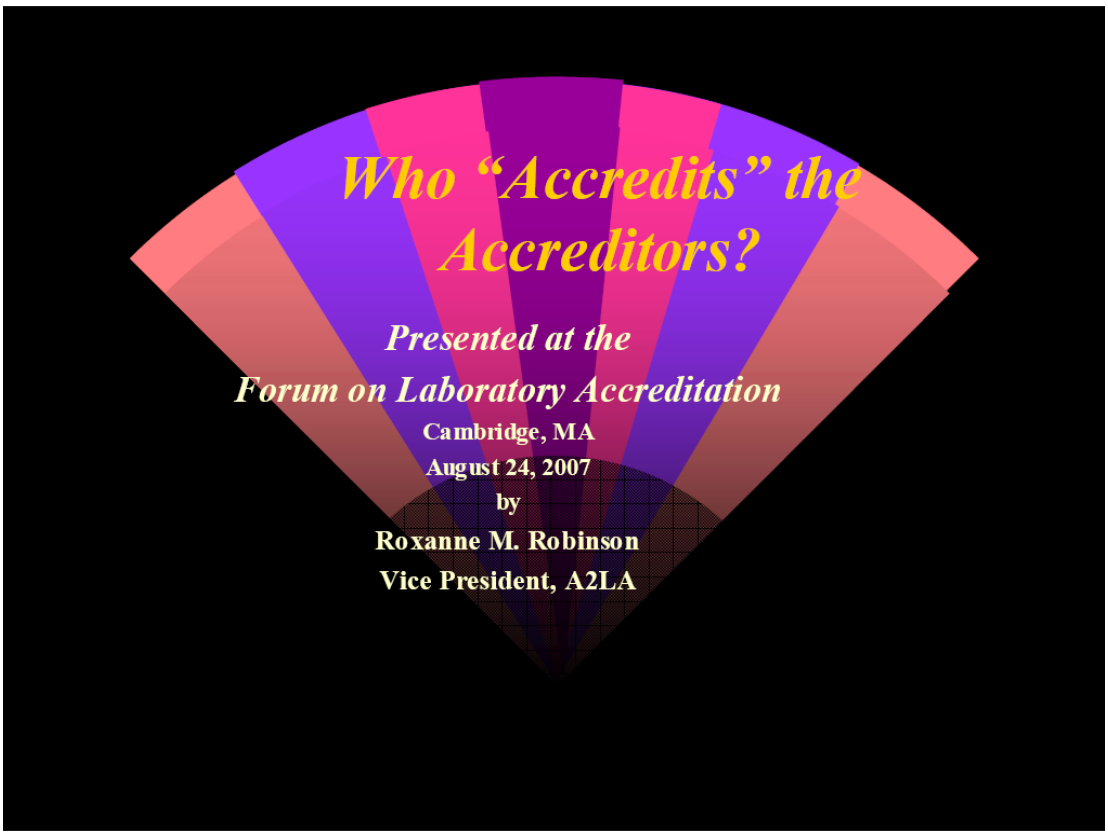
(3) Acquisition

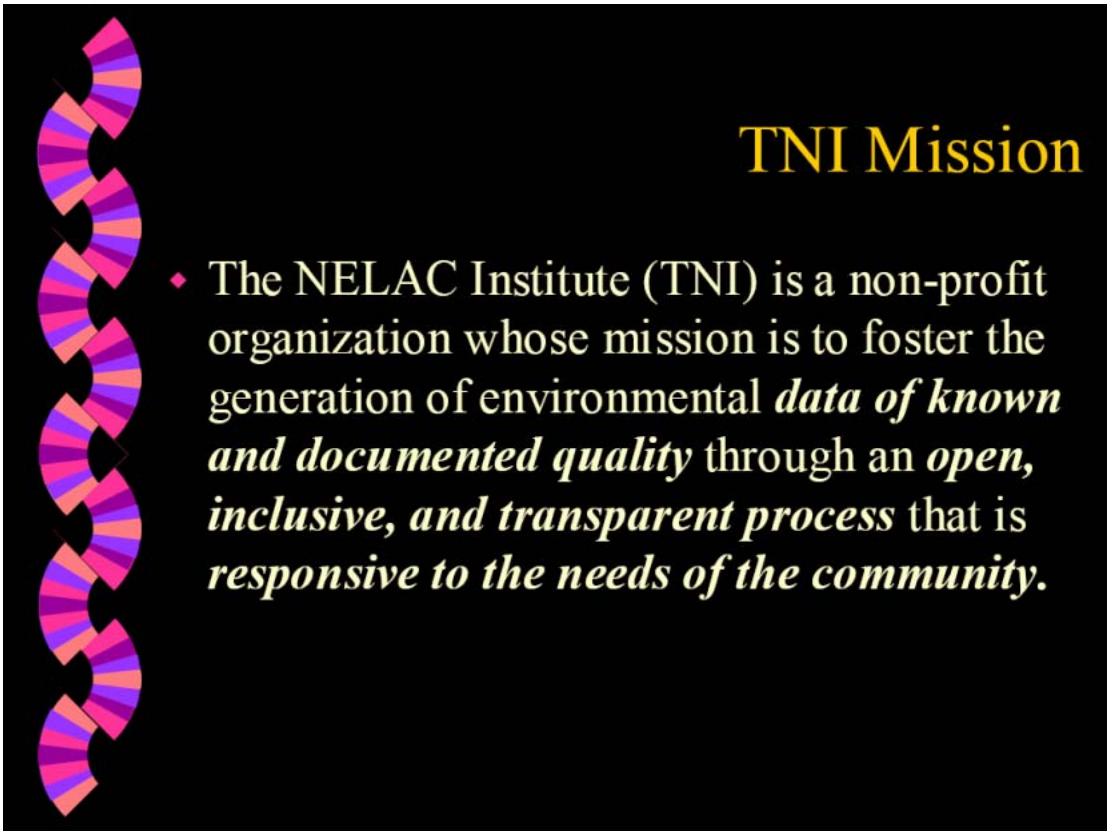
(4) Operation and Maintenance of DoD Assets

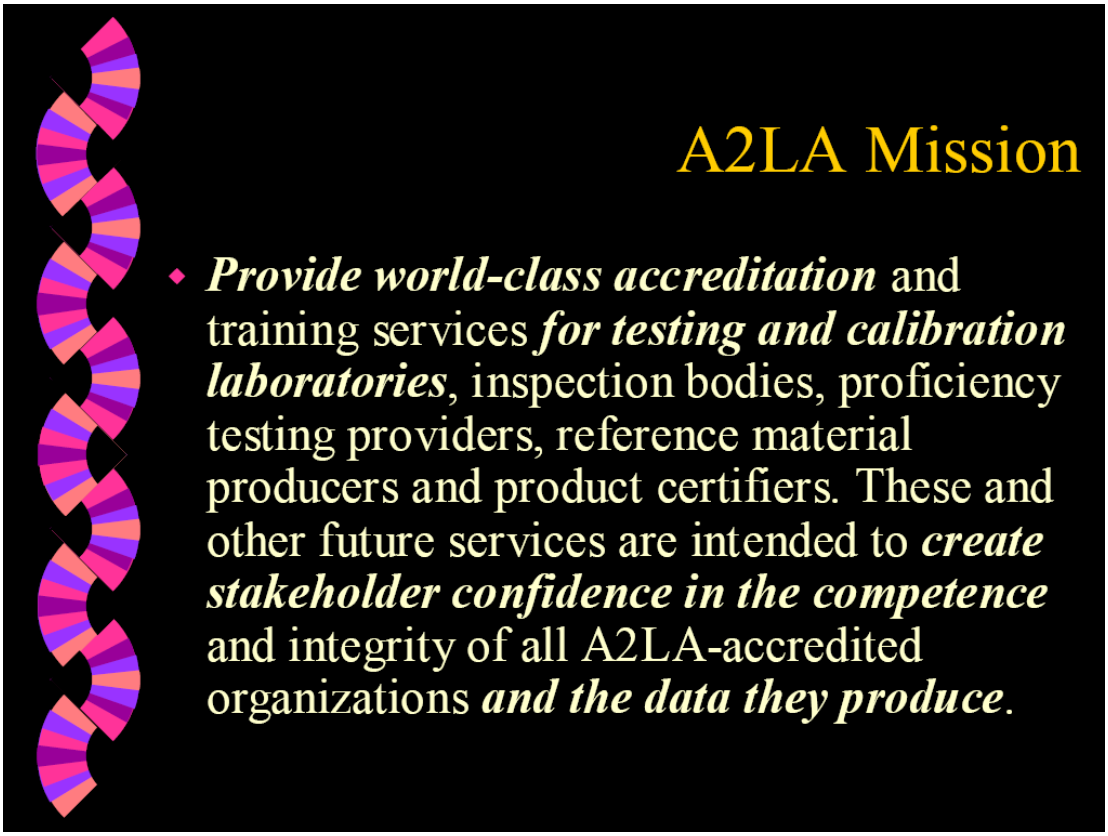
(5) Cleanup.

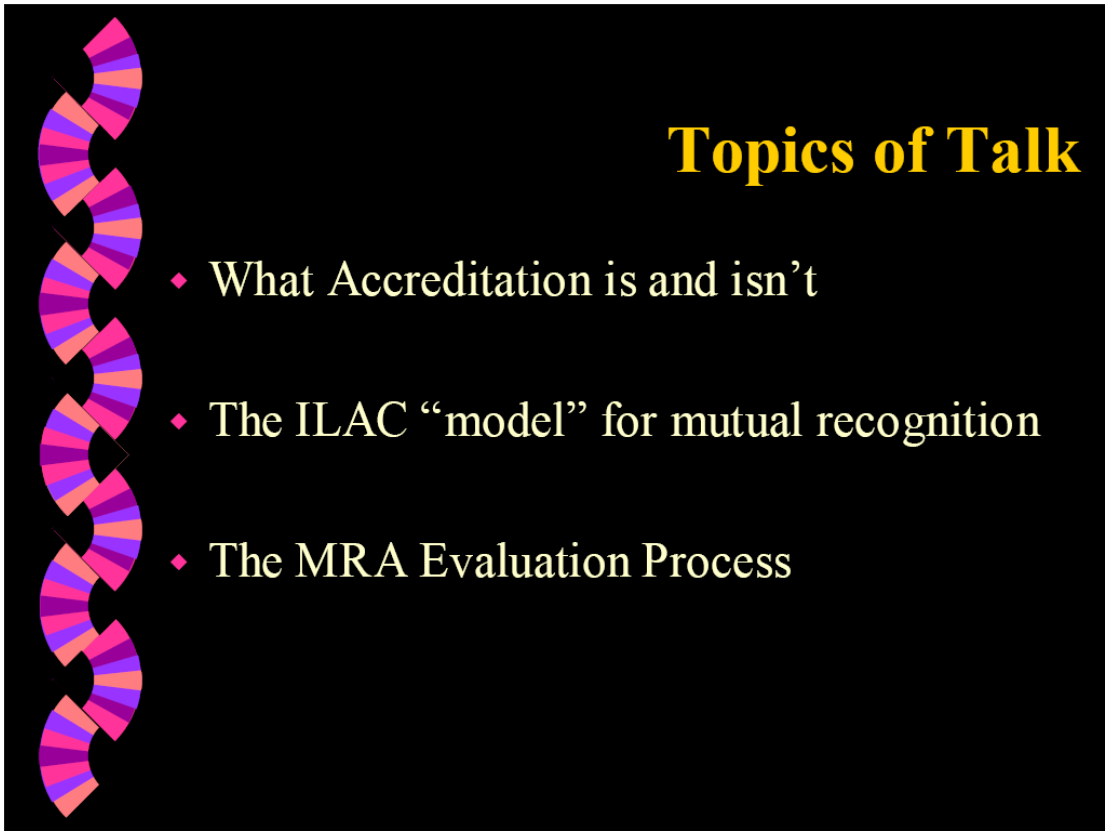
This presentation will describe the scan-watch-action list process, impact assessment methodology, and integrated risk management concept. The presentation will also display the specific ECs on the DoD watch and action lists and results of impact assessments. The impact assessments include a list of the uses of the ECs in DoD.

The DoD, EPA, and the Environmental Council of States (ECOS) have formed an EC Working Group. The group has identified a number of national policy issues requiring resolution and has prepared white papers on these issues. The presentation will conclude with a discussion of these issues and their status. Attendees will become informed about the nature of risks and issues posed by ECs and DoD's initiative to address these risks and issues.

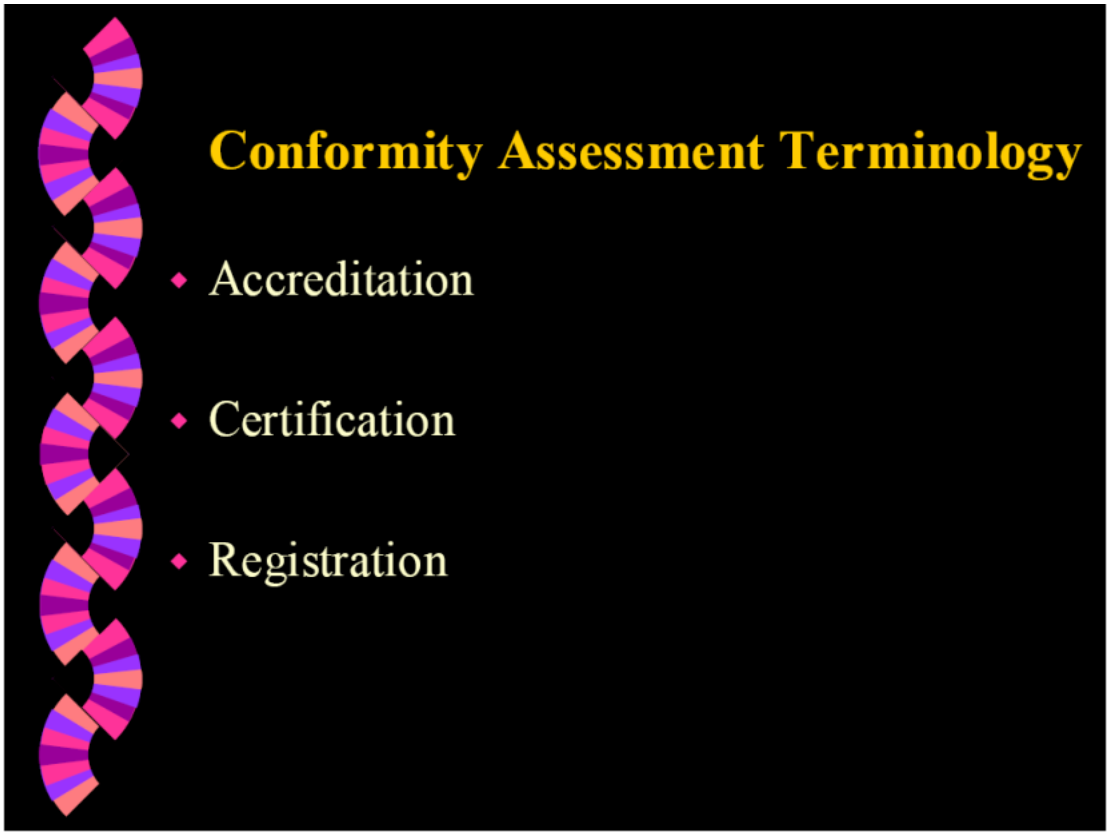

Who "Accredits" the Accreditors?
Presented at the
Forum on Laboratory Accreditation
Cambridge, MA
August 24, 2007
by
Roxanne M. Robinson
Vice President, A2LA


TNI Mission
The NELAC Institute (TNI) is a non-profit organization whose mission is to foster the generation of environmental data of known and documented quality through an open, inclusive, and transparent process that is responsive to the needs of the community.


A2LA Mission
Provide world-class accreditation and training services for testing and calibration laboratories, inspection bodies, proficiency testing providers, reference material producers and product certifiers. These and other future services are intended to create stakeholder confidence in the competence and integrity of all A2LA-accredited organizations and the data they produce.


Topics of Talk
What Accreditation is and isn't
The ILAC "model" for mutual recognition
The MRA Evaluation Process


What about me?
The evaluated (A2LA): EA, APLAC, FQA, Environmental Lead (Pb) and NELAC for PTOB
The evaluator: I am a recognized team leader for APLAC, EA, IAAC and ILAC
(Australia, New Zealand, Taiwan, Japan, India, Argentina, Canada, Greece, NVLAP etc.)


Conformity Assessment Terminology
Accreditation
Certification
Registration

Certification

- Written assurance by a ***third party*** that a product, process, or service ***conforms*** to ***specified requirements***.
  - Used internationally to include quality system (ISO 9000) and other management system (ISO 14000) certification/registration

Accreditation

- Formal recognition by **an authoritative body** that a laboratory's quality system conforms to the requirements of an appropriate standard and of a laboratory's technical competence to perform specific tests or calibrations
- ISO/IEC17025
- **Scope** of Accreditation

Accreditation vs. Certification

- Certification (Registration)
  - quality system requirements
  - ISO 9001
- Accreditation
  - 17025: quality system requirements +
  - ***technical competency requirements***
  - testing and calibration procedures

The ISO 9000 Quality Systems Auditor Asks...

- Have you defined your policies and procedures?
- Are they documented in accordance with the standard?
- Are you following them?

The Laboratory Accreditation Assessor Asks...

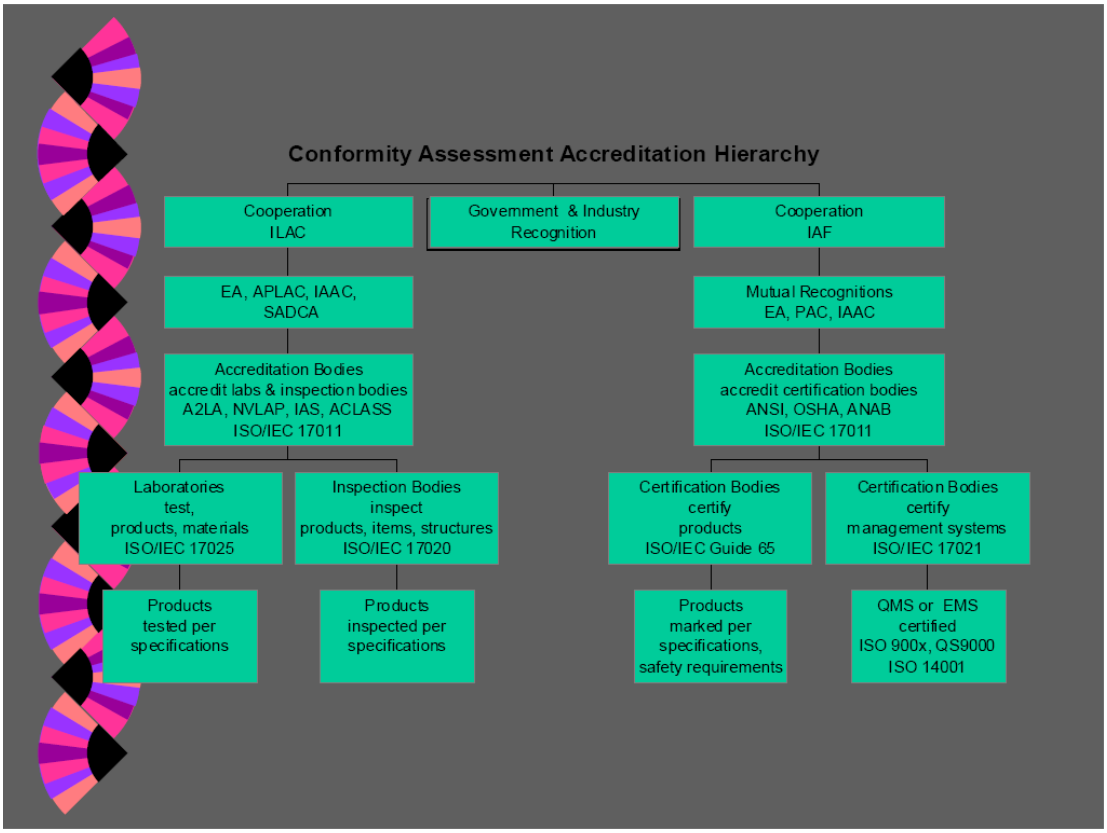
- Have you defined and *validated* your procedures?
- Are they documented in accordance with the standard?
- Are you following them?
- Do your procedures ensure *accurate* and *reliable* results?

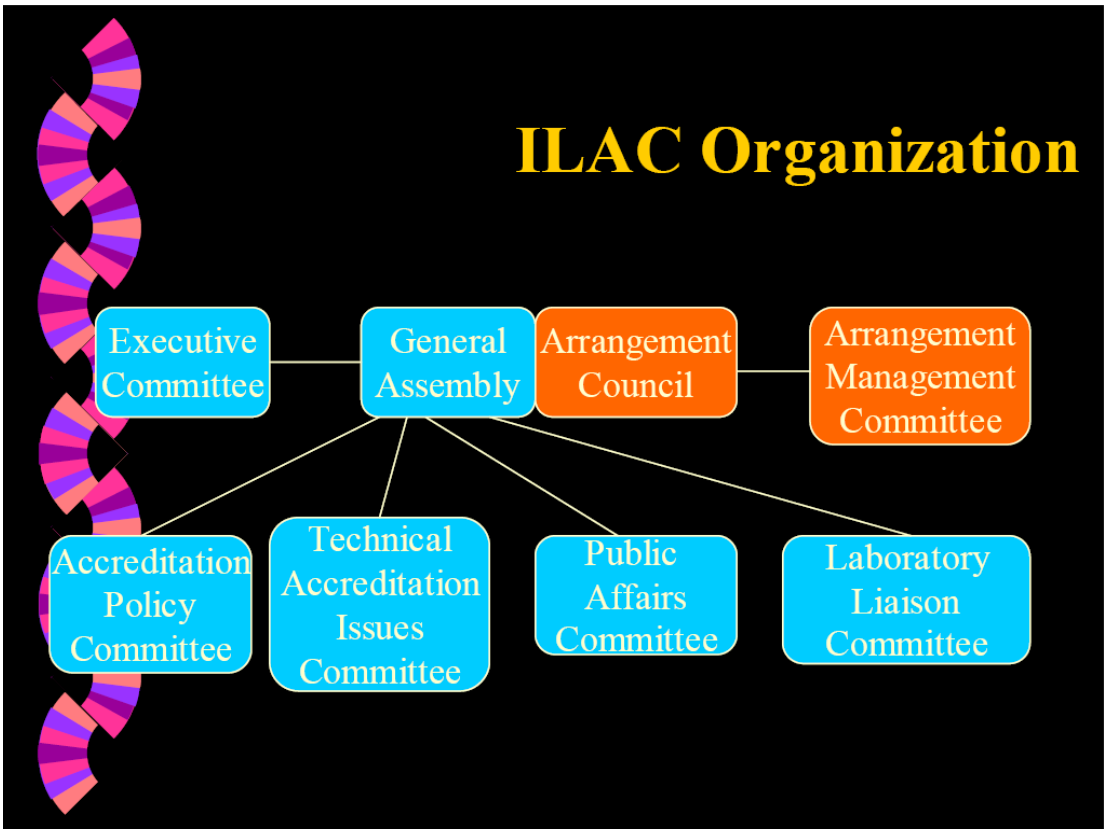
And...

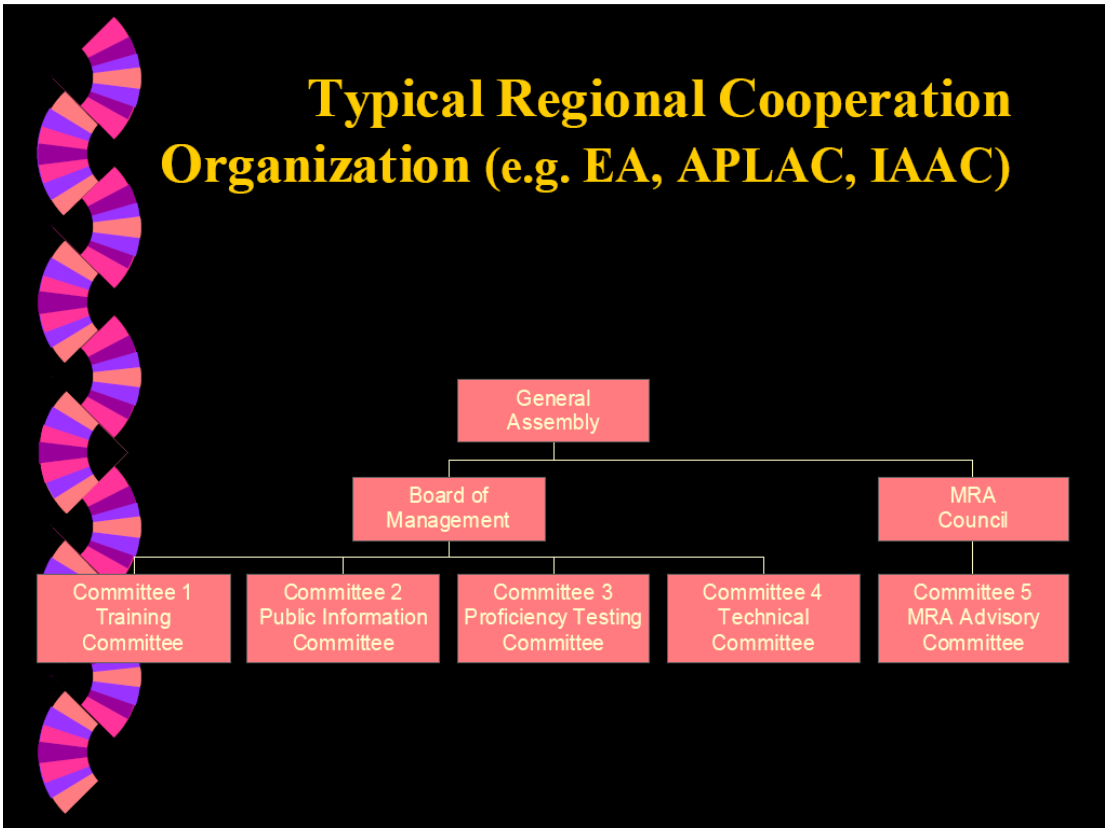
- Do you understand the science behind the procedures?
- Can you foresee and cope with any technical problems that may arise?
- Do you have the correct equipment and adequate personnel?
- Have you calculated your uncertainties?

Key Distinction

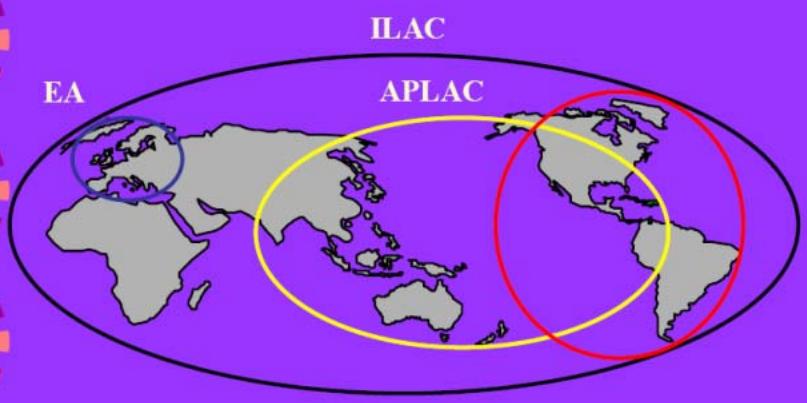
- Accreditation = competence
- Certification = conformity




ILAC Organization
Executive Committee
General Assembly
Arrangement Council
Arrangement Management Committee
Accreditation Policy Committee
Technical Accreditation Issues Committee
Public Affairs Committee
Laboratory Liaison Committee


Typical Regional Cooperation Organization (e.g. EA, APLAC, IAAC)
General Assembly
Board of Management
MRA Council
Committee 1 Training Committee
Committee 2 Public Information Committee
Committee 3 Proficiency Testing Committee
Committee 4 Technical Committee
Committee 5 MRA Advisory Committee

Mutual Recognition Arrangements

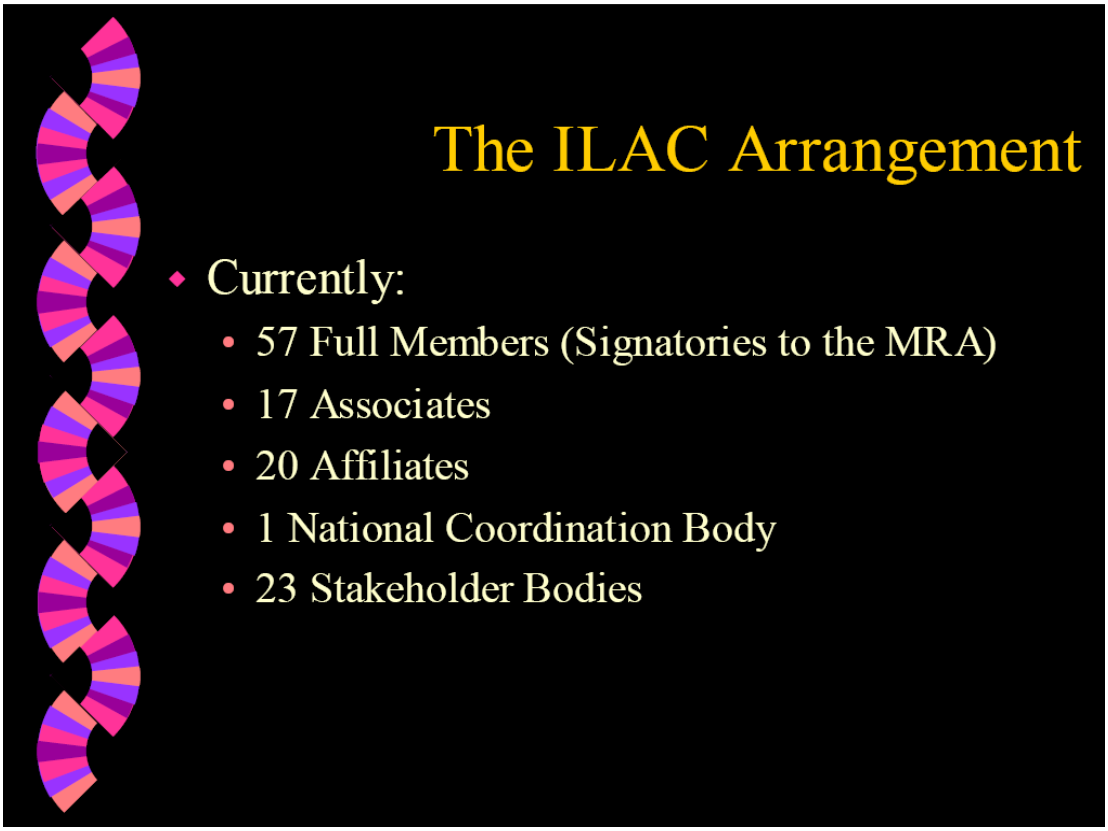


ILAC	International Laboratory Accreditation Cooperation
EA	European co-operation for Accreditation
APLAC	Asia Pacific Laboratory Accreditation Cooperation
IAAC	Inter-American Accreditation Cooperation

The ILAC Arrangement

- ILAC has signed MOUs with:
  - ISO
  - WTO
  - APEC
  - WADA
  - Bluetooth SIG
  - CDMA Certification Forum (CCF)


The ILAC Arrangement
Currently:
Regional Cooperation Bodies
2 Not Recognized
– Southern African Development Community in Accreditation (SADCA)
– Central Asian Cooperation on Metrology Accreditation and Quality (CAC-MAS-Q)


The ILAC Arrangement
Currently:
57 Full Members (Signatories to the MRA)
17 Associates
20 Affiliates
1 National Coordination Body
23 Stakeholder Bodies

New Conformity Assessment Activity included in MRA

- Reference Material Producer
  - Added to APLAC MRA March 2006
  - A2LA accepted September 2006
  - Signatories added to MRA once 4 ABs accepted by MRA Council – December 2007?
- Proficiency Testing Provider ?

Regional Cooperation Participation

- Join as a member
  - participate and learn
- Apply to be evaluated
  - ultimate goal to be an MRA signatory

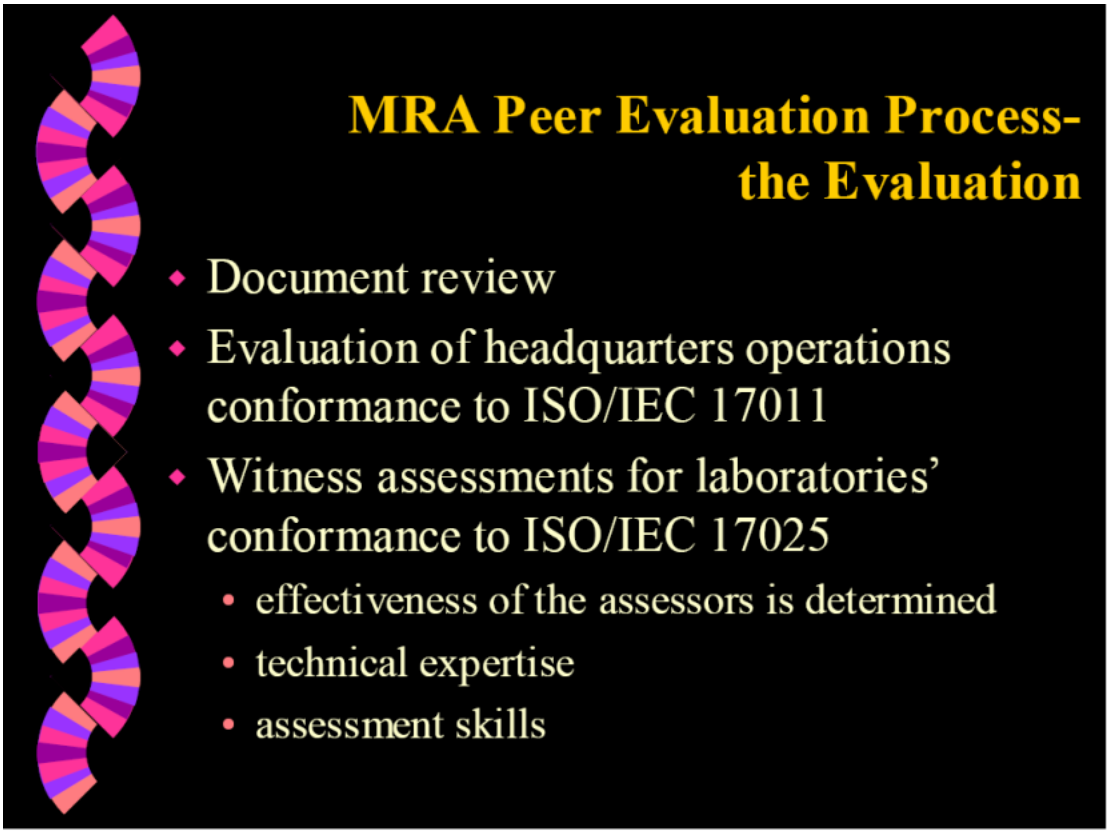
MRA Peer Evaluation Process - Application

- Submit application to secretariat of the cooperation
- Series of documents must address:
  - the ISO/IEC 17011 requirements
  - measurement traceability policy
  - laboratories' participation in proficiency testing
  - pre-evaluation is possible

MRA Peer Evaluation Process - Evaluators

- Team leader recruited/assigned
  - generally senior accreditation body staff
  - trained through observing and then serving as evaluator
  - also trained at international seminars for evaluators or specifically, team leaders


MRA Peer Evaluation Process-
Evaluators
Team leader chooses team members
Technical backgrounds coincide with kinds of laboratories that the applicant accredits
usually four, sometimes six members
If calibration is included, one team member must have a strong metrology background
often a NMI staff person joins the team


MRA Peer Evaluation Process-
the Evaluation
Document review
Evaluation of headquarters operations conformance to ISO/IEC 17011
Witness assessments for laboratories' conformance to ISO/IEC 17025
effectiveness of the assessors is determined
technical expertise
assessment skills

MRA Peer Evaluation Process – The Evaluation

- International guidelines – such as IAF/ILAC A3 – Key Performance Indicators:
  - KPI 1: Access to Expertise
  - KPI 2: Accreditation criteria, scope of the AB and extension of the scope

MRA Peer Evaluation Process – The Evaluation

- KPI's (cont'd):
  - KPI 3: AB staff, assessors and experts
  - KPI 4: Assessor support system
  - KPI 5: The assessment and the assessment team
  - KPI 6: Impartiality of Assessors, Committees and Decision-Making Bodies
  - KPI 7: Monitoring Performance of Assessors and Experts

MRA Peer Evaluation Process – The Evaluation

- KPI's (cont'd):
  - KPI 8: Dealing with non-conformities and corrective actions of the accredited bodies, including decision making on accreditation
  - KPI 9: Internal audits and management reviews
  - KPI 10: Proficiency testing

MRA Peer Evaluation Process – The Evaluation

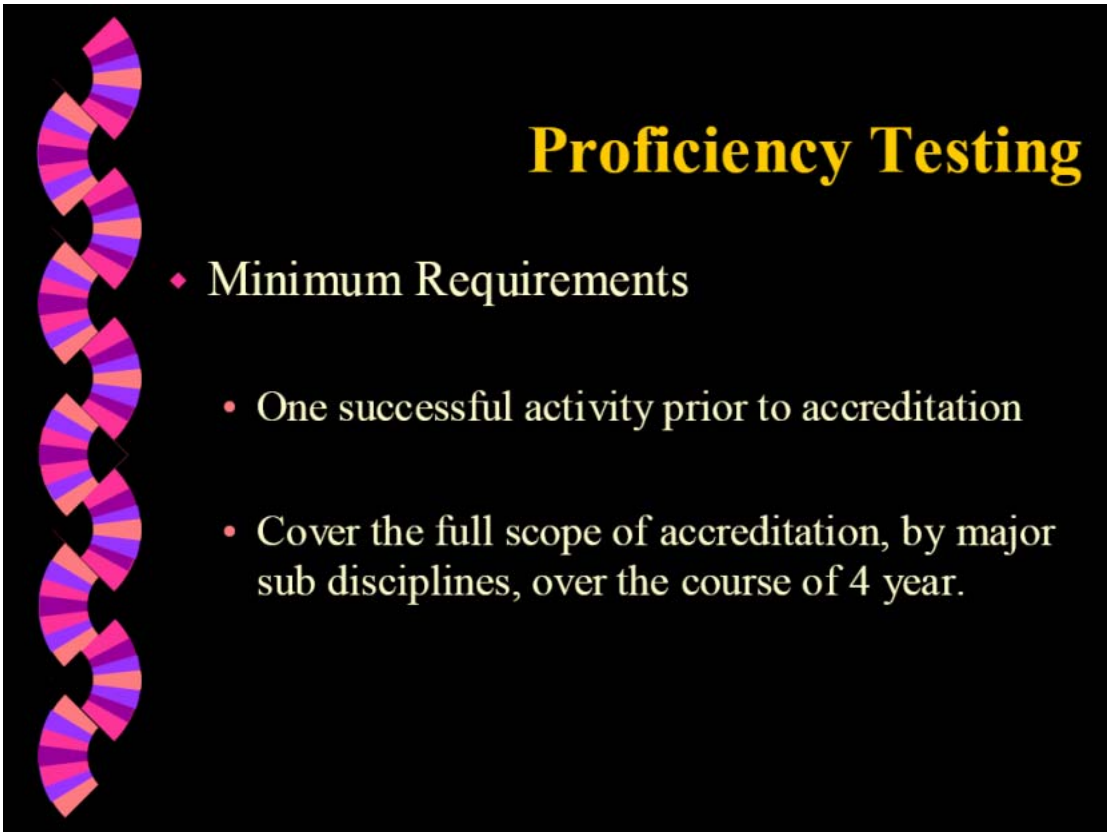
- KPI's (cont'd):
  - KPI 11: Calibration, traceability, and reference materials
  - KPI 12: Program of surveillance activities
  - KPI 13: Value-adding services

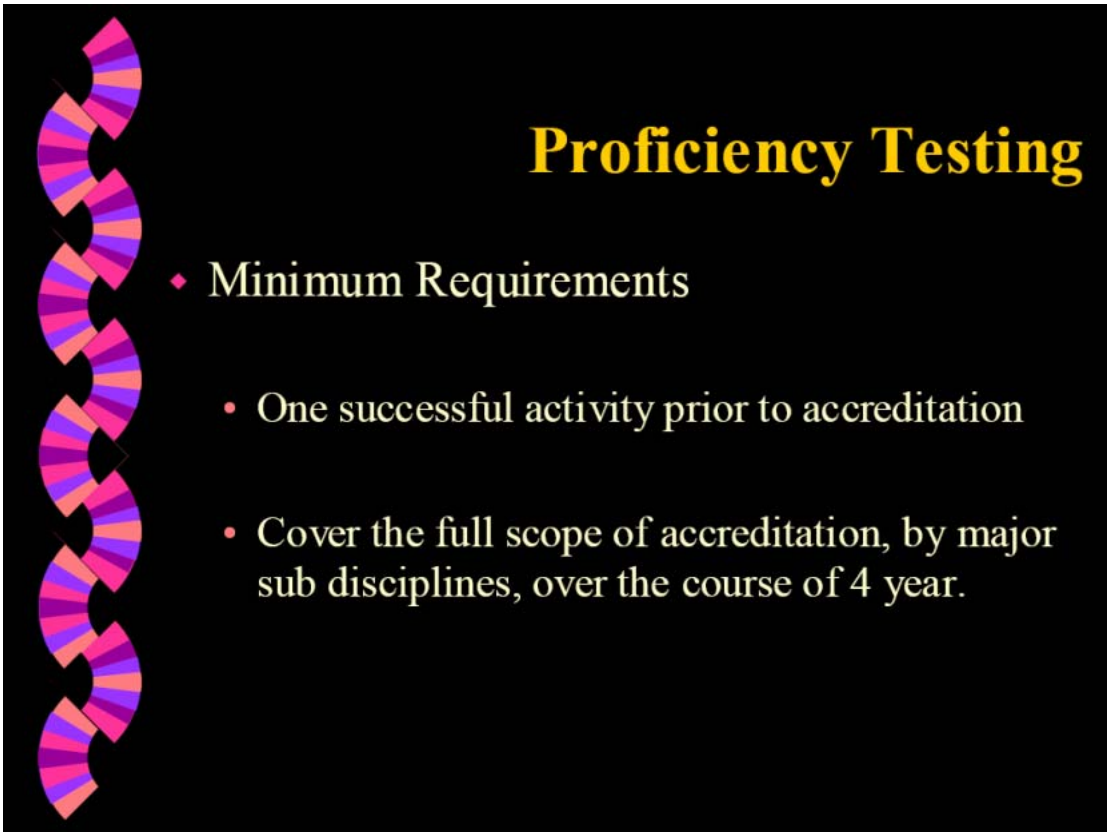
MRA Peer Evaluation Process – The Evaluation

- KPI's (cont'd):
  - KPI 11: Calibration, traceability, and reference materials
  - KPI 12: Program of surveillance activities
  - KPI 13: Value-adding services

MRA Peer Evaluation Process - the Evaluation

- Determining arrangements for ensuring traceability to the appropriate primary standards
  - visiting the National Metrology Institute
  - evaluating the level of participation in international laboratory comparisons sponsored by other NMIs or BIPM


Proficiency Testing
Minimum Requirements
One successful activity prior to accreditation
Cover the full scope of accreditation, by major sub disciplines, over the course of 4 year.


Proficiency Testing
Minimum Requirements
One successful activity prior to accreditation
Cover the full scope of accreditation, by major sub disciplines, over the course of 4 year.

Proficiency Testing

- More rigorous frequency could be prescribes by regulatory or specifier criteria
- Accreditation Bodies may also run programs or use commercial sources but must demonstrate:
  - monitoring and corrective action process
  - revocation and re-instatement of accreditation process

Use of the Accreditation Symbol

- ABs must provide limits and guidelines on use of their logo by their accredited labs
  - AB must have process for requiring corrective action
- ILAC P8 is often invoked
  - Conveys rules on use of logo on test reports, calibration certificates and business literature.

MRA Peer Evaluation Process - Signatory Status

- Respond in writing to any concerns resulting from the evaluation
- Team leader coordinates the review of the corrective action
- Full evaluation information provided to the cooperation's acceptance panel
  - Decision made to include or continue as a signatory, possibly with conditions.

Impediments to Recognition

- Assessors' technical qualifications
- Laboratory Scope content
- Separation of activities
- Sufficient assessment length and depth
- Subcontractor qualifications and oversight

MRA Peer Evaluation Process - Continue Signatory Status

- Evaluation every four years
- Appeals mechanism for negative decisions
- Alert partners to changes
- Participate in international committee work
- Provide a liaison officer
- Participate in international laboratory comparisons (ILCs)
- Promote acceptance of test data across borders

Conclusion

The International MRA Evaluation Process:

- Builds confidence between accrediting bodies
- Fosters uniformity in complying with ISO/IEC 17011 and ISO/IEC 17025
- Promotes acceptance of calibration and test results between MRA countries
- Reduces barriers to trade


Questions?
www.A2LA.org
www.ilac.org
www.aplac.org
www.european-accreditation.org
www.iaac.org.mx/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The Forum on Environmental Measurements (FEM)

Mike Shapiro, US EPA

August 22, 2007

Environmental Measurement Symposium

Overview

- Background
- Purpose/Scope
- Action Agenda
- Summary

Background

- Formed in April 2003 by the Science Policy Council (SPC)
- Composition of senior Agency managers
- Central focus for addressing measurement and methods issues with multi-program impact

Science Policy Council (SPC)

- Formed in December 1993 by the Administrator
- Composition
  - Science Advisor (chair)
  - Agency Appointees
  - Career Scientists and Managers
- Goal is to integrate policies that guide Agency decision makers in their use of scientific and technical information.

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.

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)

Improving the Quality of Agency Methods

- Policy and validation guidelines/ technical guidance documents for:
  - Chemical Methods
  - Radiochemical Methods
  - Sampling and Analysis Methods
  - Microbiology
  - Biology
- Improve system for the monitoring community to use to obtain information on methods.

Implementation of the Performance Approach

- Renewed commitment to what implementation means ten years from when it began.
- Details in the next presentation.

Technical Assistance

- Method portal for linking Agency office information on analytical methods
- Policy for the timely dissimation of information on Agency methods guidelines for posting of published methods on websites.

Method Detection/Quantitation

- Tasked to review the final product of the Federal Advisory Committee for broader Agency use.

General Laboratory Competency

- Ensuring the Competency of EPA Laboratories Agency Policy Directive was issued by the SPC in February 2004.
  - All EPA laboratories are required to document their competency through independent assessments and participation in inter-laboratory comparisons or programs.
  - The Office of Environmental Information (OEI) will provide oversight.
- All laboratories have and continue to currently implement their competency plans that were approved.

Laboratory Accreditation

- Followed the progress of the formation of The NELAC Institute (TNI) and were briefed on the organization
- Provided an Agency ex-officio member to the TNI Board
- Investigating ways to promote use of accredited laboratories

National Environmental Monitoring Conference (NEMC)

- Supported making NEMC a multi-pollutant venue to be the premier conference for environmental monitoring issues
- Supported multi-year cooperative agreement for sustainability and growth
- Promotes conference to reach target audiences (e.g., states, regions, laboratories, regulated sectors)

Summary

- The FEM is a central focus point for addressing measurement, monitoring, laboratory, and method issues with multi-program impact.
- In four years, much has been accomplished, but there is always more to do.

Contact Us

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

"The Future of the Drinking Water Laboratory Certification Program"

Environmental Measurement Symposium
NEMC/TNI
August 23, 2007

Greg Carroll
Director, Technical Support Center
U.S. Environmental Protection Agency
Office of Ground Water and Drinking Water

"EPA's Drinking Water Laboratory Certification Program: History, Status, Direction"

Environmental Measurement Symposium
NEMC/TNI
August 23, 2007

Greg Carroll
Director, Technical Support Center
U.S. Environmental Protection Agency
Office of Ground Water and Drinking Water

Background

- 1943 - US Public Health Service began to survey water bacteriology laboratories.
- 1974 - Safe Drinking Water Act (SDWA)
  - Authorized EPA to set enforceable health standards for contaminants in DW; National Primary Drinking Water Regulations
- 1978 – Drinking Water program implemented Certification Program, published "Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies"

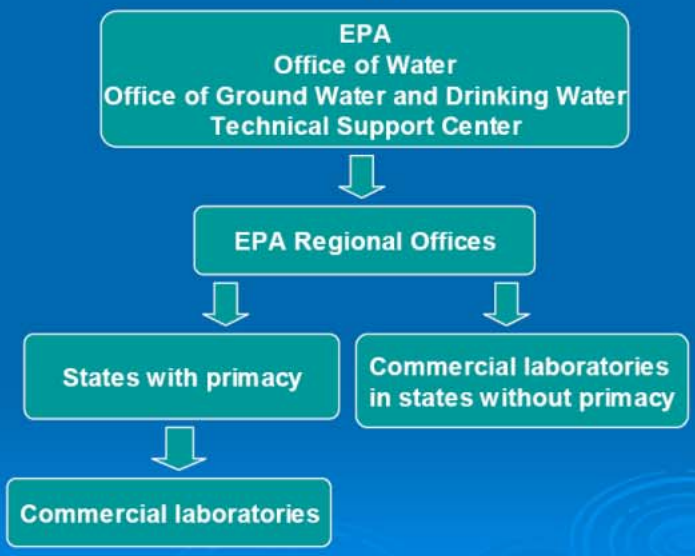
Background (cont'd)

- Code of Federal Regulations: 40 CFR
  - Subpart C- Monitoring and Analytical Requirements
    - 141.28 Certified Laboratories
      - "For the purpose of determining compliance…, samples may be considered only if they have been analyzed by a laboratory certified by the State…"
- Goal is to improve public health protection by providing more consistent, accurate, defensible results

EPA Role -- OGWDW

- Office of Ground Water and Drinking Water oversees all aspects of drinking water regulation in the US.
  - Responsible for establishing regulations and approval of methods to support regulation.
  - Oversees national drinking water laboratory certification program.
    - Reviews Regional programs
    - Conducts training of state and Regional Certification Officers
    - Maintains/updates Laboratory Certification Manual
    - Facilitates monthly conference calls with Regional COs/QAOs
    - Provides technical support regarding program, regulations, methods
    - Maintains a database of laboratory ID codes

Hierarchical Program Structure



EPA Role -- ORD

- Office of Research and Development
  - (Originally) responsible for certification of Regional laboratories
  - (Originally) responsible for audits of state radiochemistry laboratories
  - (Originally) responsible for Performance Evaluation/Proficiency Test Program.
  - Support Certification Officer Training
  - Provide technical support regarding methods
  - Develop/evaluate analytical methods to support drinking water program (shared responsibility with OGWDW)

EPA Role -- Regional Offices

- Monitor state certification programs for adequacy.
  - assess the scope, staffing, policies, procedures, and effectiveness.
- Certify principal state laboratories
- Host meetings of state certification officers
  - discuss program/implementation issues and provide current information on regulations and methods.
- Observe state on-site evaluations of local labs.
- Manage certification program and certify laboratories in the non-primacy states/territories.
- Provide technical assistance to states and certified laboratories.

State Role

- As conditions of primacy, states:
  - maintain capability to analyze regulated contaminants (in-house or via contractual arrangements)
  - manage certification program for commercial laboratories analyzing DW compliance monitoring samples
- State-designated COs review laboratory applications, conduct on-site audits of laboratories, and review laboratory PT data.
- COs provide technical assistance to laboratories.
- States may certify laboratories outside of their state through direct evaluation or reciprocity.
- Other program elements per state

Laboratory Responsibilities

- Comply with all federal regulations, including using approved methods.
- Successfully analyze Proficiency Testing (PT) samples (initial + annual)
- Successfully pass an onsite audit (initial + triennial)

Significant Program Developments

- 1978-2005 - Periodic updates to Laboratory Certification Manual
- 1997 - EPA transferred PE/PT program to private sector, with evaluation/accreditation of providers by NIST NVLAP program
- 1997 - OGWDW (Cynthia Dougherty memo) regarding NELAP accreditation as alternative to certification
  - *"….I support the use of the NELAC standards in the certification of laboratories…and encourage use of the standards based on the increased opportunity for national consistency…"*
  - *"….One of the Agency's primary goals has been to encourage states to recognize certification of laboratories by other states…(reciprocity)…"*

Significant Program Developments (cont'd)

- 1999 - Lead responsibility for Regional laboratory audits transferred from ORD to OGWDW (with ongoing ORD audit support)
- 2002 - Renewal of OGWDW (Cynthia Dougherty) support for NELAP accreditation
  - *"I continue to support the use of the NELAC standards in the certification of laboratories…"*
  - *"…I encourage future reviews…to allow continued assessment of equivalency and promote greater consistency in the program…"*
  - *"…I reiterate that the drinking water program will benefit nationwide through state participation in the accreditation program…"*

Significant Program Developments (cont'd)

- 2002 (?) - EPA decision that Regional laboratories will be accredited by NELAP.
- 2006 - NIST announced its termination of their evaluation/accreditation program for PT providers
- 2006 – OGWDW statement of support for NELAC PTOB/PTPA process to help "assure the quality of commercially-provided PTs" (i.e., in lieu of NIST-based process)

Lab Cert Program - Direction

- Implement OGWDW Action Plan per OIG review
  - Integrate fraud awareness into CO training
  - Promote data validation training, techniques
  - Enhance radiochemistry training/technical support
  - Review sample collection requirements/ vulnerabilities
- Strengthen the Quality Systems component of the Lab Cert Program/Lab Cert Manual

Significant Program Developments (cont'd)

- 2004-07 – Retirement of core OGWDW laboratory certification team members (Ed Glick, Carol Madding, Pat Hurr); hiring/reassignment of new team members (Jennifer Best, Michella Karapondo, Judy Brisbin)
- 2005-07 – OIG review/report re drinking water laboratory integrity (Report 2006-P-00036), OGWDW response/action plan

Lab Cert Program – Direction (cont'd)

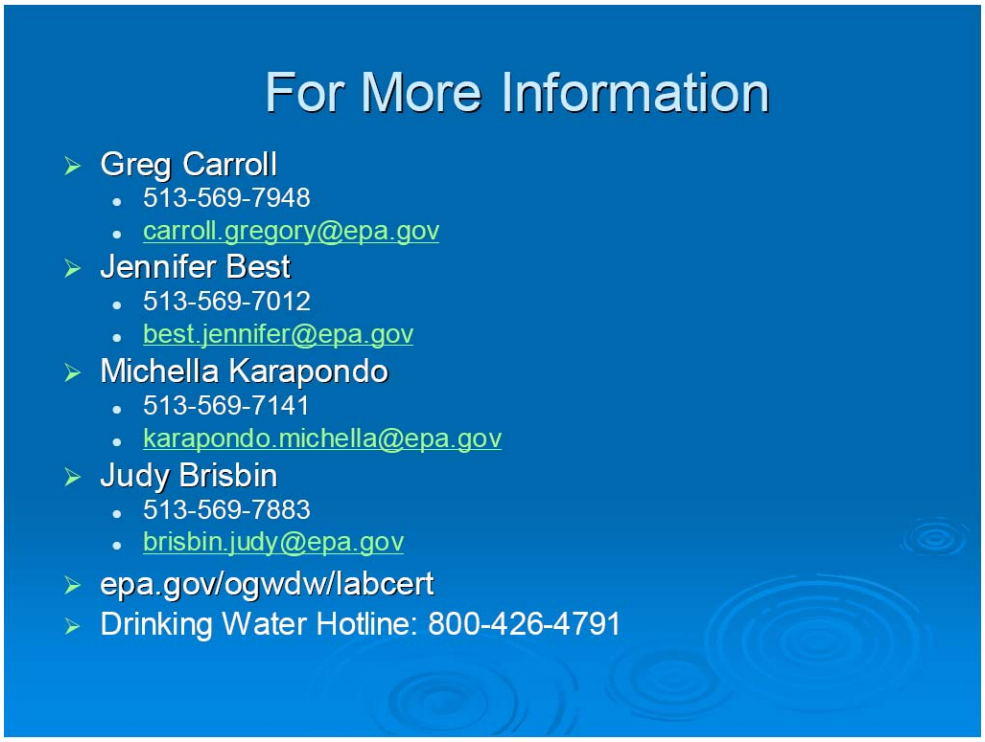
- Resolve long-term responsibility for Criteria Document
- Investigate longer-term options for LT2 (*Cryptosporidium*) lab approval
- Continue/strengthen collaboration with TNI (e.g., participate in forum/symposium, PT Board, Regional Evaluator meetings; consultation regarding Standard; networking with DW stakeholders [?])

Lab Cert Program – Direction (cont'd)

- Incorporate new/modified methods into program
  - OGWDW implementation of Expedited Method Approval approach
  - Continued OGWDW progress towards Agency's/FEM's method flexibility/ "Performance Approach" goals
  - New standards resulting from CCL/Regulatory Determination processes

Lab Cert Program – Key Elements of Approach to Future

- Adapting to change
- Collaboration
- Balancing stakeholder interests
- Commitment to public health protection
- Tech support
- Managing with limited/declining resources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Update on USEPA Methods, Regulations and Other Activities

Jerry L. Parr
Catalyst Information Resources

ABSTRACT

In 2007, the Office of Water in the Environmental Protection Agency (EPA) adopted several new regulations that will affect how water analyses are performed, including the methods update rule, the unregulated contaminant monitoring rule and the biological methods rule. Other EPA regulations, new methods and guidance documents were adopted by EPA in 2007. This presentation will review recent changes to the EPA regulations, review new EPA methods that were approved and highlight other activities within EPA's that affect the environmental monitoring industry. Other related topics, including laboratory fraud and a new handbook for the analysis of perchlorate will also be covered.

Update on USEPA Methods, Regulations and Other Activities

National Environmental Monitoring Conference

August 20, 2007

Jerry L. Parr
Catalyst Information Resources

AGENDA

- New EPA Regulations
- New SW-846 Methods
- Laboratory Fraud
- Office of Water Activities
- Other Items of Interest

For the period August 28, 2006 through August 10, 2007.

Regulations with New/Revised EPA Methods and Monitoring

- **Methods Update Rule**
- UCMR 2 Rule
- Ground Water Rule
- Biological Methods Rule

Methods Update Rule

- Finalized March 12, 2007
- Effective April 11, 2007
- New methods
- Updated versions of approved methods
- Revised method modification and analytical requirements
- Withdrawal of outdated methods
- Changes to sample collection, preservation, and holding time requirements

Regulations Changed

- **Part 122**: NPDES Permits
  - E. coli and Enterococci added (grab samples)
  - Reference to Part 136
- **Part 136**: Wastewater Methods
  - **Many, many, many changes**
- **Part 141**: Drinking Water
  - A few changes
- **Part 143**: Drinking Water
  - A few changes
- **Part 430**: Pulp & Paper NPDES
  - Approve method for chlorinated phenolics
- **Part 455**: Pesticide Manufacturing NPDES
  - Move Table 7 to Part 136
- **Part 465**: Coil Coating NPDES
  - Removal of oil and grease

Changes to Part 136

- Table 1A: Microbiologicals (SM only)
- Table 1B: Inorganics/Metals
- Table 1C: Organics
- Table 1D: Pesticides (SM & ASTM only)
- Table 1E: Radiochemistry (SM & ASTM only)
- Table 1F: Pharmaceutical Pollutants
- Table 1G: Pesticide Active Ingredients
- Table II: Preservation & Holding Time
- Section 136.6

New Chemical Test Methods

- Dissolved Inorganic **Anions** by Capillary Ion Electrophoresis, ASTM D6508
- **Cations** and Ammonium in by IC, ASTM D 6919-03,
- **Chloride** by Potentiometry, SM 4500-Cl-D.
- **Chloride** by Ion Selective Electrode, ASTM D512-89,
- **Chlorine** by Low Level Amperometry, SM 4500-Cl,
- **Cyanide** using MICRO DIST and flow injection analysis, QuikChem Method 10-204-00-1-X
- Total **Cyanide**, Acid Dissociable Cyanide, and Thiocyanate, Kelada-01,
- Available **Cyanide** by Ligand Exchange-FIA, ASTM D6888-03
- **Cyanide** by Ion Selective Electrode,
  - ASTM D2036-98 A & SM 4500-CN-F
- **Mercury** by Cold Vapor Atomic Fluorescence Spectrometry, EPA 245.7,
- **Nitrate** by Ion Selective Electrode, SM 4500-NO3-D, and
- **Sulfide** by Ion Selective Electrode.
  - SM 4500-S2-G & ASTM D4658-92

Re-proposed Chemical Test Methods

- First Proposed in 1994
  - 200.2,Total Recoverable Elements Digestion
  - 200.8, Metals by ICPMS
  - 200.9, Metals by Stabilized Temperature GFAA
  - 218.6, Hexavalent Chromium by IC
  - 300.0, Inorganic Anions by IC
  - 353.2, Nitrate and Nitrite by Colorimetry
  - Revisions to 180.1, 200.7, 245.1, 335.4, 350.1, 351.2, 353.2, 365.1, 375.2, 410.4, and 420.4.
- Equivalent ASTM and SM methods also approved

Updated Versions of Current Methods

- An errata sheet for the WET manuals
- ASTM methods
- Standard Methods
- Methods published in the 16th edition of Official Methods of Analysis of AOAC International, 1995

Method Modifications

- Replace the mercury catalyst in TKN methods
- Approve the use of styrene divinylbenzene beads and Hach StablCal as alternatives to the formazin standard for Turbidity
- Allow the use of capillary GC columns for Methods 601-613, 624, 625, and 1624B

Withdrawal of Methods

- Delete Methods 612 and 625 for dichlorobenzenes
- Withdraw approval for all oil and grease methods that use Freon-113
- Withdraw > 100 methods in MCAWW

Changes to Table 1B EPA Methods

- Deleted 52 wet chem methods
- Deleted 53 AA methods
- Approved 7 new EPA methods
- Approved 10 revisions to existing EPA methods

Table 1C: Organics

- Delete methods 612 and 625 for dichlorobenzenes
- Approve updated versions of SM, ASTM, etc.
- Add footnotes indicating EPA QC requirements apply to non-EPA methods

Table 1G: Methods for PAI

- List of 93 non-routine pesticides with method references
- Table was in Part 455
- Methods include obscure methods (e.g., 1656, 1657) as well as 500 series methods

Table II
Holding Times & Preservation

- 4 C changed to < 6 C
- Analyze immediately changed to 15 minutes
- No acid preservation for metals in field
  - Must wait 24 hours after adding acid
  - Does not apply to Hg
- Cr+6: 28 day HT, if sample buffered to pH 9.3 to 9.7
- HT starts at end of composite period
- Extensive requirements for cyanide
- Other minor changes- read carefully!

136.6: Method Modifications

- Analysts may modify methods!!!
  - Not change the "chemistry"
  - Excludes "method-defined" analytes
- Requirements for modifications:
  - Initial DOC (IPR)
  - On-going QC
  - Verification in wastewater matrices
- Reference to Pumpkin Book

Pumpkin Book **Revised!**

- **Solutions to Analytical Chemistry Problems with Clean Water Act Methods**
  - Sample Collection & Preservation
  - Method Flexibility
  - Matrix Interferences
  - Data Review
- Available at:
  - http://www.epa.gov/waterscience/methods/
- Email for method questions:
  - OSTCWAMethods@epa.gov

Changes to Drinking Water Regulations

- Parts 141 and 143
  - Approve use of current version of Standard Methods and ASTM
  - Approve 9 new methods
  - Allowable method modifications
  - Correction of holding time for coliform

New Chemical Test Methods for SDWA

- **D6508, Rev. 2**, Dissolved Inorganic Anions by Capillary Ion Electrophoresis,
- **ASTM D6888-04,** Available Cyanide by Ligand Exchange-FIA,
- **OIA-1677**, Available Cyanide by Ligand Exchange-FIA
- **ASTM D 6919-03**, Cations and Ammonium in by IC,
- **300.1, Rev. 1.0,** Chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate by IC.
- **552.3, Rev. 1.0,** Dalapon
- **Ra-226 & Ra-228 by Gamma-ray Spectrometry using HPGE of Ge(Li) detectors**, Rev. 1.2,
- **D99-003, Rev. 3**, Free Chlorine ITS test strips
- **327, Rev.1.1**, Chlorine dioxide residuals

SDWA Allowable Method Modifications

- Approve the use of styrene divinyl benzene beads and stabilized formazin as alternatives to the formazin standard for Turbidity
- Allow the use of a 450-W UV lamp in the Kelada Method-01 for Cyanide
- Allow the use of Syngenta method AG-625, with modified immunoassay testing product by Beacon Analytical System, under certain conditions.

Old Methods in Permits

- "The primacy authority should allow use of methods in the permit for the life of the permit unless the authority exercises permit reopener procedures."

Dick Redding
USEPA

Unregulated Contaminant Monitoring Rule: Phase 2

- Finalized January 4, 2007 (*72 FR 367*)
- Monitoring of drinking water for 25 chemicals using 5 methods
- Monitoring to occur 2007-2011

UCMR 2 Analytes

List 1. Assessment Monitoring

- 1,3-dinitrobenzene
- 2,2',4,4'-tetrabromodiphenyl ether
- 2,2',4,4',5-pentabromodiphenyl ether
- 2,2',4,4',5,5'-hexabromobiphenyl
- 2,2',4,4',5,5'-hexabromodiphenyl ether
- 2,2',4,4',6-pentabromodiphenyl ether
- 2,4,6-trinitrotoluene
- Dimethoate
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
- Terbufos sulfone

List 2. Screening Survey

- Acetochlor
- Acetochlor ESA
- Acetochlor OA
- Alachlor
- Alachlor ESA
- Alachlor OA
- Metolachlor
- Metolachlor ESA
- Metolachlor OA
- N-nitroso-diethylamine
- N-nitroso-dimethylamine
- N-nitroso-di-n-butylamine
- N-nitroso-di-n-propylamine
- N-nitroso-methylethylamine
- N-nitroso-pyrrolidine

Perchlorate Not Included

- "it is not clear that the Agency needs additional information on the occurrence of perchlorate in drinking water."

UCMR 2 Methods

- 521: Nitrosamines by SPE/GC/MS/MS
- 525.2: Organic Compounds by LSE/GC/MS
- 527: Pesticides and Flame Retardants by SPE/GC/MS
- 529: Explosives and Related Compounds by by SPE/GC/MS
- 535, Revision 1.1: Chloroacetanilide and Other Acetamide Herbicide Degradates by SPE/ LC/MS/MS

Other Aspects of UCMR 2

- Lowest Concentration Minimum Reporting Limit (LCMRL) adopted
- Participating laboratories must be approved by EPA

Ground Water Rule

- Adopted November 8, 2006: (*71 FR 65573)*
- Source water monitoring for:
  - E. coli, enterococci, or coliphage
- If total coliform is detected

Biological Methods Rule

- Finalized March 26, 2007 (14219)
- Membrane filter (MF) and multiple-tube fermentation (MTF) for *E. coli* and *enterococci* in wastewater
- MTF methods for fecal coliforms and *Salmonella* in sewage sludge
- Clarification holding time
  - 6 hours HT plus 2 hours processing
- Methods 1600, 1603, 1103.1, 1106.1, 1680, 1681, and 1682
- Added Table 1H to Part 136

Laboratory Fraud

- OIG Report: 9/21/2006
- *Promising Techniques Identified to Improve Drinking Water Laboratory Integrity and Reduce Public Health Risks*
  - http://www.epa.gov/oigearth/reports/2006/20060921-2006-P-00036.pdf

Most Severe Vulnerabilities

- Censoring of information based on reporting limits
- Data manipulation
- Failure to follow SOPs/reference methods
- Falsifying existing data
- Improper calibration
- Inappropriate manual integrations
- Overwriting files: peak shaving, juicing/peak enhancing, deleting
- Inadequate training
- Inappropriate collection process
- Incomplete record keeping
- Mislabeled sample
- No demonstration of competency
- No requirement for collector
- Reporting data for samples not analyzed ("dry labbing")
- Retention times not assured
- Sample integrity unknown
- Selective use of QC data
- Sequencing analysis
- Spiking samples after preparation
- Time travel (changing times and dates)

Promising Techniques

- Policy, Training, and Guidance
- Laboratory Oversight Practices
- Enforcement Practices

A Few Specific Recommendations

- Establish the use of the EPA fraud hotline for laboratories.
- Enhance audits to include techniques to identify and deter inappropriate procedures.
- Use data validation and verification techniques
- Use analyst notation on manual integration changes
- Review electronic data
- Review inventory of laboratory supplies
- Include double blind PT samples
- Develop a list of prohibited practices and incentives.
- All laboratories should have an ethics policy
- Encourage laboratories to implement a fraud detection and deterrence program

New SW-846 Methods

- **8270D**: Updated version of method for semivolatile organics
- **8260C**: Updated version of method for volatile organics
- **8261A:** Volatiles by Vacuum Distillation with GC/MS
- **8330B:** Explosives by HPLC
- **6850** Perchlorate by HPLC ME or MS/MS
- **6860:** Perchlorate by IC MS or MS/MS

Activities in the Office of Water

- Clarification on Method 625
- Use of collision cell in 200.8
- Approval of drinking water methods
- Blanket approval of discrete analyzers
- 21st Edition of *Standard Methods* approved
  - http://www.epa.gov/waterscience/methods/

Other Items of Interest

- DOD Perchlorate Handbook
  - www.navylabs.navy.mil/Archive/DODPerchlorateHandbookR1.pdf
- Comprehensive Review of Emerging Contaminants and Related Issues
  - http://pubs.acs.org/cgi-bin/sample.cgi/ancham/2007/79/i12/html/ac070719q.html
- Draft List of Pesticides for Endocrine Disruptor Effects Testing
  www.epa.gov/endo/index.htm

Jerry L. Parr

Catalyst Information Resources

The Information Resource for Environmental Professionals

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www.CatalystInfoResources.com

Activities of The NELAC Institute

Environmental Measurement Symposium
August 22, 2007
Judy Duncan, TNI Board Chair

History of Environmental Laboratory Accreditation

1976 Drinking Water Program

1980's EPA CLP

1986 Report to Congress

1990 CNAEL

1995 NELAC

2002 INELA

2005-2006 SSTG & PPT

2006 The NELAC Institute

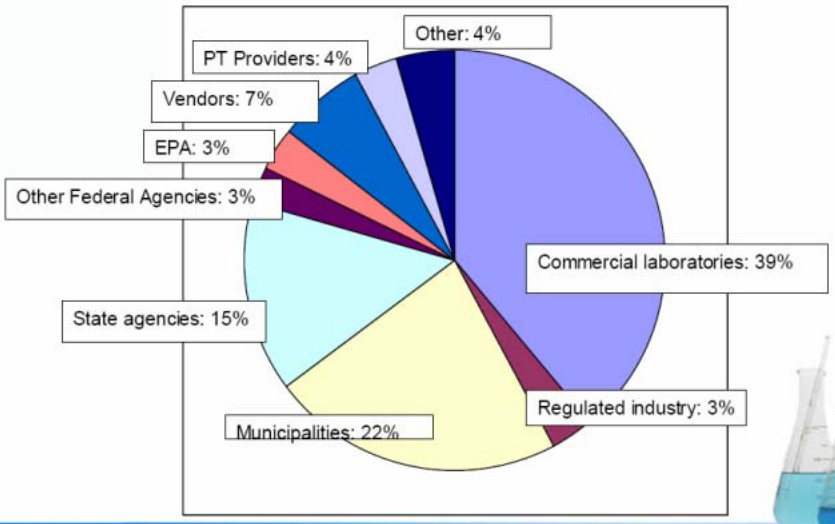
The NELAC Institute Today

- Non-profit organization with members
- Managed by a Board of Directors
- Organized into **Programs** that focus on the mission of the organization
- **Administrative** services support the programs
- **Mission** *The purpose of the organization is to foster the generation of environmental data of known and documented quality through an open, inclusive and transparent process that is responsive to the needs of the community.*

Who are our members?

- **Organizations that accredit laboratories**
  - Recognized accreditation bodies
  - States that are not recognized accreditation bodies
  - Federal agencies that operate accreditation programs
- **Accredited laboratories**
  - Commercial, Municipal, University, State, Federal, etc.
- **Others**
  - State and federal agencies that do not operate accreditation programs
  - Data users, consultants, PT Providers, vendors, etc.
  - Anyone interested in laboratory accreditation

Member Demographics



INELA & NELAC
Where are they today?

- INELA changed its Articles of Incorporation to become TNI
- NELAC discontinued some functions but will continue to exist until all key programs are fully functional in TNI
  - AA Committee discontinued as TNI NELAP Bd began to function
  - AARB still exists until TNI NELAP Bd establishes an appeal process
  - PT Boards of NELAC & TNI function in cooperation with one another

What has TNI accomplished?

- Elected our 1st Board of Directors with balanced representation from all stakeholders
- Completed a draft of a long-term strategic plan to be provided to members later this fall
- Recognized A2LA as PTOB/PTPA
- Established basic governance policies on ethics, conflict of interest, etc.

2007 TNI Board

- Judy Duncan, OK DEQ
- David Speis, Accutest
- Sharon Mertens, City of Milwaukee
- Steve Arms, FL DOH
- Joe Aiello, NJ DEP
- Jack Farrell, AEX
- Ken Jackson, NY DOH
- Barbara Finazzo, EPA
- George Detsis, DOE
- Tom McAninch, LCS
- Dave Mendenhall, UT DOH
- Judy Morgan, ESC
- Ken Olsen, Datachem
- Alfredo Sotomayor, WI DNR
- Aurora Shields, KS DHE
- Bob Wyeth, Columbia Analytical Services
- Brooke Connor, USGS

Programs of TNI

- Consensus Standards Development
- Laboratory Accreditation System
- National Environmental Laboratory Accreditation
- Proficiency Testing
- Technical Assistance
- Forum on Laboratory Accreditation
- National Environmental Monitoring Conference (NEMC)

Consensus Standards Development Program

Consensus Standards Development (CSD) Board

- Expert Committees

- Develop standards for the accreditation of environmental laboratories.
- Assist the other programs with guidance.

Expert Committees

- Accreditation Body
- Field Activities
- On-site Assessment
- Proficiency Testing
- Quality Systems

CSD Board Accomplishments

- Adoption of final standards for
  - Volume 2 Accreditation Body Requirements
    - Module 1 General Requirements
    - Module 3 On-site Assessment
- Adoption of final standards for Field Sampling and Measurement
  - Volume 1 General Requirements for Field Sampling and Measurement
  - Volume 2 General Requirements for Accreditation Bodies Accrediting Field Sampling and Measurements

CSD Bd Accomplishments, *cont.*

- Conducted membership vote on the following Draft Interim Standards
  - Volume 1 Laboratory Requirements - PT Module and 6 QS Module
  - Volume 2 Accreditation Body Requirements - Module 2 Proficiency Testing
  - Volume 3 Proficiency Testing Requirements
  - Volume 4 Oversight of Proficiency Testing
- This voting process is ongoing with Expert Committees resolving comments from voters
- These standards will then proceed to final vote and that will result in a complete "suite" of standards currently contemplated by TNI

CSD Bd Accomplishments, *cont.*

- Formed an ad hoc Uniformity of Standards Committee which has reviewed all standard modules and volumes for completeness and consistency

Laboratory Accreditation System Committee (LASC)

- Develop a system for the accreditation of environmental laboratories:
  - policies and procedures, interpretations, guidance documents, and any related tools used by ABs to implement a national environmental laboratory accreditation program.
- Subcommittees:
  - National Database Committee
  - Non-NELAP Accreditation Bodies
  - Small Organizations

LASC Accomplishments

- Organized a committee of 17 professionals with 400 collective years experience in the environmental testing industry
- LASC members participate on subcommittees and expert committees
  - Small Organizations
  - Non-NELAP Accreditation Bodies
  - National Database
  - Accreditation Body
  - Consensus Standards Development
  - ELAB

LASC Accomplishments, *cont.*

- LASC held 8 conference calls with 75% participation
- Drafted the SOP on *Standards Interpretation* for NELAP Board approval
  - SOP lays the foundation for providing quick and thorough responses to inquiries of TNI members concerning standards interpretation
- Presented the LASC Program goals and overview to an EPA audience at their annual QA Conference in Cleveland, OH

National Environmental Laboratory Accreditation Program (NELAP)

NELAP Board (representatives from accreditation bodies)

- Final authority for implementation of the program for accreditation of labs –
  - Review & approve Accrediting Bodies to become NELAP recognized.
  - Review NELAP ABs to assure conformance.
  - Recommend PT accreditor to TNI Board.
  - Adopt acceptance limits developed by PT Board.
  - Adopt the Laboratory Accreditation System for use in the Program.
- Receive complaints & direct to proper body.
- Ensure consistent application of the standard by NELAP ABs.

NELAP Board Accomplishments

- Organized 13 Accrediting Bodies from 12 states and developed processes for operation
- Recognized NELAC AAs on an interim basis as TNI ABs
- Reviewed and approved SOP for next round of AB evaluations

Proficiency Testing (PT) Program

PT Board

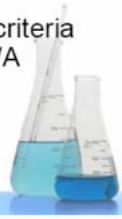
- Recommend the selection of PTOB/PTPA(s).
- Monitor the PTOB/PTPA(s) to assure that they are following the requirements set forth by the organization.
- Facilitate an annual caucus on proficiency testing.
- Review and evaluate PT data for the purpose of determining the appropriateness of study limits.
- Provide recommendations to the NELAP Board as to acceptance limits.

PT Board Accomplishments

- Developing the Quality System and SOP's for the TNI PT program
  - PT Board Charter
  - *PT Acceptance Criteria* SOP
  - *Complaint Handling* SOP
  - *PT Board Operations* SOP
  - *PTOB/PTPA Evaluation* SOP
  - *PT Caucus* SOP
  - *PT Board Voting Process* SOP

PT Bd Accomplishments, *cont.*

- Ratified as adequate and sufficient for TNI PT program in its inception -
  - The NELAC/NELAP Program PT acceptance criteria
  - The NELAC/NELAP Program approval of A2LA as the PTOB/PTPA
- Currently serving as invited guests on the NELAC PT Board as it completes its remaining current business agenda items
  - Formulation requirements of PT samples from the EPA Criteria Document
  - Request to add quantitative Microbiology PT acceptance criteria in the Drinking Water matrix to accommodate recent SDWA requirements for enumerative Microbiology test data from laboratories



Technical Assistance Program

Technical Assistance Committee (TAC)

- Develop tools and templates to assist laboratories and accreditation bodies with implementing accreditation programs.
- Ensure that training programs relevant to the needs of the stakeholder community are provided.
- Ensure that laboratory assessors have a forum to discuss common issues.
- Develop a mentoring program to assist both laboratories and accreditation bodies with implementing accreditation programs.

TAC Accomplishments

- *FAQs* SOP to be approved by the TNI Bd
- Draft of Technical SOP template
- Prepared materials for Cambridge meeting
  - Accreditation Body Fees
  - Training suggestions that led to presentations
    - Manual Integration
    - Best Calibration Practices

TAC Accomplishments, *cont*

- Mentoring Workgroup planned topics and presentations for Denver and Cambridge meetings
- Presentation and proposal of a One-on-One Mentoring Plan at Cambridge
- Assessment Forum Subcommittee organized a day of Assessment Issues for Denver and Cambridge

National Environmental Monitoring Conference

- Annual technical meeting focused on the latest innovations in environmental monitoring
- Co-hosted with EPA and the Independent Laboratories Institute
- August 20-24, 2007 Cambridge, MA
- August 11-15, 2008 Washington, DC
- www.nemc.us

Forum on Laboratory Accreditation

- Semiannual meeting where TNI committees, members, and others meet to discuss common issues
- August 20-24, 2007 Cambridge, MA
- January 18-22, 2008 Newport Beach, CA

Administration

- Advocacy Committee
- Conference Planning Committee
- Financial Audit Committee
- Nominating Committee
- Policy Committee
- Website Committee

- Administrative staff

Advocacy Committee Activities

- Establish relationships with trade organizations that have an interest in accreditation issues
- Establish relationships with EPA Program Offices
- Develop presentations and papers to promote TNI

Outreach Efforts: Trade Associations

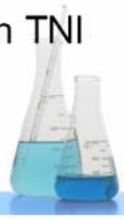
- Small focus groups with representation from :
  - American Council of Independent Laboratories (ACIL)
  - Association of Public Health Laboratories (APHL)
  - American Water Works Association (AWWA)
  - Water Environment Federation (WEF)
  - "Non-NELAP" States
- Primary focus of meetings was to identify their needs, interest and support for national laboratory accreditation

Outreach Efforts: EPA

- NELAC Special Committee letter in 2006
- TNI letter to EPA in 2006
- TNI meetings in 2007
  - Office of Solid Waste
  - Office of Water
  - Forum on Environmental Measurement (FEM)
  - Office of Inspector General
  - Office of Environmental Information
- Primary focus was to introduce TNI and indicate willingness to harmonize efforts and meet program goals

Preliminary Outcomes

- FEM designated EPA liaison to serve on Board of Directors
  - Barbara Finazzo, Region 2
- TNI requested regions to continue to provide individuals to serve as state evaluators
- Mutual interest in harmonizing drinking water certification program with TNI efforts
- Continued active participation of EPA staff in TNI activities

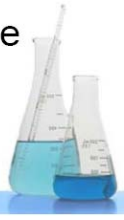


Website Committee Activities to Expand Capabilities

- Activities calendar for posting committee meetings and other events
- Posting committee minutes
- Joining TNI and paying dues electronically
- Ordering ISO standards, the generic TNI quality manual and shirts
- Finding TNI-related news as they occur
- Reviewing draft standards and voting on them
- Providing "How To" guidance for prospective ABs
- Linking to NELAC standards, lists of accredited labs and ABs

Availability of TNI Standards with ISO Language Included

- TNI Staff have worked with ASTM and ANSI to reach an agreement to make TNI Standards available with ISO language included
- Because TNI must pay a royalty fee for each integrated document, TNI Bd has instituted a pricing structure to recover these costs
- Both single copy and site licenses will be available
- Look for details on the TNI website within the next 2 months



Summary

- The NELAC Institute is poised to take national accreditation to the next level
  - Improve the accreditation requirements
  - Approve more states as accreditation bodies
  - Be responsive to stakeholder needs
  - Provide technical assistance
- We need your help!
  - Join our organization
  - Join a committee

The NELAC Institute

http://www.NELAC-Institute.org

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Recent Developments within the USEPA on the Performance Approach

Lara P. Autry
US EPA ORD
August 22, 2007

Overview

- 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

Introduction

- 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
  - Data users 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 by eliminating the need for formal rulemaking
- Improve the quality of science in the monitoring community

Redefined Steps

- The EPA is introducing a framework for flexibility and quality in environmental measurement.
- Key Goals:
  - Increased emphasis on specification of flexible 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 – demonstrates 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
  - No resources to revise regulations
  - New methods are performance based
- Ambient Air Monitoring Program
  - Performance approach methods in new areas
- Transportation and Air Quality
  - Proposed rule for sulfur in diesel
  - Proposed rule for non-diesel fuels

OPP

- Adopted and fully supported the Performance Approach for submission of methods by registrants for pesticides.
- The analyzing of samples to support the Antimicrobial Testing Program has results potentially for enforcement purposes that requires analysis using a method submitted in addition to analysis by another established lab in-house method. This needs to be addressed.

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)
- Requirements in the RCRA regulations to assist the regulatory community (i.e., removing regulatory barriers)

OW

- Method Update Rule
- Developing multiple technologies and methods for monitoring the same contaminant.
- Building flexibility into methods based on an individual- and procedure- based performance model.
- Providing transparency in method development by including more information in the method itself and in additional articles and reports.

OW (cont.)

- Operating an improved Alternate Test Procedures (ATP) program to address new, modified methods that go beyond the flexibility identified in approved methods.
- Instituting an Expedited Methods Approval approach to speed approval of newly developed or modified methods.
- Actively pursuing partnerships for methods development to bring new technologies into use faster.

Forum on Environmental Measurements (FEM)

- Action Agenda specifies implementation of performance approach
  - Action Team
  - Pilot Projects
  - Strategy Session
- Marketing and partnership development.

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 Regulations
ACIL (10% of Laboratories) →	
Regional Laboratories →	

Potential Solutions

- Omnibus regulation change
- Document that describes what one must do to demonstrate/document quality of measurement system/data
- "Marketing" strategy to implement and educate users of document
- Find ways to reduce economic and legal burden to users

Summary

- Outreach
- New Notice of Intent
- Form partnerships
- Training
- Timeline

SPECIAL SESSION ON DETECTION AND QUANTITATION LIMITS

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

The DQFAC Single laboratory Detection/Quantitation limit Procedure

Richard Burrows

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NEMC August, 2007

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DQFAC DL/QL PROCEDURE

- The procedure was developed from the ACIL procedure which was piloted for 5 methods by at least 8 labs per method.
- Modifications to the ACIL procedure were designed to address shortcomings noted during the pilot study

2

3

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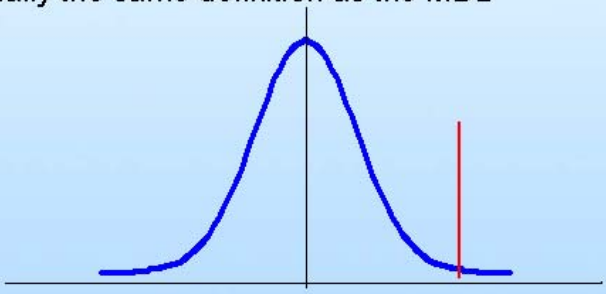
DL DEFINITION

- **Detection Limit (DL)** - The minimum result which can be reliably discriminated from a blank (for example, with a 99% confidence level).
  - ~ Essentially the same definition as the MDL



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QL DEFINITION

- **Quantification Limit (QL):** The smallest concentration of analyte demonstrated by the laboratory to meet the required precision, accuracy, false negative error rate and qualitative identification criteria for the intended purpose.

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GENERAL PRINCIPLES

- Use blanks to define the DL if numerical results are available
  - ~ Incorporate the mean of the blanks
- QL is based on a spiking level – so precision and accuracy information at the QL is obtained
- Calculate the lowest expected result (LER) from QL spikes to protect against false negatives
- Requirement to meet a given precision and accuracy at the QL is added if defined in the analytical method

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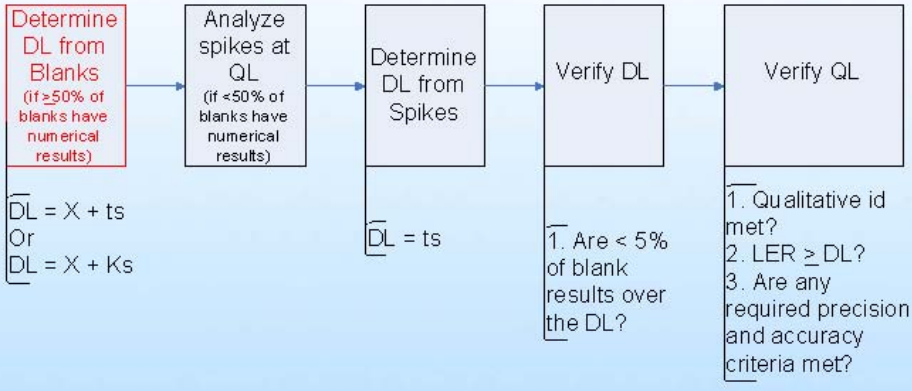
DL/QL PROCEDURE BASICS



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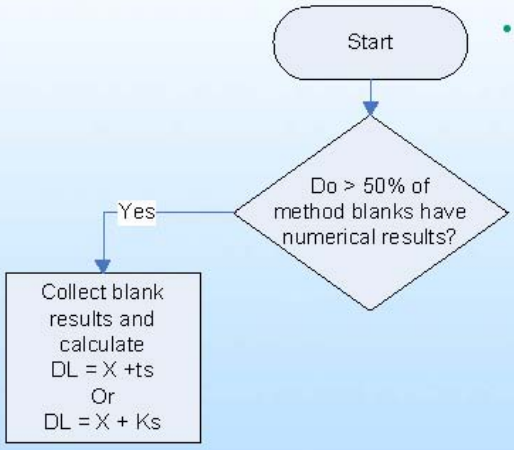
USE OF BLANKS



- Why have a different starting point when there are numerical blank values?
  - ~ Blanks provide the most accurate assessment of noise and should be used if available

8

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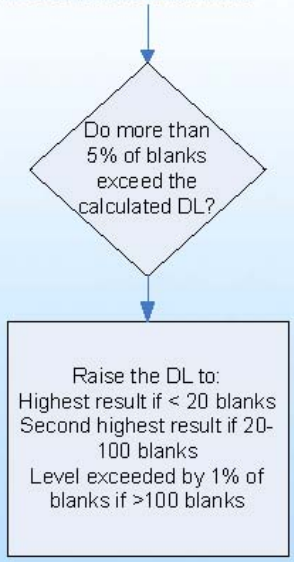
DL ADJUSTMENT



- Why a non-parametric test?
  - ~ This non-parametric test ensures that situations where non-normal distributions drive the false positive rate higher are captured

9

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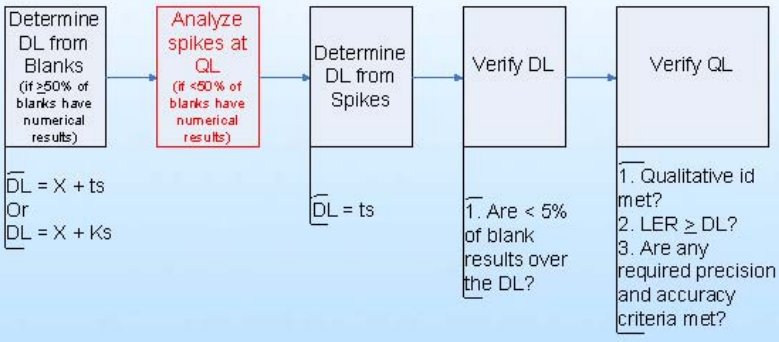

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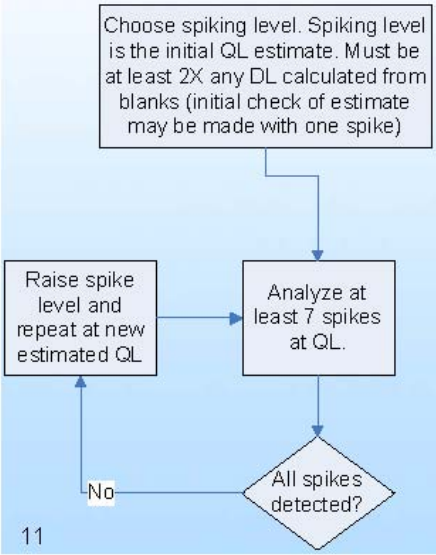
ESTABLISHING THE QL



- Spiking level is driven by the blanks if they exist, otherwise by laboratory experience
  - ~ Qualitative identification is required
- If there are MQOs for precision and accuracy, these must be met

11

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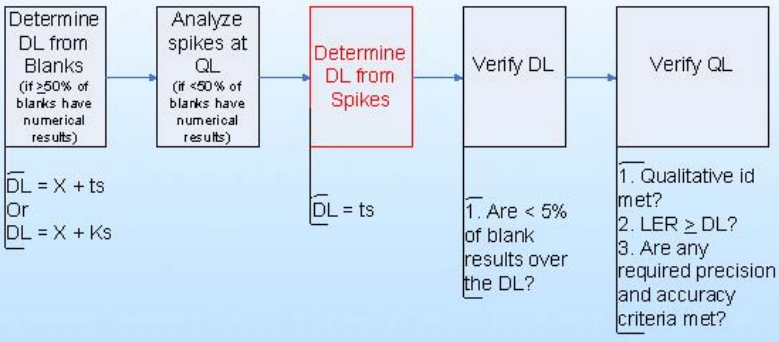

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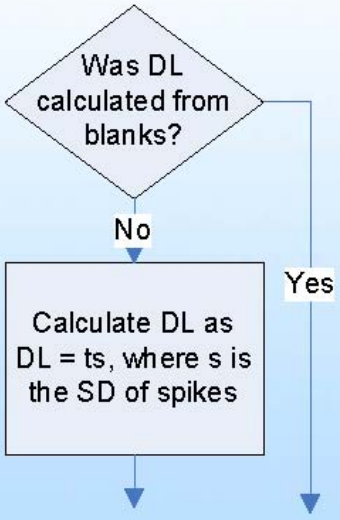
DL FOR METHODS WITH ND BLANK RESULTS



- If the DL was not calculated from blanks, then it is assessed from spikes
  - ~ These are tests where the typical blank level is within the censoring range of the method

13

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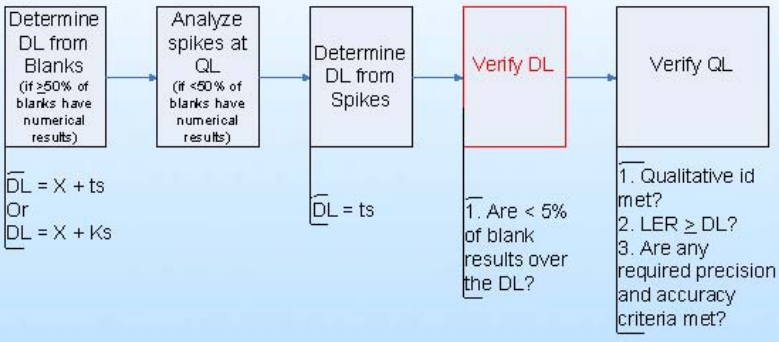

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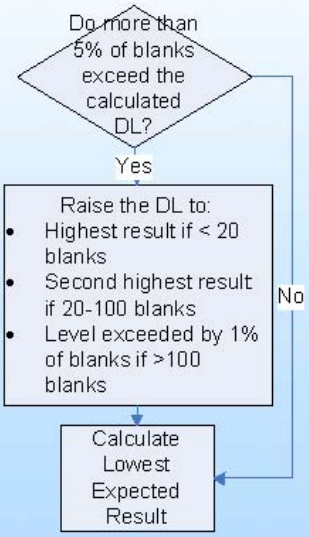
BLANK CHECK AND LER



- The non-parametric check is applied to all methods
- LER is the "Lowest Expected Result" from spikes at the QL

15

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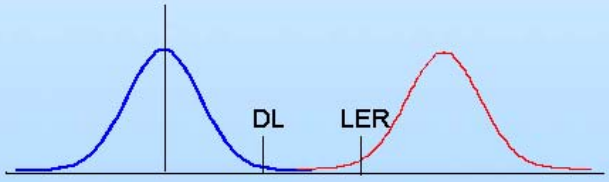
LER

Estimate the Lowest Expected Result (LER) from spikes at the QL.

$$\text{LER} = \frac{\overline{X}_s * QL}{SL} - \left(s \times t_{(n-1,1-\alpha=0.95)}\right)$$

- Where s is defined in Section 1.2.7.
- Where $\overline{X}_s$ is the mean concentration result from the QL spikes.
- $t_{(n-1,1-\alpha=0.95)}$ is the 95th percentile of a t distribution with n-1 degrees of freedom. Values for t are listed in Table 1.
- SL is the spike level used for the QL spike sample.



16

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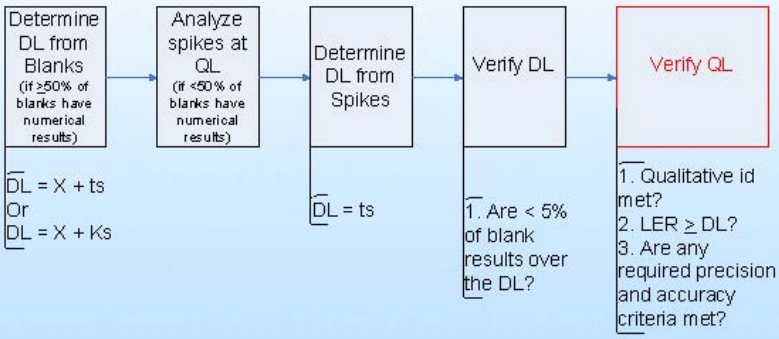

17

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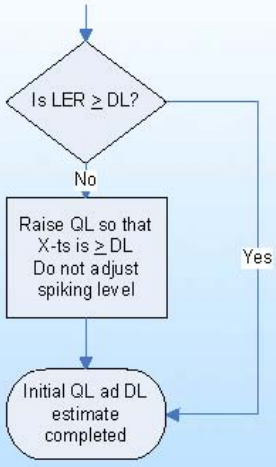
ADJUSTMENT OF QL



- QL is adjusted if necessary so that there is good confidence (95%) that a true value at the QL will return a result above the DL
- If there are precision and accuracy MQOs they must be met

18

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ONGOING CHECKS

- Data is gradually added but not discarded until over 3 years old or over 100 data points
- Intent is that DLs and QLs will become reflective of routine analysis
- If there are major instrumentation or process changes then start data collection over

19

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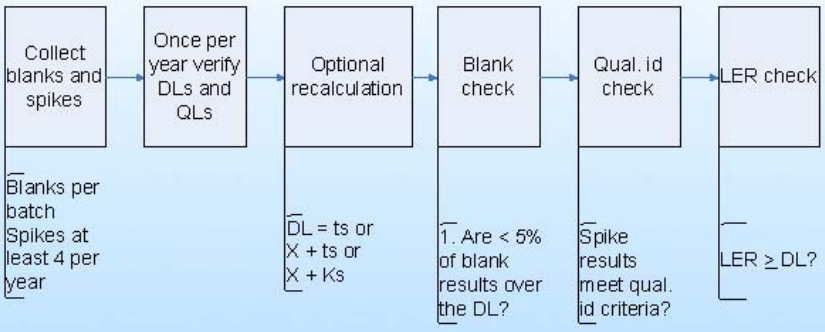
ONGOING VERIFICATION



20

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COLLECTION OF DATA

Collect method blanks with each batch and QL spikes at a frequency of 4 per 12 month period. Collect at least 2 per instrument if multiple instruments are using the same DL and QL

At least once per year, re-evaluate the DLs and QLs

- Frequency is intended to keep costs reasonable
- Re-evaluation can be more frequent at the discretion of the QA manager

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OPTIONAL RECALCULATION OF DL

Optionally, recalculate DLs using the formulas presented for the initial determination

- Recalculation is optional, since if the DL is too low, the problem will show up in the verification steps

22

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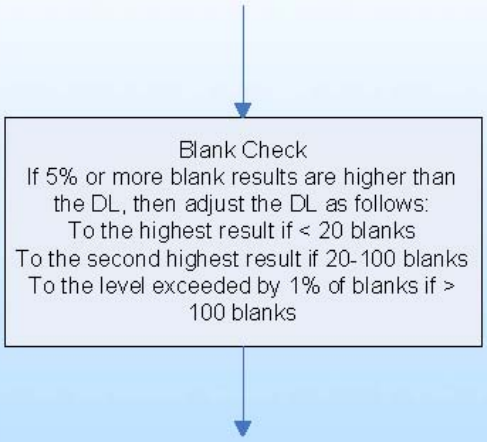
BLANK CHECK



- DL is checked based on actual method blank results

23

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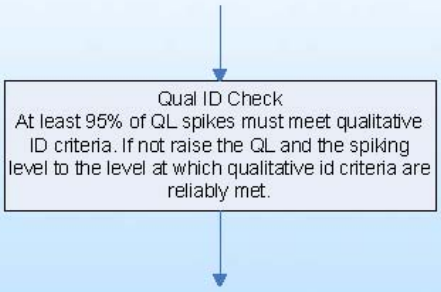
QUALITATIVE ID CHECK



- Qualitative identification criteria (qualifier ions, ratios, etc) must be met for QL level spikes

24

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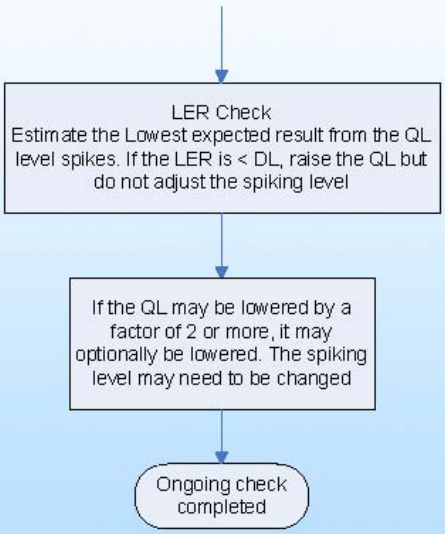
LER CHECK



- LER check to ensure that false negatives are kept under control

25

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K vs t

- t – targets a false positive rate that will average 1%
- K – targets a false positive rate that is almost always less than 1%
  - ~ The false positive rate is lower using t, but the detection limit is higher using K.

26


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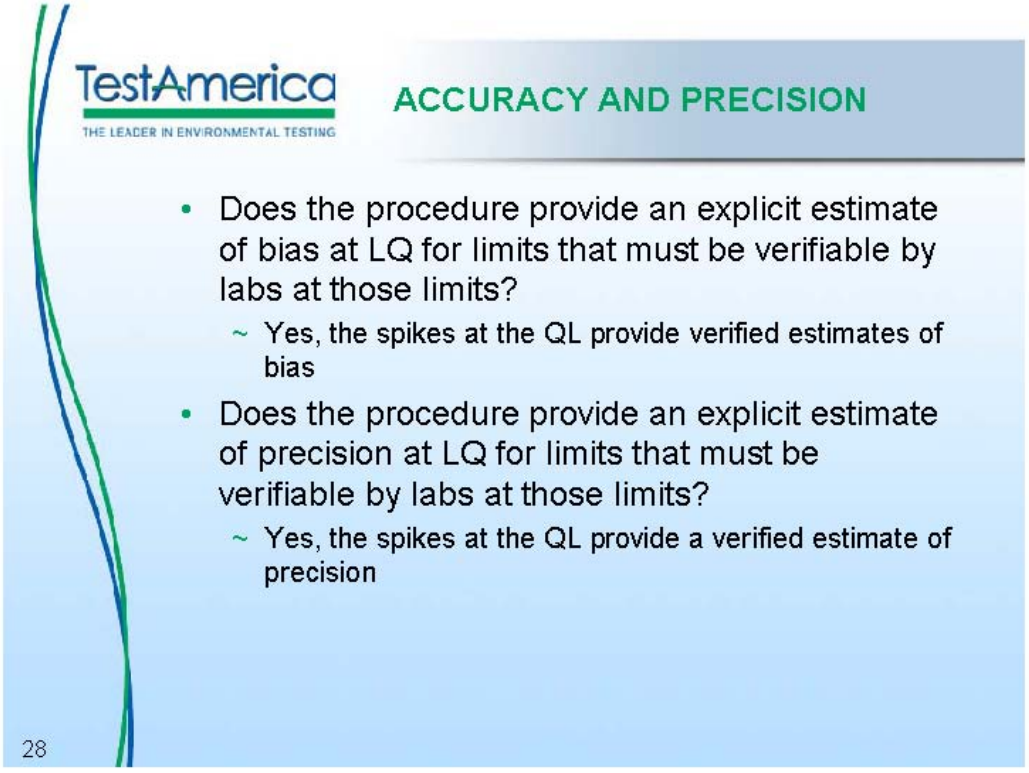
"WHAT WE WANT A PROCEDURE TO DO"
27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ACCURACY AND PRECISION
• Does the procedure provide an explicit estimate of bias at LQ for limits that must be verifiable by labs at those limits?
~ Yes, the spikes at the QL provide verified estimates of bias
• Does the procedure provide an explicit estimate of precision at LQ for limits that must be verifiable by labs at those limits?
~ Yes, the spikes at the QL provide a verified estimate of precision
28

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FALSE POSITIVE AND FALSE NEGATIVE RATES

- Does the procedure provide an explicit false positive rate for blanks?
  - ~ Yes, the procedure sets the DL at the level statistically predicted to be the 1% false positive level, and then verifies and corrects that level if necessary once sufficient data is available
- Does the procedure provide an explicit false negative rate at LC for the true value at LD or LQ that must be observed in labs at LC for the estimated values of LD or LQ?
  - ~ Yes, the procedure requires that no more than 5% of QL level spikes return false negatives

29

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QUALITATIVE IDENTIFICATION AND ROUTINE VARIABILITY

- Does the procedure provide that qualitative identification criteria defined in the analytical method are met at the determined detection and quantitation limits?
  - ~ Yes qualitative identification criteria are required to be met for any results above the DL
- Does the procedure adequately represent routine variability in lab performance?
  - ~ Yes, the procedure uses routine method blanks and spikes generated over a period of time.

30

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VERIFICATION AND MATRICES

- Does the procedure perform on-going verification of estimates?
  - ~ Yes, both false positives (through blanks) and false negatives (through spikes) are checked and the DL and QL are adjusted if the rates are too high
- Is the procedure capable of calculating limits using matrices other than lab reagent grade water?
  - ~ Yes, it is straightforward to apply the procedure to other matrices, and there is a blank/QL spike check incorporated into the procedure for individual matrices such as a specific wastewater.

31

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COMPLETE METHOD AND NON-ZERO BLANKS

- Does the procedure use only data that results from test methods conducted in their entirety?
  - ~ Yes, this is explicitly required
- Does the procedure explicitly adjust or account for situations where method blanks always return a non-zero result/response?
  - ~ Yes, the mean blank value is added to the DL estimate

32

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EASE OF USE AND COST EFFECTIVENESS

- Is the procedure clearly written with enough detail so that most users can understand and implement them?
  - ~ We believe so – the procedure is similar to that used in the pilot study
- Is the procedure cost effective?
  - ~ Yes – the procedure is more expensive than a MDL that is only performed once, but less expensive than a MDL that must be repeated each year. In addition, good QL level bias and precision information is obtained.

33

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MULTI-LAB AND GENERAL APPLICABILITY

- Does the procedure assess multi-laboratory and inter-laboratory variability when data from more than one lab is used?
  - ~ In a multi laboratory setting, the QL would be set at a level achieved by a specified proportion of the participant laboratories
- Is the procedure applicable to all users and test methods?
  - ~ Yes, we believe so, any test method for which spiking is feasible

34

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The Impact of Calibration Models on Analyte Detection and Accuracy at Low Concentrations

- Example GC/MS Data
- Example ICP/MS Data
- Example ICP Data

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GC/MS Data

- Three calibration models, average response factor, linear regression with no weighting, and linear regression with inverse square weighting.
- If a sample gave the same response as our low standard, what would we detect and report?

36

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One calibration, processed three different ways

GC/MS		inverse square	
	Avg RRF	weighted	unweighted
	%RSD	r^2	r^2
bis(2-chloroethyl)ether	4.68	0.998	0.996
bis(2-chloroisopropyl)ether	4.26	0.999	0.996
n-nitroso-di-N-propylamine	6.35	0.998	0.995
nitrobenzene	6.15	0.999	0.998
bis(2-chloroethoxy)methane	5.14	0.999	0.997
2,4-dichlorophenol	11.54	0.999	0.997
hexachlorobutadiene	3.46	0.999	0.998
2,4-dinitrotoluene	25.72	0.996	0.998
4-chlorophenyl phenyl ether	5.69	0.999	0.998
4-bromophenyl phenyl ether	5.42	0.999	0.998
hexachlorobenzene	2.4	0.999	0.998
bis(2-ethylhexyl)phthalate	22.24	0.999	0.998

37

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Three different results

GC/MS			inverse square	
		Avg RRF	weighted	unweighted
	MDL (ug/l)	0.5 ppm std	0.5 ppm std	0.5 ppm std
bis(2-chloroethyl)ether	0.405	0.53	0.5	0.12
bis(2-chloroisopropyl)ether	0.386	0.48	0.5	< 0
n-nitroso-di-N-propylamine	0.339	0.45	0.5	< 0
nitrobenzene	0.455	0.45	0.5	0.14
bis(2-chloroethoxy)methane	0.357	0.46	0.5	< 0
2,4-dichlorophenol	0.338	0.39	0.5	0.11
hexachlorobutadiene	0.362	0.49	0.5	0.38
2,4-dinitrotoluene	0.244	0.25	0.5	1.24
4-chlorophenyl phenyl ether	0.412	0.45	0.5	0.22
4-bromophenyl phenyl ether	0.267	0.46	0.5	0.38
hexachlorobenzene	0.52	0.5	0.5	0.15
bis(2-ethylhexyl)phthalate	0.232	0.28	0.5	0.47
	>20% error	>50% error		

38

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ICP/MS Data

- Compare Continuing Calibration Blank results using two different calibration models, linear regression without weighting and linear regression with 1/X weighting.

39

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The test

- If the CCB result is greater than the MDL, you have a high risk of false positives
- If the CCB result is less than the negative value of the MDL, you have a high risk of false negatives

40

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CCB 1

	MDL	not weighted	weighted
	ug/l	ug/l	ug/l
Li	0.17	-0.15	0.01
Be	0.03	-0.16	0.00
V	0.05	-0.27	-0.02
Cr	0.12	-0.15	-0.06
Mn	0.06	-0.39	0.00
Co	0.02	-0.24	0.00
Ni	0.18	-0.26	0.00
Cu	0.24	-0.28	0.04
Zn	1.25	-0.14	-0.05
As	0.28	-0.20	0.01

	MDL	not weighted	weighted
	ug/l	ug/l	ug/l
Se	0.42	-0.18	-0.04
Sr	0.03	-0.25	0.00
Mo	0.14	0.16	0.23
Ag	0.16	-0.15	0.00
Cd	0.03	-0.02	-0.01
Sb	0.20	0.10	0.13
Ba	0.07	0.00	0.00
Tl	0.06	-0.28	0.00
Pb	0.06	-0.12	0.00

41

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Method 300

Nitrate MDL 0.0082		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	2247869	339.37%	-5.43%	18.18%	0.75%
0.5	20450323	19.65%	-15.89%	-11.19%	-8.04%
2.5	1.06E+08	-6.98%	-11.82%	-9.11%	-4.16%
5	2.23E+08	-5.26%	-6.36%	-3.99%	0.94%
10	4.84E+08	1.54%	2.14%	4.22%	8.86%
	r	0.9990	0.9985	0.9985	0.9978
	RSE	182.04%	9.58%	13.04%	7.47%

42

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Summary

- DQ/QL procedure
  - ~ Uses long term data
  - ~ Takes account of blank bias
  - ~ Considers qualitative identification
  - ~ Checks actual performance against the calculated limits to accommodate non-normal data
  - ~ Develops precision/accuracy information at the QL

Whatever the DL/QL procedure, careful selection of the appropriate calibration model is vital to achieve accurate quantitation at low levels

43

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Questions?

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44

Federal Advisory Committee on Detection and Quantitation and Clean Water Act Uses

Environmental Measurement Symposium

August 22, 2007

Why does anyone care about detection and quantitation?

	Facility X	Facility Y
Analyte	Aluminum	Chromium VI
Water Quality Standard	87 ug/L (chronic) 750 ug/L (acute)	11 ug/L (chronic) 16 (acute)
WQBEL	DML = 87ug/L AML = 58 ug/L	DML = 16 ug/L AML = 8 ug/L
Method Quantitation Limit	Method 208 100 ug/L (MQL)	Method 218.4 10 ug/L (ML)

What got us started?

- Longstanding concerns about how a Method Detection Limit (MDL) or Minimum Level (ML) is calculated and used in laboratory and regulatory programs
- Industry filed suit challenging the procedures used for determining detection and quantitation levels
- EPA and Industry reached a settlement agreement in October 2000
  - Assess detection and quantitation procedures and take comments on draft
  - Take final action on assessment and any proposed rule amendments on November 1, 2004

What happened next?

- Proposed MDL and ML changes to 40 CFR Part 136
- Received 136 comments indicating EPA could do better
- On November 1, 2004, decided to withdraw rule amendments and conduct a situation assessment by a neutral third party

What did the situation assessment recommend?

- Common issues
  - Current MDL/ML does not sufficient account for variability of results within and between labs
  - Need to address background contamination, matrix and recovery effects, false positive and negative rates
  - Need for a common set of terms and definitions
  - Need for consistency use of MDL and ML in reporting and determining compliance
- Recommendations
  - Federal Advisory Committee should be formed to reach agreement on
    - Definition of terms
    - One or more approaches for detection and quantitation for Clean Water Act purposes. Pilot test most promising procedures before deciding.
    - Interpretation and uses of numbers
  - FAC should be balanced set of stakeholders; EPA should be at the table.
  - FAC recommendations should be incorporated in rulemaking
- FAC charter effective May 31, 2005 for two years.

Who is on the FAC?

4 members each

- Environmental labs
- Water Utilities
- Environmental Community (one later resigned)
- Industry
- State Government

1 member

- EPA

What's happened thus far?

- Seven face-to-face meetings of the FAC; one FAC conference call
- Over 100 meetings of several workgroups, subgroups and strike teams
- Several meetings of EPA's internal workgroup representing offices across EPA
- Pilot study of candidate detection/quantitation procedures
  - A dozen candidates narrowed to three pairs
  - Tested five methods over several weeks in 6-8 labs
- Original FAC Charter extended on May 30, 2007 to allow FAC to finish its work

What are the issues facing the FAC?

- Single lab procedure
- Laboratory verification of DL and QL -- should it be more frequent than the current practice of once per year?
- Multi lab/interlab procedure for calculating national limit -- discussions concerning number of labs, data collection time frame, calculation for the national limits
- Matrix effects – how should permitting authorities deal with these effects?
- Uses of detection and quantitation in permitting – permit limits, reporting, compliance calculation; heavy reliance on national QLs, laboratory DLs

What issues are beyond the FAC?

- Time didn't permit FAC from discussing
  - Use of detection and quantitation for other CWA uses, including reasonable potential, ambient monitoring, water quality criteria . . .
  - Updating the Alternative Test Procedures Program; but need to calculate a national quantitation limit is an issue for ATP submittals
- Should the new procedure apply to drinking water and solid waste methods?

What are the implementation issues?

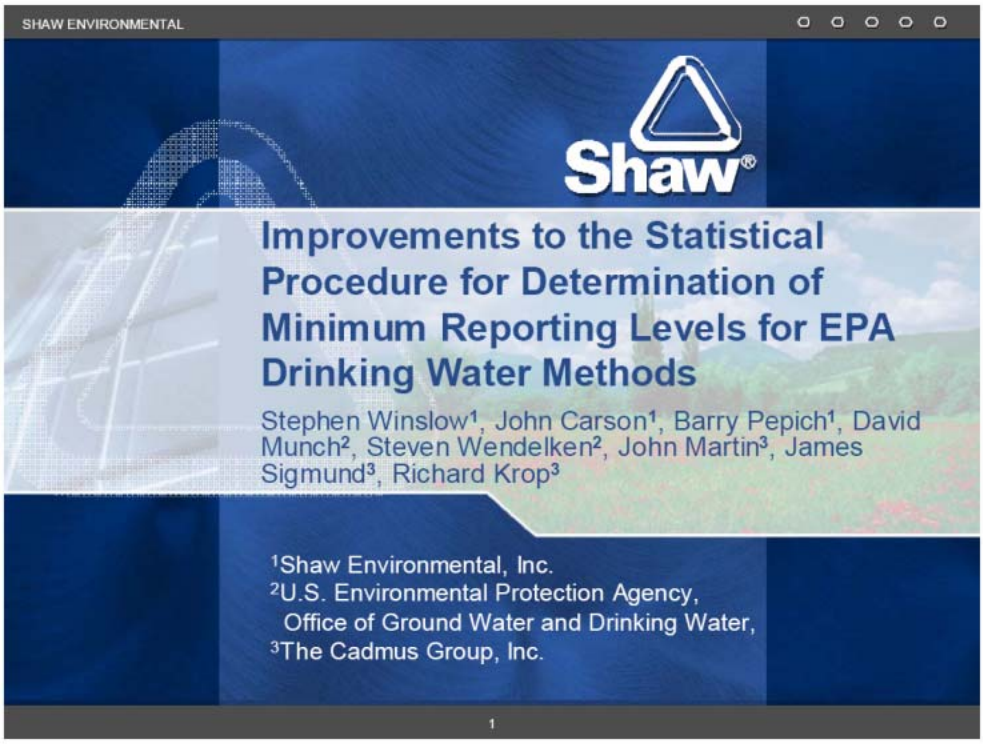
- What is the lead time labs need to learn the new procedure?
- Which states will need to make corresponding changes in their rules and should this influence the effective date of any new rule?
- How do we ensure method developers are aware of the new changes?
- The reporting and compliance determination recommendations rely heavily on the existence of national QLs which raises several issues:
  - Full implementation will take years. How do we operate a dual system in the meantime?
  - Should EPA grandfather some of existing ML into the new program, making them de facto national QLs?
  - How does EPA prioritize the creation of national QLs for existing and new methods?
  - Is there a more streamlined approach to generating national QLs? Laboratory-generated data?

More implementation issues?

- What guidance is needed for states?
  - Confusion between the old and new program, and lots of different QL types (national, state, permit, lab)
  - Guidance accompany the final rule would ensure consistent state implementation and a level playing field
  - Coordination with EPA Regions and States critical – training and workshops are needed regarding permit writing, reporting, compliance determinations
- What partnerships should EPA form to ensure smooth implementation?
  - Laboratory certifying and accrediting programs; ACIL
  - NACWA
  - ASIWPCA
  - Others?
- Will EPA have the right resources?

What are the next steps?

- Three more FACDQ meetings
  - August 28, 2007 – conference call
  - September 19-21, 2007 – key decisions meeting
  - December 5-7, 2007 – approve final report
- Post FACDQ
  - Proposed rule -- December 2008
  - Final rule – December 2009
  - Implementation
  - Methods in the rulemaking queue
    - PCB
    - Flame retardants
    - Two PPCP methods



Introduction

- Office of Ground Water and Drinking Water (OGWDW) U.S. EPA
  - OGWDW publishes quantitation level protocol for Lowest Concentration Minimum Reporting Level (LCMRL) November of 2004
  - LCMLR developed in conjunction with the second cycle of the Unregulated Contaminants Monitoring Rule (UCMR2)
  - Downloadable calculator & information available at the OGWDW website
  - LCMRL concept described in research article and in feature article in ES&T

Overview

- Why OGWDW evaluated new quantitation procedure that included precision as well as accuracy
- LCMRL Implementations to Date
- Goals for Improvements
- Results
- Improvements to LCMRL calculator
- Multi-lab Determination of Minimum Reporting Level (MRLs)
- MRL verification - simpler procedure for day-to-day operation

Why EPA evaluated new quantitation procedure

- Quantification Limit: The smallest detectable amount or concentration of analyte, greater than the detection limit, where the required precision and accuracy is achieved

Why EPA evaluated new quantitation procedure

- OGWDW needed single-lab procedure that evaluated quantitation level in terms of both precision & accuracy
  - Precision - How reproducible
  - Accuracy - How close to true value
- Quantitation level based solely on precision (using standard deviation) does not consider non-ideal processes such as:
  - Presence of analyte interferent
  - Analyte absorption or degradation by instrument
  - Loss of analyte in extraction step
  - Matrix enhancement

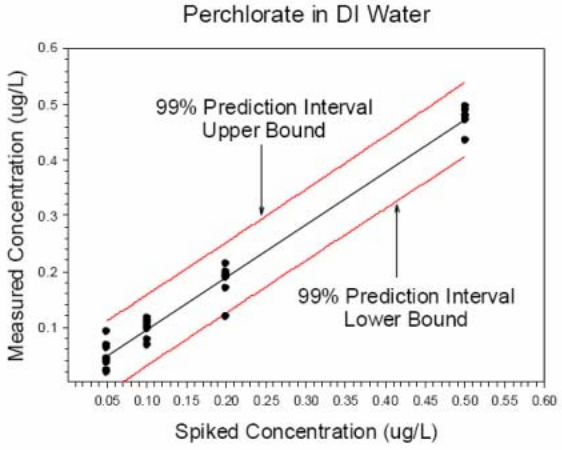
Lowest Concentration Minimum Reporting Level (LCMRL) Determination

- Definition: The lowest concentration MRL (LCMRL) is the lowest true concentration for which future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery
- Although the LCMRL is defined in terms of a probabilistic statement of coverage, it is in practice determined by precision and accuracy

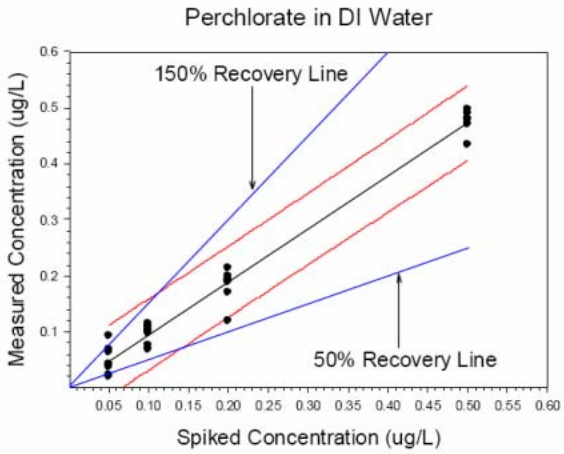
LCMRL Determination

- LCMRL takes into account precision and accuracy, simultaneously applied
- Multiple-concentration regression approach
- Created for OGWDW, but flexible to meet other program designs
- LCMRL determined during method development
- Simpler MRL verification procedure to be used to evaluate lab capability at predetermined level

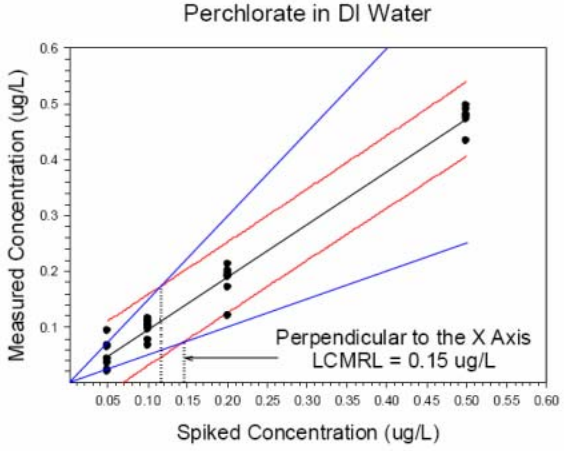
Present LCMRL Calculator



Present LCMRL Calculator

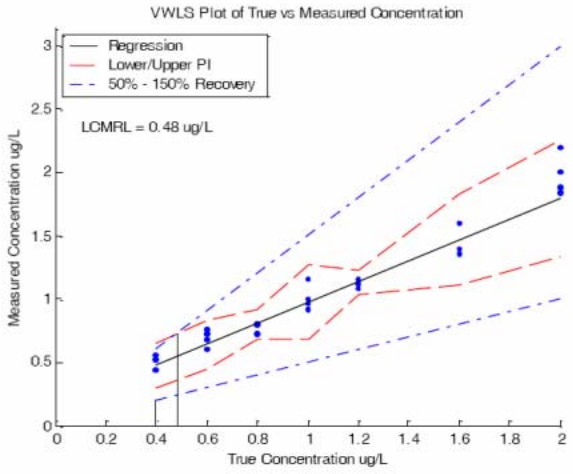


Present LCMRL Calculator



Present LCMRL Calculator

- Case of non-constant variance
- Use variance weighted least squares (VWLS)
- Prediction interval taken at each point
- Model linked point-to-point

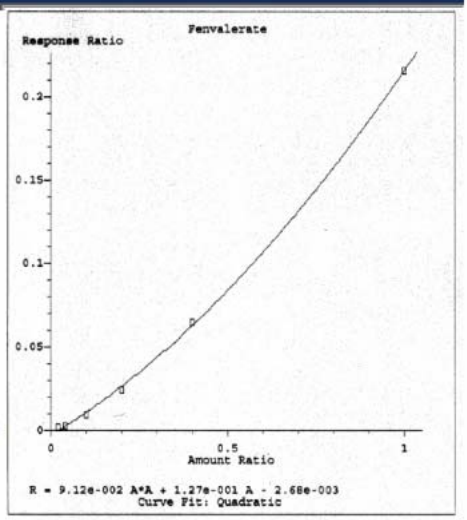


Why Accuracy, too

- Both precision & accuracy are needed for a quantitation level
- But quantitation level often defined as 10 times the standard deviation
  - Takes into account precision only
- When non-ideal process occur, such as analyte absorption, degradation, and extraction loss, a precision multiplier may not be adequate

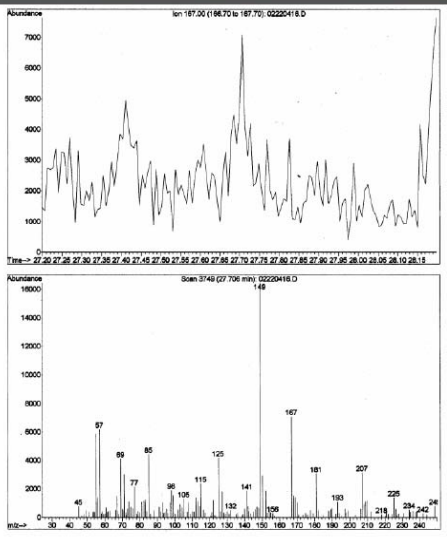
Why Accuracy, too

- Example:
  - At right, Fenvalerate instrument calibration curve
  - At low-level concentration, fenvalerate is prone to adsorption/degradation by injection port active sites
  - Non-linearity and lack of fit at low end of curve are evidence of non-ideal processes



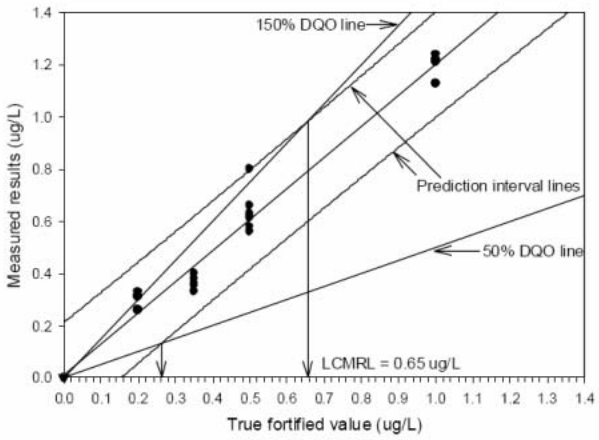
Why Accuracy, too

- Fenvalerate:
  - QL_{10xSD} = 0.25 ug/L
- At upper right, 0.20 ug/L chromatogram
- At lower right, spectrum showing quant ion m/z 167



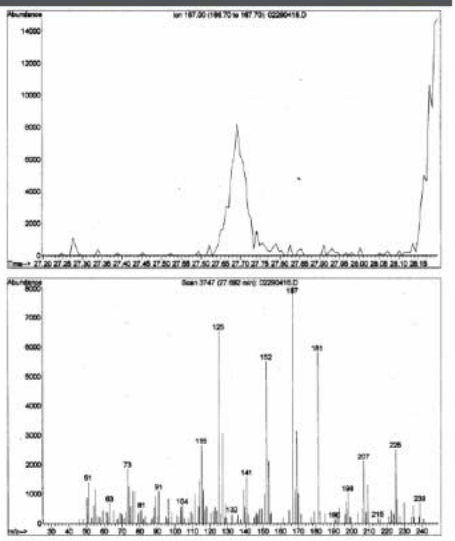
Why Accuracy, too

- **Determined by LCMRL, Fenvalerate quantitation level = 0.65 ug/L**



Why Accuracy, too

- Fenvalerate
  - LCMRL = 0.65 ug/L
  - At right, chromatogram and ion trace at 0.5 ug/L
  - Quant ion m/z 167 now largest ion
- LCMRL and QL_{10xSD} tend to be dissimilar when low-level accuracy is an issue



LCMRL Uses to Date

- LCMRL approach promulgated in second cycle of OGWDW's Unregulated Contaminant Monitoring Rule (UCMR2)
- LCMRL reported in EPA Methods 314.1, 331.0, 332.0, 521, 527, and 535
- New methods coming out with LCMRLs
- For initial demonstration of laboratory capability, MDL determination is optional, only MRL verification required

Improvement Goals for LCMRL Calculator

- More robust
- Simpler to implement, or as easy to use
- No additional burden
- Readily available

Results

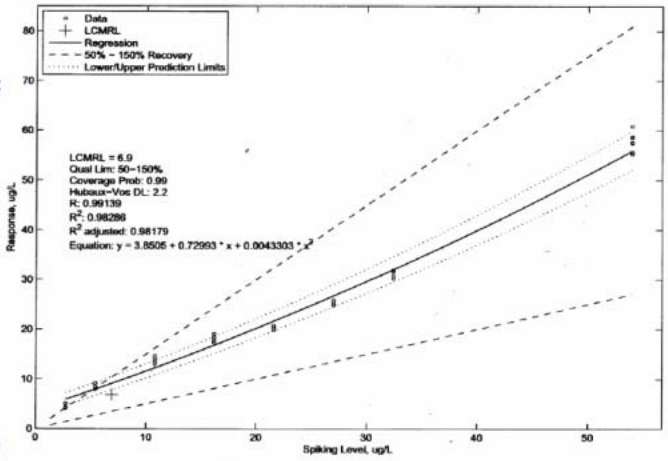
- **Modeling capacity was improved**
  - **New variance function covers both cases of constant and non-constant variance**
    - **No need to distinguish between OLS and VWLS conditions**
    - **Variance modeled by continuous function rather than using point-to-point estimation about each spiking level**
  - **Mean regression line now has quadratic option in addition to linear**

Results

- Calculator handles wider range of real world situations
  - Not as particular about selection or range of concentration
  - Reduces effect of aberrant results at highest level
    - Outliers included, but influence on mean & standard deviation models down-weighted
- Simpler, or as easy to use
  - Don't need to decide about apparent outlier
  - Statistics are more sophisticated, but no additional work required
  - Previously four levels of seven replicates (28 total), now seven levels of four replicates (28 total)

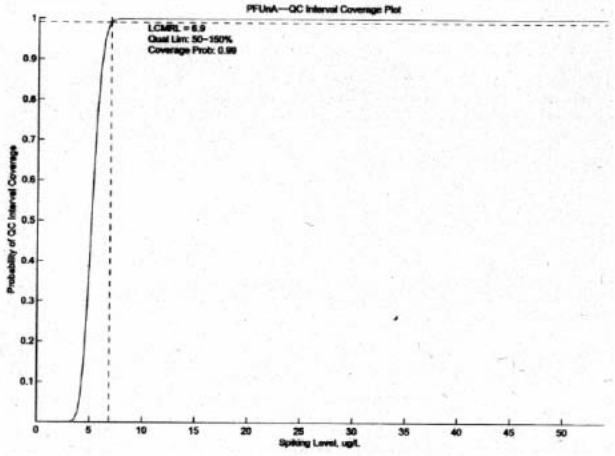
Results

- Graphical example of new calculator
- Actually solved by probability coverage (next slide)



Results

- Mean & variance functions used to create coverage probability function, used to solve for LCMRL
- LCMRL found at 99% probability that spiking at that level will result in recovery between 50 & 150%, inclusive



LCMRL Flexibility

- OGWDW uses 50 to 150% recovery with 99% confidence, but data quality parameters can be adjusted to program needs
  - Use of data below the quantitation level is up to data user to decide
  - Data can be generated over time to incorporate temporal variability
  - Number of replicates at each level don't have to be the same as long as minimum number met
  - Data can be generated using particular matrix

Multi-Lab MRL

- Multi-lab LCMRLs are used to generate minimum reporting levels (MRLs),
  - MRLS are nationally attainable quantitation levels determined by regulatory agency such as OGWDW
- For UCMR2, MRLs were defined as:
  - Three labs
    - MRL = Mean + three standard deviations
  - Two labs
    - MRL = Mean + 3 X absolute value (LCMRL 1 - LCMRL2)
  - MRLs rounded to one significant figure

Multi-Lab MRL

- Multi-lab MRL procedure is work-in-progress
- Challenges
  - Add more labs, five labs instead of three
  - Get more information about distribution by using data generated during LCMRL determination instead of just using the final LCMRL value
  - Previous procedure (mean + 3 sigma) uses "tail" of distribution when uncertain of distribution itself
- Further models considered
  - Composite model
  - Random Effects model
  - Bayesian Bootstrap: strongest candidate

MRL Verification Procedure

- The LCMRL procedure is a sophisticated model that accounts for a complex world
  - Performed during method development and used to generate multi-laboratory MRLs
- The MRL Verification procedure is much simpler than LCMRL determination
  - Performed in analytical lab initial demonstration of capability
  - Not necessary to re-determine the lowest limit
  - Used to make a decision at pre-defined MRL, either DQOs are met or not

MRL Verification Procedure

- Seven replicate samples are fortified at single concentration at the MRL or below, and taken through entire method procedure
  - MRL verification is not iterative like the MDL
  - Only single level used
- A prediction interval of results (PIR) calculated:
- PIR = $Mean \pm s \times t_{df,1-\frac{1}{2}\alpha} \times \sqrt{1+\frac{1}{N}}$

  where *S* = standard deviation, *t* = students *t*, *N* = # of samples
- Laboratories simply need to verify that PIR interval is between 50 and 150%

Summary

- New LCMRL calculator version more statistically robust, easier to use
  - No increased burden on labs,
  - Takes into account precision & accuracy
  - Ready to be applied to more challenging matrices
- A simpler procedure for MRL verification is available for day-to-day lab operation
- Currently working on procedure for multi-lab MRL determination
- Work now in-progress to make revised calculator available on-line: www.epa.gov/safewater/methods/sourcalt

Acknowledgements

- This work has been funded in part by the United States Environmental Protection Agency under contract (contract no. 68-C-01-098) to Shaw Environmental, Inc and under contract (contract no. 68-C-02-026) to the Cadmus Group, Inc.

Extra Slides: Multi-Lab MRL Work in-Progress

- Composite model
  - Creates mixed function from mean & variance functions of individual LCMRLs
  - Mixed function run through LCMRL calculations to compute MRL
  - Tricky aspects
    - Assumes mean and variance functions are independent
    - Difficult to find algorithm that averages distribution of mean and variance functions

Extra Slides: Multi-Lab MRL Work in-Progress

- Random effects Model
  - Extension of variance model, how intercept & slope vary
  - Form mixture model from individual mean & variance functions of single-lab LCMRL determinations
  - Search routine used to synthesize an aggregate mean & variance function
  - Process through calculations similar to LCMRL
  - Theoretically best model
  - Weaknesses
    - Possibility of non-convergence to solution
    - Difficult to implement

Extra Slides: Multi-Lab MRL Work in-Progress

- Bootstrap Model: Creates additional data sets by randomly "resampling" values from existing data to repopulate levels for new dataset
- Bootstrapping example:
  - Given original data set of one concentration level: 6, 7, 8, 10
  - Random sampling from this set might be 7, 6, 10, 7
  - A value can be selected more than once
  - Resample to repopulate all levels; solve for LCMRL
  - For 4 replicates @ 7 levels,
    - Max number of resampled LCMRLs = 4! times 7 = 168
  - Rank 168 values from each of 5 labs in ascending order (total 848)
  - Upper limit cut-off with 95% confidence = 0.95 x 848 = 806
  - MRL is 806th highest bootstrap LCMRL

Extra Slides: Multi-Lab MRL Work in-Progress

- Bootstrapping
  - Does not assume normal distribution
  - Can use small sample sizes <20
  - Easiest to implement
  - Shown reliable use

Detection and Quantitation Procedures Pilot Study (2006 – 2007)

Study Design

Federal Advisory Committee for Detection and Quantitation Uses in Clean Water Act Programs

Timothy W. Fitzpatrick
Florida Dept. of Environmental Protection

Study Design Team

Representative	Caucus Group
Zonetta English	Public Utilities
Richard Rediske	Environmental
Richard Burrows	Laboratories
Larry LeFleur	Industry
Richard Reding	EPA
Bob Avery	States

Terminology

- **Procedure** – a set of written, step-by-step procedures for establishing a detection or quantitation (D/Q) limit;
- **Method** – written instructions describing the preparation and analysis of a sample for the measurement of an analyte or analytes;

More Terminology

- **Censored Method** – methods that produce no quantitative response below a certain signal threshold
- **Uncensored Method** – methods that produce a quantitative response for every measurement regardless of analyte concentration

Procedures Terminology

- **Single Lab** – a procedure that establishes D/Q limits using data from a single lab and that are applicable only to that lab;
- **Multi-Lab** – a procedure that pools single lab D/Q *limits* to establish 'consensus' D/Q limits across labs;
- **Inter-Lab** – a procedure that pools single lab *measurements* to establish 'consensus' D/Q limits across labs;

D/Q Limits Terminology

- Lc – Critical Level or Detection Limit (DL)
  The minimum result that can reliably be discriminated from a blank (e.g., with a 99% confidence level);
- Ld – Detection Limit
  The lowest concentration that will almost always be detected (controls false positives and false negatives);
- Lq – Quantitation Limit **(proposed definition)**
  The smallest concentration greater than the DL demonstrated by the laboratory to meet the required precision, accuracy, FN error rate and qualitative ID criteria for the intended purpose;
- Yc – 'Signal Level'
  A decision level similar to Lc (in the measurement domain); Used in the Hubaux-Vos and ASTM IDE procedures;

How Were Procedures Evaluated?

- Against Defined Measurement Quality Objectives;
- Against 15 Desired Characteristics of a Procedure Defined by the FACDQ;

It was not the intent to compare the D/Q limits derived by each procedure to one another;

Four Pilot Study MQOs

1. </= 1% False Positive Rate at DL;
2. </= 1% False Negative Rate at the QL relative to the DL;
3. Precision at QL of +/- 20% RSD;
4. Accuracy at QL of 50% - 150%

Detection Procedures Tested

Procedure	Type
EPA OGWDW Hubaux-Vos Yc	Single and Multi-Lab* (Regression)
ACIL MDL	Single Lab (Non-regression)
ASTM IDE	Inter-Lab* (Regression)

* Tested as a single and inter-lab procedure;

Quantitation Procedures Tested

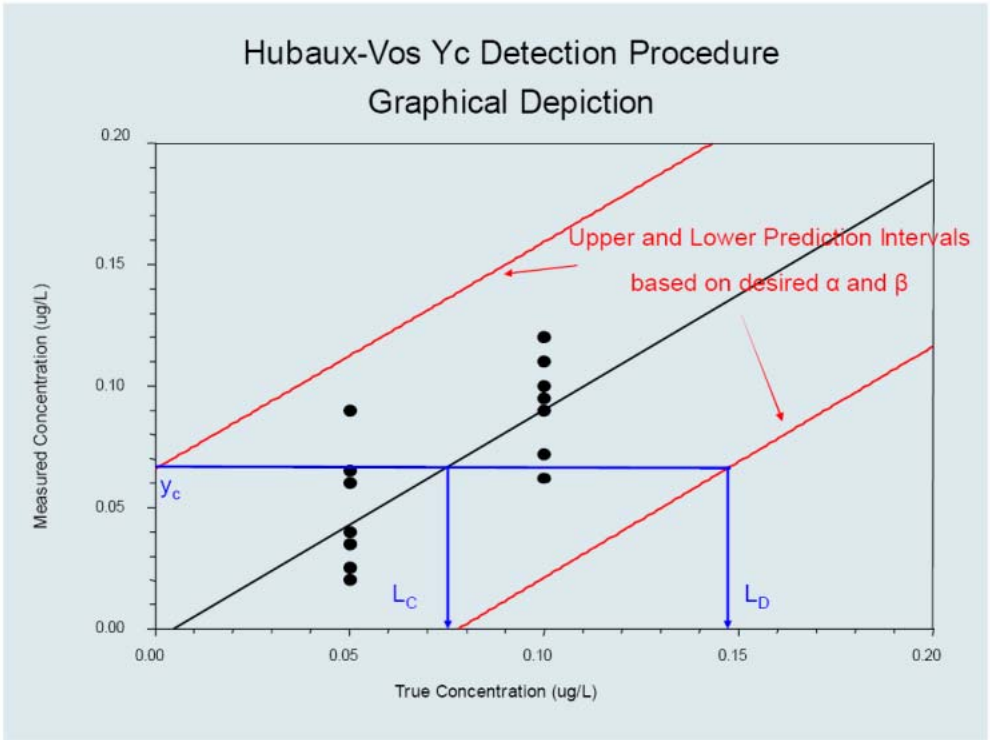
Procedure	Type
EPA OGWDW LCMRL	Single Lab or Multi-Lab* (Regression)
ACIL ML	Single Lab (Non-regression)
ASTM IQE	Inter-Lab* (Regression)

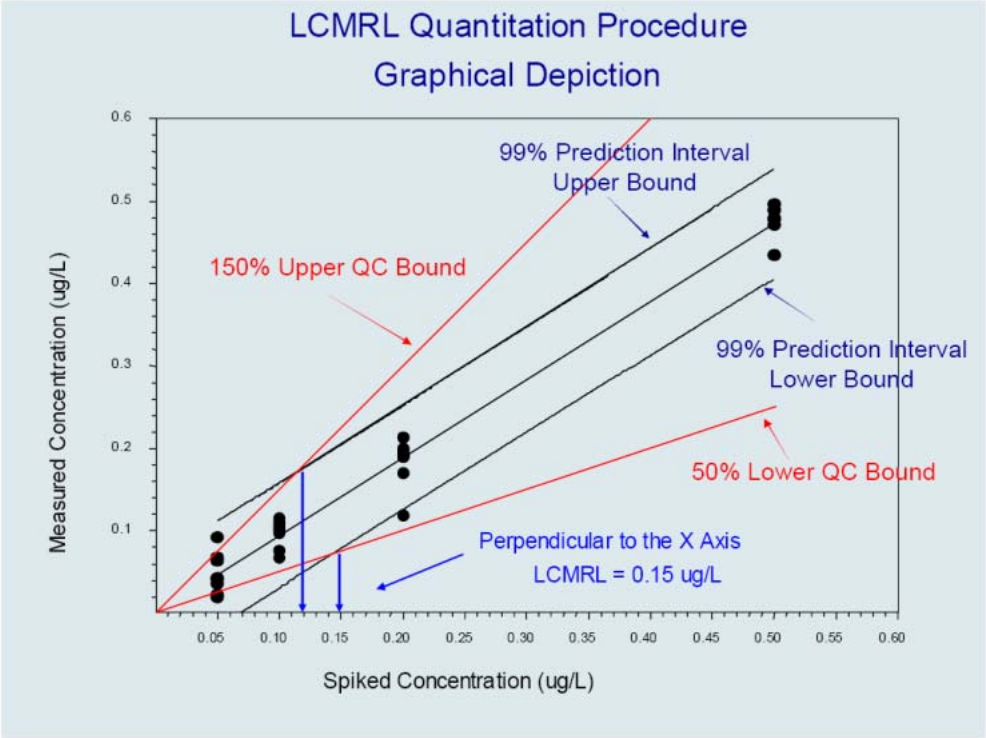
* Tested as a single and inter-lab procedure;

ACIL Detection and Quantitation Procedure Operational Overview

Methods divided between uncensored and censored;

- **Uncensored**
  - Lab estimates Lc as mean plus K times standard deviation of blanks
  - Lab chooses Lq spiking level. This must be at least 2xLc
  - Spikes at Lq must meet quantitation MQOs: 50-150% average recovery and 20% RSD for the pilot study
  - Ongoing spikes at least once per quarter
  - Reassess at least once per year
- **Censored**
  - Lab chooses Lq spiking level
  - Spikes at Lq must meet MQOs: 50-150% average recovery and 20% RSD for the pilot study
  - Lc calculated as K times standard deviation of the spikes
  - Lq must be at least 2xLc and qualitative ID criteria must be met
  - Ongoing spikes at least once per quarter
  - Reassess at least once per year





ASTM IDE/IQE
Operational Overview

- A minimum of one sample at each of a minimum of five concentrations are analyzed by a minimum of six laboratories;
- The concentrations must range from less the L_C to the linear range of the method at specified intervals;
- Optionally outlying laboratories and/or data points may be removed per ASTM D2777;
- The response curve is statistically evaluated and the appropriate standard deviation vs. concentration model is selected;
- The L_C, L_D, and IQEs are calculated based on the model selected;
- "The IDE is computed to be the lowest concentration at which there is 90 % confidence that a single measurement from a laboratory…will have a true detection probability of at least 95 % and a true nondetection probability of at least 99 % (when measuring a blank sample)."
- IQE – Lowest conc. with estimated Z% RSD (20%, 30% tested);

Methods Included in the Pilot Study Test

Method	Analytes Targeted
200.7 (ICPAES)	24 Elements (including P)
300.0 (IC)	7 Anions
335.4	Total Cyanide
608 (GC)	18 Chlorinated Cmpds + 2 Aroclors
625 (GC/MS)	52 Compounds

Method	Class Analyte	Number of Labs*	Number of Analytes Evaluated
EPA 200.7	Trace elements via ICPAES	8	11
EPA 300.0	Determination of Anions by Ion Chromatography (Method A)	7	7
EPA 335.4	Total Cyanide Distillation with Semi-Automated Spectrophotometry	7	1
EPA 608	Organochlorine Pesticides and PCBs by GC/ECD	6	18
EPA 625	Extractable Semivolatiles Capillary Column GC/MS	7	18

How was the study conducted?

- Labs were vetted following their response to a solicitation (8 labs per method targeted);
- Lab-specific information collected
  - Workload/Experience with the analysis;
  - Instrumentation;
  - Calibration levels;
  - Estimated spiking levels for ACIL and LCMRL procedures;
  - Historical blank data (30 batches or 6 months of data for FP rate assessment) to assess long term variability;

How was the study conducted?

- Labs Prepare/Analyze Samples for ACIL MDL/ML Determination;
- Labs Analyze 'Blind' Samples
  - 120 blind samples analyzed over a period of 3 weeks to assess 'long-term' variability;
  - Concentrations cover the expected range of LCMRL spike levels cited by labs (10 replicates of 12 concentrations incl'd blank)
- Aroclor Confirmation Samples Analyzed;

How was the study conducted?

- Labs determine their own short-term ACIL D/Q estimates and LCMRL quantitation estimate; (Hubaux-Vos software wasn't available yet);
- Electronic Data Submitted for other D/Q estimates to be determined by contractor (H-V, ASTM IDE/IQE);

Post Pilot Study Evaluation Other Procedures and Data Considered

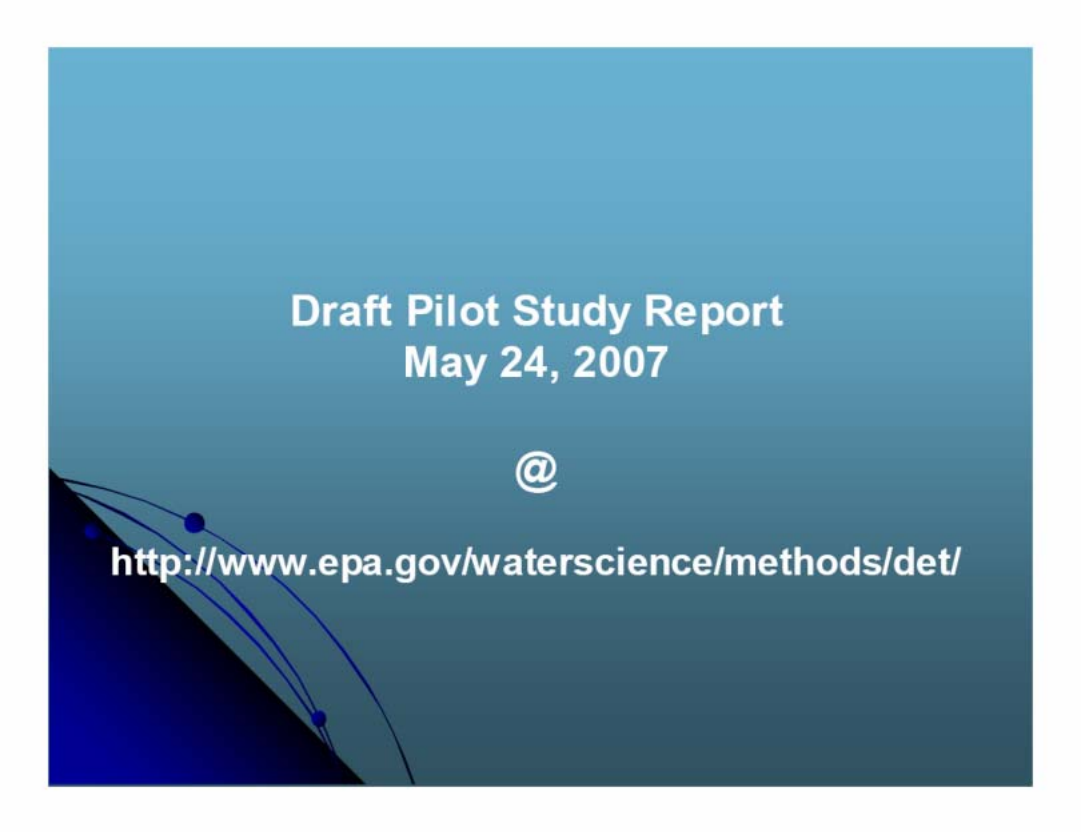
- **Procedures Evaluated (Not Pilot Tested)**

  Consensus Group Procedures for Evaluating the Critical Level and Quantitation Limit

  East Bay Municipal Utility District Lab QC Procedure

- **Other Data Sets Evaluated**

  Michigan Manufacturers Association (MMA) PCB Data used to Evaluate Regression based Procedures


Draft Pilot Study Report
May 24, 2007
@
http://www.epa.gov/waterscience/methods/det/

Detection and Quantitation Procedures Pilot Study (2006 – 2007) Lessons Learned

Federal Advisory Committee for Detection and Quantitation Uses in Clean Water Act Programs

Timothy W. Fitzpatrick
Florida Dept. of Environmental Protection

Recap - Detection Procedures Tested

Procedure	Type
EPA OGWDW Hubaux-Vos Yc	Single and Multi-Lab* (Regression)
ACIL MDL	Single Lab (Non-regression)
ASTM IDE	Inter-Lab* (Regression)

* Tested as a single and inter-lab procedure;

Recap - Quantitation Procedures Tested

Procedure	Type
EPA OGWDW LCMRL	Single Lab or Multi-Lab* (Regression)
ACIL ML	Single Lab (Non-regression)
ASTM IQE	Inter-Lab* (Regression)

* Tested as a single and inter-lab procedure;

Method	Class Analyte	Number of Labs*	Number of Analytes Evaluated
EPA 200.7	Trace elements via ICPAES	8	11
EPA 300.0	Determination of Anions by Ion Chromatography (Method A)	7	7
EPA 335.4	Total Cyanide Distillation with Semi-Automated Spectrophotometry	7	1
EPA 608	Organochlorine Pesticides and PCBs by GC/ECD	6	18
EPA 625	Extractable Semivolatiles Capillary Column GC/MS	7	18

Recap - Pilot Study DQIs/MQOs

1. </= 1% False Positive Rate at DL;
2. </= 1% False Negative Rate at the QL relative to the DL;
3. Precision at QL of +/- 20% RSD;
4. Accuracy at QL of 50% - 150%;

Ongoing discussion regarding what confidence limits were intended for MQOs;

Evaluation against 15 criteria identified by the FACDQ as desirable characteristics

'What we need a procedure to do'

- Address bias, precision, FP, FN;
- Address qualitative identification;
- Represent routine lab variability;
- On-going verification steps;
- Address non-zero blank response;
- Address intermittent contamination;
- Be cost effective and clearly written;
- Applicable to all users and test methods;

Information Overload…

- 3 DL & 3 QL Tested Procedures + 2 Additional Procedures Evaluated (not pilot tested);
- Single-Lab and Inter-Lab Evaluation;
- 5 Analytical Methods;
- > 100 Analytes (55 analytes evaluated plus the MMA PCB dataset and PCB verification data);
- 6 – 8 Labs per Method;
- 120 Blind Spikes per Analyte at 12 Concentrations;
- Historical Blank Results (30 Batches or 6 Months);
- 4 DQIs;
- Data Evaluation w/ & w/o Outlier Removal;
- Laboratory Comments and Test Information;

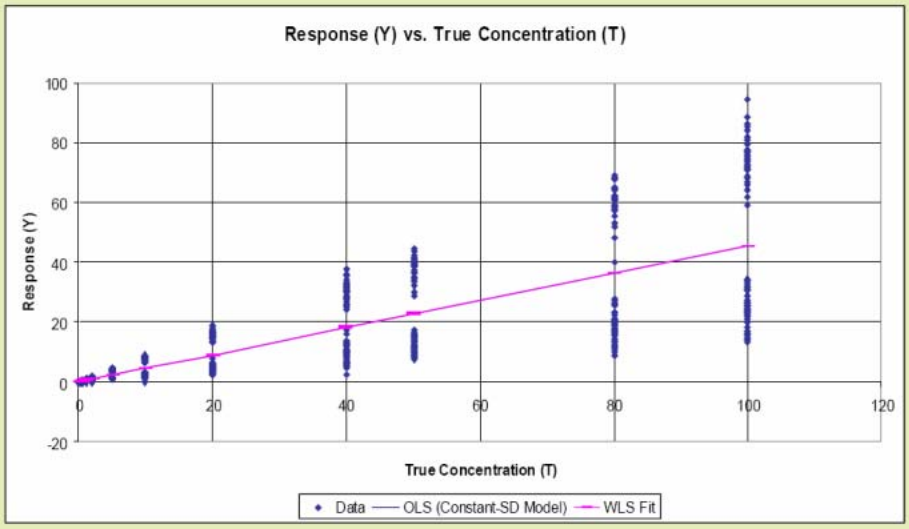
General Observations

- Labs generally did not generally express difficulty following the single-lab procedures (although not all labs interpreted or implemented the procedures in the same manner);
- Computer analysis was needed for regression procedures; Some difficulties expressed;
- Most of the MQOs were met most of the time;
  - The likelihood of meeting the target MQOs depended on what the procedure targeted; Where a procedure targets a less stringent MQO than tested by the study, that study criterion would not be expected to be achieved most of the time; (e.g., IQE doesn't target accuracy and targets a 5% FN rate);

General Observations – MQOs

- Large differences in achieving MQOs were observed between labs;
  - As might be expected, differences in MQO success were observed among analytes for a given method;
  - Some MQO differences among labs could be attributed to how the method was applied (e.g., phenols recovered better with CLL vs. separatory funnel extraction);

Phenol by Method 625



General Observations – MQOs

- Regardless of procedure, the concentration at which MQOs for precision and recovery were met varied with method, analyte and lab;
  - For Method 300.0, the RSD target was achieved at a lower concentration than the recovery; For 608 and 625, the trend was reversed;
- Data censoring and non-normally distributed data may have affected the MQO success in some cases;
  - Partially censored data sets can result in biased D/Q limits by obscuring the 'true' distribution; Non-normally distributed data was often observed at the low concentration region for regression procedures;

Normality Test for 200.7 Pilot Study Spikes

(P – Pass; F – Fail)

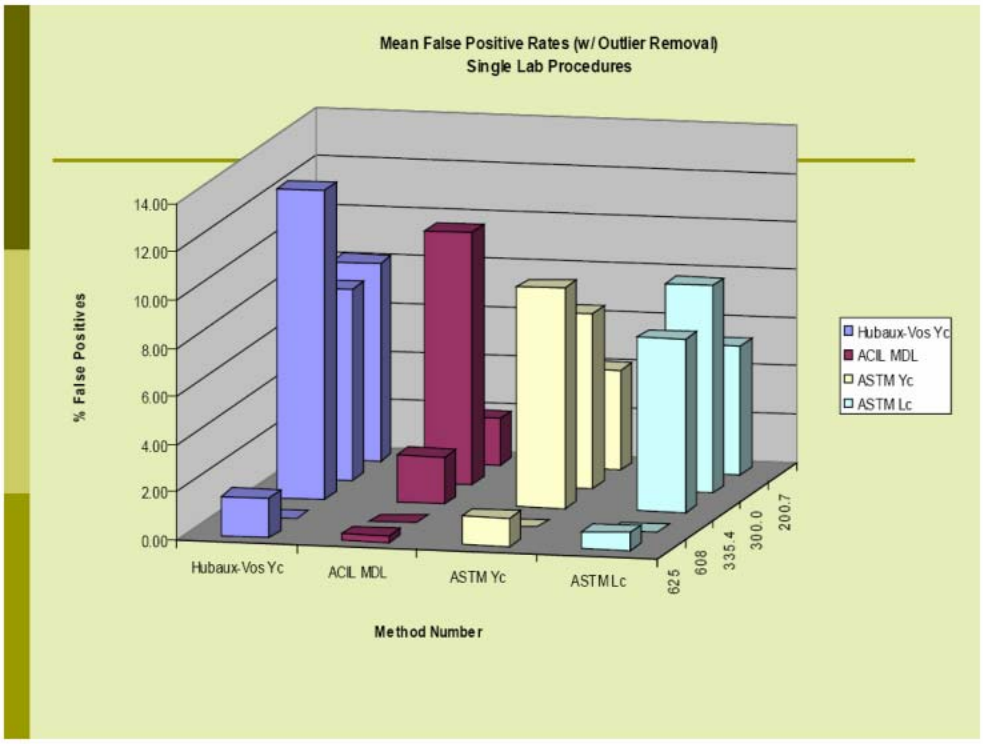
	Spike Level (1 – lowest; 12 – highest)											
	1	2	3	4	5	6	7	8	9	10	11	12
Al	F	F	F	F	F	F	P	P	F	F	F	P
As	F	F	F	F	F	F	F	F	F	P	F	P
Be	F	F	F	F	F	F	P	F	P	P	P	P
Cd	F	F	F	F	P	P	F	F	P	F	F	F
Ca	F	F	F	F	F	F	F	F	P	P	P	P
Cu	F	F	F	F	P	P	F	F	F	F	F	P
Pb	F	F	F	F	F	F	F	F	P	F	F	P
Mn	F	F	F	F	F	F	F	F	F	F	P	P
K	F	F	F	F	F	F	F	F	F	F	F	F
Ag	F	F	F	F	F	F	F	F	F	F	F	F
Zn	F	F	F	F	F	F	F	F	P	F	P	P

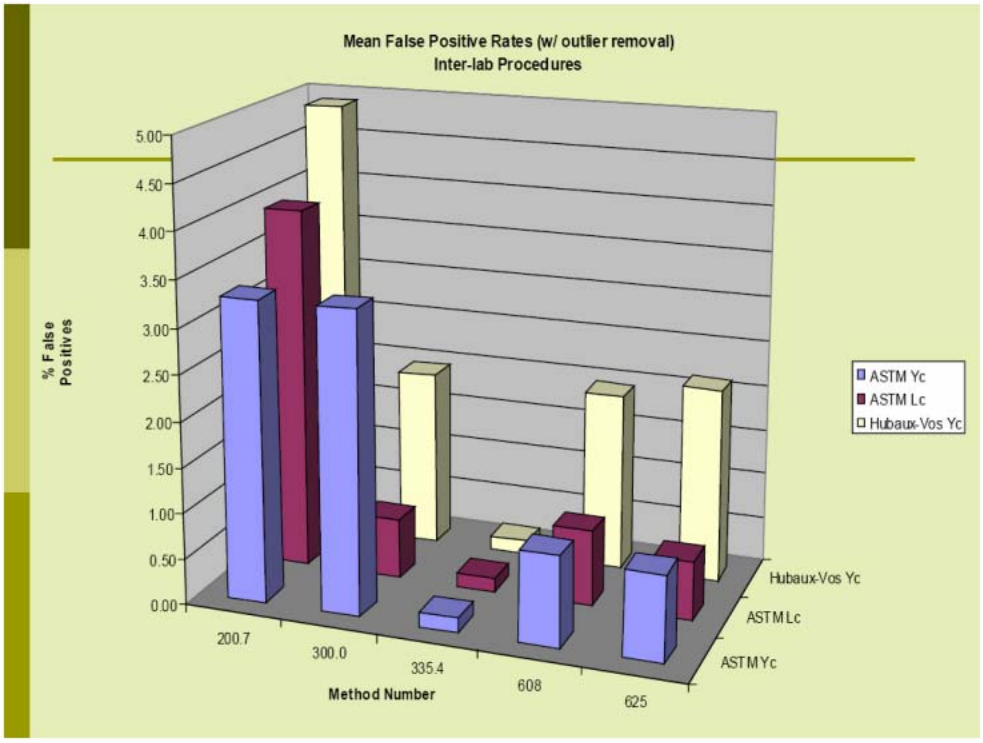
General Observations – False Positive Rates

- Procedures based on extrapolation from spiked samples were more prone to unexpected false positive rates;
  - For censored methods, the relationship between recovery and concentration may not be linear in the region around D/Q as assumed by regression procedures
  - The level of apparent background contamination varied widely among labs;
  - The method blank data and study data were not from the same time period;

General Observations – False Positive Rates

- The ACIL procedure for uncensored methods performed very well;
  - The ACIL procedure was developed to target a specific false positive rate from long-term method blank data;
  - The data used to determine the ACIL detection limit incorporated much of the variability observed in the longer term record used to measure FP rates;
- Intermittent blank contamination was most often responsible for FP rate failures;


Mean False Positive Rates (w/ Outlier Removal)
Single Lab Procedures
% False Positives
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
Hubaux-Vos Yc
ACIL MDL
ASTM Yc
ASTM Lc
625
608
335.4
300.0
200.7
Method Number
Hubaux-Vos Yc
ACIL MDL
ASTM Yc
ASTM Lc


Mean False Positive Rates (w/ outlier removal)
Inter-lab Procedures
% False Positives
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
200.7
300.0
335.4
608
625
Method Number
Hubaux-Vos Yc
ASTM Lc
ASTM Yc
ASTM Yc
ASTM Lc
Hubaux-Vos Yc

General Observations - False Negative Rates

- The false negative (FN) rate was the most difficult to achieve and failed most often;
  - the FN rate depends on two limits: detection and quantitation; a bias in either limit will affect the FN rate;
  - For the ASTM procedure, FN rates depended on the detection criterion used (Lc vs. Yc);
  - The ACIL procedure performed very well (when implemented correctly); Some procedures had problems with this MQO;

General Observations - Accuracy

- Mean recovery failures were seldom outside the 50% - 150% criterion range;
  - Failures were observed on both the high and low side;
  - Low side failures were mainly for a few problematic analytes in Method 625 and 608;
  - High failures were primarily for Method 300.0 analytes;
  - Some analytes failed for accuracy throughout the study range;

General Observations - Precision

- For some methods and analytes, the MQO for precision failed throughout the concentration range;
  - This phenomenon was observed for several analytes in Methods 608 and 625;

General Observations – D/Q Limits

- Large differences were observed among calculated D/Q limits;
  - The differences were greater among labs than among procedures in individual labs;
  - Part of the observed differences might be attributable to labs targeting different limits in their studies (e.g., the ACIL procedure did not require labs to target the lowest limits achievable);

Procedure Performance

- ACIL MDL & ML
  - Met the study MQOs more frequently than other procedures (since it was designed to meet study MQOs);
  - Most failures to meet MQOs were due to improper implementation by the lab (indicating a need for clarification);
  - Met more of the FACDQ desired procedure criteria than the other procedures;
  - Recommended by FACDQ for modification into a robust, single-lab procedure;

Procedure Performance

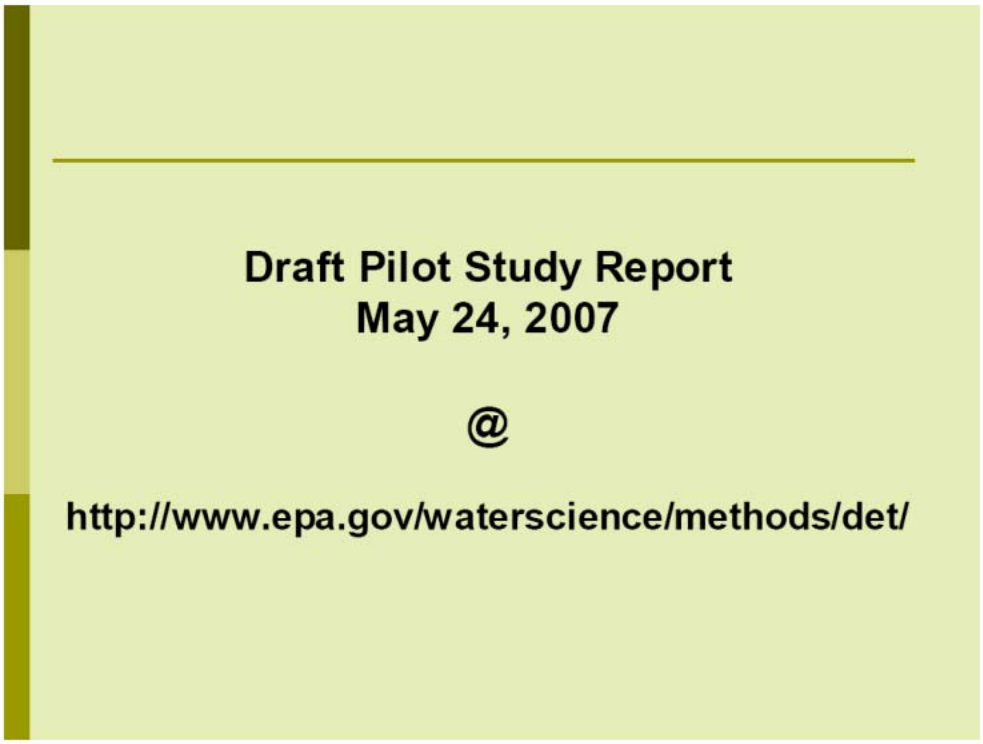
- Hubaux-Vos & LCMRL
  - Hubaux-Vos did not perform well overall as a detection procedure and was not recommended for pairing with the LCMRL quantitation procedure;
  - LCMRL would need to be paired with another detection procedure (such as ACIL) to evaluate FP/FN rates;
  - LCMRL did not establish quantitation limits for a number of 625/608 analytes (primarily due to recovery limits not being attained);
  - A weakness in the study design was that the MRL portion of the LCMRL procedure was not tested;

Procedure Performance

- IDE/IQE
  - Large differences among laboratories were observed with these procedures, probably because of differing lab capabilities to control interferences and contamination;
  - Failed to meet study MQOs more frequently than other procedures (due to procedure MQOs differing from study MQOs);
  - Good at assessing MQOs across the range of concentrations;
  - Considered useful for method evaluation studies across laboratories;

Procedure Performance

- Consensus Group Procedure
  - Not pilot tested;
  - More complex version of the ACIL procedure;
  - Concepts from this procedure should be used to improve the ACIL procedure;
- East Bay Municipal Utility District Procedure (a.k.a. Lab QC)
  - Not pilot tested;
  - Concepts similar to ACIL procedure;
  - Concepts from this procedure should be used to improve the ACIL procedure;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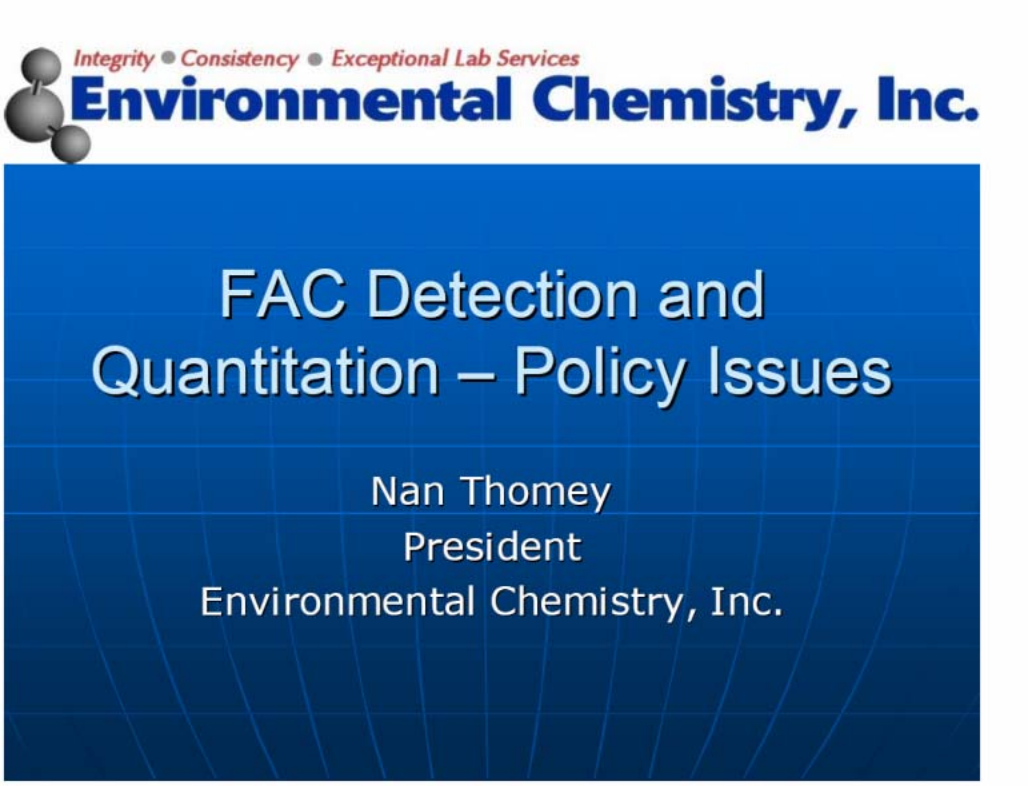
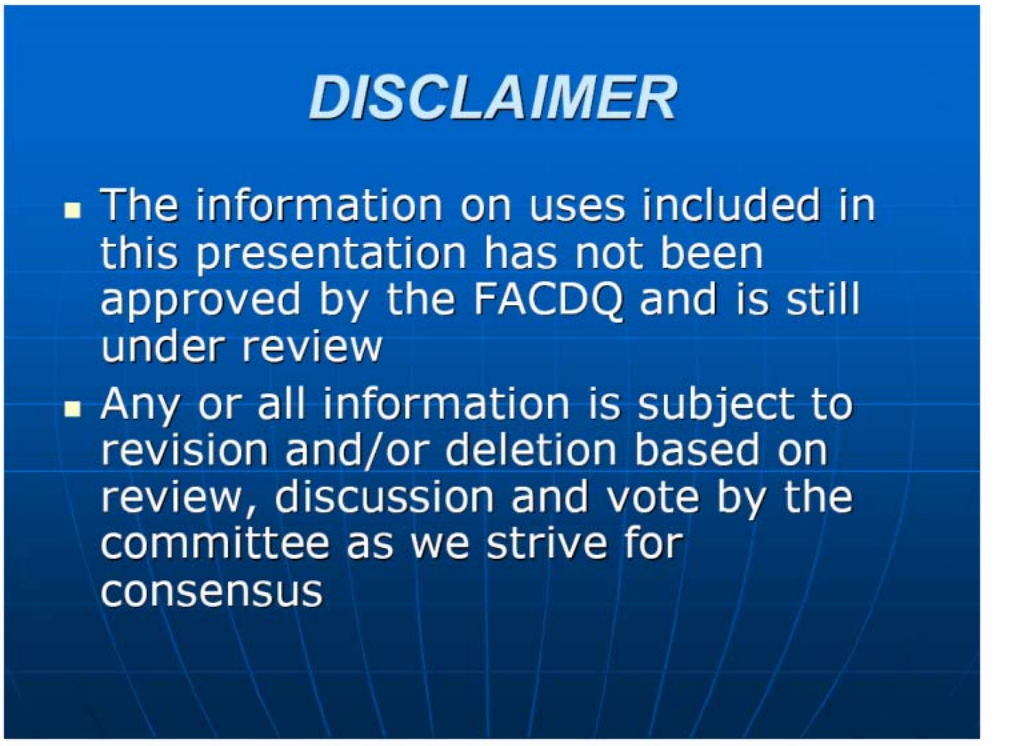

Integrity • Consistency • Exceptional Lab Services
Environmental Chemistry, Inc.
FAC Detection and Quantitation – Policy Issues
Nan Thomey
President
Environmental Chemistry, Inc.


DISCLAIMER
The information on uses included in this presentation has not been approved by the FACDQ and is still under review
Any or all information is subject to revision and/or deletion based on review, discussion and vote by the committee as we strive for consensus

Lab-Determined Detection Limits and Quantitation Limits

- Promulgate the descriptive single-lab procedure recommended by the FACDQ for individual labs to determine their actual detection and quantitation limits
- Use instead of 40 CFR Part 136 Appendix B in CWA program

Lab-Determined Detection Limits and Quantitation Limits

The modified ACIL procedure has the following two capabilities:

- Demonstrates the lab's performance at a specified level
- Determines the lowest possible value achievable by the lab while meeting the measurement quality objectives (MQOs)

National Quantitation Limits

- Foundation of Uses "Package" for setting permit limits and evaluating compliance
- Shall be the upper bound for lab performance
- Originally envisioned to be by method and analyte
- Alternative view is to have single NQL for each analyte, regardless of method

National Quantitation Limits

- Should not be disincentive for new technology
- Should not stifle or further delay development/promulgation of new methods
- Level playing field for permittees

New Method Promulgation

- Use a multi-lab or inter-lab procedure for determining National QLs
- When EPA promulgate future analytical methods in 40 CFR Part 136, should National QLs be created and included with the methods?
- A National QL would be created for each method/analyte combination

Verification of Laboratory Proficiency of Detection and Quantitation Limits

- Develop process for separate initial and on-going verification of DLs and QLs by labs
- Strive for feasibility, practicality, representativeness and cost-effectiveness.
- The process should verify that the method meets the chosen MQOs
- The Lab QL must be $\leq$ the National QL if a National QL exists.

Future Updates of Promulgated Analytical Method DLs/QLs

Periodically review current capabilities of methods and update on priorities :

- Methods with significant improvements in DLs or QLs
- Methods with no National QLs
- Cases where QLs are critical to the permit program (e.g., those required for very low WQBELs)

Future Updates Priorities

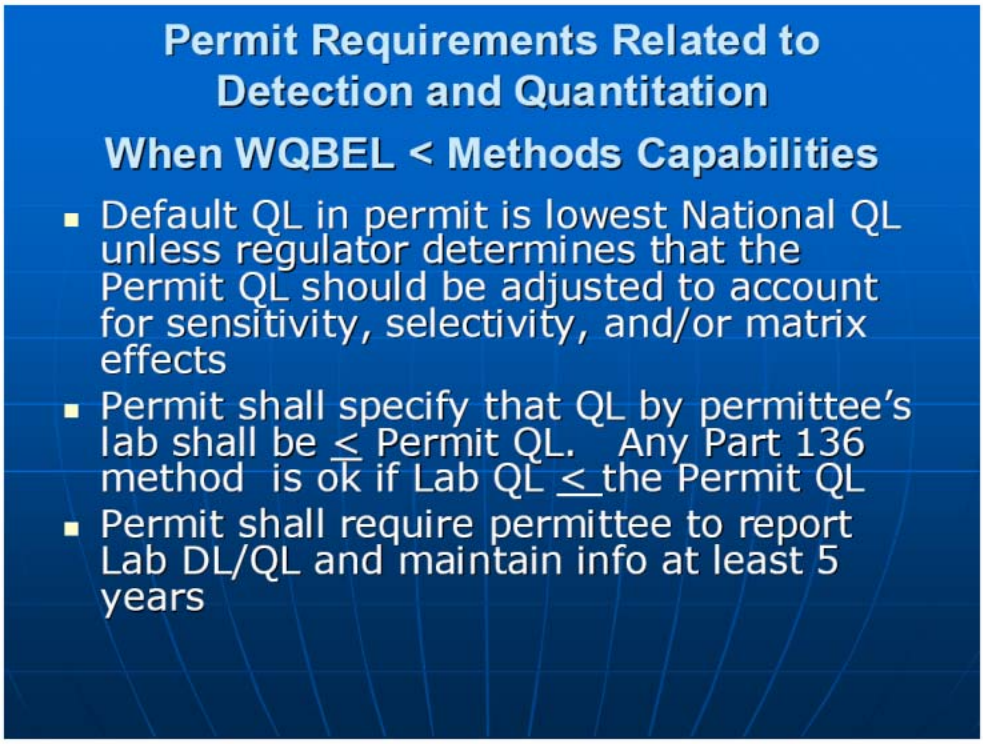
- Analytes for which current methods provide poor performance or otherwise do not meet program needs
- Cost and resource considerations
- Information submitted by states and/or other qualified third parties

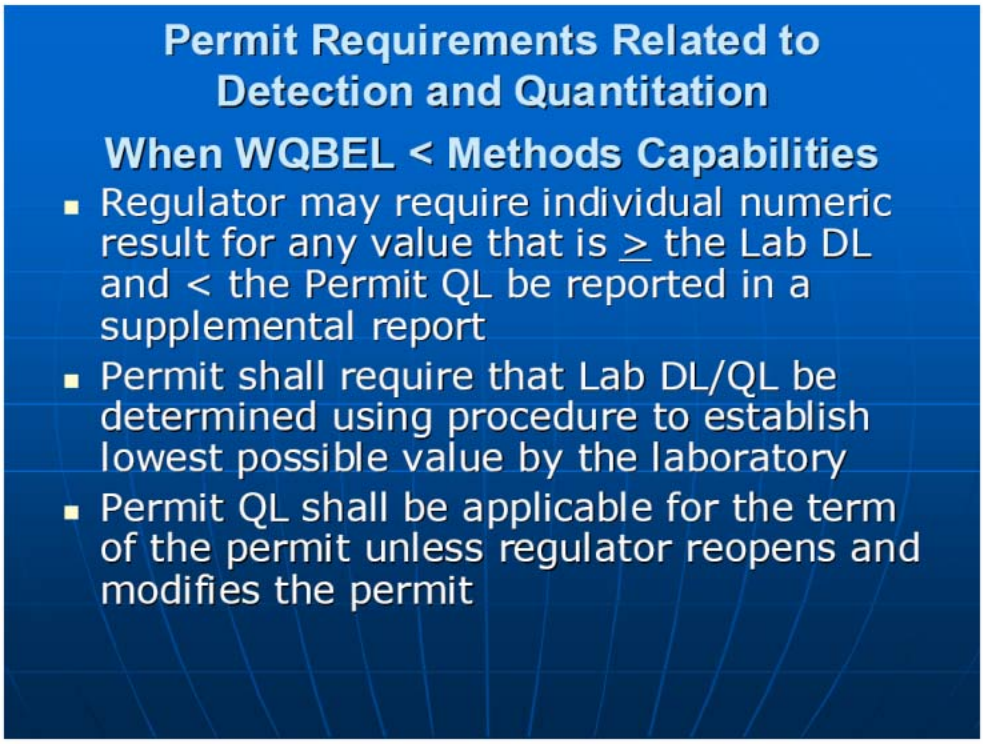
Policy Issues

- Calculating monthly averages
- Determining compliance with daily maximum limits and monthly average limits
- Reporting data
- Appropriate compliance response in light of data uncertainty and the need for the protection of public health and the environment

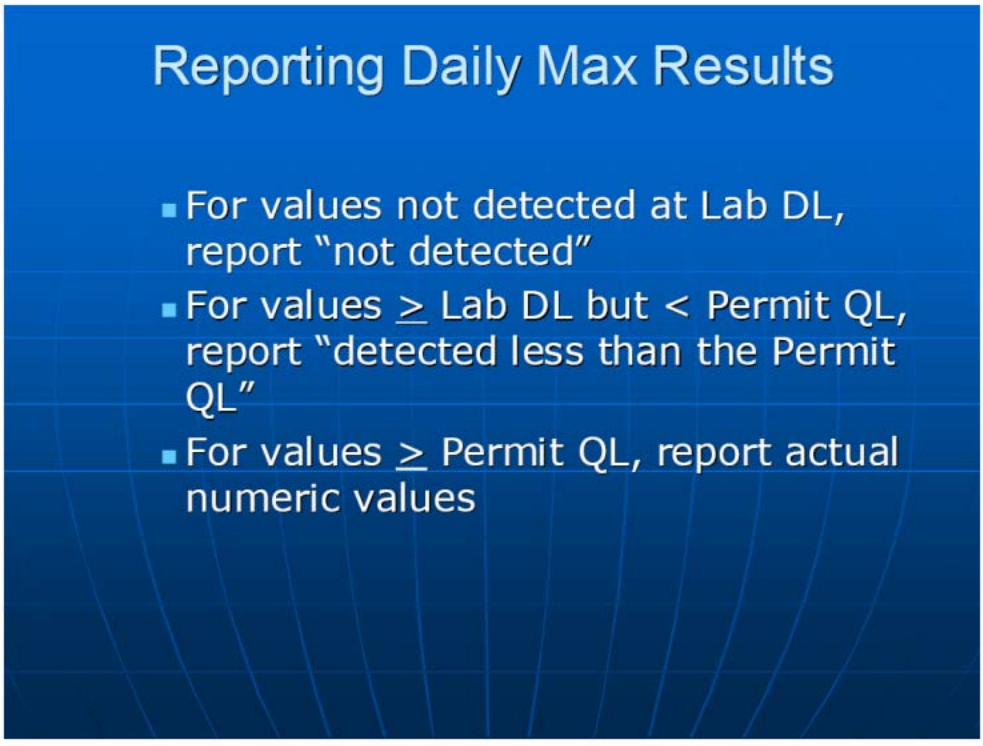
NPDES Permits and Compliance Uses for WQBELs Below QL

- WQBELS at concentrations < method QLs presents a number of NPDES-related issues
- Values between a given lab's DL and QL have higher level of uncertainty
- Assigning non-zero value where analyte is <QL would have significant compliance/enforcement implications


Permit Requirements Related to Detection and Quantitation
When WQBEL < Methods Capabilities
Default QL in permit is lowest National QL unless regulator determines that the Permit QL should be adjusted to account for sensitivity, selectivity, and/or matrix effects
Permit shall specify that QL by permittee's lab shall be ≤ Permit QL. Any Part 136 method is ok if Lab QL ≤ the Permit QL
Permit shall require permittee to report Lab DL/QL and maintain info at least 5 years


Permit Requirements Related to Detection and Quantitation
When WQBEL < Methods Capabilities
Regulator may require individual numeric result for any value that is ≥ the Lab DL and < the Permit QL be reported in a supplemental report
Permit shall require that Lab DL/QL be determined using procedure to establish lowest possible value by the laboratory
Permit QL shall be applicable for the term of the permit unless regulator reopens and modifies the permit


Establishing Compliance Thresholds and Determining Compliance
• Regulators will set average and daily max permit limits at WQBEL
• Permittees must report all information in the following manner on the DMR:


Reporting Daily Max Results
For values not detected at Lab DL, report "not detected"
For values ≥ Lab DL but < Permit QL, report "detected less than the Permit QL"
For values ≥ Permit QL, report actual numeric values

To Report Average Sample Results

- When all values used to calculate an average are not detected at Lab DL, report "not detected"
- When all values used to calculate an average are "detected < Permit QL," report "detected less than the Permit QL"
- When values used to calculate average are a combination of "not detected" and "detected < Permit QL", report "detected less than the Permit QL"
- When any value used to calculate an average is ≥ Permit QL, report the calculated numeric average after assigning zero to any individual value reported either as "not detected" or "detected < Permit QL"

Compliance Determination

- To determine NPDES permit compliance with results reported on the DMR, regulators will:
  - Determine that any daily maximum or monthly average results reported as either "not detected" or "detected less than the Permit Quantitation Limit" are in compliance with the effluent limitation
  - Compare any numeric results directly to the WQBEL

Other Reporting Requirements

- Permits shall include language that triggers steps when "significant number of" DNQs are reported
- May include additional monitoring, matrix studies, pollutant minimization programs, or other permit conditions
- Reports under such provisions will be done outside of the DMR reporting process

Permits and Compliance When No National QL Exists

(Or if the Permitting Authority Requires Use of a Method More Sensitive than the Method for Which a National QL exists)

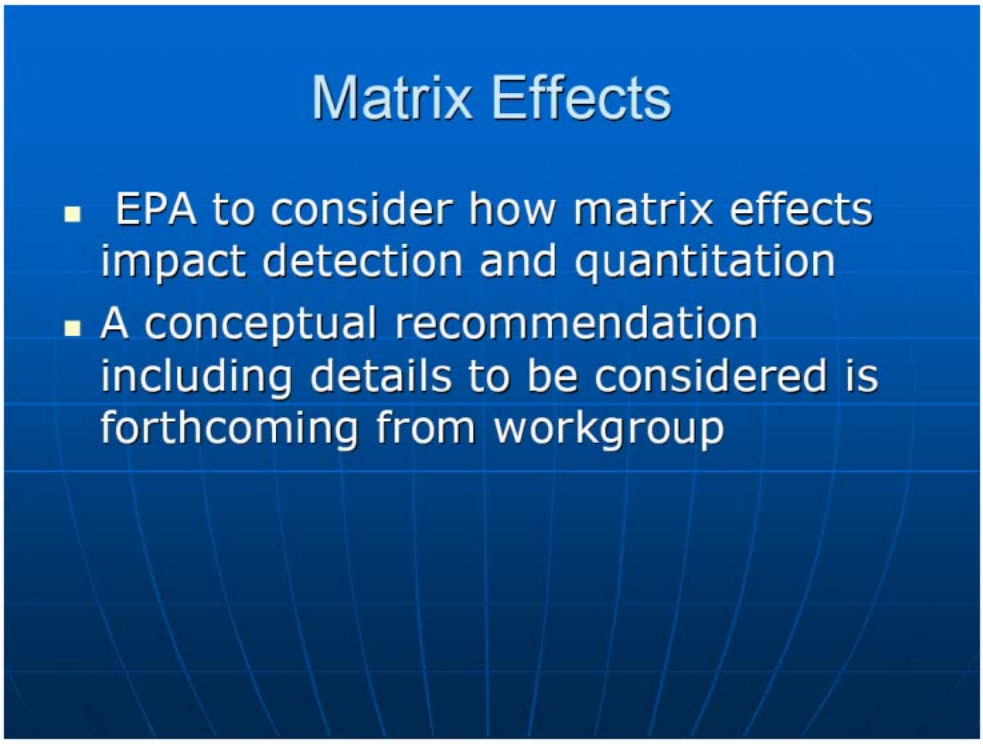
- Permitting authority is free to establish its method for determining compliance for analytes that have limits/water quality standards at a level lower than that which can be detected and/or quantified

Permits and Compliance When No National QL Exists

- For a list of analytes defined by EPA, permit shall require that Lab DL/QL be determined using steps of procedure to establish lowest possible value by the lab
- EPA will require Lab DL/QL and Permit QL be reported by the regulator to the Integrated Compliance Information System (ICIS) for purposes of updating 40 CFR Part 136 National QLs

Most Sensitive Method Issue

- Current EPA guidance for implementing permit limits for WQBELs that challenge current analytical capabilities stipulates that the permit should specifically reference the most sensitive method
- Modify this reference to "the most appropriate method, taking into account sensitivity, selectivity and matrix effects" (i.e., "best method")


Matrix Effects
EPA to consider how matrix effects impact detection and quantitation
A conceptual recommendation including details to be considered is forthcoming from workgroup


Method Quality Objectives
False positive
False negative
Precision
Accuracy

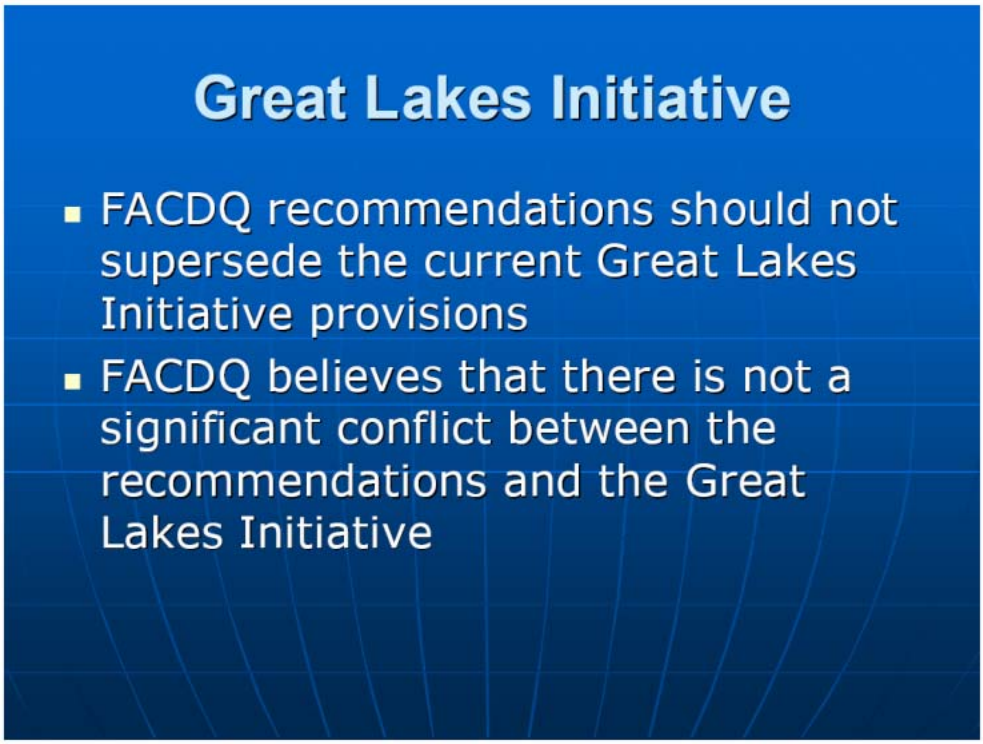
Other Uses

The FACDQ tabled the following list of additional uses:

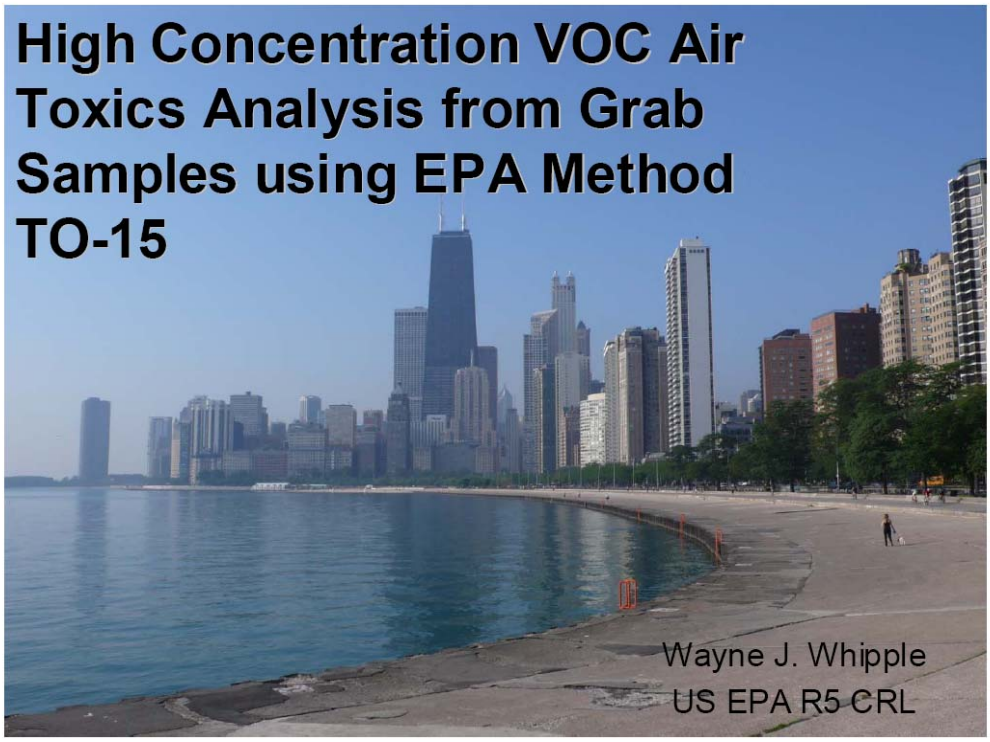
- ambient monitoring 305(b)
- pretreatment
- non-regulatory operational monitoring
- stormwater monitoring
- other studies, such as fish tissues or biosolids characterization
- reasonable potential analysis

Alternative Test Procedure

- The FACDQ tabled the option of developing recommendations to EPA on updating the Alternative Test Procedures (ATP) program


Great Lakes Initiative
FACDQ recommendations should not supersede the current Great Lakes Initiative provisions
FACDQ believes that there is not a significant conflict between the recommendations and the Great Lakes Initiative

AIR



Presentation Goals

- **Fundamentals of High Concentration Technique**
  - What is the technique
  - Why use it
  - Limitations
- **Practical Usage**
  - Equipment
  - Methodology
- **Results**
  - Demonstration of Capability
  - Amber Bottle Stability Study

Purpose

- *This technique allows* **highly concentrated samples** *to be analyzed using a routine* **ambient air analytical system** *without diluting the sample thereby* **minimizing extra work** *in the laboratory for canister cleaning and checking while* **maintaining the precision and accuracy** *of measurements.*

Fundamentals

- Use an Entech 7100 preconcentrator
- Sample in glass bottles with Micro-QT™ valve
- Use syringe to inject sample into sample transfer line, flush with blank gas
- Calibration is normal TO-15 calibration
- Extremely similar to a 400x dilution at 1 mL
- Extremely reproducible and accurate at 1 mL injection volume

Benefits and Drawbacks

- Technique does not require dilutions (+)
- Reproducible and Accurate (+)
- Manual Injection (-)
- Still a possibility of active sites in syringe (-)
- Limited Injection Volume (~)
  - > 1 mL

Sampling

- Sample in Stainless Steel Canister, Tedlar Bags or Bottles
- Use Micro-QT™ instead of Valco® valve with Swagelock® connector
- Bottles cheaper than canisters and reusable
- Surrogate can be added in laboratory before sampling

Sampling bottles and Micro-QT™

Sample procedure

- Evacuate clean bottles in laboratory
- Leak check bottles
  - Preferably over expected time period of leaving the lab to sampling
- Add surrogate
- Monitor sampling time for grab sample
- After sampling pressurize vessel 1.5X in the laboratory

Analysis

- Calibrate using 40 to 800 cc injection of 10 ppbv standard
- 1 mL of 1 ppmv standard (blank spike)
  - ± 30% recovery limits
  - Laboratory control sample, blank spike
  - Second Source and CCV
- Flush with 100 cc of nitrogen from canister
- Analytical blank of 100 cc flush
- Sample injections containing F-152 surrogate
- Final 1 mL blank spike

Analytical Instrumentation

- Entech 7100 preconcentrator
  - micro-scale purge and trap mode
- Agilent 6890/5973 GC/MS
  - full scan mode
- DB-VRX separation column
  - 60 m x 0.25 mm ID x 1,4 µm film thickness

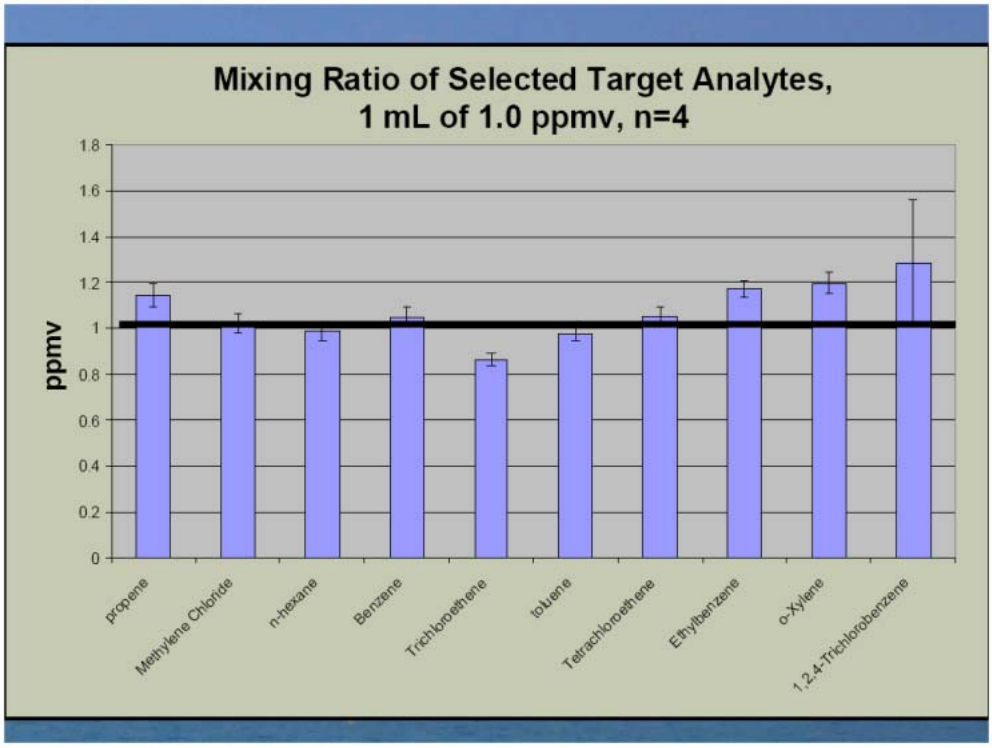
Quality Assurance

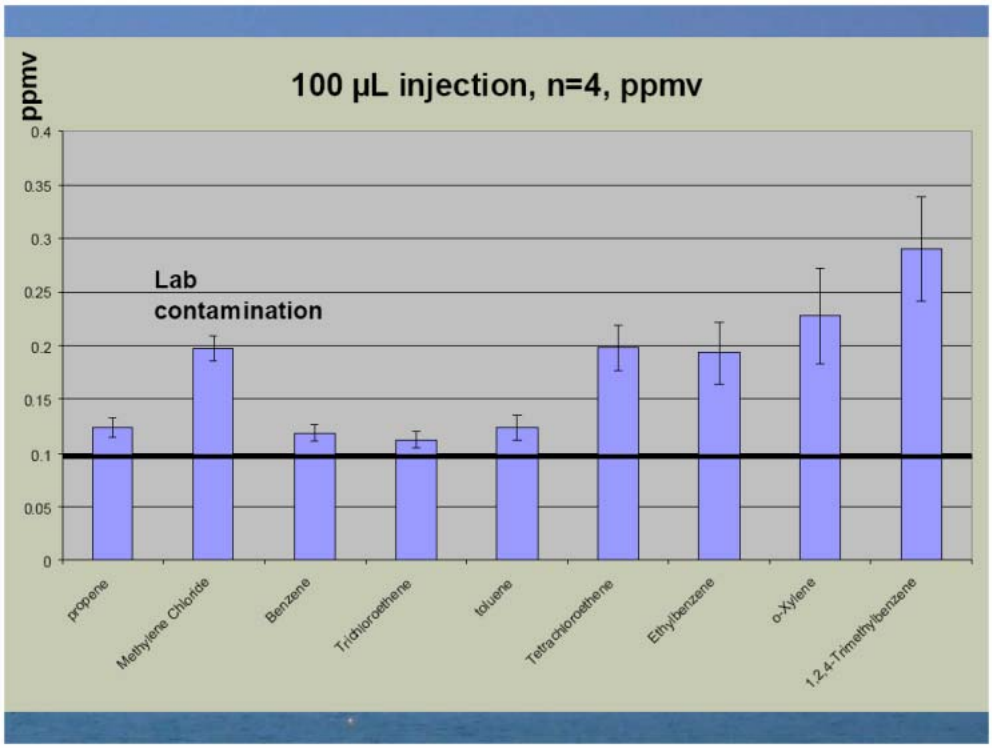
QA Type	Description	Limits
BFB	analytical blank or lab air for BFB check	BFB specifications in SOP
IC	40 to 800 cc of normal AT ~ 10 ppbv calibration standard	Calibration Specs in SOP
ICV/CCV† (-BS1)	1 mL of 1 ppmv standard from separate source or lot number than the initial calibration	± 30% of expected target analyte concentration, no limits set on surrogate
MB (-BLK1)	100 cc of make up gas used to flush sample and also used as a BFB check after 24 hour period	no compound greater than reporting limit
Samples	check surrogate concentration and linear range	surrogate concentration greater than 10% (tighter specifications will be provided)
BSD-1	1 cc of 1 ppmv standard run at end of batch or after 24 hour period	TO-15 recovery and precision

†If existing initial calibration is utilized from a prior run the 1 ppmv can be used as a CCV and passes expected concentration within ± 30%.:

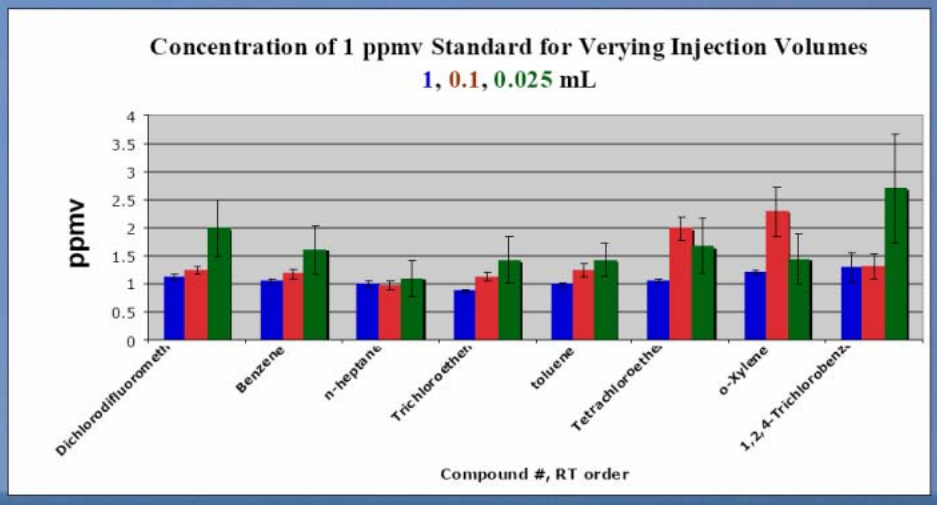
Compiled Injection Results

1 ppmv expected	25 µL n=8	100 µL n=4	1 mL n=4
average ppmv/ CV	1.95 ± 16%	1.64 ± 10%	1.11 ± 5%


Mixing Ratio of Selected Target Analytes,
1 mL of 1.0 ppmv, n=4
ppmv
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
propene
Methylene Chloride
n-hexane
Benzene
Trichloroethene
toluene
Tetrachloroethene
Ethylbenzene
o-Xylene
1,2,4-Trichlorobenzene


100 µL injection, n=4, ppmv
ppmv
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Lab
contamination
propene
Methylene Chloride
Benzene
Trichloroethene
toluene
Tetrachloroethene
Ethylbenzene
o-Xylene
1,2,4-Trimethylbenzene

Comparison of Injection Volumes for Selected Compounds



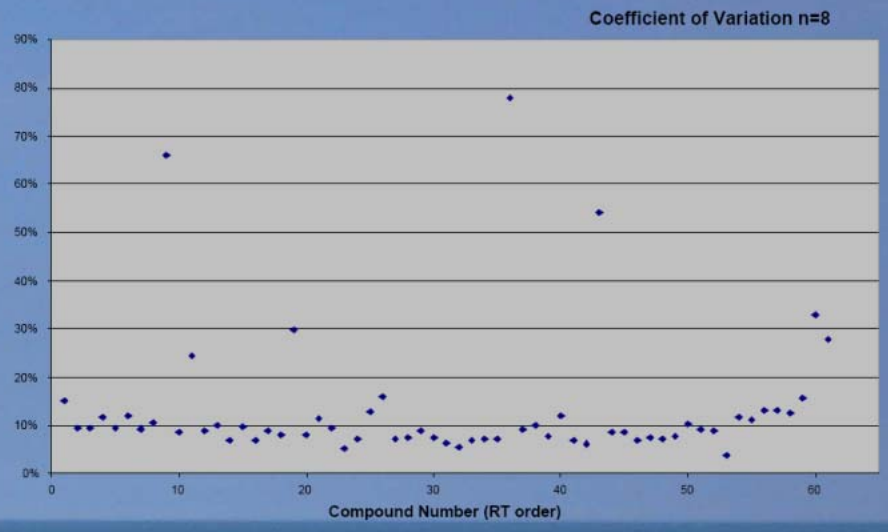
F-152 (1,1-difluoroethane) Surrogate

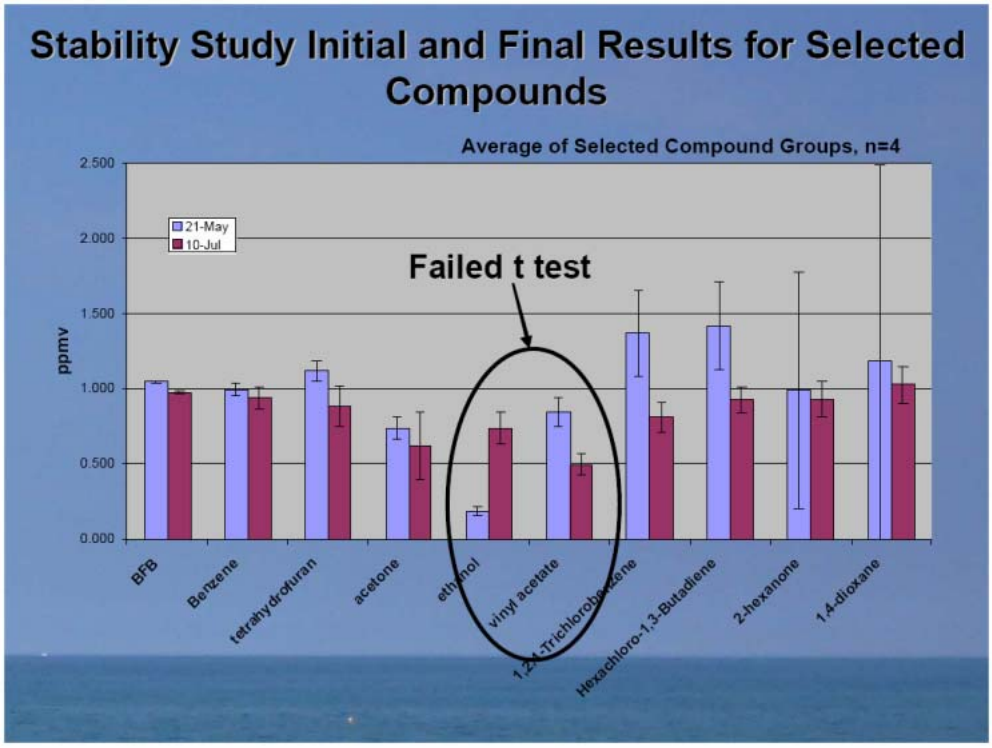
- 10 µL neat F-152 added to vacuumed bottle before going to field (20 ppmv in 0.5 L bottle)
- Single point calibration with ICV or CCV
- Semi-quantitative, although very reproducible, Tenax trap carryover
- Future attempt to lower F-152 concentrations, 1:5 dilution

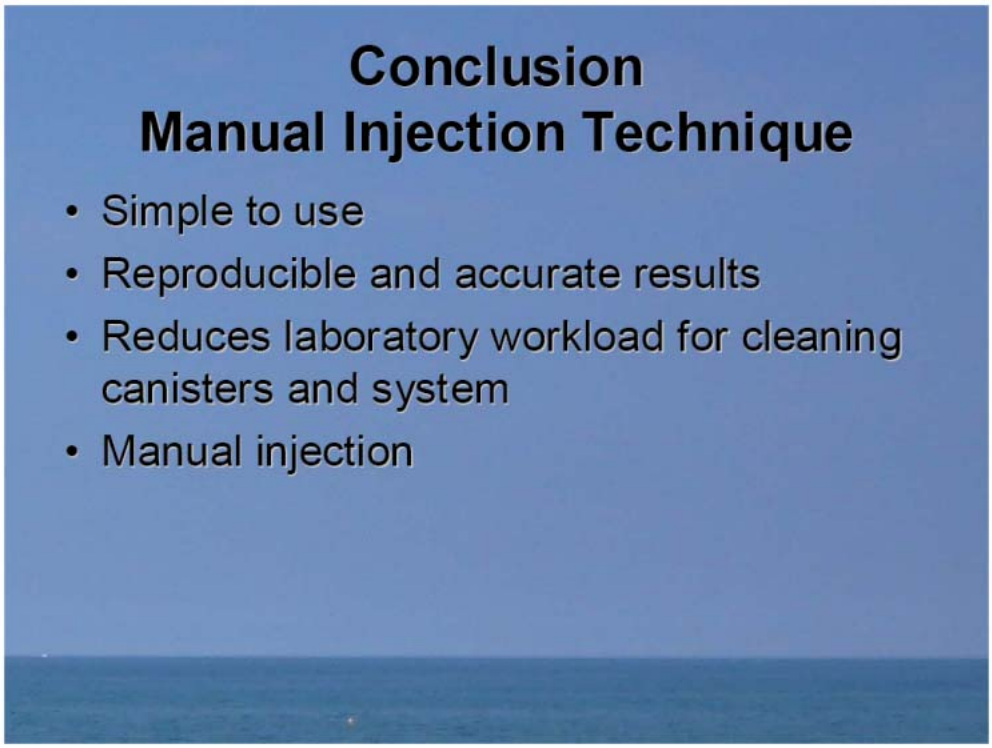
VOC Stability Check in Bottles

- Four 1 mL injections of 1 ppmv standard into bottles
- Bottles analyzed one day after injection
- Same samples analyzed after 8 weeks
- Single point calibration, 62 compound 1 ppmv air toxics standard

Compound vs. coefficient of variation (CV) for initial and final measurements




Stability Study Initial and Final Results for Selected Compounds
Average of Selected Compound Groups, n=4
21-May
10-Jul
Failed t test
ppmv
2.500
2.000
1.500
1.000
0.500
0.000
BFB
Benzene
tetrahydrofuran
acetone
ethanol
vinyl acetate
1,2,4-Trichlorobenzene
Hexachloro-1,3-Butadiene
2-hexanone
1,4-dioxane


Conclusion
Manual Injection Technique
• Simple to use
• Reproducible and accurate results
• Reduces laboratory workload for cleaning canisters and system
• Manual injection

Conclusion
Sampling procedure

- Glass bottles are less expensive, reusable and inert for most compounds
- Glass bottles have longer storage time then Tedlar bags
- Easy to transport and use
- Surrogate can be used for samping

Conclusion
Bottle Stability Study

- Initial results suggest most compounds are stable in bottles for over eight weeks.
- Ethanol and vinyl acetate have measurable degradation in study
- More work should be done
  - Whole air spikes or humidified zero air
  - Fresh standard should be made with each measurement


Appreciation
• Region 5 Chicago Regional Laboratory Staff
• NEMC staff and attendees, Thank You

Accreditation of Air Emission Testing Bodies with ASTM D7036

QuickTime™ and a decompressor are needed to see this picture.

Presented by Scott Evans
Director
Stack Testing
Accreditation Council

NEMC 2007 Cambridge, MA

What's Happening?

App. A § 6.1.2(a)	(a) Any Air Emission Testing Body (AETB) conducting relative accuracy test audits of CEMS and sorbant trap monitoring systems under this part must conform to the requirements of ASTM D7036-04. This section is not applicable to daily operation, daily calibration error checks, daily flow interference checks, quarterly linearity checks or routine maintenance of CEMS.
App. A § 6.1.2(b)	(b) The AETB shall provide to the affected source(s) certification that the AETB operates in conformance with, and that data submitted to the Agency has been collected in accordance with, the requirements of ASTM D7036-04. This certification may be provided in the form of: (1) A certificate of accreditation of relevant scope issued by a recognized, national accreditation body; or (2) A letter of certification signed by a member of the senior management staff of the AETB.
App. A § 6.1.2(c)	(c) The AETB shall either provide a Qualified Individual on-site to conduct or shall oversee all relative accuracy testing carried out by the AETB as required in ASTM D7036-04. The Qualified Individual shall provide the affected source(s) with copies of the qualification credentials relevant to the scope of the testing conducted.

CLEAN AIR MARKET PROGRAMS

Who is STAC?

GOLDEN SPECIALTY CONSULTING, LTD.

Hoefler CONSULTING GROUP | AMTEST AIR QUALITY

ONE TEAM. ONE COMMITMENT.

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CONSOL ENERGY

Mostardi Platt Environmental

AIR SAMPLING ASSOCIATES, INC. THERE'S A WORLD OF DIFFERENCE

CleanAir ENGINEERING

Air Compliance Testing, Inc.

Delta Air Quality Services, Incorporated

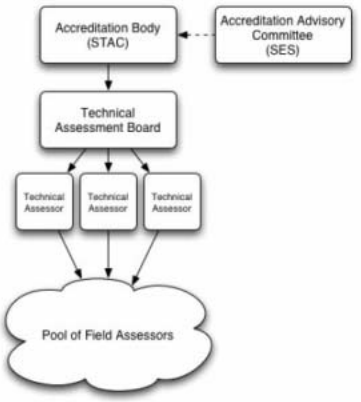
TestAmerica AIR DIVISION

Western Enviromental Services and Testing Inc.

AirTech Environmental

STAC STACK TESTING ACCREDITATION COUNCIL

How is STAC Structured?



- ISO 17011
- National program (not state-by-state)
- Assessors experienced in stack testing

STAC STACK TESTING ACCREDITATION COUNCIL

STAC Technical Assessment Board

Air and Waste Engineering

How Does STAC Accreditation Work?

How Does STAC Accreditation Work?

Application
Quality Plan
Experience Matrix
SOPs

Electronic Submittal
No paper
Application Fee

Completeness Determination
Assessment Fee

TAB Review and Vote

Do you walk the walk?

Implementation Assessment
In the field
2x during term

Ongoing
state observer supplement

Do you talk the talk?

Conformity Assessment
ASTM D7036
No on-site visit

Final Accreditation

Interim Accreditation

Future Plans

THE NELAC INSTITUTE

Open issues

- Use of ASTM D7036
- National program (not state-by-state)
- STAC accreditation process approach

Future Plans

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology

July 16, 2007

Dr. William L. Tilmon
President, National Cooperation for Laboratory Accreditation (NACLA)
c/o Forensic Quality Services International (FQS-I)
7881 114th Ave. N
Largo, FL 33773

Dear Dr. Tilmon:

Subsequent to the recent discussion between representatives of the National Institute of Standards and Technology (NIST) and NACLA, I would like to reiterate the longstanding

Standards and Technology (NIST) and NACLA, I would like to reiterate the longstanding NIST policy to encourage laboratory accreditation bodies to seek NACLA recognition. of government-to-government mutual recognition agreements and arrangements (MRAs) specifically call out NACLA recognition as a qualification. You can view this

Mary H. Saunders, Chief
Standards Services Division

cc:
Anthony Anderson, Executive Director
NACLA
1802 Commerce St., Suite 101
Lake Mary, FL 32746

NIST

STACK TESTING ACCREDITATION COUNCIL

Questions?

STACK TESTING ACCREDITATION COUNCIL

Air Toxic Emissions from Snowmobiles in Yellowstone National Park

Barkley Sive
University of New Hampshire

ABSTRACT

The spatial distribution of emissions associated with over-snow travel in Yellowstone National Park during the periods February 12-16, 2002 and February 12-16, 2003 will be presented. Whole air samples collected throughout the Park and exhaust samples were analyzed by gas chromatography using flame ionization and electron capture detection in conjunction with mass spectrometry to determine the mixing ratios of eighty-five volatile organic compounds, carbon monoxide and methane.

The findings indicate that 2-stroke snowmobile engine emissions in Yellowstone National Park and West Yellowstone contributed large quantities of air toxics and hazardous air pollutants to the Park's air shed. Benzene, toluene, ethyl benzene, xylenes, and hexane, which are major components of 2-stroke engine exhaust, exhibited significant enhancements between the high traffic and low traffic sampling periods as well as on subsequent days. The observed enhancements were a direct result of the increased snowmobile use between these two periods. Evaluation of the photochemical history of air masses sampled in the Park reveals that emissions of these compounds were i) recent, ii) persistent throughout the region and iii) are consistent with the 2-stroke exhaust sample fingerprints. Using a simple box model, the annual fluxes of these gases from snowmobile usage in the Park are estimated to be 0.35, 1.12, 0.24, 1.45, and 0.36 Gg/yr for benzene, toluene, ethyl benzene, xylenes, and hexane, respectively. The results derived from the box model are comparable to estimates of emissions based on actual snowmobile usage and the emission measurements made in 2003. These results yielded flux estimates of 0.23, 0.77, 0.17, and 0.70 Gg/yr for benzene, toluene, ethyl benzene, and xylenes.

By extrapolating these results to the U.S., annual emissions from snowmobile usage appear to be significant (~14-21%) with respect to EPA estimates of air toxics by non-road vehicles. The results from this study have been used by the National Park Service in order to support their current winter use plan for managing snowmobile and snowcoach traffic within the Park.

Collection and Analysis of Polycyclic Aromatic Hydrocarbons using Compendium Method TO-13A

Mitchell Howell, Julie L. Swift, and Donna Tedder
Eastern Research Group, Inc.

ABSTRACT

Semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), have received increased attention due to interest from the U.S. Environmental Protection Agency (EPA) and the National Air Toxic Trends Stations (NATTS) program. Many of these compounds are highly carcinogenic or mutagenic. Eastern Research Group, Inc. (ERG) has demonstrated exceptional performance of SVOC analysis using Compendium Method TO-13A[1] with Gas Chromatography/Mass Spectroscopy (GC/MS) and selective ion monitoring (SIM). The sensitivity of GC/MS SIM allows comparison of typical rural, suburban, and urban PAH content in ambient air. Data using Method TO-13A collection and analysis of ambient air across the United States will be presented to show recovery of PAHs in the ambient air.

INTRODUCTION

PAHs are a group of chemicals that are formed during incomplete combustion. These compounds generally occur in the environment as complex mixtures and not as individual compounds. PAHs can enter the environment from volcanoes, forest fires, residential wood burning, stationary combustion sources, cigarette smoke and exhaust from automobiles and trucks. Some PAHs are present in the atmosphere as vapors, but most are associated with particulate matter.

In general, PAHs having two to three benzene rings are present in ambient air in the vapor phase. PAHs that have four benzene rings exist in both the vapor and particulate phase, and the PAHs having five or more benzene rings are found in the particulate phase. PAHs can travel long distances in the particulate phase before returning to earth by rain or gravity, or degrading by chemical reaction. The EPA has determined that many of the PAH compounds are probable human carcinogens or mutagens with benzo(a)pyrene having the highest level of risk.

METHODOLOGY

ERG has been collecting and analyzing PAH samples from different urban sites by EPA Method TO-13A using a GCMS operating in SIM. The sampling sites were located in diverse locations including rural and metropolitan areas. ERG has used several types of sample cartridge media including XAD-2®, PUF and a combination of cartridges containing XAD-2® and PUF. With the addition of a quartz filter preceding the sample cartridge, both gaseous and particulate containing PAHs are captured more efficiently using the XAD-2® and PUF cartridge combination.

The following data presents the results, trends, and concentrations of the PAHs found in ambient air from 2005 and 2006 at the various monitoring sites.

TO-13A RESULTS

Field and Laboratory Surrogate & Blank Spike Recoveries

The surrogate results, expressed as percent recovery, were extracted from field blanks, method blanks and field samples during 2005 through 2006. The field surrogates benzo(a)pyrene-d12 and fluoranthene-d10 had an average of 67.9% and 84.1% recovery, respectively. The percent recovery for the laboratory surrogates, fluorene-d10 and pyrene-d10, were 80.0% and 79.6%, respectively. In addition to surrogates, one blank spike sample was prepared for every twenty samples extracted. The blank spike contains all of the TO-13A compounds and was prepared from a second source. The average recovery for all compounds spiked into the blank was 84.1%.

Site Location

Samples were collected from rural and metropolitan areas which allows compound specific comparisons between the PAHs. The sample collection in rural areas provides background concentrations for compounds without the influence of industry and urban sources. However, it is possible that the PAHs found at the rural sites are transported by particulate from the metropolitan areas.

The following table (Table 1) provides site descriptions for samples analyzed at ERG from 2005 and 2006:

Table 1. Sampling Site Descriptions

UATMP Code	Sampling Site	AQS Site Code	Land Use	Location Setting	Population Within 10 Miles of Site
ITCMI	Sault Sainte Marie, MI	26-033-0901	Residential	Rural	22,188
PVAL	Providence, Al	01-073-1009	Residential	Rural	28,665
ETAL	East Thomas, Birmingham, AL	01-073-0028	Residential	Suburban	399,149
GPMS	Gulfport, MS	28-047-0008	Commercial	Rural	173,435
KELA	Kenner, LA	22-051-1001	Residential	Suburban	302,165
NBAL	North Birmingham, AL	01-073-0023	Commercial	Urban	394,649
SAMS	Stennis Airport, MS	28-045-8201	Military Reservation	Suburban	39,443
SIAL	Sloss Industries, Birmingham, AL	01-073-6004	Residential	Urban	394,649
YFMI	Yellow Freight, Detroit, MI	26-163-0027	Industrial	Urban	1,154,943

Sample Results

Table 2 presents the average result for each compound detected at the sites from 2005 through 2006. Values were determined using different types of collection media. The sample collection using an all XAD-2® sample cartridge and filter was performed at ETAL, NBAL, PVAL, and SIAL. The sample collection using a PUF/XAD-2®/PUF sandwich and filter was performed at GPMS and SAMS. The sample collection using PUF and filter only was performed at ITCMI. The results from the different sampling media and the capture of the lower molecular weight PAHs (involving less than three members rings, i.e. naphthalene, acenaphthylene and acenaphthene) is not as efficient on PUF only cartridges as those containing all XAD-2® or PUF/XAD-2®/PUF sandwich cartridges. These compounds have approximately 35% recovery when using PUF as the sorbent[1].

Table 2. Average PAH Concentrations (ng/m^3) for Sites 2005 – 2006

	Rural Site			Suburban Site		Urban Site		
	ITCMI	PVAL	GPMS	ETAL	SAMS	NBAL	SIAL	YFMI
Compound	PUF	XAD	XAD/PUF	XAD	XAD/PUF	XAD	XAD	XAD/PUF
Acenaphthene	0.33	1.02	5.05	14.61	1.24	16.30	15.13	10.66
Acenaphthylene	0.33	0.25	1.71	6.65	0.33	14.51	12.48	3.40
Anthracene	0.62	2.00	1.64	7.02	0.43	8.30	7.94	2.93
Benzo(a)anthracene	0.13	0.06	0.24	0.60	0.06	3.31	3.14	0.65
Benzo(a)pyrene	0.13	0.09	0.26	0.49	ND	**2.39**	**2.24**	0.54
Benzo(b)fluoranthene	0.19	0.07	0.21	0.63	0.07	2.54	3.31	0.79
Benzo(e)pyrene	0.15	0.06	0.22	0.52	0.06	2.04	2.41	0.66
Benzo(g,h,i)perylene	0.13	0.06	0.15	0.42	0.05	1.38	1.61	0.48
Benzo(k)fluoranthene	0.16	0.09	0.20	0.55	0.06	2.22	2.63	0.70
Chrysene	0.27	0.08	0.38	1.01	0.09	4.10	4.55	1.02
Coronene	0.07	0.05	0.11	0.21	ND	0.47	0.53	0.15
Dibenz(a,h)anthracene	0.04	0.03	0.07	0.20	ND	**0.93**	0.65	0.22
Fluoranthene	1.93	0.73	2.06	5.70	0.65	12.25	16.44	7.27
Fluorene	1.01	1.55	5.17	11.86	1.44	17.64	18.97	10.22
Indeno(1,2,3-cd)pyrene	0.15	0.07	0.18	0.45	0.09	1.99	2.33	0.56
Naphthalene	1.51	17.02	**49.18**	**265.53**	9.44	**286.40**	**495.52**	**181.23**
Perylene	0.05	ND	0.12	0.27	ND	1.10	0.81	0.17
Phenanthrene	5.45	2.25	8.61	23.84	2.40	40.70	44.51	27.38
Pyrene	1.04	0.37	1.56	3.83	0.38	7.68	9.91	4.47

Note: Compound concentrations listed in bold text are above risk levels provided in EPA IRIS.[2]

Health Risk

Studies[3] have shown that PAHs can cause harmful effects on body fluids, the skin, and the body's system for fighting disease after both short- and long- term exposure. EPA has determined that benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene, and napthalene are probable human carcinogens and that acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, phenathrene and pyrene are not classifiable to their carcinogenicity to

humans. This is, in part, due to the inadequate data to either support or refute human carcinogenicity. Table 3 contains the results associated with exceeding the risk level. The EPA risk level was compared to the calculated values of the median, average, and maximum value seen at each sampling site from 2005 through 2006. This table contains only the compounds that exceeded the risk level.

Table 3. PAH Risk Levels Exceeded

Site	Risk Level	Compounds						
		Benzo (a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Dibenz(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Naphthalene
ETAL	Median							✓
	Average							✓
	Maximum		✓					✓
ITCMI	Median							
	Average							
	Maximum		✓					
NBAL	Median							✓
	Average		✓			✓		✓
	Maximum	✓	✓	✓	✓	✓	✓	✓
PVAL	Median							
	Average							
	Maximum							✓
SIAL	Median		✓					✓
	Average		✓					✓
	Maximum	✓	✓	✓	✓	✓	✓	✓
YFMI	Median							
	Average							✓
	Maximum		✓					✓
GPMS	Median							
	Average							✓
	Maximum							✓
SAMS	Median							
	Average							
	Maximum							✓

CONCLUSION

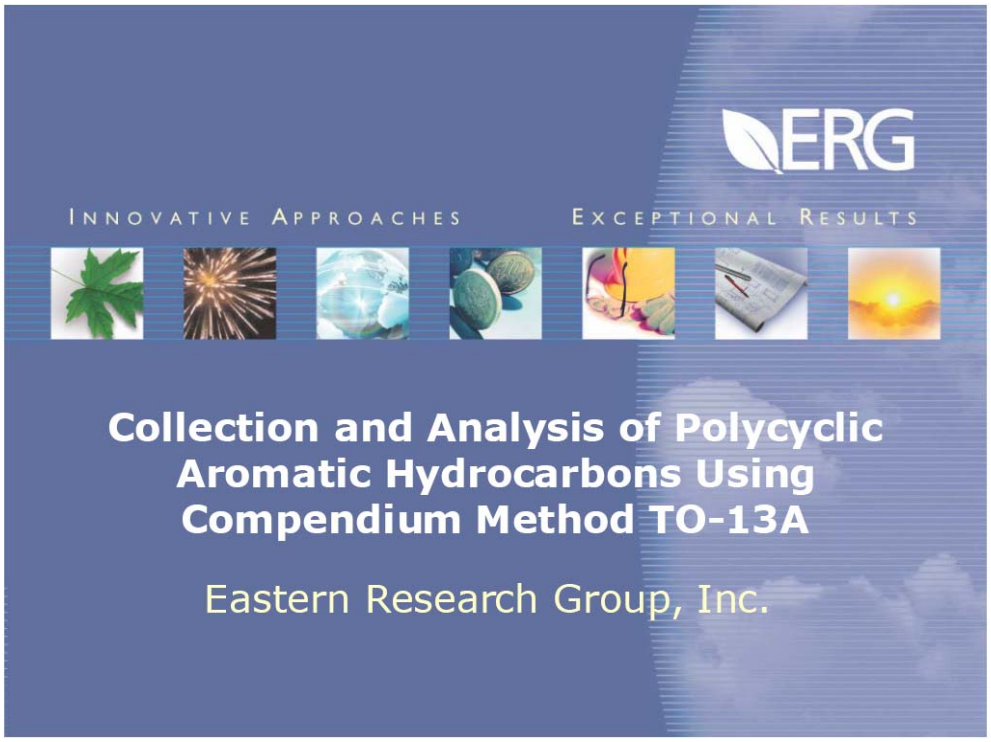
In conclusion, EPA has declared that PAHs are a risk to human health and has determined risk levels for each of the TO-13A compounds. These compounds are in the ambient air in three different physical states. The sampling sites reported here used different types of collection media. The results demonstrate that urban air contains much higher concentrations of PAH, often above risk threshold values. The collection of the gaseous and particulate PAHs seems more efficient when XAD-2® is used in combination with PUF. Data from the sampling sites provide support that PAH compounds are being detected above the risk levels in ambient air and the continuing need to monitor for the presence of PAHs.

REFERENCES

1. *Compendium Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography / Mass Spectrometry (GC/MS)*, EPA-ORD, Cincinnati, Ohio; U. S. Environmental Protection Agency, 1999.

2. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency, www.epa.gov/ttn/atw/toxsource/table1.pdf, 2005.

3. *Risk Assessment for Carcinogens*, U.S. Environmental Protection Agency, Technology Transfer Network Air Toxics Website, www.epa.gov/ttn/atw/toxsource/carcinogens.html.



Collection and Analysis of PAHs Using Method TO-13A

- Introduction
- Methodology
- ERG TO-13A Results
- Health Effects
- Conclusions

ERG

Introduction

- What are Polycyclic Aromatic Hydrocarbons?
- How do they occur in ambient air?
- What states do they exist in the ambient air?
- Probable human carcinogens?

ERG

Methodology

- Collection and analysis of samples (2005-2007)
- Types of media
- Urban, Suburban, and Rural sites
- SIM vs. Full Scan

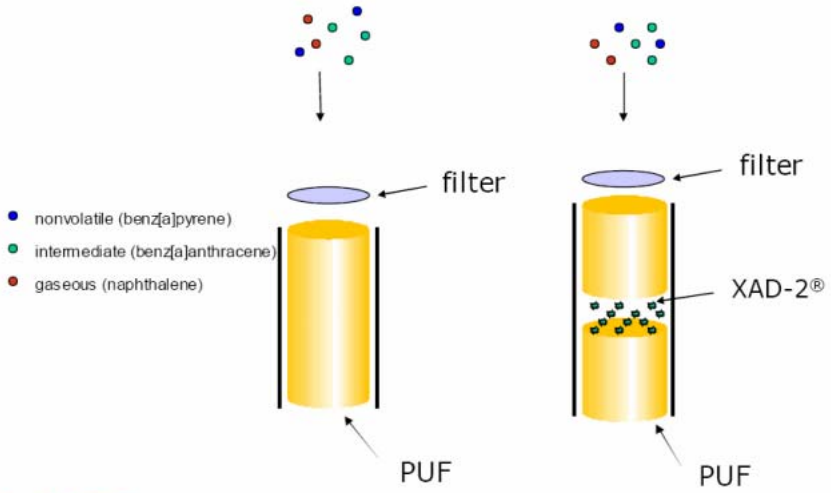
ERG

Media Types

- XAD-2®
- PUF
- PUF/XAD-2® Combination

ERG

Media Demonstration



ERG

Urban, Suburban, and Rural sites Page 1 of 2

UATMP Code	Monitoring Site	Land Use	Location Setting	Population w/in 10 Miles of Site
CELA	N. Main St, Los Angeles, CA	Residential	Urban/City Central	3,764,677
ETAL	East Thomas, Birmingham, AL	Residential	Suburban	399,149
GPMS	Gulfport, MS	Commercial	Rural	173,435
ITCMI	Sault Sainte Marie, MI	Residential	Rural	22,188
KELA	Kenner, LA	Residential	Suburban	302,165
NBAL	North Birmingham, AL	Commercial	Urban	394,649

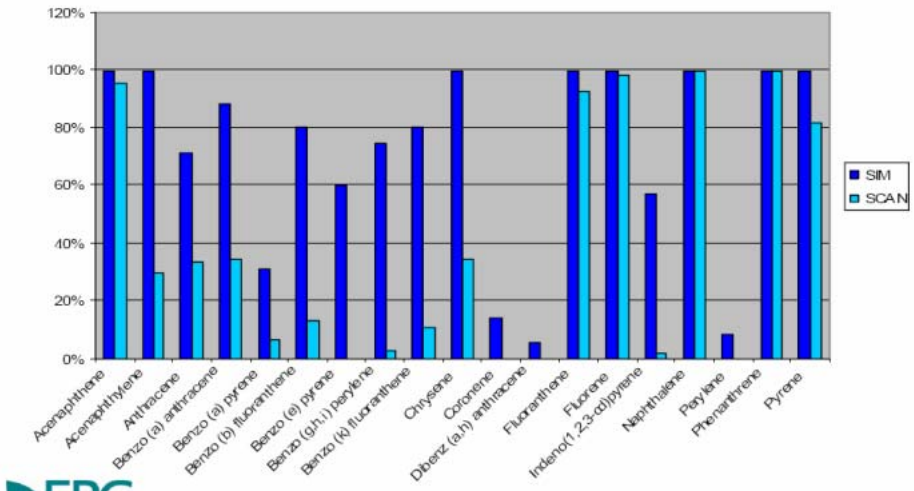
ERG

Urban, Suburban, and Rural sites Page 2 of 2

UATMP Code	Monitoring Site	Land Use	Location Setting	Population w/in 10 Miles of Site
PVAL	Providence, Al	Residential	Rural	28,665
RUCA	Riverside-Rubidoux, CA	Residential	Urban/City Central	968,736
SAMS	Stennis Airport, MS	Military Reservation	Suburban	39,443
SDGA	Atlanta, GA, Decatur Co	Residential	Suburban	720, 699
SIAL	Sloss Industries, Birmingham, AL	Residential	Urban	394,649
YFMI	Yellow Freight, Detroit, MI	Industrial	Urban	1,154,943

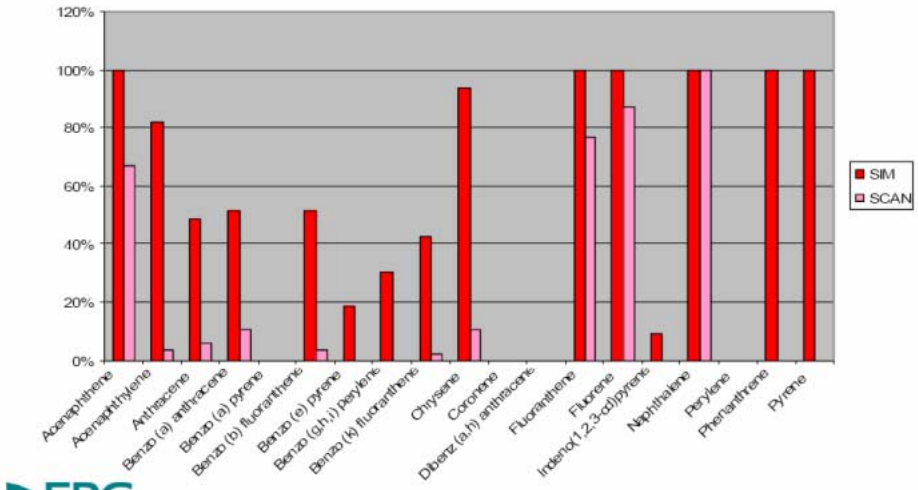
ERG

SIM vs. Full Scan - GPMS



ERG

SIM vs. Full Scan - SAMS



ERG

ERG TO-13A Average Results (ng/m^3) Page 1 of 4

	ITCMI	PVAL	SAMS	GPMS	NBAL	SIAL
	PUF	XAD	PUF/XAD-2®	PUF/XAD-2®	XAD	XAD
Compound	**22K**	**29K**	**39K**	**173K**	**395K**	**395K**
Acenaphthene	0.33	1.02	1.24	5.05	16.30	15.13
Acenaphthylene	0.33	0.25	0.33	1.71	14.51	12.48
Anthracene	0.62	2.00	0.43	1.64	8.30	7.94
Benzo(a)anthracene	0.13	0.06	0.06	0.24	3.31	3.14
Benzo(a)pyrene	0.13	0.09	ND	0.26	**2.39**	**2.24**
Benzo(b)fluoranthene	0.19	0.07	0.07	0.21	2.54	3.31
Benzo(e)pyrene	0.15	0.06	0.06	0.22	2.04	2.41
Benzo(g,h,i)perylene	0.13	0.06	0.05	0.15	1.38	1.61
Benzo(k)fluoranthene	0.16	0.09	0.06	0.20	2.22	2.63
Chrysene	0.27	0.08	0.09	0.38	4.10	4.55

ERG

ERG TO-13A Average Results (ng/m^3) Page 2 of 4

	ITCMI	PVAL	SAMS	GPMS	NBAL	SIAL
	PUF	XAD	PUF/XAD-2®	PUF/XAD-2®	XAD	XAD
Compound	**22K**	**29K**	**39K**	**173K**	**395K**	**395K**
Coronene	0.07	0.05	ND	0.11	0.47	0.53
Dibenz(a,h)anthracene	0.04	0.03	ND	0.07	0.93	0.65
Fluoranthene	1.93	0.73	0.65	2.06	12.25	16.44
Fluorene	1.01	1.55	1.44	5.17	17.64	18.97
Indeno(1,2,3-cd)pyrene	0.15	0.07	0.09	0.18	1.99	2.33
Naphthalene	1.51	17.02	9.44	49.18	**286**	**495**
Perylene	0.05	ND	ND	0.12	1.10	0.81
Phenanthrene	5.45	2.25	2.40	8.61	40.70	44.51
Pyrene	1.04	0.37	0.38	1.56	7.68	9.91

ERG

ERG TO-13A Average Results (ng/m^3) Page 3 of 4

	ETAL	SDGA	RUCA	YFMI	CELA
	XAD	PUF/XAD-2®	PUF/XAD-2®	PUF/XAD-2®	PUF/XAD-2®
Compound	**399K**	**721K**	**969K**	**1,155K**	**3,765K**
Acenaphthene	14.61	1.79	1.49	10.66	2.33
Acenaphthylene	6.65	ND	ND	3.40	0.24
Anthracene	7.02	7.13	2.32	2.93	0.12
Benzo(a)anthracene	0.60	0.02	0.02	0.65	0.03
Benzo(a)pyrene	0.49	0.19	0.18	0.54	0.13
Benzo(b)fluoranthene	0.63	0.05	0.04	0.79	0.04
Benzo(e)pyrene	0.52	0.17	0.11	0.66	0.05
Benzo(g,h,i)perylene	0.42	0.07	0.05	0.48	0.06
Benzo(k)fluoranthene	0.55	0.03	0.02	0.70	0.03
Chrysene	1.01	0.08	0.08	1.02	0.10

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ERG TO-13A Average Results (ng/m^3) Page 4 of 4

	ETAL	SDGA	RUCA	YFMI	CELA
	XAD	PUF/XAD-2®	PUF/XAD-2®	PUF/XAD-2®	PUF/XAD-2®
Compound	**399K**	**721K**	**969K**	**1,155K**	**3,765K**
Coronene	0.21	0.04	0.05	0.15	0.05
Dibenz(a,h)anthracene	0.20	ND	ND	0.22	ND
Fluoranthene	5.70	0.96	1.13	7.27	1.35
Fluorene	11.86	3.18	3.35	10.22	2.95
Indeno(1,2,3-cd)pyrene	0.45	ND	0.03	0.56	0.04
Naphthalene	**266**	**79.2**	**44.60**	**181**	**47.51**
Perylene	0.27	ND	ND	0.17	ND
Phenanthrene	23.84	5.79	6.04	27.38	6.49
Pyrene	3.83	0.47	0.62	**4.47**	0.85

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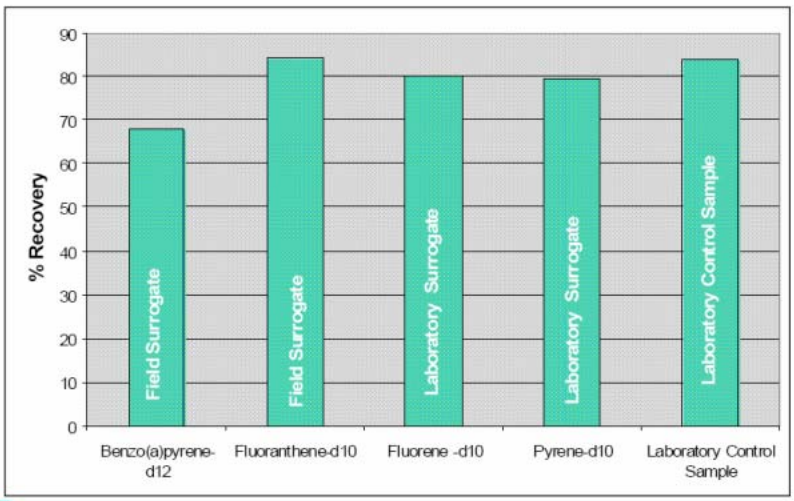
Surrogate & Laboratory Control Recoveries



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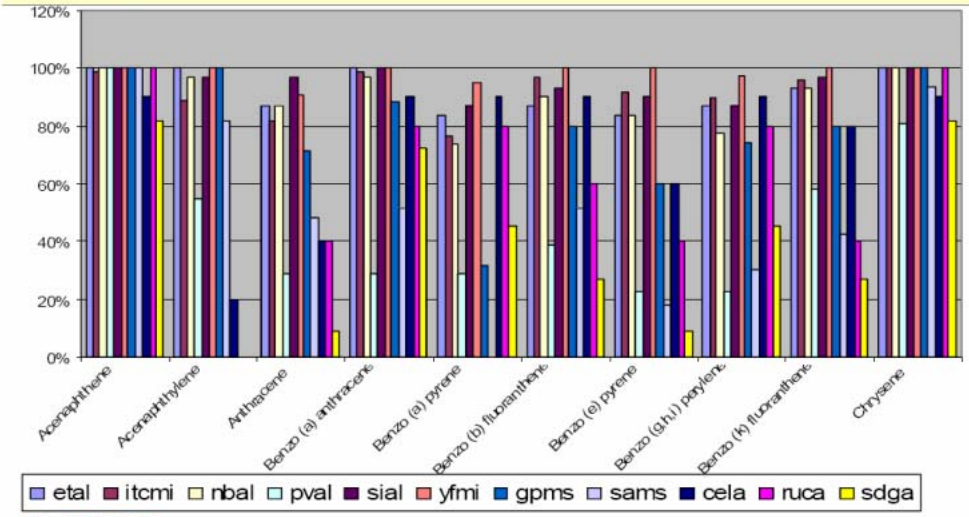
% Frequency at UATMP/NATTS Sites Page 1 of 2



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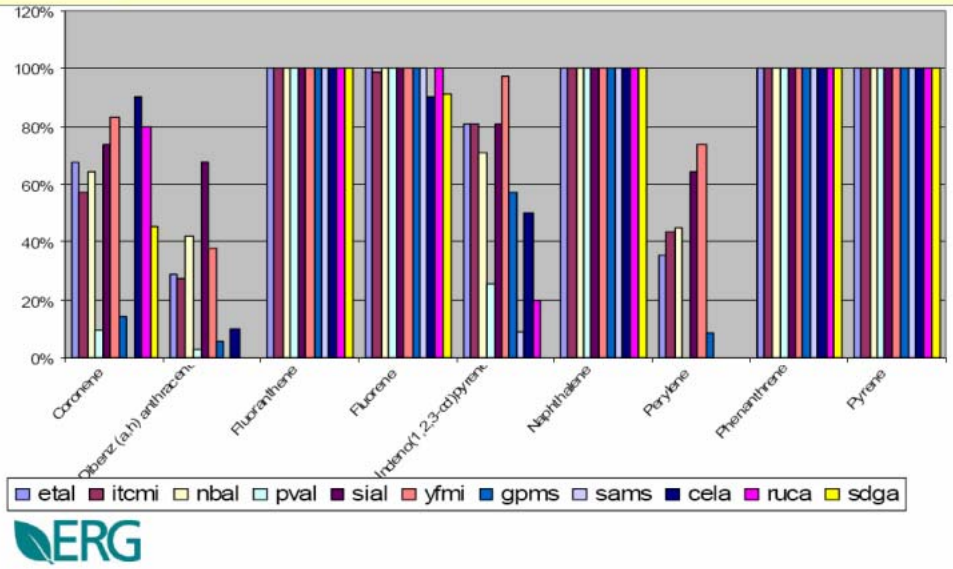
% Frequency at UATMP/NATTS Sites Page 2 of 2



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Health Effects
Page 1 of 3

Site		Benzo(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Dibenz(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Naphthalene
ETAL	Median							✓
	Average							✓
	Maximum		✓					✓
NBAL	Median							✓
	Average		✓			✓		✓
	Maximum	✓	✓	✓	✓	✓	✓	✓
PVAL	Median							
	Average							
	Maximum							✓
SIAL	Median		✓					✓
	Average		✓					✓
	Maximum	✓	✓	✓	✓	✓	✓	✓

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Health Effects
Page 2 of 3

Site		Benzo(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Dibenz(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Naphthalene
ITCMI	Median							
	Average							✓*
	Maximum		✓					✓*
YFMI	Median							
	Average							✓
	Maximum		✓					✓
GPMS	Median							
	Average							✓
	Maximum							✓
SAMS	Median							
	Average							
	Maximum							✓

✓* - Only detected after switching from PUF only to PUF/XAD-2 ® cartridge

Health Effects
Page 3 of 3

Site		Benzo(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Dibenz(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Naphthalene
SDGA	Median							✓
	Average							✓
	Maximum							✓
RUCA	Median							
	Average							✓
	Maximum							✓
CELA	Median							
	Average							✓
	Maximum							✓

Conclusions

- Risk levels have been determined for the PAHs
- Gaseous and particulate PAHs collect best on PUF/XAD-2®
- Need more PAH measurements

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  - Donna Tedder
  - Julie Swift

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Comparison of Naphthalene Measurements between Laboratory Methods and an Ultra-Fast Field Gas Chromatograph

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ABSTRACT

Naphthalene, especially as it relates to odors, can be a significant issue during the remediation of former Manufactured Gas Plant (MGP) sites. The zNose® Model 4200 Ultra-Fast Gas Chromatograph has been used at several sites to monitor airborne naphthalene concentrations in real-time during remedial activities. This paper presents the results of a side-by-side comparison of field and conventional laboratory analysis techniques for measuring naphthalene. Test results for samples analyzed using the zNose® are compared with test results for samples collected with evacuated fused-silica lined canisters and analyzed using US EPA TO-15, and samples collected on a PUF/XAD resin cartridge and analyzed using US EPA TO-13.

INTRODUCTION

Odors from remediation activities, particularly from former Manufactured Gas Plant (MGP) sites, have typically been difficult to quantify. Currently there are methods such as the ASTM (American Society for Testing Materials) E544-99 for Referencing Suprathreshold Odor Intensity[1] that use airborne n-butanol concentrations as a reference standard for comparison to ambient emissions. Instruments such as the Scentometer[2] also can be used to give a quantifiable measure of odor based on the dilution to threshold ratio. Initial work by the Gas Research Institute[3] indicated that a suspected principal odorant in coal tar at former MGP sites was naphthalene. There has been an increasing awareness and interest in measuring odors from remediation sites to prevent community complaints that could force remedial activities to stop. More recently, a reevaluation of the toxicity of naphthalene by the US EPA has lead to increased interest in measuring naphthalene in real-time.

EPRI conducted an evaluation of field emission measurement techniques in 2002.[4] During the evaluation, an open-path Fourier transform infra-red (OP-FTIR) spectrometer and the zNose® Model 4100 Ultra-Fast Gas Chromatograph (Electronic Sensor Technologies, Newbury Park,

CA) showed the capability to measure naphthalene concentrations in real-time during remedial activities. Since 2004, GEI Consultants, Inc. (GEI) has used the zNose® to monitor odor intensity as a function of naphthalene concentration.[5,6]

The current Environmental Protection Agency (EPA) methodology lists TO-13[7] as the primary method for measuring naphthalene in ambient air. Although TO-15 is often used for the analysis of naphthalene, it does not classify as a VOC as defined in the method. Per method TO-15, "VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25 °C and 760 mm Hg."[8] Recent advances in canister passivation, however, have demonstrated acceptable recovery for naphthalene by method TO-15.

Fused silica lined (FSL) canisters and SUMMA canisters are both used for TO-15 analysis. Both are passivation techniques applied to the interior surface of the canisters, the FSL being an inert coating that is applied to the stainless steel surface while the SUMMA is a patented electropolishing technique that deactivates the stainless steel surface.

This study presents a side-by-side comparison of analytical results generated using fixed-lab analytical methods and the zNose® Ultra-Fast Gas Chromatograph. The study also compares collection and storage of naphthalene using FSL canisters and SUMMA canisters. The advantages and disadvantages of all three methodologies (field GC, canisters, and cartridges) are also discussed.

Experimental Methods

An Entech 4600 Dynamic Diluter was used to prepare a sampling stream containing low part-per-billion by volume (ppbV) concentrations of naphthalene. A diagram of this is shown in Fig. 1. A photograph of the setup is shown in Fig. 2.

Figure 1: Standard Preparation System

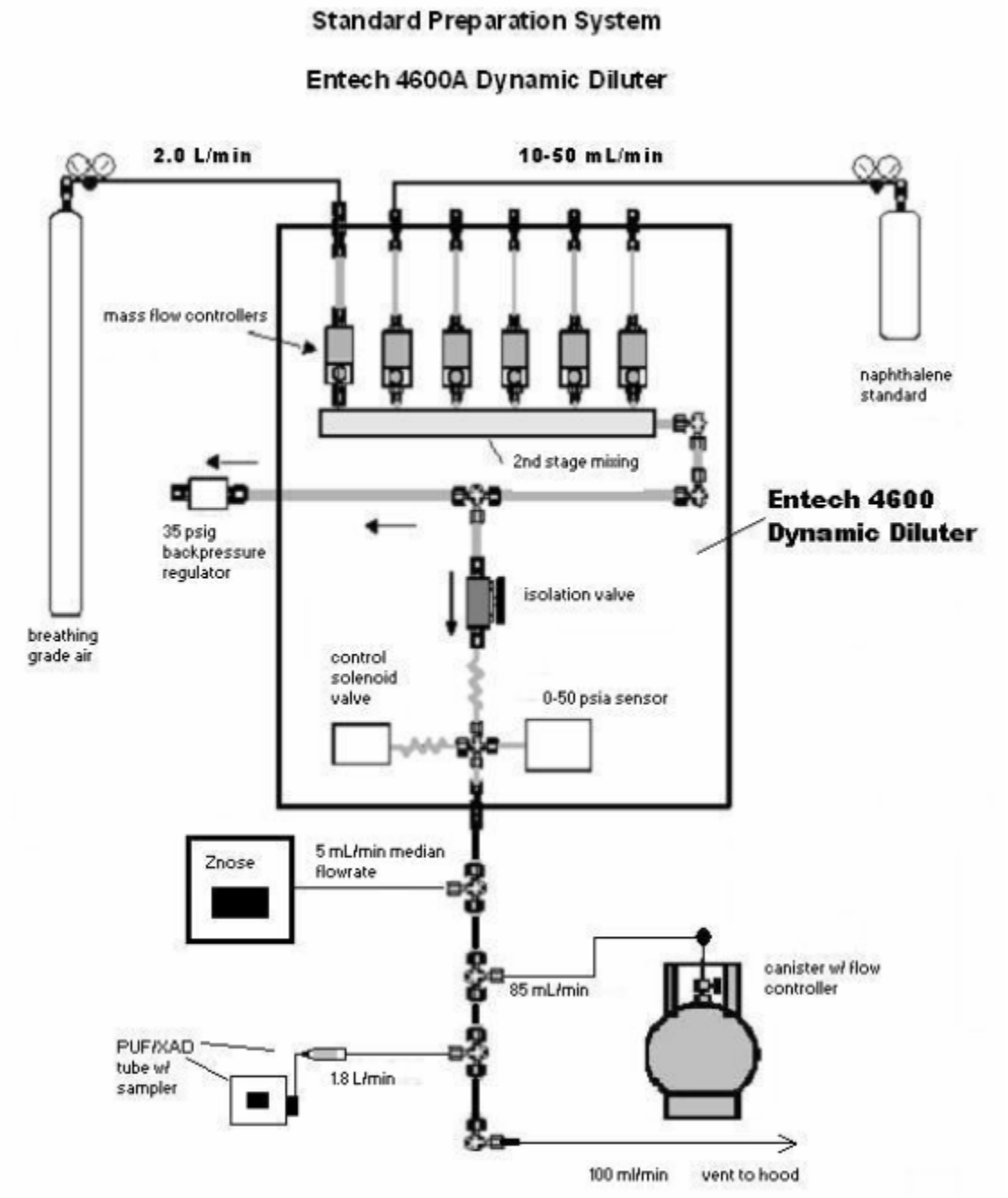
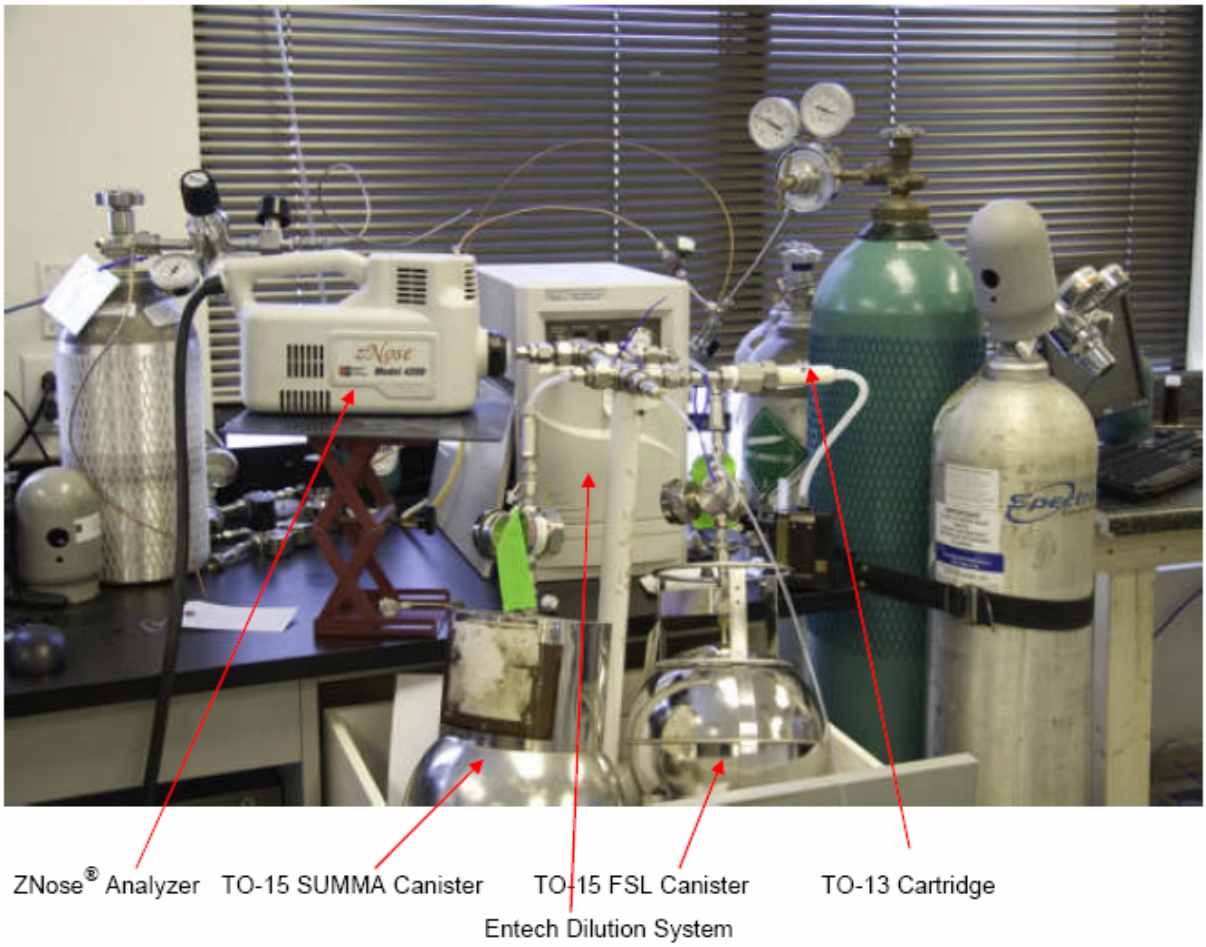


Figure 2: Photograph of Sampling System



Zero air and a naphthalene standard at 1 ppmV were mixed in the diluter to produce two different naphthalene concentrations for use in performing the tests. Tests 1 and 2 had a calculated final gas stream concentration of 4.5 ppbV (23.3 µg/m^3) and Tests 3 and 4 had a calculated final gas stream concentration of 23.8 ppbV (123.7 µg/m^3). Test 5 was a blank run of zero grade air. The zero air was humidified to a relative humidity of 30%. The system parameters are in Table 1.

The sampling system consisted of ¾ inch stainless steel tubing with three tees in-line for the various sampling apparatus. The tubing size was reduced to ⅛ inch to create backpressure in the ¾ inch tubing. Backpressure on the system was approximately 15 psia. The zNose® was fitted with a luer needle that was inserted through a septa.

Table 1: System Parameters

System Parameter	Flow or Sampling Rate
Dilution air flow rate	2.010 L/min
Naphthalene standard flow rates	9 mL/min (Tests 1 and 2) 49 mL/min (Tests 3 and 4)
PUF/XAD cartridge flow rate	1.8 Liters/min
Canister flow rate	85 mL/min
zNose® sampling flow rate	31 mL/min (5 mL/min median flow)

As the gas mixture exited the diluter, it was sampled by the zNose®, a fused silica lined (FSL) canister, and a low volume-PUF (Polyurethane Foam)/XAD resin cartridge. On Test 4, a SUMMA canister was added to the sample train for comparison to the FSL canister. During each test, the canisters and PUF/XAD samplers collected a single integrated sample over a 1 hour period. During each approximately 1 hour test period, the zNose® collected discrete samples over 30 second periods and produced analytical results approximately every three minutes yielding a total 21 to 22 discrete results for each test period. During the 30 second sampling period the flow rate to the zNose® was 31 mL/min. Over the three minute analysis time the calculated median flow rate to the zNose® was 5 mL/min.

The canisters were analyzed via EPA method TO-15 using an Entech 7100 Concentrator coupled to an Agilent 6890/5973 GC/MS system. The PUF/XAD cartridges were extracted and analyzed via EPA method TO-13, which calls for a Soxhlet extraction of the PUF/XAD cartridge. The extract was concentrated to a final volume of 1.0 mL and analyzed using an Agilent 6890/5973 GC/MS system. The mass spectrometer was set to acquire data in the SIM (selective ion monitoring) mode.

zNose® Operation

Real-time direct measurements of the gas mixture described above were made using the zNose®. Samples analyzed consisted of either injected standards or air samples. Analytes of interest were collected on a 1.0 mg Tenax trap before being desorbed onto a DB-624 column.

Prior to data collection, a five point naphthalene calibration curve was prepared and ranged from 4.96 ppbV to 99.3 ppbV. A calibration curve plotting peak response as area versus concentration was linear with $r^2 = 0.990$. Continuing calibration checks of 4.96 ppbV and 24.8 ppbV were analyzed after data collection Test 3 and at the end of testing. Continuing calibration checks were within ± 15% of the mass injected.

Results

Table 2 summarizes the results for the zNose® runs taken during each test. Figure 3 is a plot of zNose® concentration over time for the four test runs. Table 3 shows the results of the TO-13 and TO-15 analysis, and the average zNose® concentration for each test. Table 4 presents the percent recovery of the estimated initial concentration for each measurement method. Table 5 is the percent difference comparison of the average zNose® concentrations and the TO-15 results to the TO-13 concentrations.

Table 2: Summary Statistics of zNose® Test Runs

Parameter	Test 1		Test 2		Test 3		Test 4	
	µg/m^3	ppbV	µg/m^3	ppbV	µg/m^3	ppbV	µg/m^3	ppbV
Estimated Feed Concentration	23.2	4.5	23.2	4.5	123.7	23.8	123.7	23.8
Mean	20.3	3.9	18.9	3.6	58.0	11.1	71.2	13.6
Median	20.1	3.8	18.8	3.6	60.3	11.5	70.6	13.5
High	22.7	4.3	23.5	4.5	65.5	12.5	82.0	15.7
Low	18.5	3.5	16.5	3.2	38.8	7.4	63.6	12.1
Standard Deviation	1.3	0.2	1.5	0.3	6.6	1.3	4.1	0.8
Relative Standard Deviation	6%		8%		11%		6%	
Number of Samples	22		22		21		22	

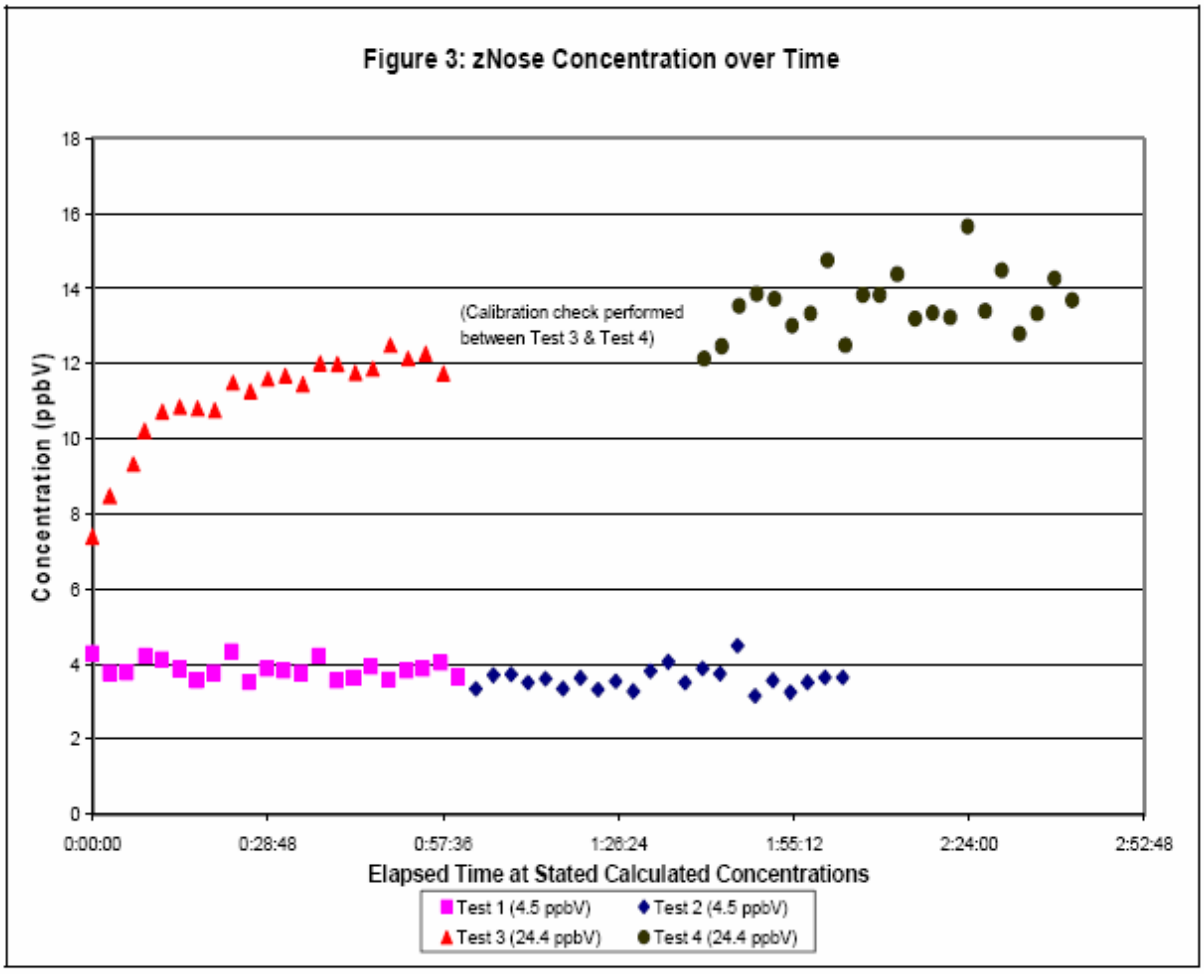


Table 3: Summary of TO-15 Results

Parameter	Test 1 (FSL)	Test 2 (FSL)	Test 3 (FSL)	Test 4 (FSL)	Test 4 (SUMMA)	Blank
Bromoform	14.6	14	62.5	63.6	56.3	ND
True Value, ppbV	13.5	13.5	69.9	69.9	69.9	
% Recovery	108%	104%	89%	91%	81%	
Naphthalene	2.64	2.96	12.6	15.8	6.46	2.47
True Value, ppbV	4.5	4.5	23.8	23.8	23.3	
% Recovery	59%	66%	54%	68%	28%	

Table 4: Naphthalene Analysis Method Results

Parameter	Test 1		Test 2		Test 3		Test 4	
	µg/m^3	ppbV	µg/m^3	ppbV	µg/m^3	ppbV	µg/m^3	ppbV
Estimated Feed Concentration	23.2	4.5	23.2	4.5	123.7	23.8	123.7	23.8
TO-13 PUF/XAD Cartridge	19.1	3.7	18.2	3.5	100.2	19.3	90.2	17.4
TO-15 FSL Canister	13.8	2.6	15.5	3.0	65.9	12.6	83.0	15.8
Mean zNose® Concentration	20.3	3.9	18.9	3.6	58.0	11.1	71.2	13.6

Table 5: Percent Recovery of Estimated Initial Feed Concentration

Analysis Method	Test 1	Test 2	Test 3	Test 4
TO-13 PUF/XAD Cartridge	82%	79%	81%	73%
TO-15 FSL Canister	59%	66%	54%	68%
Mean zNose® Concentration	87%	82%	47%	58%

Table 6: Percent difference comparison to US EPA Method TO-13

Analysis Method	Test 1	Test 2	Test 3	Test 4
TO-15 FSL Canister	-28%	-15%	-14%	-8%
Mean zNose® Concentration	6%	4%	-42%	-21%

Discussion

zNose®

Results from the zNose® are provided in Table 2 and Figure 3. For the 4.5 ppbV calculated concentration analysis, the mean naphthalene concentration measured by the zNose® was 3.9 ± 0.2 ppbV (n = 22; 87% recovery) for Test 1 and 3.6 ± 0.3 ppbV (n = 22; 80% recovery) for Test 2. The percent relative standard deviation (RSD) was 6% for Test 1 and 8% for Test 2. While the results were consistent between Tests 1 and 2, the data did exhibit a slight decrease in measured concentration over the course of the two tests (Figure 3). In general, the zNose® measurements were stable for the duration of Tests 1 and 2.

Similar reproducibility was observed for the 24.4 ppbV sample analysis, although the percent recovery was lower. The mean naphthalene concentration measured during Test 3 was 11 ± 1.3 ppbV (n = 21; 45% recovery) and 14 ± 0.8 ppbV (n = 22; 56% recovery). Percent RSDs, 11 % for Test 3 and 6% for Test 4, were comparable to those from Tests 1 and 2. There does appear to be a significant increase in measured concentration over time, particularly at the beginning of Test 3 (Figure 3). The increase in concentration observed over the first five measurements from Test 3 appears to be the source of most of the variability in this test; after 0:14:23 of elapsed time the zNose® measurements are much more stable (standard deviation ± 0.50, n = 16). Comparing the last 16 measurements from Test 3 to Test 4, there is a slight increase in variability as expressed by standard deviation (0.50 compared to 0.8) and percent RSD (5% compared to 6%).

The results from the FSL canisters analyzed by Method TO-15 are listed in Table 3, and in Table 4 along with the mean zNose® concentrations. Tests 1 and 2 had naphthalene results of 2.6 ppbV and 3.0 ppbV respectively, with a Relative Percent Difference (RPD) of 14 %, while Tests 3 and 4 had measured naphthalene concentrations of 12.6 ppbV and 15.8 ppbV (RPD = 23 %). These results are in good agreement with the mean zNose® concentrations of 3.9 ppbV and 3.6 ppbV for Tests 1 and 2, and of 11.1 ppbV and 13.6 ppbV for Tests 3 and 4.

A comparison of FSL canisters (aka Silcosteel, Silonite) versus the traditional SUMMA electropolished canister was performed during Test 4 (Table 3). While the bromoform exhibited acceptable recovery in both the SUMMA and FSL canister, the naphthalene had much lower recovery in the SUMMA canister (28%) when compared to the FSL canister (68%).

The calibration standard used for the study was prepared by a vendor certified for preparing EPA protocol gases (Spectra Gases). Since naphthalene is a solid at ambient temperature, preparing gaseous phase standards is challenging and many standard vendors will not guarantee stability of the naphthalene in the gaseous standard. The standard used for this study was prepared by first dissolving the naphthalene into bromoform and volatilizing the liquid into high purity nitrogen and storing it in a cylinder at approximately 2500 psig. The resulting concentration of bromoform was 3 ppmV and for naphthalene was 1 ppmV. The presence of bromoform, which is a standard analyte for TO-15 analysis, allowed for it to be used as a surrogate for the sampling system. Recovery of bromoform (Table 3) was well within the acceptable recovery range of TO-15 analysis (70-130%), and also demonstrated that the sampling system was working properly.

A canister blank was analyzed after all spiked samples were collected, yielding a detectable concentration of naphthalene at 2.47 ppbV. The same flow controller used for the collection of the spiked samples was used for the collection of the blank, which indicates that some residual naphthalene may have been present in the flow controller or possibly the sampling manifold. Data from the TO-13 PUF/XAD cartridges are also listed in Table 4, and this method exhibited better recovery than either the TO-15 or zNose®. The concentration as measured by TO-13 for Tests 1 and 2 was 3.7 ppbV (82%) and 3.5 ppbV (79%) with a RPD of 6%, and for Tests 3 and 4 was 19.3 ppbV (81%) and 17.4 ppbV (73%) with a RPD of 10%.

When the data is evaluated in terms of percent recovery of naphthalene from the calculated concentration, naphthalene was under recovered by all of the techniques used to varying degrees, as seen in Table 5. Average percent recovery for Tests 1 and 2, based on a calculated concentration of 4.5 ppbV, was 85 % for the zNose®, a little better than the 63 % for the FSL canisters. For Tests 3 and 4, where the calculated concentration was 23.8 ppbV, the average zNose® recovery was 53%, while the FSL canisters averaged 62%. TO-13 average recoveries were 81% for Tests 1 and 2, and 77% for Tests 3 and 4. Both the zNose® and TO-15 compared favorably with method TO-13 (Table 6).

The lower naphthalene recoveries observed using TO-15 and the zNose® may be associated with the nature of naphthalene. This compound is known to be "sticky", and therefore may have adsorbed onto the stainless steel tubing used to construct the sample delivery system manifold depicted in Figures 1 and 2. Adsorption of naphthalene onto portions of the sample delivery system is also indicated by the steep portion of the plot of zNose® concentration over elapsed time as illustrated by Figure 3; as the manifold system becomes coated with naphthalene, the plot of concentration over time begins to level off. Recoveries using the TO-13 method are increased, possibly due to the concentrating effect of the cartridges. In this method, all the naphthalene that enters the system is available for analysis as it is concentrated by the cartridge, resulting in an increased load. In the zNose® and TO-15, some concentration does take place but not to the same extent as in TO-13.

CONCLUSIONS

Naphthalene is regularly measured in air samples to monitor the health and safety of workers at a job site and the people living in the surrounding community. Currently, both EPA Method TO-13 and TO-15 (utilizing either SUMMA canisters or FSL canisters) are used to measure airborne naphthalene concentrations, with the turnaround time (TAT) for these methods being on the order of 5 – 10 days. There is often a need for "real time" information to manage the risk of exposure to both workers and the community. The zNose® can provide a large data set of reliable screening information in the field, and these data can be used to optimize TO-13/TO-15 sampling locations and the analytical budget. The advantages and disadvantages of the methods compared in this study are listed in Table 7.

This study has demonstrated that the zNose® is capable of delivering "real time" data, in less than three minutes, that is comparable to data obtained using Methods TO-15 and TO-13, and is ideal for field screening air samples to identify locations where collecting samples for more comprehensive TO-15 or TO-13 analysis will provide the most benefit. Additionally, this study

has demonstrated that naphthalene can be accurately measured using the TO-15 method, thereby supporting the use of method TO-15, TO-13, or both, to measure naphthalene concentrations with the final selection being dependant on the other compounds of interest and the goals of the project. Finally, based on the single comparison performed in this study, it appears that FSL canisters are better suited for the collection of air samples with potential naphthalene contamination than standard un-lined SUMMA canisters.

Table 7: Comparison of Naphthalene Measurement Methods

Analysis Method	Advantages	Disadvantages
TO-13 PUF/XAD Cartridge	• Designated by US EPA as the primary method for naphthalene detection • Concentration method allows for lower detection limits than TO-15 • Allows for changes in sampling time in the field • Relatively simple operation • Analysis by GCMS gives added confidence in results and minimizes matrix interference	• Sample requires refrigeration or loss of analytes possible • TAT of 5 – 10 days • Use of sampling pumps which may require electrical service or have mechanical failures • Analytical range does not include VOCs
TO-15 Canister	• Passivated sampling yields simplest operation • Most field rugged sampling system • Analysis by GCMS gives added confidence in results and minimizes matrix interference	• TAT of 5 – 10 days • Analytical range does not include heavier PAHs • Less sensitive than TO-13 • Increased shipping costs incurred • Flow controller failures and potential canister leakage
zNose® Ultra-Fast Gas Chromatograph	• Rapid results comparable to TO-13 and TO-15 • Possible to screen numerous samples in the field generating a large data set • Can analyze for a select range of both VOC and semivolatile • Provides "real time" information that can be used to optimize TO-13/TO-15 sampling locations and budgets • Low per unit cost	• Trained operator required • Screening data only, results should be confirmed by TO-15/TO-13 analysis

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KEY WORDS

Air Monitoring
Manufactured Gas Plant (MGP) Sites
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Odors
US EPA TO-13
US EPA TO-15
zNose®

Comparison of Naphthalene Measurements between Laboratory Methods and Field Gas Chromatograph

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Overview

- Study Design and Objective
- Overview of zNose Ultra Fast Field GC and lab methods (TO-15, TO-13)
- Dilution system overview
- Summary of results
- Results & Discussion
- Conclusions

Study Objective and Design

- Use the Entech Dynamic Dilution System to provide a consistent naphthalene feed concentration
- Performed four test runs at two feed concentrations (4.5 and 23.8 ppbv)
- A Fused-Silica Line (FSL) evacuated canister and TO-13 cartridge collected a sample over one hour

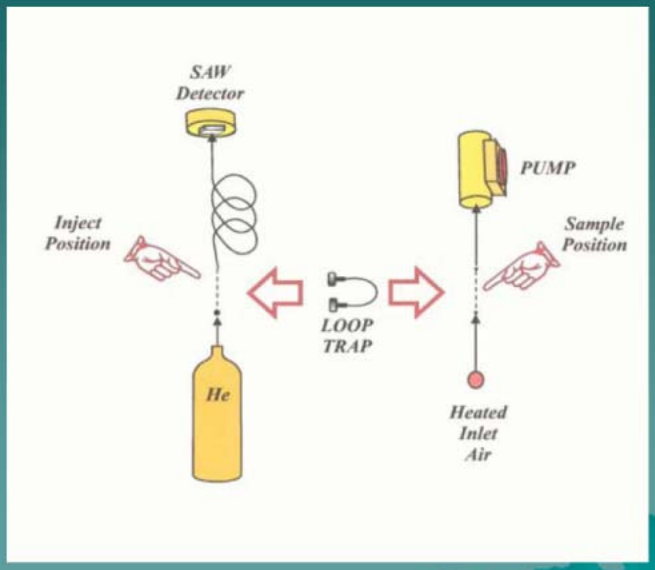
Study Objective and Design

- The zNose analyzed over 20 samples throughout the each test
- A SUMMA canister was added in test run on the Test 4

zNose GC Overview

- Manufactured by Electronic Sensor Technology, Inc. (Newbury Park, CA)
- Uses GC principles but on a smaller scale (1-meter column)
- The electronic nose portion of the zNose® consists of a Surface Acoustic Wave (SAW) detector

zNose GC Overview

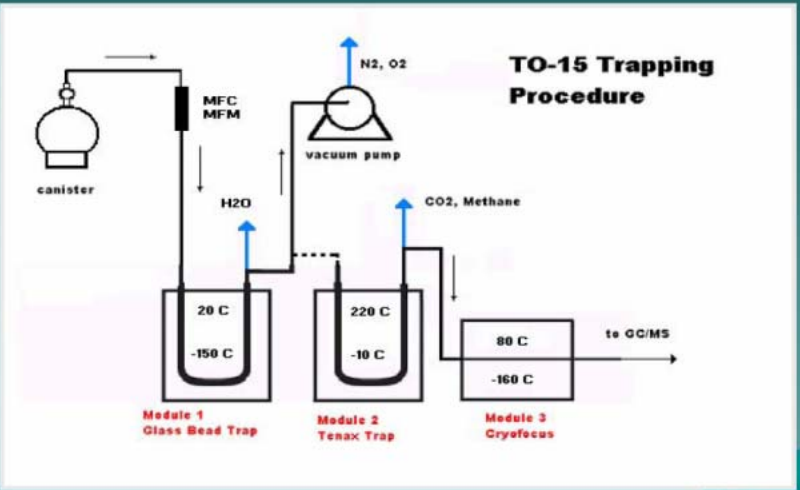


EPA Method TO-15

- EPA test method for sampling and analysis of VOC's in ambient air
- Samples collected using passivated (i.e. SUMMA vs. FSL) stainless steel canisters
- Analysis performed via a multi-stage trapping procedure for sample prep, then GC/MS
- Naphthalene is not an "official" analyte as prescribed in TO-15

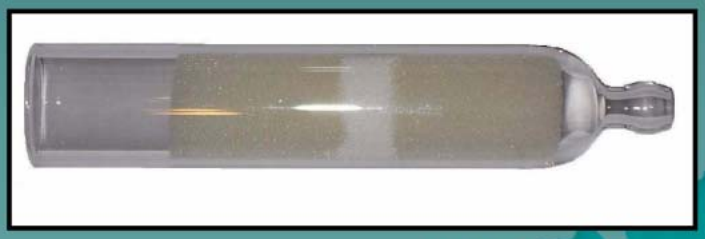
EPA Method TO-15

Entech Concentrator



EPA Method TO-13

- EPA test method for sampling and analysis of semi-volatile PAH's in ambient air
- Sampling is conducted by drawing air through a cartridge packed w/ sorbent material (poly-urethane foam (PUF) or XAD resin)
- Cartridge is then sent to lab, extracted, and analyzed via GC/MS
- Modified cartridge used for this test, low flow volume (1-5 L/min) and PUF/XAD sandwich

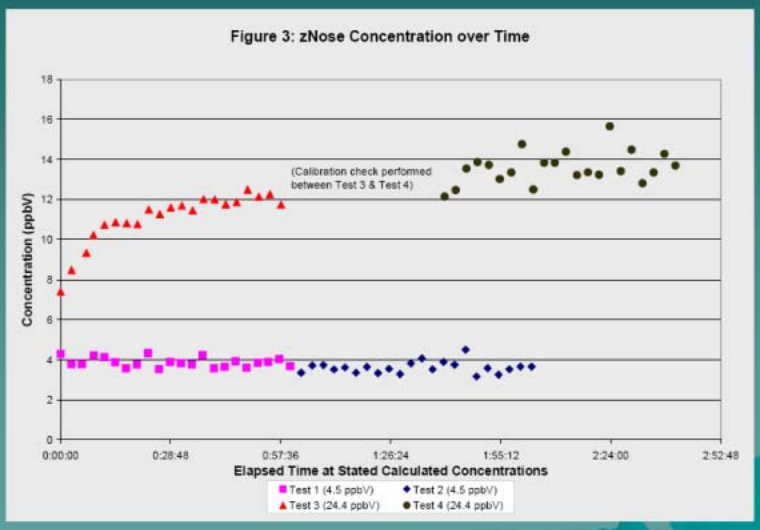


Dilution System Overview

Summary of zNose Results

Parameter	Test 1	Test 2	Test 3	Test 4
Estimated Feed Concentration	4.5	4.5	23.8	23.8
zNose Mean Concentration	3.9	3.6	11.1	13.6
zNose Standard Deviation	0.2	0.3	1.3	0.6
Relative Standard Deviation	6%	8%	11%	6%
Number of Samples	22	22	21	22

Summary of zNose Results



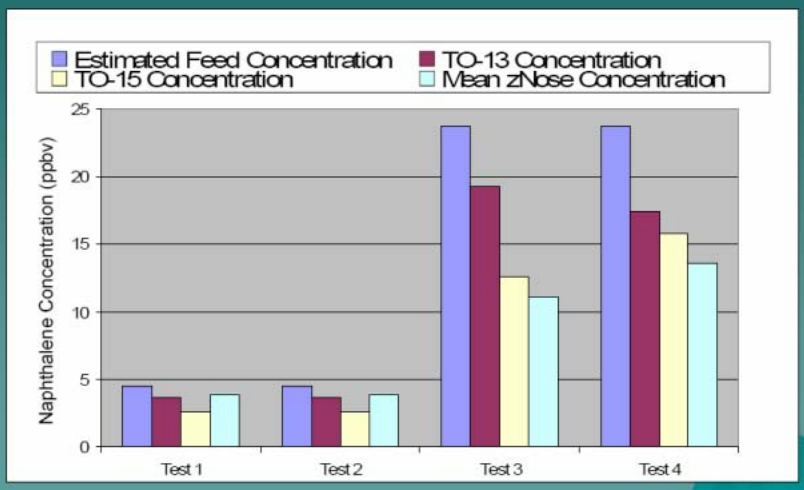
Summary of Results – TO-15

	Test 1	Test 2	Test 3	Test 4A	Test 4B
Parameter	(FSL)	(FSL)	(FSL)	(FSL)	(SUMMA)
Bromoform	14.6	14	62.5	63.6	56.3
True Value, ppbV	13.5	13.5	69.9	69.9	69.9
% Recovery	108%	104%	89%	91%	81%
Naphthalene	2.64	2.96	12.6	15.8	6.46
True Value, ppbV	4.5	4.5	23.8	23.8	23.3
% Recovery	59%	66%	54%	68%	28%

Summary of TO-13 Results

Parameter	Test 1	Test 2	Test 3	Test 4
Estimated Feed Concentration (ppbv)	4.5	4.5	23.8	23.8
TO-13 PUF/XAD Cartridge	3.7	3.5	19.3	17.4
Percent Recovery	87%	82%	81%	73%

-Comparison of Results- zNose vs. TO-15 vs. TO-13



-Comparison of Results- zNose and TO-15 vs. TO-13

Analysis Method	Test 1	Test 2	Test 3	Test 4
TO-15	-28%	-15%	-14%	-8%
zNose	6%	4%	-42%	-21%

Conclusions

Analysis Method	Advantages	Disadvantages
TO-13 PUF/XAD Cartridge	➢Designated by US EPA as the primary method for naphthalene detection ➢Concentration method allows for lower detection limits than TO-15 ➢Allows for changes in sampling time in the field ➢Relatively simple operation ➢Analysis by GCMS gives added confidence in results and minimizes matrix interference	◆Sample requires refrigeration or loss of analytes possible ◆TAT of 5 – 10 days ◆Use of sampling pumps which may require electrical service or have mechanical failures ◆Analytical range does not include VOCs

Conclusions

Analysis Method	Advantages	Disadvantages
TO-15 Canister	◆Passivated sampling yields simplest operation ◆Most field rugged sampling system ◆Analysis by GCMS gives added confidence in results and minimizes matrix interference	◆TAT of 5 – 10 days ◆Analytical range does not include heavier PAHs ◆Less sensitive than TO-13 ◆Increased shipping costs incurred ◆Flow controller failures and potential canister leakage

Conclusions

Analysis Method	Advantages	Disadvantages
zNose® Ultra-Fast Gas Chromatograph	◆Rapid results comparable to TO-13 and TO-15 ◆Possible to screen numerous samples in the field generating a large data set ◆Can analyze for a select range of both VOC and semivolatile compounds ◆Provides "real time" information that can be used to optimize TO-13/TO-15 sampling locations and budgets ◆Low per unit cost	◆Trained operator required ◆Screening data only, results should be confirmed by TO-15/TO-13 analysis

Questions

?

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Mike Marando's reaction that it worked

Low Concentration Measurements with EPA Reference Methods: A Case Study

Scott Evans
Clean Air Engineering

ABSTRACT

Many of the EPA Reference Methods for stack sampling were developed decades ago for pollutant concentrations many times higher than are typically found today. In addition, some of these methods were validated in one stack matrix but are routinely used in other stack matrices where interferences and detection limits may be dramatically different.

Clean Air Engineering recently conducted a Method Detection Limit study on EPA Reference Method 8 "Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources." This method was originally developed for use in Sulfuric Acid Plants with bone-dry, particulate-free gas streams with relatively high acid mist concentrations. However, permit writers routinely specify Method 8 for power plants with wet, particulate-laden gas streams and sub-ppm levels of acid mist. The purpose of this study was to determine the method detection limit in this matrix.

This presentation will also address some of the general issues regarding the limitations of a prescriptive approach to specifying test methods in operating permits and the advantages to moving towards a DQO/performance approach in permit writing.

NEMC 2007

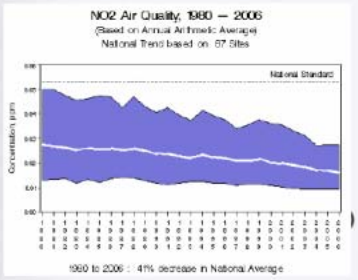
Low Concentration Measurements with EPA Reference Methods

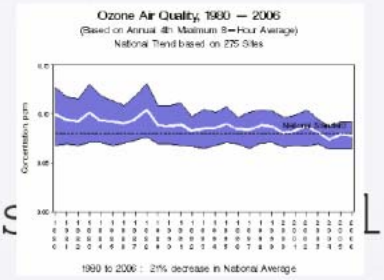
Test Methods, Issues and Uncertainty

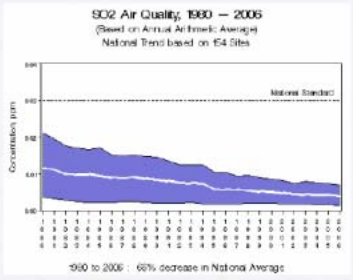
Presented by
Scott Evans
Vice President, Regulatory Affairs
Clean Air Engineering
Palatine, Illinois

CleanAir.

The Problem







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The Problem

Methods designed for a specific gas matrix are generalized to all matricies with no validation testing

Pollutant concentrations are, in some cases, three orders of magnitude lower than those used for validation testing

Establishment of emission limits is now divorced from development of test methods

EPA has little money for method development or validation testing

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An Example...

- EPA Method 8 "Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources"
- **However...**
- It was never validated on any source other than sulfuric acid plants
- **Nevertheless...**
- It is turning up in permits for measuring SO_3 in power plants in the sub-ppm range

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Method 8 Origins

- Variations have been used since the early 1900's.
- EPA version promulgated... for use on sulfuric acid plants.
- These gas streams have no moisture and no particulate matter.
- The method was generalized and adopted by the EPA as the compliance method for sulfuric acid determination from stationary sources.

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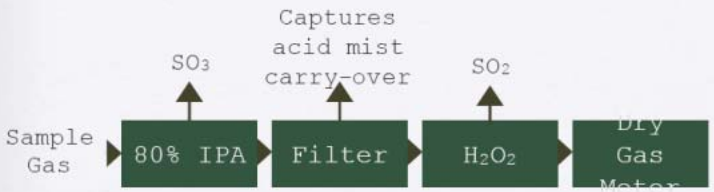
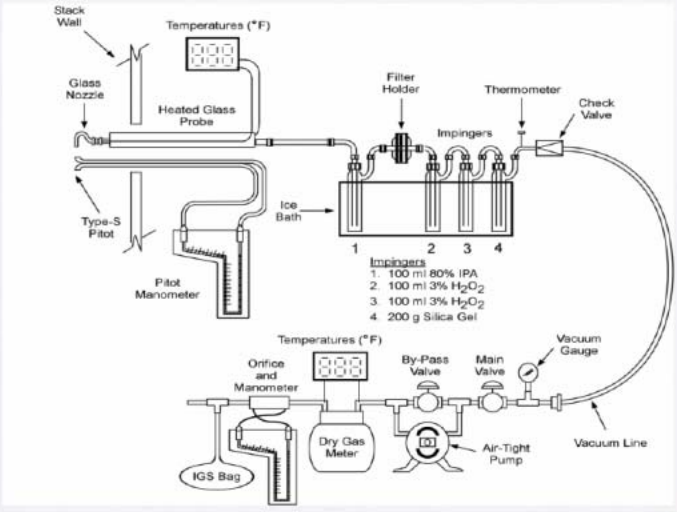
Method 8 Basics

Works by differential absorption



IPA minimizes absorption and oxidation of SO_2

Method 8 Sample Train



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Clean Air Method 8 Validation Study

- Method 8 performance in simulated flue gas matrix
- Fixed parameters: NOx, HCl, CO, CO_2
- Variables: H_2O, SO_2, SO_3, O_2
- Focused on measuring SO_3 in the 0.1 to 0.5 ppm range

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Detection Limits

excluding bias considerations

Basis	ppm	$\mu g/m^3$
Claimed in Method	0.01	0.05
Blank	0.0004	0.0013
SO_3 in clean, dry air	0.03	0.10
SO_3 in simulated flue gas	0.16	0.62

Standard deviation of 7 replicate runs x 3.143 (99% Student's t, n-1 df) following 40 CFR 136 Appendix B

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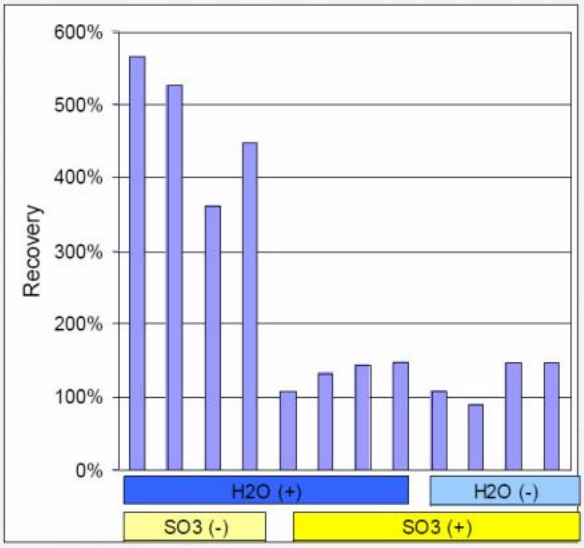
Speaking of Bias



M8 Bias Overview

- Flue gas bias (compared to clean, dry air) -- **+32%**
- IPA titration -- **+31%**
- Glass filter bias (IC analysis only) -- **+0.25 ppm**
- Water/Low SO_3 effect -- **+600%**

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Other Bias Effects

- Ammonia
  - England showed ammonia biases of up to 2.5 ppm.
  - Positive correlation with SO_2 and NH_3 concentrations
- Particulate
  - Method 8 typically has no filter therefore PM collects in IPA impinger
  - Tends to have positive bias from catalyzation of SO_2 to SO_3 due to trace metals in the ash.

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Method 8 Conclusions

- Detection limit about 0.2 ppm -- PLQ about 0.5 ppm
  - Under tightly controlled conditions
  - Likely to be higher in practical application
- Many positive bias effects -- Some correctable
- Longer runs amplify bias effects
- Analysis at sub-ppm levels very sensitive - small analytical errors lead to large positive biases
- All bets are off with NH_3 in matrix

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Implications

Method 8 is almost always the wrong method to use.
But if you have to...

- Use only quartz filters
- Adjust IPA to 80% before titration
- Use well-trained analysts experienced with titration.

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Another Example...

HCl Methods

- Method 26, 26A (isokinetic)
  - Wet method
  - Precision - 0.25 to 0.50 ppm @ 15 ppm max. conc. (CleanAir ~0.02 ppm)
  - Bias - <8%
  - Ammonium chloride positive bias
  - Significant (~ 50%) negative bias when using Method 5 sampling configuration with low HCl concentrations (<5 ppm)
  - Significant deterioration in precision and accuracy below 5 ppm

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Improvements

- NEVER use glass filter
- Increase probe and filter temp to 400 °F if no ammonia is present
- Eliminate filter with inertial probe or ESP

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EPA Guidance

EMISSION MEASUREMENT TECHNICAL INFORMATION CENTER
GUIDELINE DOCUMENT

Guideline Document 038
Description of In-Stack Detection Limit

$$ISDL = \frac{A \times B}{C}$$

where, ISDL = In-stack detection limit
A = Analytical detection limit
B = Amount of analyte analyzed
C = Volume of stack gas sampled

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Observations/ Recommendations

Many test methods must be modified to provide accurate results at low concentrations

Strict adherence to Reference Methods does not always result in data of known and documented quality

Test method must be evaluated for use considering the limitations of the test method and the sampling matrix

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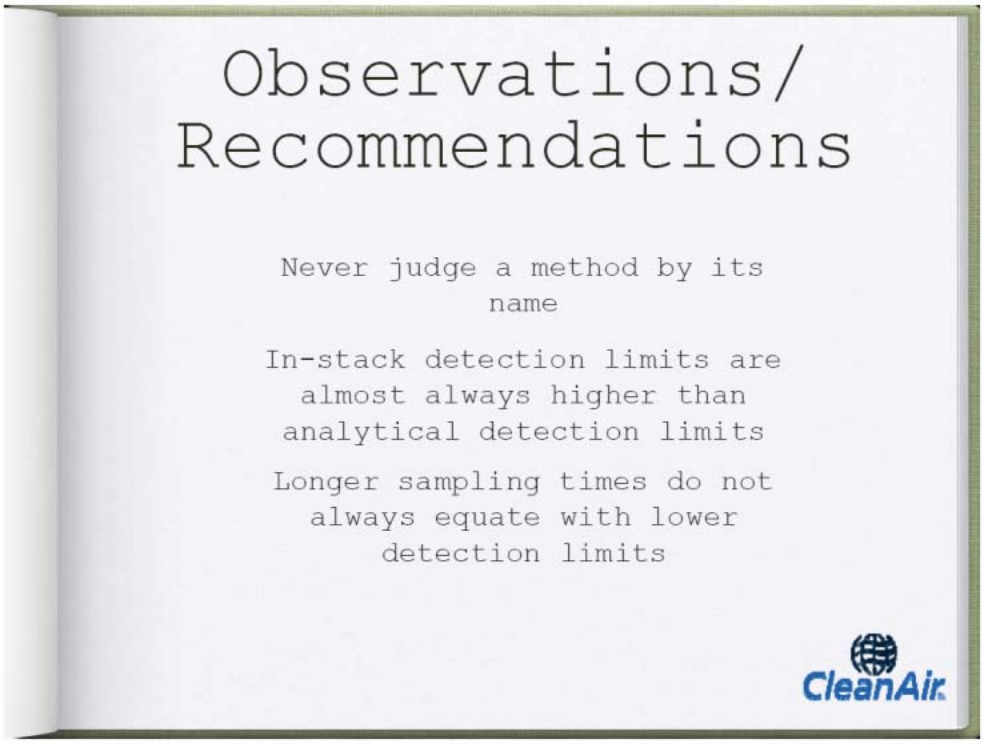
Observations/
Recommendations
Never judge a method by its name
In-stack detection limits are almost always higher than analytical detection limits
Longer sampling times do not always equate with lower detection limits
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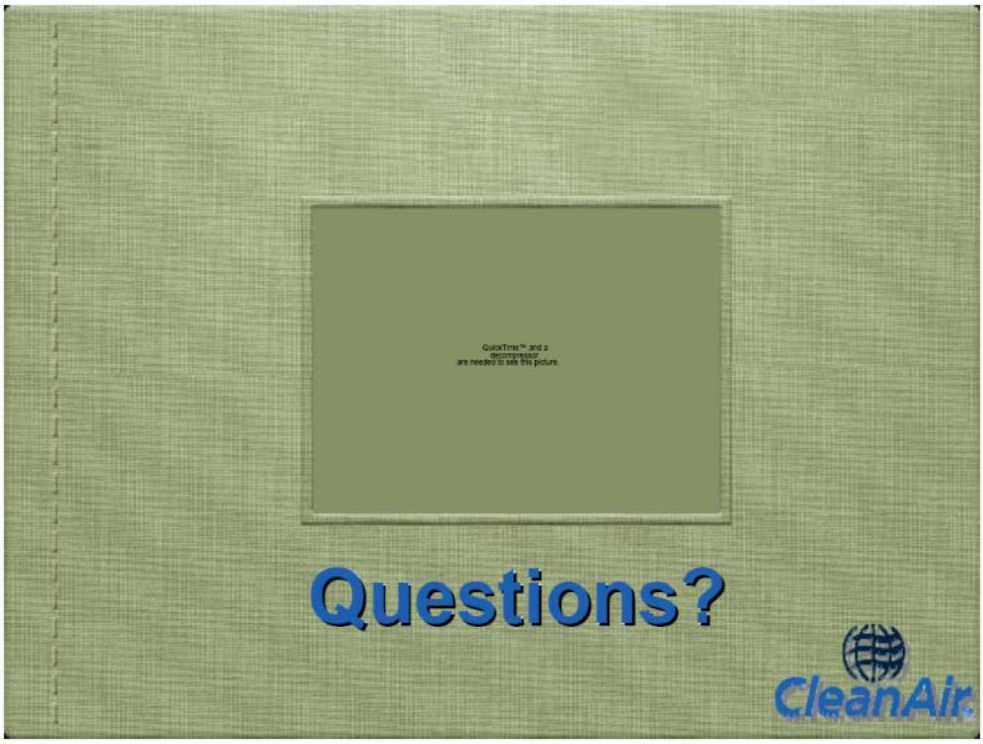

Questions?
CleanAir

Mercury Monitoring Methods and Techniques for Ambient Air

Frank Schaedlich
Tekran Instruments Corporation

ABSTRACT

The US Environmental Protection Agency (EPA) has recently implemented regulations limiting and reducing the emissions of mercury from coal fired power plants. The aim is to reduce annual emissions from this source from forty-eight to eighteen tons per year by 2018. Hopefully, this will reduce the mercury loading in freshwater fish, which is the primary pathway by which mercury finds its way to humans.

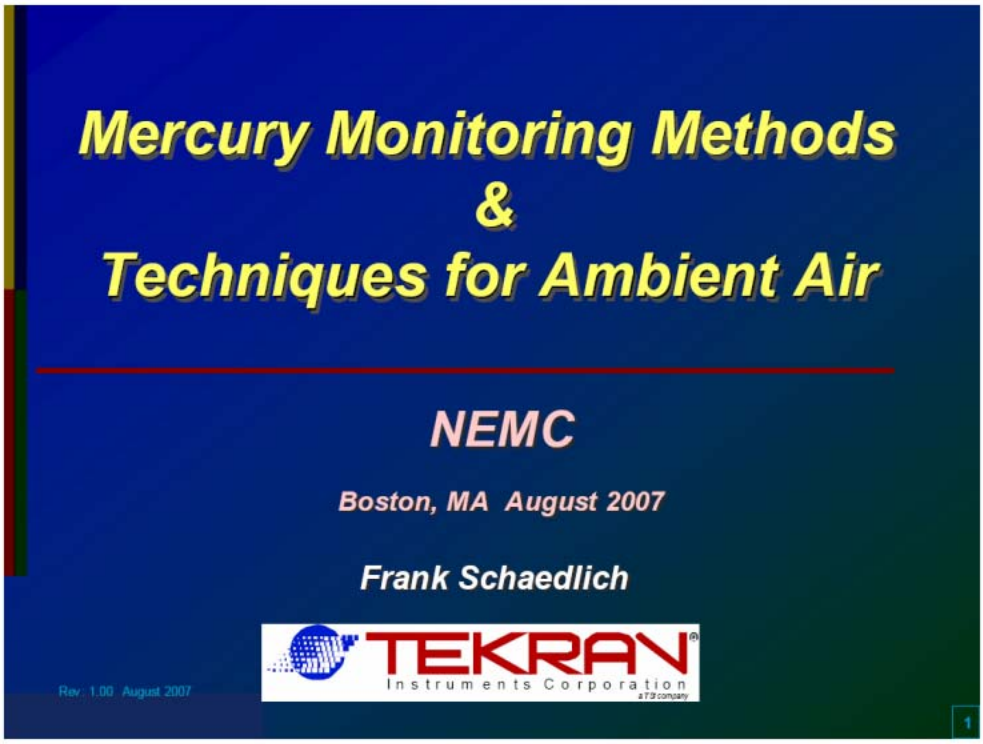
But, will this regulation make a difference? The answers are far from obvious. Unlike many pollutants, mercury is naturally present in the lithosphere and much of the mercury emitted is due to natural sources. Also, many of the atmospheric mercury emissions from other continents have lengthy residence times and are deposited in the US. A further complication is that the form of mercury, elemental, particulate or gaseous ionic, makes a vast difference in the deposition rates. Mercury is also interconverted during transport. It can be stored in various natural reservoirs and reemitted, possibly in a different form.

Determining the local effects of atmospheric mercury pollution requires measurement of the concentrations, dry deposition rates and wet deposition rates of the various species. This has caused an ever increasing interest in making accurate, low level ambient mercury measurements.

The monitoring of elemental mercury vapor and mercury compounds in ambient air is one of the most challenging continuous monitoring applications. The global background concentration of elemental mercury is only 1.5 ng/m3 (<0.1 parts per trillion) yet even these low levels have measurable biological effects. Reactive ionic mercury species can have measurable biological effects at values in the low picogram (pg/m3) range.

It has taken decades for researchers to develop methods capable of measuring these low levels accurately yet a range of reliable, rugged equipment now exists. For low level total mercury measurements, preconcentration onto pure gold followed by analysis using atomic fluorescence has proven to be sensitive, selective and capable of operating reliably under field conditions. Automated measurement of particulate bound and ionic gaseous mercury species requires additional equipment to separate and further preconcentrate these fractions.

This presentation provides a survey of the various methods that have allowed these low level measurements to become routine.


Mercury Monitoring Methods
&
Techniques for Ambient Air
NEMC
Boston, MA August 2007
Frank Schaedlich
TEKRAN
Instruments Corporation
Rev. 1.00 August 2007
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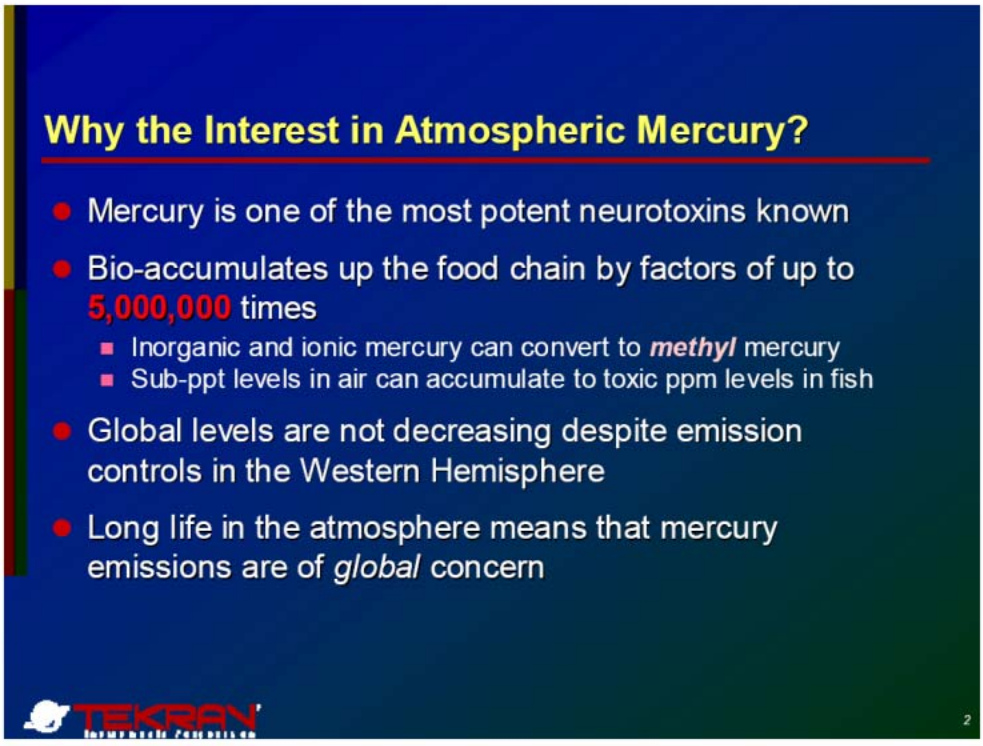
Why the Interest in Atmospheric Mercury?
Mercury is one of the most potent neurotoxins known
Bio-accumulates up the food chain by factors of up to 5,000,000 times
Inorganic and ionic mercury can convert to methyl mercury
Sub-ppt levels in air can accumulate to toxic ppm levels in fish
Global levels are not decreasing despite emission controls in the Western Hemisphere
Long life in the atmosphere means that mercury emissions are of global concern
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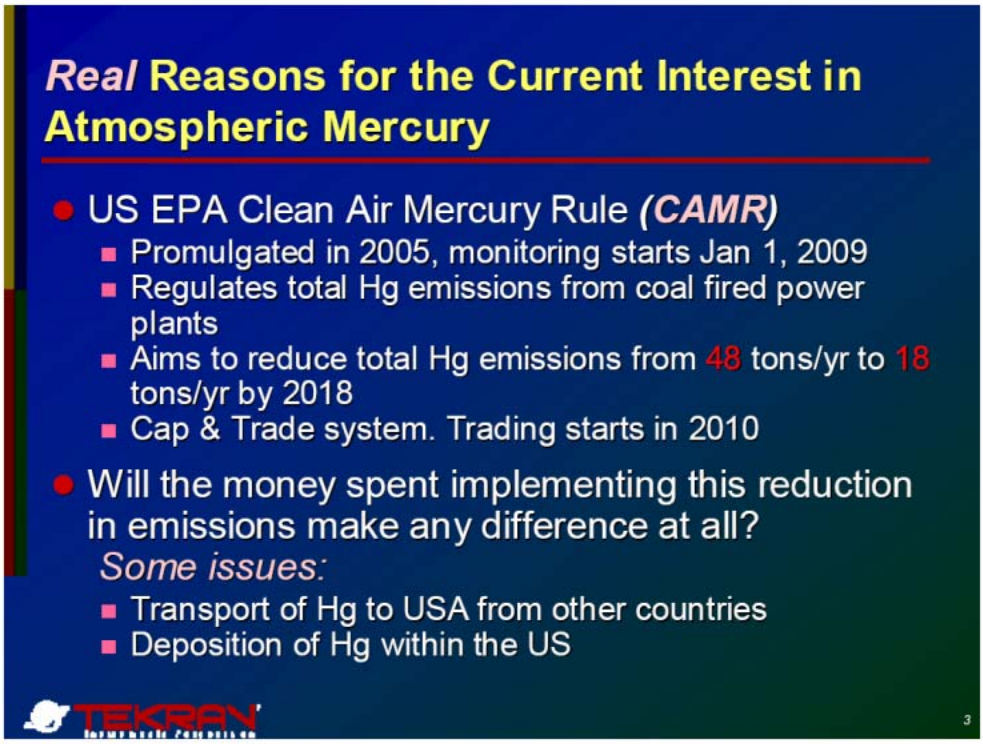
Real Reasons for the Current Interest in Atmospheric Mercury
US EPA Clean Air Mercury Rule (CAMR)
Promulgated in 2005, monitoring starts Jan 1, 2009
Regulates total Hg emissions from coal fired power plants
Aims to reduce total Hg emissions from 48 tons/yr to 18 tons/yr by 2018
Cap & Trade system. Trading starts in 2010
Will the money spent implementing this reduction in emissions make any difference at all?
Some issues:
Transport of Hg to USA from other countries
Deposition of Hg within the US
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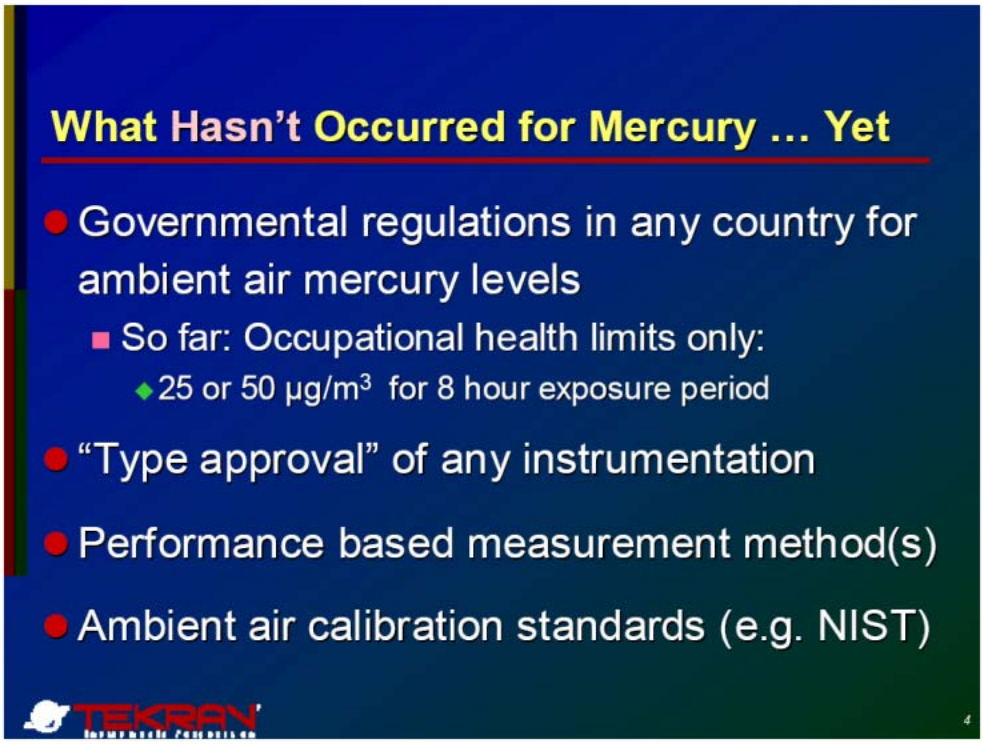
What Hasn't Occurred for Mercury … Yet
Governmental regulations in any country for ambient air mercury levels
So far: Occupational health limits only:
25 or 50 µg/m3 for 8 hour exposure period
"Type approval" of any instrumentation
Performance based measurement method(s)
Ambient air calibration standards (e.g. NIST)
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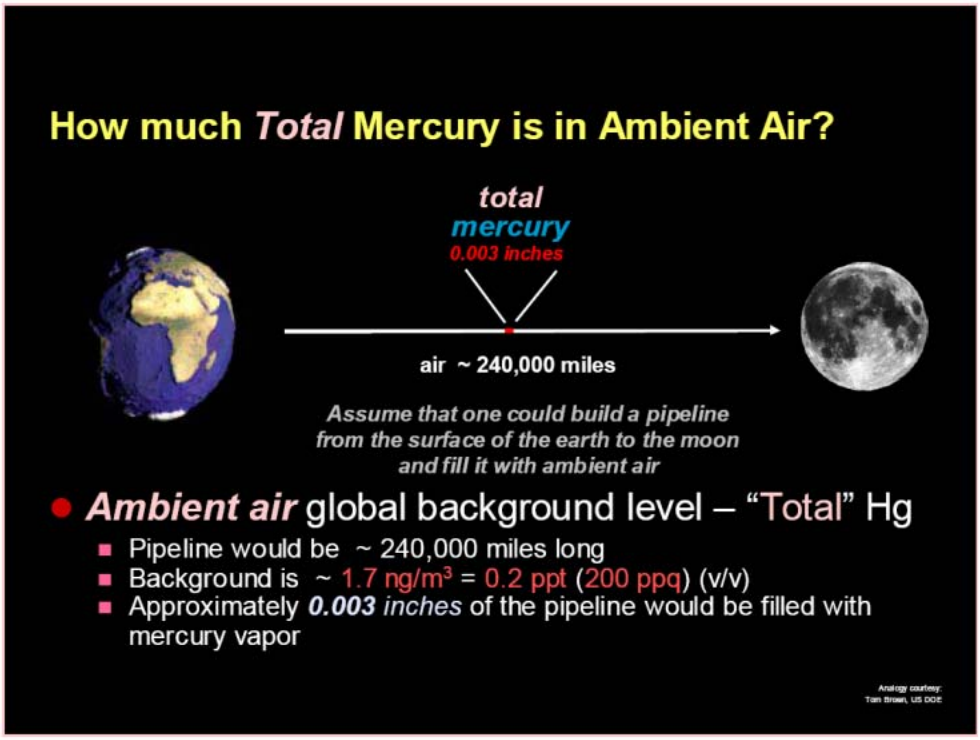
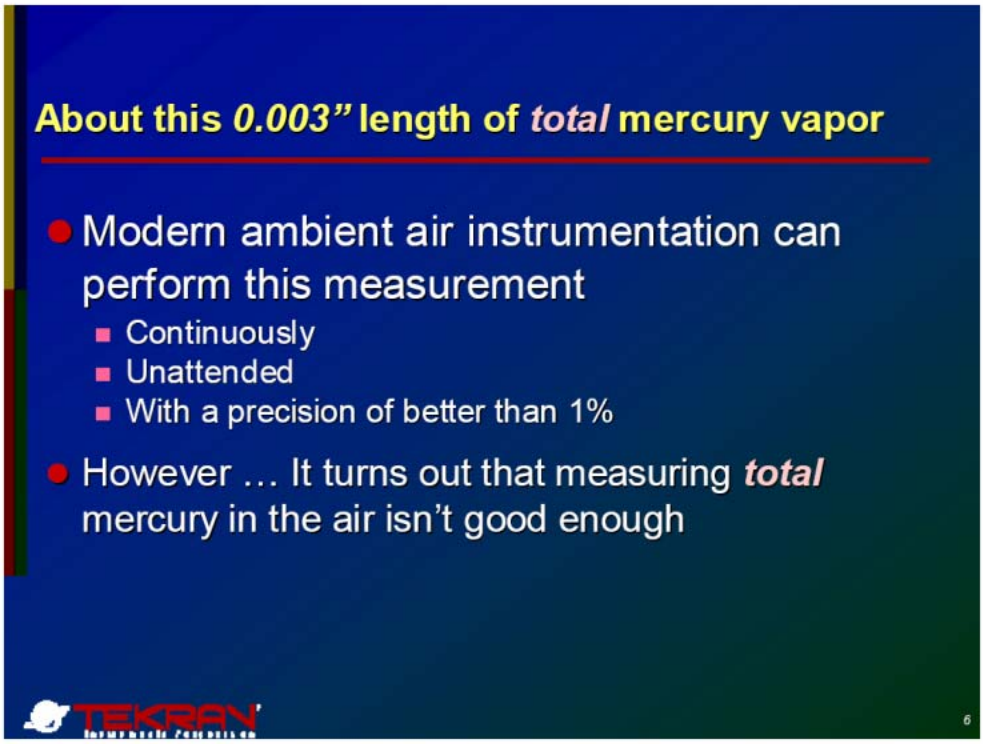

How much Total Mercury is in Ambient Air?
total
mercury
0.003 inches
air ~ 240,000 miles
Assume that one could build a pipeline from the surface of the earth to the moon and fill it with ambient air
Ambient air global background level – "Total" Hg
Pipeline would be ~ 240,000 miles long
Background is ~ 1.7 ng/m3 = 0.2 ppt (200 ppq) (v/v)
Approximately 0.003 inches of the pipeline would be filled with mercury vapor
Analogy courtesy: Tom Brown, US DOE


About this 0.003" length of total mercury vapor
Modern ambient air instrumentation can perform this measurement
Continuously
Unattended
With a precision of better than 1%
However … It turns out that measuring total mercury in the air isn't good enough
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Ambient Air Mercury Speciation – Why?

- Types of mercury in ambient air:
  - Elemental mercury: Hg^0
  - Reactive (ionic) mercury: Hg^{II}, RGM, Hg^{2+}
  - Particulate bound mercury: Hg^P, TPM
- Different forms of gaseous Hg have very different behaviors
  - Atmospheric deposition (and hence biological uptake) is highly dependent on RGM & Hg^P levels
- Forms can interconvert in the atmosphere and in various reservoirs

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Elemental Mercury: Hg^0

- Typically 95+% of atmospheric Hg loadings
- Relatively slow to react
  - Estimated 6 – 12 month residence time
- Hg^0 sources impact large areas
- Sources: chlor-alkali plants, gold and Hg mining, coal-fired power plants

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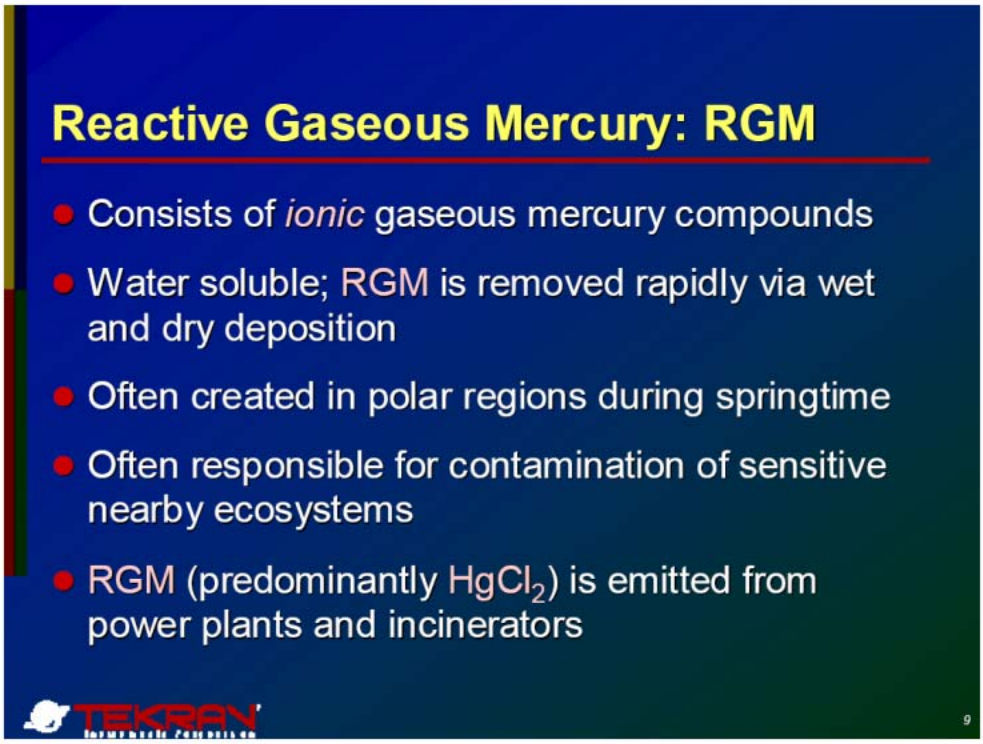
8


Reactive Gaseous Mercury: RGM
Consists of ionic gaseous mercury compounds
Water soluble; RGM is removed rapidly via wet and dry deposition
Often created in polar regions during springtime
Often responsible for contamination of sensitive nearby ecosystems
RGM (predominantly $HgCl_2$) is emitted from power plants and incinerators
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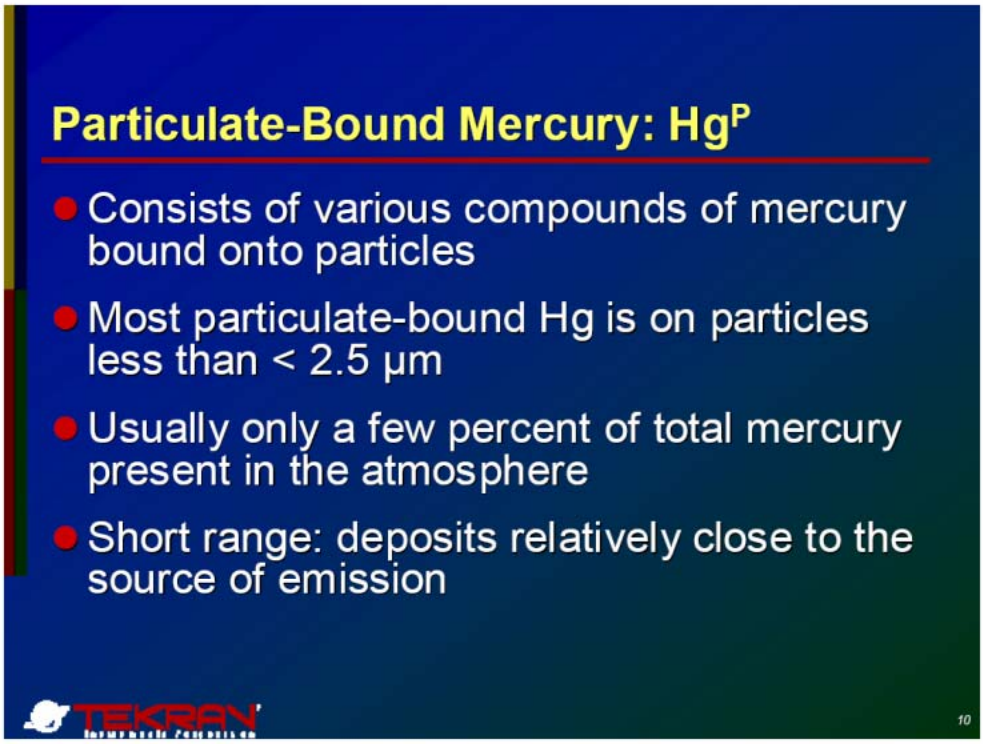
9


Particulate-Bound Mercury: Hg^P
Consists of various compounds of mercury bound onto particles
Most particulate-bound Hg is on particles less than < 2.5 µm
Usually only a few percent of total mercury present in the atmosphere
Short range: deposits relatively close to the source of emission
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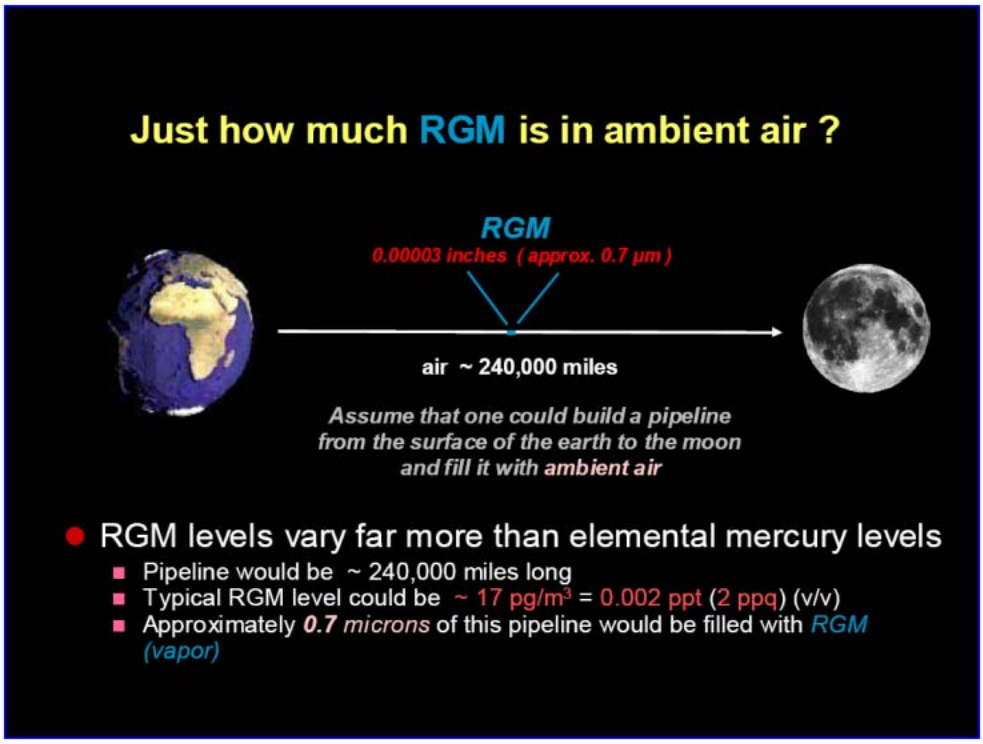
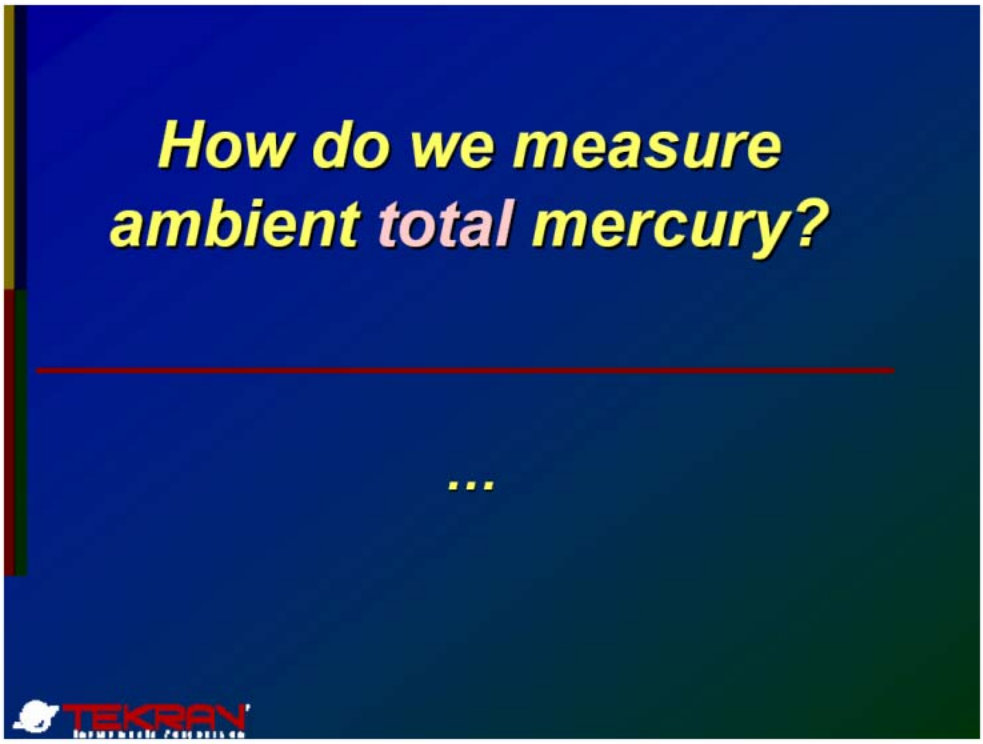
10


Just how much RGM is in ambient air ?
RGM
0.00003 inches (approx. 0.7 µm)
air ~ 240,000 miles
Assume that one could build a pipeline from the surface of the earth to the moon and fill it with ambient air
RGM levels vary far more than elemental mercury levels
Pipeline would be ~ 240,000 miles long
Typical RGM level could be ~ 17 pg/m3 = 0.002 ppt (2 ppq) (v/v)
Approximately 0.7 microns of this pipeline would be filled with RGM (vapor)


How do we measure ambient total mercury?
...
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Manual Total Gaseous Mercury Monitoring

- Manual method developed in late 1980's
  - Developed and used by researchers
  - Eventually documented by US EPA as IO-5
- Method Overview:
  - Adsorb Hg onto gold coated silica field cartridges
  - Typical exposure time required: ***6-24 hours***
  - Analysis using dual stage thermal desorption with CVAFS (atomic fluorescence) detection

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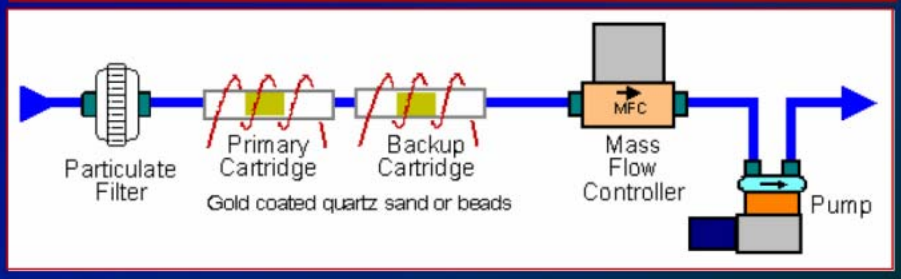
13

Manual Total Hg Sampling



- Gold coated silica adsorbent trap
  - Backup trap tests for breakthrough
- Mass flow controller and pump
  - Measures total volume drawn through cartridges

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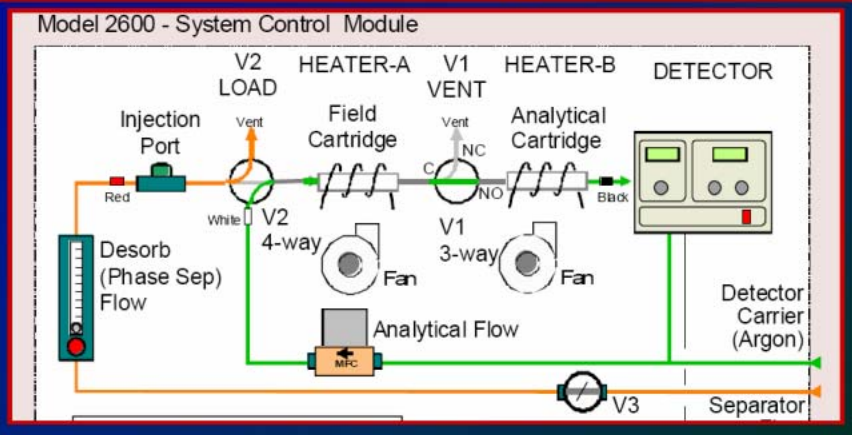
14

Manual Cartridge Analysis



- Dual stage thermal desorption
- Atomic Fluorescence (AF) detection

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15

Why Atomic Fluorescence?

- Much more sensitive than atomic adsorption
  - MDL < 0.1 pg absolute
- Not subject to interferences
  - AA requires some sort of compensation/correction scheme
  - Interfering compounds (e.g. SO_2, O_3, organics) often present in concentrations *thousands* of times higher than Hg
- Inherently linear
  - Detector linear over >5 orders of magnitude
- Simple, rugged and low cost
  - Capable of continuous field operation

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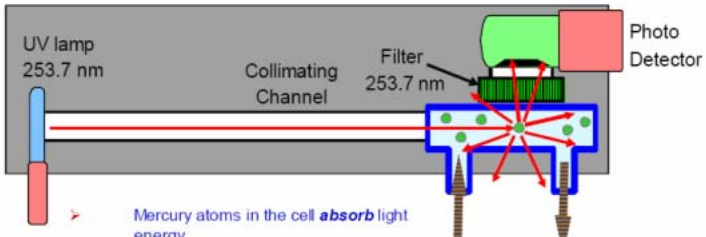
16

Atomic Fluorescence (AF) Detector



- Mercury atoms in the cell ***absorb*** light energy
- They re-emit radiation (***fluoresce***) at the same wavelength
- Re-emission is ***omnidirectional***
- Photo detector measures ***increase*** in intensity against a dark background

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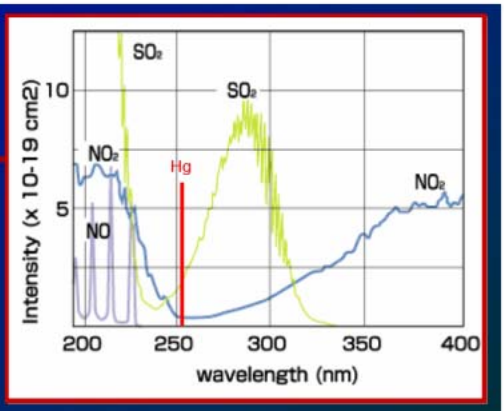
17

Why not AA?



- Amount of absorption is set by Beer's law
  - Logarithmic response
  - Limited dynamic range
  - Main reason EPA has traditionally insisted on all those 5 point linearity checks
- Not particularly sensitive
  - Looking for very small decreases in a bright lamp signal
- Inherently cross sensitive to any molecular species that absorbs in the UV at 253.7 nm
  - There are lots ! Organics, SO_2, O_3, NO_2 to name but a few

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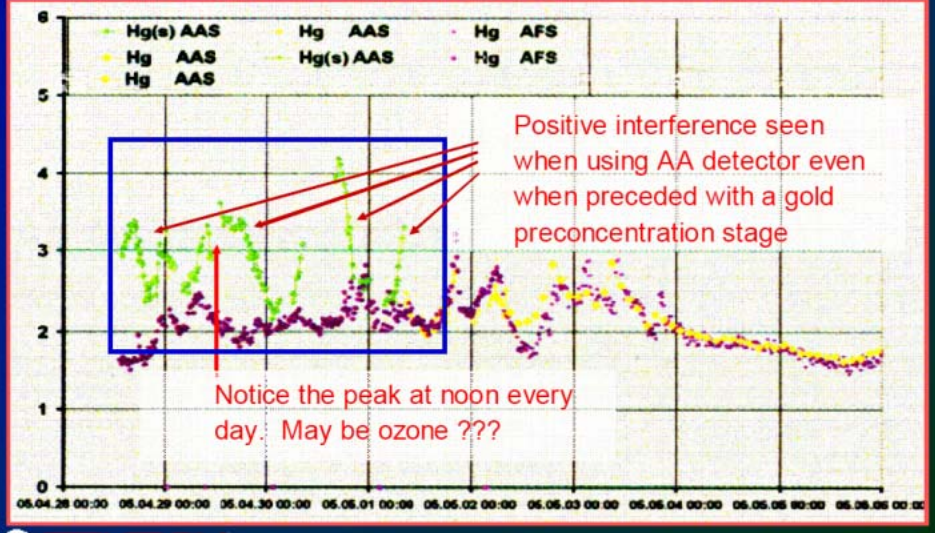
18

Interference when using AA Based Hg Analyzer



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19

Automated Total Mercury Analyzer

- Automated implementation of gold/AF manual method
- Has largely supplanted manual cartridge methods
- Provides continuous total gaseous (TGM) readings with update rate as low as ***2.5*** minutes
- Detection limit ***< 0.1 ng/m³*** *(5 min. samples)*
- Automatic recalibration with internal Hg^0 permeation source
- Capable of unattended operation for extended periods
- Two cartridges are used to alternately sample and desorb
  - No gaps in data stream

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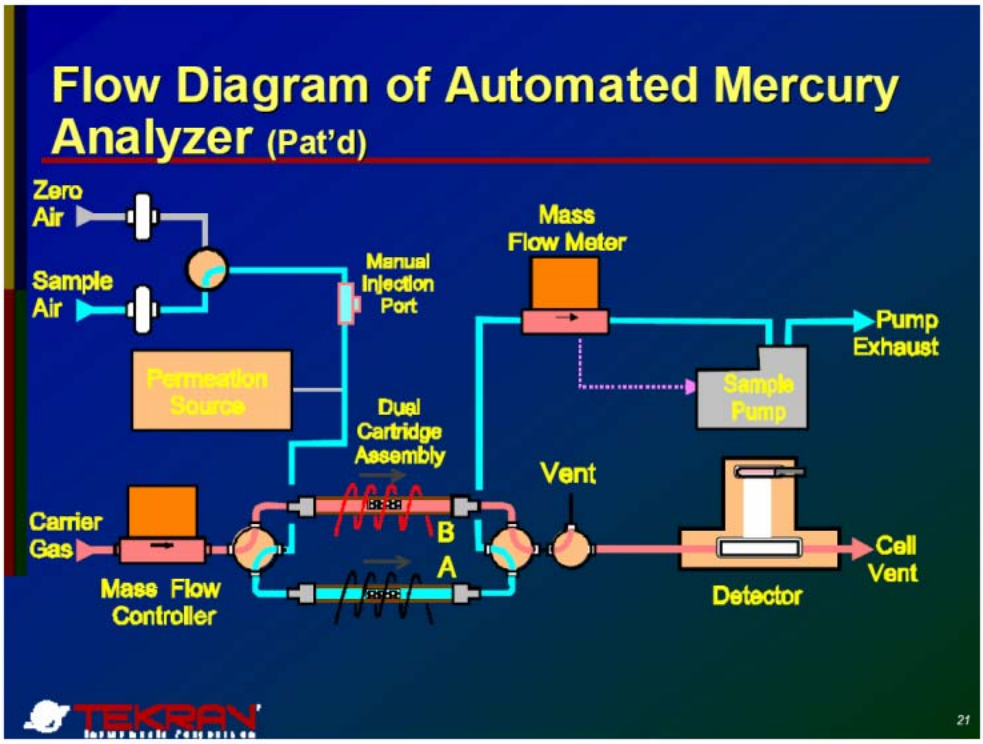
20


Flow Diagram of Automated Mercury Analyzer (Pat'd)
Zero Air
Sample Air
Manual Injection Port
Mass Flow Meter
Pump Exhaust
Permeation Source
Dual Cartridge Assembly
Sample Pump
Vent
Carrier Gas
B
A
Cell Vent
Mass Flow Controller
Detector
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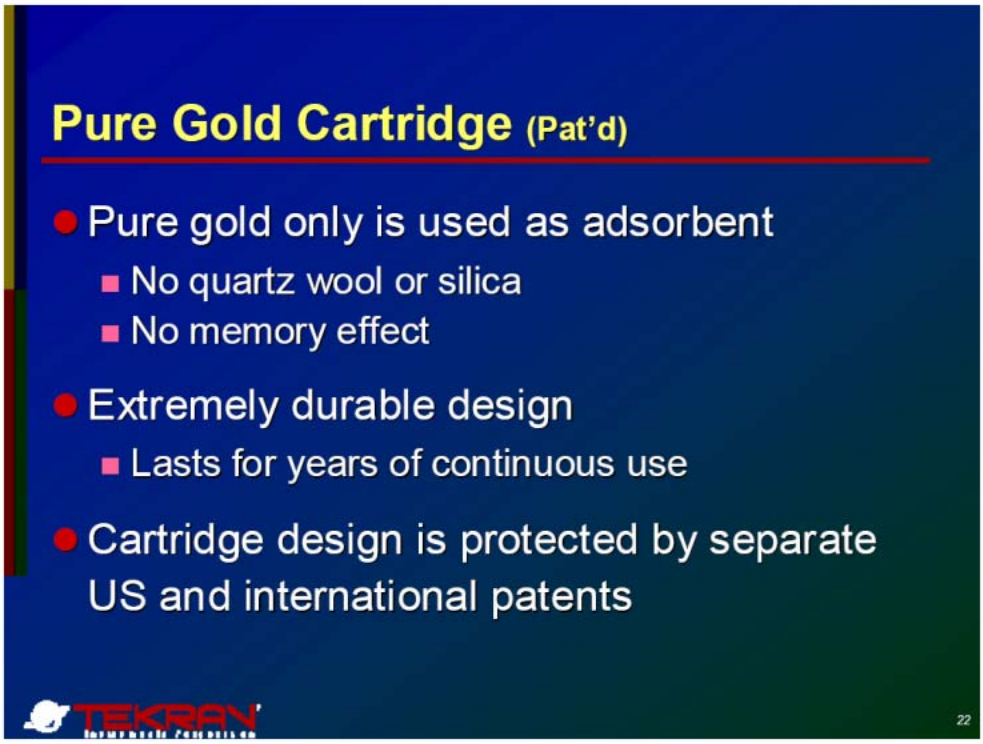
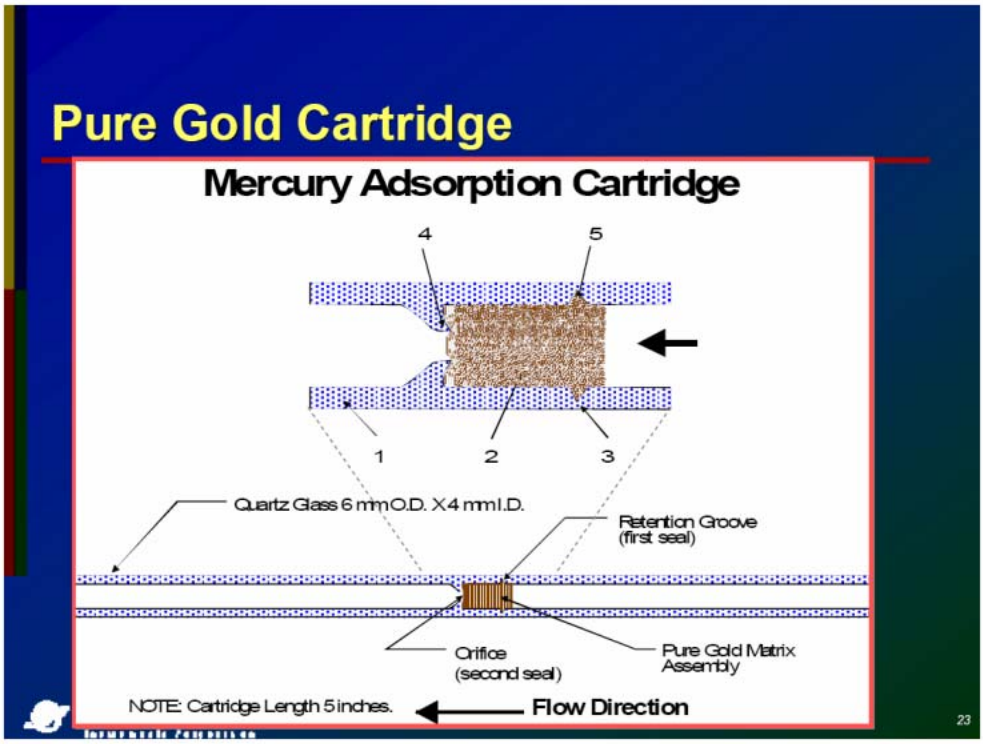
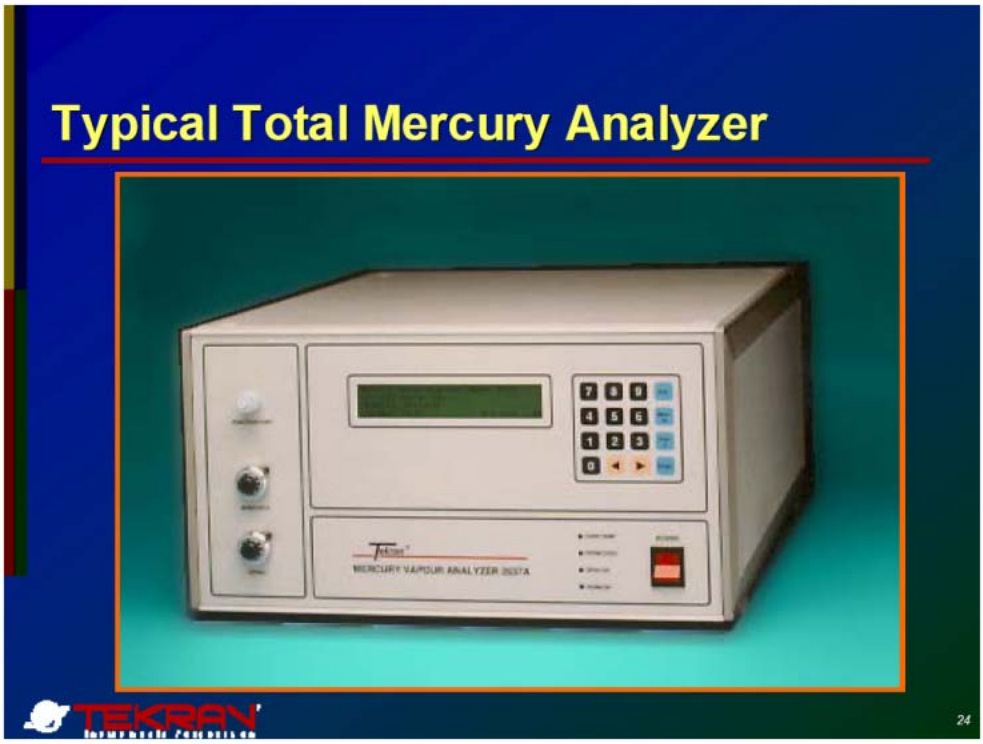
21


Pure Gold Cartridge (Pat'd)
Pure gold only is used as adsorbent
No quartz wool or silica
No memory effect
Extremely durable design
Lasts for years of continuous use
Cartridge design is protected by separate US and international patents
TEKRAN
22


Pure Gold Cartridge
Mercury Adsorption Cartridge
4
5
1
2
3
Quartz Glass 6 mm O.D. X 4 mm I.D.
Retention Groove
(first seal)
Orifice
(second seal)
Pure Gold Matrix
Assembly
NOTE: Cartridge Length 5 inches.
Flow Direction
23


Typical Total Mercury Analyzer
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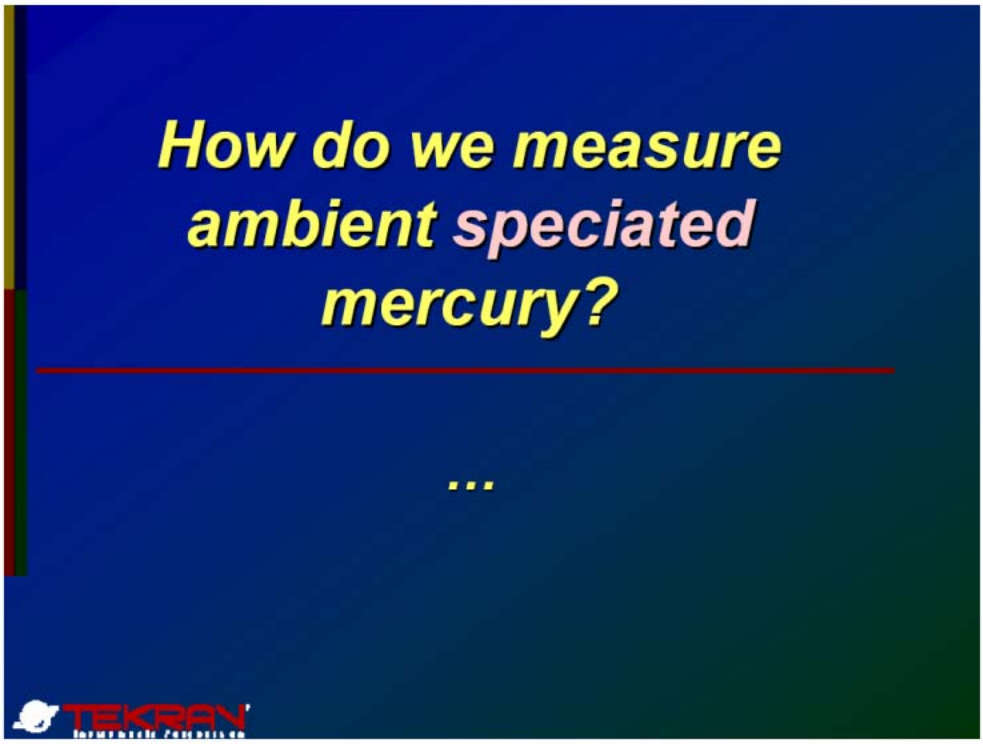
24


How do we measure ambient speciated mercury?
...
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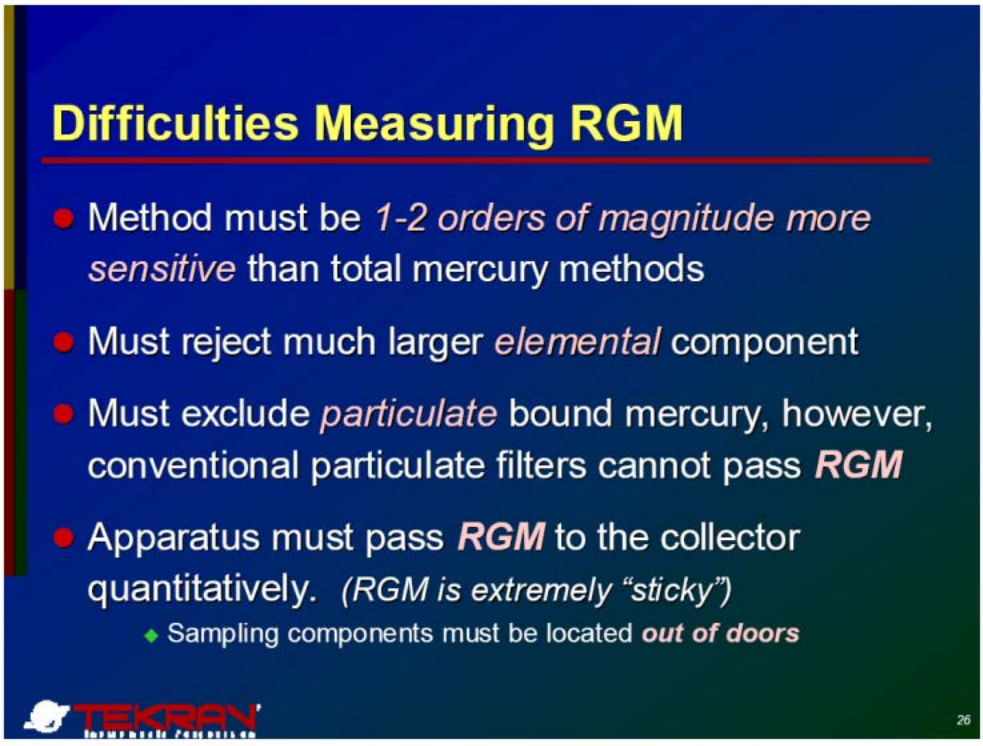
Difficulties Measuring RGM
Method must be 1-2 orders of magnitude more sensitive than total mercury methods
Must reject much larger elemental component
Must exclude particulate bound mercury, however, conventional particulate filters cannot pass RGM
Apparatus must pass RGM to the collector quantitatively. (RGM is extremely "sticky")
Sampling components must be located out of doors
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RGM Monitoring - Principles of Operation

- Automated RGM monitoring instrumentation now exists
  - Quartz, KCl coated annular denuder is thermally desorbed and regenerated
  - Sampling Phase
    - Absorbs RGM while passing all elemental and particulate Hg
    - Model 2537A reads ***Hg^0*** during this phase
  - Desorption/Analysis Phase
    - Denuder heated to 500 °C
    - RGM released as ***elemental*** mercury

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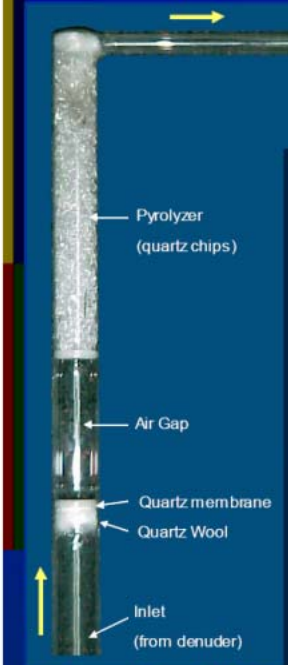
27

Hg^P Monitoring – Principles of Operation



- Sampling Phase
  - Sample passes through impactor to eliminate coarse particles
  - Coated denuder captures RGM and eliminates it *before* passing sample gas to particulate collector
  - Quartz, regenerable particulate filter (***RPF***) captures fine fraction (***< 2.5 um***) particulates
- Desorption/Analysis Phase
  - Zero air used as carrier
  - Downstream ***pyrolyser*** is activated first
  - RPF is then heated to desorb captured particulates

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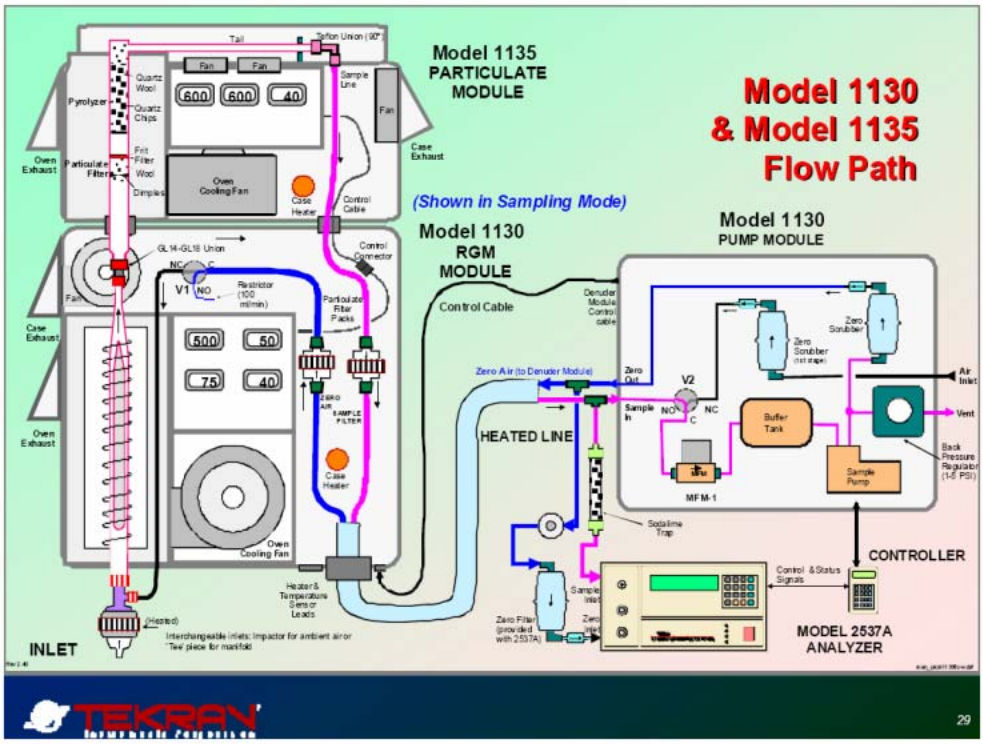
28


Model 1135
PARTICULATE
MODULE
Model 1130
& Model 1135
Flow Path
(Shown in Sampling Mode)
Model 1130
RGM
MODULE
Model 1130
PUMP MODULE
Control Cable
HEATED LINE
CONTROLLER
MODEL 2537A
ANALYZER
INLET
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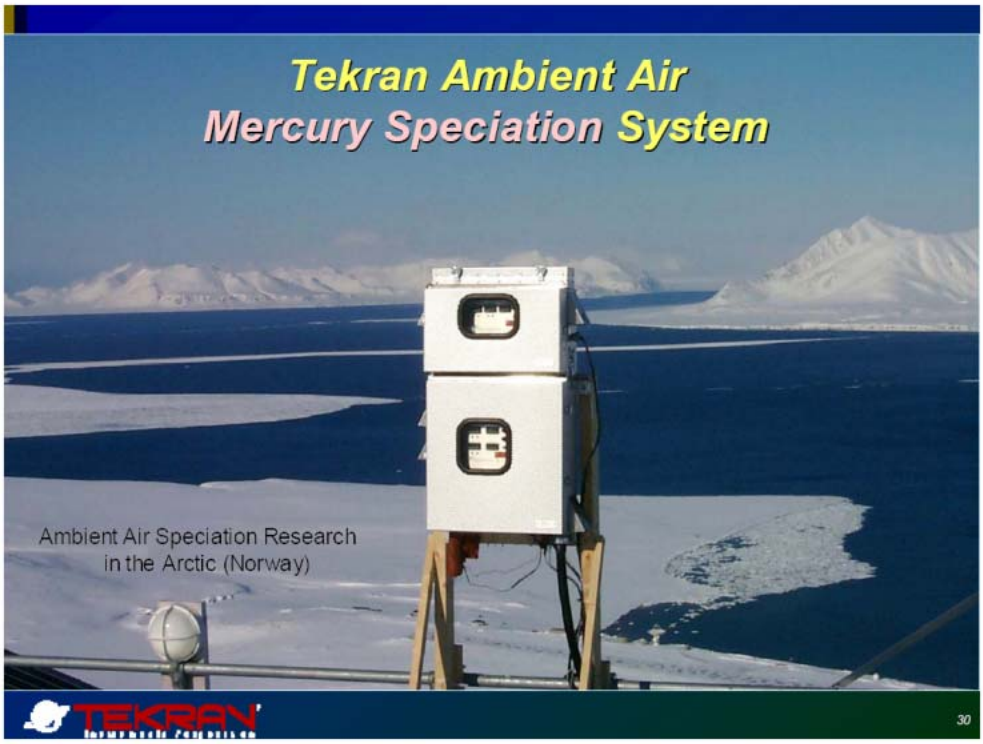
29


Tekran Ambient Air
Mercury Speciation System
Ambient Air Speciation Research
in the Arctic (Norway)
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30

Sample Mercury Results

Do these very low mercury levels actually have any measurable effects?

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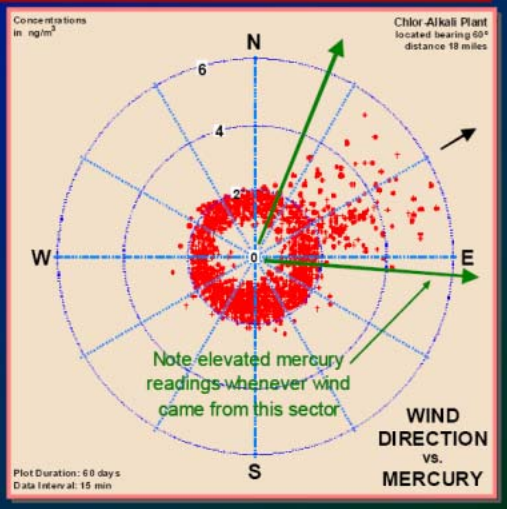
Sample Hg^0 Data: Chlor-Alkali Plant

Plot of wind direction vs. ambient mercury values

- Two months of continuous monitoring
- Plant is located 18 miles to the north-east
- Fish consumption advisories in effect
  - Global background: ~1.7 ng/m³
  - Bio-accumulation is non-linear: Even slight increases in background levels cause large increases in the concentrations of biota
  - Fish levels in this area were > *1.5 ppm* even though air readings were only slightly elevated
  - Eating too much fish with these concentrations may cause irreversible neurological damage



This bio-accumulation is due to RGM!

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1
32

Case Study: Florida Everglades

- Had been found in early 1990's to be severely contaminated with mercury
  - Case of senior predators (panther) dying of mercury poisoning
- Years of sampling 'total mercury' did not reveal causes of problem
  - Total mercury numbers were not significantly elevated above other, non-affected areas

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33

Florida Everglades Crisis

- Tests using the ***Model 1130*** confirmed that virtually all mercury deposition in the Everglades was due to RGM from nearby sources. *(Landis et. al. 1998)*

RGM emission controls were placed on Florida sources. Decreases in the levels of mercury contamination in the Everglades have already been observed. *(Atkeson, 2003)*

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34

Polar Mercury Depletion Events

- Discovered in Alert, Canada in early 1990's
  - Sudden disappearance of elemental mercury over short time scales
  - Starts: After polar sunrise
  - Ends: After snow melt
  - Transformations are occurring locally
- Subsequent studies using Tekran automated equipment:
  - Confirmed that mercury was being oxidized and partitioning into either gaseous and particulate phases
- Phenomenon has since been observed in ***all*** polar regions around the globe, both Arctic and Antarctic

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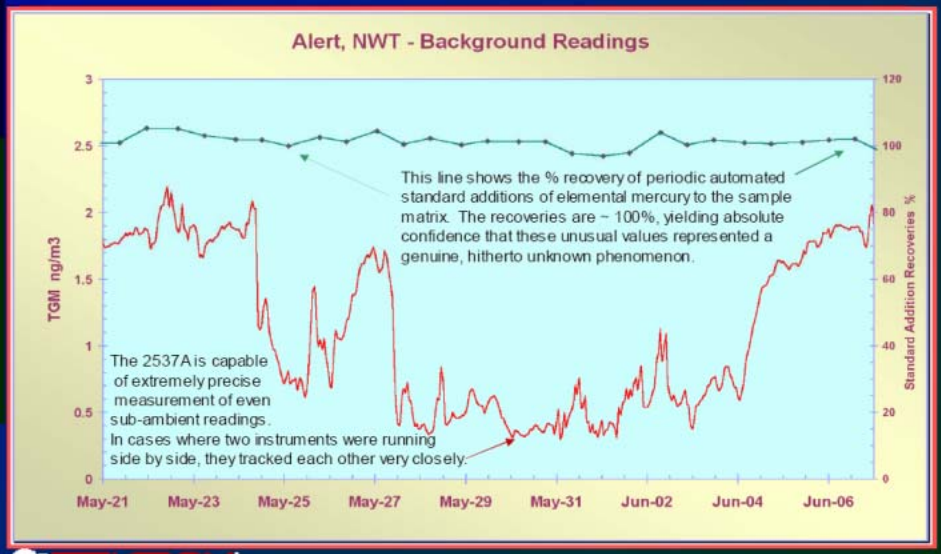
35

Depletions of Elemental Mercury in Alert, Nunavut (Canada)



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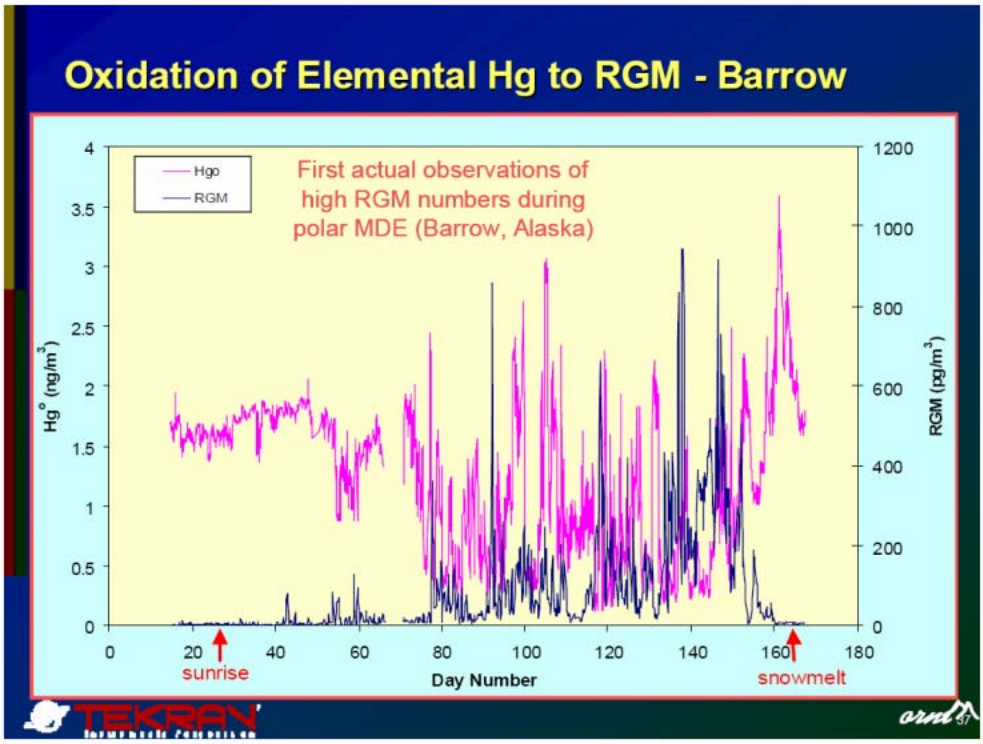
36


Oxidation of Elemental Hg to RGM - Barrow
Hgo
RGM
First actual observations of high RGM numbers during polar MDE (Barrow, Alaska)
Hg° (ng/m³)
RGM (pg/m³)
Day Number
sunrise
snowmelt
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In
Summary
...
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Further Topics - Mercury Monitoring

- The preceding is just an overview. There are many topics that have not even been addressed in the foregoing presentation. e.g.
  - *Calibration* of mercury instrumentation
  - NADP (National Atmospheric Deposition Program)
    - Network measuring deposition of Hg in precipitation *(collection and lab analysis)*
    - Soon to measure RGM and Hg^P and Hg^0
      http://nadp.sws.uiuc.edu/mtn/
  - Global mercury transport and species interconversion
  - Measurement of mercury in flue gas

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39

References

1. Landis, Stevens, Prestbo and Schaedlich, (2002) Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air, *Env. Sci and Technol.*, 36:3000
2. Ebinghaus R., Jennings S.G., Schroeder W.H., Berg T., Buttermore L., Donaghy T., Ferrara R., Guentzel J., Kenny C., Kock H.H., Kvietkus K., Mazzolai B., Mühleck T., Munthe J., Prestbo E.M., Schneeberger D., Sommar J., Urba A., Wallschläger D. and Xiao Z. (1997) "International Field Intercomparison Measurements of Atmospheric Mercury Species at Mace Head, Ireland," *Atmos. Environ.*, 33:3063
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4. Weiss-Penzias P., Jaffe D.A., McClintick A., Prestbo E.M. and Landis M.S. (2003) "Gaseous elemental mercury in the marine boundary layer: evidence for rapid removal in anthropogenic pollution," *Environ Sci Technol.* 37(17):3755-63
5. Munthe, Wängberg,Pirrone, Iverfeldt, Ferrara, Ebinghaus, Feng, Gårdfeldt, Keeler, Lanzillotta, Lindberg, Lu, Mamane, Prestbo, Schmolke, Schroeder, Sommar, Sprovieri, Stevens, Stratton, Tuncel and Urba (2001) "Intercomparison of methods for sampling and analysis of atmospheric mercury species." *Atmos. Env.* 35:3007.
6. Lyman, S.N., Gustin M.S., Prestbo E.M. and Marsik F.J. (2007) Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods, *Environ. Sci. Technol.* 41:1970.
7. Friedli H.R., Radke L.F., Prescott R., Hobbs P.V. and Sinha P. (2003) Mercury emissions from the August 2001 wildfires in Washington State and an agricultural waste fire in Oregon and atmospheric mercury budget estimates, *Global Biogeochemical Cycles*, 17:1039.
8. Lynam M.M. and Keeler G.J. (2006) Source–receptor relationships for atmospheric mercury in urban Detroit, Michigan, *Atmospheric Environment*, 40:3144.
9. Poissant L., Pilote M., Xu X. and Zhang H. (2004) Atmospheric mercury speciation and deposition in the Bay St. Francois wetlands *J. Geophys. Res.* 109:11301
10. Yatavelli R.L.N., Fahrnia J.K., Kim M., Crist K.C., Vickers C.D., Winter S.E. and Connell (2006) Mercury, PM2.5 and gaseous co-pollutants in the Ohio River Valley region: Preliminary results from the Athens supersite, *Atmospheric Environment* 40:6650.

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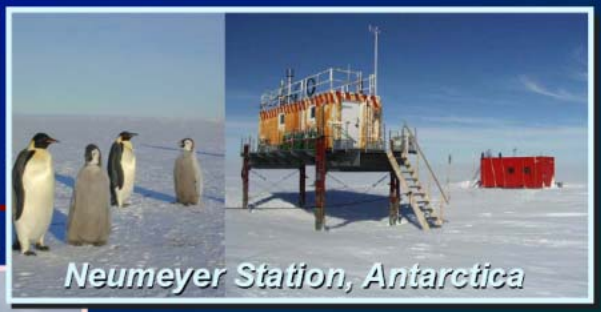
40

Mercury Research Continues …



- *Researchers around the world are still busy trying to solve basic issues regarding mercury transport, deposition and cycling*

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For More Information

Contact *fschaedlich@tekran.com*

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42

Monitoring Emissions from Animal Feeding Operations

Steven Trabue[1], Hong Li[2], Robert Burns[2], and Hongwei Xin[2]
[1]USDA Agricultrual Research Service, National Soil Tilth Laboratory
[2]Iowa State University, Department of Biosystems and Agricultural Engineering

ABSTRACT

The EPA air consent agreement with animal feeding operations (AFO) specifies the use of EPA TO-15 for the speciation of VOCs emitted from these facilities. Sorbent tube sampling may be a more effective technique in the speciation of VOCs from AFOs due to its ability to capture both volatile and highly polar compounds. The technique is limited by the types of sorbent material used and ambient air matrix (temperature, relative humidity and dust levels). In particular, relative humidity (RH) affects both field sampling and analysis of air samples. The objectives of this study were to determine the effect RH had on the recovery and analysis of various compounds emitted from AFO using different sorbent materials (Tenax, graphitized carbon, and carbon molecular sieves) and report major compounds detected from a poultry facility. Test atmospheres were generated at ambient temperatures (23 $\pm$ 1.5°C) and 25, 50, and 80% RH. A custom designed sorbent tube containing graphitized carbon materials performed best with quantitative recovery of most compounds tested for all RHs and sampling volumes tested. Tenax sorbent tubes gave quantitative results for most compounds except acetic acid. Sorbent tubes with carbon molecular sieve (CMS) material performed poorly at both 50 and 80% RH due to excessive sorption of water. Major compounds detected at a poultry facility included volatile fatty acids, carbonyl or oxy containing compounds and phenolic compounds most of which would be difficult to measure using canister based sampling techniques.

INTRODUCTION[1]

The report by the National Research Council (NRC) highlighted the need for more research in the area of animal emission (1). In fact, this report was a major basis for the EPA's animal feeding operations (AFO) consent agreement referred to as Air Compliance Agreement (2). The NRC report highlighted the need for standardized protocols for sampling and analysis of volatile organic compounds (VOC), but offered little guidance. While the Air Compliance Agreement does give guidance in terms of sampling protocol, the method it specified, TO-15, may not be the best choice for agricultural VOCs or sampling in agricultural environments. Compounds typically associated with AFO are semi-volatile and polar (3-5) two properties that limit the effectiveness of TO-15 for use in speciation of VOCs in air. Weaknesses in using TO-15 for monitoring AFO include poor recovery of polar compounds (6) and potential loss of polar compounds due to water condensation in canister or during sampling (7).

[1] Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the USDA or ISU and does not imply approval to the exclusion of other products that may be suitable.

An alternative sampling method that may capture many of these polar compounds is EPA TO-17 and this method has previously been used in a number of air quality studies monitoring AFOs (3,4, 8-10). However, sorbent tubes also have a weakness when sampling in humid environments with excess water sorption limiting quantitation (8). This weakness can be mitigated by techniques that can minimize water sorption during sampling (11-12) and post sampling (11) or the use of hydrophobic sorbents during sampling. The purpose of this study is to report the use of EPA TO-17 for speciation of VOCs from a poultry facility. This work investigates water sorption on sorbent tubes during sampling, techniques and sorbents used to minimize water sorption, and recovery of compounds typically associated with AFO during sampling. In addition, the speciation of VOC emitted from a poultry facility using sorbent tubes is reported.

MATERIALS AND METHODS

Method Validation

The following method validations were performed: 1) safe sampling volume (SSV) and 2) storage stability. The SSV for the sorbent tubes was tested by loading sorbent tubes with reference standards and challenged sorbent tubes with 12 L of air (nitrogen). Storage stability of volatile fatty acids, phenols and indoles were tested by loading known quantity of a reference standard mix onto 10 sorbent tubes. Sorbent tubes were immediately stored in freezer (< 25°C) prior to analysis. Following storage, sorbent tubes were analyzed along with sorbent tubes that were recently (less than 1 day) loaded. Due to the number of compounds detected and the exploratory nature of this study, it can only be assumed that the other compounds behaved similarly in terms of storage stability.

Air Sampling

All samples were collected on glass sorbent tubes (178 x 6 mm diameter). Four types of sorbent tubes were used: 1) Custom tube containing sorbent packing of Carbopack C and Carbopack X (1:2 ratio v/v); 2) Tenax tubes (includes by Tenax TA and Tenax GR); 3) Carbotrap 300™ (Supelco, Inc., Bellafonte, PA) multi-bed containing (Carbopack C:Carbopack B: Carbosieve S-III); and 4) Custom tube containing a sorbent packing of Tenax TA and Carboxen 569 (1:1 ratio v:v). Characteristics of each sorbent material are shown on Table 1. Air samples from the laboratory and poultry facility were sampled at 100 mL min^{-1} for 12 L (sampling time approximately 2 hours). Sampled sorbent tubes were stored at ambient temperatures within the sampling turrent of the GS1 gas sampler (Gerstel, Inc, Baltimore, MD) and placed into sample tube holders and stored (<-20°C) until analyzed. All samples were analyzed within 30 days of the time they were sampled in the field.

Table 1: Properties of tested sorbents

Adsorbent	Adsorbent Class[a]	Mesh Size[b]	Surface Area[b] $m^2\ g^{-1}$ material	Water Saturation Capacity[c] mg water g^{-1} material
Carbosieve S-III	CMS	60/80	820	200.5
Carboxen-569	CMS	20/45	400	280.1
Carbopack-B	GCB	60/80	100	<1.2
Carbopack-C	GCB	60/80	10	<0.5
Carbopack-X	GCB	60/80	240	-
Tenax TA	POP	60/80	35	<3.3
Tenax GR	POP	60/80	24	<2.0

[a]CMS: carbon molecular sieves, GCB; graphitized carbon black, POP; porous organic polymers. [b]Manufacturer's data. [c]Reference 11

Water Sorption

Sorbent tubes were connected to a Teflon cylindrical manifold (i.d., 4.1 cm, Savillex, Co., Minnetonka, MN) maintained at ambient temperatures (23°C±2) and pressures. Humidified air was introduced into the manifold using zero grade air passing through an Alpha-MOS 720 (Alpha-MOS, Hanover, MD) sampling chamber. Total flow in the manifold system was set at 5 L min^{-1} and relative humidity set at 25, 50, and 80%. The relative humidity and temperature of the diluting zero grade air was verified at the end of the manifold using Traceable® Hydrometer/Temperature recorder (Fisher Scientific, New Castle, DE). Sorbent tubes were connected to the manifold and air flow from the manifold to each sorbent tube was controlled using a field gas sampler (GS1, Gerstel, Inc, Baltimore, MD). The GS1 collected samples at 100 mL min^{-1} for 2, 4, 6, and 12 L. Each sorbent tube was weighed before starting the experiment and after passing the predetermined volume of humidified air through the sorbent tube with total water sorbed determined by difference.

Two water sorption mitigation techniques were tested on sorbent tubes containing carbon molecular sieve (CMS) material. The first technique involved heating sorbent tubes to 40°C (approximately 15°C above ambient temperature) during sampling. The second method was a dry purge technique using nitrogen gas to remove excess water from the sorbent tube following sampling. The technique involved attaching sorbent tubes to an ATIS™ system (Supleco, Inc., Bellafonte, PA) in which a dry nitrogen stream of gas was flushed through the sorbent material at 100 mL min^{-1} for 2 L.

Field Sampling

Poultry House: The commercial broiler house where air samples were taken had a dimension of 13.1 x 155.5 m (43 x 510 ft) and an east-west orientation. Mechanical ventilation of the house was achieved by either sidewall fans (four, 0.9-m diameter) or tunnel fans (10, 1.2-m diameter), depending on the climate and bird age. Rice hull was used as the bedding material. After each flock, caked litter (mixture of bedding and manure) along the drinker and feed lines was

removed. The GS1 samplers were placed on the litter floor and samples collected at 100 mL min^{-1} for 12 L with sample tubes being transported to the laboratory for analysis in less than 18 hours. During sample collection, air temperature was 25°C with an RH of 50%.

Analytical Analysis

Reference Standards and Calibration

All reference chemicals were purchased from either Aldrich (Sigma-Aldrich, St. Louis, MO), Fluka (Sigma-Aldrich, St. Louis, MO), Fisher Scientific (Thermo Fisher Scientific, Waltham, MA), or Cole Palmer (Cole-Parmer Instrument Company, Vernon Hills, IL) with a minimum purity of 97% or greater (GC grade). Methanol and Water used to dilute reference standards were HPLC grade and were purchased from Sigma-Aldrich and Burdican and Jackson (Mustegon, MI), respectively.

Calibration curves were generated using external standards loaded onto sorbent tubes using an ATIS™ system. The ATIS™ system was maintained at 110°C and purged with nitrogen at 100 mL min^{-1} for a minimum total volume loading of 250 mL (five times volume of ATIS™ holding tube). A minimum of a four point calibration curve was generated for each compound. However several compounds were quantified off calibration curves generated from other compounds this included: 3-hydroxy-2-butanone (2-butanone)[2]; dimethyl sulfone (sulfone); and itaconic acid ethyl ester (diethyl ethylindenmalonate).

Sorbent Tube Analysis

Sorbent tubes were analyzed by thermal desorption (TDS) using an Agilent 6890N GC (Agilent Technologies, Inc.). Two different 6980N GC instruments were used one contained only a 5973N Inert MSD (Agilent Technologies) the other 5975N Inert MSD (Agilent Technologies). Both GC systems used a Gerstel TDSA (Gerstel, Inc., Baltimore, MD) as its TDS unit, each were equipped with PTV (programmed temperature vaporizer) inlets (CIS 4, Gerstel, Inc.) and both separated compounds on a 30m x 0.25mm x 0.25µm FFAP column (J&W Scientific, Inc., Wilmington, DE) using a helium gas set at a maximum of 1.2 mL min^{-1} constant flow. Thermal desorption (TDS) parameters were the following: splitless mode; initial temperature, 60°C; final temperature, 300°C; initial time 0.5 min; final hold time 3 min; ramp, 60°C min^{-1}; with a transfer line temperature of 320°C. The inlet was packed with glass bead/Carbopack C material with the following parameters: solvent vent mode; initial temperature, 30°C, final temperature, 320°C, initial time, 0.2 min, final time, 3 min; ramp, 12°C sec^{-1}, vent flow 20 mL min^{-1}, and purge split flow 20 mL min^{-1}. The GC instrument oven temperature program was: 1) initial temp, 45°C hold 0.05 min; 2) ramp 10°C min^{-1} to 220°C; and 3) ramp 50° C min^{-1} to 240°C and hold 5 min.

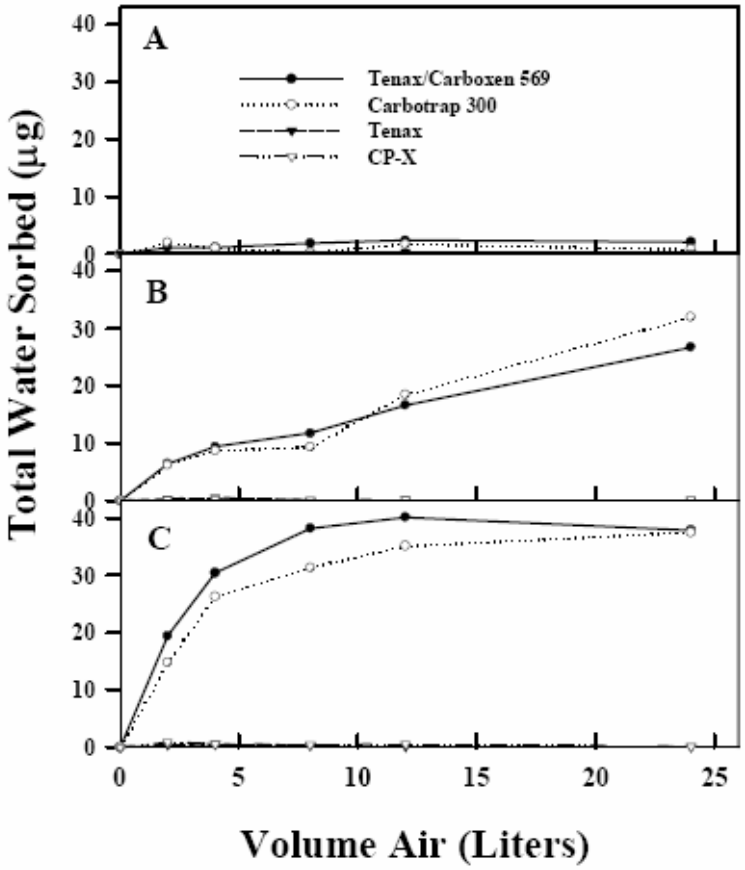
[2] Compound in the parenthesized is surrogate compound used

RESULTS AND DISCUSSION

Water Sorption

The type of sorbent material used had a significant effect on the amount of water sorbed during sampling as did the test atmosphere's relative humidity and total volume of air sampled (Figure 1). Sorbent tubes containing CMS material sorbed significantly more water than tubes containing either Tenax or Carbopack material. There was no significant difference in water sorption between sorbent tubes containing Tenax material or Carbopack material. Relative humidity conditions had a significant effect on water sorbed for CMS material but no affect on either Tenax or Carbopack material. Total volume of air sampled had a significant effect on water sorbed for CMS material but no affect on either Tenax or Carbopack material. Water sorption on CMS containing material is well documented (11-13) with relative humidity conditions controlling sorption. In fact, Gawrys et al. (12) determined that relative humidity conditions between 30-45% as the critical junction for increased water sorption on CMS material.

Figure 1: Sorption of Water on Various Sorbent Tubes



A) 25% RH (relative humidity); B) 50% RH; and C) 80% RH.

In this study, our results mirror these finding since tubes containing CMS material sorbed little water at 25% RH while significantly more water was sorbed at 50 and 80% RH (Figure 1). Kimura et al (14) have shown this increased sorption is due to cluster formation on surfaces at these higher RH which leads to greater sorption and eventual pore water filling of the CMS. Given that RH conditions inside animal production facilities is typically maintained at around 50% (15) with outside summer condition at many of these facilities above 70% (3,4, 10, 16), the use of sorbent tubes containing CMS should be avoided since excess sorption of water on sorption tubes is known to affect the sampling and analysis of sorbent tubes (17).

Studies by Helmig et al. (11) and Gawrys et al. (12) have demonstrated techniques such as heating sorbent tubes during sampling or dry purging of sorbent tubes following sampling can significantly reduce the amount of water sorbed. In this study, we tried both methods of water mitigation. Sorbent tubes heated to 40°C during sampling reduced water sorption by more than 87%, while sorbent tubes dry purged with 2 L of nitrogen removed over 38 µL of water. It should be noted that removal or prevention of water sorption does result in the loss of some compounds. Heating of sorbent tubes during sampling resulted in the loss of acetic acid (68% recovery), but recovery of all other compounds tested was 98%. Dry purging of sorbent tubes resulted in the loss of acetic (51% recovery), propanoic (45% recovery), and 2-methyl propanoic acids (85% recovery) with an overall recovery of all other compounds tested of 98%. This indicates that heating of sorbent tubes is a better sampling practice than dry purging of tubes containing CMS material in humid environments.

Sampling Validation

Due to problems associated with excessive water sorption, sorbent tubes containing CMS material were not tested for their capacity to retain standards under various RH conditions and sample volumes. Relative humidity had a significant impact on the performance of the sorbent tubes containing Tenax material; however, the impact was only on the trapping efficiency of acetic acid (Table 2). At RH of 80%, Tenax (Tenax TA) and graphitized Tenax (Tenax GR) tubes gave excellent recoveries for most of the VFAs compounds tested averaging 97.5% (Table 2). However, recovery of acetic acid was less than 50% for both Tenax sorbent tubes, and its measure of reproducibility was lower than the other VFAs with an RSD average value of 19.2% (Table 2). At 50% RH, Tenax sorbent tubes gave excellent results again for all compounds except acetic acid with an average recovery of 97% (excluding acetic acid). At 25% RH, recovery was excellent for all VFA except acetic acid with an average recovery of 90%. Due to the loss of acetic acid larger sampling volume of more than 2 L was not attempted on Tenax sorbent tubes.

Relative humidity did not have a significant impact on the performance of the Carbopack C/Carbopack X (CP-X) sorbent tubes (Table 3). Recovery of VFA on CP-X sorbent tubes averaged 91% over all RHs with an average RSD value of 5%. The RSD value for acetic acid was significantly higher than the other VFAs averaging 12% compared to 4% for all other VFA. Consequently, analysis of samples was excellent with good reproducibility. Higher sampling volumes of 6 and 12 L were also tested with these tubes. Since RH did not affect recovery of VFAs on CP-X tubes, SSV for 12 L were tested at 50% RH only.

Table 2: Recovery (%) of Volatile Fatty Acids after Passage of 2 L of Humidified Air

Volatile Fatty Acids	Sorbent Tube					
	Tenax TA		Tenax GR		CP-X[a]	
	Recovery	RSD[b]	Recovery	RSD	Recovery	RSD
	80% Relative Humidity					
acetic acid	47.8	22.9	46.4	15.6	94.3	14.1
propanoic acid	118.1	3.9	86.5	5.1	103.1	6.9
2-methyl propanoic acid	116.8	4.0	97.0	3.3	95.0	1.7
butanoic acid	112.6	2.7	96.7	3.5	92.9	2.8
3-methyl butanoic acid	110.6	3.8	102.8	3.1	95.8	4.6
pentanoic acid	102.4	3.9	98.0	4.0	93.6	2.2
	50% Relative Humidity					
acetic acid	19.4	14.6	29.0	8.8	97.9	18.5
propanoic acid	90.3	3.3	103.6	6.8	92.9	8.5
2-methyl propanoic acid	87.1	3.9	104.1	6.5	86.7	7.8
butanoic acid	94.2	1.9	105.9	4.7	90.1	0.9
3-methyl butanoic acid	94.1	1.9	105.8	4.7	89.5	1.1
pentanoic acid	92.2	3.1	100.0	4.9	93.1	3.0
	25% Relative Humidity					
acetic acid	23.6	31.8	ND[c]	-	96.2	2.4
propanoic acid	90.0	2.2	ND	-	85.1	2.1
2-methyl propanoic acid	89.5	2.2	ND	-	82.0	4.7
butanoic acid	91.0	2.7	ND	-	81.6	3.2
3-methyl butanoic acid	91.9	1.9	ND	-	84.1	2.4
pentanoic acid	89.5	3.6	ND	-	84.4	3.8
	Dry					
acetic acid	15.9	16.7	ND	-	ND	-
propanoic acid	84.7	1.7	ND	-	ND	-
2-methyl propanoic acid	81.1	3.9	ND	-	ND	-
butanoic acid	81.0	2.6	ND	-	ND	-
3-methyl butanoic acid	83.6	1.9	ND	-	ND	-
pentanoic acid	83.6	3.2	ND	-	ND	-

[a]CP-X (Carbopack C/Carbopack X). [b]RSD (relative standard deviation). [c]ND (not determined)

Total recovery of VFAs, phenols, and indole was excellent averaging 94% (84-102%). Consequently, CP-X sorbent tubes were chosen for monitoring of emissions from a poultry facility.

Speciation of VOCs from Poultry Facility

Table 4 is a list of the most abundant compounds identified by GC/MS using sorbent tubes. Acetic acid was by far the most abundant compound emitted from poultry facility. Its concentration is four times that of 2,3-butodione, which is the next most abundant compound emitted. In fact, the top six compounds compromised close to 80% of the quantifiable material on sorbent tubes. Two major chemical classes were associated with sorbent tubes volatile fatty acids (63%) and oxy compounds (21%). The volatile fatty acids were expected since they have been associated with AFO, but the importance of the oxy compounds was unexpected since these compounds are not typically reported in air quality studies with AFO. The highest concentration of compounds was detected in the region of the building with an active flock (SW1). A curtain was placed in the portion of the building separating SW1 from SW3 and Tunnel ventilated portion of the building. The concentration levels of the different compounds varied more spatially than temporally.

Table 4: Concentrations of Top 20 Volatile Organic Compounds Detected from Poultry Facility Using TO-17

Compound	Overall	SW1	SW3	Tunnel
	$\mu g\ m^{-3}$			
Acetic Acid	773.9	1936.7	457.9	138.0
2,3-Butandone	187.8	309.7	119.6	147.5
Butanoic Acid	62.2	164.2	29.5	10.3
Dimethyl disulfide	57.0	121.9	27.2	30.7
3-Hydroxyl-2-butanone	52.9	167.5	2.2	0.8
2-Methyl-3-Pentanone	50.1	83.2	26.3	43.2
Propanoic acid	39.7	112.3	13.6	5.1
3-Methyl butanoic acid	35.9	100.4	11.0	6.1
Hexane	34.3	50.5	39.9	19.3
Tetramethyl pyrazine	23.9	66.9	7.3	4.1
2-methyl propanoic acid	22.6	74.2	5.9	2.6
Trimethyl Oxzaole	21.8	67.3	1.7	0.9
Acetamide	21.6	50.3	15.6	7.0
2-Butanone	19.2	42.0	12.9	6.9
Dimethyl sulfone	17.0	31.1	12.0	10.1
Indole	16.9	55.8	0.5	0.6
Pentanoic acid	15.1	41.9	5.3	5.1
Dodecane	14.2	21.9	18.0	7.8
Benzene	13.9	13.5	19.5	10.0
Diethyl ethylindenmalonate	13.1	17.1	15.6	8.3
4-Methyl phenol	9.3	19.3	10.2	1.2

CONCLUSION

We determined that sorbent tubes containing Carbopack X material was superior to other sorbent material if sampling in humid environments. Techniques that reduce the sorption of water while effective at lowering the water content of the sorbent material also lose the more volatile compounds. It was determined that thermal desorption is an excellent technique to use when quantifying semi-volatile compounds emitted from AFOs. The major compounds detected at a poultry facility were volatile fatty acids and oxy compounds with the areas of the facility containing an active flock having higher concentration of compounds than portions of the facility containing no birds.

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Monitoring VOC Emissions from Animal Feeding Operations (AFO)

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Outline

- Background Information
- Method Development TO-17
- Speciation of VOC TO-17
- Comparison of TO-17 vs TO-15

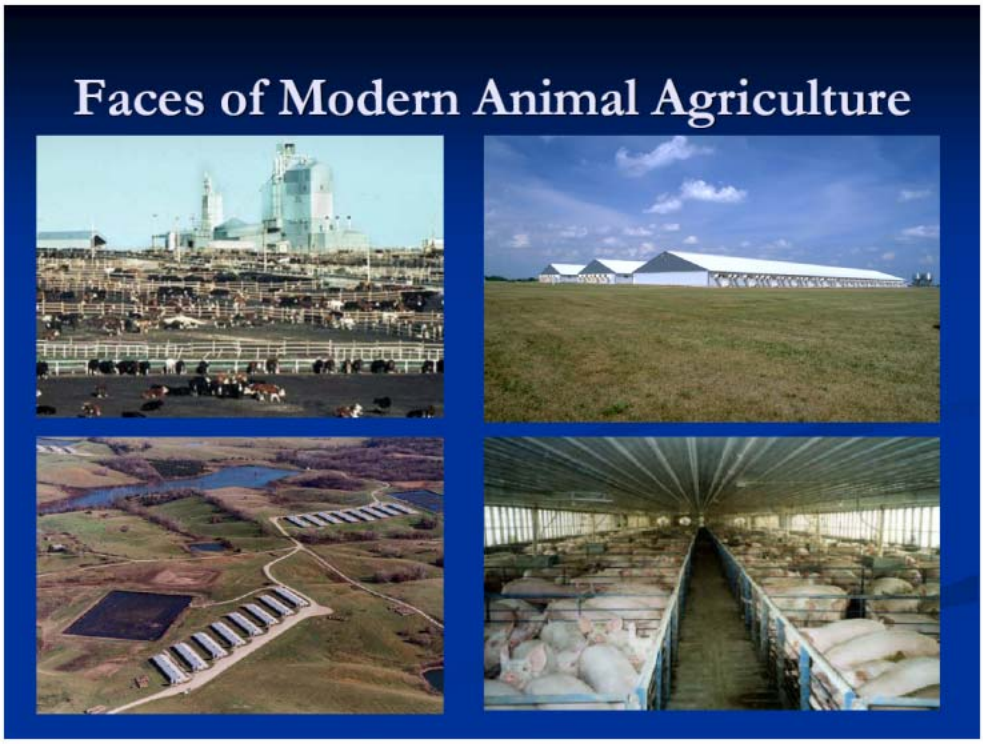
Animal Agriculture

Major Changes in last several decades

- 1982-2002 Total Number of AFOs fell by 25%[1]
  - Total number cattle: -9%
  - Total number dairy cows: -15%
  - Total number of swine: 9%
  - Total number of meat birds: 143%

Total No.	1982-2002	Large AFO	Last 5 Years
Poultry	6%	99%	17%
Swine	-73%	70%	29%
Dairy	-67%	35%	49%

[1]USDA, National Agricultural Statistical Service, 2002 Census


Faces of Modern Animal Agriculture

EPA's Air Compliance Agreement

Purpose: determine if AFOs are in compliance with various EPA regulations

- Clean Air Act
- Release Reporting Requirements
  - Comprehensive Environmental Response, Compensation and Liability Act (Superfund)
  - Emergency Planning and Community Right-to-Know Act

VOC Emission Methodology

National Research Council (2003)[1]

- More research needed
- Lack of standardized methods in sampling and analysis of VOCs
- Offered little in terms of guidance
- Methods described were validated with stable, non-polar hydrophobic compounds associated with industrial pollutants

[1]NRC. Air emission from animal feeding operations current knowledge future needs.

EPA Air Compliance Agreement[2]

- Nonmethane Hydrocarbon (NMHC)
  - EPA Method 25A (FID)
- Speciation of VOC based off TO-15 canister
  - Top 20 compounds

[2]Fed. Regist. 2005 70:4958-4977

Agricultural Air Quality Studies

Major VOC Categories from AFOs[1]

1. Organic Acids
2. Alcohols
3. Carbonyl/Ketones
4. Phenols
5. Sulfides

[1]Blunden et al. 2005 Atmos Environ.; Zahn et al. 1997, 2001 J. Environ. Qual.; Schiffman et al. 2001 Agric. For. Meteorol.; Rabud et al. 2003 Atmos. Environ. and Filipy et al. 2006 Atmos. Environ.

Physical chemical properties of VOCs

1. **Range of Volatility**
2. **Reactivity**
3. **Polarity**
4. **Sorption to surfaces**

Method Development

EPA TO-17

Sorbent Tubes

Zahn et al. 1997 J. Environ. Qual.

1. Demonstrated the effectiveness of using sorbent tubes for analysis of agricultural emissions at the source and ambient air.
2. Method used a multi-bed sorbent tube containing carbon molecular sieve sorbent material.
3. This paper has become a standard for measuring emissions from animal feeding operations.

Carbon Molecular Sieve (CMS)

Sorption Studies[1]

1. Sorption occurs on surface functional groups (Low P/P_o)
2. Water sorption increases as vapor concentration of water increases with water sorbing into previous sorbed water with subsequent cluster formation
3. Pore filling occurs at 50% (P/P_o)
4. Plateau at high P/P_o when all pores are filled

[1]Brennan et al. 2001. Colloids and Surf. A.

Inside Animal Facility

Swine Barn[1]

23°C

51% RH (39-78%)

[1]Jerez et al. 2005 AWMA

Broiler House[2]

30°C

57% RH

[2]Heber et al. 2005 AWMA

Outside Conditions

Swine Facility[3]

18-23°C

78-85% RH

[3]Zahn et al. 2001 J. Environ. Qual.

Cattle Feedlot

20-37°C

19-85% RH

Objectives

1. Determine the effect relative humidity has on the sampling and analysis of VOCs on sorbent tubes.

2. Develop water mitigation techniques for sampling in humid environments.

Compounds Tested

1. Volatile fatty acids (VFA)
   - C_2-C_7
2. Phenolic Compounds
   - p-cresol
   - 4-ethylphenol
3. Indolic Compounds
   - Indole
   - 3-methylindole

Sorbent Tubes

1. Carbon Molecular Sieve
   - Tenax TA/Carboxen 569 (CMS 569)
   - Carbopack C/Carbopack B/Carbosieve SIII (Carbotrap 300)
2. Tenax TA (Tenax)
3. Graphitized Carbon
   - Carbopack C/Carbopack X (Carbopack X)

Properties of Sorbent Material

Adsorbent	Surface Area ($m^2\ g^{-1}$)	Water Holding Capacity (mg water g^{-1})[1]
Carbosieve SIII	820	200.5
Carboxen 569	400	280.1
Carbopack-B	100	<1.2
Carbopack-C	10	<0.5
Carbopack-X	240	---
Tenax TA	35	<3.3
Tenax GR	24	< 2.0

[1]Helmig and Vierling, Anal. Chem. 1995 67:4380-4386

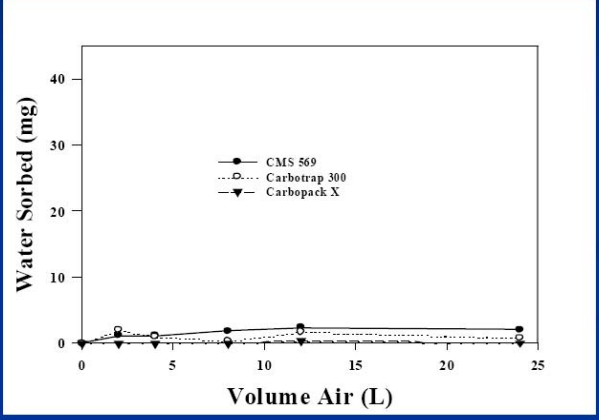
Sampling Condition

1. Air Matrix
   a) Temperature (23°C)
   b) Relative Humidity: 25, 50, 80%
2. Sampling Parameters
   a) Sampling Flow Rate: 100 mL min^{-1}
   b) Total Volume: 2, 4, 8, 12, 24 L
3. Tube Loading (100-600 ppbv)

Analysis

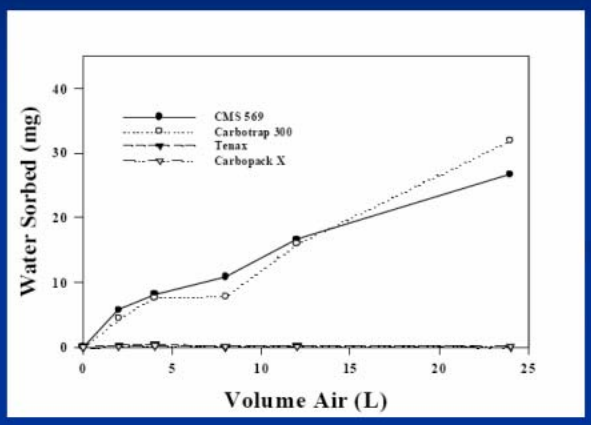
1. Thermal Desorption (Gerstel TDSA)
   - Splitless Mode
   - Desorption flow: 40 mL min^{-1}
   - Temperature: 60-300°C
2. GC/MS (Agilent 6890 w/5973 MSD)
   - GC Column: FFAP (30 m)
   - Column Flow: 1.3 mL min^{-1}
   - MS: SIM mode

25% Relative Humidity



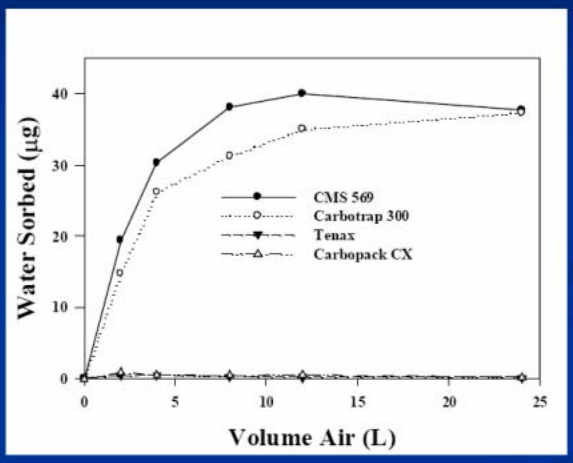
- CMS 569
  0.3-2.0 mg water
- Carbotrap 300
  1.2-2.3 mg water
- Carbopack X
  <0.5 mg water

50% Relative Humidity



- CMS 569
  5.8 mg 2 L
  26.8 mg 24 L
- Carbotrap 300
  4.4 mg 2 L
  32.0 mg 24 L
- Tenax TA
  0.05-0.5 mg
- Carbopack X
  0.1-0.25 mg

80% Relative Humidity



- CMS 569
  19.9 mg 2 L
  40.1 mg 24 L
- Carbotrap 300
  16.5 mg 2 L
  37.5 mg 24 L
- Tenax TA
  0.1-0.5 mg water
- Carbopack X
  0.1-0.8 mg water

Carbon Molecular Sieve

Critical RH for CMS Sorbent Material[1]

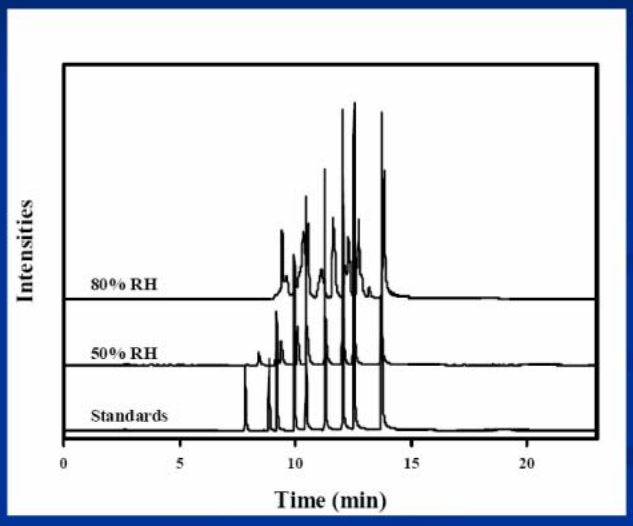
- 45% RH Carboxen 1000
- 35% RH Other CMS

[1]Fastyn et al. 2005 J. Chromatogr. A.

Recovery of Compounds from Sorbent Tubes

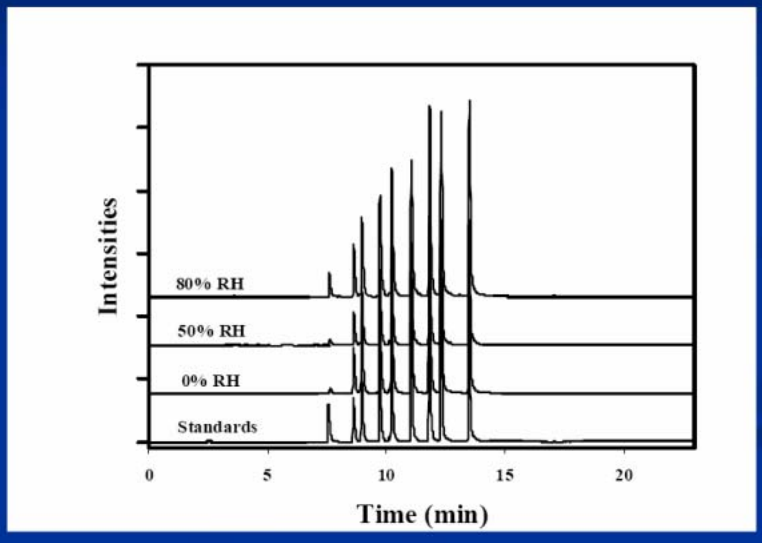
Carbotrap 300

1. 80% Relative Humidity
   - Inability to integrate peaks (lost data)
2. 50% Relative Humidity
   - 83% Recovery
   - 27.5% RSD
3. 25% Relative Humidity
   - 108% Recovery
   - 5.8% RSD



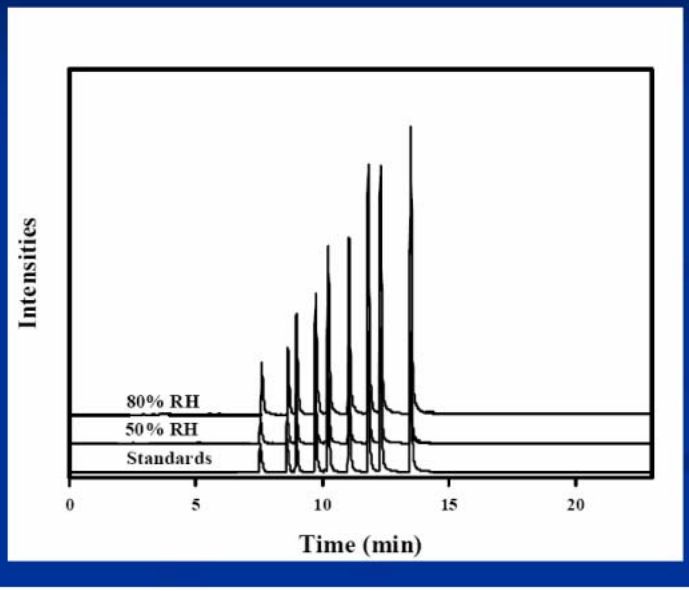
Tenax TA

1. Low water sorption at all RH tested
2. Generally excellent recovery of all compounds (except acetic acid and indole)
   - 99.8% Recovery (80% RH) from 2-12 L
   - 5.2% RSD
   - Lower recovery of acetic acid at lower RH.



Carbopack X

1. Low water sorption at all RH tested
2. Best results in terms of recovery and reproducibility
   - 90% Recovery for all compounds (2-12 L at 80% RH).
   - 8.6% RSD



Conclusion

1. Multi-bed sorbent tube containing graphitized carbon material (Carbopack X) was capable of quantitatively recovering all compounds tested at all RH.
2. Tenax generally trapped/quantified all compounds except acetic acid and indole.
3. Sorbent tubes containing carbon molecular sieve material should be avoided in humid environments.

Water Management Techniques

Dry Purge (Post Processing)

- Temperature: 23°C
- Flow: 100 mL min^{-1}
- Volume: 2 L

- Reduced Water Content
  - 38 mg to < 0.5 mg
- Recovery: 89.8% Acetic acid and propanoic acid were less than less than 50% (96.7%).
- High RSD 24%

Heating of Tube

- Temperature: 41°C
- Flow: 100 mL min^{-1}
- Volume: 12 L

- Reduced Water Content
  - 37.5 mg to < 1.0 mg
- Recovery: 91%
- RSD: 12.9%

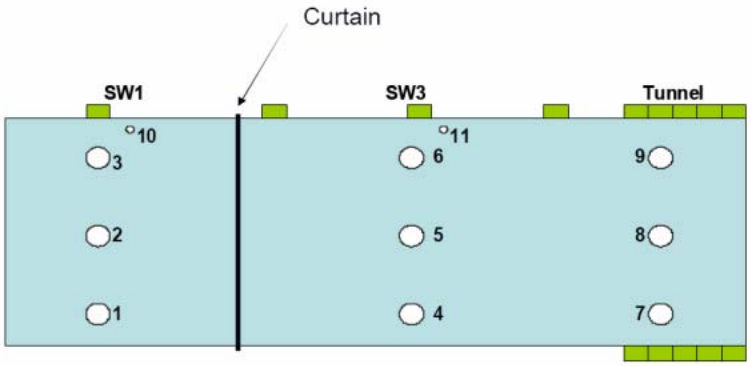
Conclusion

Heating of CMS sorbent tubes is preferred over dry purging of CMS sorbent tubes.

- Greater Recovery of compounds
- Lower RSD compared to dry purging

Speciation of VOCs

Production Facility



Commercial broiler house. 43 x 510 ft.
Ventilation: 1) sidewall fans (four, 0.9-m d); or 2) tunnel fans (10, 1.2-m d).
Rice hull was used as the bedding material with caked litter being removed
The litter was allowed to accumulated 2-4 flocks of production.

Results

Top 10 VOC Determine TO-17				
	Overall	SW1	SW3	Tunnel
Compound	$\mu g\ m^{-3}$			
Acetic acid	773.9	1936.7	457.9	138.0
2,3-Butandone	187.8	309.7	119.6	147.5
Butanoic acid	62.2	164.2	29.5	10.3
Dimethyl disulfide	57.0	121.9	27.2	30.7
3-Hydroxyl-2-butanone	52.9	167.5	2.2	0.8
2-Methyl-3-pentanone	50.1	83.2	26.3	43.2
Propanoic acid	39.7	112.3	13.6	5.1
3-Methyl butanoic acid	35.9	100.4	11.0	6.1
Hexane	34.3	50.5	39.9	19.3
Tetramethyl pyrazine	23.9	66.9	7.3	4.1

VOC TO-17 Information

% Total	Top 1	Top Tier	Top 10	Top 20
Overall:	51.1%	79.0%	87.8%	>96%
■ SW1:	54.0%	82.1%	88.3%	>95%
■ SW3:	53.0%	71.5%	89.0%	>97%
■ Tunnel:	31.0%	79.6%	89.4%	>98%

Variability RSD (CV)

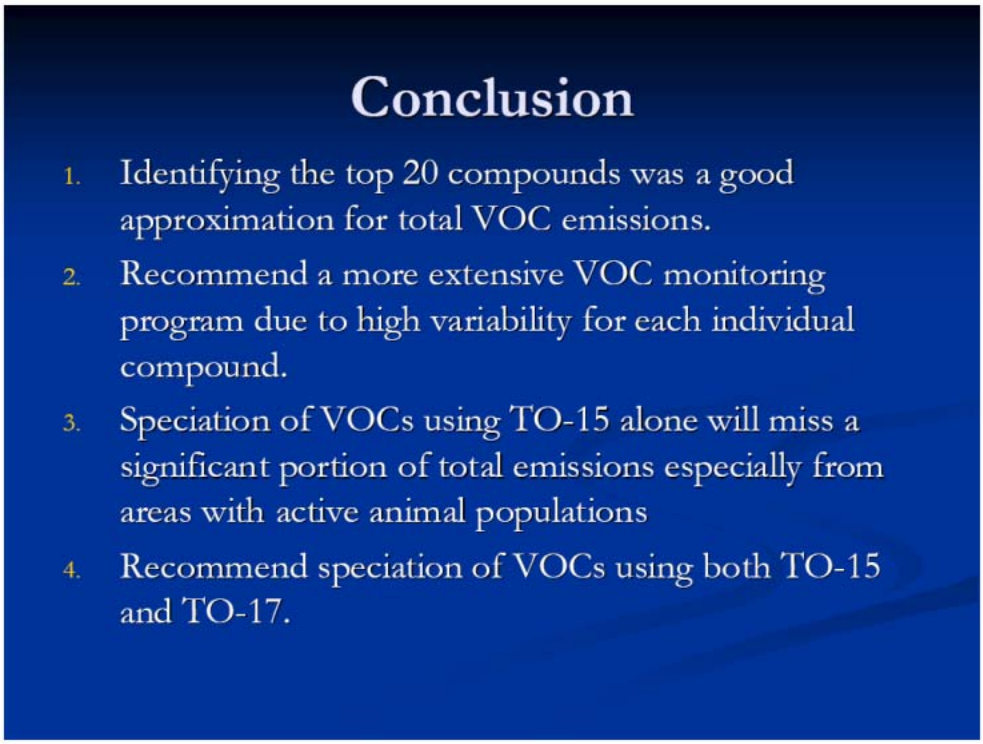
- Location: 56%
- Section: 95%
- Overall: 181%

TO-17 and TO-15 Compound Overlap

	TO-17	TO-15
	$\mu g\ m^{-3}$	
2,3-Butandione	201.2	917.4
2-Butanone	20.6	44.0
Hexane	34.3	37.0
Toluene	5.4	5.1
Benzene	13.9	14.9

TO-15 vs TO-17

VOC Emissions:	TO-15 (%)	TO-17 (%)
Overall	59	73
SW1	50	78
SW3	70	72
Tunnel	73	46


Conclusion
1. Identifying the top 20 compounds was a good approximation for total VOC emissions.
2. Recommend a more extensive VOC monitoring program due to high variability for each individual compound.
3. Speciation of VOCs using TO-15 alone will miss a significant portion of total emissions especially from areas with active animal populations
4. Recommend speciation of VOCs using both TO-15 and TO-17.

Seasonal and Diurnal Variations of Hg° over New England: Implications for Regional Budgets

Huiting Mao
University of New Hampshire

ABSTRACT

Three-year total gaseous mercury (TGM) measurements at a near-coastal site in southeastern New Hampshire exhibited distinct seasonality with a maximum level of 160 parts per quadrillion (ppqv) in spring and a 100 ppqv minimum in fall. Coincident depletion of O3 and TGM on summer nights suggested strong dry depositional loss of Hg° with a deposition velocity of 0.12-0.14 cm s-1. Using measurements from a central New England 700 m altitude site, we obtained a regional biogenic contribution of 13 ppqv to the daily TGM level, ~50% greater than the anthropogenic one. The significantly lower TGM mixing ratios near the coast compared to inland appear to be mediated by reactions with marine-derived halogen compounds. Overall, the significant multiple loss pathways for Hg° support a lifetime of only several weeks in the coastal boundary layer. Moreover, we propose that the steep decreasing warm season trend in TGM during 2005 may have been driven by inter-annual variability in the large-scale background level.

The Impact of Passive Sampling Methodologies Used in the DEARS

Ron Williams
US Environmental Protection Agency

ABSTRACT

The Detroit Exposure and Aerosol Research Study (DEARS) was a three-year field monitoring study completed in February 2007 that was designed to characterize spatial and temporal exposure relationships involving air toxics, particulate matter (PM) components, PM from specific sources, and criteria pollutants in Wayne County, Michigan. Daily (24-hr) personal, residential indoor, residential outdoor and community-based outdoor air measurements were major components of the study design. A primary data collection need of the study was to collect approximately 1200 participant monitoring days. Use of traditional active samplers for collecting some of the desired metrics would not have been cost effective or would have represented unwanted monitoring burden to the participants. Therefore, low burden passive dosimeters were employed for the collection of many of the desired environmental pollutants. In particular, diffusive sampling tubes (PerkinElmer) containing Carbopack X (Supelco) were deployed for the collection of twenty-five volatile organic compounds (VOCs), Ogawa diffusion badges were used for SO^2, NO^2, and O^3 measurements and the Passive Aldehyde and Ketones Sampler (PAKS) were used for the collection of acrolein, acetaldehyde and formaldehyde.

This presentation will provide information on the use of passive monitors to collect nearly 6000 criteria gas samples, as well as approximately 4000 carbonyl and VOC measurements each during field deployment in the DEARS. In particular, data will be presented showing the ability of the passive monitors to successfully collect data across the various spatial settings. Detailed descriptions of how the methodologies were deployed, operating conditions, comparisons of results for passive and standard methods, artifacts observed, limits of detection, precision and analyte recovery statistics will be reported. Field measurement data from the DEARS are still being recovered and validated. We will discuss some of the early environmental findings from the first two years of the study to showcase the ability of these passive samplers to detect real-world concentrations of select pollutants.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

BEST PRACTICES FOR INSTRUMENT CALIBRATION

Calibration Best Practices Defined in United Kingdom

Marlene Moore
Advanced Systems, Inc.

ABSTRACT

International organizations and ASTM publish best practices for calibrations used in testing laboratories. This presentation will highlight the best practices developed and published by one organization in the United Kingdom. Some comments on current ASTM guidance will also be summarized for comparison. In 2003, a study in the United Kingdom found many pitfalls encountered in calibration studies. The information was published in an Industry Guide titled: "Preparation of Calibration Curves, A Guide to Best Practices, September 2003." The pitfalls identified include the following:

- the concentration range is not adequate to cover the range of sample concentrations;
- the calibration standards concentration are not evenly spaced across the calibration range;
- the uncertainty associated with the calibration standards concentration is too large due to preparation practices or standards purity;
- the wrong regression formula is applied;
- the calibration line is fitted through zero even though the intercept is not zero;
- instrument software is used to carry out the regression without looking at the plot of the data;
- the full standard error of prediction calculation is not performed; and
- the performance of the instrument is not within specification.

Suggested steps are presented in the reference document to avoid the above problems. An overview of these steps and the related ASTM guidance are presented.

Calibration Best Practices

Defined in United Kingdom

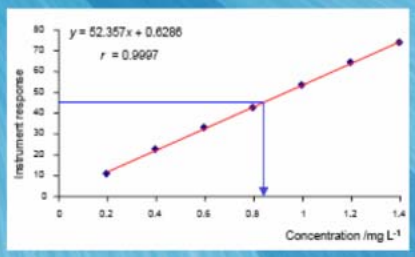
Presented by:
Marlene Moore

Reference

- ***Preparation of Calibration Curves, A Guide to Best Practices,*** September 2003
  LGC/VAM/2003/032

Pitfalls during Studies

- Common pitfalls were identified
- Linear Systems
  - Response to concentration



Pitfalls

- Concentration range is not adequate to cover the range of sample concentrations
- Calibration standards concentration are not evenly spaced across the calibration range
- Uncertainty associated with the calibration standards concentration is too large due to preparation practices or standards purity
- Wrong regression formula is applied

Pitfalls

- Calibration line is fitted through zero even though the intercept is not zero
- Instrument software is used to carry out the regression without looking at the plot of the data
- Full standard error of prediction calculation is not performed
- Performance of the instrument is not within specification

Avoid Problems By:

- Plan the calibration study
- Analyze a standard with zero analyte concentration (i.e., method blank or calibration blank)
- Use appropriate materials and apparatus for preparation of calibration standards
- Define the equipment specifications appropriate for the calibration

Avoid Problems By:

- Plot and examine calibration results and specify the acceptable residual;
- Use validated software to perform the linear regression;
- Define when to set the intercept to zero (e.g. when is the intercept and zero insignificant);
- Calculate the uncertainty for test sample concentrations from the calibration curve as one component of the estimated uncertainty.

Plan the Study

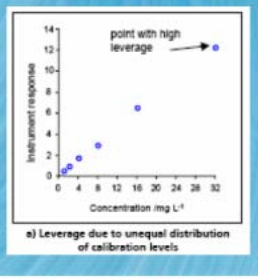
- Number of calibration standards
- Concentration of each standard
- Number of replicates of each measurement
- Preparation of calibration standards

Making Measurements

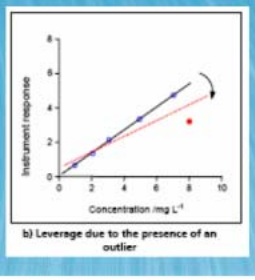
- Equipment Qualification
  - Fit for purpose
- Standards in a random order
  - Not decreasing or increasing

Plotting the Results

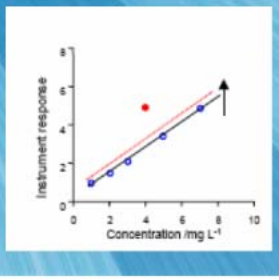
- View in a plot
- Evaluate the scatter plot
- Points of influence
  - Leverage or bias



a) Leverage due to unequal distribution of calibration levels



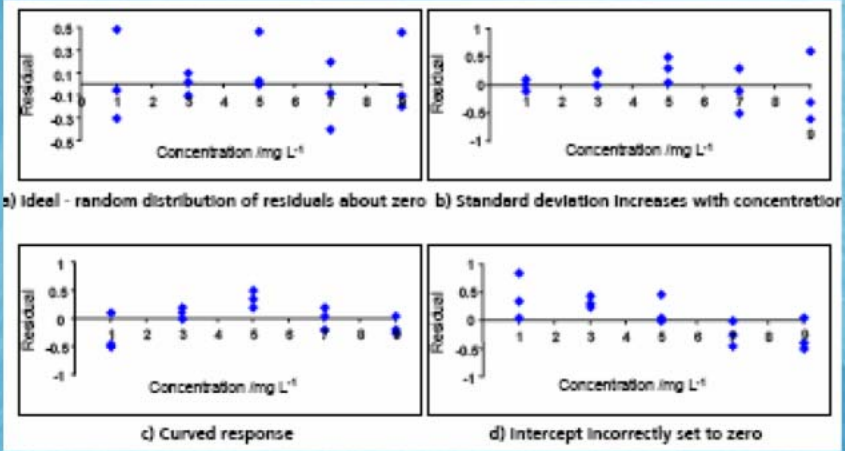
b) Leverage due to the presence of an outlier



Regression Analysis

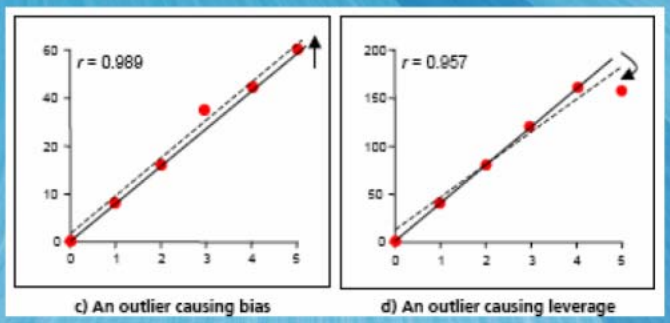
- y = mx+b
  - x = concentration
  - y = response
- Residuals
  - y measured versus y calculated
  - How well the line fits the data
  - Least squares regression - minimize the sum of squared residuals
  - Normal distribution, equal weight to all points
    - Standard deviation is the same across all points

Analyze Residual Plots



Correlation Coefficient, r

- Measure of correlation not linearity
- Closer to 1 the better the correlation



Residual Standard Deviation

- Deviation of data from fitted regression line
- ANOVA table to assess regression
- Fitting line through origin

$$s(r) = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-2}}$$

Regression Analysis

Regression Statistics	
Multiple R	0.999955883
R Square	0.999911768
Adjusted R Square	0.999889709
Standard Error	0.005164622
Observations	6

ANOVA	*df*	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.2091	1.2091	45330.79	2.93×10^{-9}
Residual	4	0.00010669	2.67×10^{-5}		
Total	5	1.2092			

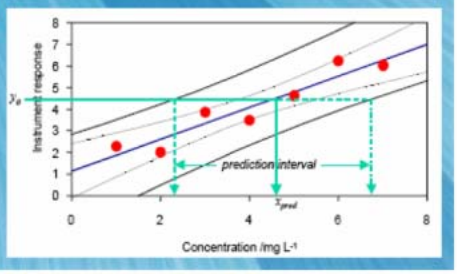
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.0021129	0.0037548	0.56270	0.60368	-0.008312	0.012538
X Variable 1	0.10441	0.00049038	212.91	2.92×10^{-9}	0.10304	0.10577

Estimate Sample Values

- Satisfactory regression analysis
- m and y used to calculate test sample results
- Samples analyzed multiple times
- Same conditions as standards

Estimate Uncertainty

- Confidence interval for regression line
- Less certain near extremes
- Prediction interval calculation provides estimate of uncertainty associated with predicted values of x



Calibration Today

- Robust statistical techniques not always used in the method validation when test developed
- Laboratory method validation data does not present study of calibration process to support laboratory method

Method Validation

- Reference test methods must define
  - specific conditions of test or define acceptable statistical parameters of performance
  - selection of number of data points
  - calibration range
  - origin
  - uncertainty
  - number of standard and sample runs to reduce standard error of prediction

Thank you

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302 368 1211
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Calibration in Environmental Analysis: Issues and Proposals for Improvement

Richard Burrows
Severn Trent Laboratories

ABSTRACT

The instrument is calibrated in order to translate a response to the concentration or amount of a compound of interest. Ideally, the model that we use to describe the relationship of response to amount should minimize any errors that are introduced. There also needs to be a measure of how effectively the calibration model describes the analyte/response relationship. Limits are set for the quality of the calibration model before use for analysis of environmental samples is allowed. Ideally these limits should be set based on an understanding of the method and data quality objectives. In practice they are almost always set by reference to a published EPA method. Almost all EPA methods use average response factors or least squares regression as the calibration model. Percent relative standard deviation is used to measure the quality of the average RF model and the correlation coefficient or coefficient of determination is used as a model of the least squares model.

In this paper we show that unweighted regression curves are a very poor calibration model for environmental analysis, and that the correlation coefficient is completely inadequate as a measure of the quality of the fit, despite its wide use not only in environmental analysis, but also in pharmaceutical and general chemical methods. We will introduce alternative statistics for the evaluation of calibration curves, designed to ensure that curves that pass the criterion will be appropriate for environmental analysis.

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THE LEADER IN ENVIRONMENTAL TESTING

Calibration in Environmental Analysis

Issues and Proposals for Improvement

Richard Burrows

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NEMC August, 2007

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Premise

- The impact of calibration models on the ability to detect and quantify analytes is substantial.
  - ~ Nonetheless, use of the appropriate calibration models is poorly understood and poorly controlled, and in many cases we are instructed to use calibration models that produce false positives, false negatives, and wildly inaccurate quantitation.

2

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Instrument Calibration

- What do we want from the calibration?
  - ~ Accurate translation of instrument response to analyte amount
  - ~ Minimize the errors introduced by the calibration itself

3

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What kind of Errors?

- Relative or Absolute?
  - ~ Characteristics of other errors in the measurement system
  - ~ What kind of error are we measuring with our QC?
  - ~ Which is most important from the risk standpoint?

4

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Characteristics of variance

- Method 3520/8270, 8 replicates prepared and analyzed at 100ppb, 10ppb, 1ppb
  Average of 84 analytes

	100ppb	10ppb	1ppb
Std. Dev.	4.163	0.610	0.042
SD relative to 1ppb SD	88	13	1

Unweighted regression is only valid if the standard deviation is constant across the range

5

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What do we care most about?

- Calibration curve 1-100ppb
  - Do we prefer and expect)
  - +/- 5ppb at all levels, (Absolute error)
  - +/- 10% at all levels, (Relative error)

True	1	10	25	50	100
+/- 5	(-4) - 6	5-15	20-30	45-55	95-105
+/-10%	0.9-1.1	9-10	22.5-27.5	45-55	90-110

6


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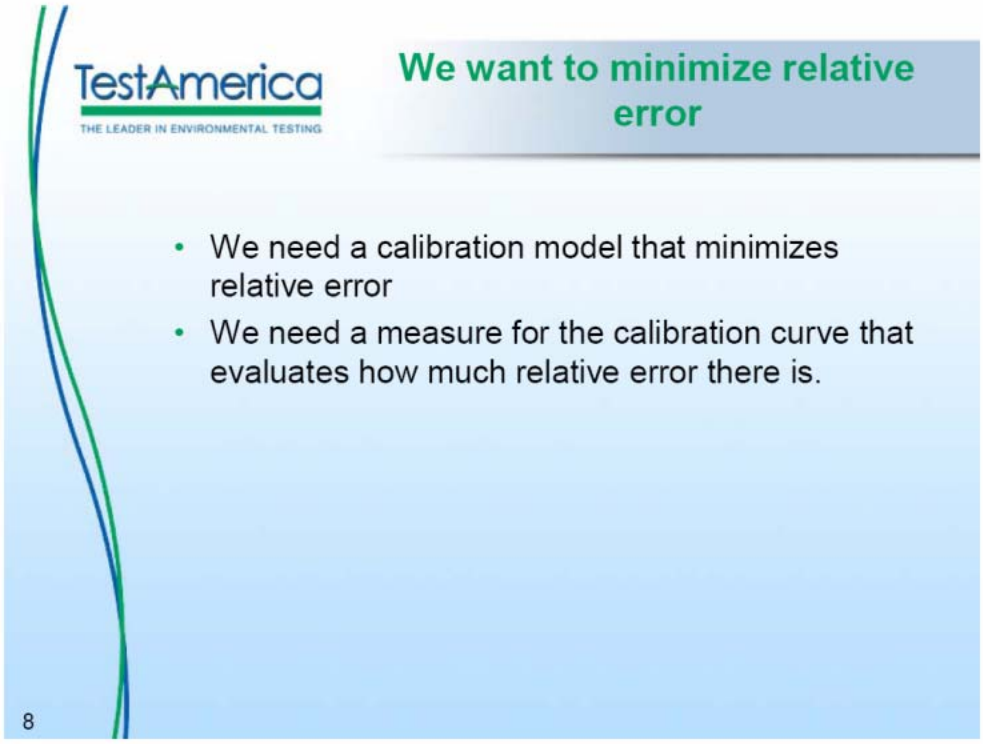
Risk
The difference in risk level between a concentration of 100 and 110 is small, but the difference between 0 and 1 may be very large
7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We want to minimize relative error
• We need a calibration model that minimizes relative error
• We need a measure for the calibration curve that evaluates how much relative error there is.
8

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Calibration approaches

- SW-846 Method 8000B
  - ..begin with the simplest approach, the linear model through the origin, and progress through other options until calibration criteria are met
    - If RSD is < 20%, linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations

9

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Linear regression

- SW-846 Method 8000B
  - If the RSD is > 20% then linearity through the origin cannot be assumed. In this case the analyst may employ a regression equation that does not pass through the origin
- 8000C
  - Linear least squares regression may be employed based on past experience or at the discretion of the analyst

10

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Weighting

- 8000B
  - The analyst may also employ a weighted least squares regression if replicate multi point curves have been performed $1/SD^2$
- 8000C
  - Weighting may significantly improve the ability of the regression to fit the linear model to the data.
    - The mathematics used in the least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated will tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels

11

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Method 8000C

- Weighting
  - Examples of weighting factors which can place more emphasis on numbers of smaller value are:
  - $wi = 1/y_i$ or $wi = 1/y_i^2$
  - These weighting factors are recommended if weighting other than $w_i = 1$ is to be used

12

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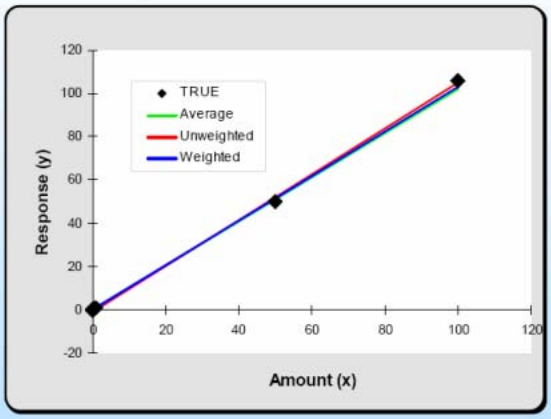
A simple calibration curve



True conc	Response
1	1
50	50
100	106

13

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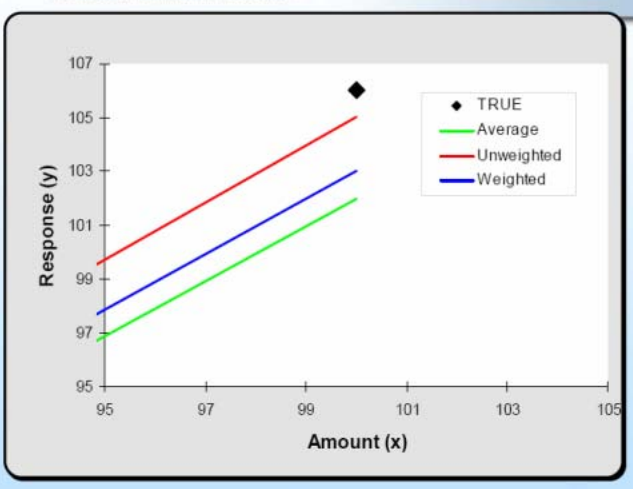
Effect of weighting



Average	
Point	Error
1	2%
50	2%
100	3.8%

Unweighted	
Point	Error
1	100%
50	4%
100	0.92%

Weighted	
Point	Error
1	0.03%
50	3%
100	2.8%

14

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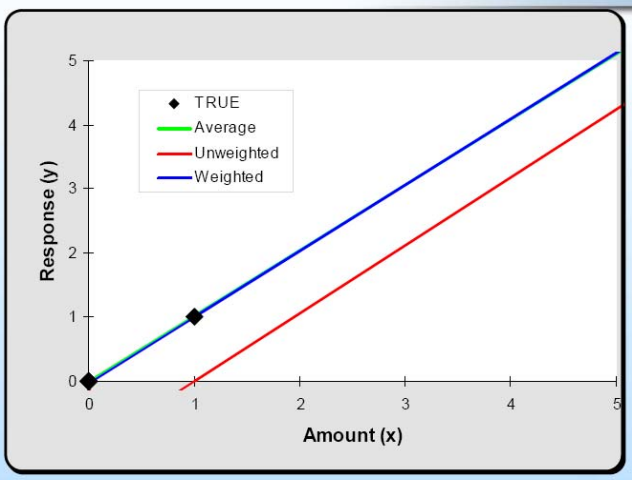
Effect of weighting



Average	
Point	Error
1	2%
50	2%
100	3.8%

Unweighted	
Point	Error
1	100%
50	4%
100	0.92%

Weighted	
Point	Error
1	0.03%
50	3%
100	2.8%

15

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Method 1631 guidance

- Weighting
  - ~ "An unweighted regression is incorrect for nearly all instruments and analytical systems."
  - ~ "The calibration included a data point at the Method 1631 MDL (0.2 ng/L). The RSD for the CF/WR approach was 7.8 percent. The coefficient of determination (r2) for the unweighted approach was 1.000, indicating no error in calibration. The reason for the indication of zero error is that the low calibration points are, essentially, unweighted. Therefore, the unweighted regression is equivalent to a single-point calibration at the highest calibration point. We do not believe that this form of calibration is consistent with the best science."

16

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Weighted Regressions

- Unweighted Σ [(predicted – actual)^2]
- 1/X Weighting $\Sigma \left[\left[(\text{predicted} - \text{actual})/ \text{conc}\right]^2\right]$
- 1/X^2 Weighting $\Sigma \left[\left[(\text{predicted} - \text{actual})/ (\text{conc})^2\right]^2\right]$
- Weighted regressions tend to minimize relative error as opposed to absolute error

17

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Unweighted linear regression

- Unweighted regressions minimize the **absolute** residuals
  - ~ In a calibration from 1-100, an error (residual) of 5 at the 1.0 point has the same weight as an error of 5 at the 100 point.
- 1/ (Conc)^2 weighted regressions minimize the **relative** residuals
  - ~ In a calibration from 1-100, an error (residual) of 5% at the 1.0 point has the same weight as an error of 5% at the 100 point.

18


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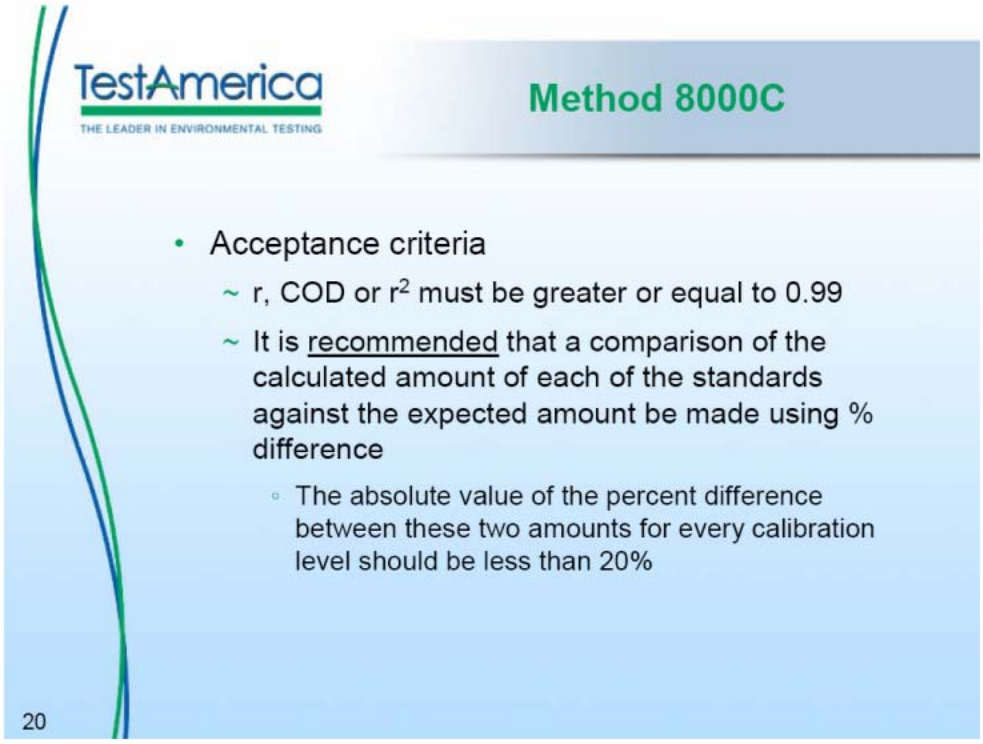
Acceptance Criteria
19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Method 8000C
• Acceptance criteria
~ r, COD or r2 must be greater or equal to 0.99
~ It is recommended that a comparison of the calculated amount of each of the standards against the expected amount be made using % difference
◦ The absolute value of the percent difference between these two amounts for every calibration level should be less than 20%
20

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Second Premise

- The Correlation coefficient (and the coefficient of determination) are pretty much useless for evaluating the suitability of a calibration curve

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Correlation coefficient

- For most applications, and calibration curves in particular, the correlation coefficient must be regarded as a relic of the past
  - ~ Meier and Zund, Statistical Methods in Analytical Chemistry, 2000

22

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Correlation coefficient

- "The correlation coefficient in the context of linearity testing is potentially misleading and should be avoided"
  - ~ Royal Society of Chemistry, Technical brief
- "The author has seen cases where a correlation coefficient of 0.997 was believed to be a better fit than 0.996 of a 5 point calibration curve. One can even find requirements in quality assurance plans to recalibrate if the correlation coefficient is less than 0.995!"
  - ~ Taylor, Statistical Techniques for Data Analysis, 1990

23

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IUPAC

- Guidelines for calibration in Analytical Chemistry, 1998
  - ~ "The correlation coefficient which is a measure of relationship of two random variables, has no meaning in calibration….because the values x are not random quantities in the calibration experiment"

24

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Correlation coefficient

- "One practice that should be discouraged is the use of the correlation coefficient as a means of evaluating goodness of fit of linear models"
  - ~ Van Arendonk and Skogerboe, Anal. Chem. 53, 1981, 2349-2350

25

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- What alternatives are available?

26

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Calibration objectives

- The calibration model should minimize relative error
- The calibration measure(s) should determine how well this objective is met

27

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One additional requirement

- If we accept different ways of evaluating the curve, we want some consistency.
- We don't want one measure to say a curve is good, and another measure to say that it is bad

28

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RSD and RSE

$$\%RSD = 100 \times \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{\bar{C}x_i - y_i}{\bar{C}x_i}\right)^2}{n-1}}$$

C = curve coefficient

x = Concentration

y = response

$$\%RSE = 100 \times \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{\hat{y}_i - y_i}{\hat{y}_i}\right)^2}{n-p}}$$

$\hat{y}$ = predicted response from curve

RSE = RSD when calculated for the average

COULD USE THE SAME CRITERIA

29

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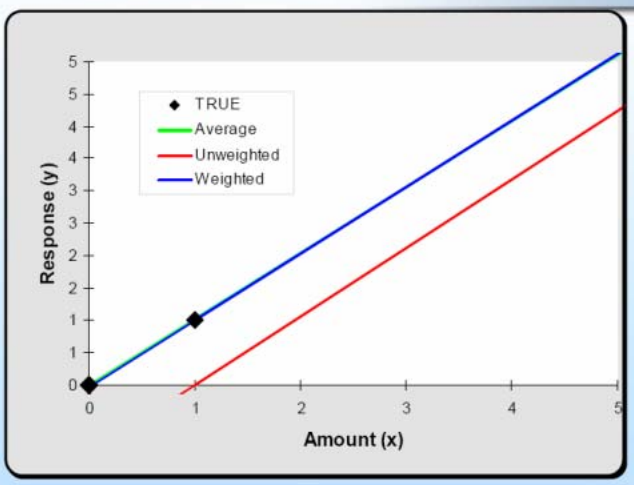

r = .999 RSE = 3.4%	
Average	
Point	Error
1	2%
50	2%
100	3.8%

r= .999 RSE = 94%	
Unweighted	
Point	Error
1	100%
50	4%
100	0.92%

r = .999 RSE = 4.1%	
Weighted	
Point	Error
1	0.03%
50	3%
100	2.8%

30

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EPA clarification memo on the use of SW-846 methods, Aug 7 1998

- "Further, the Agency recognizes that the relative standard error (RSE) is a useful measure of the goodness of fit of a calibration model that the Agency had not previously considered. The RSE is useful for both linear regression models as well as non-linear models, as it considers the error at each point in the calibration model as a function of the concentration of that standard."

31

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EPA clarification memo on the use of SW-846 methods, Aug 7 1998

- "Using the RSE as a metric has the added advantage of allowing the same numerical standard to be applied to the calibration model, regardless of the form of the model. Thus, if a method states that the RSD should be <20% for the traditional linear model through the origin, then the RSE acceptance limit can remain 20% as well. Similarly, if a method provides an RSD acceptance limit of 15%, then that same figure can be used as the acceptance limit for the RSE."

32

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The Calibration Curve that Can't Fail! (A Digression)

- "We really want to make sure we carefully define the low end of the curve."

Conc	Resp
1	0.82
2	2.23
3	2.75
4	4.34
5	4.27
10	8.55
100	117
slope	0.84419
corr	0.99968
int	0.91870

33

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Reporting limit corresponds to the low point on the curve

Population mean is very near low end of curve. Irrespective of results, the line is close to the data points.

Conc	Resp
1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
10	0.00
100	117
slope	0.81564
corr	0.99679
int	4.16667

RSE = 149%

34

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The Impact of Calibration Models on Analyte Detection and Accuracy at Low Concentrations

- Example GC/MS Data
- Example ICP/MS Data
- Example IC data Data

35

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GC/MS Data

- Three calibration models,
  - ~ Average response factor
  - ~ Linear regression with no weighting
  - ~ Linear regression with inverse square weighting.
- If a sample gave the same response as our low standard, what would we detect and report?

36

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One calibration, processed three different ways

GC/MS		inverse square	
	Avg RRF	weighted	unweighted
	%RSD	r^2	r^2
bis(2-chloroethyl)ether	4.68	0.998	0.996
bis(2-chloroisopropyl)ether	4.26	0.999	0.996
n-nitroso-di-N-propylamine	6.35	0.998	0.995
nitrobenzene	6.15	0.999	0.998
bis(2-chloroethoxy)methane	5.14	0.999	0.997
2,4-dichlorophenol	11.54	0.999	0.997
hexachlorobutadiene	3.46	0.999	0.998
2,4-dinitrotoluene	25.72	0.996	0.998
4-chlorophenyl phenyl ether	5.69	0.999	0.998
4-bromophenyl phenyl ether	5.42	0.999	0.998
hexachlorobenzene	2.4	0.999	0.998
bis(2-ethylhexyl)phthalate	22.24	0.999	0.998

37

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Three different results

GC/MS			inverse square	
		Avg RRF	weighted	unweighted
	MDL (ug/l)	0.5 ppm std	0.5 ppm std	0.5 ppm std
bis(2-chloroethyl)ether	0.405	0.53	0.5	0.12
bis(2-chloroisopropyl)ether	0.386	0.48	0.5	< 0
n-nitroso-di-N-propylamine	0.339	0.45	0.5	< 0
nitrobenzene	0.455	0.45	0.5	0.14
bis(2-chloroethoxy)methane	0.357	0.46	0.5	< 0
2,4-dichlorophenol	0.338	0.39	0.5	0.11
hexachlorobutadiene	0.362	0.49	0.5	0.38
2,4-dinitrotoluene	0.244	0.25	0.5	1.24
4-chlorophenyl phenyl ether	0.412	0.45	0.5	0.22
4-bromophenyl phenyl ether	0.267	0.46	0.5	0.38
hexachlorobenzene	0.52	0.5	0.5	0.15
bis(2-ethylhexyl)phthalate	0.232	0.28	0.5	0.47
	>20% error	>50% error		

38

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ICP/MS Data

- Compare Continuing Calibration Blank results using two different calibration models, linear regression without weighting and linear regression with 1/X weighting.

39

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The test

- If the CCB result is greater than the MDL, you have a high risk of false positives
- If the CCB result is less than the negative value of the MDL, you have a high risk of false negatives

40

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CCB 1

		not	
	MDL	weighted	weighted
	ug/l	ug/l	ug/l
Li	0.17	-0.15	0.01
Be	0.03	-0.16	0.00
V	0.05	-0.27	-0.02
Cr	0.12	-0.15	-0.06
Mn	0.06	-0.39	0.00
Co	0.02	-0.24	0.00
Ni	0.18	-0.26	0.00
Cu	0.24	-0.28	0.04
Zn	1.25	-0.14	-0.05
As	0.28	-0.20	0.01

		not	
	MDL	weighted	weighted
	ug/l	ug/l	ug/l
Se	0.42	-0.18	-0.04
Sr	0.03	-0.25	0.00
Mo	0.14	0.16	0.23
Ag	0.16	-0.15	0.00
Cd	0.03	-0.02	-0.01
Sb	0.20	0.10	0.13
Ba	0.07	0.00	0.00
Tl	0.06	-0.28	0.00
Pb	0.06	-0.12	0.00

41

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Weighted versus unweighted

- Unweighted – 50% fail test. CCB results are either > MDL or < -MDL
- Weighted – 1.2% fail test. One high result for molybdenum
- Same data, same instrument same sensitivity, only difference is calibration model

42

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Method 300 example

Fluoride MDL 0.040					
Conc.	Response	Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	1497075	266.11%	0.63%	16.43%	0.78%
0.5	12858983	13.30%	-15.69%	-12.09%	-9.10%
2.5	67621646	-6.11%	-9.99%	-7.83%	-3.19%
5	1.43E+08	-3.50%	-4.38%	-2.47%	2.14%
10	3.02E+08	1.13%	1.62%	3.35%	7.80%
	r	0.9994	0.9991	0.9990	0.9979
	RSE	152.00%	8.47%	12.47%	7.24%

43

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Nitrite MDL 0.011		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	2180491	205.76%	5.67%	12.56%	0.55%
0.5	18572459	11.28%	-10.75%	-8.54%	-6.22%
2.5	93858389	-6.50%	-9.58%	-7.90%	-4.17%
5	2.01E+08	-1.87%	-2.56%	-1.05%	2.61%
10	4.16E+08	0.79%	1.18%	2.60%	6.22%
	r	0.9996	0.9994	0.9993	0.9986
	RSE	124.30%	7.32%	10.09%	5.85%

44

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Bromide MDL 0.021		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	1606620	358.50%	-5.30%	24.17%	1.29%
0.5	13366717	14.44%	-26.57%	-20.67%	-16.15%
2.5	76229872	-5.90%	-10.97%	-8.09%	-1.64%
5	1.59E+08	-5.28%	-6.44%	-3.96%	2.54%
10	3.46E+08	1.50%	2.14%	4.29%	10.40%
	r	0.9990	0.9985	0.9983	0.9955
	RSE	192.13%	12.30%	17.49%	10.65%

45

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Nitrate MDL 0.0082		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	2247869	339.37%	-5.43%	18.18%	0.75%
0.5	20450323	19.65%	-15.89%	-11.19%	-8.04%
2.5	1.06E+08	-6.98%	-11.82%	-9.11%	-4.16%
5	2.23E+08	-5.26%	-6.36%	-3.99%	0.94%
10	4.84E+08	1.54%	2.14%	4.22%	8.86%
	r	0.9990	0.9985	0.9985	0.9978
	RSE	182.04%	9.58%	13.04%	7.47%

46

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Phosphate MDL 0.048		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	651248	218.38%	-25.53%	9.91%	0.30%
0.5	7605083	12.10%	-7.49%	-3.50%	-2.15%
2.5	38175481	-4.32%	-7.07%	-5.43%	-3.23%
5	79141773	-2.66%	-3.29%	-1.99%	0.23%
10	1.66E+08	0.85%	1.21%	2.33%	4.50%
	r	0.9997	0.9995	0.9996	0.9995
	RSE	99.36%	11.37%	6.06%	3.48%

47

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Method 300

- In every case, the unforced, unweighted linear regression introduced error of over 200% for the low point of the curve.
- Despite this, in every case the correlation coefficient for the unweighted unforced curve is better than 0.999!
- The unweighted forced curve gives lower error
- Unforced weighted curves (1/Concentration or $1/Concentration^2$) give the lowest error across the range of the calibration
- The RSE does a good job of identifying which curves are acceptable for environmental analysis.

48

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Summary

- The correlation coefficient and coefficient of determination are inadequate as QC measures for calibrations curves for environmental analysis
- Relative Standard Error is one good measure that could be used and assesses relative error across the curve
- Unweighted regressions are almost always bad – a good QC measure would indicate this

49

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Questions?

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50

Higher Accuracy Analysis by Direct Mathematical Determination without a Traditional Calibration Curve

H. M. "Skip" Kingston[1], Mizanur Rahman[1], John Kern[2], Timothy Fahrenhoz[1], Matt Pamuku[1], Laura Reyes[1], Greg Zinn[1], Panxi Zhao[1], Gonzalo Monchego[1], Scott Faber[3], and Jingyan Sun[2]

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[3]Children's Institute

ABSTRACT

The critical role of "measurement" was defined in the 1800s by Lord Kelvin: "If you can measure what you speak of and can express it by a number, you know something about your subject; but if you cannot measure it, your knowledge is meager and unsatisfactory..." How are methods and instruments integrated into useful, higher-utilitarian and reliable systems that are able to produce legally defensible environmental forensic measurements? Integration of methods and instruments frequently begins in sample preparation which is always the key to achieve accuracy and precision. Effective new tools, must have reliable automation steps, as well as methods that uniquely integrated into the system for instrumental implementation.

Quantitative elemental and molecular speciation of dynamic and reactive chemical species are relatively difficult and new class of metrology. It is one of the most difficult fields in analytical measurement, challenging both methods and instrumentation. A new fundamental approach to sample preparation and method integration aiming for higher degrees of automation, as well as quantitative and qualitative measurement is being investigated for its benefits and advantages.

Among the roadblocks that inhibit progress are lack of much needed new, accurate standard reference materials and diagnostic tools. Some elemental and molecular species undergo conversion and form other species or the species of interest degrade to other species during sampling, storage, calibration and the measurement processes. Traditional calibration is impossible in many of these cases.

Until recently, there have been no effective diagnostic tools to trace the fate of dynamically unstable species, the effectiveness of methods and accuracy of measurements. The ability to measure the transformation of the species is critical in the preparation and certification of standard reference materials and for accurate speciated analysis. Countries, such as China, Korea and twenty-five members of the European Community have reached conclusions and now strongly support enriched stable isotopically-traceable solutions and identify them specifically.

A newly updated and revised EPA RCRA Method (designated as 6800) known as Speciated Isotope Dilution Mass Spectrometry (SIDMS, and several variations on this name) provides internationally legally defensible accuracy in new automated measurement methods. SIDMS has also been used

recently as a diagnostic tool for validation of the speciated protocols for three species, measured simultaneously while nine interconversions are taking place. The updated EPA Method 6800 also includes other species and applications in tissues, food, environmental toxicology, clinical and instrumentation automation for homeland defense. Fundamentals of sample preparation and integration of SIDMS as Method 6800 in the fields of environmental toxicology, medicine and nutrition will be discussed and examples presented.

High Accuracy Analysis by Direct Mathematical Determination without a Traditional Calibration Curve

- *H. M. Skip Kingston,*
- *Research Group - Mizanur Rahman, Laura Reyes, Timothy Fahrenholz, Matt Pamuku^, John Kern, Scott Faber (MD)*, Panxi Zhao, Greg Zin, Bryan Seybert, Dengwei Huo*
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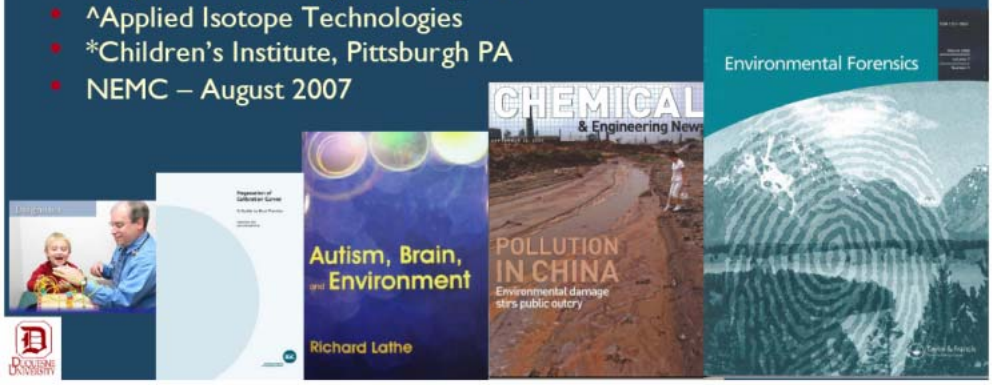
- NEMC – August 2007



Accuracy and Precision in Instrumental Analysis

- **Accuracy and Precision depends on the calibration protocol**
  - **Internal standardization**
  - **Standard addition**
  - **Matrix matching**
  - **Isotope dilution (a type of internal standard that is an enhanced isotope of the same element being measured)**
  - **Determinative speciated isotope dilution**
- **Errors – both fixed and random – can be introduced through the use of different calibration techniques**
- **The measured accuracy of the unknown analyte can only be worse (greater) than the uncertainty in the calibration**

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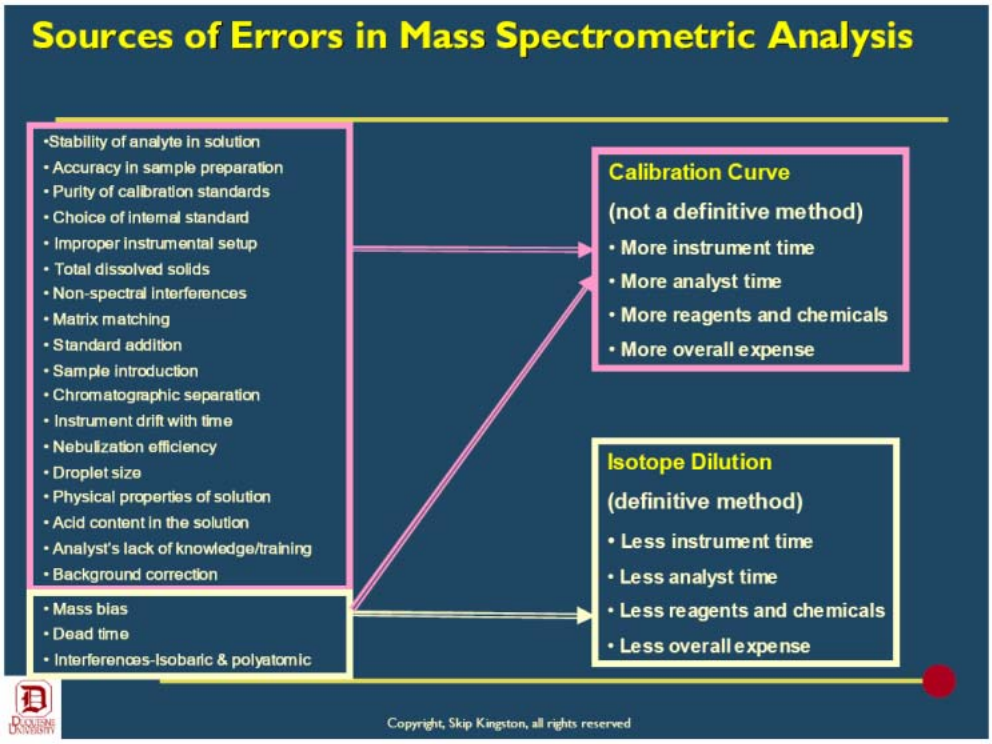
Sources of Errors in Mass Spectrometric Analysis
•Stability of analyte in solution
• Accuracy in sample preparation
• Purity of calibration standards
• Choice of internal standard
• Improper instrumental setup
• Total dissolved solids
• Non-spectral interferences
• Matrix matching
• Standard addition
• Sample introduction
• Chromatographic separation
• Instrument drift with time
• Nebulization efficiency
• Droplet size
• Physical properties of solution
• Acid content in the solution
• Analyst's lack of knowledge/training
• Background correction
• Mass bias
• Dead time
• Interferences-Isobaric & polyatomic
Calibration Curve
(not a definitive method)
• More instrument time
• More analyst time
• More reagents and chemicals
• More overall expense
Isotope Dilution
(definitive method)
• Less instrument time
• Less analyst time
• Less reagents and chemicals
• Less overall expense
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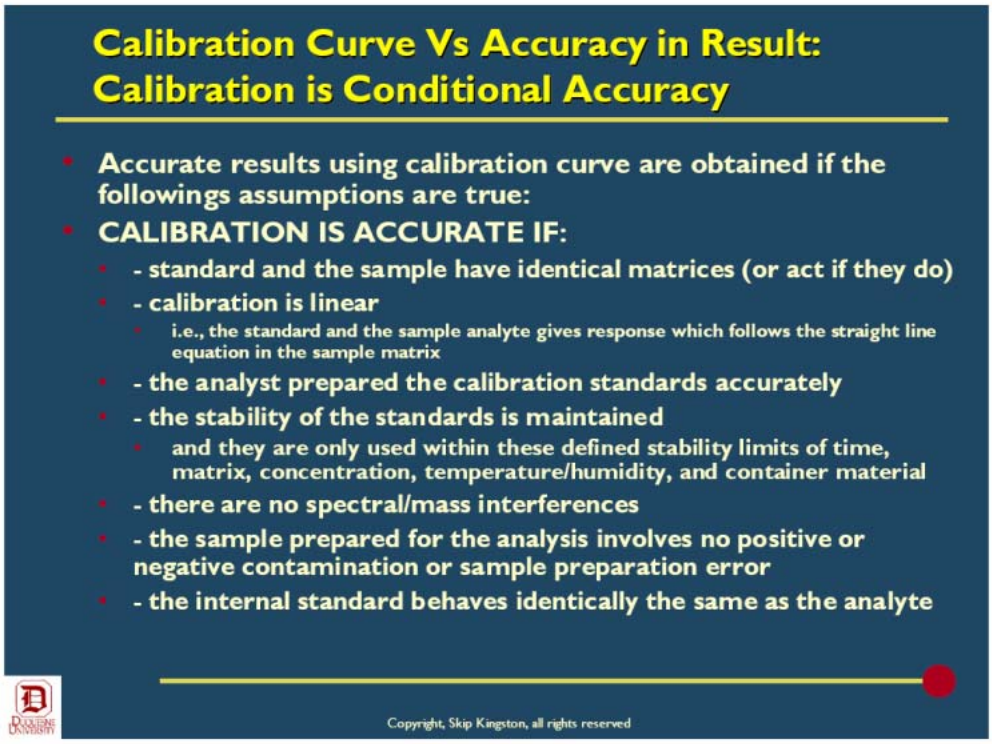
Calibration Curve Vs Accuracy in Result:
Calibration is Conditional Accuracy
• Accurate results using calibration curve are obtained if the followings assumptions are true:
• CALIBRATION IS ACCURATE IF:
• - standard and the sample have identical matrices (or act if they do)
• - calibration is linear
• i.e., the standard and the sample analyte gives response which follows the straight line equation in the sample matrix
• - the analyst prepared the calibration standards accurately
• - the stability of the standards is maintained
• and they are only used within these defined stability limits of time, matrix, concentration, temperature/humidity, and container material
• - there are no spectral/mass interferences
• - the sample prepared for the analysis involves no positive or negative contamination or sample preparation error
• - the internal standard behaves identically the same as the analyte
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Matrix Matching in Spectrometry Analysis

- Matrices of the standard and the samples should be identical
  - Match the acid content, type and concentration in calibration standard and sample
  - Match the elemental matrix component of calibration standard and sample
- The matrix influence
  - Nebulization efficiency
  - Droplet size, which is influenced by the physical properties of solution (surface tension, viscosity and density)
  - Effect of acid matrix upon nebulization (5-10% v/v will cause a decrease in efficiency of 10-35%)
  - Plasma temperature, which is related to signal intensity
  - Ionization potential

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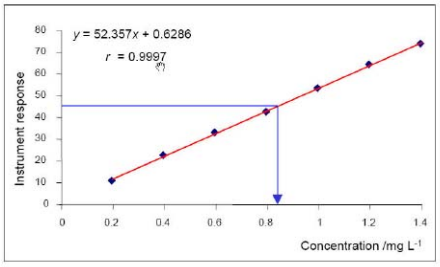
Calibration and quantification in MS (example ICP-MS[1] or GC/MS or LC-MS

•Calibration curve is a relationship between the analytical signal (response) and the concentration of analyte.

•Response function can be linear, but non-linear models, are also observed.

•The response function is obtained using calibration standards (CSs) prepared in absence or presence of matrix sample and relating the response and the concentration.

1. External calibration[2]



The regression analysis of the analytical signal (Y) on the analyte concentrations (**Z**) yields the calibration curve for the predicted responses ($\hat{Y}$). The linear model predict responses according to Equation (1):

$$\hat{Y} = a + bZ \qquad (1)$$

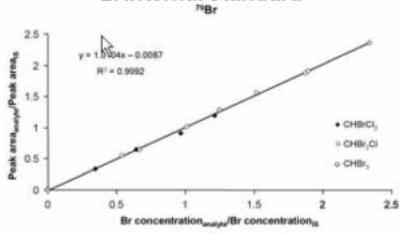
Where:

a is the intercept and **b** the slope, with standard deviations sa and sb, respectively.

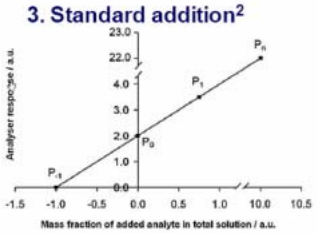
[1]González A.G., Herrador M. A., Trends in Analytical Chemistry, 2007, 26 (3), 227-238.
[2]Preparation of calibration curves, a guide to best practices. LGC, September 2003.

Calibration and quantification in MS & others

2. Internal standard[1]



3. Standard addition[2]



1González-Gago A., et al, J. Anal. At. Spectrom., 2007, DOI: 10.1039/b705035f
2Brown R. J.C., et al, Anal. Chimica Acta, 2007, 587(21):158-163

External calibration

The ICP-MS produces results with a maximum precision (i.e., complex matrices) in the range of 5 to 10%. The main problems associated with external calibrations are:

1) Dynamic range: Typically in the commercially available ICP-MS instruments, the linear dynamic range, the range over which the response of the instrument is linear with respect to analyte concentration, is greater than six orders of magnitude. As such, the curve fitted to the standard data should be linear. The slope of the line defined by the standards is proportional to the concentration in the standards. The unknown sample is run and its signal intensity is plotted against the curve to determine the concentration.

2) Matrix effects: The role that matrix plays is complex and varied, and can lead to dramatically diminished accuracy. Complex matrices generally result in a suppression of the analyte, although enhancements have been observed.

3) Drift: It can have a dramatic effect on all analyses performed using ICP-MS. Drift arises when an instrument response changes with time.

Matrix effects (Observation and mechanisms)

- **High dissolved solids**
  - Blockage of the entrance aperture of the sampling cone
  - The deposition of salts leads to a decrease in the aperture diameter, so that the sensitivity worsens and the signals gradually decrease as a function of time.
  - Ionization enhancements
  - Ionization suppression

Suppression and enhancement effects

- ***Ionization suppression***:

  $M = M^+ + e^-$

  Introduction of an easily ionized element contributes strongly to the electron density in the plasma and therefore shifts the ionization equilibrium so that the analyte elements are ionized to a lesser extent.

- ***Space charge effects***:

  Lighter analyte ions can be expected to suffer more from this effect than heavier ones, and are thus preferentially lost from the transmitted ion beam.

Methods to correct for or overcome matrix effects

- **Dilution**
  - Easy
  - Detection limits sacrificed
- **Matrix matching**

When the analyzed matrix is also added to the standards, correction for matrix effects is possible. This method can only be applicable for simple matrices, e.g. metals, but is clearly not applicable for complex matrices of varying composition.

The Determination of Mercury in Microwave Digests of Foodstuffs by ICP- MS[1]

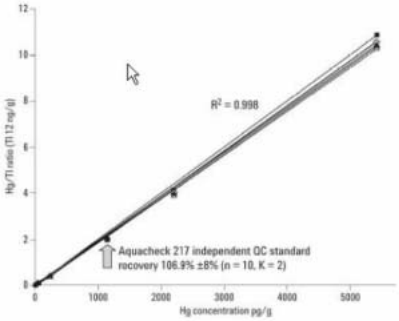


Figure 2 Calibrations over 36 hr of continuous operation.

Use of thallium (12 ng/g) as internal standard

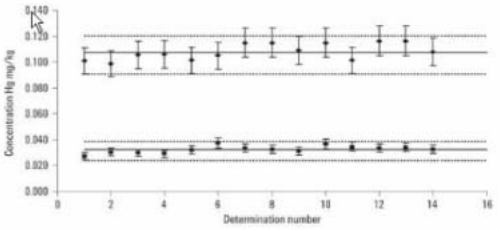


Figure 3 NIST 1547 peach leaves (lower trace) and LGC 7160 crab paste (top trace) analyzed 14 times over a period of one month. Each point represents a separate digest. LGC 7160 certified value 0.096 = ±0.108 mg/kg; NIST 1547 certified value 0.031 = ±0.007 mg/kg. The dotted lines are established in-house acceptance limits.

[1]Entwisle J., American laboratory, March 2007, 11-14

Standard addition

☺It is used when the matrix is quite variable and/or when an internal standard that corrects for plasma related effects couldn't be found.

☺ It offers the best possible solution to matrix interference through plasma related effects.

☺ It is a safe method for samples of unknown composition and thus unknown matrix effect.

☹ However, it is a time consuming approach.

The following considerations may prove useful in performing the technique of standard additions:

- The technique of standard additions requires a linear response (It is therefore important to work within the linear working range for each analyte).
- Many analysts prefer to make more than one spiked level.

Standard addition: Application to the determination of chromium in blood samples

• Except at very low concentrations, when standard additions are used, the bias and the reproducibility are less than 20%.

The method is sufficiently precise to enable quantitative determination of chromium, even in a complex matrix such as whole blood.

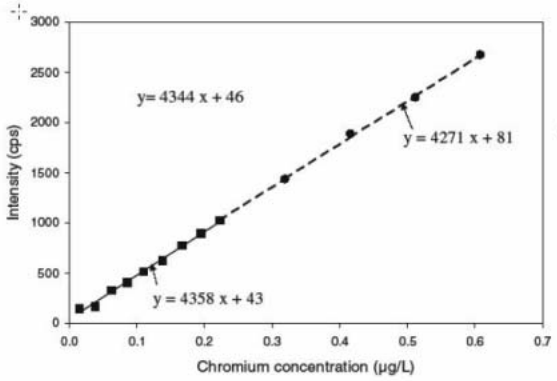


Fig. 3 Comparison of the slopes for the three levels of Seronorm QC samples mixed two by two (*squares with solid line*) and for the standard additions (*circles with broken line*), as a function of chromium concentration. The two linear regression equations are given, along with the equation corresponding to a single straight line

Bonnefoy C., et al, Anal Bioanal Chem, 2005, 383: 167–173

Comparison between hydride generation and nebulization for sample introduction in the determination of lead in plants and water samples by inductively coupled plasma mass spectrometry, using external calibration and isotope dilution[1]

Table 3
Analytical results for matrix CRMs and spiked high-salt solutions (recoveries/R% in parentheses)

Material	Certified concentration/μg g^{-1}	Uncertainty/μg g^{-1} [a,b]	Found Neb (R%)[c]	Found HG (R%)[c]	Found Neb+ID (R%)[c]	Found HG+ID (R%)[c]
SRM 1572	13.3	2.4	11.6±0.8 (87±6)	13.0±0.1 (98±1)	13.3±0.05 (99.9±0.4)	13.5±0.1 (101.8±0.8)
GBW 08501	0.99	0.08	0.58±0.03 (59±3)	NA[d]	0.92±0.16 (93±16)	0.98±0.19 (99±19)
BCR 60	63.8	3.2	43.4±1.9 (68±3)	45.9±11.5 (72±18)	64.4±1.9 (101±3)	66.3±3.2 (104±5)
NIST 1643	19.6[a]	0.2[a]	17.7±1.3 (90.3±6.4)	25.5±0.02 (130.1±0.1)	19.4±0.6 (99±3)	19.7±0.02 (100.3±0.8)
Sea water	–	–	n.a.[e]	<LOD	n.a.[e]	0.17±0.08
Sea water	–	–	n.a.[e]	8.9±6.6 (89±66)[f]	n.a.[e]	9.9±1.4 (99±14)[f]
20% m/v NaCl	–	–	n.a.[e]	4.1±0.6 (41±6)[f]	n.a.[e]	10.2±0.04 (102.2±0.4)[f]

[a] For aqueous samples/μg L^{-1}.
[b] 95% statistical confidence intervals.
[c] ±2 SD, based on 2 parallel sample digests, each measured 5 times.
[d] Not acceptable: too high value caused by difference in pH of sample and standards, see Section 3.3.1.
[e] Not analyzed.
[f] Spiked with 10 μg L^{-1} Pb.

[1]Panayot K., et al, Spectrochim. Acta Part B (2006) 61: 50 – 57

Internal Standard

- ✓ Ideally, internal standards should be non-interfered and mono-isotopic species. Commonly used internal standards include ^{9}Be, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In and ^{209}Bi.
- ✓ In solution ICP-MS the internal standard element chosen should not be present in the samples and should be added to all blanks, standards and samples in equal concentrations (typically ~ 10 ppb).
- ✓ In order to effectively correct for temporal variations in signal intensity (largely dependent on variations in the physical behavior of the analytes in the plasma), the physical properties of the internal standards must be carefully matched to those of the isotopes they are applied to (i.e. internal standards should have similar mass and ionisation efficiency as the elements they are applied to).
- ✓ Allows correction for systematic variations of the analytical signal in samples and standards due to matrix effects.

Minimizing interferences in the quantitative multielement analysis of trace elements in biological fluids by ICP-MS using internal standard[1]

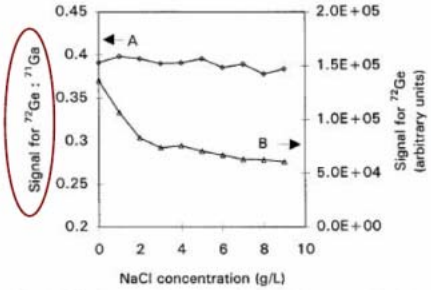


Fig. 1. Effectiveness of an internal calibrator to correct for signal suppression caused by various NaCl concentrations: *A*, signal ratio for the analyte ^{72}Ge to the internal calibrator ^{71}Ga and *B*, signal for the analyte ^{72}Ge.

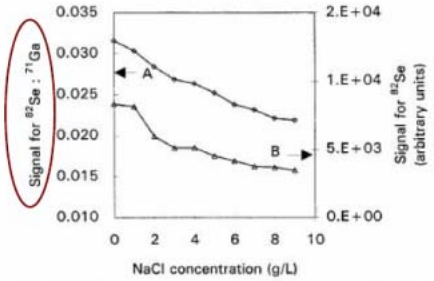


Fig. 2. Effectiveness of an internal calibrator to correct for signal suppression caused by various NaCl concentrations: *A*, signal ratio for the analyte ^{82}Se to the internal calibrator ^{71}Ga and *B*, signal for the analyte ^{82}Se.

[1]Hsiung Chiung-Sheng, et al, Clin. Chem., 1997, 43 (12): 2303–2311.

Primer and reference on Calibration Curve Best Practices

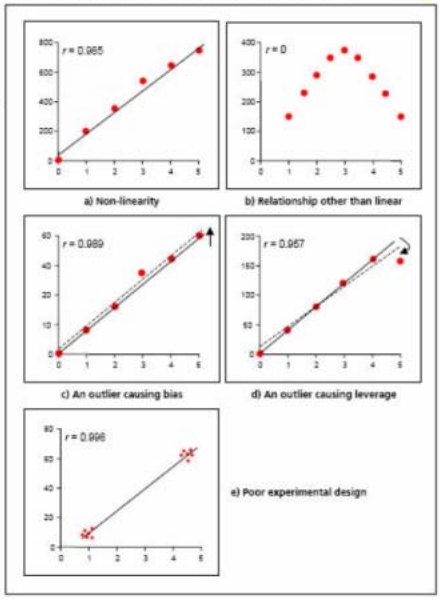


Figure 9: Interpreting the correlation coefficient

Reference:– "Preparation of Calibration Curves: A guide to Best Practice," September 2003, LGC/VAM/2003/032, LGC, Vicki Barwick

r requires that there is a straight line to have an *r*

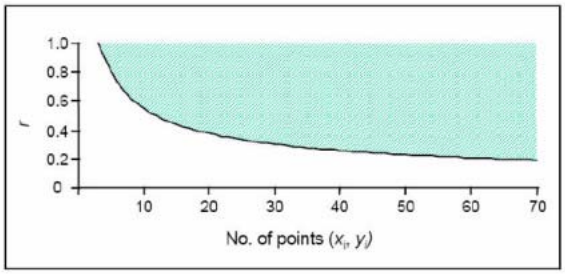


Figure 10: Statistically significant values of *r* (shaded area) at the 95% confidence level

The parameters related to r are r^2 and adjusted r^2. r^2 is often used to describe the fraction of the total variance in the data which is contributed by the line that has been fitted. Ideally, if there is a good linear relation, the majority of variability can be accounted for by the fitted line. r^2 should therefore be close to 1.

Reference:– "Preparation of Calibration Curves: A guide to Best Practice," September 2003, LGC/VAM/2003/032, LGC, Vicki Barwick

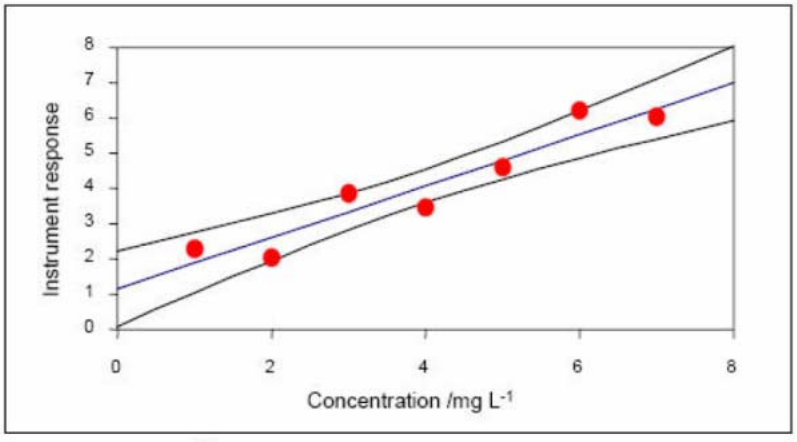


Figure 12: 95% confidence interval for the line

References

1. *Inductively Coupled Plasma Mass Spectrometry*; Mantaser, A., Ed.; Wiley-VCH: New York, 1998
2. *Plasma Source Mass Spectrometry - Developments and Applications*; Holland, G., Tanner, S. D., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1997.
3. Taylor, H. E. *Inductively Coupled Plasma Mass-Spectrometry, Practices and Techniques*; Academic Press: New York, 2001.
4. González A.G., Herrador M. A., Trends in Analytical Chemistry, 2007, 26 (3), 227-238.
5. Preparation of calibration curves, a guide to best practices. *LGC*, September 2003.
6. González-Gago A., et al, *J. Anal. At. Spectrom.*, 2007, DOI: 10.1039/b705035f
7. Brown R. J.C., et al, *Anal. Chimica Acta*, 2007, 587(21): 158-163
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9. Hsiung Chiung-Sheng, et al, *Clin. Chem.*, 1997, 43 (12): 2303–2311.
10. Entwisle J., *American laboratory*, March 2007, 11-14
11. Rodríguez-González P., et al, *Spectrochim. Acta Part B*, 2005, 60,151-207.
12. Rottmann L. and Heumann K.G., *Fresenius J. Anal. Chem.*, 1994, 350: 221-227.
13. Vicki Barwick, Preparation of Calibration Curves: A guide to Best Practice, LGC/VAM/2003/032, LGC, September 2003.

Relative vs. Primary Methods

Isotope Dilution Mass Spectrometry – IDMS

Speciated Isotope Dilution Mass Spectrometry – SIDMS

EPA Method 6800

Isotope Dilution Analysis

- A primary analytical method for the determination of trace metals in a variety of sample types.
- ID-ICP-MS is of particular interest to the

DRAFT TECHNICAL COMMITTEE REPORT

PROPOSED ISO/TC 102/ TCR 12	
Date 2007-7-23	Reference number ISO/TC 102 **N 587E**
Supersedes document	

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PROPOSED ISO/TC 102/ TCR 12	
Date 2007-7-23	Reference number ISO/TC 102 **N 587E**
Supersedes document	

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…"Methods presented in the literature as potentially capable of being classified as primary are gravimetry, titrimetry, coulometry, and isotope-dilution mass spectrometry (IDMS)." …

"…Primary Method of measurement is a method having the highest metrological qualities, whose operation is completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units, and whose results are, therefore, accepted without reference to a standard of the quantity being measured." …

Isotope Dilution Analysis

- Elements that are monoisotopic ^{9}Be, ^{23}Na, ^{27}Al, ^{45}Sc, ^{55}Mn, ^{75}As, ^{89}Y, ^{103}Rh, ^{127}I, ^{133}Cs, ^{141}Pr, ^{159}Tb, ^{165}Ho, ^{169}Tm, ^{197}Au, and ^{232}Th
- Radiogenic U, Pb

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Isotopes Amenable to IDMS and SIDMS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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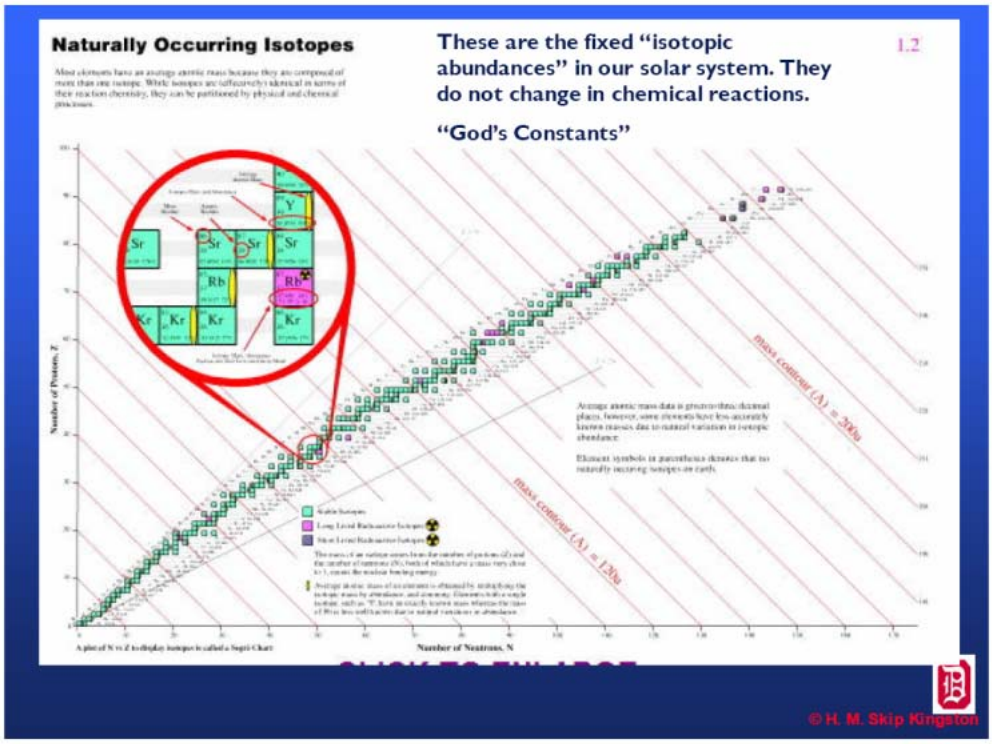
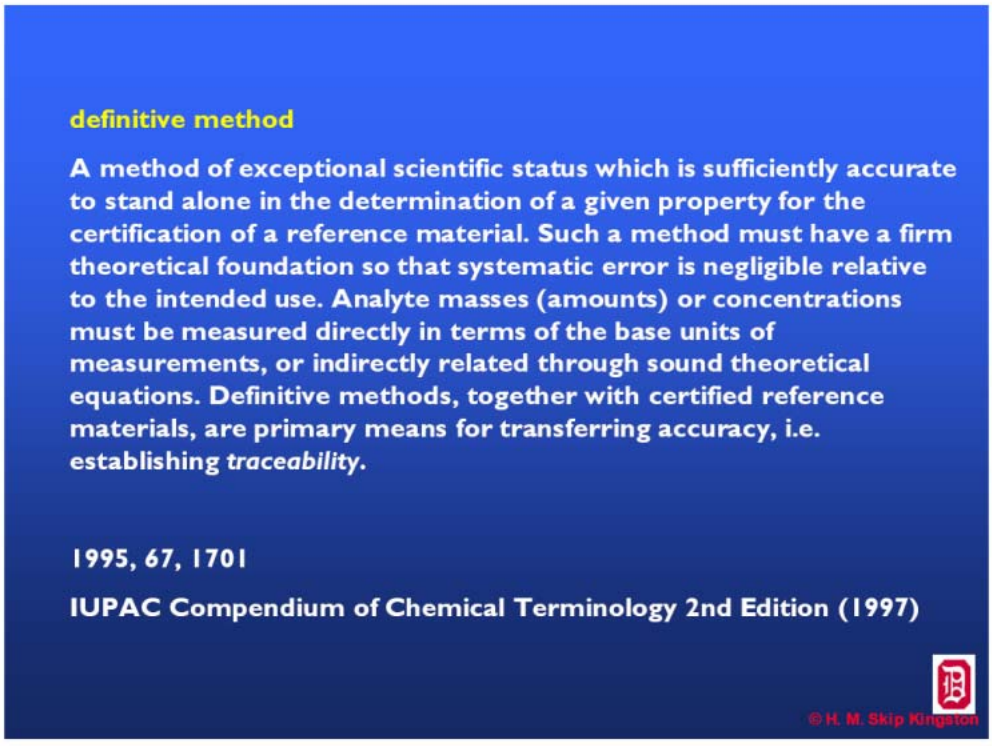

Naturally Occurring Isotopes
These are the fixed "isotopic abundances" in our solar system. They do not change in chemical reactions.
"God's Constants"
1.2
Number of Protons, Z
Number of Neutrons, N
© H. M. Skip Kingston


definitive method
A method of exceptional scientific status which is sufficiently accurate to stand alone in the determination of a given property for the certification of a reference material. Such a method must have a firm theoretical foundation so that systematic error is negligible relative to the intended use. Analyte masses (amounts) or concentrations must be measured directly in terms of the base units of measurements, or indirectly related through sound theoretical equations. Definitive methods, together with certified reference materials, are primary means for transferring accuracy, i.e. establishing traceability.
1995, 67, 1701
IUPAC Compendium of Chemical Terminology 2nd Edition (1997)
© H. M. Skip Kingston

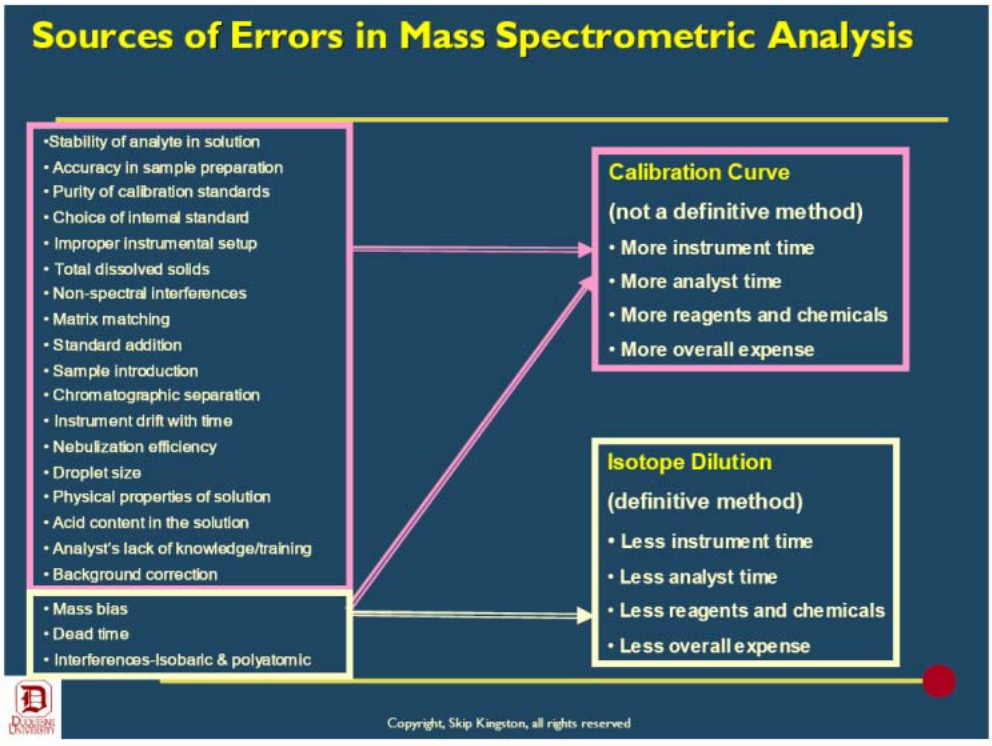
INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

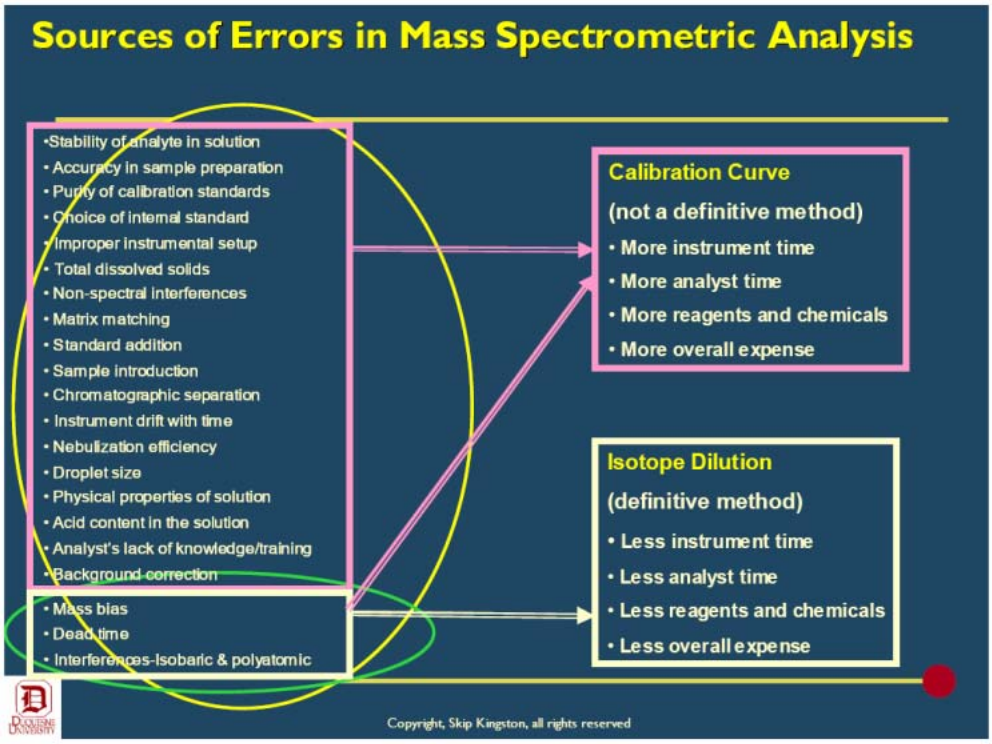
IUPAC/ISO 1997

INORGANIC CHEMISTRY DIVISION
COMMISSION ON ATOMIC WEIGHTS AND ISOTOPIC ABUNDANCES*

TABLE 1. Isotopic compositions of the elements as determined by mass spectrometry

Atomic Number 1	Symbol 2	Mass Number 3	Range of Natural Variations (Atom %) 4	Annotations 5	Best Measurement from a Single Terrestrial Source (Atom %) 6	Reference (App. A) 7	Available Reference Materials[a] (App. B) 8	Representaive Isotopic Composition (Atom %) 9
80	Hg	196			0.15344(19) 1s N	89ZAD1		0.15 (1)
		198			9.968 (13)			9.97 (20)
		199			16.873 (17)			16.87 (22)
		200			23.096 (26)			23.10 (19)
		201			13.181 (13)			13.18 (9)
		202			29.863 (33)			29.86 (26)
		204			6.865 (7)			6.87 (15)
24	Cr	50			4.3452 (85) 2s C	66SHI1	NIST-SRM979*	4.345 (13)
		52			83.7895 (117)			83.789 (18)
		53			9.5006 (110)			9.501 (17)
		54			2.3647 (48)			2.365 (7)




Sources of Errors in Mass Spectrometric Analysis
•Stability of analyte in solution
• Accuracy in sample preparation
• Purity of calibration standards
• Choice of internal standard
• Improper instrumental setup
• Total dissolved solids
• Non-spectral interferences
• Matrix matching
• Standard addition
• Sample introduction
• Chromatographic separation
• Instrument drift with time
• Nebulization efficiency
• Droplet size
• Physical properties of solution
• Acid content in the solution
• Analyst's lack of knowledge/training
• Background correction
• Mass bias
• Dead time
• Interferences-Isobaric & polyatomic
Calibration Curve
(not a definitive method)
• More instrument time
• More analyst time
• More reagents and chemicals
• More overall expense
Isotope Dilution
(definitive method)
• Less instrument time
• Less analyst time
• Less reagents and chemicals
• Less overall expense
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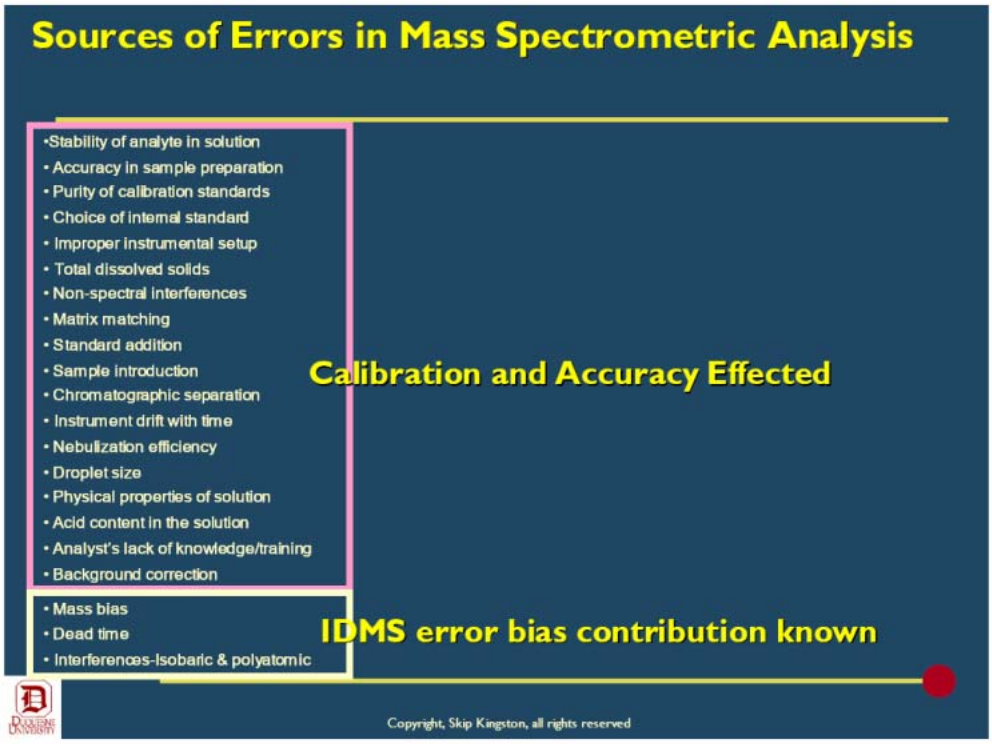
Sources of Errors in Mass Spectrometric Analysis
•Stability of analyte in solution
• Accuracy in sample preparation
• Purity of calibration standards
• Choice of internal standard
• Improper instrumental setup
• Total dissolved solids
• Non-spectral interferences
• Matrix matching
• Standard addition
• Sample introduction
• Chromatographic separation
• Instrument drift with time
• Nebulization efficiency
• Droplet size
• Physical properties of solution
• Acid content in the solution
• Analyst's lack of knowledge/training
• Background correction
Calibration and Accuracy Effected
• Mass bias
• Dead time
• Interferences-Isobaric & polyatomic
IDMS error bias contribution known
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Primary Definitive Methods in Mass Spectrometry

Isotope Dilution
(definitive method)
- Less instrument time
- Less analyst time
- Less reagents and chemicals
- Less overall expense

IDMS - definitive method
- Total element measurement
- Calibration curve-less accuracy
- Legally defensible

SIDMS - definitive method
- Simultaneous species measurement (one, two or three)
- Interconversions are calculated mathematically
- Calibration curve-less accuracy
- Calculated corrections are legally-defensible

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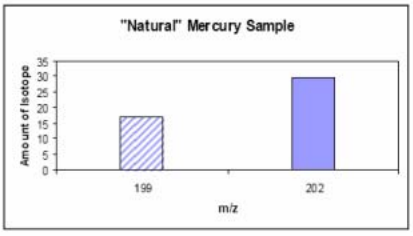
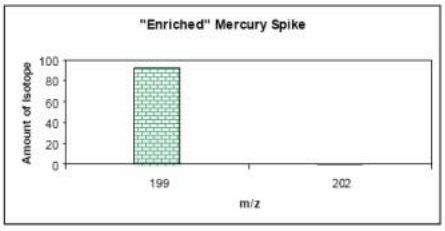
Quantification Method
(Simplest example is a one IDMS determination)
Isotope Dilution Mass Spectrometry (IDMS)
(Example of how it works)



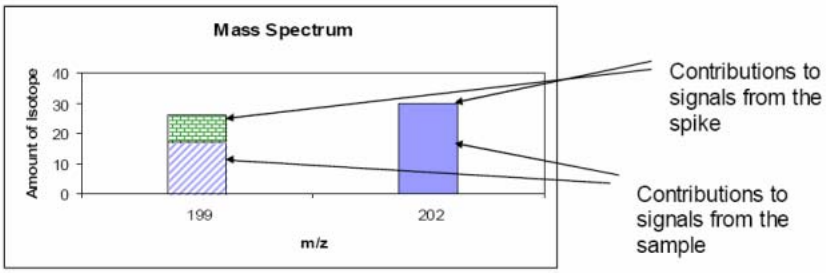


^{199}Hg & ^{202}Hg occur naturally in a **16.87:29.86** abundance ratio.

Isotopically-enriched solutions are commercially available (*e.g.* **91.95:0.73**).

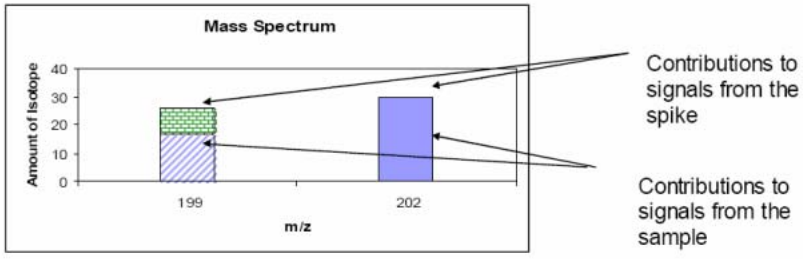
Quantification Method
Using IDMS

A sample of mercury of unknown concentration is 'spiked' with a known concentration and known amount of isotopically enriched mercury standard, and analyzed by ICP-MS



Quantification Method
Using IDMS

$$\text{Ratio}\left(\frac{\text{Isotope A}}{\text{Isotope B}}\right) = \left(\frac{\text{Amount of A from SAMPLE} + \text{Amount of A from SPIKE}}{\text{Amount of B from SAMPLE} + \text{Amount of B from SPIKE}}\right)$$



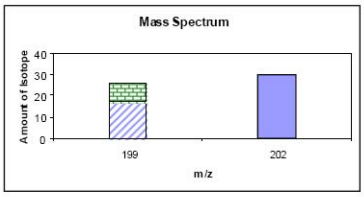
IDMS Calculation & Formula

... cntd

$$\text{Ratio}\left(\frac{\text{Isotope A}}{\text{Isotope B}}\right) = \frac{(\text{Amount of A from Sample} + \text{Amount of A from Spike})}{(\text{Amount of B from Sample} + \text{Amount of B from Spike})}$$

So ...

$$\text{Ratio} = \frac{(A_s C_s V_s + A_{sp} C_{sp} V_{sp})}{(B_s C_s V_s + B_{sp} C_{sp} V_{sp})}$$

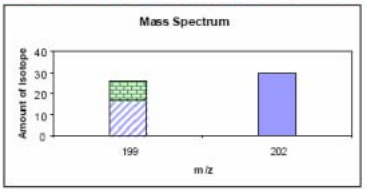


Where:

		Known?
A_s	= Fraction of isotope A in sample (natural)	✓
B_s	= Fraction of isotope B in sample (natural)	✓
A_{sp}	= Fraction of isotope A in spike (altered)	✓
B_{sp}	= Fraction of isotope B in spike (altered)	✓
C_s	= **Concentration of element in sample**	✗
C_{sp}	= Concentration of element in spike	✓
V_s	= Volume of the sample	✓
V_{sp}	= Volume of the spike	✓

Solve for C_s, (the concentration of the element in the sample) ...

IDMS Quantitation of Cu



... contd

$$\text{Ratio} = \frac{(A_s C_s V_s + A_{sp} C_{sp} V_{sp})}{(B_s C_s V_s + B_{sp} C_{sp} V_{sp})}$$

Rearrange the equation to solve for C_s

$$C_s = C_{sp}\left(\frac{V_{sp}}{V_s}\right)\frac{(A_{sp} - \text{Ratio} \times B_{sp})}{(\text{Ratio} \times B_s - A_s)}$$

Known & Measured Values

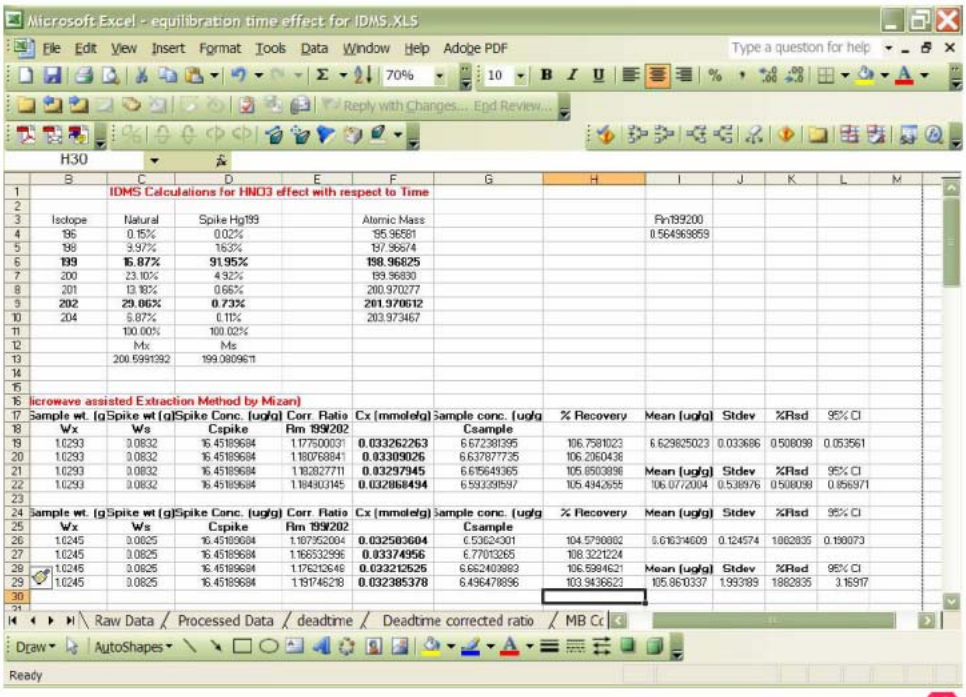
1) The isotope ratio in the enriched spike standard,
   = 0.73 : 91.95 (^{199}Hg:^{202}Hg) (A_{sp} & B_{sp})
2) The concentration of the spike standard solution,
   = 4.95 µg/g (C_{sp})
3) The relative masses of the spike and sample
   = 0.10 (spike / sample) (V_{sp} / V_s)
4) Measured Isotope Ratio
   = 0.9256 (^{199}Hg / ^{202}Hg) (*Ratio*)
5) Natural Isotope Ratio
   = 16.87 : 29.86 (^{199}Hg : ^{202}Hg) (A_s & B_s)

$$C_s = 4.95 \times 0.10 \times \frac{(0.73 - 0.9256 \times 91.95)}{(0.9256 \times 29.80 - 16.87)}$$

C_s = 4.23 µg/g

So ...

Element	Conc.
Hg	4.23 ppm

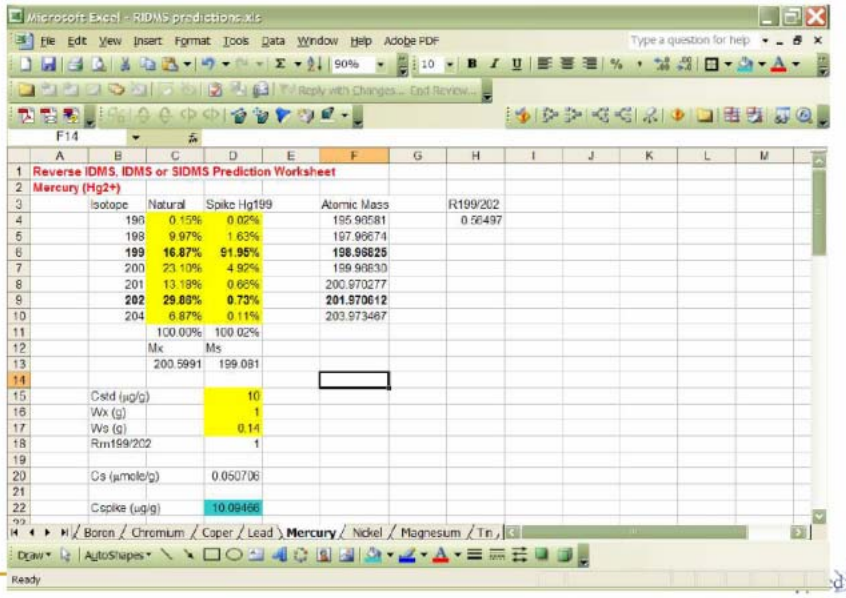


Calibration and IDMS 6800 Analysis of Human Urine

Element	ICP-MS (External Calibration) (ppb)	ICP-MS (IDMS) (ppb)
Cr	127.8 ± 2.2	124.4 ± 5.1
Ni	16.7 ± 0.9	15.6 ± 1.5
Cu	57.36 ± 0.6	43.1 ± 2.5
Zn	342.3 ± 3.4	349.3 ± 6.9
Cd	3.6 ± 0.3	3.9 ± 0.4
Sn	2.0 ± 0.1	1.9 ± 0.4
Ba	2.4 ± 0.2	2.5 ± 0.2
Hg	428.6 ± 30.8	440.8 ± 35.5
Pb	7.5 ± 0.4	8.7 ± 0.7

Uncertainties are at 95% CI, n = 4

Mercury Isotopic Calculation Keyed Software



Microsoft Excel - RIDMS predictions.xls

	A	B	C	D	E	F	G	H
1	Reverse IDMS, IDMS or SIDMS Prediction Worksheet							
2	Mercury (Hg2+)							
3		Isotope	Natural	Spike Hg199		Atomic Mass		R199/202
4		196	0.15%	0.02%		195.96581		0.56497
5		198	9.97%	1.63%		197.96674		
6		**199**	**16.87%**	**91.95%**		**198.96825**		
7		200	23.10%	4.92%		199.96830		
8		201	13.18%	0.66%		200.970277		
9		**202**	**29.86%**	**0.73%**		**201.970612**		
10		204	6.87%	0.11%		203.973467		
11			100.00%	100.02%				
12			Mx	Ms				
13			200.5991	199.081				
14								
15		Cstd (µg/g)		10				
16		Wx (g)		1				
17		Ws (g)		0.14				
18		Rm199/202		1				
19								
20		Cs (µmole/g)		0.050706				
21								
22		Cspike (ug/g)		10.09466				

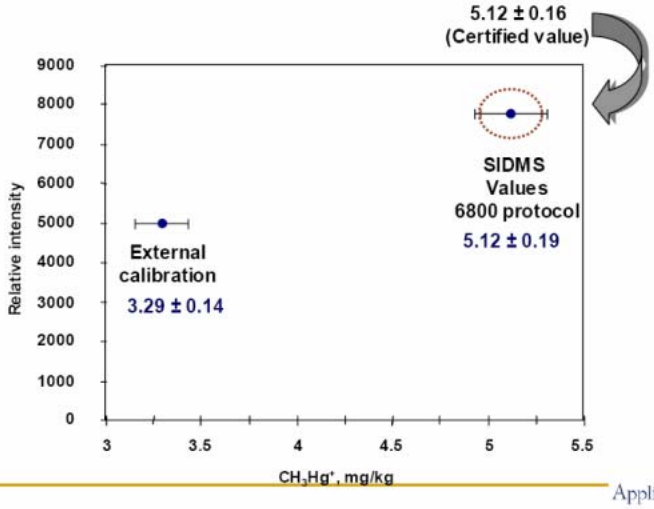
Boron / Chromium / Caper / Lead / **Mercury** / Nickel / Magnesium / Tin /

Ready

Applied Isotope Technology

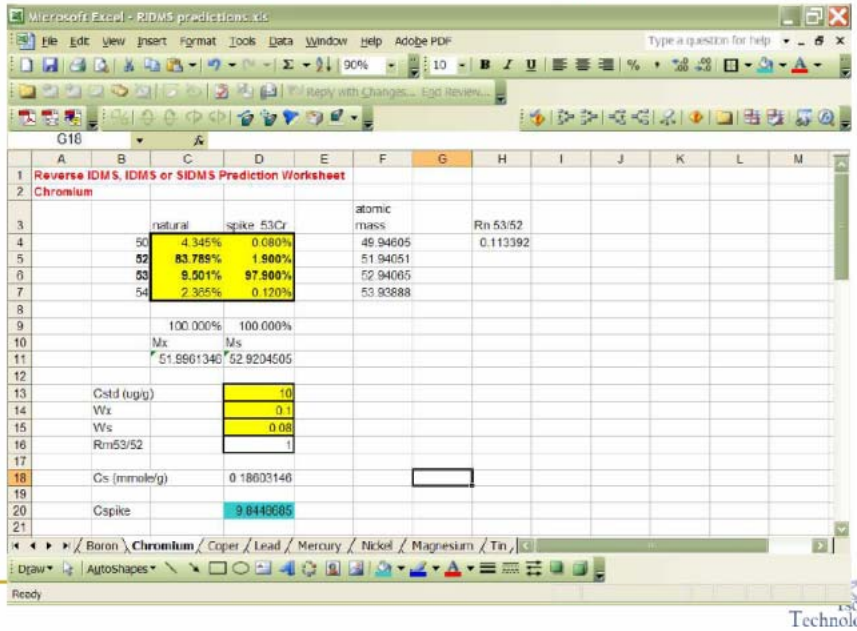
Methylmercury concentration in CRM-464 after microwave extraction with CH_3COOH.

36% Species Conversion



Applied Isotope Technology

Chromium Isotopic Calculation Keyed Software



Microsoft Excel - RIDMS predictions.xls

File Edit View Insert Format Tools Data Window Help Adobe PDF

G18

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Reverse IDMS, IDMS or SIDMS Prediction Worksheet												
2	Chromium												
3			natural	spike 53Cr		atomic mass		Rm 53/52					
4		50	4.345%	0.080%		49.94605		0.113392					
5		52	83.789%	1.900%		51.94051							
6		53	9.501%	97.900%		52.94065							
7		54	2.365%	0.120%		53.93888							
8													
9			100.000%	100.000%									
10			Mx	Ms									
11			51.9961346	52.9204505									
12													
13		Cstd (ug/g)		10									
14		Wx		0.1									
15		Ws		0.08									
16		Rm53/52		1									
17													
18		Cs (mmole/g)		0.18603146									
19													
20		Cspike		9.8449685									
21													

Boron | Chromium | Coper | Lead | Mercury | Nickel | Magnesium | Tin

Draw Autoshapes

Ready

Isotope Technology

2007 Update Method EPA 6800 (SIDMS)

Species Analyses including Chemical Marker and Biomarkers

METHOD 6800

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application.

1.0 SCOPE AND APPLICATION

1.1 This method consists of two approaches: isotope dilution mass spectrometry (IDMS) for the determination of total metals and speciated isotope dilution mass spectrometry (SIDMS) for the determination of elemental species. This method is applicable to the determination of total metals and metal species at sub µg/L levels in water samples or in waste extracts or digests. In general, elements that have more than one available stable isotope can be analyzed by IDMS. SIDMS may require more isotopes of an element, depending on the number of interconvertable species. The following analytes have been determined by this method:

Element	CASRN*
Antimony	(Sb)
Boron	(B)
Barium	(Ba)
Cadmium	(Cd)
Calcium	(Ca)
Chromium	(Cr)
Copper	(Cu)
Iron	(Fe)
Lead	(Pb)
Magnesium	(Mg)
Mercury	(Hg)
Molybdenum	(Mo)
Nickel	(Ni)
Potassium	(K)
Selenium	(Se)
Silver	(Ag)
Strontium	(Sr)
Thallium	(Tl)
Vanadium	(V)
Zinc	(Zn)

* Chemical Abstract Service Registry Number

6800 - 1

Revision 0
April 2004

Excerpt from Item-1.5:

"Aqueous samples such as drinking water, ground water, and other aqueous samples may be directly spiked and analyzed. **Solid samples such as soils, sludges, sediments, industrial materials, biological tissues, botanicals, lysed cells, foods, mixed samples, blood, and urine and other samples containing solid matrices require spiking before or after extraction or digestion prior to analysis to solubilize and equilibrate the species prior to introduction to the mass spectrometer.** The Method 6800/IDMS/SIDMS has also been used to **certify reference materials and for environmental forensic analysis such as water, soil, air and other samples for detecting chemical and biological agents for homeland defense and homeland security purposes."**

2007 Promulgation method update

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Characterization of waste — State of the art document — specification in solid matrices - PD CEN/TR 14589:2003 – Independent Review

"SIDMS (EPA Method 6800) is the first method to evaluate species conversion and to correct mathematically for them (using additional degrees of freedom). This is a fundamentally different approach and its accuracy, value and reliability was demonstrated [19, 20, 27-33]."

4.3.2 Application of SIDMS for Cr(VI) determination on solid matrices

Theoretically, IDMS method is applicable to elements with more than one stable isotope. USEPA SW-846 Method 6800 lists the elements of interest, namely: Sb, B, Ba, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Hg, Mo, Ni, K, Se, Ag, Sr, Tl, V and Zn. Other elements with multiple isotopes may also be analysed by means this method. For an extensive review on the derivation of the SIDMS calculations we refer to the USEPA SW-846 Method 6800 [31] (see Annex D)

Characterization of waste — State of the art document —specification in solid matrices - PD CEN/TR 14589:2003 – Independent Review

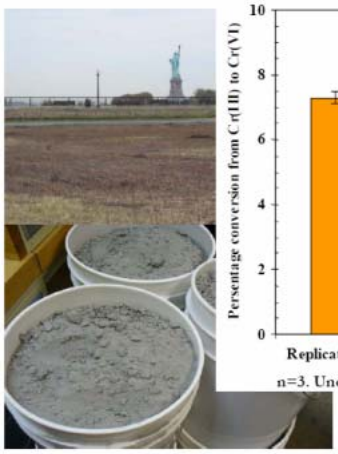
5 Final conclusions

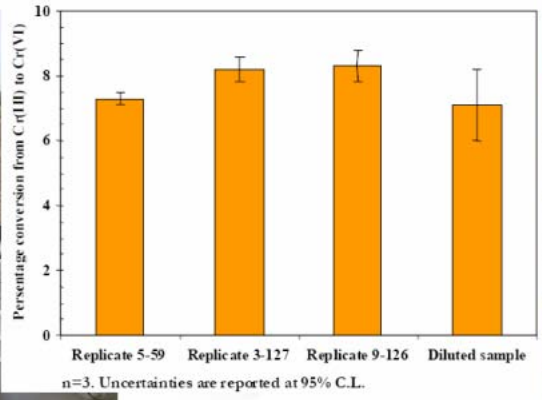
Currently, the reliability of speciated data measurements is discredited in the courts. There has not been a diagnostic method previously to provide quality assurance for speciated measurements of such elements as Cr(VI) and other transformable and highly reactive species. The proposed method of speciation isotope dilution, SIDMS, permits the monitoring of species shifts that have occurred during analysis and also during other portions of sample handling if they are included in the method protocol. This could provide both a measurement technique and a diagnostic tool to validate or calibrate other speciation measurements methods for a variety of different species.

EU Members Signing: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom

First SIDMS Speciated Standard underdevelopment - NIST, NJDEP, EPA, DU, AIT, Others

Conversion from original SRM and diluted SRM, 2007 National Validation
1st SRM that may have to be analyzed only by a single method.
Only EPA 6800 obtains the correct value on the dynamic species





"Application of Double Spike Isotope Dilution for the Accurate Determination of Cr(III), Cr(VI) and Total Cr in Yeast"(EPA6800, SIDMS)

5% of Cr in Yeast is Cr(VI), Yeast to be placed in medicin
Cr(III) transformed to Cr(VI) during measurement and
Cr(VI) transformed to Cr(III) during measurement
"and EPA method 6800 was able to sort it all out"

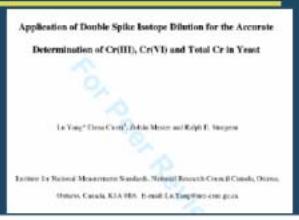

Application of Double Spike Isotope Dilution for the Accurate Determination of Cr(III), Cr(VI) and Total Cr in Yeast

Table 2. Results for Speciation of Cr in Yeast

Sample	^{Nat}Cr(III) added, mg/kg	^{Nat}Cr(VI) added, mg/kg	Measured Cr(III), mg/kg (n=3)	Measured Cr(VI), mg/kg (n=3)	^{Nat}Cr(III) Recovery, % (n=3)	^{Nat}Cr(VI) Recovery, % (n=3)	Measured Cr(III)+Cr(VI) mg/kg (n=3)	Measured Total Cr, mg/kg (n=4)
Yeast	0	0	1952±103	76±48	NA	NA	2028±57	2014±16
Spiked Yeast	1784	2398	3749±43	2466±40	101±2	100±2	NA	NA

Ref: Lu Yang, Zoltan Mester and Ralph E. SturgeonmApplication of double-spike isotope dilution for the accurate determination of Cr(III), Cr(VI) and total Cr in yeast, Analytical and Bioanalytical Chemistry, 386, pgs 1673-1680, 2006. – Nat. Research Council of Canada, by permission,

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Extraction method that does not need quantitative recovery for accuracy and automation – examples uses alkyl mercury and other mercury speciation in fish CRM

Drs. Laura H. Reyes, G. Mizanur Rahman, Skip Kingston

Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA.

Eight extraction methods for alkylmercury species in biological samples, literature summary (Methylmercury and Inorganic Hg)

Extracting Reagents:

1. Basic Leaching
- 25% (w/v) KOH (with or without methanol)
- 25% (w/v) TMAH (with or without methanol)

2. Acidic Leaching
- 5M HCl
- 6M HCl/0.1M NaCl
- 1M HCl/saturated NaCl solution
- 4M HNO_3
- CH_3COOH

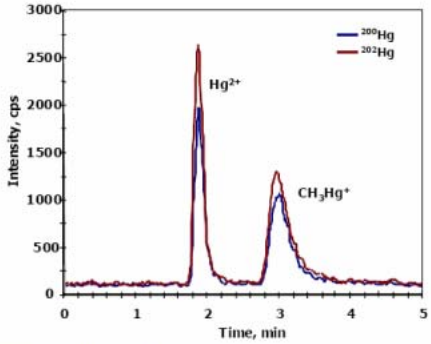
3. Sulfhydryl group reagents extraction
- 1% (w/v) L-Cysteine-HCl
- 0.05% (w/v) L-cysteine and 0.05% (v/v) β-mercaptoethanol
- 5% thiourea with 5% HNO3

4. Enzymatic hydrolysis
- Protease type XIV
- Trypsin

Extraction technique

1. Room Temperature
2. Conventional heating
3. **Ultrasonic assisted extraction**
4. **Microwave assisted extraction**

HPLC-ICP-MS chromatogram for 10 ppb Hg^{2+} and CH_3Hg^+



Chromatographic conditions[1]:

Column:	150 mm x 4.6 mm, 2 µm (DVB-C18, Metrohm Peak) serial number: 06520308 TRANSGENOMICS BIOCONSUMABLES
Mobile phase:	50 mM pyridine, 0.5 % cysteine, 5% methanol, pH 3
Elution:	Isocratic
Flow rate:	1 ml/min
Sample loop:	100 µl

[1]V. Vallant, R. Kadnar and W. Goessler, *J. Anal. At. Spectrom.*, 2007, 22, 322-325.

Total mercury in CRM-434 extracts using conventional method

Procedure	Certified value		ICP-MS	
	Total Hg, µg g^{-1}	CH_3Hg^+, mg kg^{-1}	Total Hg, mg kg^{-1}	Total Hg Recovery, %
A	5.24±0.10	5.12±0.16	5.24±0.34	99±6
B	5.24±0.10	5.12±0.16	5.19±0.59	98±5
C	5.24±0.10	5.12±0.16	4.82±0.20	91±4
D	5.24±0.10	5.12±0.16	4.25±0.49	80±9
E	5.24±0.10	5.12±0.16	4.00±0.13	76±2
F	5.24±0.10	5.12±0.16	3.62±0.47	69±9
G	5.24±0.10	5.12±0.16	4.58±0.43	87±8
H	5.24±0.10	5.12±0.16	4.60±0.55	87±10

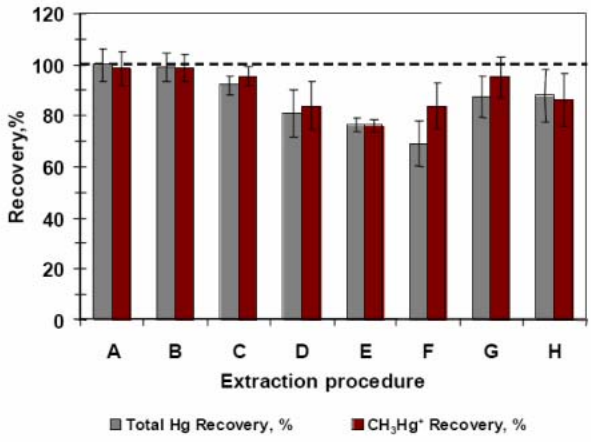
[1]Uncertainties are reported at 95% CL (n=3)

Mercury speciation in CRM-434 extracts using conventional method

Procedure	Certified value		HPLC-ICP-MS			
	Total Hg, μg g^{-1}	CH_3Hg^+, mg kg^{-1}	Hg^{2+}, mg kg^{-1}	CH_3Hg^+, mg kg^{-1}	CH_3Hg^+ Recovery, %	sum of species
A	5.24±0.10	5.12±0.16	0.06±0.02	5.05±0.13	99±3	5.11±0.13
B	5.24±0.10	5.12±0.16	0.12±0.03	5.05±0.18	99±4	5.17±0.18
C	5.24±0.10	5.12±0.16	0.18±0.05	4.88±0.17	95±3	5.06±0.18
D	5.24±0.10	5.12±0.16	0.07±0.02	4.29±0.39	84±8	4.36±0.39
E	5.24±0.10	5.12±0.16	0.07±0.02	3.90±0.12	76±2	4.00±0.13
F	5.24±0.10	5.12±0.16	0.35±0.08	3.29±0.14	84±8	3.64±0.16
G	5.24±0.10	5.12±0.16	0.45±0.10	4.87±0.20	95±4	5.32±0.22
H	5.24±0.10	5.12±0.16	0.16±0.07	4.42±0.14	86±3	4.58±0.16

[1]Uncertainties are reported at 95% CL (n=3)

Comparison of the results obtained in CRM-434 by conventional method*



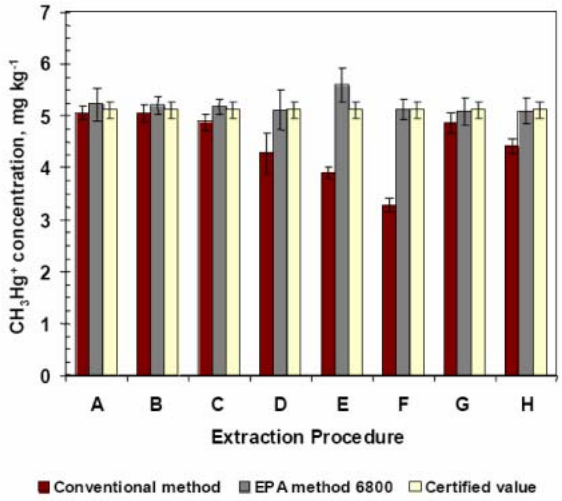
*Total mercury and CH_3Hg^+ recovery are compared with those corresponding to the certified value in CRM-434 (uncertainties are reported at 95% CL, n=3).

Comparison of the results obtained in CRM-434 using SIDMS (EPA Method 6800)1*

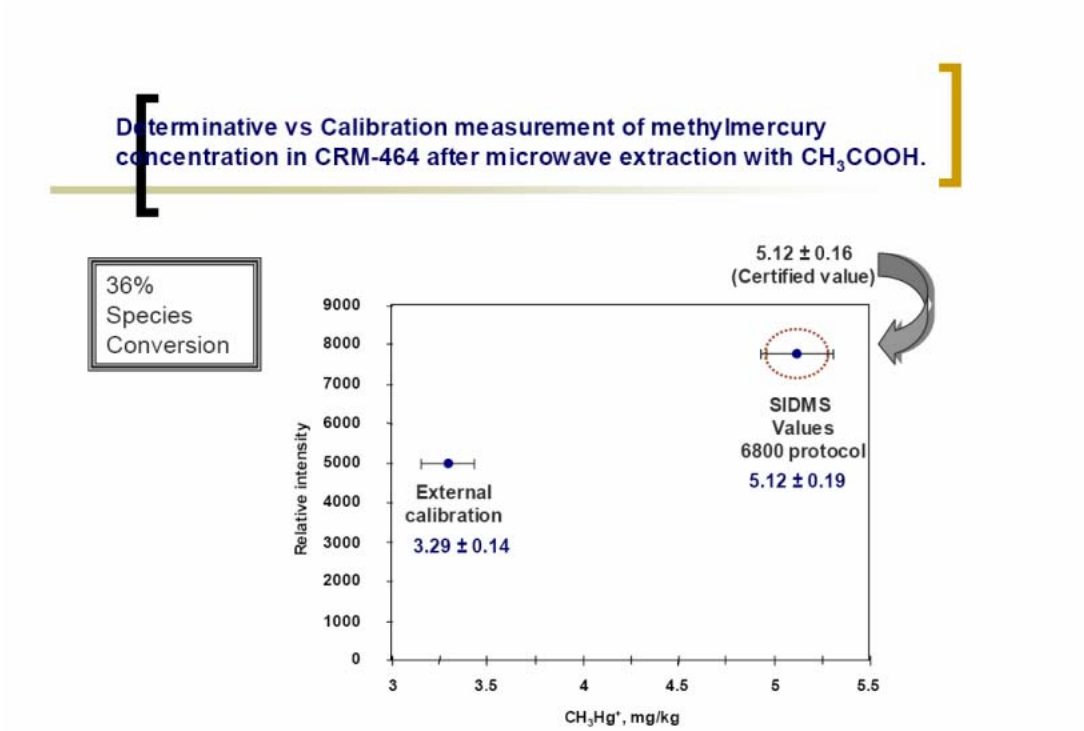
Extraction Procedure	CH_3Hg^+ Certified value, mg kg^{-1}	EPA METHOD 6800 - SIDMS (HPLC-ICP-MS)					
		Hg^{2+}, mg kg^{-1}	CH_3Hg^+, mg kg^{-1}	Apparent CH_3Hg^+ Recovery, %	Sum of species, mg kg^{-1}	Mean degree of transformation ± 95% CL, %	
						Hg^{2+} to CH_3Hg^+	CH_3Hg^+ to Hg^{2+}
A	5.12±0.16	0.07±0.02	5.22±0.31	102±6	5.3±0.3	5±3	6±1
B	5.12±0.16	0.07±0.03	5.20±0.18	102±4	5.3±0.2	6±2	4±1
C	5.12±0.16	0.30±0.07	5.18±0.13	101±3	5.5±0.1	3±2	6±2
D	5.12±0.16	0.13±0.05	5.11±0.38	100±7	5.2±0.4	5±3	3±1
E	5.12±0.16	0.11±0.07	5.60±0.33	109±6	5.7±0.3	18±4	0.8±0.6
F	5.12±0.16	0.27±0.12	5.12±0.19	100±4	5.4±0.2	4±2	27±5
G	5.12±0.16	1.05±0.14	5.08±0.25	99±5	6.1±0.3	4±3	4±1
H	5.12±0.16	0.15±0.05	5.09±0.24	99±5	5.2±0.2	4±2	1.4±0.5

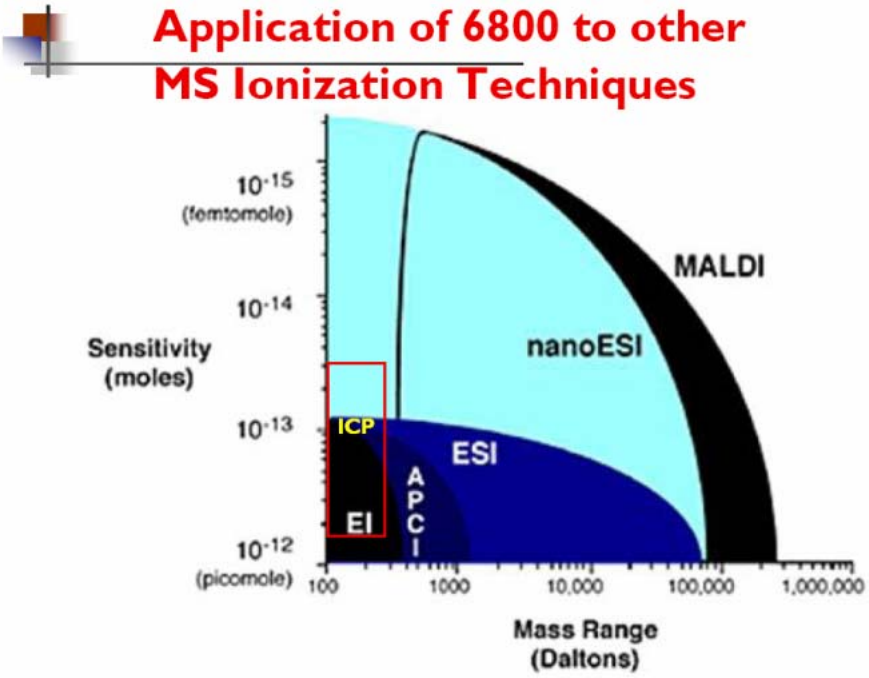
*CH_3Hg^+ recovery are compared with those corresponding to the certified value in CRM-434 (uncertainties are reported at 95% CL, n=3).

Evaluation of extraction procedures using SIDMS (EPA Method 6800)1



[1]Uncertainties are reported at 95% CL (n=3)


Determinative vs Calibration measurement of methylmercury concentration in CRM-464 after microwave extraction with CH_3COOH.
36% Species Conversion
5.12 ± 0.16 (Certified value)
SIDMS Values 6800 protocol
5.12 ± 0.19
External calibration
3.29 ± 0.14
Relative intensity
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
3
3.5
4
4.5
5
5.5
CH_3Hg^+, mg/kg

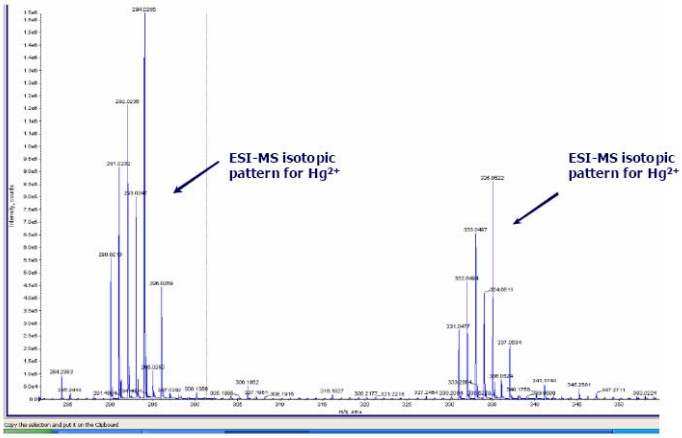

Application of 6800 to other MS Ionization Techniques
10^{-15} (femtomole)
10^{-14}
10^{-13}
10^{-12} (picomole)
Sensitivity (moles)
MALDI
nanoESI
ESI
ICP
EI
APCI
100
1000
10,000
100,000
1,000,000
Mass Range (Daltons)

Further in Work

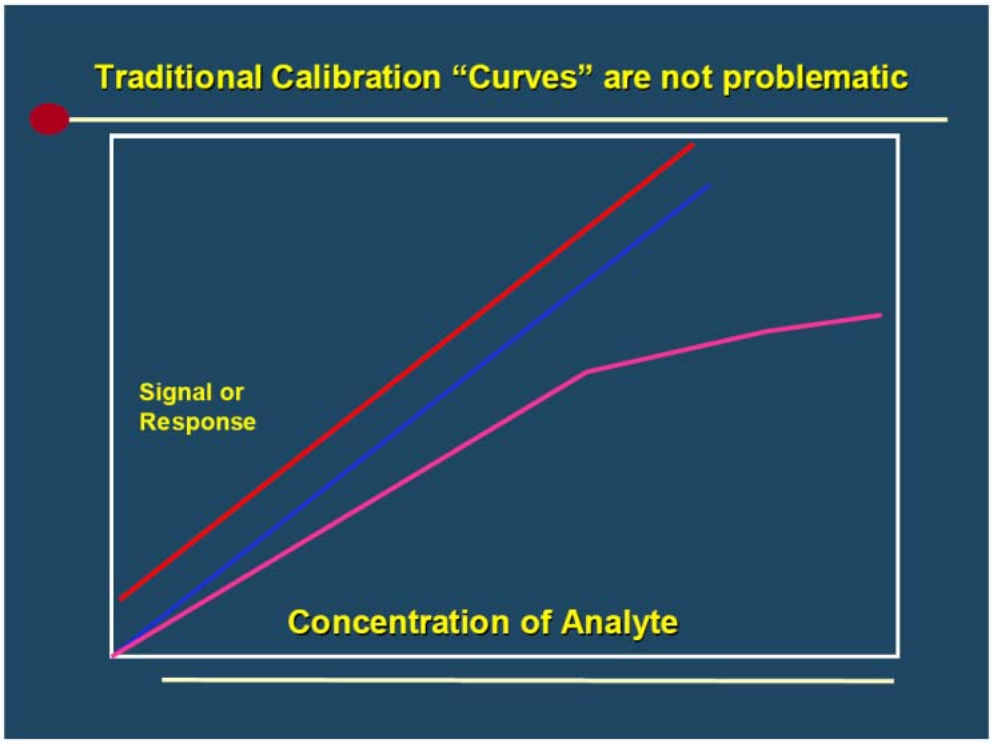
4) Demonstrate and validate these analyses error correction advantages function on all mass spectrometric platforms

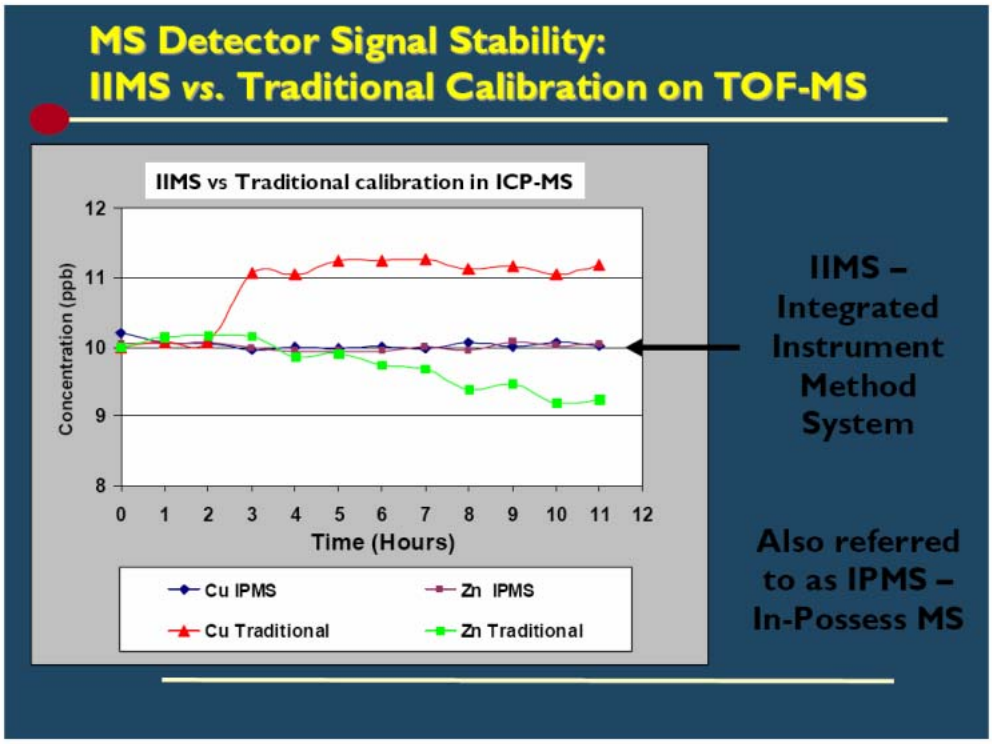
- **(i.e. ESI-MS, MALDI-MS, LC-MS, GC-MS, ICP-MS,)**

ESI-MS spectrum of 10 ppm $MeHg^+$ in 0.005 % cysteamine: acetonitrile (50:50)

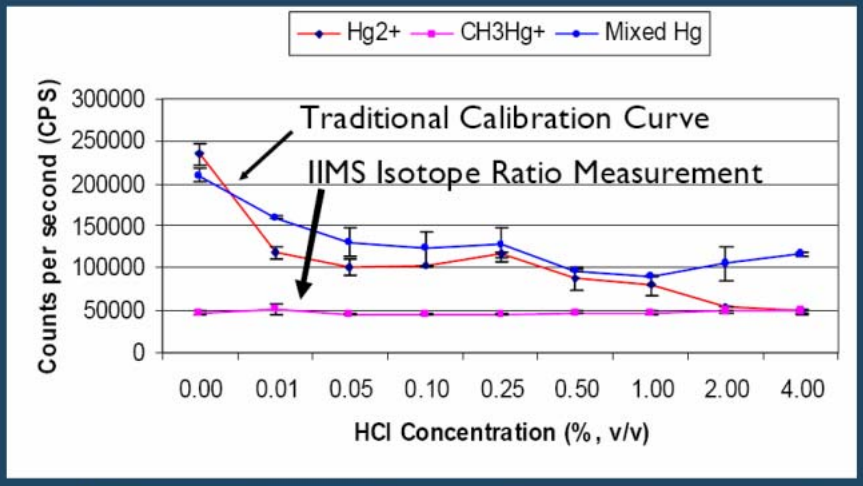


Integrating QA and Automation into DIDMS and DSIDMS Speciation and Enabling the Correction of Instrumental Errors


Traditional Calibration "Curves" are not problematic
Signal or Response
Concentration of Analyte

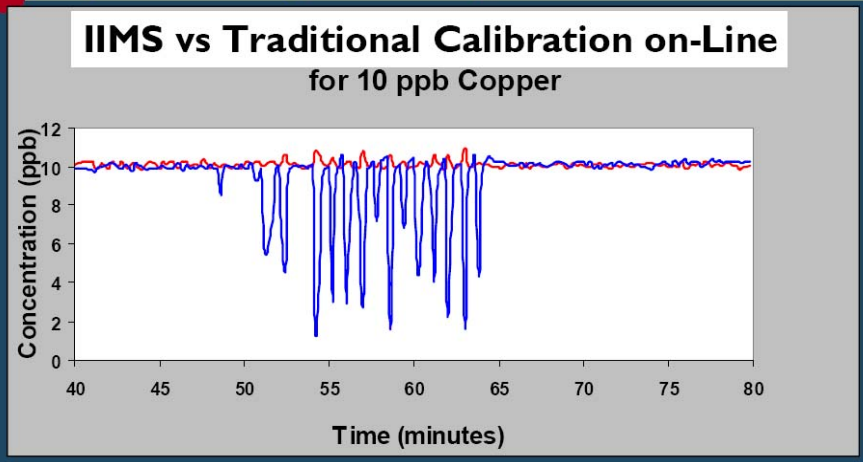

MS Detector Signal Stability:
IIMS vs. Traditional Calibration on TOF-MS
IIMS vs Traditional calibration in ICP-MS
Concentration (ppb)
12
11
10
9
8
0 1 2 3 4 5 6 7 8 9 10 11 12
Time (Hours)
Cu IPMS
Zn IPMS
Cu Traditional
Zn Traditional
IIMS – Integrated Instrument Method System
Also referred to as IPMS – In-Possess MS

Accuracy is independent of instrumental matrix influence and time drift and signal response in EPA method 6800 (SIDMS)



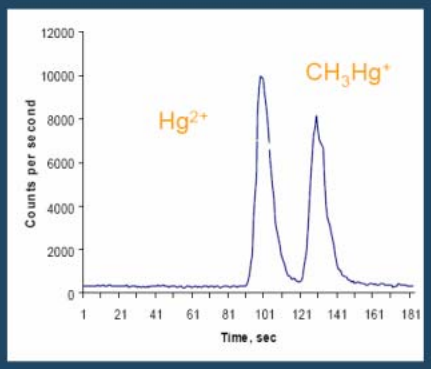
IIMS/SIDMS/IPMS are independent of MS drift for quantification
IIMS – Integrated Instrument Method System

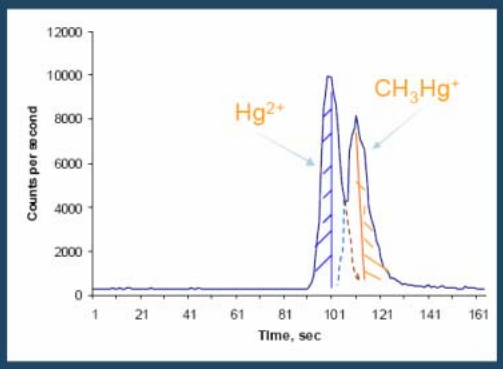
Automated EPA Method 6800 uses IIMS and sample preparation accuracy robustness: Independent of Signal Stability Enables MS Automation



With a typical analytical instrument, air bubbles in the sample introduction system would cause dramatic instability and/or decrease in signal. *However, with IIMS-SIDMS technology, MS detector signal remains constant.*

Accuracy Independent of Separation

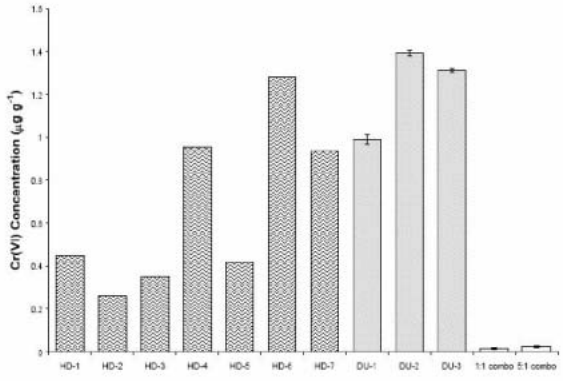




Field spiked with enriched Cr (VI) 95% Cr(VI) destroyed before returning to the laboratory

FIGURE 6

HEXAVALENT CHROMIUM CONCENTRATIONS IN FLY ASH LEACHATE OBTAINED FROM HISTORICAL DATA (HD), STUDY WITH SIDMS (DU), AND BEFORE AND AFTER COMBINATION WITH ACID MINE DRAINAGE (AMD) (Ref. 14)



Cr(VI) concentration in leachate before and after combination with AMD, which illustrate the dramatic and statistically significant decrease in Cr(VI) concentrations in the fly ash leachate as a result of treating with AMD. Observations from HD-1 to HD-7 (dark gray bars) were historical data obtained from the power plant. Observations from DU-1 to DU-3 (light gray bars) were obtained from the SIDMS analysis at Duquesne University during current study, and observations '1:1 combo' and '5:1 combo' were obtained by mixing leachate and AMD with the ratios of 1:1 and 5:1 (leachate to AMD), respectively. Error bars are shown at 95% confidence intervals with n = 3.

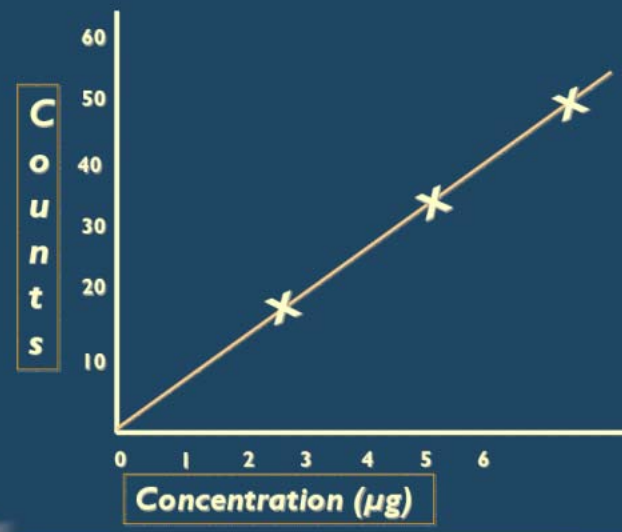
2007 Update of EPA 6800

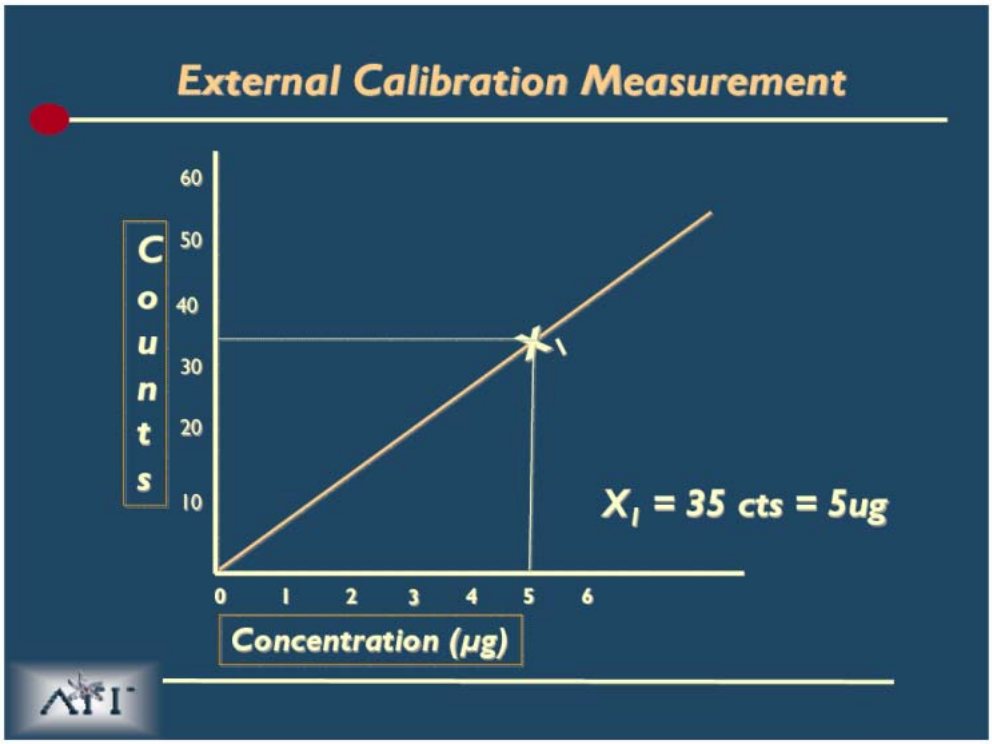
Figure 6 example of field spiking for sample preparation QA

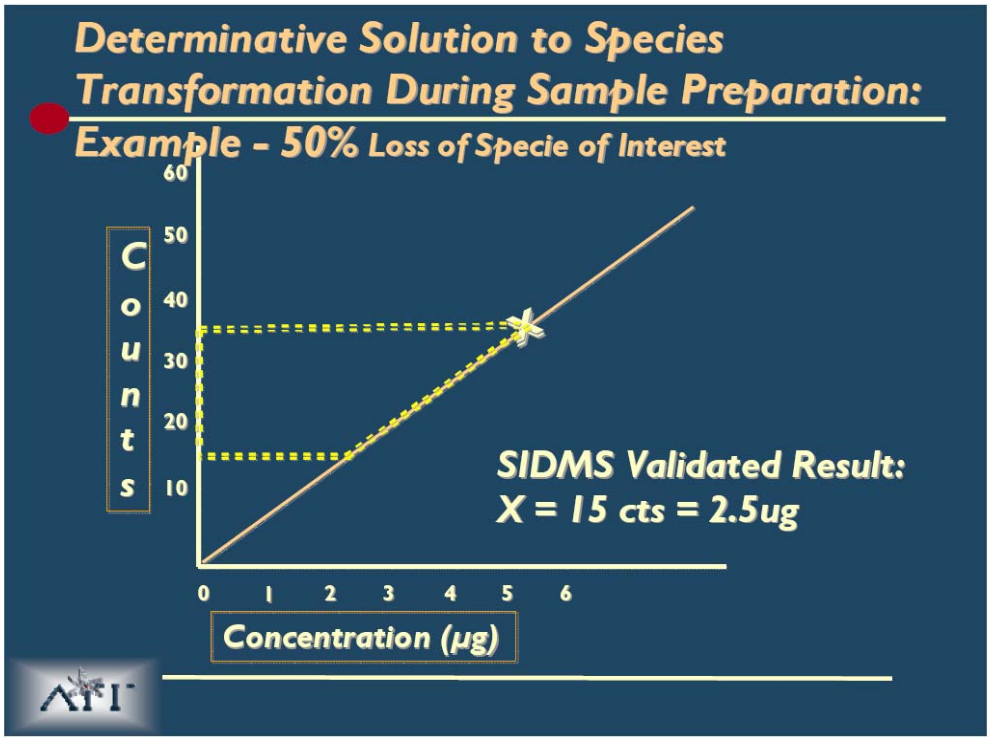
Methods of Quantitation

- External Standard
  - Calibration curve
- Internal Standard
  - A Different molecule or species (Response Factor)
- Isotope Dilution*
  - 1. calibration curve made from isotopic analogue
  - 2. direct isotope ratio between analyte and isotopic analogue
- Speciated Isotope Dilution*
  - Direct isotope ratio between analyte and isotopic analogue
  - Deconvolution and correction for transformed analyte species
- *Forms of Determinative IDMS & Determinative SIDMS
  - DIDMS and DSIDMS

External Calibration Technique




External Calibration Measurement
Counts
60
50
40
30
20
10
0
1
2
3
4
5
6
Concentration (µg)
X_1 = 35 cts = 5ug


Determinative Solution to Species Transformation During Sample Preparation:
Example - 50% Loss of Specie of Interest
Counts
60
50
40
30
20
10
0
1
2
3
4
5
6
Concentration (µg)
SIDMS Validated Result:
X = 15 cts = 2.5ug

Blood Sample Spiked with Hg^{2+} and CH_3Hg^+ - Deliberate Biase Correction

Blood Sample	Hg^{2+} conc. in ppb	CH_3Hg^+ conc. in ppb	Sum of Hg^{2+} and CH_3Hg^+ conc. in ppb	Hg^{2+} to CH_3Hg^+	CH_3Hg^+ to Hg^{2+}
Original sample	220 ± 11	168 ± 9	388 ± 16	1.08% ± 3.01%	1.50% ± 1.55%
Sample mimicking 25% reduction in recovery- Deliberate bias	218 ± 9	161 ± 11	379 ± 17	2.02% ± 2.74%	0.14% ± 2.06%

"Deconvolution" Simplified Equations for 2 species

- For Hg^{2+}

$$R^{In}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

$$R^{In}_{201/202} = \frac{\left({}^{201}A_n N^{In}_n + {}^{201}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{201}A_n N^{Me}_n + {}^{201}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

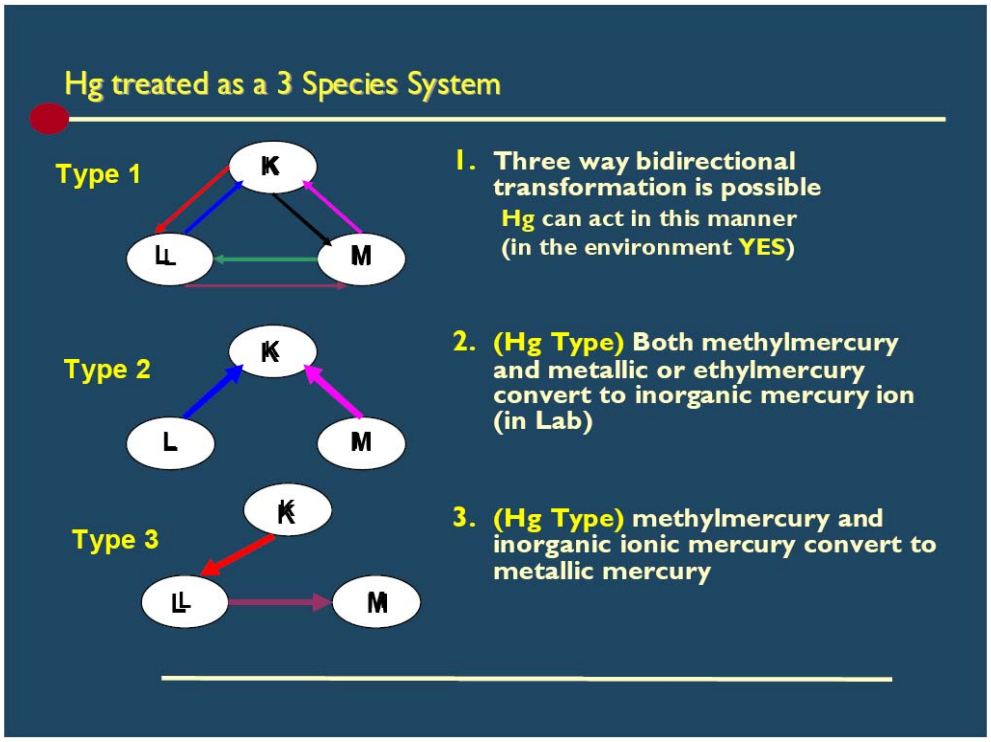
- For CH_3Hg^+

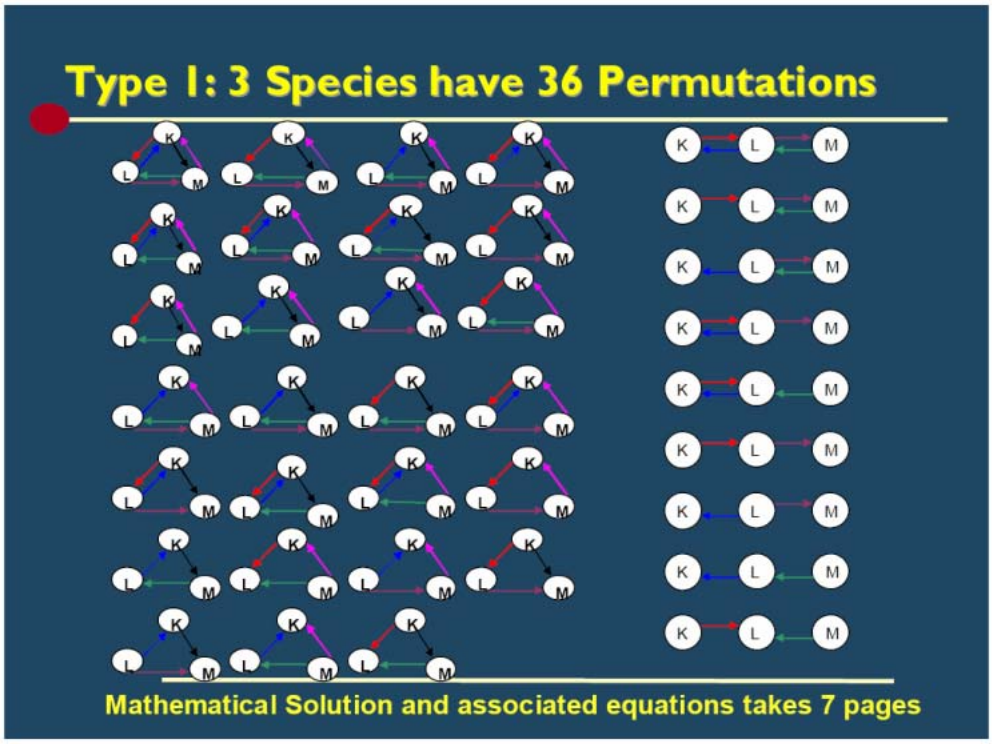
$$R^{Me}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)\alpha + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

$$R^{In}_{201/202} = \frac{\left({}^{201}A_n N^{In}_n + {}^{201}A^{In}_s N^{In}_s\right)\alpha + \left({}^{201}A_n N^{Me}_n + {}^{201}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

α fraction of $Hg^{2+} \longrightarrow CH_3Hg^+$ and β fraction of $CH_3Hg^+ \longrightarrow Hg^{2+}$

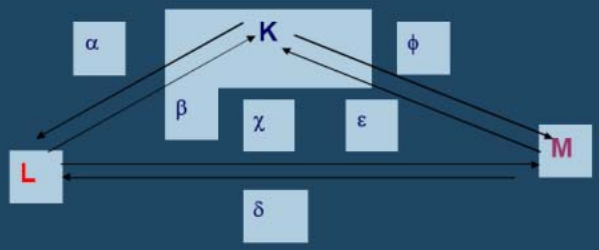
N^{In} is Concentration of Hg^{2+}, and N^{Me} is Concentration of CH_3Hg^+


Hg treated as a 3 Species System
Type 1
K
L
M
1. Three way bidirectional transformation is possible
Hg can act in this manner
(in the environment YES)
Type 2
K
L
M
2. (Hg Type) Both methylmercury and metallic or ethylmercury convert to inorganic mercury ion (in Lab)
Type 3
K
L
M
3. (Hg Type) methylmercury and inorganic ionic mercury convert to metallic mercury


Type 1: 3 Species have 36 Permutations
Mathematical Solution and associated equations takes 7 pages

EPA Method 6800 validated for Three Species
Simultaneously Inorganic-, Methyl-, Ethyl-Mercury

Three Species
(Species *L*)



$$R^K_{F/R} = \frac{\left({}^F A_x C_x^K W_x + {}^F A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^F A_x C_x^L W_x + {}^F A_s^L C_s^L W_s^L\right)\beta + \left({}^F A_x C_x^M W_x + {}^F A_s^M C_s^M W_s^M\right)\varepsilon}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\beta + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\varepsilon}$$

$$R^K_{G/R} = \frac{\left({}^G A_x C_x^K W_x + {}^G A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^G A_x C_x^L W_x + {}^G A_s^L C_s^L W_s^L\right)\beta + \left({}^G A_x C_x^M W_x + {}^G A_s^M C_s^M W_s^M\right)\varepsilon}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\beta + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\varepsilon}$$

$$R^K_{H/R} = \frac{\left({}^H A_x C_x^K W_x + {}^H A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^H A_x C_x^L W_x + {}^H A_s^L C_s^L W_s^L\right)\beta + \left({}^H A_x C_x^M W_x + {}^H A_s^M C_s^M W_s^M\right)\varepsilon}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)(1-\alpha-\phi) + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\beta + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\varepsilon}$$

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EPA Method 6800 - SIDMS Equations for Three Species Simultaneously

(Species *K*)

$$R^L_{F/R} = \frac{\left({}^F A_x C_x^K W_x + {}^F A_s^K C_s^K W_s^K\right)\alpha + \left({}^F A_x C_x^L W_x + {}^F A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^F A_x C_x^M W_x + {}^F A_s^M C_s^M W_s^M\right)\delta}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\alpha + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\delta}$$

$$R^L_{G/R} = \frac{\left({}^G A_x C_x^K W_x + {}^G A_s^K C_s^K W_s^K\right)\alpha + \left({}^G A_x C_x^L W_x + {}^G A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^G A_x C_x^M W_x + {}^G A_s^M C_s^M W_s^M\right)\delta}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\alpha + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\delta}$$

$$R^L_{H/R} = \frac{\left({}^H A_x C_x^K W_x + {}^H A_s^K C_s^K W_s^K\right)\alpha + \left({}^H A_x C_x^L W_x + {}^H A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^H A_x C_x^M W_x + {}^H A_s^M C_s^M W_s^M\right)\delta}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\alpha + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)(1-\beta-\chi) + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)\delta}$$

(Species *M*)

$$R^M_{F/R} = \frac{\left({}^F A_x C_x^K W_x + {}^F A_s^K C_s^K W_s^K\right)\phi + \left({}^F A_x C_x^L W_x + {}^F A_s^L C_s^L W_s^L\right)\chi + \left({}^F A_x C_x^M W_x + {}^F A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\phi + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\chi + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}$$

$$R^M_{G/R} = \frac{\left({}^G A_x C_x^K W_x + {}^G A_s^K C_s^K W_s^K\right)\phi + \left({}^G A_x C_x^L W_x + {}^G A_s^L C_s^L W_s^L\right)\chi + \left({}^G A_x C_x^M W_x + {}^G A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\phi + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\chi + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}$$

$$R^M_{H/R} = \frac{\left({}^H A_x C_x^K W_x + {}^H A_s^K C_s^K W_s^K\right)\phi + \left({}^H A_x C_x^L W_x + {}^H A_s^L C_s^L W_s^L\right)\chi + \left({}^H A_x C_x^M W_x + {}^H A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}{\left({}^R A_x C_x^K W_x + {}^R A_s^K C_s^K W_s^K\right)\phi + \left({}^R A_x C_x^L W_x + {}^R A_s^L C_s^L W_s^L\right)\chi + \left({}^R A_x C_x^M W_x + {}^R A_s^M C_s^M W_s^M\right)(1-\delta-\varepsilon)}$$

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Applied Isotope Technologies, Inc.

Mercury Speciated Analysis Calculation Software (*)

Answer the following questions by filling the appropriate information in the bordered cells:

(A)	How much sample did you double spikes?	1.0000	g	User Entry is Required
(B)	How much $^{199}Hg^{2+}$ did you spike?	1.0000	g	User Entry is Required
(C)	How much $^{200}CH_3Hg^+$ did you spike?	1.0000	g	User Entry is Required
(D)	What is the concentration of $^{199}Hg^{2+}$ spike?	10.0000	pg/g	User Entry is Required
(E)	What is the concentration of $Me^{200}Hg^+$ spike?	10.0000	pg/g	User Entry is Required

(D) What are the isotope ratios you obtained after analyzing the sample extract or the sample with an appropriate instrument?

Analysis Replicates	Hg2+ $^{199}Hg/^{202}Hg$	Hg2+ $^{202}Hg/^{201}Hg$	MeHg+ $^{199}Hg/^{201}Hg$	MeHg+ $^{202}Hg/^{201}Hg$
1	1.161925	1.004248	0.6403534	1.03356108
2	1.144258	0.990021	0.6123047	1.01719221
3	1.08226	0.993098	0.6231401	1.03792597
4	1.123481	0.995789	0.6252661	1.02955975

Place the mouse cursor on any of the four cells on the "Analysis Replicates, 1 line" to see User Entry Instructions.

Deconvoluted Concentration and Interconversion

Analysis Replicate	Deconvoluted Hg2+	Deconvoluted MeHg+	Interconversion Hg2+ to MeHg+	Interconversion MeHg+ to Hg2+
1	11.888	121.3938	22.467%	25.291%
2	12.142	130.3882	14.554%	26.819%
3	16.368	118.8004	15.762%	30.583%
4	13.364	123.3662	17.606%	27.450%
Average	13.440	123.487	17.598%	27.540%

Place the mouse cursor on any of the four cells on the "Analysis Replicates, 1 line" to see User Entry Instructions.

SIDMS Calculation

SIDMS Analysis of Three Mercury Species from Hair (IAEA-085) Measured by 3 species SIDMS 6800

	Hg^{2+} (µg/g)	$MeHg^{+}$ (µg/g)	$EtHg^{+}$ (µg/g)	Hg^{2+} to $MeHg^{+}$ (%)	Hg^{2+} to $EtHg^{+}$ (%)	$MeHg^{+}$ to Hg^{2+} (%)	$MeHg^{+}$ to $EtHg^{+}$ (%)	$EtHg^{+}$ to Hg^{2+} (%)	$EtHg^{+}$ to $MeHg^{+}$ (%)
Certified value	0.3 ±0.2	22.9±1.4	****	NA	NA	NA	NA	NA	NA
Measured value	1.3 ±0.7	22.1±0.4	21.1±1.0	8.3 ± 0.9	1.2 ± 0.4	5.4 ± 0.8	1.7 ± 0.3	74.3±4.0	6.8 ± 0.7

Uncertainties are at 95% CI, n = 8.

**** sample spiked with EtHgCl (22.7 ± 1.0 µg as Hg / g Hair)

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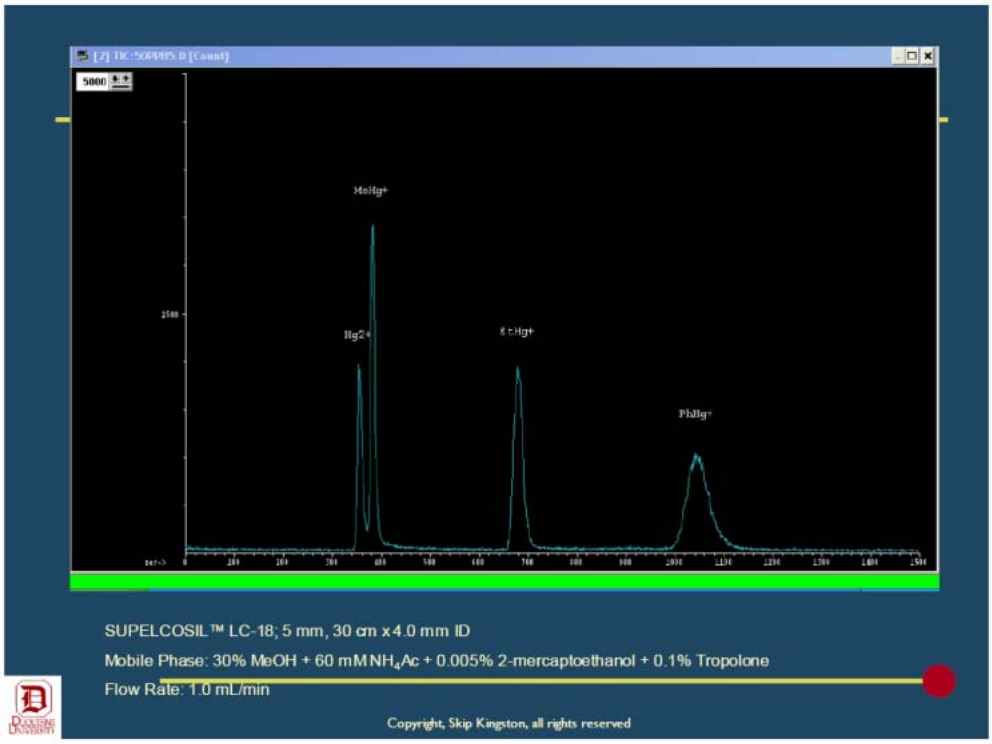
Inorganic-, Methyl- and Ethyl-, Mercury

CRM Human Hair Study (H-9)

	Deconvoluted Concentration			Interconversion in (%)			Interconversion in (%)		
Analysis Reps	Hg2+	MeHg+	EtHg+	Hg2+ to MeHg+	MeHg+ to Hg2+	MeHg+ to EtHg+	EtHg+ to MeHg+	EtHg+ to Hg2+	Hg2+ to EtHg+
1	0.218	21.9816	22.2375	8.866%	5.08%	0.93%	7.11%	77.77%	1.54%
2	3.216	21.3193	19.3977	9.045%	6.07%	1.85%	7.97%	81.10%	1.10%
3	0.937	21.5255	22.0858	6.743%	6.97%	2.02%	6.44%	78.50%	1.05%
4	0.817	22.3988	22.5879	9.512%	4.03%	1.31%	7.80%	77.47%	0.64%
Average	1.297	21.806	21.5772	8.54%	5.54%	1.53%	7.33%	78.71%	1.08%
Stdev	1.317448	0.482319	1.4682	1.23%	1.27%	0.50%	0.70%	1.65%	0.37%
95% CL	2.094742	0.766887	2.3344	1.95%	2.02%	0.79%	1.12%	2.63%	0.58%


MeHg+
Hg2+
PhHg+
SUPELCOSIL™ LC-18; 5 mm, 30 cm x 4.0 mm ID
Mobile Phase: 30% MeOH + 60 mM NH_4Ac + 0.005% 2-mercaptoethanol + 0.1% Tropolone
Flow Rate: 1.0 mL/min
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Homeland Security: Updated EPA 6800 applied to Drinking Water Toxins
An equivalent act in drinking water could be 100 -10,000 times worse in lost lives
Michael Gritzuk, P.E.
Director
City of Phoenix, AZ
Water Service Authority
July 19, 2004
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2007 Update Method EPA 6800 (IDMS/SIDMS)

METHOD 6800

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application.

1.0 SCOPE AND APPLICATION

1.1 This method consists of two approaches: isotope dilution mass spectrometry (IDMS) for the determination of total metals and speciated isotope dilution mass spectrometry (SIDMS) for the determination of elemental species. This method is applicable to the determination of total metals and metal species at sub µg/L levels in water samples or in waste extracts or digests. In general, elements that have more than one available stable isotope can be analyzed by IDMS. SIDMS may require more isotopes of an element, depending on the number of interconvertable species. The following analytes have been determined by this method:

Element		CASRN*
Antimony	(Sb)	7440-36-0
Boron	(B)	7440-42-8
Barium	(Ba)	7440-39-3
Cadmium	(Cd)	7440-43-9
Cobalt	(Co)	7440-48-4
Chromium	(Cr)	7440-47-3
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

* Chemical Abstract Service Registry Number

6800 - 1 Revision 0 April 2004

Excerpt from Item-1.5:

"Aqueous samples such as drinking water, ground water, and other aqueous samples may be directly spiked and analyzed. **Solid samples such as soils, sludges, sediments, industrial materials, biological tissues, botanicals, lysed cells, foods, mixed samples, blood, and urine and other samples containing solid matrices require spiking before or after extraction or digestion prior to analysis to solubilize and equilibrate the species prior to introduction to the mass spectrometer.** The Method 6800/IDMS/SIDMS has also been used to **certify reference materials and for environmental forensic analysis such as water, soil, air and other samples for detecting chemical and biological agents for homeland defense and homeland security purposes."**

2007 Promulgation method update

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Flexible methods and New tools make the scientists toolbox

Electrospray Ionization (ESI)

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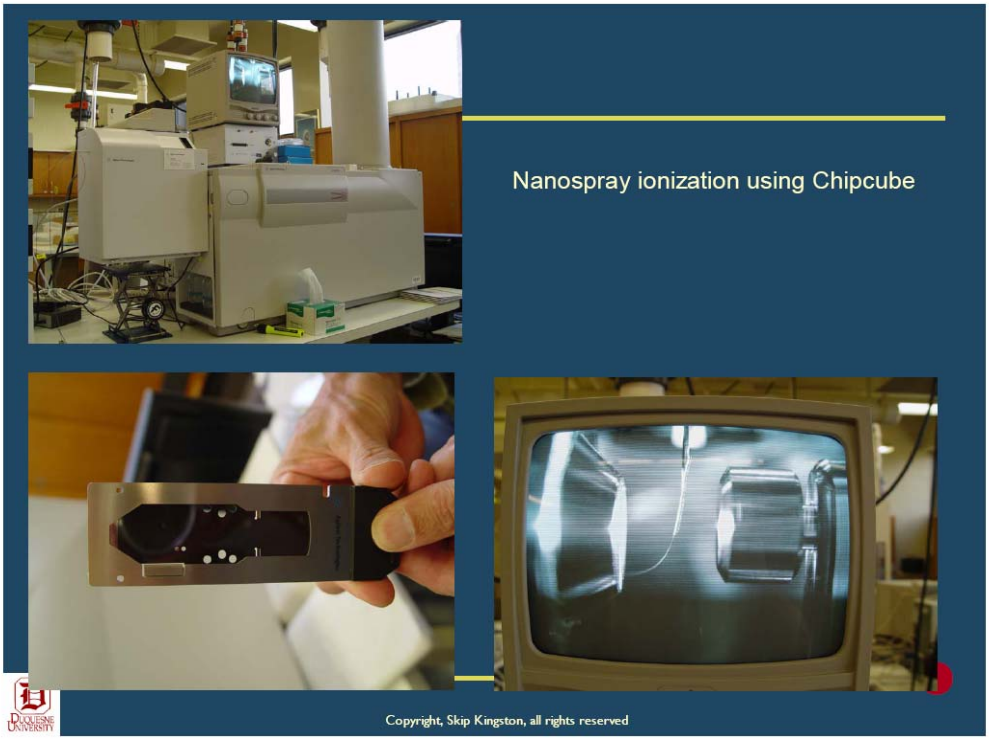

TOXICOLOGICAL PROFILE FOR MERCURY
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, CDC

Public Health Service, Agency for Toxic Substances and Disease Registry, March 1999

- A person can be exposed to mercury from breathing in contaminated air, from swallowing or eating contaminated water or food, or from having skin contact with mercury.
- A large part of this mercury is in the form of methylmercury and probably comes from eating fish. Methylmercury is the form of mercury most easily absorbed through the gastrointestinal tract (about 95% absorbed).
- When you breathe in mercury vapors, however, most (about 80%) of the mercury enters your bloodstream directly from your lungs, and then rapidly goes to other parts of your body, including the brain and kidneys.
- Analyses Methods to measure mercury levels in the body - involve taking blood, urine, or hair samples.
- Additional research will be needed to validate the determination of individual mercury species (i.e., methylmercury, phenyl mercury, mercury acetate, etc.)
- Effects: Metallic mercury vapors or organic mercury may affect many different areas of the brain and their associated functions, resulting in a variety of symptoms. These include personality changes (irritability, shyness, nervousness), tremors, changes in vision (constriction (or narrowing) of the visual field), deafness, muscle incoordination, loss of sensation, and difficulties with memory.

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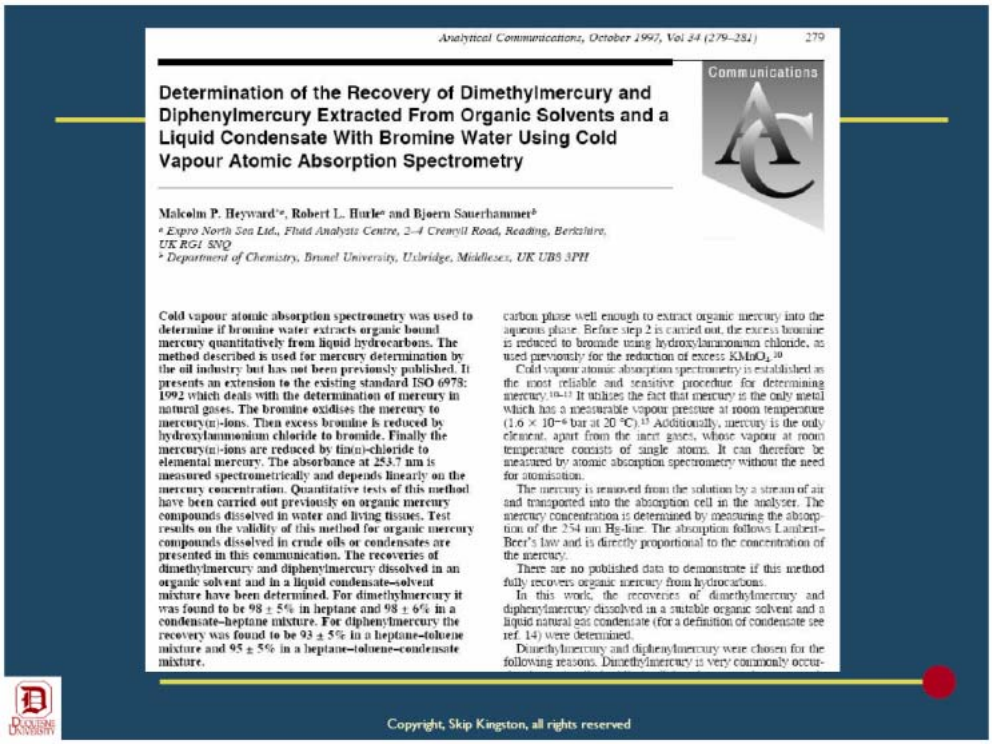

Analytical Communications, October 1997, Vol 34 (279–281) 279

Communications

Determination of the Recovery of Dimethylmercury and Diphenylmercury Extracted From Organic Solvents and a Liquid Condensate With Bromine Water Using Cold Vapour Atomic Absorption Spectrometry

Malcolm P. Heyward[a]*, Robert L. Hurle[a] and Bjoern Sauerhammer[b]
[a] Expro North Sea Ltd., Fluid Analysis Centre, 2–4 Cremyll Road, Reading, Berkshire, UK RG1 8NQ
[b] Department of Chemistry, Brunel University, Uxbridge, Middlesex, UK UB8 3PH

Cold vapour atomic absorption spectrometry was used to determine if bromine water extracts organic bound mercury quantitatively from liquid hydrocarbons. The method described is used for mercury determination by the oil industry but has not been previously published. It presents an extension to the existing standard ISO 6978: 1992 which deals with the determination of mercury in natural gases. The bromine oxidises the mercury to mercury(II)-ions. Then excess bromine is reduced by hydroxylammonium chloride to bromide. Finally the mercury(II)-ions are reduced by tin(II)-chloride to elemental mercury. The absorbance at 253.7 nm is measured spectrometrically and depends linearly on the mercury concentration. Quantitative tests of this method have been carried out previously on organic mercury compounds dissolved in water and living tissues. Test results on the validity of this method for organic mercury compounds dissolved in crude oils or condensates are presented in this communication. The recoveries of dimethylmercury and diphenylmercury dissolved in an organic solvent and in a liquid condensate–solvent mixture have been determined. For dimethylmercury it was found to be 98 ± 5% in heptane and 98 ± 6% in a condensate–heptane mixture. For diphenylmercury the recovery was found to be 93 ± 5% in a heptane–toluene mixture and 95 ± 5% in a heptane–toluene–condensate mixture.

carbon phase well enough to extract organic mercury into the aqueous phase. Before step 2 is carried out, the excess bromine is reduced to bromide using hydroxylammonium chloride, as used previously for the reduction of excess $KMnO_4$.[10]

Cold vapour atomic absorption spectrometry is established as the most reliable and sensitive procedure for determining mercury.[10–13] It utilises the fact that mercury is the only metal which has a measurable vapour pressure at room temperature (1.6×10^{-6} bar at 20 °C).[13] Additionally, mercury is the only element, apart from the inert gases, whose vapour at room temperature consists of single atoms. It can therefore be measured by atomic absorption spectrometry without the need for atomisation.

The mercury is removed from the solution by a stream of air and transported into the absorption cell in the analyser. The mercury concentration is determined by measuring the absorption of the 254 nm Hg-line. The absorption follows Lambert–Beer's law and is directly proportional to the concentration of the mercury.

There are no published data to demonstrate if this method fully recovers organic mercury from hydrocarbons.

In this work, the recoveries of dimethylmercury and diphenylmercury dissolved in a suitable organic solvent and a liquid natural gas condensate (for a definition of condensate see ref. 14) were determined.

Dimethylmercury and diphenylmercury were chosen for the following reasons. Dimethylmercury is very commonly occur-

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Homeland Defense and Homeland Security Measurements of Common Toxins and Combinations of Toxins

- Cyanide
- Azide
- Dimethylmercury
- Methylmercury
- Combinations of Alkylmercury and other Toxins, in Water, Air, Food, Ware Fighter
- Methylmercury and Dimethylmercury
  - In Solvents (methanol)
  - From Land Fills
  - In food with other toxins
  - In water and air as terrorist chemical agents and threats

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Research on Alkyl Mercury and Other Bulk Toxins

- Dimethylmercury – Scenario presented to President Bush
  - – E. Floyd Kvamme-Office of Technology Policy
- Cyanide
- Azide
- Alkylmercury species
- Combinations
- Reduction of False Positives and False Negatives
- Automation and QA

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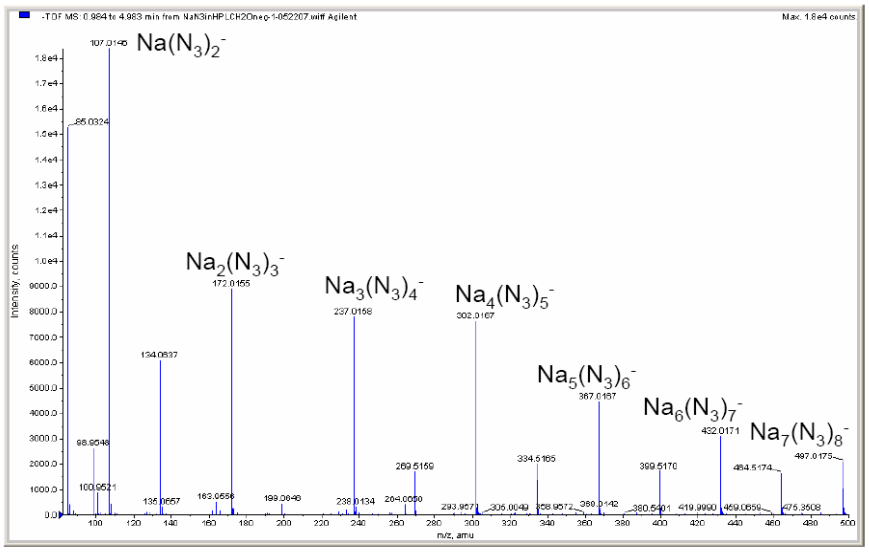
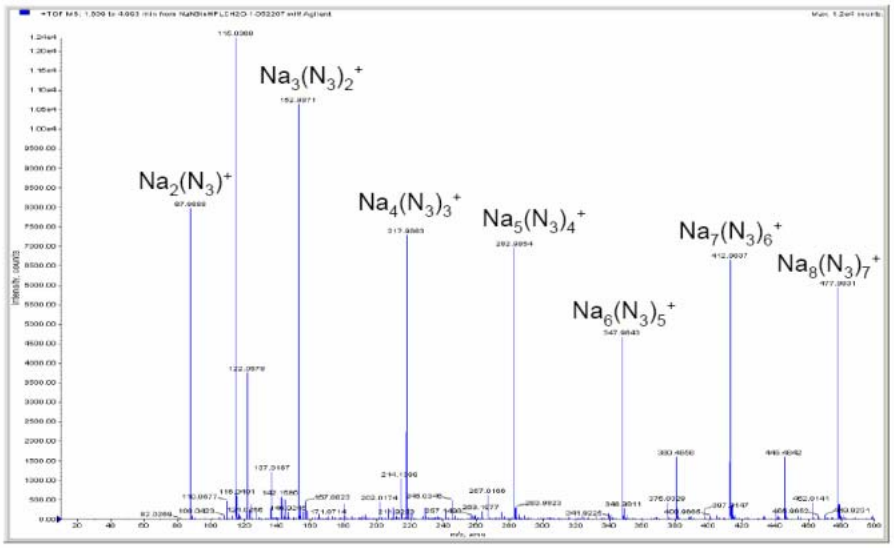
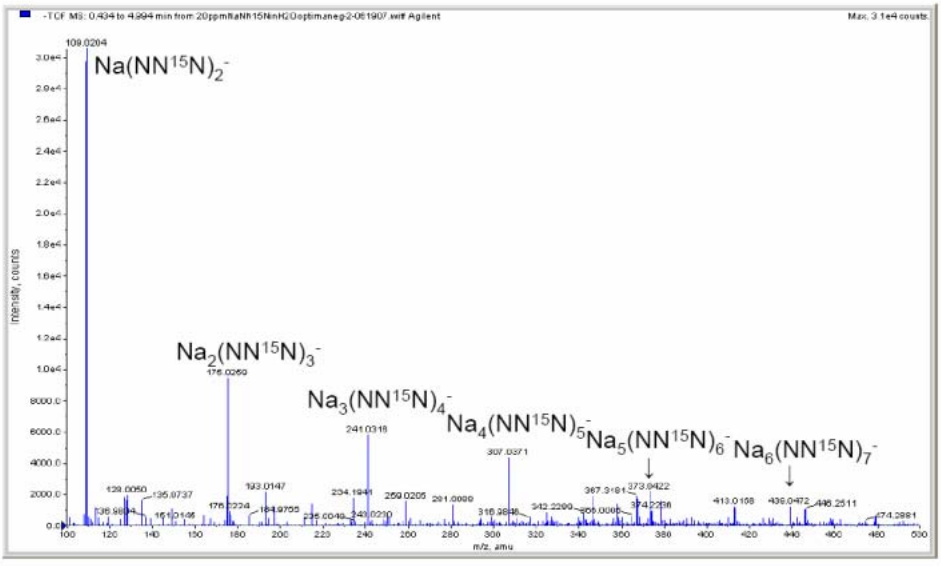
NaN_3 in HPLC H_2O negative mode



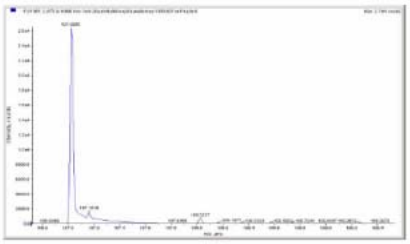
NaN_3 in HPLC H_2O positive mode

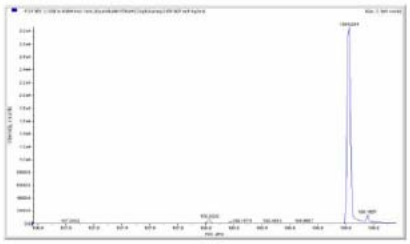


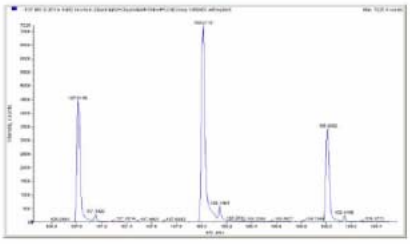
20ppm $NaNN^{15}N$ in HPLC H_2O negative mode



Close up of first peak, Na(N3)2- in negative mode upper left-natural, upper right-isotope, lower left- mix 20 ppm in HPLC H2O



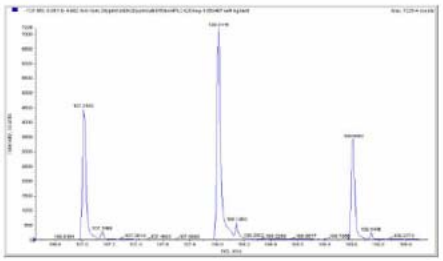




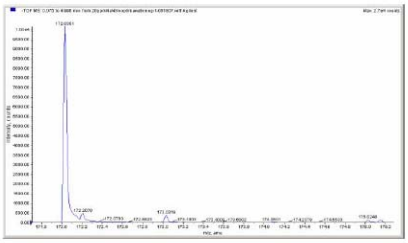
- Possible Combinations for Na(N3)2-,
- Na15N3 + 15N3
- Na15N3 + N3
- NaN3 + 15N3
- NaN3 + N3

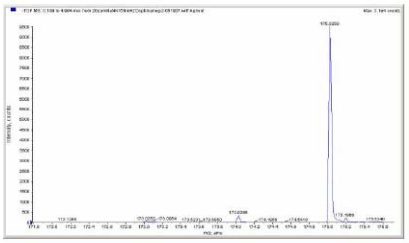
Quantification of $Na(N_3)_2^-$

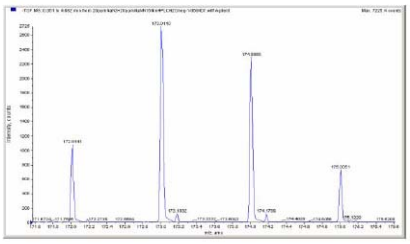
- For $Na(N_3)_2^-$, there are four possible combinations with natural and isotopically labeled azide anion
  - $Na^{15}N_3 + {}^{15}N_3^-$
  - $Na^{15}N_3 + N_3^-$
  - $NaN_3 + {}^{15}N_3^-$
  - $NaN_3 + N_3^-$
- Expect a 2:1 ratio of peaks 108 and 109
- After integration of the peaks, the ratio was determined to be: 2.05:1
- From this ratio and integration, the natural concentration was determined to be 21.9 ppm when the actual value was 20 ppm



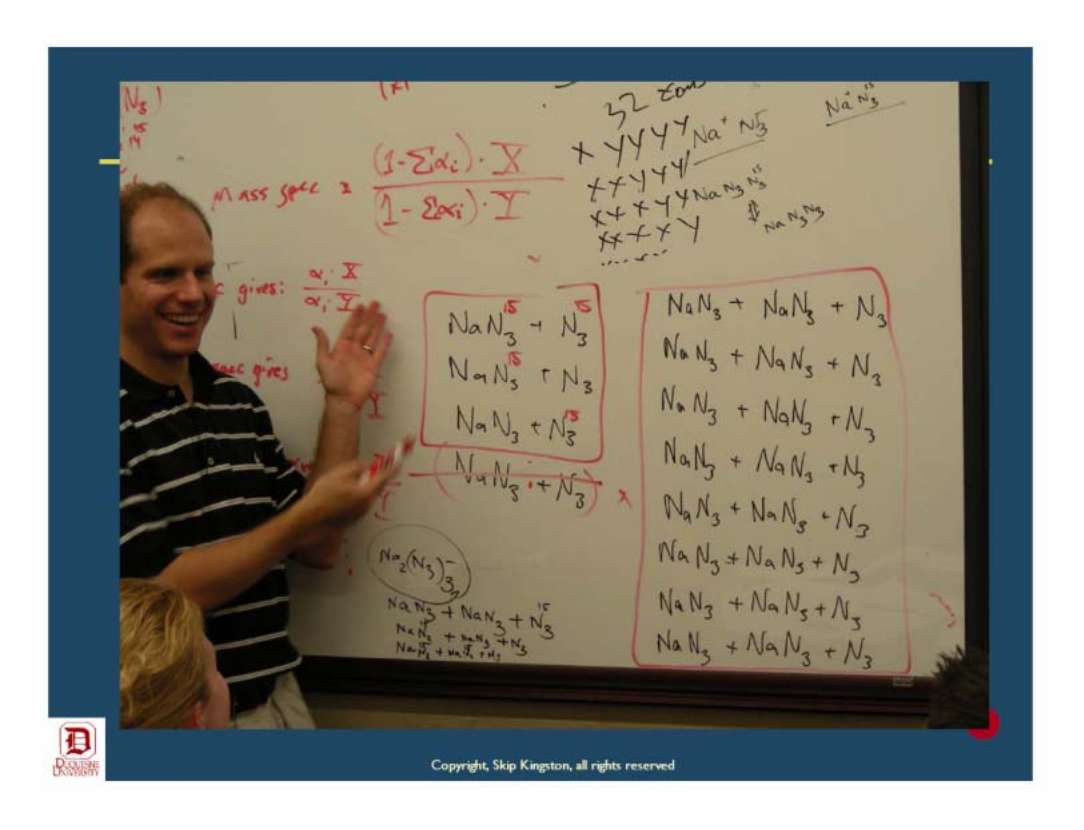
Close up of second peak, Na2(N3)3- in negative mode upper left-natural, lower left-isotope, right- mix
20 ppm in HPLC H2O



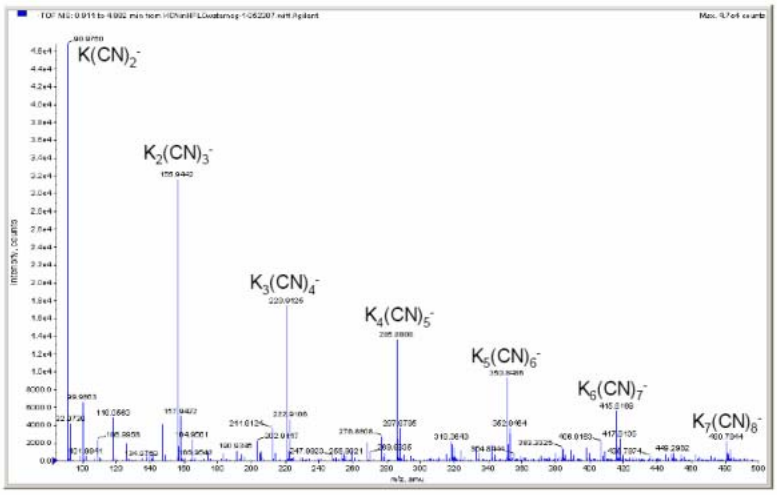




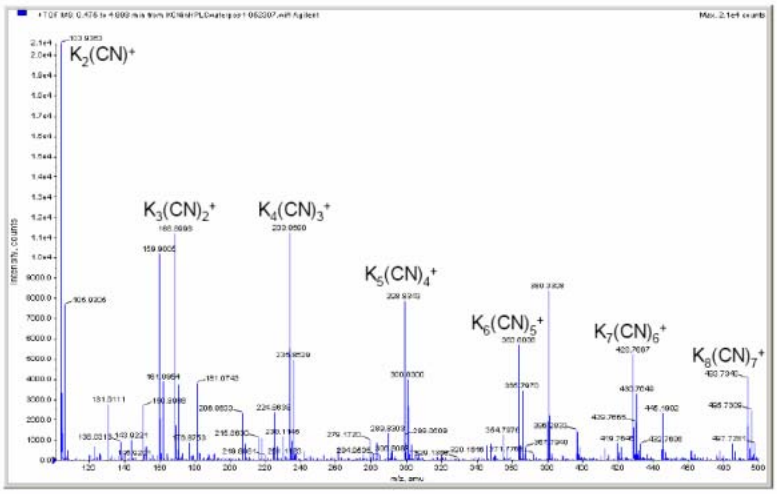
- Possible Combinations for Na2(N3)3-,
- Na15N3 + Na15N3 + 15N3
- Na15N3 + Na15N3 + N3
- Na15N3 + NaN3 + 15N3
- NaN3 + Na15N3 + 15N3
- Na15N3 + NaN3 + N3
- NaN3 + Na15N3 + N3
- NaN3 + NaN3 + 15N3
- NaN3 + NaN3 + N3



KCN in HPLC H2O in negative mode
Shows the expected spectrum for KCN in negative mode

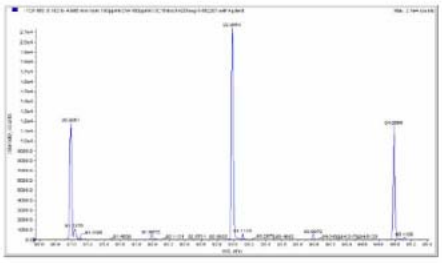


KCN in HPLC H2O in positive mode
Shows clearly the expected spectrum for KCN in positive mode



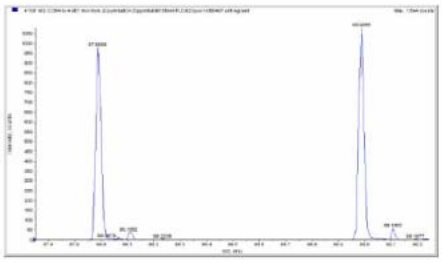
Quantification of $K(CN)_2^-$

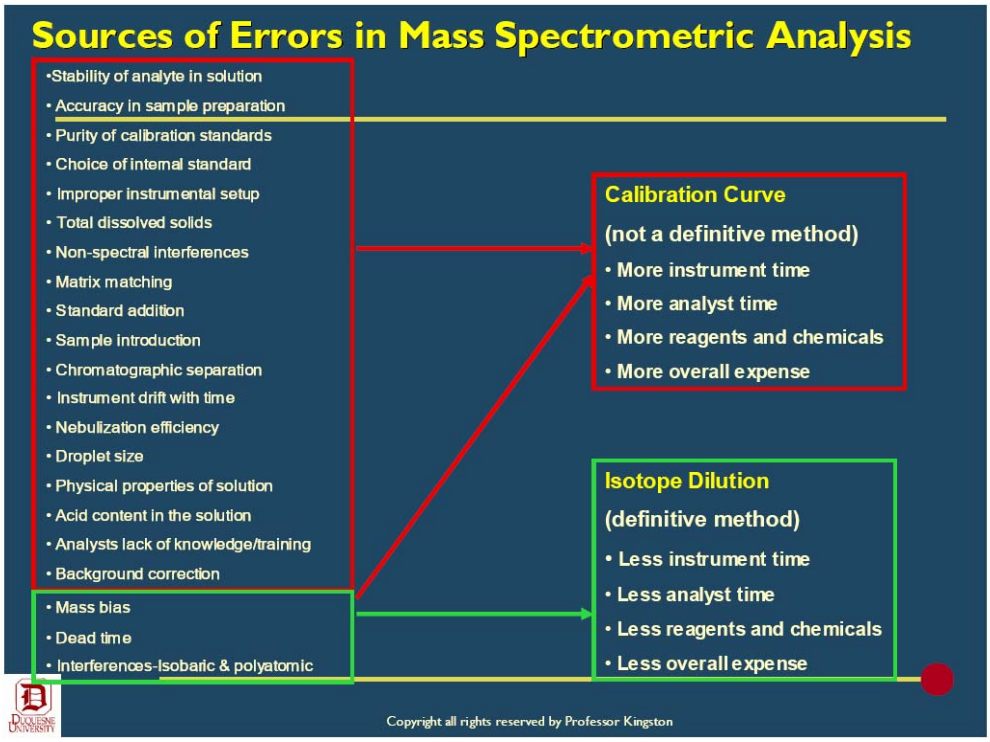
- For $K(CN)_2^-$, there are four possible combinations with natural and isotopically labeled cyanide anion
  - $K^{13}C^{15}N + {}^{13}C^{15}N^-$
  - $K^{13}C^{15}N + CN^-$
  - $KCN + {}^{13}C^{15}N^-$
  - $KCN + CN^-$
- Expect a 2:1 ratio of peaks 93 and 95
- After integration of the peaks, the ratio was determined to be: 1.997:1
- From this ratio and integration, the natural concentration was determined to be 108.3 ppm when the actual value was 100 ppm



Quantification of K_2CN^+

- For $K_2(CN)^+$, there are 2 possible combinations with natural and isotopically labeled cyanide anion
  - $K^{13}C^{15}N + K^+$
  - $KCN + K^+$
- Expect an approximate 1:1 ratio of peaks 104 and 106
- After integration of the peaks, the ratio was determined to be: 1.03
- From this ratio and integration, the natural concentration was determined to be 102.7 ppm when the actual value was 100 ppm.




Sources of Errors in Mass Spectrometric Analysis
•Stability of analyte in solution
• Accuracy in sample preparation
• Purity of calibration standards
• Choice of internal standard
• Improper instrumental setup
• Total dissolved solids
• Non-spectral interferences
• Matrix matching
• Standard addition
• Sample introduction
• Chromatographic separation
• Instrument drift with time
• Nebulization efficiency
• Droplet size
• Physical properties of solution
• Acid content in the solution
• Analysts lack of knowledge/training
• Background correction
• Mass bias
• Dead time
• Interferences-Isobaric & polyatomic
Calibration Curve
(not a definitive method)
• More instrument time
• More analyst time
• More reagents and chemicals
• More overall expense
Isotope Dilution
(definitive method)
• Less instrument time
• Less analyst time
• Less reagents and chemicals
• Less overall expense
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Current and Former Research Group Contributors
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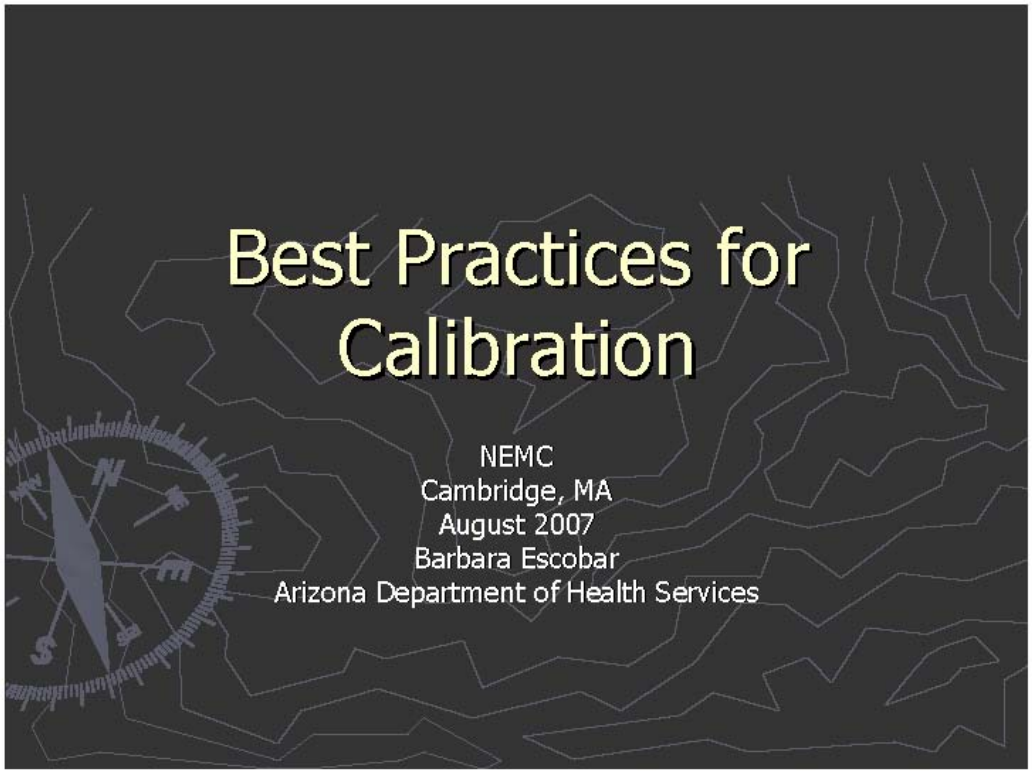
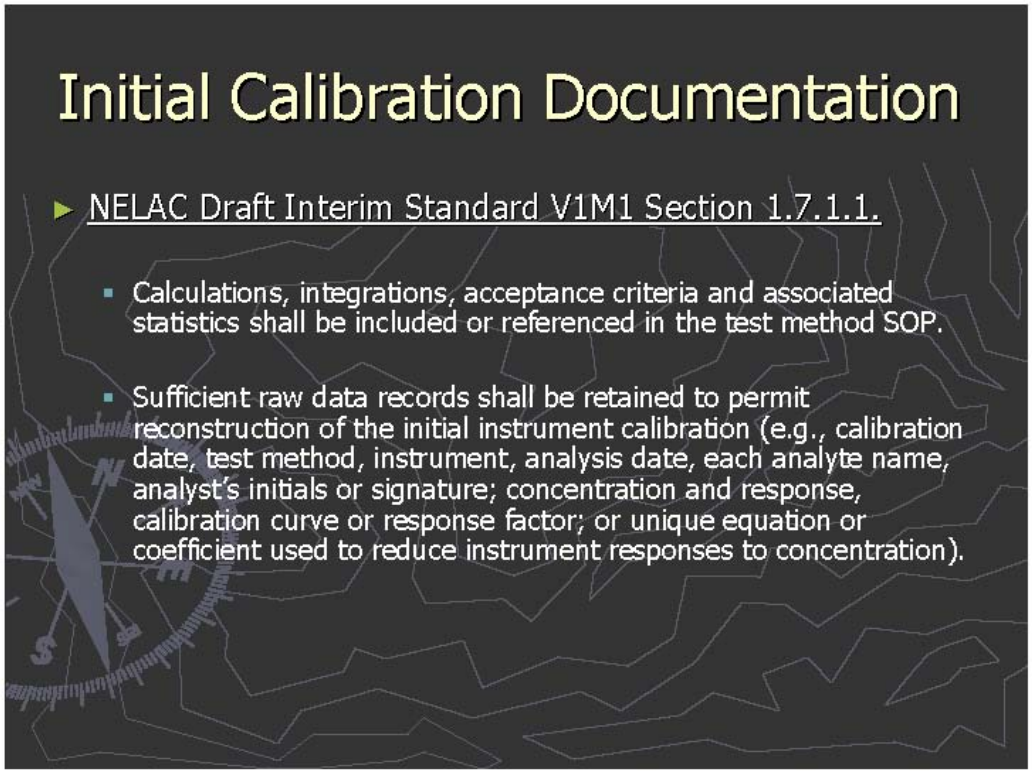
US Air Force
EPA
Allegheny Energy Supply Co.
Milestone Inc
Agilent Technologies.
Duquesne University


Best Practices for Calibration
NEMC
Cambridge, MA
August 2007
Barbara Escobar
Arizona Department of Health Services


Initial Calibration Documentation
NELAC Draft Interim Standard V1M1 Section 1.7.1.1.
Calculations, integrations, acceptance criteria and associated statistics shall be included or referenced in the test method SOP.
Sufficient raw data records shall be retained to permit reconstruction of the initial instrument calibration (e.g., calibration date, test method, instrument, analysis date, each analyte name, analyst's initials or signature; concentration and response, calibration curve or response factor; or unique equation or coefficient used to reduce instrument responses to concentration).

Initial Calibration Documentation

- EPA Manual for the Certification of Laboratories Analyzing Drinking Water, 5th Ed. Chapter IV
  - ***8.4.5 Analytical Records.*** Calibration and standards information should be readily available.
  - ***8.5 Reconstruction of Data:*** Adequate information should be available to allow the auditor to reconstruct the final results for compliance samples and PT samples.
  - ***8.6 Computer Programs:*** Computer programs should be verified initially and periodically by manual calculations and the calculations should be available for inspection.

Initial Calibration Documentation

- Office of Solid Waste SW-846 Chapter One, Rev. 1
  - Section 4.3.4 The documentation of the actual laboratory procedures for analytical methods should include instrument standardization - This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.
  - Section 4.4.6 All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date.

Calibration Data Audits

Challenges:

- When laboratories don't specify algorithm used, or specify a wrong one (e.g. stating linear but actually using weighted linear).
- When data provided during an on-site doesn't provide all of the raw data needed. (e.g. response factor reports that don't show all of the cal standards).
- Can't tell what calibration standard levels are used since they aren't current in SOP or data headers don't specify.

State Assessor's Bimonthly Teleconference Meetings

- State Assessors from all environmental programs from all States are invited to participate on a bimonthly call to share auditing information and challenges.
- It was decided that a general calibration guidance document should be created that could be used to help both assessors and laboratories when the actual method or regulation was not detailed enough.

State Assessor's Calibration Protocol

- State Assessor's Calibration Group presented a preliminary draft of the protocol to the State Assessors Forum for review and comment in 2004. The final version of the protocol incorporated changes resulting from comments received.
- Current Version Dated 1/18/07; to be revised as needed based on comments and suggestions received from its users.
- Although not mandatory, the authors hope that assessors and laboratories use it widely as a resource and reference.
- Posted http://www.azdhs.gov/lab/license/tech/infoup.htm

AZDHS Instrument Calibration Policy

- On-site survey findings dictated the need for an AZDHS Director Approved Calibration Policy approved on 7/18/03 and subsequently incorporated into the regulation.

http://www.azdhs.gov/lab/license/tech/ollct.htm

AZDHS Instrument Calibration Policy

- Instrument calibration allowed is based on method specified or instrument manufacturer if allowed.
- QAP specifies all general procedures for analytical instrument calibrations, have records available that demonstrate the calculations performed by the calibration model and have the calibration model being used specified in a current standard operating procedure for all licensed methods.

AZDHS Instrument Calibration Policy

- The laboratory must train all lab personnel about the specific calibration models that each individual is utilizing or reviewing data for.
- This training must also document what specific aspects of each calibration model being used might compromise the data quality, rendering the data to be not scientifically valid and defensible.
- Some of these specific aspects could include detector saturation, detector sensitivity, the calibration model not accurately reflecting the calibration points, inappropriate extension of the calibration range, weighting factors and the inappropriate dropping of mid-level calibration points without justification. In all of the above cases, the calibration model utilized cannot be used simply to avoid needed instrument maintenance.

Meeting Calibration Documentation Requirements

- The proper training of analysts on the types of calibrations used in the lab, as well as the familiarization and ability to confirm calibration used and acceptance criteria is very challenging:
  - Higher order calibrations
  - Complex IS corrected responses (e.g. ICP-MS)
  - Manufacturer's software that will not provide actual raw data responses, or state that their algorithms are proprietary

AZDHS Calibration CD

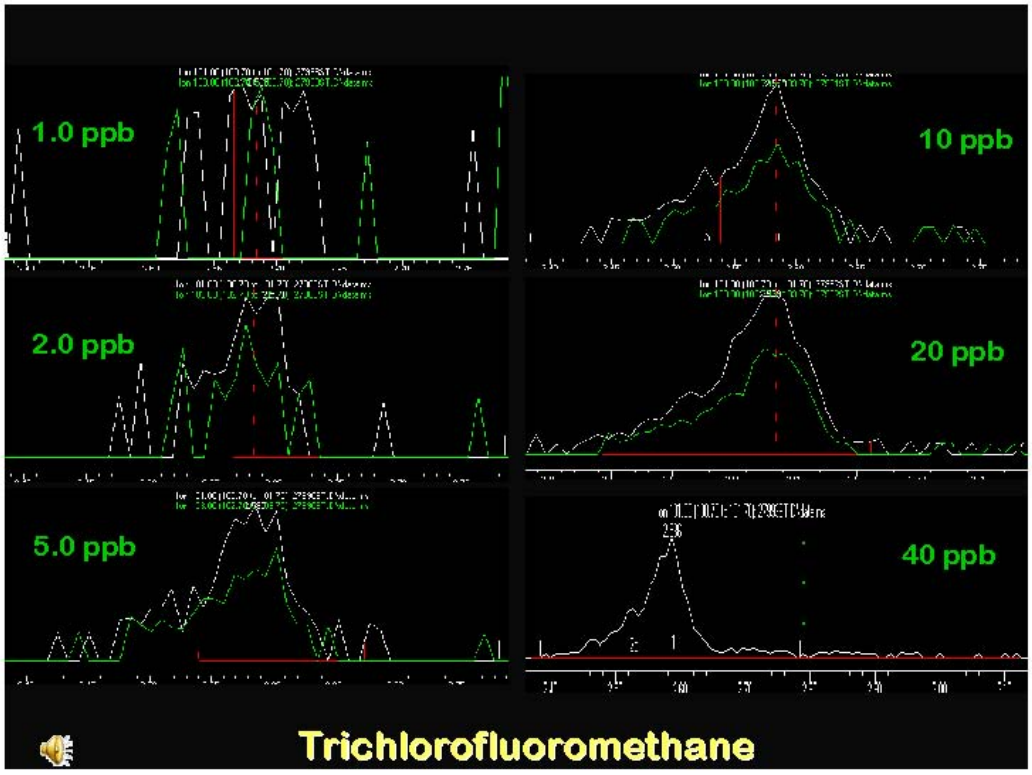
- AZDHS has attempted to pull together much of the information that it had available about calibration in the training CD so that this would not be a presentation of AZDHS's opinion on calibration, but the opinions of the wider scientific community.
- Just like the State Assessor's Calibration Protocol, The Calibration CD is a living document and that other resources may be found to change or add to the training CD at a later date.
- Section 1 of the CD discusses calibration in general, the requirements of the Arizona regulations and more specific information about the most common calibration models used in environmental laboratories.
- Section 2 of the CD discusses conditions that may compromise calibration of an instrument.

AZDHS Calibration CD

- In addition, the CD contains an EXCEL spreadsheet developed by AZDHS assessors that aids in confirming several calibration calculations commonly used in the laboratory.
- AZDHS greatly appreciates Dale Rushneck of Interface, Inc. for his assistance in reviewing and commenting on the contents of various sections of this Calibration CD.

The following are examples from the AZDHS Calibration CD…

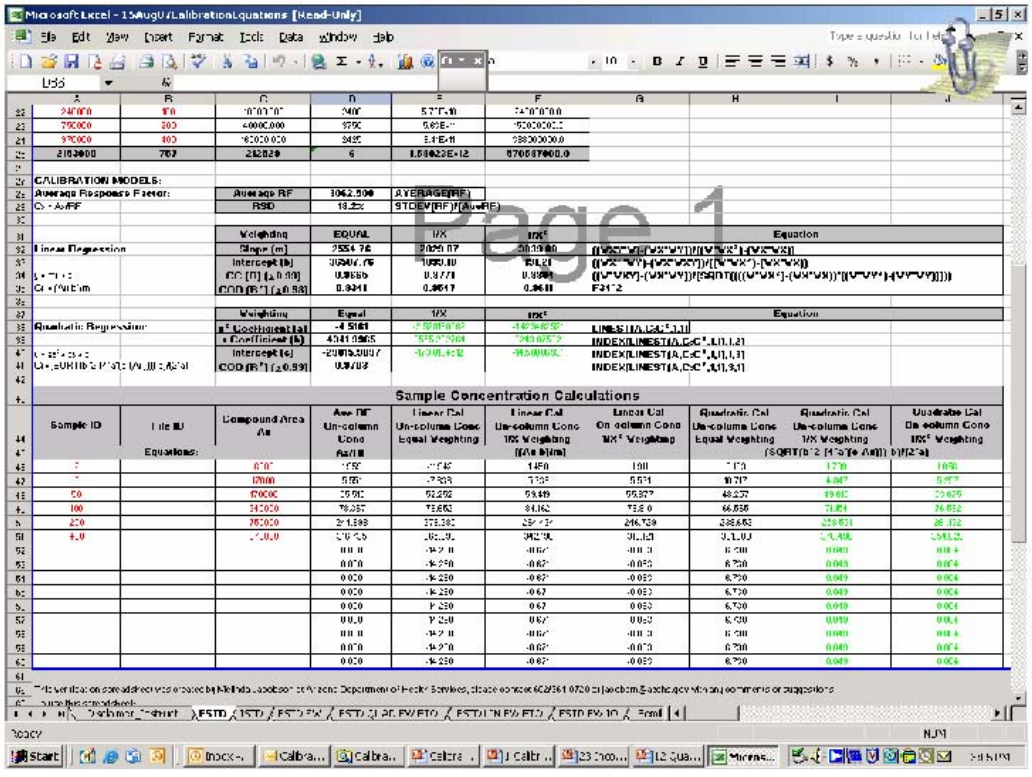
- Power and Exponential Calibration
- Point to Point Calibration
- Linear Calibrations
  - Response/Calibration Factor
  - Linear Calibration Using A Least Square Regression
  - Linear Forced through Zero
  - Method of Standard Additions
  - Weighted Least Square Regression
- Non-Linear/Quadratic



Quadratic Regression Equation

$$y = ax^2 + bx + c$$

Where: y = Response A_x for External Standard
or A_x/A_{is} for Internal Standard
x = Concentration C_x for External Standard
or C_x/C_{is} for Internal Standard

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Training for the Environmental Professional

How to Properly & Scientifically Calibrate Analytical Systems

A Presentation by:

Jack Farrell and Patricia Snyder
Analytical Excellence, Inc.

Analytical Excellence, Inc.

Calibration Practices and Irregularities

Excerpts from a technical training program

Calibration Issues & Irregularities

- "Historical" ICALs
- Random points removed from the center of the curve
  - A level of the curve can be statistically removed
- Duplicate points added to the curve
- Data insertions
  - Improperly manipulating responses or concentrations in a calibration file
  - Responses added from standards without the associated internal standards

Calibration Issues & Irregularities

- Using low concentration standards with insufficient response
- Improper manual integrations
- Changing computer generated integration parameters so that the low to high points are not integrated the same
- Analyzing a low level standard immediately after a high level standard or priming solution to enhance response from carryover
- Changing instrument conditions during an ICAL

Points Removed from the Curve

Response Factor Report MS01

Method : W:\RWL\MS01\METHODS\BEFORE\8260620.M
Title : Volatile Organic Compounds 8260
Last Update : Sun Jun 22 16:43:24 1997
Response via : Initial Calibration

Calibration Files
1 =0620002.D 2 =0620003.D 3 =0620004.D
4 =1101004.D 5 =1001002.D 6 =1201005.D

		Compound	1	2	3	4	5	6	Avg	%RSD
1)	I	pentafluorobenzene	ISTD							
2)	T	Dichlorodifluoromet	1.537	1.319	1.387	1.561	1.576	1.468	1.481	6.49
3)	T	Chloromethane	0.597	0.506	0.521	0.642	0.574	0.568	0.563	8.38
4)	T	Vinyl Chloride	0.924	0.776	0.802	0.890	0.929	0.907	0.872	6.88
5)	T	Bromomethane	0.640	0.543	0.562	0.713	0.460		0.584	16.55
6)	T	Chloroethane	0.276	0.261	0.264	0.394		0.296	0.308	17.78
7)	T	Trichlorofluorometh	2.284	1.979	2.105	2.489	2.296	2.398	2.266	7.61
8)		Dichlorotrifluoroet	0.580	0.519	0.563	0.629	0.622	0.612	0.587	7.17
9)	M	1,1-Dichloroethene	0.232	0.216	0.225	0.228	0.209	0.236	0.223	4.53
10)		carbon disulfide	0.869	0.779	0.832	0.835	0.879	0.930	0.859	5.60
11)	T	Freon 113	0.581	0.507	0.534	0.518	0.503	0.534	0.528	4.94
12)		ACROLEIN							0.000	-1.00
13)	T	Acetone	0.637	0.610	0.467	0.566		0.386	0.533	19.60
14)		acrylonitrile		0.037	0.030	0.038		0.026	0.032	15.44
15)	T	Methylene Chloride	0.338	0.285	0.295	0.294	0.285	0.310	0.299	6.67
16)	T	Vinyl Acetate	0.158	0.162	0.134	0.156		0.132	0.146	10.05
17)	T	tr-1,2-Dichloroethe	0.345	0.324		0.235	0.249	0.260	0.295	17.90
18)		Methyl-Tert-Butyl-E	1.765	1.587	1.649	1.647	1.373	1.545	1.596	7.52
19)	T	1,1-Dichloroethane	1.011	0.865	0.865	0.863		0.871	0.883	7.41
20)		Diisopropyl ether							0.000	-1.00
21)	T	cis-1,2-Dichloroeth	0.503	0.446	0.467	0.464	0.434	0.469	0.458	5.62

Duplicate Points Added to the Curve

Calibration Status Report MS03

Method : F:\KSH\MS03\METHODS\091598.M
Title : VOA Standards for 5 point calibration
Last Update : Fri Oct 16 16:40:38 1998
Response via : Initial Calibration

From original method

#	ID	Conc	ISTD Conc	Path\File
1	1	1	25	J:\MS03\DATA\091598\0915013.D
2	3	2	25	J:\MS03\DATA\091598\0915006.D
3	5	10	25	J:\MS03\DATA\091598\0915008.D
4	6	20	25	J:\MS03\DATA\091598\0915009.D
5	7	50	25	J:\MS03\DATA\091598\0915010.D
6	8	100	25	J:\MS03\DATA\091598\0915011.D
7	9 *	100	25	J:\MS03\DATA\091698\0916005.D
8	4 *	10	25	J:\MS03\DATA\092098\0920002.D
9	2 *	10	25	J:\MS03\DATA\101698\1016002.D

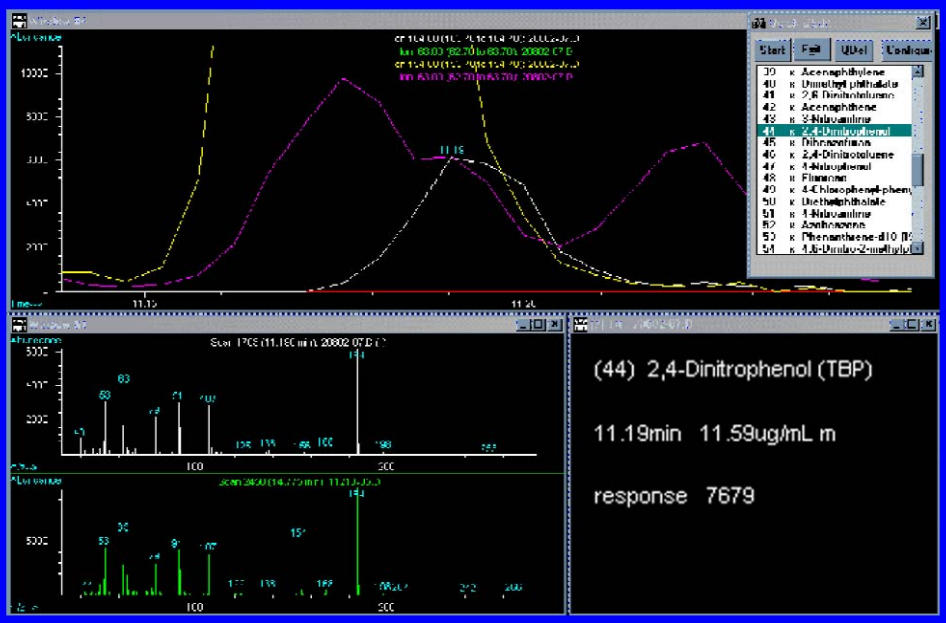
pkd 10/7/98

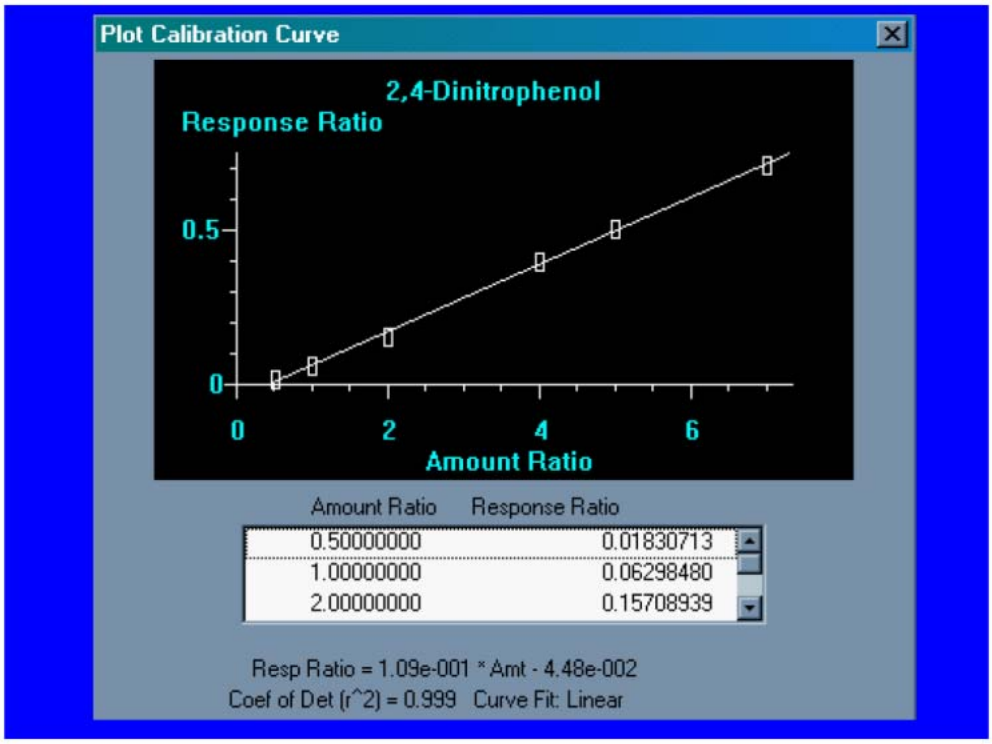
added later - duplicate levels.

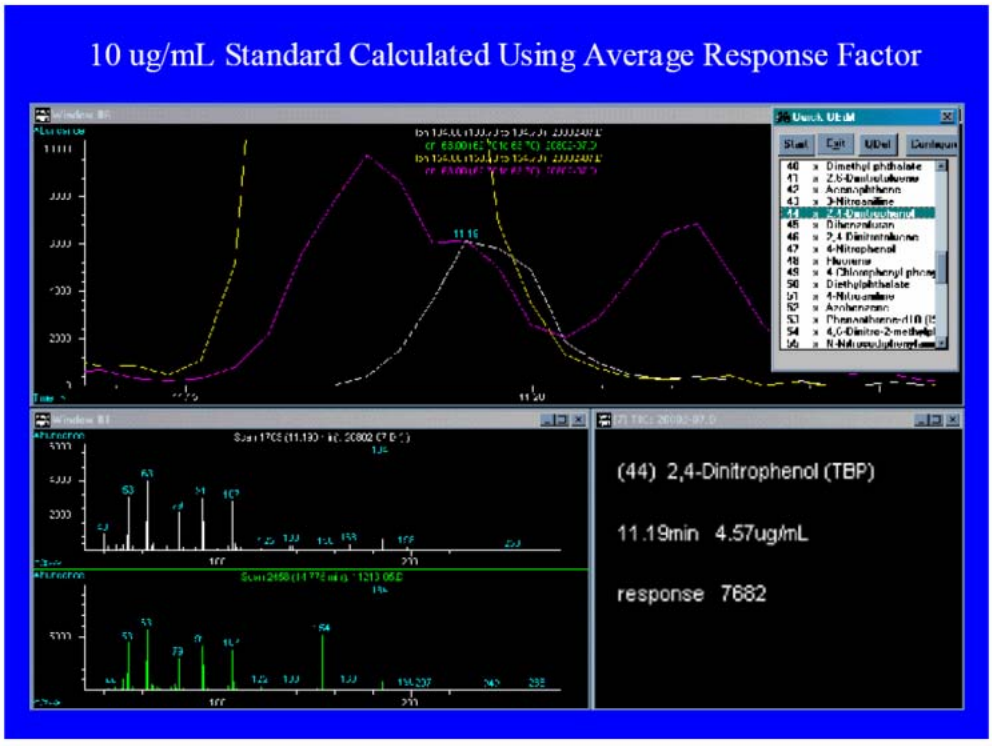
#	ID	Update Time	Quant Time	Acquisition Time
1	1	Sep 16 09:12 1998	Sep 16 08:24 1998	16 Sep 98 2:00 am
2	3	Sep 16 09:13 1998	Sep 16 08:48 1998	15 Sep 98 9:40 pm
3	5	Sep 16 09:13 1998	Sep 16 09:10 1998	15 Sep 98 10:53 pm
4	6	Sep 16 09:14 1998	Sep 16 08:38 1998	15 Sep 98 11:31 pm
5	7	Sep 16 09:14 1998	Sep 16 08:40 1998	16 Sep 98 12:08 am
6	8	Sep 16 09:15 1998	Sep 16 08:44 1998	16 Sep 98 12:45 am
7	9	Sep 16 15:44 1998	Sep 16 15:46 1998	16 Sep 98 3:04 pm
8	4	Sep 21 16:37 1998	Sep 21 16:36 1998	20 Sep 98 9:33 am
9	2	Oct 16 16:14 1998	Oct 16 16:13 1998	16 Oct 98 3:40 pm

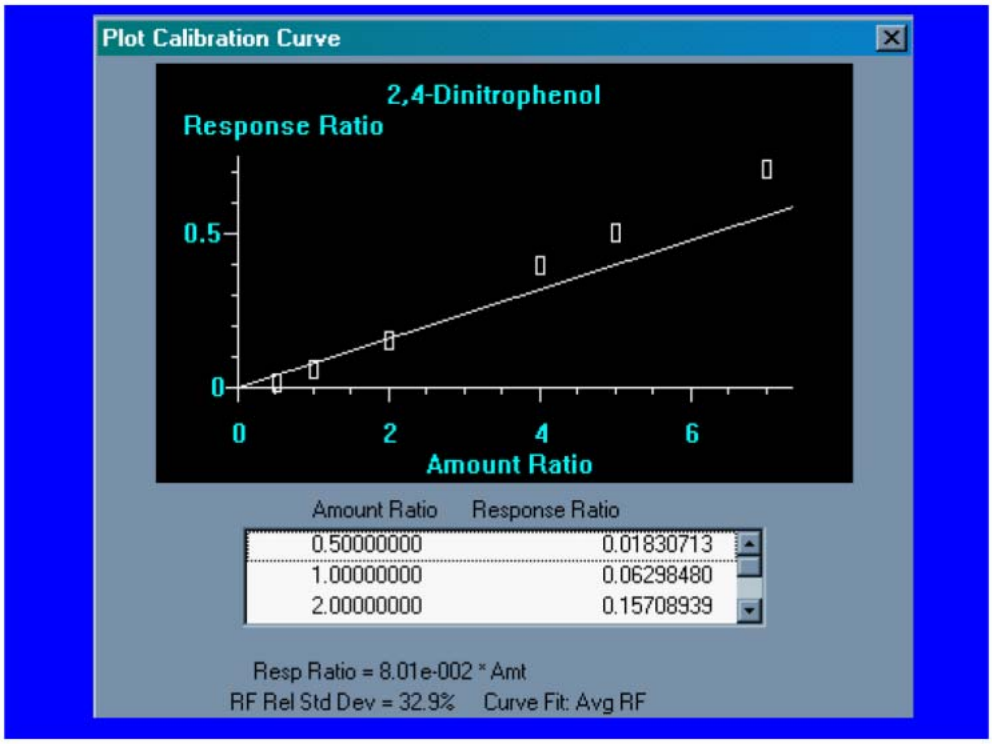
Artificially High or Low Calculated Concentrations

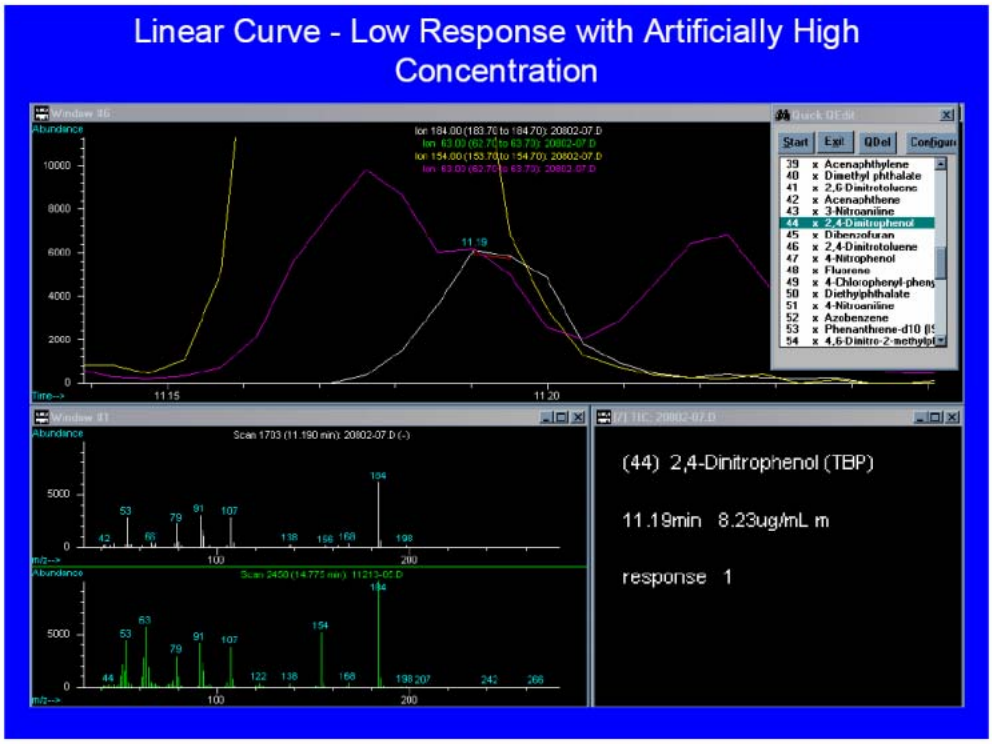
10 ug/mL Standard Calculated Using a Linear Curve

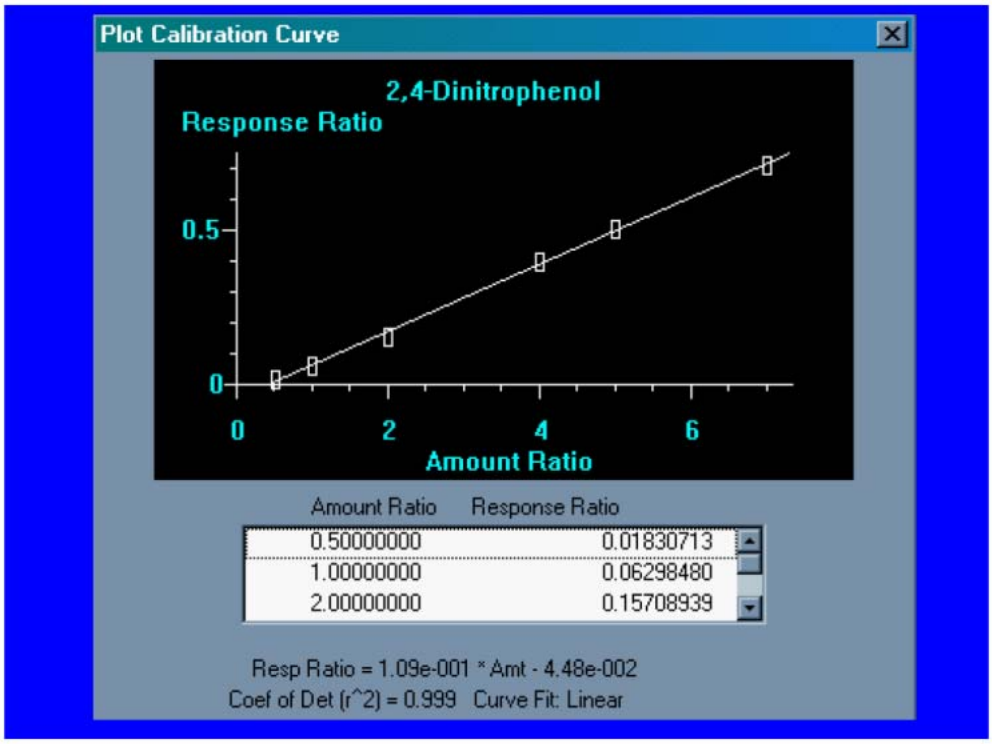


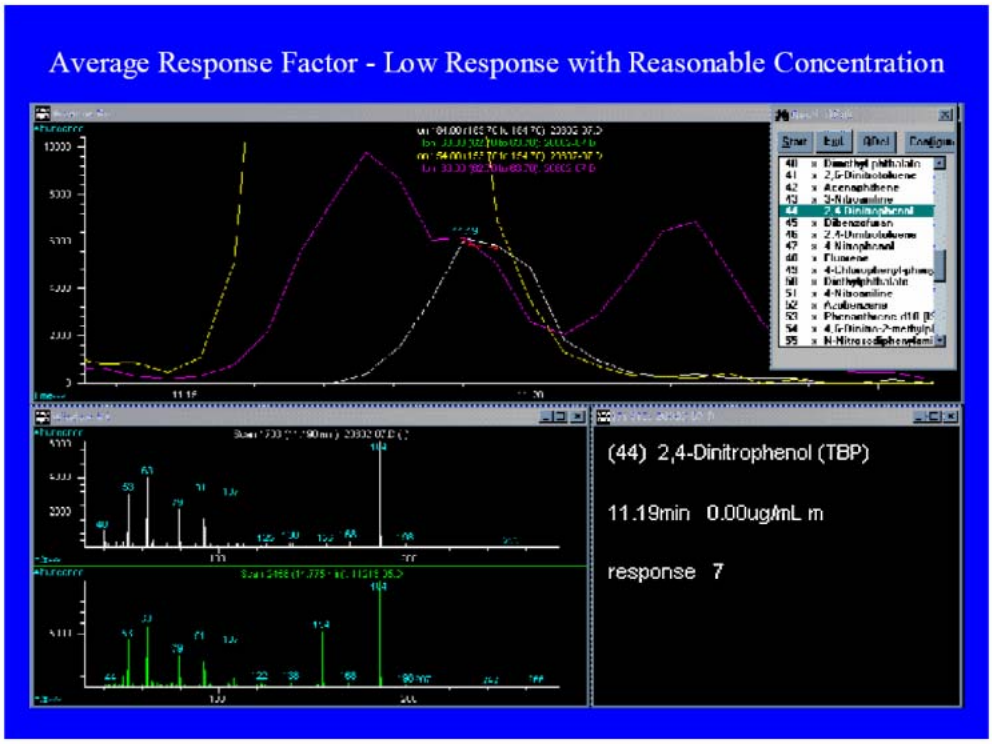

Plot Calibration Curve
2,4-Dinitrophenol
Response Ratio
0.5
0
0
2
4
6
Amount Ratio
Amount Ratio
Response Ratio
0.50000000
0.01830713
1.00000000
0.06298480
2.00000000
0.15708939
Resp Ratio = 1.09e-001 * Amt - 4.48e-002
Coef of Det (r^2) = 0.999 Curve Fit: Linear

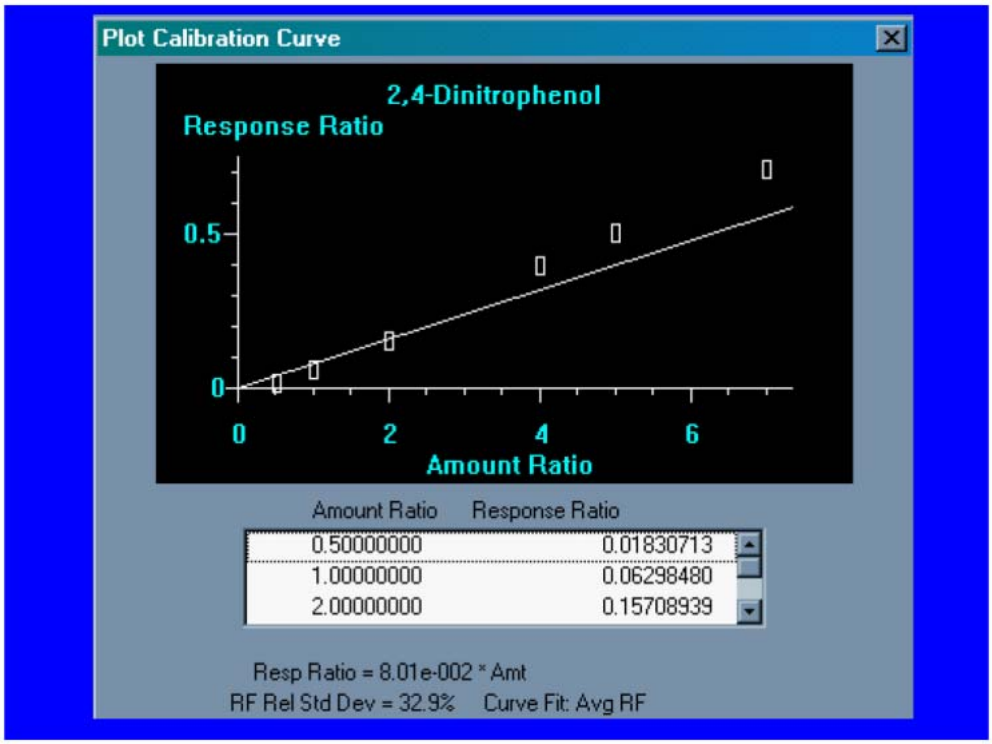

10 ug/mL Standard Calculated Using Average Response Factor
(44) 2,4-Dinitrophenol (TBP)
11.19min 4.57ug/mL
response 7682


Plot Calibration Curve
2,4-Dinitrophenol
Response Ratio
0.5
0
0
2
4
6
Amount Ratio
Amount Ratio
Response Ratio
0.50000000
0.01830713
1.00000000
0.06298480
2.00000000
0.15708939
Resp Ratio = 8.01e-002 * Amt
RF Rel Std Dev = 32.9%
Curve Fit: Avg RF


Linear Curve - Low Response with Artificially High Concentration
(44) 2,4-Dinitrophenol (TBP)
11.19min 8.23ug/mL m
response 1

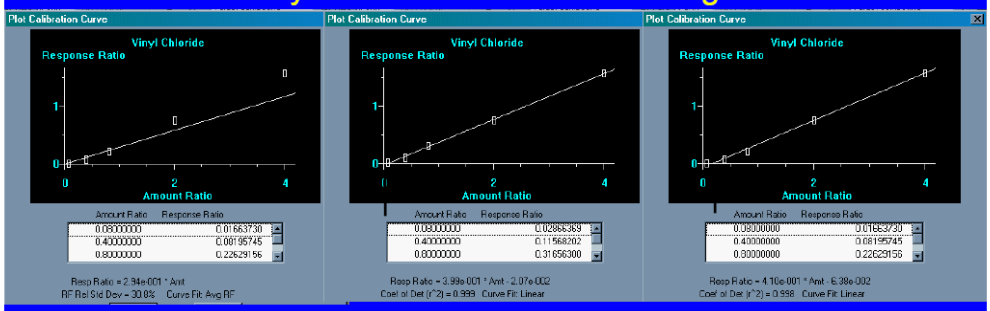

Plot Calibration Curve
2,4-Dinitrophenol
Response Ratio
0.5
0
0
2
4
6
Amount Ratio
Amount Ratio
Response Ratio
0.50000000
0.01830713
1.00000000
0.06298480
2.00000000
0.15708939
Resp Ratio = 1.09e-001 * Amt - 4.48e-002
Coef of Det (r^2) = 0.999 Curve Fit: Linear


Average Response Factor - Low Response with Reasonable Concentration
(44) 2,4-Dinitrophenol (TBP)
11.19min 0.00ug/mL m
response 7



Example - Curve Intercept Issues

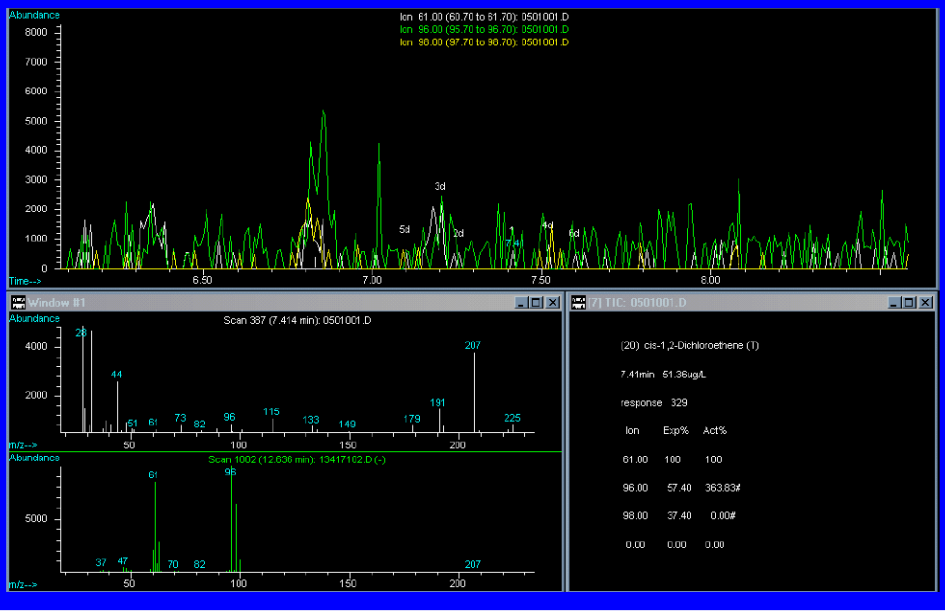
Vinyl Chloride standard at 2.0 ug/L



Average Response Factor	Linear - curve intercepts near 0,0	Linear - curve intercepts on positive X-axis
Calculated concentration	Calculated concentration	Calculated concentration
2.22 ug/L	2.93 ug/L	5.49 ug/L

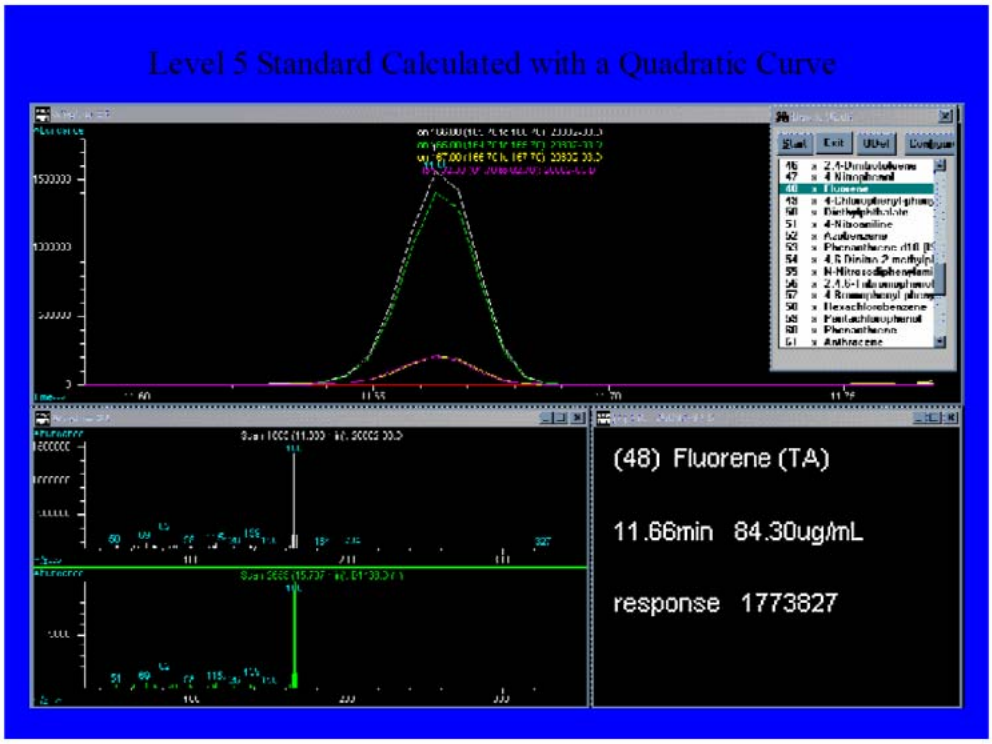
Non-existent Peaks

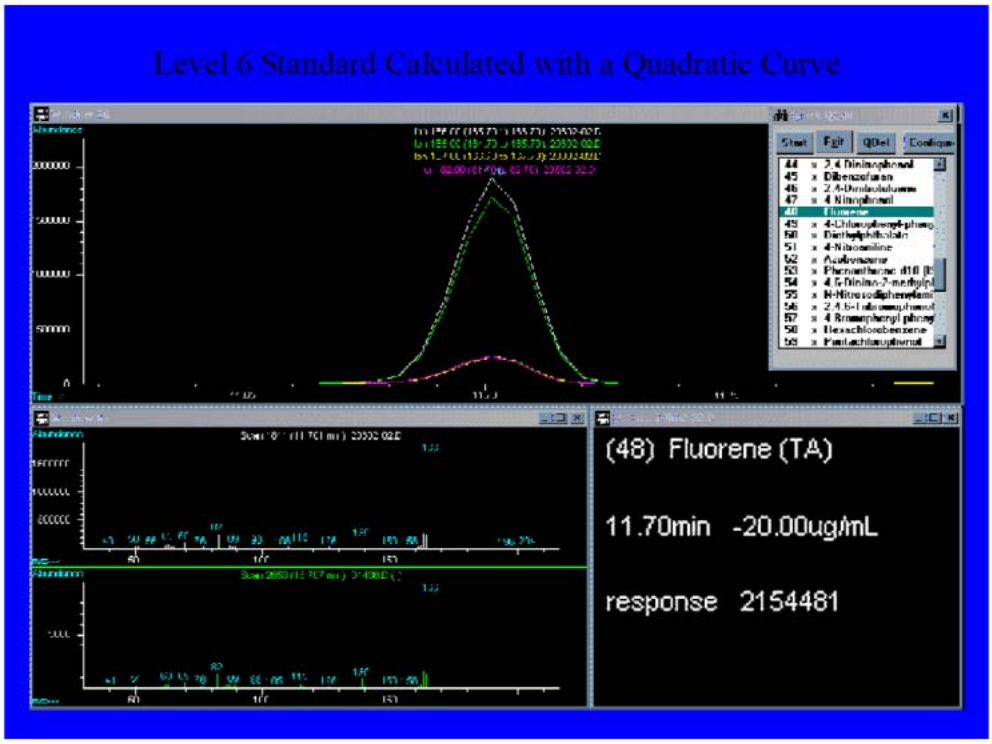
Insufficient Signal to Noise Ratio

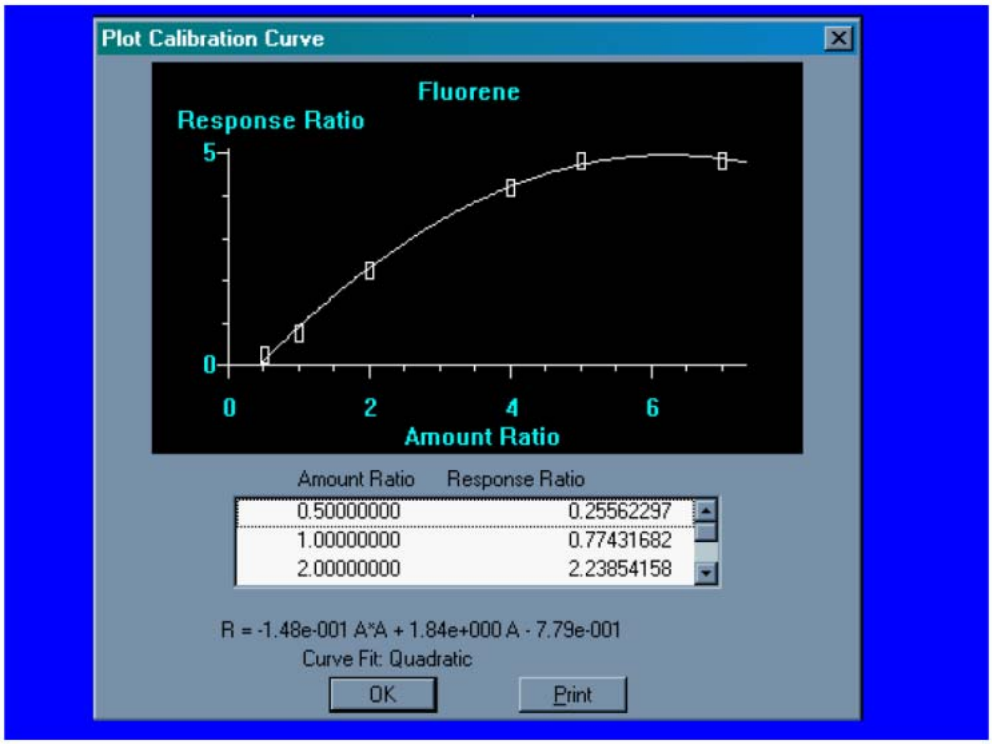


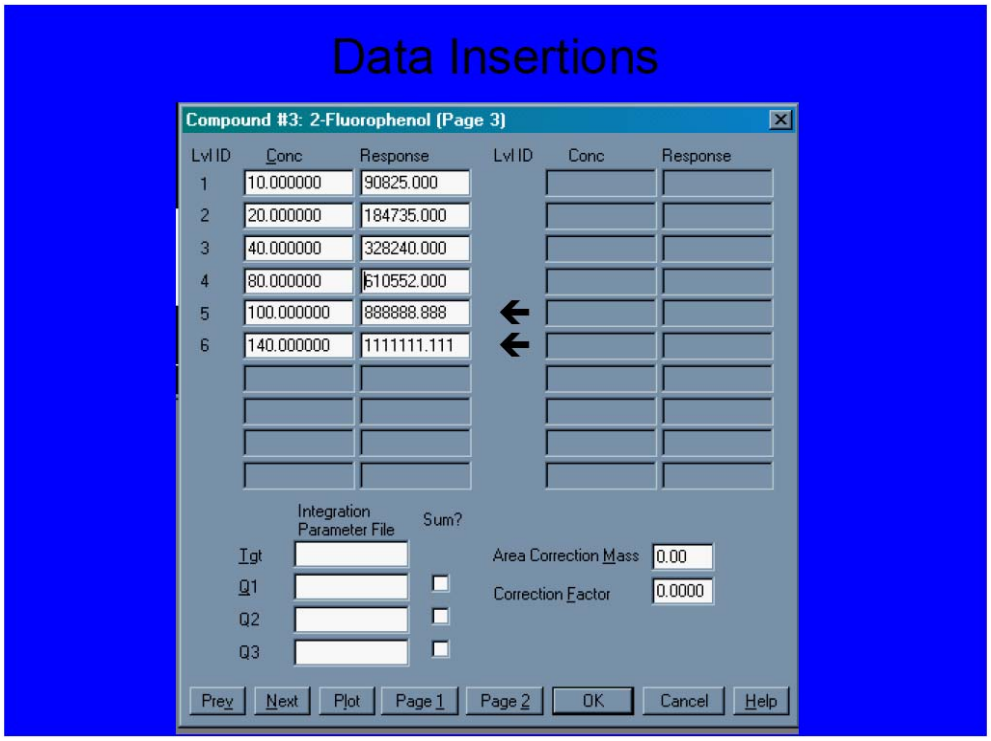
Quadratic Curve Reversal

(Parabolic Shaped Curves)


Level 5 Standard Calculated with a Quadratic Curve
(48) Fluorene (TA)
11.66min 84.30ug/mL
response 1773827


Level 6 Standard Calculated with a Quadratic Curve
(48) Fluorene (TA)
11.70min -20.00ug/mL
response 2154481

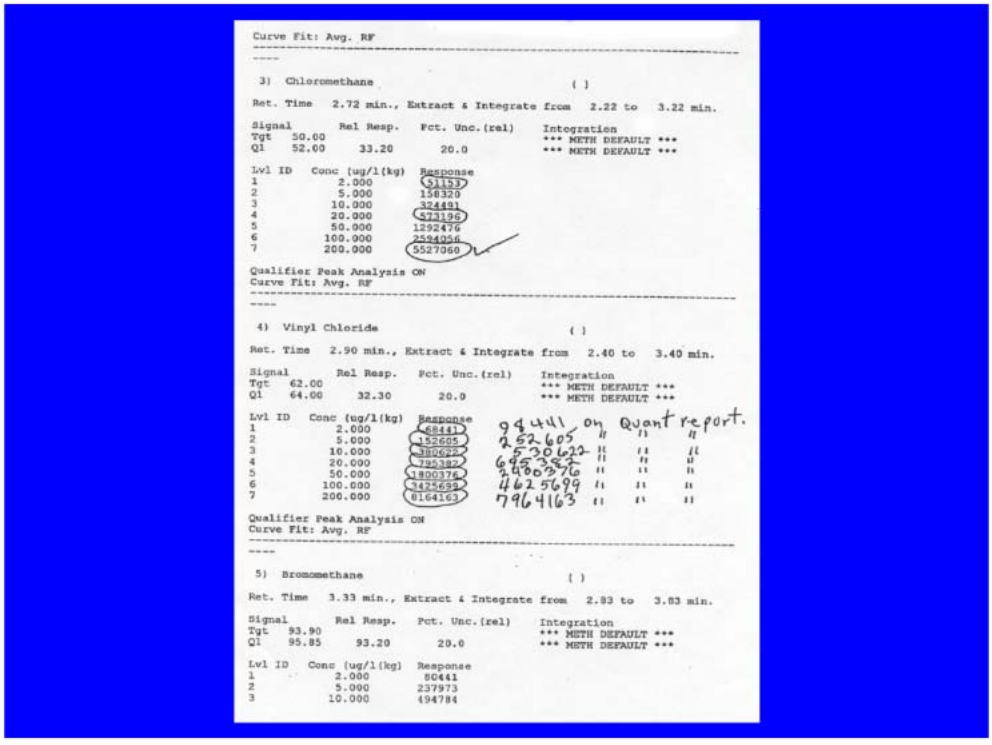

Plot Calibration Curve
Fluorene
Response Ratio
5
0
0
2
4
6
Amount Ratio
Amount Ratio
Response Ratio
0.50000000
0.25562297
1.00000000
0.77431682
2.00000000
2.23854158
R = -1.48e-001 A*A + 1.84e+000 A - 7.79e-001
Curve Fit: Quadratic
OK
Print


Data Insertions
Compound #3: 2-Fluorophenol (Page 3)
Lvl ID
Conc
Response
1
10.000000
90825.000
2
20.000000
184735.000
3
40.000000
328240.000
4
80.000000
610552.000
5
100.000000
888888.888
6
140.000000
1111111.111
Integration Parameter File
Sum?
Tgt
Q1
Q2
Q3
Area Correction Mass
0.00
Correction Factor
0.0000
Prev
Next
Plot
Page 1
Page 2
OK
Cancel
Help

Initial Calibration MS03, 7/14/97, Method 8260JL14.m		Original Method File Data	Original Quant Report Data
Compound	Conc. Level	Response (area)	Response (area)
Toluene	2 ppb	62291	162291
Toluene	5 ppb	163187	183187
Toluene	10 ppb	330812	330812
Toluene	50 ppb	1527891	1527891
Toluene	100 ppb	4017537	4017537
Toluene	200 ppb	8761296	8761296
% RSD		9.48	53.76
% RSD Method Criteria		30%	30%

```
2            5.000        83766
3           10.000       155819
4           50.000       875102
5          100.000      1996673
6          200.000      3284031

Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
----

40)  trans-1,3-Dichloropropene                    ( )

Ret. Time  17.50 min., Extract & Integrate from  17.30 to  17.70 min.

Signal       Rel Resp.    Pct. Unc.(abs)     Integration
Tgt   75.00                                  *** METH DEFAULT ***
Q1    77.00      35.10        20.0          *** METH DEFAULT ***

Lvl ID   Conc (ug/l)   Response
1            2.000        39348
2            5.000       106293
3           10.000       206056
4           50.000      1326062
5          100.000      2908037
6          200.000      6415236

Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
----

41)  Toluene                                      ( )

Ret. Time  18.19 min., Extract & Integrate from  17.99 to  18.39 min.

Signal       Rel Resp.    Pct. Unc.(abs)     Integration
Tgt   92.00                                  *** METH DEFAULT ***
Q1    91.00     171.70        20.0          *** METH DEFAULT ***

Lvl ID   Conc (ug/l)   Response
1            2.000        62291   ✓ 162291 on Quant report.
2            5.000       163187   ✓ 183187 on Quant report.
3           10.000       330812
4           50.000      1527891
5          100.000      4017537
6          200.000      8761296

Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
----

42)  1,1,2-Trichloroethane                        ( )

Ret. Time  17.80 min., Extract & Integrate from  17.60 to  18.00 min.

Signal       Rel Resp.    Pct. Unc.(abs)     Integration
Tgt   97.00                                  *** METH DEFAULT ***
Q1    99.00      69.10        20.0          *** METH DEFAULT ***
```

Initial Calibration MS01, 6/03/96, Method 8260JUN1.m		Original Method File Data	Original Quant Report Data
Compound	Conc. Level	Response (area)	Response (area)
1,2-Dichloropropane	1ppb	21780	21780
1,2-Dichloropropane	2 ppb	47914	47914
1,2-Dichloropropane	5 ppb	150649	100649
1,2-Dichloropropane	10 ppb	327622	203401
1,2-Dichloropropane	20 ppb	550539	450539
1,2-Dichloropropane	50 ppb	1661507	1361507
1,2-Dichloropropane	100 ppb	2814651	2814651
1,2-Dichloropropane	200 ppb	5792739	4792739
% RSD		13.13	7.68
% RSD Method Criteria		30%	30%
Initial Calibration MS01, 8/20/97, Method 8260820.m		Original Method File Data	Original Quant Report Data
Compound	Conc. Level	Response (area)	Response (area)
Vinyl Chloride	2ppb	68441	98441
Vinyl Chloride	5 ppb	152605	252605
Vinyl Chloride	10 ppb	380622	530622
Vinyl Chloride	20 ppb	795382	695382
Vinyl Chloride	50 ppb	1800376	2400376
Vinyl Chloride	100 ppb	3425699	4625699
Vinyl Chloride	200 ppb	8164163	7964163
% RSD		7.18	19.49
% RSD Method Criteria		30%	30%



Curve Fit: Avg. RF

3) Chloromethane ( )

Ret. Time 2.72 min., Extract & Integrate from 2.22 to 3.22 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 50.00			*** METH DEFAULT ***
Q1 52.00	33.20	20.0	*** METH DEFAULT ***

Lvl	ID	Conc (ug/l(kg)	Response
1		2.000	51153
2		5.000	156329
3		10.000	324491
4		20.000	673196
5		50.000	1292476
6		100.000	2594056
7		200.000	5527060

Qualifier Peak Analysis ON
Curve Fit: Avg. RF

4) Vinyl Chloride ( )

Ret. Time 2.90 min., Extract & Integrate from 2.40 to 3.40 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 62.00			*** METH DEFAULT ***
Q1 64.00	32.30	20.0	*** METH DEFAULT ***

Lvl	ID	Conc (ug/l(kg)	Response
1		2.000	68441
2		5.000	152605
3		10.000	380622
4		20.000	795382
5		50.000	1800376
6		100.000	3425699
7		200.000	8164163

98441 on Quant report.
252605 " " "
530622 " " "
695382 " " "
2400376 " " "
4625699 " " "
7964163 " " "

Qualifier Peak Analysis ON
Curve Fit: Avg. RF

5) Bromomethane ( )

Ret. Time 3.33 min., Extract & Integrate from 2.83 to 3.83 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 93.90			*** METH DEFAULT ***
Q1 95.85	93.20	20.0	*** METH DEFAULT ***

Lvl	ID	Conc (ug/l(kg)	Response
1		2.000	80441
2		5.000	237973
3		10.000	494784

How do you know that you have a proper or scientifically sound calibration?

How do you balance meeting client and company requirements and proper scientific practices and techniques?

What to Look for in a Proper Calibration

- Minimum number of required points present for the method
- No points removed from the middle of the calibration
- No duplicate curve points, especially at the low end
- Responses from the standards match those used in the curve
- Concentrations of the standards match those used in the curve
- Sufficient signal to noise ratio in the low level standards

What to Look for in a Proper Calibration

- No detector saturation in the high level standards
- Low standard concentration at the reporting limit
- RSD or correlation coefficient requirements met
- Internal standard responses consistent
- Retention times stable
- CCV area responses comparable from one to the next
- X/Y intercepts on calibration curve close to the origin to minimize low level concentration bias

CONTAMINATED SEDIMENTS

A Modeling Methodology to Assist in Assessing Historical Data Quality for Sediment Characterization

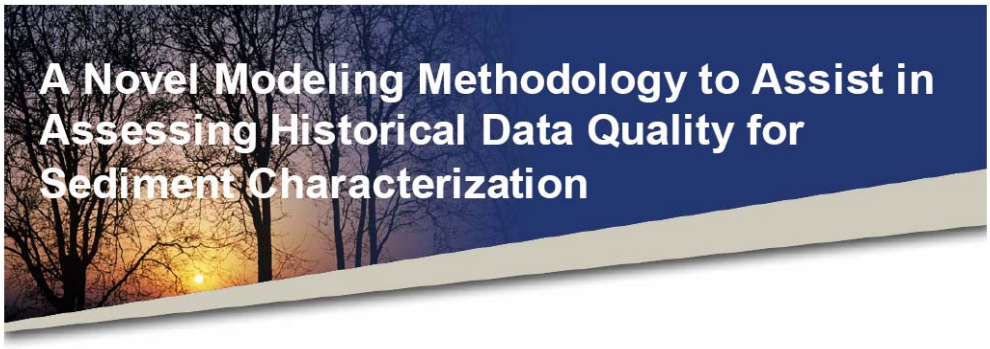
Rock Vitale
Environmental Standards, Inc.

ABSTRACT

Characterization projects involving sediments contained within various river systems often encompass numerous historical site owners, consultants, and laboratories and a variety of sampling and analytical efforts conducted over a period of many years. The resulting reports and laboratory data, which were generated for purposes other than obtaining a current, comprehensive sediment assessment, typically are of various levels of quality. In addition, laboratory data for a single project is commonly documented in a wide variety of data formats, including both hardcopy and electronic versions. The quality and format of data have direct bearing on its usefulness.

A current assessment of laboratory data of unknown quality can represent a significant challenge. The individual project consultants and laboratories may no longer be in business and the level of the data deliverable can be highly variable. Data can either be in the form of summarized tables, abbreviated laboratory reports, electronic spreadsheets, or fully "validatable" data packages. The processes of sorting through the various types of historical data, systematically "gauging" and "grading" data quality, and, ultimately, assessing overall data usability will be presented.

In addition, the use of three-dimensional (3-D) modeling software to visualize historical analytical data, which has proven to be a powerful tool in assessing historical data quality and the identification of data gaps, will be presented. The use of 3-D modeling is particularly useful in measuring data sufficiency, determining whether or not a site is adequately characterized, and ensuring that sample locations have been properly georeferenced. Project-specific examples regarding the use of 3-D modeling for these purposes will be presented.



A Novel Modeling Methodology to Assist in Assessing Historical Data Quality for Sediment Characterization

Rock J. Vitale, CEAC, CPC
Dennis P. Callaghan
Joseph P. Kraycik, P.G.

Environmental Standards, Inc.
Valley Forge, Pennsylvania
www.envstd.com

ENVIRONMENTAL STANDARDS

Introduction

- There are numerous rivers, harbors, and waterways throughout the US that contain sediments that have been impacted by industrialized activities.
- It is estimated that approximately 10% of the sediment in US waterways contains contamination at sufficient quantities to negatively impact aquatic organisms or impair the health of organisms that ingest contaminated fish.

ENVIRONMENTAL STANDARDS

Introduction

- Historical sediment sampling and characterization activities have been conducted by various parties for many of these waterways.
- Analytical data from these historical events significantly vary in quality and can exist in a variety of hardcopy and electronic formats.
- Historical data may be useful during current, comprehensive investigations depending on the data quality and the current data quality objectives.

ENVIRONMENTAL STANDARDS

Establishing Objectives

Identifying the Drivers

Sediment contaminants can be placed into the following five categories:

- Nutrients – *e.g.,* phosphorous, nitrogen
- Bulk Organics – *e.g.,* oil and grease
- Halogenated Hydrocarbons – *e.g.*, pesticides, PCBs
- Polycyclic Aromatic Hydrocarbons
- Metals

ENVIRONMENTAL STANDARDS

Identifying the Drivers

- Current investigations typically involve one or more of these contaminant categories.
- It is important to identify investigative drivers as early as possible based on historical information and site-specific knowledge.

ENVIRONMENTAL STANDARDS

Establishing Data Quality Objectives

- Historically, the incorrect application of soil sample collection and analysis techniques to sediment sampling has adversely impacted data quality.
- Significant advances have been made in the collection and analytical techniques applicable to sediments.
- Clear data quality objectives must be established for current investigations prior to assessing historical sediment data.

ENVIRONMENTAL STANDARDS

Prioritizing Data Gathering Efforts

- Searching for and accessing historical data sets can be a major challenge.
- The efforts and resources associated with accessing historical data must be balanced with the likelihood of identifying data in usable formats and the potential costs to search for, obtain, and assess the quality of the historical data.

ENVIRONMENTAL STANDARDS

Inventorying Available Data

- An inventory of the available analytical data and formats should be conducted.
- The types of analysis, format of data, and documentation have a direct bearing on the usefulness of the data.

ENVIRONMENTAL STANDARDS

In general, in order to effectively use historical laboratory data, the following items are needed:

- Original laboratory reports (CLP-like data packages)
- Chain-of-custody records
- Field sampling records
- Boring logs for accurate stratigraphic information
- Geo-referenced location data

ENVIRONMENTAL STANDARDS

Historical data can be placed into the following categories for current data use:

- Screening Data – use to guide sampling locations for current investigations
- Estimated Data – use in model with estimated qualifications
- Potentially Quantitative Data – possibly reliable/usable analytical data

ENVIRONMENTAL STANDARDS

- It may be possible to "upgrade" data that are initially placed in the screening or estimated categories.
- In order to upgrade data, the previous consultants and laboratories must be contacted to obtain the required information, if available.
- Need to balance the costs involved vs. merely collecting new data.

ENVIRONMENTAL STANDARDS

- Estimated data should be subjected to quality screening (verification).
- Potentially quantitative data should be subjected to rigorous data validation by qualified chemists.
- Based on verification and validation efforts, data may be rejected or placed into one of the three historical data categories.

ENVIRONMENTAL STANDARDS

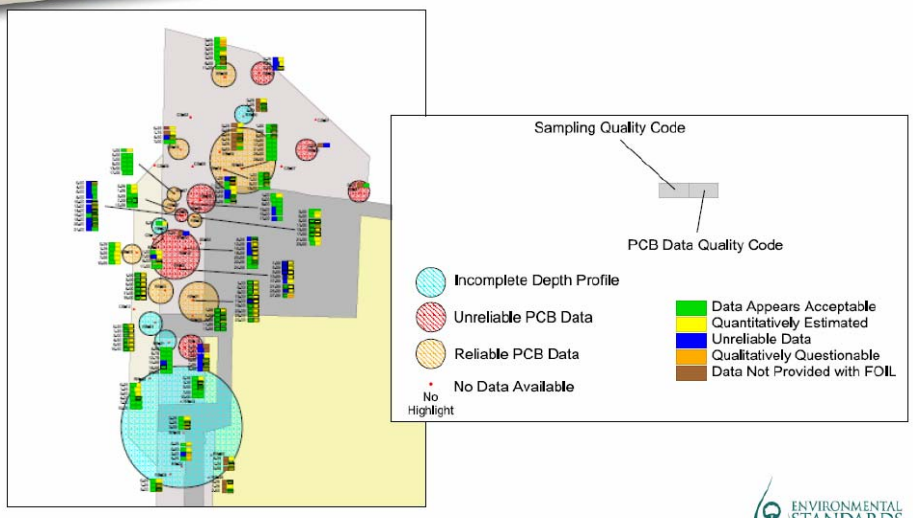
Visualization and Modeling

Geographic Information Systems (GIS)

- GIS can be a highly effective method of screening data prior to use in a 3-D model.
- GIS can be used to determine if sufficient and appropriately qualified data exist in areas of interest prior to modeling.

ENVIRONMENTAL STANDARDS

Visualization and Modeling



ENVIRONMENTAL STANDARDS

- 3-D contaminant distribution modeling can also be used to provide a more refined assessment and evaluation of analytical data.
- Software tools such as the Mining Visualization System (MVS) and Environmental Visualization System (EVS) produced by CTech, Inc. can be used.
  - Extensively used by US EPA, other regulatory agencies, and industry

ENVIRONMENTAL STANDARDS

- Appropriate data from the data screening activity are combined to create the modeling data set and can include data identified as screening, estimated, and potentially quantifiable.
- Data determined to be unusable during the data assessment are not included in the modeling data set.

ENVIRONMENTAL STANDARDS

Data operations to yield modeling data set:

- Geo-reference all data points (X, Y, Z)
  - Boring logs indicate appropriate data based on recoveries
- Assign a numeric value to non-detects
  - Some percentage of the method detection limit

ENVIRONMENTAL STANDARDS

- Once the modeling data set is compiled and operations are complete, data are input into visualization software for the initial modeling run.
- The modeling results for each contaminant of concern are displayed as 3-D sampling locations and volumes based on project-specific action levels.

ENVIRONMENTAL STANDARDS

- To enhance understanding of the site, stratigraphic data can be incorporated into the model.
- After interpreting stratigraphic data and creating a geological file, MVS/EVS is used to create geological surfaces resulting in a “geological model”.
- The generation of a geological model allows an assessment of the extent of contamination within each geological unit and the identification of anomalous stratigraphic data.

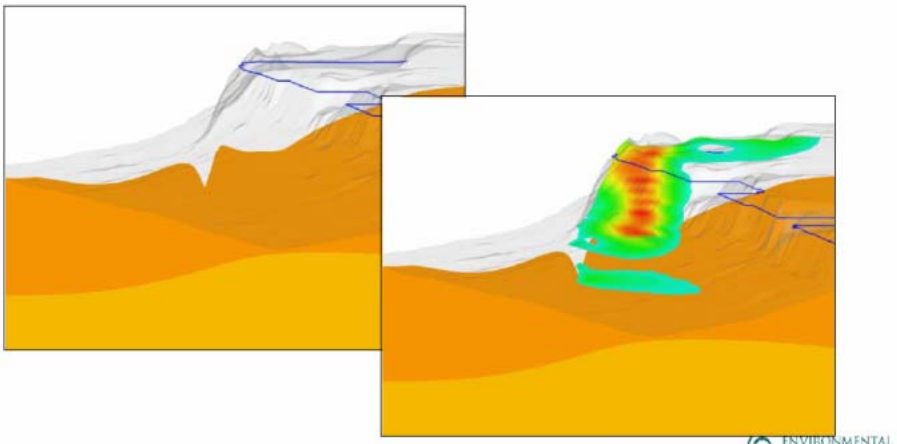
ENVIRONMENTAL STANDARDS

- The MSV/EVS modeling environment is very strong in visualization and provides high-level or large-area mass and volume calculations.
- By reviewing the completed model, questionable data, data errors, and data gaps are often obvious.
- Model can be used to identify low data density and low data confidence areas for guiding future assessments.

ENVIRONMENTAL STANDARDS

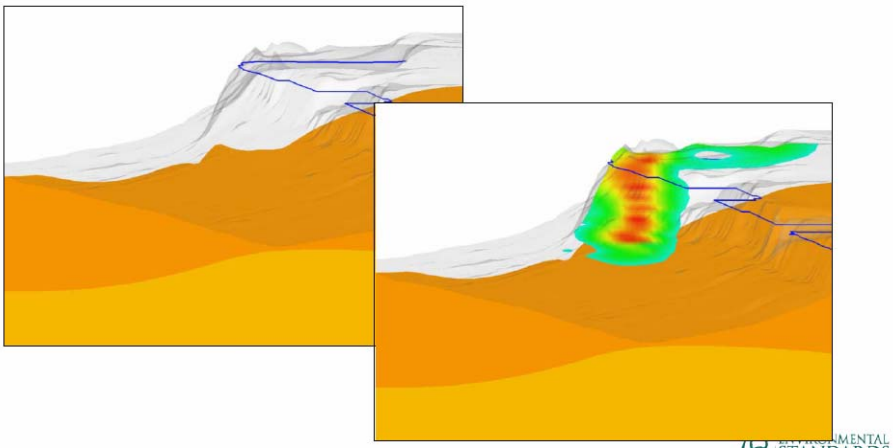
Example Project Issue

Note the stratigraphic trap and the contamination anomaly….



Example Project Issue

Revised model after data collection ….



Conclusions

- When planning sediment investigations, consider that useful existing historical data may be available.
- In order to determine the usability of the available historical data, a data quality assessment of the historical data must be performed.

Conclusions

- After data quality has been assessed and data preparation / normalization operations performed, a 3-D contaminant distribution model can be produced.
- The 3-D model can be used as a powerful tool to identify low-quality or anomalous data and data gaps for risk assessment, remediation, and engineering purposes.

Setting the Standards for Innovative Environmental Solutions

ENVIRONMENTAL STANDARDS

Applying Flocculation and Isotope Dilution-Solid Phase Microextraction for Determining Freely Dissolved Nonionic Organic Contaminants in Pore Waters

David Thai
TestAmerica Severn Trent Laboratories

ABSTRACT

The US Environmental Protection Agency (EPA) has developed equilibrium sediment benchmarks and risk assessment guidance based on a commonly accepted strategy for determining exposures of benthic receptors (i.e., estimating the freely dissolved pore water concentrations from sediment organic carbon concentrations) in accordance with equilibrium partitioning theory. In this strategy, estimates of freely dissolved pore water concentrations of nonionic organic contaminants are derived from the organic carbon concentrations, based on organic carbon-water equilibrium partition coefficients (KOCs), which are given by octanol-water partition coefficients (KOWs). This indirect approach has emerged due to the logistical problems of generating adequate volumes of pore water for analysis, and the absence of a method to selectively extract freely dissolved analytes. The validity of this approach depends on the degree to which organic carbon controls the equilibrium. A steadily increasing body of literature reveals that, for sites in which various forms of black carbon are present, the black carbon, rather than the organic carbon, controls the equilibrium positions. Indeed, the use of KOW-based KOCs can result in thousand-fold overestimates of the freely dissolved PAH concentrations. Recent studies of black carbon have shown that it exists in varied mixtures of heterogeneous forms. As a result, it is unlikely that reliable, generic black carbon partitioning coefficients can be developed.

Fortunately, new techniques and methods are emerging that provide for more direct analysis of freely dissolved concentrations. Hong & Ghosh *et al.* have demonstrated a straightforward flocculation/centrifugation method for removing particulate and colloidal components, leaving the dissolved concentrations essentially unaffected and available for analysis. Hawthorne *et al.* have applied this technique to generate pore waters that are amenable to analysis by isotope dilution-solid phase microextraction (ID-SPME). They developed and reported a method which provides freely dissolved concentrations at sub µg/L to low ng/L, with greater sensitivities for the more hydrophobic analytes. It is significant to note that these sensitivities, which rival those from a 1 L liquid-liquid extraction, are achieved using less than 2 mL of pore water per analysis.

An interlaboratory validation study was recently completed, and ASTM Committee D19.06 has scheduled balloting of the method (ASTM WK10122) for July 1 2007. This presentation provides more specific information on the difficulties with the traditional approach, and reports on our experience as a commercial laboratory in setting up for the analysis, learning the analytical techniques and participating in interlaboratory validations. It provides an evaluation of the performance capabilities of the method and recommended quality assurance elements and discusses broader applications of the approach.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THE LEADER IN ENVIRONMENTAL TESTING
Applying Flocculation and Isotope Dilution-Solid Phase Microextraction for Determining Freely Dissolved Nonionic Organic Contaminants in Pore Waters
2007 National Environmental Monitoring Conference
David Thal
Operations Manager - Sediments and Tissue Program
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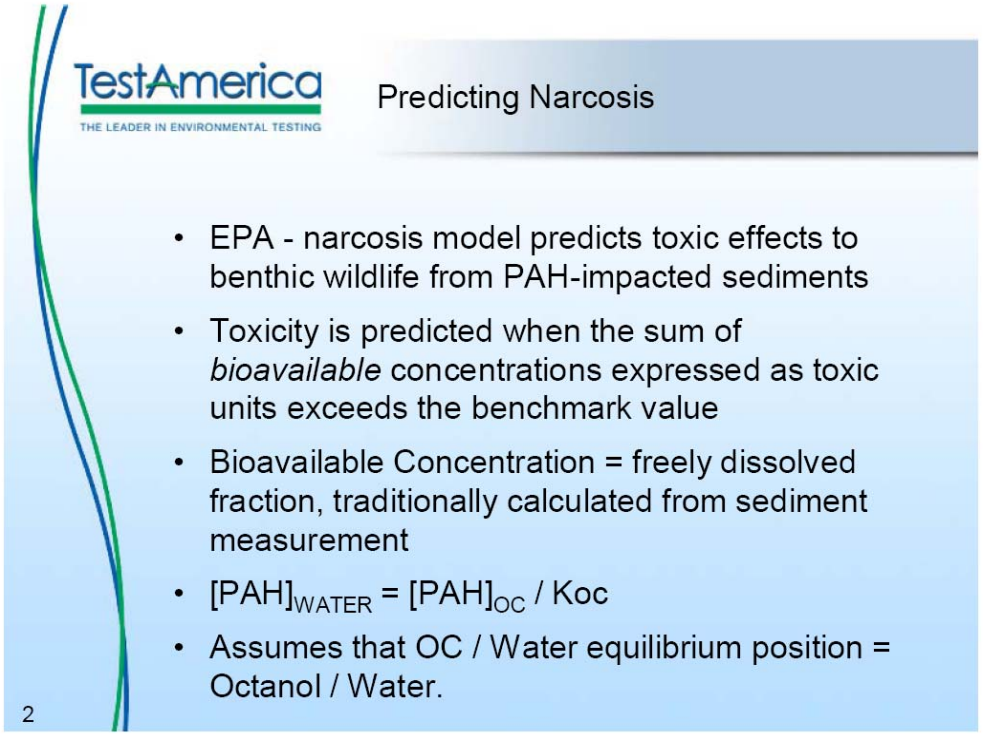
Aug 23, 2007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Predicting Narcosis
• EPA - narcosis model predicts toxic effects to benthic wildlife from PAH-impacted sediments
• Toxicity is predicted when the sum of *bioavailable* concentrations expressed as toxic units exceeds the benchmark value
• Bioavailable Concentration = freely dissolved fraction, traditionally calculated from sediment measurement
• $[PAH]_{WATER} = [PAH]_{OC} / Koc$
• Assumes that OC / Water equilibrium position = Octanol / Water.
2

March 2007 - EPA Proposed Revised ERA Guidelines

- Recognizes that pore water methods are logistically difficult and may be expensive
- Refines the traditional approach (sediment to pore water conversion).
- Recommends sediment testing for 18 parent and 16 alkyl homologs. (EPA 34 PAH List)
- Recognizes that no EPA method is available to address the homologs
- Identifies Lauenstein & Cantillo (1998) as a method. [aka NOAA Method]
- Clarifies conversion of sediment conc's to sum of toxic units (ΣTU).

3

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Where to Measure?

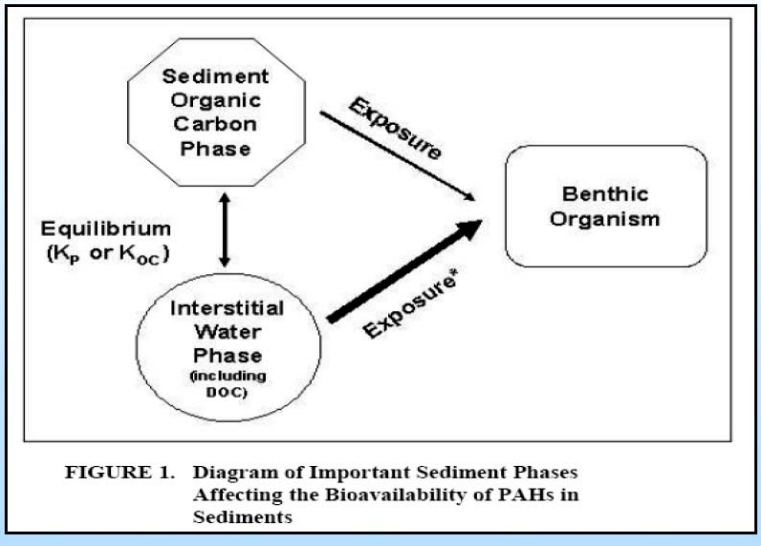

FIGURE 1. Diagram of Important Sediment Phases Affecting the Bioavailability of PAHs in Sediments

4

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Why not simply perform direct analysis of pore water?

- Isolating 1 L porewater by centrifugation or pressing can require 5-10 kg of sediment/site water slurry.
- Once isolated, the pore water can contain significant amounts of suspended particulate and colloidal agglomerates.
- Suspensions/dispersions can't be removed by centrifugation, due to (primarily) cationic charges.
- Filtration is avoided due to two types of bias.
  - failure to remove colloids <0.1 µm
  - "SPE phase" forms as oil sheen builds on filter

5

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Flocculation (Coagulation)

- Alum, $Al_2(SO_4)_3$. Is used within a controlled pH range. Other Al and Fe salts, including poly-aluminum chloride, ferric chloride, and ferric sulfate, may be used as well for flocculation processes.
- Salts react w/ cations on suspended clays, humates and organic matter-complexed cations, forming solid precipitates
- Method as described by Hong, Ghosh & Hawthorne effective at removing colloids. But does it also remove dissolved PAHs?

6

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2003 Hong & Ghosh Perform Direct Measures of Dissolved Phase

- Air bridge studies allow direct measures of freely dissolved concentrations.
- Air bridge studies provide standard against which to evaluate impact of flocculation on dissolved concentrations.
- Gives the ability to empirically determine K_{OC}s.
- Observed significant scatter in partitioning behavior.
- SEM imaging of sediment components.

7

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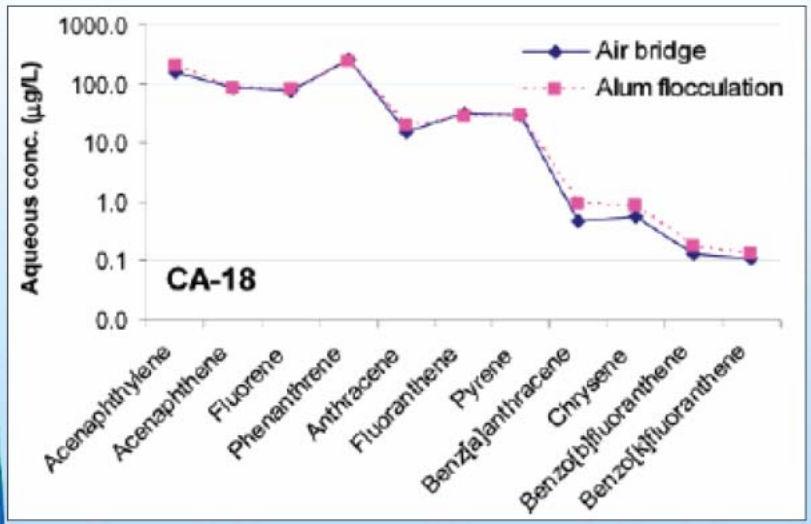
Dissolved Concentrations Unaffected by Flocculation



Hong, Ghosh *et al.*, 2003

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Now that freely dissolved concentration can be measured, some dissolved concentrations observed 100 to 1000 times below predicted

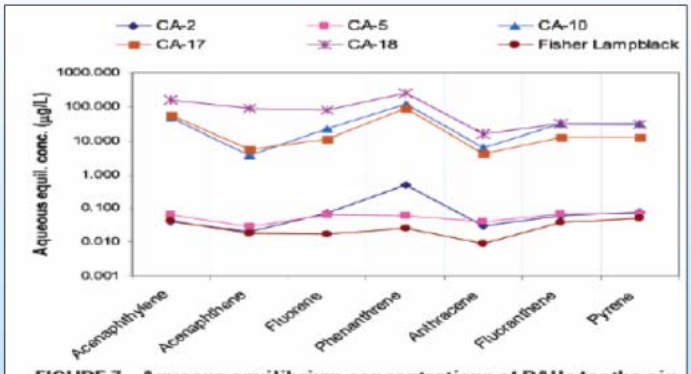

FIGURE 7. Aqueous equilibrium concentrations of PAHs for the six study materials as measured by the air-bridge technique. CA-2, CA-5, and Fisher lampblack show nearly 2—3 orders of magnitude lower PAH concentrations in the aqueous phase as compared to the other lampblack-impacted soils including CA-10, CA-17, and CA-18.

9

Hong, Ghosh *et al.*, 2003

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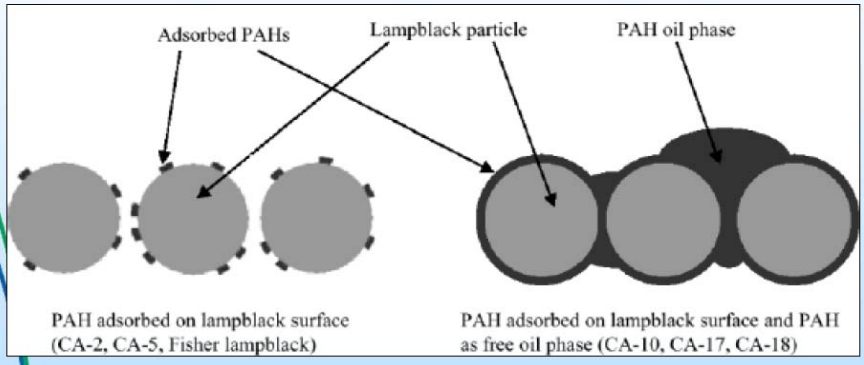
Is this why observed K_{OC} >> K_{OW}?



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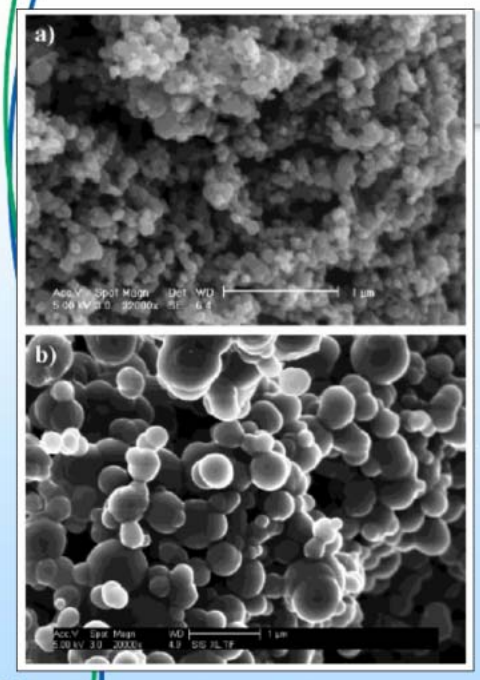
Hong, Ghosh *et al.*, 2003



Scanning Electron Microscopy

← Standard black carbon
vs.
← impacted sediment black carbon

11

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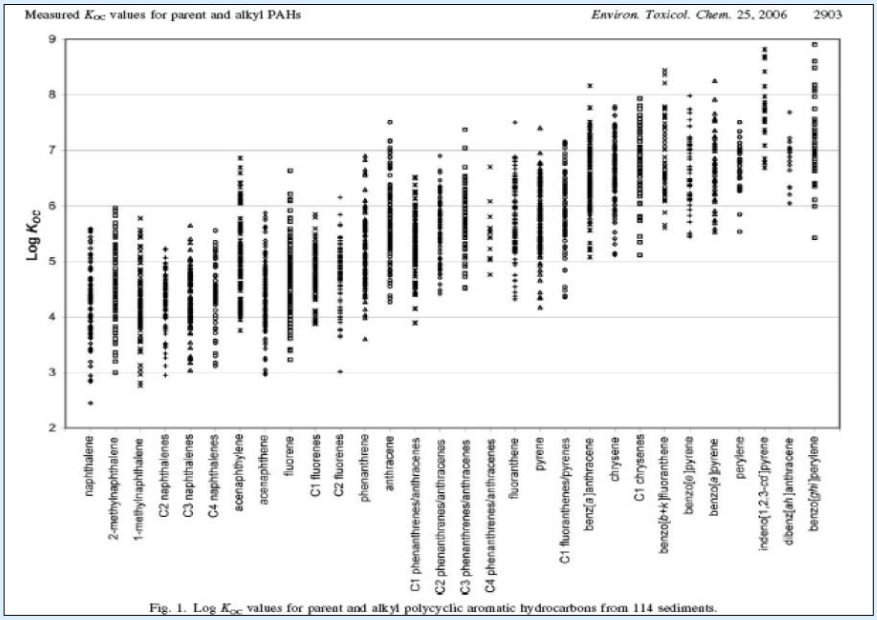
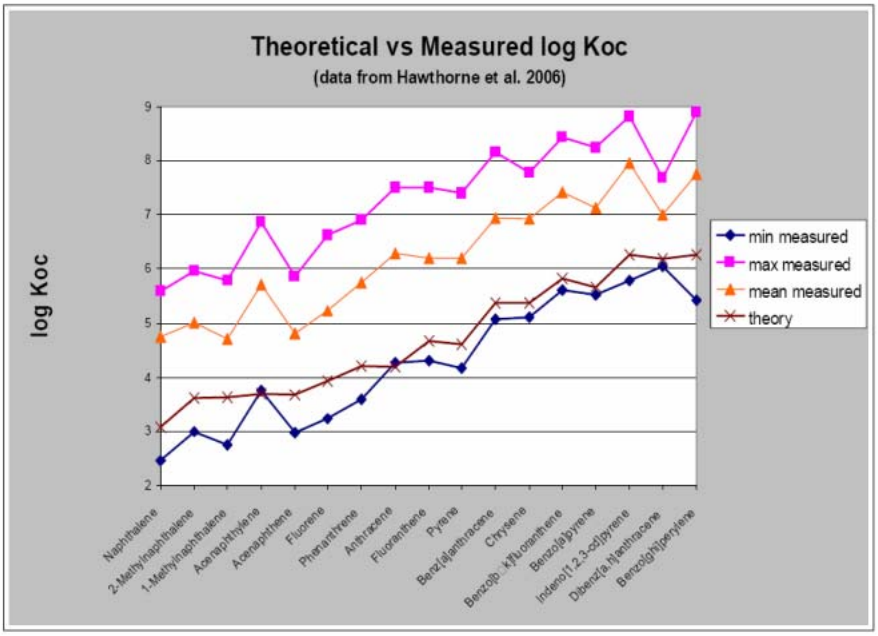
2005, 6 – Hawthorne Reports PAH Partitioning Behavior Using New Method

- Isotope Dilution-Solid Phase Microextraction performed on flocculated pore waters.
- Measures only freely dissolved PAHs.
- Addresses EPA 34 list, uses homolog-RRFs rather than RFs from parent.
- Method requires only a 4 oz jar of slurry.

12



13 Hawthorne et al., 2006



14

Method shows better specificity, and overall prediction efficiency for toxicity to H. azteca.

TABLE 2. Survival Predictions for *H. azteca* using Total Extractable, SFE Rapidly Released, and Pore Water PAH_{34} Concentrations from 97 Field Sediments

method	15–85% survival range (μmol/g of lipid)[a]	no. of sediments in 15–85% range	prediction efficiencies: sensitivity[b] (%)	specificity[c] (%)	overall[d] (%)	Goodman–Kruskal γ
PAH_{13} concn > 1.6 mg/kg (TEC)[e]			100	6	30	0.73
PAH_{13} concn > 22.8 mg/kg (PEC)[f]			96	32	48	0.75
PAH_{34} concn	36–315	26	80	81	80	0.78
SFE rapidly released PAH_{34}	0.9–43	40	92	64	71	0.80
pore water PAH_{34}	15–75	17	92	89	90	0.95

[a] Lower 95% confidence interval for 85% survival and upper 95% confidence interval for 15% survival. [b] Sensitivity is the extent to which a test correctly classifies a toxic sample as toxic and is therefore protective of the environment. [c] Specificity is defined as the rate at which a test correctly classifies a nontoxic sample as nontoxic. [d] Overall efficiency is the fraction of correct predictions for all samples. [e] TEC is the sum of 13 parent PAH concentrations below which toxicity is considered unlikely (1). [f] PEC is the sum of 13 parent PAH concentrations above which toxicity is considered likely (1).

Hawthorne, Azzolina, Neuhauser & Kreitinger ES&T Aug 4, 2007

15

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Regulatory Situation

- Proof of Concept Study, completed in 2006. TestAmerica Knoxville served as non-development lab
- ASTM has approved the provisional method **WK10122**. To publish it as a full standard with limited validation data - 2008 Annual Book of Standards Section 11.
- Following publication of that standard, 5 years is allowed to complete the full interlab study with 7 labs.
- EPA Interlab Validation study as **EPA Draft Method 8272** was just completed under the guidance of Mr. Barry Lesnik, with funding from Alcoa. Three non-development labs participated. (TAL, UMBC, Meta)
- Results will be published in a peer reviewed paper as well as presented in the next NEMC conference.

16

Sediment Contaminant Bioavailability Alliance

- Formed in 2004, is a multi-industry group being led by Alcoa, Central Hudson Gas and Electric, National Grid, New York State Electric and Gas Company, the Northeast Gas Association, and ENSR Corporation (dba the RETEC Group, Inc.)
- Also Supported by Dow, NiSource and US Steel.
- Bioavailability Research Team Participants include representatives of ENSR, University of ND Energy and Environment Research Center, USACE ERDC, AquaTox, University of Maryland Baltimore County, TestAmerica

17

SCBA Purpose

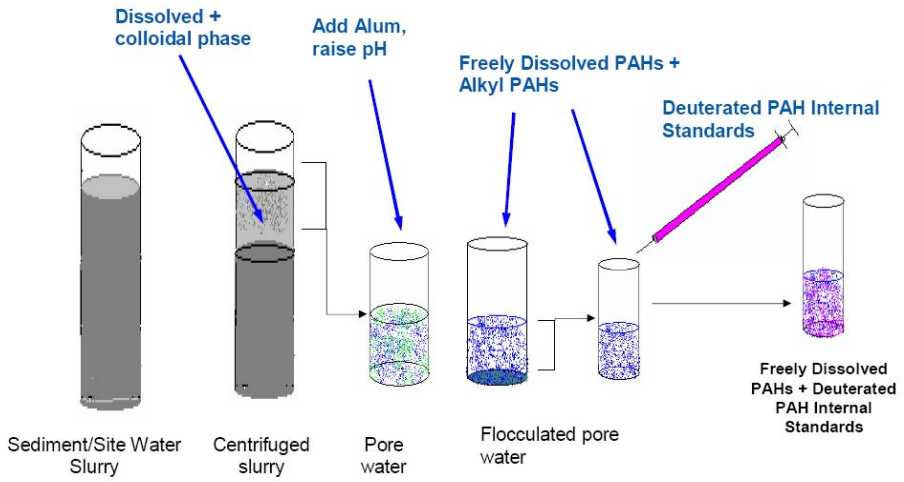
Increase scientific understanding of chemical exposure to aquatic organisms in sediments

Develop site-specific chemical measures that estimate the bioavailability of sediment-bound organic chemicals to these organisms

Use this improved scientific understanding within existing regulatory frameworks to make more informed sediment management decisions

18

Centrifuge, Flocculate, Separate, Spike w/ Isotopically Labeled PAHs



19

Fig. 1 - Extraction Procedure for SPME

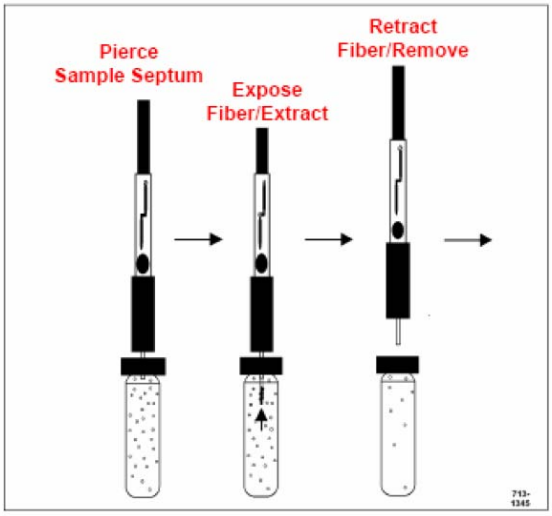
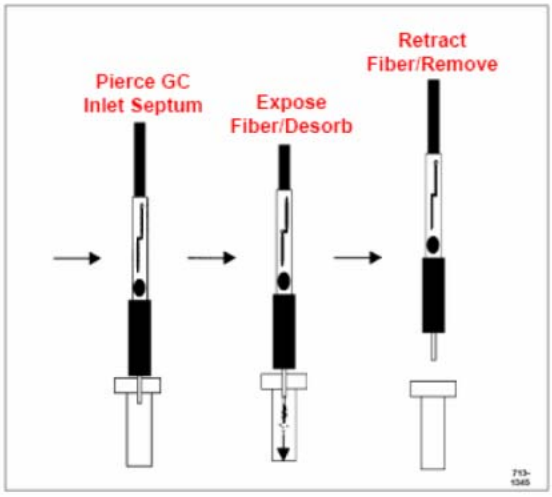
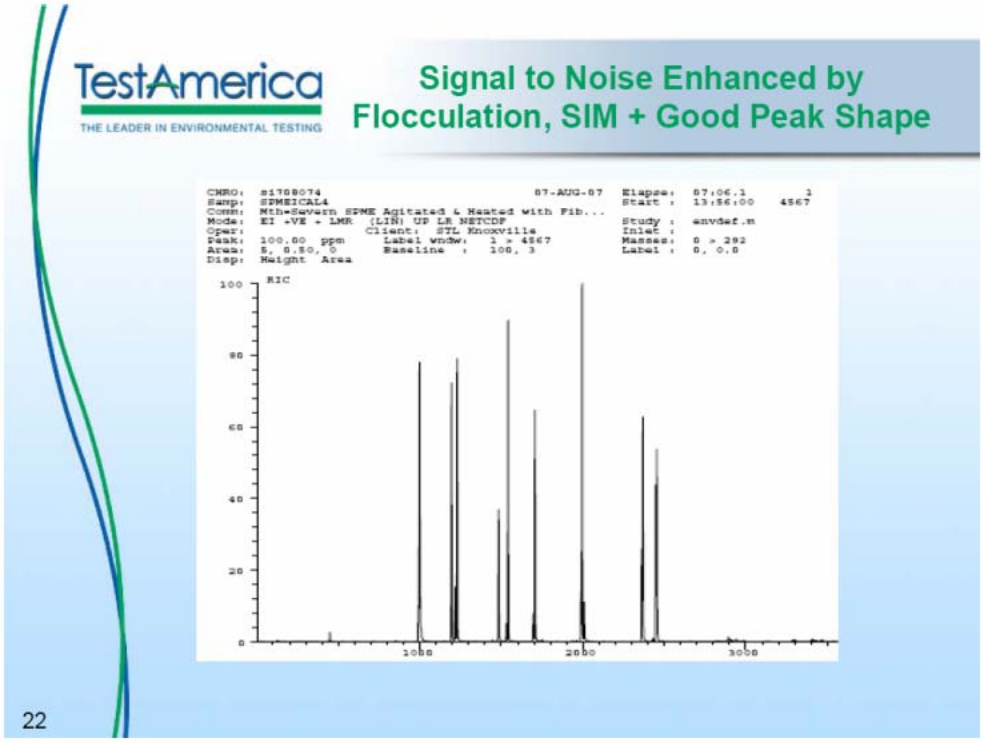
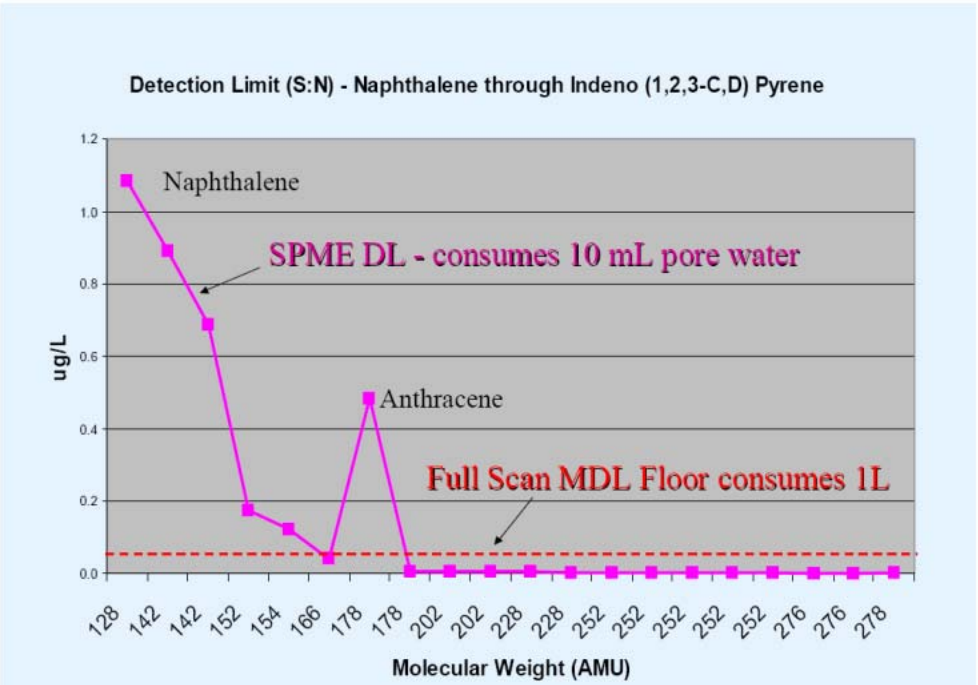


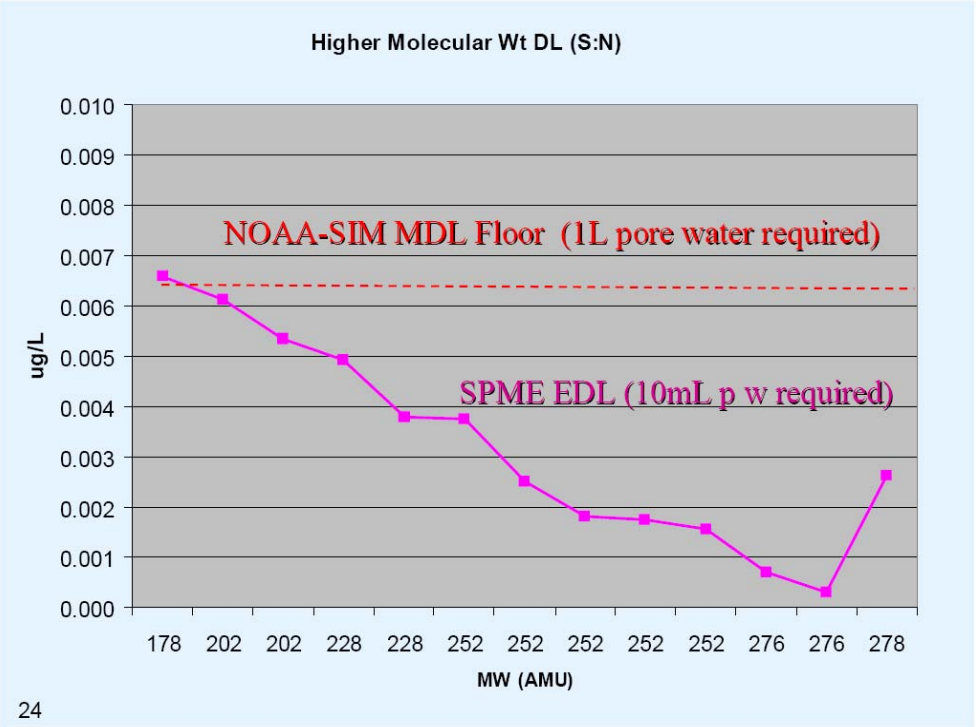
Fig. 2 - Desorption Procedure for SPME



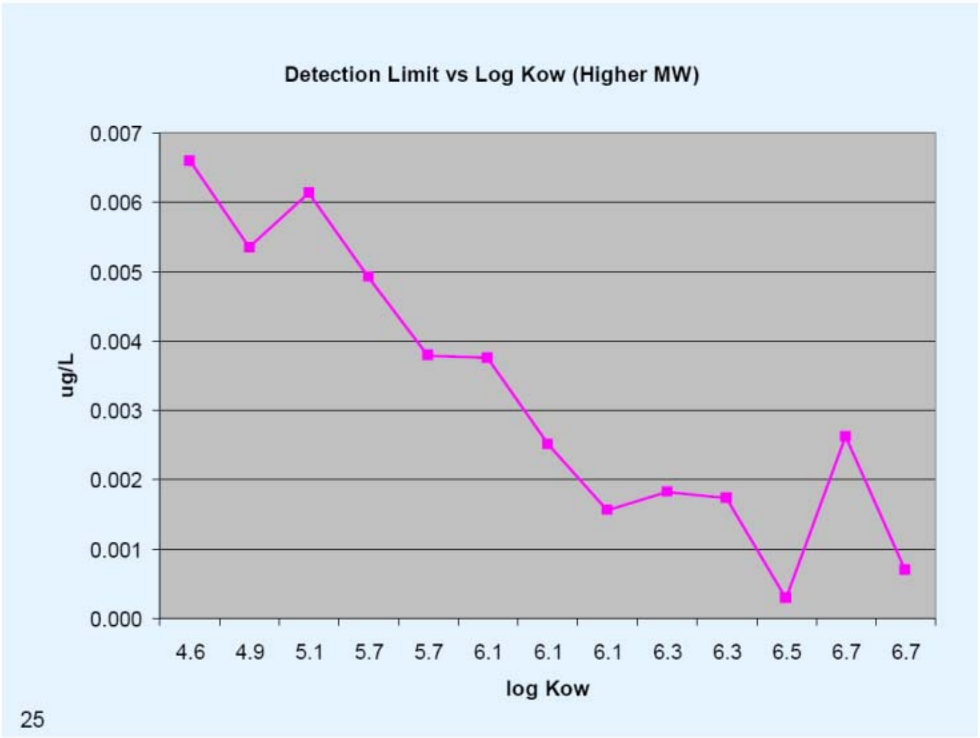



Detection Limit (S:N) - Naphthalene through Indeno (1,2,3-C,D) Pyrene
Naphthalene
SPME DL - consumes 10 mL pore water
Anthracene
Full Scan MDL Floor consumes 1L
ug/L
1.2
1.0
0.8
0.6
0.4
0.2
0.0
128 142 142 152 154 166 178 178 202 202 228 228 252 252 252 252 252 276 276 278
Molecular Weight (AMU)

23


Higher Molecular Wt DL (S:N)
NOAA-SIM MDL Floor (1L pore water required)
SPME EDL (10mL p w required)
ug/L
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
178 202 202 228 228 252 252 252 252 252 276 276 278
MW (AMU)

24



25

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Data Reduction

- The concentrations for 18 parent PAHs is obtained using isotope dilution quantitation (15 labeled analogs).
- The concentrations for 16 groups of alkyl PAHs are determined using relative response factors provided by Hawthorne (2005) .
- Each concentration is converted to Toxic Units (TU), (TU = Conc/FCV).
- The TU for each of the 34 concentrations is summed, to provide ΣTU.
- Alternatively, the results can be expressed in terms of µmole/g lipid.

26

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Advantages

- Improved predictive efficiency of narcosis
- Reduces uncertainty about partitioning.
- Very Sensitive: Working with 10 mLs, similar to sensitivity to 1L 8270 for 2-3 rings.
- Much lower sensitivity for 4-6 rings. Comparable to NOAA-SIM at 1 L.
- Requires 4 oz jar of sediment site water slurry.
- Turnaround time can be short. For 8 samples, sample receipt to data acquisition can be done in 2 days.

27

Challenges

- Lab had to upgrade to a good Agillent 5973 series was required. New electronics, new inert source ~$15K.
- Specialized autosampler required unless instrument is to be continually staffed. ~$34K.
- Special standards must be formulated, with native and deuterated standards adjusted for solubility.
- Background air sources must be controlled.
- Requires change in liner, septum, very clean ion source.
- Learning curve - senior analyst and instrument 3-wks - 1 month to get going for low molecular weight targets.
- 1-2 add'l months for high molecular weight targets.
- Multiple runs required, separated by multiple blanks - minimum 4 runs per sample. Almost 1h per run.

28

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Summary

- Narcosis model predicts narcosis toxicity
- Literature/Modeled K_{OW}s can overestimate bioavailable concentrations by several orders of magnitude.
- EPA is considering a revision of PAH ecological risk assessment to include 34 alkyls and parents.
- Flocculation is a useful analytical tool for removing colloids & suspensions.
- ID-SPME is a new way to directly measure dissolved phase.
- Used in concert, these techniques provide and important new line of evidence for site specific KOCs.
- Methodology is being taken through necessary steps for regulatory acceptance.

29

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- Hawthorne, S.B., Azzolina, N., Neuhauser, E., Kreitinger, J.P., Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to Hyalella Azteca Using Equilibrium Partitioning, Supercritical Fluid Extraction and Pore water Concentrations. *Environ. Sci. Technol.* 2007, online edition Aug 4 2007.

30

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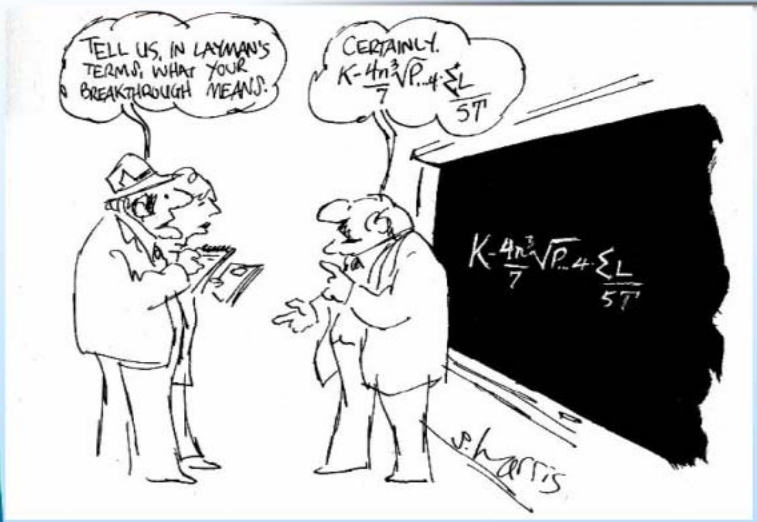


31

Estimating the Bioavailability of PAHs (parent and aklylated) in Sediment Based on Direct Measures of PAHs in Sediment Pore Water Using Solid Phase Microextraction (SPME)

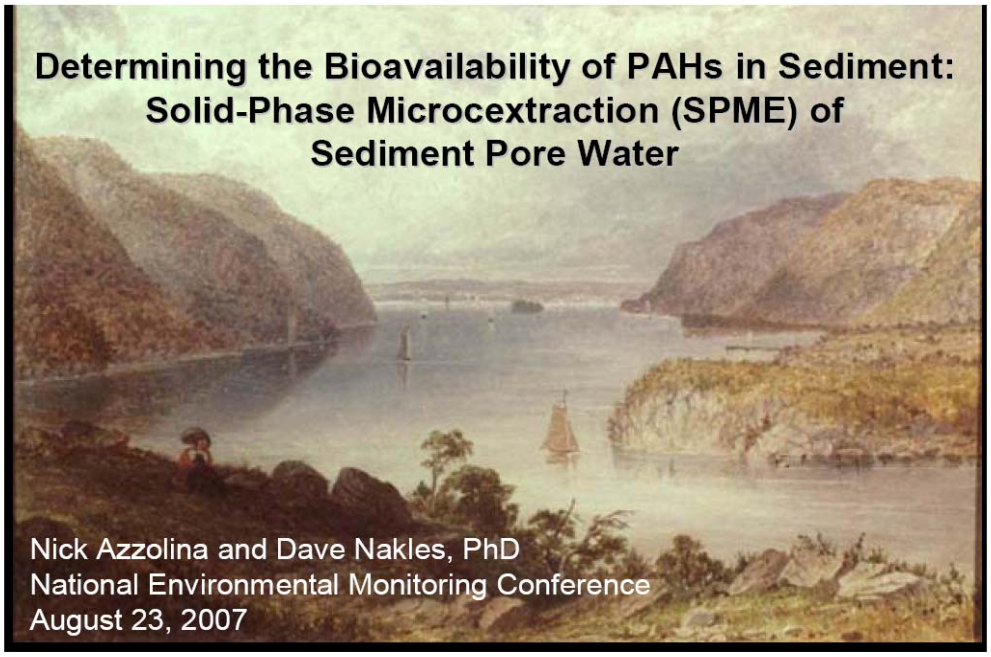
David Nakles
ENSR/AECOM

ABSTRACT

In December 2005, the US Environmental Protection Agency (EPA) released a guidance document, "Contaminated Sediment Remediation Guidance at Hazardous Waste Sites." This document cites the importance of understanding the bioavailability of sediment-bound contaminants for evaluating the efficacy of remedial strategies, such as monitored natural recovery, as well for managing the residual risk following dredging. However, at no point in the document is a method for measuring bioavailability provided. More recently, on March 2, 2007, the EPA released a "Notice for Public Comment Period" for an external review draft, "Evaluating Ecological Risk to Invertebrate Receptors from PAHs in Sediments at Hazardous Waste Sites." This draft document notes that the measurement of PAHs in sediment pore water provides the "most accurate indicator of the bioavailable exposure concentration." However, it continues by noting that available analytical methods for measuring pore water concentrations are "logistically impractical and expensive", forcing an EPA policy that recommends predicting these pore water concentrations based on bulk sediment concentrations and literature-based partitioning coefficients.

The Sediment Contaminant Bioavailability Alliance (SCBA), an industrial consortium, has developed an analytical method for accurately measuring the concentration of 34 PAHs (18 parent PAHs and 16 clusters of alkylated PAHs) in sediment pore water using solid phase microextraction (SPME). Using as little as 1 to 2 ml of pore water, parts per trillion detection limits can be achieved using this method. Based on twelve industrial field case studies, which characterized 160 sediments and their pore water, the SCBA has demonstrated that these measurements can be used to accurately predict the toxicity of PAH-impacted sediment to aquatic organisms. Currently, the SCBA is pursuing ASTM and EPA approval of this analytical method, with the assignment of a provisional ASTM method, as well as EPA methods for both the Office of Water and the Office of Solid Waste and Emergency Response, expected in CY 2007.

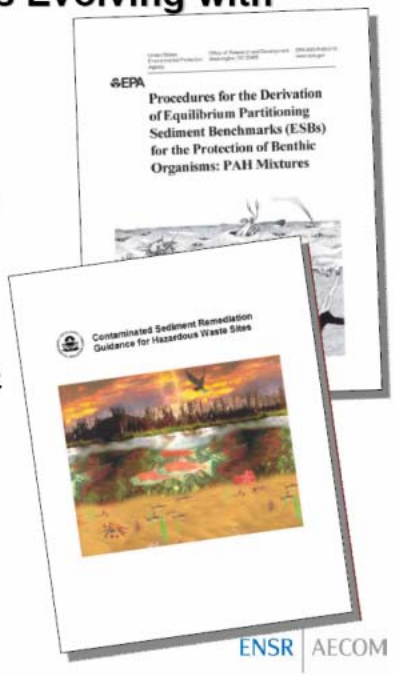
This presentation provides an overview of the results of the twelve field case studies of the SCBA, describes the use of the SPME pore water analytical measurements for the prediction of sediment toxicity, and discusses the status of the current efforts to secure ASTM and EPA approval of this analytical method.



SCBA ENSR | AECOM

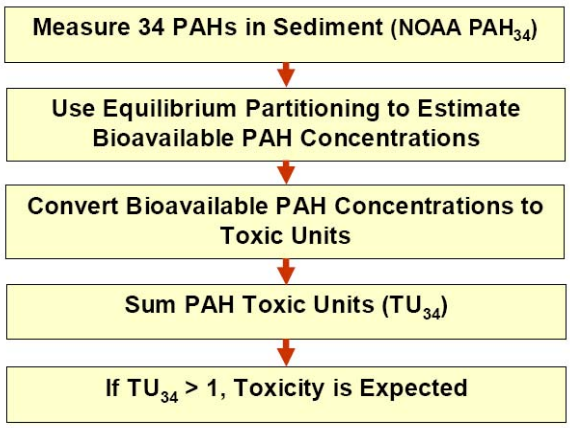
Use of Bioavailability Concepts Evolving with Regulatory Guidance

- NOAA [1990's] – Sediment screening values: No consideration of bioavailability
- USEPA 2003 - Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures
- USEPA 2005 - Contaminated sediment remediation guidance - Extensive reference to bioavailability
- USEPA 2007 - Evaluating ecological risk to invertebrate receptors from PAHs in sediments at hazardous waste sites - Explicit accounting of bioavailability



SCBA ENSR | AECOM

Proposed U.S. EPA Approach For Predicting Toxicity of PAHs to Benthic Organisms [U.S. EPA, 2007]



U.S. EPA (2007 Draft) *Evaluating ecological risk to invertebrate receptors from PAHs in sediments at hazardous waste sites*

SCBA ENSR | AECOM

Critical Technical Issues

- Use of Literature Equilibrium Partition Coefficients (Koc)
- Sediment pore water PAH concentration
- Quantification of 16 clusters of alkyl PAHs
- Presence of dissolved organic carbon (DOC)
- Default Toxic Threshold Value of 1 Toxic Unit
- Value of Benthic Community Surveys

SCBA ENSR | AECOM

SPME Provides Accurate Determination of Bioavailable PAHs

- Porewater is "the most accurate indicator of bioavailable exposure concentration" (USEPA 2007)
- SCBA method has been applied to >200 sediment samples
  - ✓ Solid-Phase Microextraction (SPME)
  - ✓ Rapid – 30 minutes
  - ✓ Small sample size:
    - ✓ ~ 20 ml of sediment
    - ✓ ~ 1.5 ml of pore water
  - ✓ Low detection limit: ~ pg/mL (ppt)

These direct measurements of bioavailable PAHs
reduce the uncertainty of their estimation by a factor of 100 to 1,000

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Survey of Hudson River Sediments Shows a Wide Range of Natural and Anthropogenic Carbon

The PAH binding (Koc) is very different for these different types of carbon

(Ghosh et al., 2003)

SCBA

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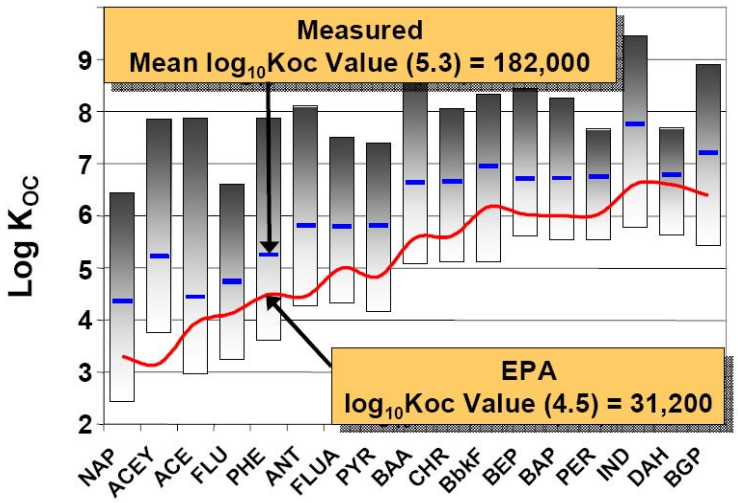
Actual Koc Increases by 1,000-fold in MGP Sediments



N=114
(Hawthorne *et al.* 2006)

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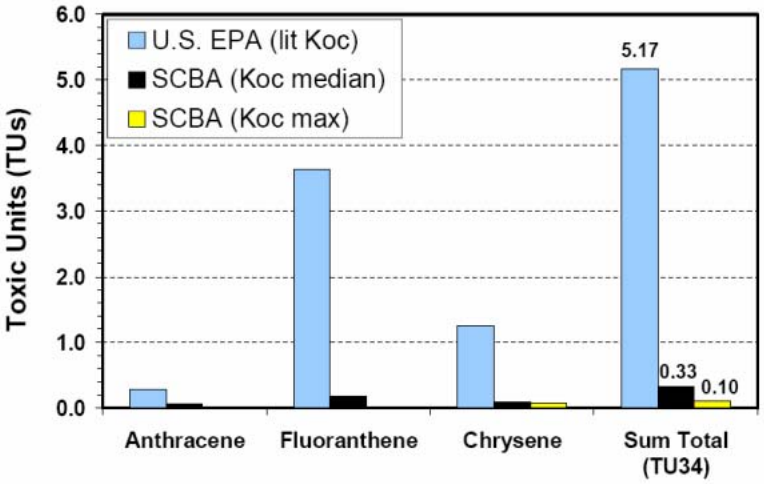
Measured Koc Provide Significantly Lower Toxic Unit Calculations Versus Literature Koc Values



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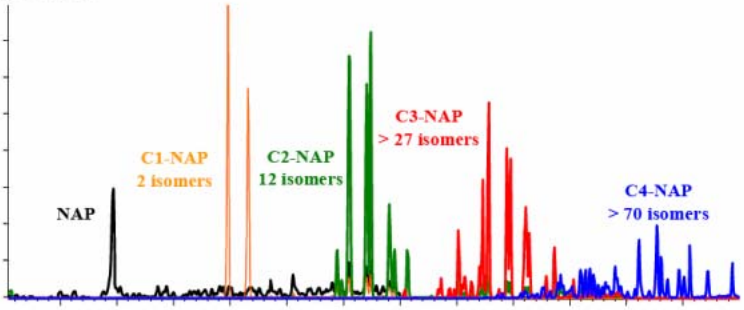
US EPA Referenced Analytical Method [NOAA, 1998] Underestimates Alkylated PAHs

- No calibration standards exists for 11 of the 16 groups of alklyated PAHs, which forces the use of GC/MS response factors for parent compounds



- Underestimates highly alklyated (C_3 to C_4) PAHs, which are some of the more toxic.
- The SCBA has developed appropriate response factors for the alkylated PAHs, reducing the uncertainty by a factor of 2 to 3.

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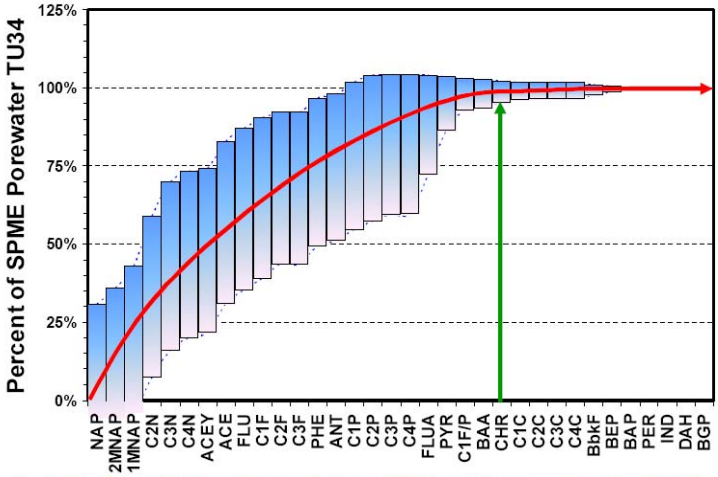
Presence of DOC Does Not Significantly Affect the Determination of the Bioavailable PAHs [Hawthorne, 2005]



2- to 4-ring PAHs account for ~90% of the pore water TU_{34}

2- to 4-ring PAHs do not strongly partition to DOC

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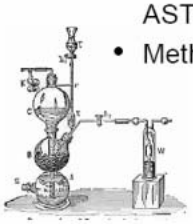
SPME Analytical Method Standardization

- EPA (OSWER [SW-846] and Office of Water)
  - Accepted Proof-of-Concept Study – Fall 2006
  - Completed Inter-laboratory Validation Study – April 2007
  - Assigned an EPA Method Number – Method 8272
  - Review with EPA Analytical Work Group – August 2007
- ASTM Method Standardization
  - Method with limited validation data approved in June 2007
  - Method with limited validation data to be published in 2008 ASTM Standards for Water (Section 11)
  - Method with full validation data needs to completed by 2013



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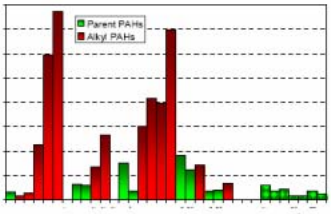
Why both EPA and ASTM?

- EPA
  - Requires recoveries for all compounds based on *standards*
  - No standards for 11 of the 16 groups of alkylated PAHs (NOAA list)
    - EPA method approves only parent compounds + methyl napthalenes
    - However, same method could be used to analyze the remaining alkylated PAHs
  - Requires proof-of-concept (POC study) using 1 lab followed by an ILV study using 3 labs
- ASTM
  - Permits approval of a method for all 18 parent + 16 groups of alkylated PAHs (PAH_{34})
  - Requires 7 labs for full blown ILV study



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EPA POC and ILV Studies Demonstrated that the SPME Method is Reproducible

- POC data showed that a commercial lab like STL (TestAmerica), could produce results that were comparable to EERC (developer lab)

EERC → SEVERN TRENT STL TestAmerica

- EPA ILV results showed excellent precision and bias from the 3 participating test labs

EERC (custodial lab)

META Environmental, Inc. UMBC SEVERN TRENT STL TestAmerica

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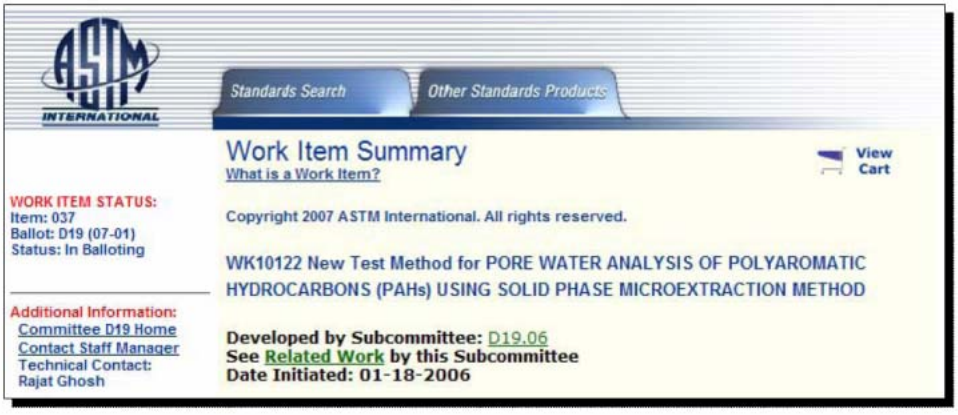
ASTM Accepted a Single Lab Study by EERC as a Standard with Limited Validation Data

- 5 years to complete the full-blown 7-lab ILV



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SCBA Vision: CY 2007

By the end of CY 2007 the SCBA will have:

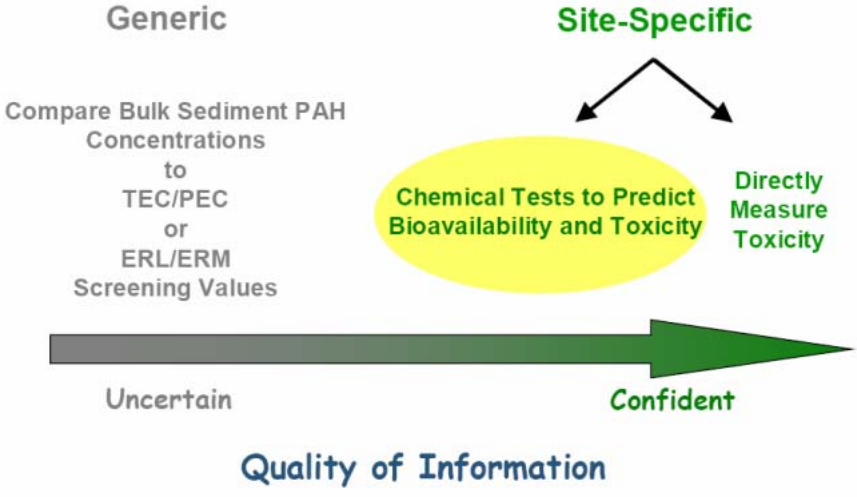
1. A SW-846 method for porewater PAH analysis via SPME

and

2. An ASTM standard for porewater PAH analysis via SPME with limited validation data.

SCBA ENSR | AECOM

SCBA Approach for Predicting Sediment Toxicity



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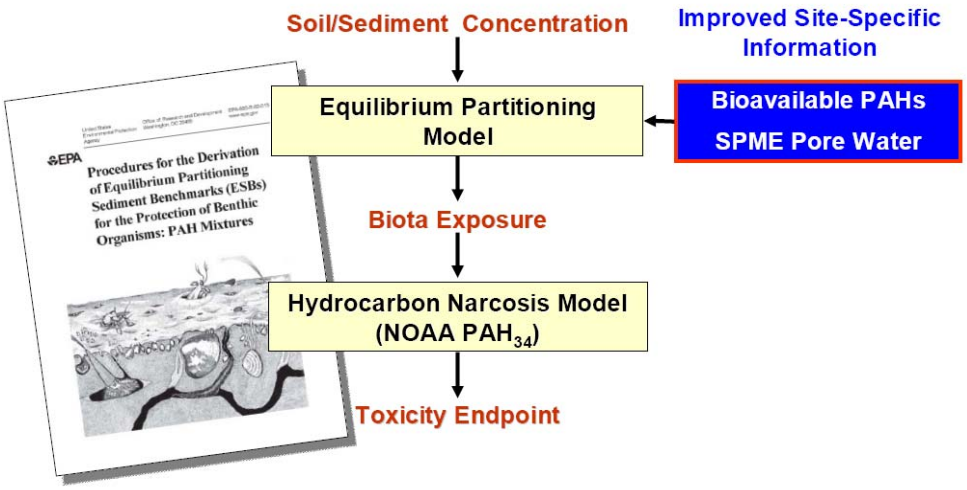
Site-Specific Measures of PAH Bioavailability Are Used to Determine Screening Benchmarks (ESBs)



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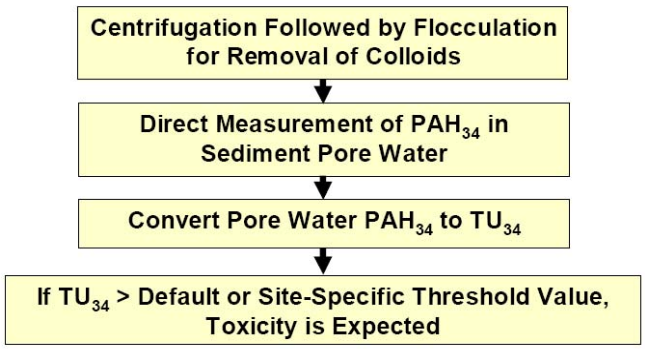
SCBA Approach For Predicting Toxicity of PAHs to Benthic Organisms



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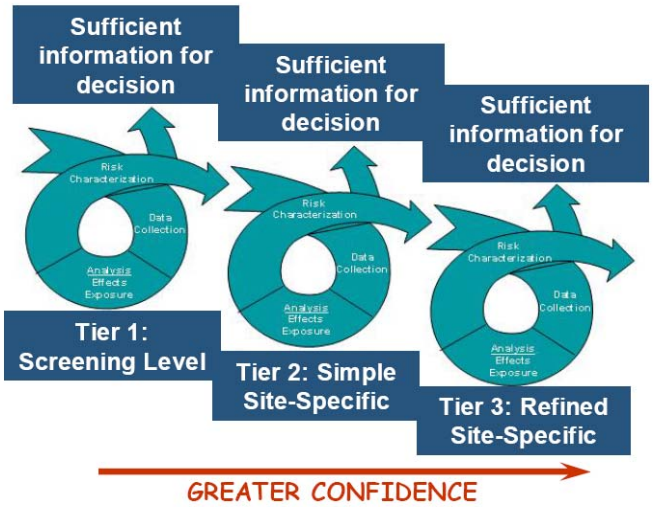
Tiered Approach for Ecological Risk Assessment [U.S.EPA 1996]



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Acknowledgements

ALCOA Northeast GAS ASSOCIATION

Alcoa and the Northeast Gas Association provided support for the EPA and ASTM method standardizations.

SCBA ENSR | AECOM

Extended Sediment Sample Characterization for PCB, PCN, and PCT Contaminated Sites: A Case Study

Bryce Stearns
Severn Trent Laboratories

ABSTRACT

Characterization of polychlorinated biphenyls (PCBs) is generally performed either as an evaluation based on Aroclor pattern, or one based on individual congeners. Routinely, SW-846 Method 8082 has been a primary technique in the analytical evaluation, with the results reported as one or more Aroclors from a standard list. Certain manufacturing processes create and/or used PCB mixtures that can not be accurately characterized in terms of classical Aroclor patterns. Additionally, certain formulations may have included constituents that may not be well characterized in a strict assessment of PCB congeners. These formulations were designed to impart specific material properties and may include, as process by-products or additives, polychlorinated naphthalenes (PCNs) and polychlorinated terphenyls (PCTs).

PCBs were generated at the site to provide for insulation material as part of the manufacturing process. In order to obtain the required physical properties, the reaction process was designed to provide for a higher degree of chlorination than what might be characterized as Aroclor 1262 or Aroclor 1268. Additionally, highly chlorinated PCTs were used in the process. The resulting formulation was highly characteristic of the site activity, and provided a means for source evaluation. A brief history of the site, a summary of the investigative work that was performed by Environmental Standards, and a discussion of the analytical method that was developed by STL Burlington will be presented.

PAH Source Identification: A Multiple Methods Approach

Stephen Emsbo-Mattingly
Newfields

ABSTRACT

Distinguishing the origin of pyrogenic PAH from multiple sources in sediment presents numerous technical challenges. Principally, the source identification difficulties begin with the fact that PAHs are ubiquitous. Secondly, the chemical signatures of natural, point and non-point PAH sources are potentially very similar especially when measured for priority pollutant analytes only ($n < 20$). Thirdly, the effects of environmental weathering and matrix interferences in environmental media often confound the signature of various proximate sources. For these reasons, multiple lines of environmental forensic evidence and the creative use of alternative measurement techniques are often needed to isolate an individual PAH source among others.

Several emerging environmental forensic methodologies have been reviewed and tested for identifying the sources of pyrogenic materials in the environment generated by the manufacture of gas, coke, and tar products in the presence of urban background. The demonstrated effectiveness of these methods in sediment samples offers similar opportunities for source identification projects involving soil, waters, and tissue samples. This cross media capability is important for risk assessment and natural resource damage assessments.

The analytical methods that will be featured in this talk include priority pollutant PAHs (GC/MS), extended PAHs (GC/MS), biomarkers (GC/MS), organic petrology, and compound-specific isotope ratio mass spectrometry (GC/IRMS). This presentation will discuss the utility of complementary methods for PAH source identification purposes in sediments down to the 5 mg/kg total PAH concentration range.

DATA USABILITY

Assessing the Stability of Pesticides and VOCs Under Various Preservation Conditions

Dr. Andrew Eaton
MWH Labs

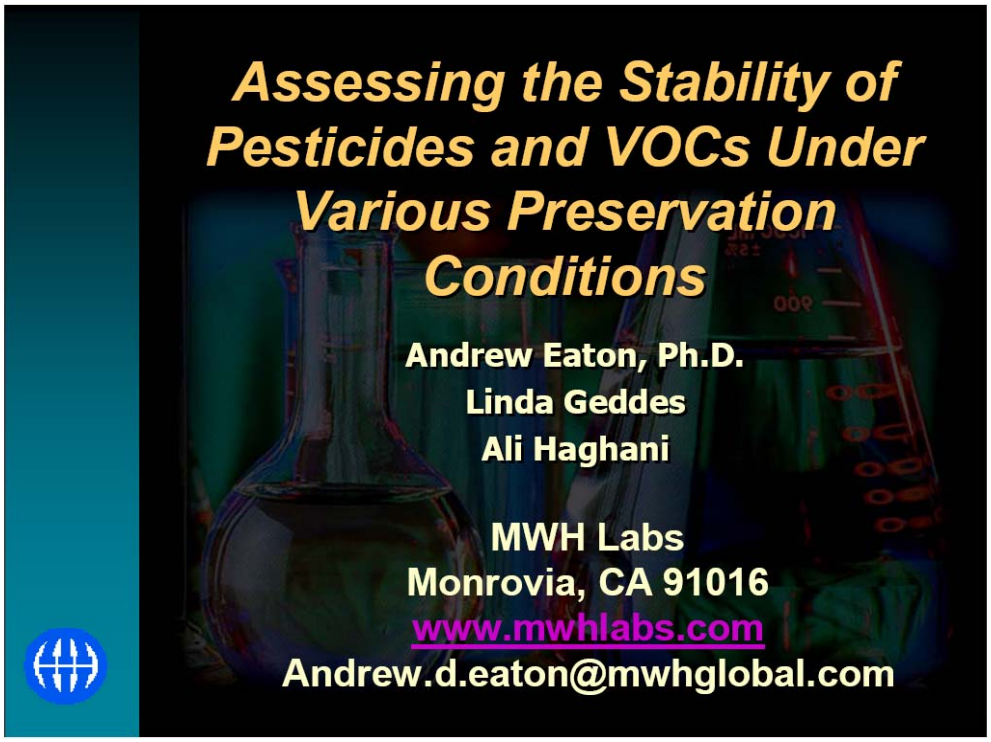
ABSTRACT

EPA Methods such as 508/524.2/525.2 have specified preservation and holding time conditions for compliance monitoring, but there are inconsistencies between the methods in terms of preservation and holding time requirements. In more recent studies, EPA has begun holding samples at 10 degrees for 48 hours, to simulate transport without optimum refrigeration, but many existing drinking water compliance methods have not been evaluated in this same manner. EPA has not evaluated the impact of room temperature storage during transit, which would greatly simplify shipping logistics for samplers. When shipping from outside the USA, there are difficulties maintaining low temperatures or regulatory constraints limiting the use of hazardous preservatives. Additionally there are pesticides that are regulated under WHO that are not even listed in EPA methods and therefore have no data on preservation or holding time. An evaluation of holding time and various preservation options for nearly 200 analytes of interest for several water matrices was conducted as part of a global water quality study. This paper focuses on the VOCs and Pesticides/SOCs tested using methods 524.2, 525.2, 505, and 532. Preservation options listed in some EPA methods were shown to not always be appropriate for many of the target analytes.

Samples representing four distinct matrices, a chlorinated tap water, packaged water, a sample that had been processed through conventional water treatment processes, and high ionic strength raw water were selected for testing. Each sample was split into four aliquots, preserved according to several different possible schemes and aliquots were spiked with a comprehensive mixture of pesticides and VOCs at levels of approximately 2 ppb. Samples were held for varying periods of time under different temperatures and analyzed by methods 524.2, 505, 532, and 525.2.

Most VOCs were stable for up to twenty-eight days without refrigeration or acidification, using only ascorbic acid as a dechlorinating agent pre-added to the bottles. However there were some significant exceptions where refrigeration was critical for stability, whereas acidification was less important. For nearly all target VOCs refrigeration during transit was not necessary if samples were chilled within seven days.

Pesticide and SOC stability was highly dependent on the compound and preservation options selected. Some pesticides were more stable at neutral pH and others were only stable under low pH conditions. Refrigeration had a large positive effect on stability of the pesticides and SOCs in general and stability was demonstrated for many compounds for up to twenty-eight days. To optimize results for pesticide/SOC analysis it is beneficial to analyze two fractions, both dechlorinated, but one acidified and the other maintained at neutral pH because some compounds


Assessing the Stability of Pesticides and VOCs Under Various Preservation Conditions
Andrew Eaton, Ph.D.
Linda Geddes
Ali Haghani
MWH Labs
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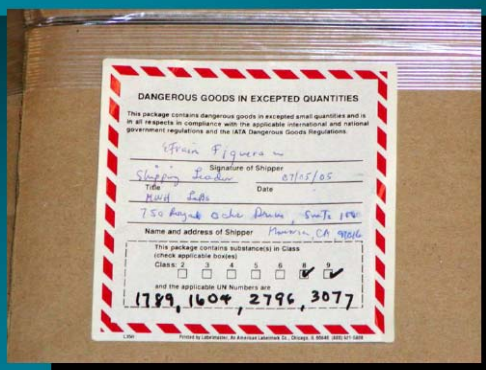
Current Testing Methods for Compliance Require a Lot of Bottles

Current Preservation Techniques Require the Use of Dangerous Goods and International Transport Can be a Challenge



Goals Of The Project – To Understand the Impact of Not Strictly Following EPA Guidelines for Preservation and Storage

- Evaluate impact of extended storage at room temperature on analyte stability
  - e.g. simulate long transit times
- Evaluate impact of eliminating "dangerous goods" from preservation
  - e.g. to facilitate international transport
- Eliminate dual stage preservation
  - e.g. De-chlorination followed by acidification

Evaluating the Impact of Sample Type on Stability

- 4 Matrices, each analyzed in quadruplicate
  - Chlorinated tap water
    - (free chlorine ~1 ppm)
  - Bottled Water sample
  - Treated Water sample
    (further treatment to remove THMs, etc)
  - Ground Water with high TDS
    (unchlorinated)

Evaluated Numerous Storage Conditions

- Analyzed samples under various conditions over time
  - Day 0 – Immediate
  - Day 7 – Held at Room Temperature for 7 D
  - Day 14 – Held at Room Temperature for 14 D
  - Day 28 – Refrigeration for 28 D
- Also evaluated the impact of acidification, where EPA methods require it.
  - Day 7 and Day 14 without acid, at Room temp.
  - Day 7 – without acid, refrigerated

What Compounds Did We Test?

- Nearly 200 different compounds
  - EPA 524.2 volatiles/THMs
  - EPA 525.2 semivolatiles and pesticides
  - EPA 532 Phenylurea Pesticides
  - EPA 505 pesticides
  - EPA 515 and 555 Herbicides
  - Epichlorohydrin, Acrylamide
  - DBPs (551.1, SM6251B)
  - Phenolics, Cyanide
  - Plus a lot more methods/analytes….

How Did We Analyze the Data?

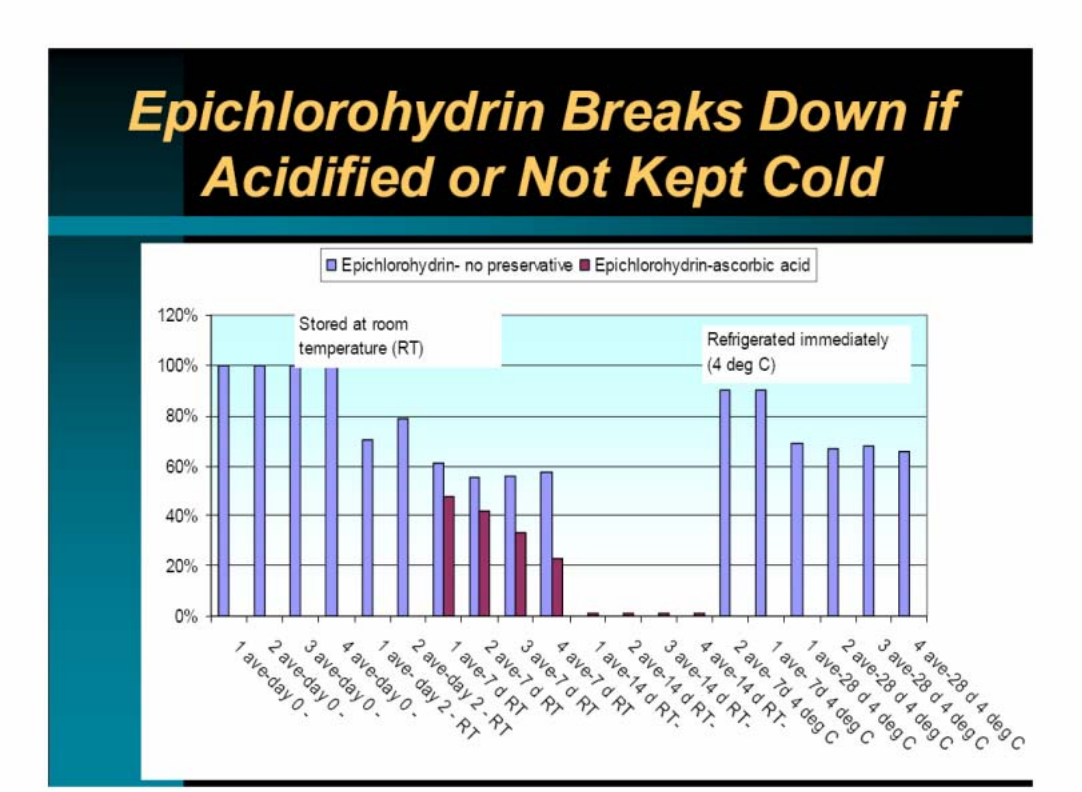
- Compared results to Day 0 and also to the initial spike level
- We set arbitrary limits to determine whether compounds were stable (75-125% recovery over time indicated no significant change)
- We also looked to see if there were any differences as a result of matrix.

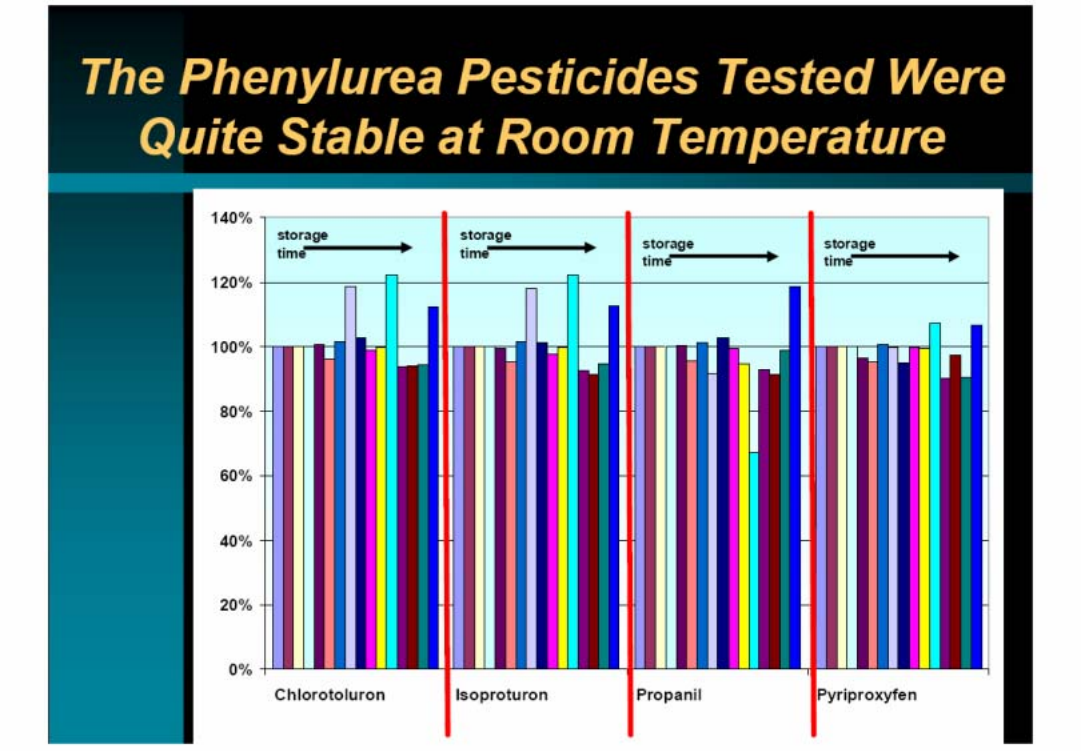
Which Analytes Will We Discuss Today?

- Volatiles (524.2) and Pesticides (525.2)
  - Both currently require "2 step" preservation and entail the use of "dangerous goods" for transport
  - Both have high visibility as concerns
- Phenylurea pesticides and epichlorohydrin
  - Neither currently regulated by EPA, but both regulated by WHO and EU

In Some Cases, Interpretation of Results is Straightforward

- A lot of compounds are quite stable, even under extreme transport conditions
- Differences in behavior among matrices in general are minor compared to the impact of changing preservation.

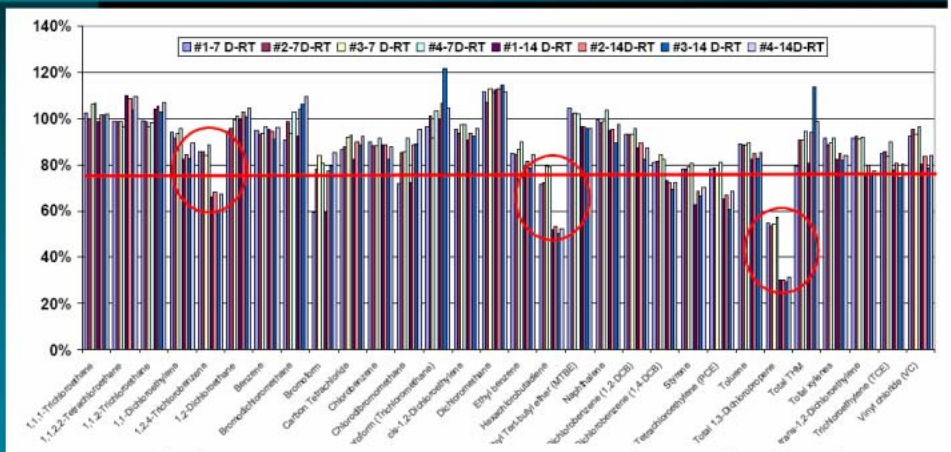

Epichlorohydrin Breaks Down if Acidified or Not Kept Cold
Epichlorohydrin- no preservative
Epichlorohydrin-ascorbic acid
120%
100%
80%
60%
40%
20%
0%
Stored at room temperature (RT)
Refrigerated immediately (4 deg C)
1 ave-day 0 -
2 ave-day 0 -
3 ave-day 0 -
4 ave-day 0 -
1 ave- day 2 - RT
2 ave-day 2 - RT
1 ave-7 d RT
2 ave-7 d RT
3 ave-7 d RT
4 ave-7 d RT
1 ave-14 d RT-
2 ave-14 d RT-
3 ave-14 d RT-
4 ave-14 d RT-
2 ave- 7d 4 deg C
1 ave- 7d 4 deg C
1 ave-28 d 4 deg C
2 ave-28 d 4 deg C
3 ave-28 d 4 deg C
4 ave-28 d 4 deg C


The Phenylurea Pesticides Tested Were Quite Stable at Room Temperature
140%
120%
100%
80%
60%
40%
20%
0%
storage time
storage time
storage time
storage time
Chlorotoluron
Isoproturon
Propanil
Pyriproxyfen

Those Were the Simple Ones, Compared to Pesticides and VOCs

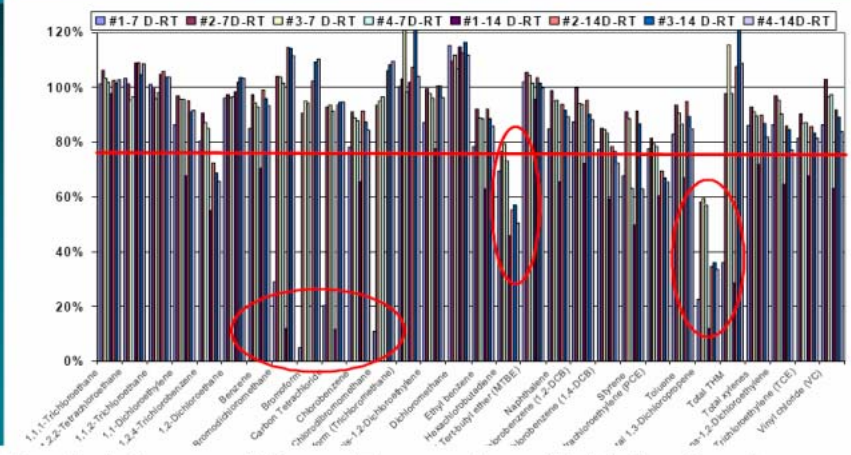
- Volatiles and Chlorinated Pesticides/PAHs are much more challenging in terms of evaluating acceptable preservation schemes
- EPA preservation instructions for these are quite inconsistent for the same compound when analyzed by different methods.

While Many VOCs are Stable at Room Temperature, Several are Not



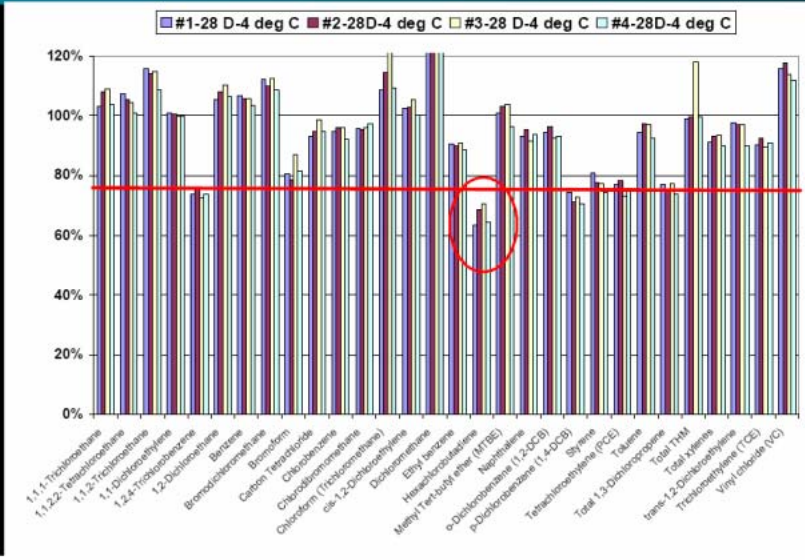
Extended storage at Room Temperature (7-14 days), using ascorbic acid only as a preservative for volatiles, results in significant losses for some groups of compounds.

Acidification Leads to Even More Degradation at Room Temperature



Extended storage at Room Temperature (7-14 days), using ascorbic acid followed by HCl, results in significant losses of analytes.

Refrigeration (with acidification) Stabilizes Most Volatile Target Analytes Up to 28 Days

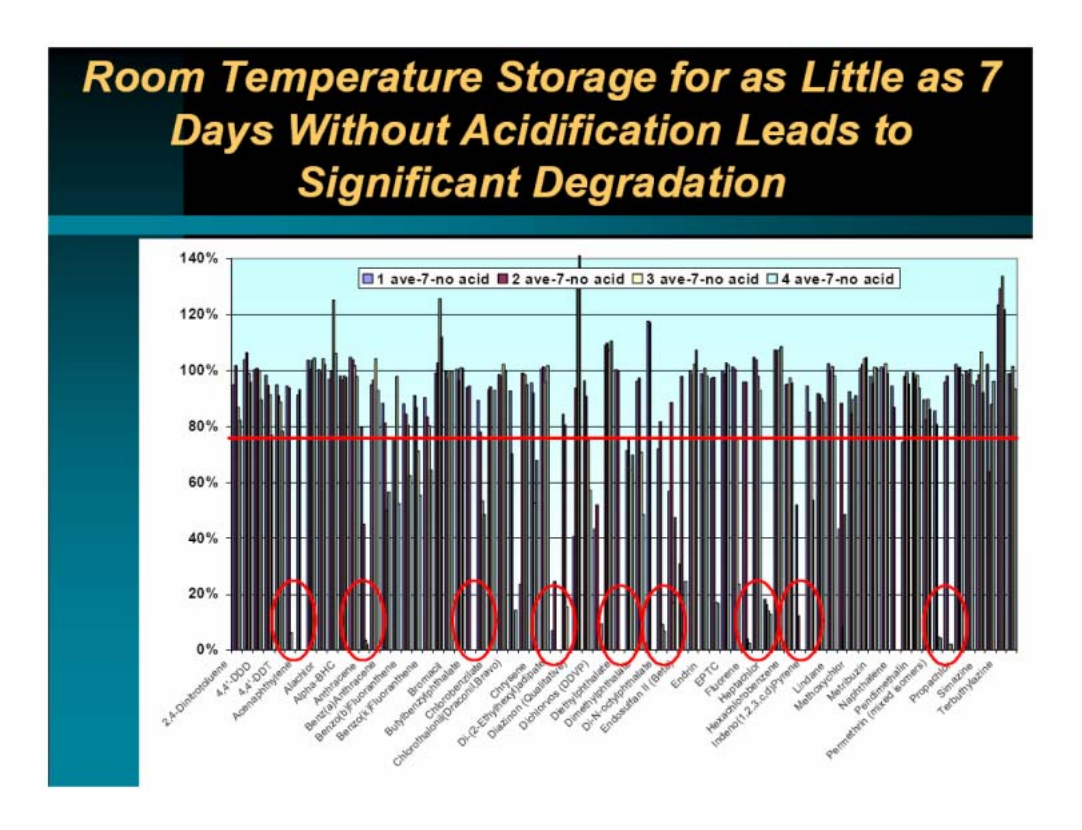


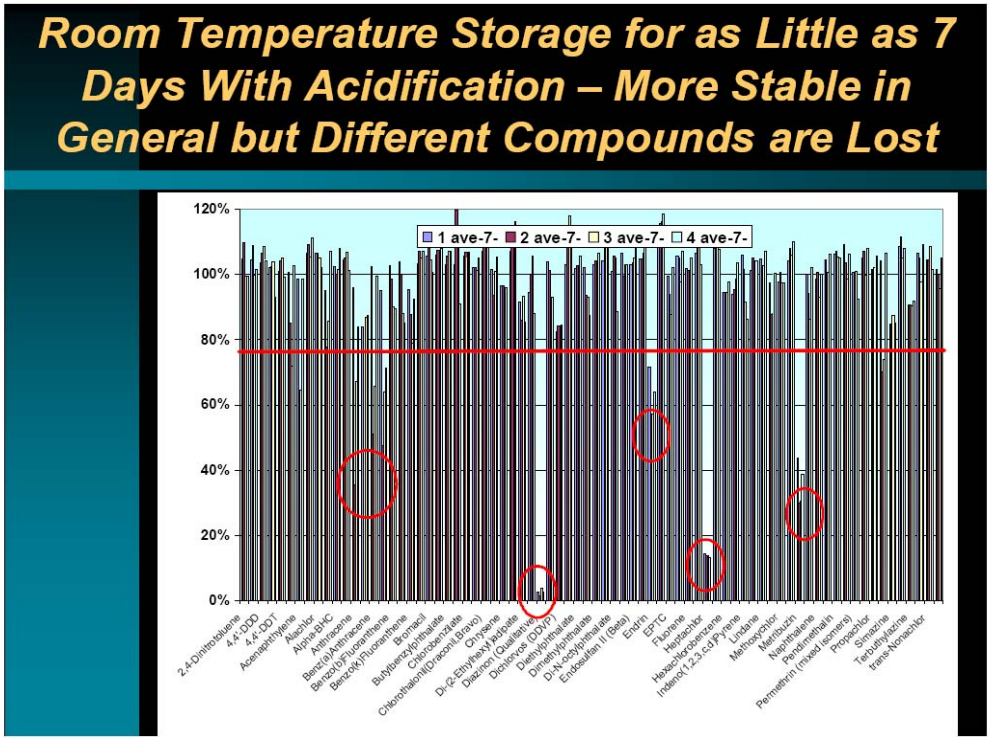
What is the Recommendation for Volatiles for International Transport?

- Keep them cold if at all possible
- Don't worry about acidifying with HCl – use of ascorbic acid as a dechlorinating agent is generally effective (and note work by Shaw and EPA on a new preservation scheme).
- Get them to the lab as soon as possible to avoid high temperatures in transit.
- Most compounds are stable for up to 7 days at room temperature even if you can't hold to these conditions, but some (the Dichloropropenes) are very unstable without refrigeration.

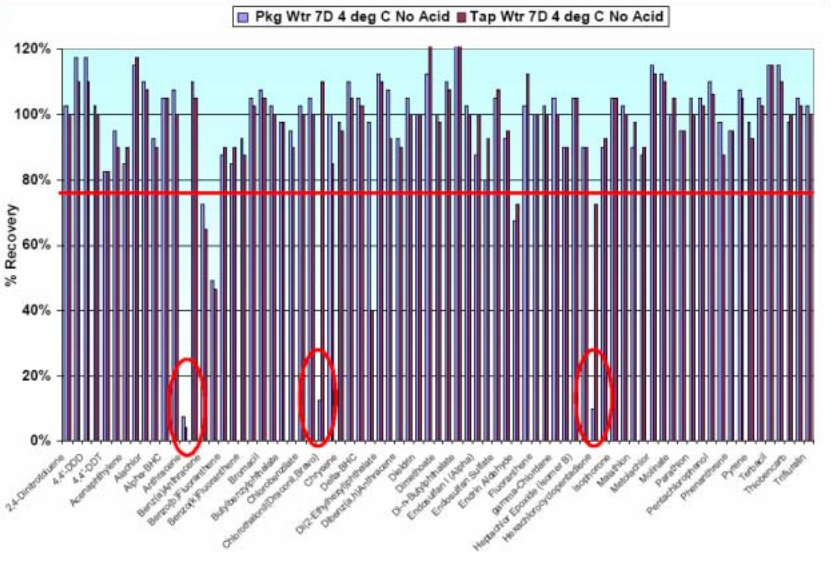
Pesticides/SOCs/PAHs are More Challenging to Stabilize

- More target analytes (>75) which are all in different classes.
  - PAHs
  - Chlorinated Pesticides
  - Phthalates/Adipates
  - Nitrogen and Phosphorus pesticides
- EPA methods for these all have inconsistent preservation schemes
  - (acidify/don't acidify, choice of dechlorinating agent)

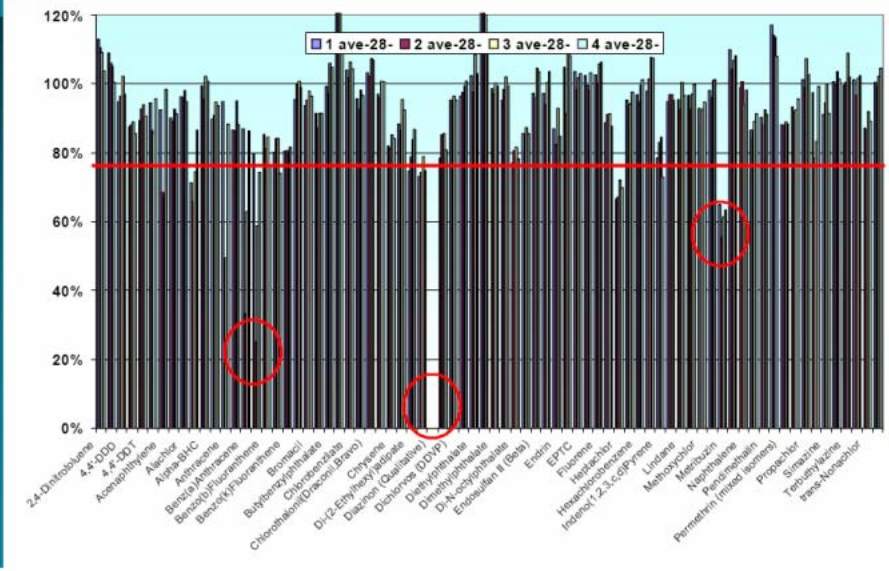

Room Temperature Storage for as Little as 7 Days Without Acidification Leads to Significant Degradation
1 ave-7-no acid
2 ave-7-no acid
3 ave-7-no acid
4 ave-7-no acid
140%
120%
100%
80%
60%
40%
20%
0%


Room Temperature Storage for as Little as 7 Days With Acidification – More Stable in General but Different Compounds are Lost
1 ave-7-
2 ave-7-
3 ave-7-
4 ave-7-
120%
100%
80%
60%
40%
20%
0%

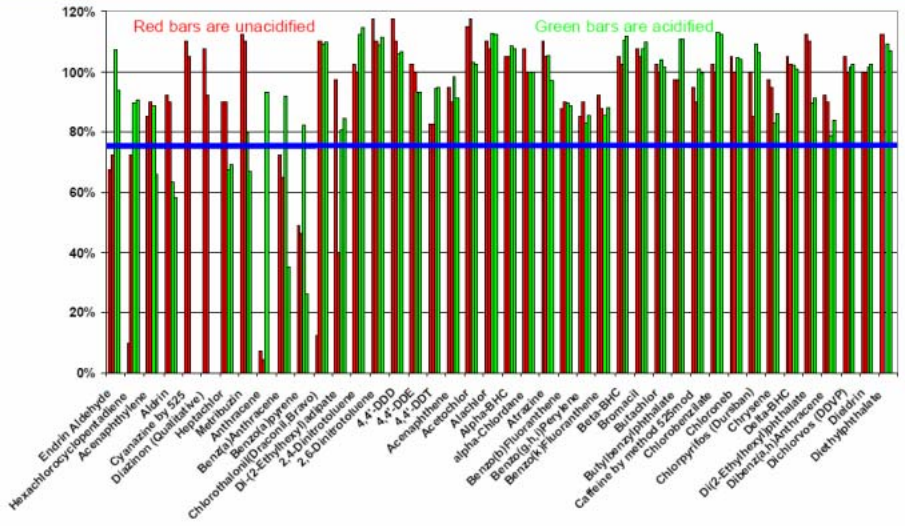
Refrigeration is Much More Critical Than Acidification – 7 Days Chilled Without Acid: a Few Compounds Still Degrade, But Most Are Stable



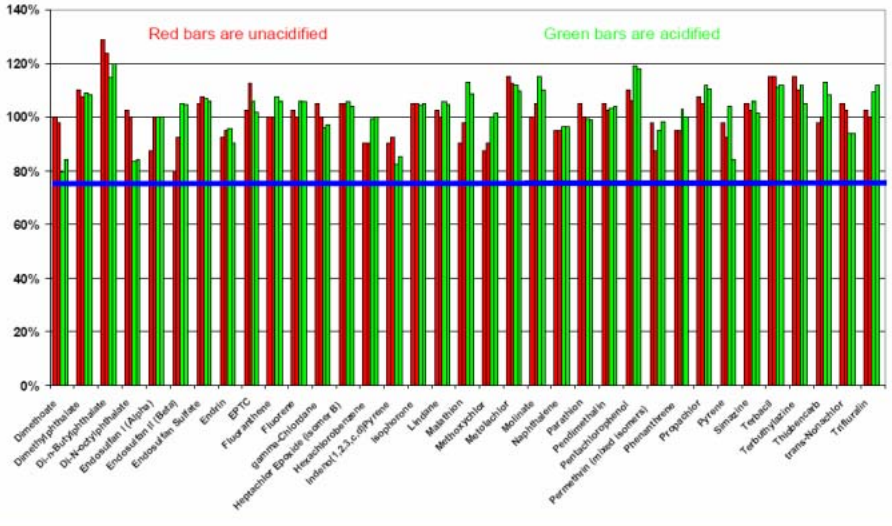
With Refrigeration and Acidification MOST Compounds are Stable for at Least 28 days (but not all)



When Refrigerated, Stability of Some Compounds is Impacted by Acidification (Positive or Negative)



As Long as Samples are Refrigerated, Most Compounds Show No Difference in Stability With or Without Acidification



Impact of Acidification at Room Temperature Storage-Different Compounds Degrade (duh!)

Preservative	Sulfite Only								Sulfite followed by HCl							
Storage Conditions	1 - 7 D RT	2 - 7 D RT	3 - 7 D RT	4 - 7 D RT	1 - 14 D RT	2 - 14 D RT	3 - 14 D RT	4 - 14 D RT	1 - 7 D RT	2 - 7 D RT	3 - 7 D RT	4 - 7 D RT	1 - 14 D RT	2 - 14 D RT	3 - 14 D RT	4 - 14 D RT
4,4'-DDD	100%	101%	100%	89%	104%	105%	103%	52%	103%	107%	109%	104%	101%	102%	107%	101%
4,4'-DDE	98%	94%	91%	77%	98%	99%	85%	37%	102%	103%	104%	93%	95%	96%	96%	88%
4,4'-DDT	95%	91%	89%	78%	73%	99%	84%	35%	101%	104%	105%	99%	94%	96%	96%	93%
Alachlor	100%	99%	104%	102%	102%	100%	106%	108%	106%	107%	105%	102%	100%	99%	102%	100%
Aldrin	97%	100%	125%	106%	106%	104%	130%	65%	95%	78%	86%	107%	102%	86%	98%	105%
alpha-Chlordane	105%	104%	102%	96%	96%	103%	97%	56%	104%	105%	107%	101%	104%	106%	110%	105%
Atrazine	95%	96%	104%	93%	98%	101%	107%	104%	84%	83%	87%	88%	65%	62%	62%	58%
Benzo(a)pyrene	76%	53%	98%	52%	80%	25%	106%	33%	95%	48%	64%	71%	73%	37%	67%	51%
Chlorpyrifos (Dursban)	23%	99%	98%	95%	6%	93%	97%	77%	101%	93%	101%	105%	93%	78%	93%	98%
Di-(2-Ethylhexyl)adipate	7%	24%	0%	0%	8%	106%	0%	0%	92%	86%	93%	85%	70%	66%	71%	70%
Di(2-Ethylhexyl)phthalate	84%	80%	16%	0%	86%	88%	23%	7%	95%	100%	106%	88%	88%	93%	87%	83%
Dieldrin	109%	110%	107%	110%	109%	113%	116%	97%	103%	110%	118%	110%	106%	111%	111%	112%
Dimethoate	71%	76%	65%	70%	73%	92%	70%	85%	102%	93%	93%	87%	49%	65%	74%	74%
Endrin	99%	88%	101%	98%	105%	110%	113%	94%	72%	57%	57%	64%	45%	30%	33%	32%
gamma-Chlordane	105%	104%	98%	93%	100%	108%	97%	52%	107%	109%	109%	103%	102%	104%	103%	102%
Heptachlor	18%	16%	14%	13%	3%	3%	1%	3%	14%	14%	14%	13%	8%	8%	7%	7%
Heptachlor Epoxide (isomer B)	107%	107%	107%	109%	101%	105%	106%	91%	108%	107%	110%	108%	105%	105%	108%	109%
Hexachlorobenzene	95%	95%	97%	96%	94%	94%	94%	86%	94%	93%	95%	98%	93%	91%	91%	94%
Hexachlorocyclopentadiene	52%	12%	0%	0%	35%	3%	0%	0%	94%	95%	99%	103%	80%	83%	79%	89%
Lindane	102%	99%	101%	96%	99%	101%	96%	104%	105%	102%	103%	107%	98%	96%	97%	99%
Methoxychlor	92%	85%	90%	91%	87%	86%	90%	63%	96%	101%	97%	97%	93%	94%	94%	97%
Metolachlor	101%	102%	104%	105%	103%	101%	110%	116%	104%	108%	106%	110%	100%	99%	102%	104%
Molinate	101%	100%	102%	99%	105%	99%	107%	107%	100%	94%	86%	102%	99%	76%	94%	95%
Naphthalene	94%	87%	0%	0%	99%	101%	0%	0%	98%	101%	93%	100%	94%	94%	93%	96%
Pendimethalin	99%	97%	98%	94%	96%	97%	101%	82%	106%	107%	105%	105%	101%	99%	100%	100%
Simazine	96%	98%	107%	92%	105%	104%	112%	107%	85%	84%	87%	85%	65%	61%	61%	56%
Terbuthylazine	123%	129%	134%	122%	102%	106%	114%	112%	91%	91%	90%	92%	91%	91%	89%	85%
trans-Nonachlor	102%	101%	99%	88%	97%	104%	96%	44%	105%	104%	109%	102%	102%	101%	104%	100%
Trifluralin	102%	97%	98%	92%	96%	90%	96%	74%	102%	100%	96%	105%	99%	96%	94%	99%
Cyanazine	97%	90%	101%	98%	96%	97%	106%	106%	26%	15%	19%	24%	12%	9%	11%	12%

Compounds that are unstable under one or more conditions are shown in pink

Observations on Pesticide/SOC Analysis and Degradation

- Under refrigeration, almost all target analytes are stable for 28 days when acidified.
- However without acidification, but with refrigeration, almost all target analytes are stable for at least 7 days.
- Without refrigeration there are significant differences by compound class with acidification vs neutral pH. It is also somewhat matrix dependent.
- For some compounds acidification enhances degradation whereas de-chlorination does not.

A Conservative Approach to Analysis of Pesticides and SOCs

- If samples are not received cold within a few days of sample collection, there should be analysis of BOTH an un-acidified and an acidified aliquot, because sensitivity to degradation at room temperature is different for each pesticide as a function of storage.

What Does This All Mean?

- Much existing data on water quality for pesticides and VOCs may be suspect, depending on the analytical method and the preservation/storage.
- It's critical to educate samplers on proper packaging and transport options, particularly for international shipments.

If we can get fresh fish we can get fresh samples!


Grandpa,
enough
already…

Commercial Laboratory Perspectives on Automated Analytical Data Validation

Brad Mosakowski
Air Toxics, Ltd.

ABSTRACT

Due to the various levels and complexity requested for electronic data deliverables (EDD), the ability of laboratories to deliver analytical data in an electronic format has been subject to variability. At a minimum, the multitude of formats require continued investment and commitment from the individual laboratories. The introduction of Staged Electronic Data Deliverables (SEDD) attempts to correct this problem by offering a universal complete and consistent format data transfer format.

The SEDD format can fulfill a number of objectives: Improved transparency, confidence in the data by supplying the complete set of raw data, and the ability to perform automated data validation. Future oversight and scrutiny on many projects demonstrate the need for a laboratory that can respond to these needs with advances in technology that permit flexibility and performance in providing data of the highest quality.

Presented is a commercial laboratory perspective supporting the format as well as a software tool that validates 100% of the SEDD deliverable. The use of such tools offers improvements in data gathering, response time, and ultimately focusing the user into the areas that need professional judgment.

Air Toxics LTD
Laboratory Services Since 1989

Commercial Laboratory Perspective on Automated Analytical Data Validation

2007 National Environmental Monitoring Conference
August, 2007

Brad Mosakowski
President, Air Toxics Ltd.

Obsolete

- **Main Entry:**
  - **1ob·so·lete**
- **Function:**
  - *adjective*
- **Etymology:**
  - Latin *obsoletus*, from past participle of *obsolescere* to grow old, become disused, perhaps from *ob-* toward + *solēre* to be accustomed
- **1 a:** no longer in use or no longer useful **<an *obsolete* word> b:** of a kind or style no longer current : old-fashioned **<an *obsolete* technology>**

Cause

- Aging analytical data systems
- Limited database structures
  - Laboratory Information Management System (LIMS)
  - Environmental Information Management System (EIMS)
- Proprietary EDDs
- Hardcopy data validation
- Resistance to change

…prevents maximum efficiency and effectiveness

Why Review Data?

- Assure quality and data usability
- Agency requirement
- Assume human error
- Perceived data fraud

Industry Norm

- Considerable resources are used to manually validate laboratory analytical data
- Guidelines vary from program to program
- Unavailable data
- Difficult to share data
- Inconsistency of manual review

Laboratory Norm

- 100s of electronic formats
- No standardization of deliverables
- Industry lacks common approach to data
- Limited client acceptance of new technology
- Dated LIMS

Manual Review Steps

- Data Verification: evaluating the completeness, correctness, consistency, and compliance of a data package
- Data Validation: assessment in accordance with EPA regional or national functional guidelines or project-specific guidelines
  (typically recalculation in addition to verification)
- Data Usability Review: determining whether the quality of the data produced meets the intended use of the data

Is Manual Review Effective?

- With manual resources, how much data is actually reviewed?
- What is the cost?
- What is the time required to determine usability?

"Data validation has been used to detect fraud, but it should be noted that the nature of fraudulent reporting is to make hard copy data packages appear compliant and, therefore, data manipulation in most cases will not be detected by this tool."

1997, California Military Environmental Coordination Committee in association with Chemical Data Quality/Cost Reduction Process Action Team

Staged Electronic Data Deliverable (SEDD)

- Non-proprietary standard (XML)
- Portable
- Long-term storage
- Agency and program neutral

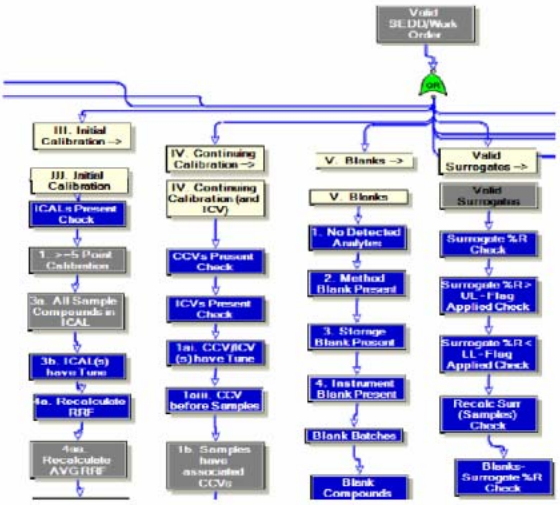
SEDD Benefits

- Complete raw analytical data
- Enables full recalculation
- Standardized data sharing and delivery
- All databases can be populated with SEDD
- Automate data verification/validation

"Use of electronic data deliverables and electronic data validation, wherever possible, will promote objectivity, substantially reduce costs, and facilitate data exchange."

1997, California Military Environmental Coordination Committee in association with Chemical Data Quality/Cost Reduction Process Action Team

Software



Example Rules

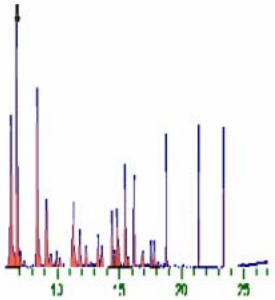
- Manual integrations?
  - Standards?
  - Samples?
  - Check compounds?
- Multiple analysis of standards?
  - Tune checks?
  - Initial calibrations?
  - Ongoing calibration checks?
- Initial calibration after sample analysis?
- Aborted run time?
- Clock-time discrepancy?
- Removal of a detection or negative proof present?

Laboratory Validation

- 100% Automated Data Review
- Bench level
- Errors are corrected before SDG is released
- Eliminates 95% of manual review time
- Integrates within laboratory processes

Does it Work?

- Vapor Intrusion Investigation
  - Inside homes
  - >6000 TO-15 analyses, 800 SDGs
  - Laboratory performed automated validation
  - Client performed full manual Level IV review for all SDGs



Comparison	Manual	Computer
Hours	2400	27
Cost	$70,000	electricity
Result	*No Findings*	*No Findings*

Reality of Manual Review

- It's a feel good thing
  - Expensive
  - Perceived value
  - Minimal benefit

Roadblocks

- "I'll lose my job" – *Data Validator*
- "Labs can't do Stage 3, don't ask" – *EPA*
- "You need human judgment" – *Project Chemist*
- "I like it the way it is" – *Varied*
- "We've tried before, it never worked" – *Consulting Firms*
- "It reduces billable hours" - *Consulting Firms*

Required Change

- Laboratories must innovate
  - Embrace SEDD
- SEDD must become the standard
  - Remove reliance on proprietary EDDs
- Improve efficiency of data flow
  - Upgrade Data Systems
- Focus on usability
  - Automate verification/validation

Future Benefits

- Enhanced confidence in data usability
- Consistent sharing of data
- Continued automation
- Mutual benefit to all parties
- Rapid decision making

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Experiences with Data Usability versus Project Planning

Andrew F. Beliveau
Sleeman Hanley & DiNitto

ABSTRACT

This paper will discuss practical elements of project planning that ultimately yield usable data. Key to project planning is having a well-qualified diverse project team familiar with the site or environmental situation and brings their experience to the table. The various elements that determine what data are needed and for what purpose will be discussed. Included in the paper will be short descriptions of projects that demonstrate how good data usability was achieved as well as descriptions of projects where the data generated had questionable data usability. The five examples will include projects having environmental problems needing solutions such as: volatile organic chemicals (VOCs) in soil, PCBs in air, PCBs in seafood tissue, the analysis of highly wet sediments, and a dioxin in sediments project.

INTRODUCTION

What Is Data Usability?

Assessing data usability allows the project team to determine whether the data is good enough to use in making project decisions. In the practical sense, useable data are the data you where looking for when you started the project. When project personnel investigate a site or environmental situation in any medium, they will have to answer some or all of the following questions:

- Do the data to be collected just need to address immediate concerns or will they be used in future site solutions?
- Do the data have to cover all contaminants of interest?
- Do the data need to meet some set of required detection limits?
- Can we answer all the questions about the site that need answering?

So the project team must decide what type of data are needed and how much data are needed to answer some set of questions about the site or the environmental problem.

The environmental investigators will have to first answer some questions about how the data will be used and define the purpose of the study. Some of the types of data and how the data will be used are as follows:

- Data to determine if the site is contaminated and what are the contaminants of interest (COI)?

- If the COIs are known then, what data are needed to determine the remedial alternatives or remedial design?
- Are the data going to be used to determine if there are human health risks or ecological risks at the site or the area surrounding the site?
- And, are the data going to be used to determine if the remediation was successful?

The investigators may already have answers to some of these questions, but these questions will lead to answering the following questions:

- How much data are needed; how many samples to collect; and how to collect these samples?
- What compounds must be analyzed; how the COIs will be analyzed; and by whom?
- What sensitivity is needed in these analyses to meet the detection limits for all the purposes stated above?
- What PARCCS (precision, accuracy, representativeness, comparability, completeness and sensitivity) criteria are needed to support the project requirements for the specific COIs?

In this author's experience in Superfund work, the most important factor in getting usable data is meeting the detection limit requirements. In some cases this may mean increasing the sample volume, lengthening the collection time for sample compositing, or having to wait for a severe weather condition to collect samples. Attaining low enough detection limits in many cases ultimately controls the project data usability. In some cases the investigators may find that the detection limit they need is unattainable with the current analytical technology. The data users will have to determine if they can live with the higher detection limit that is available. In some cases the very low detection limit can be attained by some method but the cost may be prohibitive.

So How Do We Get Usable Data?

The first thing to be done is to scope out the project with a team of QA chemists, scientists, including data reviewers, hydrologists, geologists, human health and ecological risk assessors, science specialists and engineers, and don't forget to include representatives of the laboratory that will be generating the data. There may be a need to have multiple scoping sessions that will scope out the initial questions and then follow-up sessions to finalize the plans. It's always helpful to document the decisions that the team agree to in meeting notes, so there is no confusion about issues in the future. This team must visit the site and do a "walk over" to observe the field conditions, discuss the issues together and then return to the office to start the planning process. One planning/scoping person must investigate the site history in detail and come to the table with answers about:

- What was manufactured or performed at the site?
- How long was the period of site use for each type of manufacturing type?
- What chemicals were used at the facility(ies)?
- What disposal practices were used to remove waste?
- What is the site topography or where there changes in the site topography over time?

- What are the soil conditions? Is there evidence of soil staining?
- Where are the locations of surface water and groundwater?
- Are there abutting industries that could influence the site conditions?
- What are the prevailing weather conditions?

When the project team does sit down to plan the project they must always keep in mind that the plan they design must meet the data usability goals. These data usability goals (or project objectives) and all the planned technical activities including the sampling design and sampling and analysis procedures are then documented in a QA Project Plan. The UFP-QAPP workbook (include website on slide) includes worksheets that can be used to collect and document necessary project planning information. And the worksheets can then be directly incorporated into the final QAPP. Some of the critical information that is collected on the worksheets includes:

- Where to collect samples (vertically and horizontally)?
- How many samples need to be collected?
- When to sample especially when environmental conditions change seasonally?
- What sample collection method to use Such as using Method 5035 or using Low Flow Ground Water Collection techniques)?
- What analytical methods/SOP to use?
- What detection limits are needed to meet project action limits.
- Will documented standard method achieve the needed results?
- Are special methods and laboratories needed to achieve some of the results and what will those special techniques cost.
- How will data be reviewed / checked before it is assessed for usability?

I recommend that you take a look at the UFP-QAPP guidance and the workbook book at http://www.epa.gov/fedfac/documents/qualityassurance.htm.

Planning doesn't guarantee perfect data especially when unknown conditions, contaminants, etc. are discovered during the process. However in most cases, if enough is known about the site history from previous investigations, the planning process will yield data that are usable for making site decisions. Some of the following examples demonstrate that insufficient planning results in rework, other examples show how good planning with an experienced and diverse project team results in successful projects.

The ABC River Project

The ABC River was previously studied by an EPA Superfund field contractor. The contractor did not adequately plan even though they had been advised by and EPA chemist not to proceed with their plan because it would not yield the data they needed. The contractor's data indicated sediments with percent solids varying from 8% to 12% solids (88-92 percent moisture). The data generated were rejected by the data validators because the actual samples collected and analyzed had only one tenth of the solid dry sample required by the laboratory method used. The laboratory that performed the work could not be instructed to analyze more sample volume or

remove the moisture prior to sample preparation due to contractual reasons. The detection limits for all wet samples for all organics were elevated due to the low % solids and did not meet the risk- based detection limits required by the project scope.

A new project team that included EPA chemists and contractor chemists and sample collection experts was convened. The group went out and collected representative samples of sediment to experiment on removing moisture without changing the integrity of the sample. In the laboratory these pre-samples were tested to determine the best method for sample collection and analysis. Literature studies were also conducted to determine how other investigators had dealt with similar high moisture conditions. The laboratory tests and the literature study provided information to determine what modifications were needed in the sample collection techniques and sample preparation techniques to achieve lower "usable" detection limits needed for risk assessment. The following was developed and later performed in the field:

- Sample collection methods included removal of the surface moisture in the field,
- The laboratory sample preparation methods were modified to include freeze drying or air drying the sediments for some analytes.
- Method 5035 with methanol was used to collect larger quantities of wet sample to meet dry weight sample requirements,
- More sample was collected to meet method sample dry weight requirements,
- The modified methods were documented and agreed upon by the laboratory performing the work.

The resulting data yielded analyte detections of the COIs at much lower detection levels than any previous investigations and the data met the risk assessment requirements for both human health and ecological risk. This successful approach became a model for further studies with fresh water river low solids sediment projects. Not only did the project team generate more usable data, but the team discovered COIs not found in previous investigations. The team discovered better ways to collect samples and prepare and analyze highly wet sediments.

The key to acquiring usable data for this project was the team work, experimentation and literature search and knowing that special sample handling was required for this type of sample.

Courtyard VOC Project

For many years EPA was at odds with a PRP group over the investigation and treatment of halogenated volatile organic chemicals (VOCs) at the Courtyard Site. Significant amounts of VOCs were discharged to the ground when the operation was in business. The PRP group had initially used Method 8240 to analyze VOCs in the contaminated soils. Using that data they designed a soil VOC vacuum extraction system and a water, pump and treat system. After five years of running the systems, they stopped the treatments and decided to test the soils again to determine if they were successful. During the time interval the EPA had set aside Method 8240 because they had developed the new Method 5035 and Method 8260. The PRP collected new samples using Method 5035 and analyzed the samples with Method 8260. The resulting VOC data for the soils was significantly higher than the levels of VOCs before remediation. The reason for this startling discovery was the new methods prevent VOC losses during sample

collection, sample preparation and analysis whereas Method 8240 did not prevent VOC losses during the initial sample collection. The new higher concentration data created heated arguments between the PRP lawyers, the PRP engineering firm and EPA as to whether the new data were valid. After two years, the EPA, the PRP engineering firm, and the state agencies agreed to plan a new project. This project would evaluate the total VOCs in soils and whether the remaining VOCs would leach into groundwater. The collection of samples would be performed using a portable drilling device, and cores in plastic sleeves would be retrieved. The plastic core liners containing the soil would be cut at specific intervals and sampled for total VOCs. Samples would be collected at the ends using the method described in Method 5035A. The innovative part of the project would be the collection of samples from the core liners in a similar manner for TCLP analysis. Instead of using a Zero Headspace Extractor (ZHE) where there can be VOC losses in transferring the soil to the reactor, the team planned to use a larger volume coring device that would be immediately discharged into a larger jar containing the TCLP extraction fluid and immediately sealed with a lid having a septum to remove the analytical sample after extraction. The jar would be shaken over the 24 hours extraction period instead of the ZHE apparatus. This new procedure eliminated VOC losses in sample collection and during customary TCLP extraction. The Zero Headspace Extraction Technique in Method 1311 still allows for the initial VOC losses during sample collection and in sample weighing and transfer to the ZHE apparatus.

This operation was performed in the field and within seconds of the core sleeve being removed from the ground the soil samples were collected and preserved to measure total VOCs and TCLP VOCs. The same operation was performed in borings over the entire site and especially in those known high concentration areas that had not been successfully remediated. The final analytical results showed little correlation between total VOCs and TCLP VOCs. However, the results indicated that the only remediation strategy that would be successful would be excavation of the high concentration soils followed by soil treatment at an off site destruction facility. The collaborative planning approach allowed all vested parties to evaluate the actual VOC contamination at the site in a new light. The new data led to a new and less expensive remedial strategy – one that the EPA and state partners could live with. The cooperative effort generated usable data for both total VOC as well as TCLP VOCs without the question of accuracy surrounding the earlier VOC data. The project also generated data that could be used to propose a new sample collection and extraction procedure to measure TCLP VOCs.

WXYZ River Dioxin in Sediment Project

The WXYZ River project needed to know the depth of 2,3,7,8 TCDD concentrations in sediment to be able to determine how much sediment was contaminated and what the remedial alternative would be to remove the contamination. This project took very careful planning to determine the overall depth of contamination from sediment surface to an unknown horizon where there was no TCDD. To accomplish this task, a diverse project team was assembled that included analytical chemists, geochemists, experienced sample collection personnel, eco risk assessors, geo sediment dating scientists, specialized age dating laboratories, and High Resolution GC/ High Resolution MS dioxin laboratories. All personnel sat down and designed a process where cores of sediment would be collected from a barge platform and then transported to a laboratory. At the laboratory the cores were split in half lengthwise, and then sliced into 2 centimeter slices for

age dating and dioxin analysis. Each core would be documented in photographs as well as evaluated visually and documented from surface (Top) to core refusal (Bottom). Slices from one half were sent to a laboratory for age dating using specific radionuclides. The opposite half slices were frozen for later dioxin analysis. The sample collection and slicing went very well considering the difficulties encountered with the loose sediments found in some cores.

Knowing that the chemical company discharged considerable concentrations of 2,3,7,8 TCDD dioxin waste (2, 3, 7, 8 TCDD only was known to be the primary contaminant of concern) to the river from 1960 to 1970, those slices that indicated that approximate age horizon would eventually be sent for dioxin analysis. In addition, the slice layer just below that horizon was analyzed to confirm that the dioxin was not present in the sediment below. The initial age dating data came back from the laboratory and was evaluated by the geo-sediment dating scientist on the team. After each boring was mapped, the entire team reconvened to determine which slices would be sent for dioxin analysis. Once those samples were analyzed for TCDD the results were compared to the location of the age dated slices in each boring. The new TCDD data were mapped and showed that there was dioxin at the sediment surface. This dioxin was deposited in recent years probably due to erosion of surface soils at the chemical site as well as 2,3,7,8 TCDD down to 1.5 feet below the sediment surface. The 2,3,7,8 TCDD was predominantly in the 1960-1970 horizons. Below that point there was no telltale site specific 2,3,7,8 TCDD in the older sediment. In some shallower cores the TCDD was only at depth of ten inches mainly due to the sediment thickness in that area.

Despite the complexity of this project, it was very successful in terms of not requiring additional sampling or analysis (rework). The small amount of additional time spent planning the project was well worth it. This type of special sample collection, core splitting, slicing and age dating had not been performed successfully before. The second phase of choosing slices for dioxin analysis yielded much more important data that will be used in the future for defining a remedial strategy as well as performing a sediment stability study. Without the diverse experienced team working in concert with each other, the data would not have been as useful to each participant. The project proved that you can get the most usable data when the project team works together and plans the project down to the last detail. The overall data usability for this effort was very high and will allow future WXYZ projects to proceed toward remediation.

Bay Seafood PCB Project

Seafood from a New England Bay contaminated with moderately to high concentrations of PCBs is periodically tested to determine if the seafood is safe to eat. The project planning team made up of the project manager, state representatives, sample collection personnel, EPA PCB chemists, laboratory personnel and several tissue scientists met and scoped out the project from start to finish. The data generated would determine whether the previously inedible seafood still had PCB concentrations that were a health risk. The laboratory that was chosen to do the work was the new entity in the mix of participants. The laboratory professed that they knew how to perform congener specific PCB analysis. The analysis to be performed was to quantitate the 18 NOAA congeners (The most prolific congeners found in aquatic environments) and the 12 World Heath Organization dioxin-like congeners in several types of seafood collected in various

zones in the BAY. (This analysis is actually quantitating 28 congeners as two congeners; BZ 105 and BZ 118 are included on both lists.)

As I was the EPA chemist that would review the Project QAPP and ultimately QC check the PCB congener data, the laboratory sent to me the initial findings. The first look indicated that they had found very high concentrations of BZ #77, a WHO dioxin-like congener in almost all samples. This indicated to me that there was a considerable health risk. I immediately called the laboratory to check on the results. I knew that BZ #77 co-eluted with BZ #110 (a non dioxin-like, non-NOAA congener found in relatively high concentrations in most Aroclors) on a DB-5 capillary column. BZ #110 is not a high risk congener but is usually about 500 to 1000 times higher than BZ#77 in most PCB mixes. I asked the laboratory manager if he used a DB-5 column and had he calibrated and quantitated BZ #110 on his GC system. He had, in fact, used a DB-5 column and had not taken into account the co-elution of BZ #77 and BZ #110. Luckily none of this initial data was given to anyone but me.

This is an example of a project where the utmost planning was performed, but one element failed. However, using the diverse team approach, there was one team member there to recognize the problem and bring it to light. The laboratory was able to go back and reanalyze the samples using a different GC column where there was no co-elution problem and all the congeners planned could be quantitated with certainty. The final data were found to be usable and were subsequently used in determining that the seafood was indeed edible. Unfortunately the lobster omalley was not edible so the lobster meat was found also to be inedible. The right team saved the data usability.

PCB Landfill Air Sampling

This site example is about generating data for risk assessment use without the benefit of a diverse project team composed of data users and data generators. The PRP owner of the landfill has been collecting T04 (Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Ambient Air) quarterly samples for PCB analysis at stations placed around the landfill. The landfill has received high volumes of solid waste, soils and sediment that are contaminated with Aroclor 1260. The air sampling is being performed to show that PCBs are not migrating into the air and ultimately into the surrounding residences. There has been a total PCB upset limit set by the state using risk assessments that must not be exceeded.

The analytical results indicate that Aroclor 1254 and Aroclor 1248 could be present in the air even though Aroclor 1260 was disposed in the landfill. The analytical data package has quantities of Aroclor 1254 flagged with a code flag noting that: "Aroclor 1254 is the best match. The sample exhibits an altered PCB pattern." The Aroclor 1248 results reported are flagged as well indicating an altered PCB pattern as well: "Actual Aroclor 1248 is not present in the sample but is reported to more accurately quantify PCB present in the sample that has undergone environmental alteration."

Closer examination of the GC/ECD chromatograms indicates a plethora of PCB peaks ranging from the lower chlorinated peaks found in Aroclor 1016 and Aroclor1242 up to higher chlorinated peaks found in Aroclor 1254 and Aroclor 1260. There is no pattern indicating a

specific Aroclor PCB pattern. The first rule of PCB Aroclor pattern recognition analysis is that the GC analyst must identify a sample Aroclor pattern, and then choose an Aroclor standard that matches the sample pattern in order to properly quantify the PCB concentration. In this case there is no distinct PCB pattern. The quantitation performed by the laboratory using either of the 1248 or 1254 standards may under estimate the true concentration of PCBs in air surrounding the landfill.

It is quite well known that lower chlorinated PCB congeners having 1, 2, 3 or 4 chlorines can volatilize from soils into the air. Moderately higher chlorinated PCB congeners in air usually indicate that the PCB is attached to very fine particles that are picked up by the wind and end up in the air. The results of the air analyses indicate that both volatile PCBs and PCBs bound to particulates are present in the air collected around the landfill.

The question we must ask is: Is data generated in this manner usable for risk purposes? Obviously if full congener analysis (quantitation of all peaks in a chromatogram) were used, each GC/ECD chromatogram peak would have been evaluated and quantitated and the sum of all the concentrations of all peaks found would yield a much more accurate concentration of PCB in air to compare to the risk based limit.

The owner of the landfill indicates that the Aroclor analysis is much less expensive than full congener analysis and the Aroclor analysis shows that the PCB level is five times lower than the risk based limit. The owner figures that a 5X margin of error is enough to indicate that the PCB levels are under the limit.

Scientifically, I do not believe that the Aroclor data are usable given that no pattern exists and not all of the peaks are evaluated using Aroclor analysis. If a side by side study, congener analysis versus Aroclor analysis, were performed everyone interested in the results would really know what the actual level of PCB is in the air surrounding the landfill. This is an example of a project where planning was performed but not amongst all parties that are interested and the data is scientifically compromised and possibly unusable.

CONCLUSIONS

Assessing the "usefulness" of project data before it is used is essential to good project management and for making defensible site decisions. Data usability is a complex process and includes many steps. If each of those steps is planned well, utilizing the correct personnel on a team, attaining usable data to make project decisions will become a reality. The above examples are only a few that show that knowing all you can about the site, site contamination, or environmental situation are crucial to planning how to get the right data to use in making decisions. One facet that has not been discussed here is the cost to get enough of the right data to answer the site situation questions. In most cases the cost to get the best data all at once is too much. The project team must decide what they can collect with the budget at hand at that time and then collect further data when more money is available. Answering some of the project's questions with the most usable data is better than doing the entire project and getting questionable or not enough data. Some projects will require several iterations or phases to finally get enough usable data to make all the decisions.

Experiences with Data Usability versus Project Planning

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What is Data usability?

Assessing data usability allows the project team to determine whether data are good enough to use in making project decisions.

Project Team Questions

- Does the data to be collected just need to address immediate concerns or will they be used in future site solutions?
- Do the data have to cover all contaminants of interest (COI)?
- Do data need to meet some set of required detection limits?
- Can we answer all the questions about the site that need answering?

Define the use of the data and project purpose

Types of data and how the data will be used:

- Data to determine if the site is contaminated and with what COIs,
- If COIs are known, what data will be needed to determine remedial alternatives or remedial design?
- Are the data going to be used to determine HH or eco risk?
- Are data going to be used to determine if the remediation is successful?

Questions that must be answered by the project team

- How much data are needed, number of samples to collect, and how to collect the samples?
- What COIs to be analyzed, how to analyze, and by whom?
- What sensitivity is needed to meet detection limits?
- What PARCCS criteria are needed to support project requirements for COIs?

The most important factor in Superfund work

- Detection limits control usability

  Are they low enough?

  Project may need to collect more sample, composite longer, or collect samples during severe weather events.
- What to do when standard methods cannot meet required detection limits?
- Cost of meeting detection limits?

How to get usable data?

- Scope the project out fully, Collect a team of QA chemists, scientists, data reviewers, hydrologists, geologists, HH and eco risk assessors, engineers and managers (field and office),
- Take entire team to a site walk-over,
- You may need multiple scoping sessions to develop a Conceptual Site Model (CSM),

How to get usable data (continued)

Investigate site history in depth for the CSM:

- What was manufactured at the site?
- How was the site used over entire time?
- Chemicals used at the site over time?
- Waste disposal practices?
- Site topography?
- Soil conditions and staining?
- Location of surface and groundwater?
- Abutting industry influences on the site?
- Prevailing weather conditions?

Planning sessions must meet data usability goals

Write a QAPP with UFP-QAPP worksheets that detail:

- Where to collect samples,
- How to collect samples,
- When to sample (seasonal issues),
- What sample collection method to use (such as 5035 or low flow water collection)?

Planning sessions must meet project usability goals (continued)

- What analytical methods to use/
- What detection limits are needed to meet project action limits?
- Will general SOPs meet needed results?
- Are special analytical methods needed?
- Are special laboratories needed and at what cost/
- How will the data be reviewed and assessed for usability?

ABC River Sediment Project

- Sediments studied by EPA Superfund contractor, DQO was data for risk assessment,
- Contractor did not take into account low % solids (8%-12%) in samples,
- CLP lab generated data that was rejected by validators due to not meeting dry weight solids requirements for the region,
- Only 10% of the method required solids in the sample meant increased detection limits. not meeting DQOs

New Project Team for the ABC River Project

EPA, a new contractor, chemists, and sample collection experts convened a scoping meeting to plan new ways to get usable data. The results were:

- Collect more sample,
- Sample collection procedure included removal of surface water in the field,
- Modified methods were documented for labs to follow,
- Laboratory would use freeze drying and air drying to increase solids content,
- 5035 with methanol would be used to collect larger quantities of sample for VOC analysis

ABC River Data Usability Results

- COIs detections found at much lower concentrations,
- Data met Risk assessment requirements,
- Discovered COIs not found previously,
- New ways to collect and analyze very wet samples were documented,
- Project was a model for future wet sediment projects,
- Discovered an error in way EPA calculates methanol VOC data. Incorporated in Method 5035A.

WXYZ River Dioxin Sediment Project

Questions to answer:

- How deep in sediments is the site specific 2,3,7,8 TCDD?
- How much sediment must be remediated to get to no risk limits?
- How much TCDD contaminated sediment could erode during high water flow events?

Site History and Project Team

- 2,3,7,8 TCDD was a byproduct of Hexachlorophene manufacture released into the WXYZ River between 1960-1970.
- A project team convened of dioxin analytical chemists, geochemists, sample collection experts, eco and HH risk assessors, geo-sediment dating scientists, and age dating laboratories and HRGC/HRMS laboratories.

What was Planned

The team designed a process for:

- sample collection with clear plastic sleeved cores,
- splitting cores lengthwise,
- Logging and documenting core morphology,
- Collecting 2 cm slices from both halves,
- Age dating slices from one half, freezing corresponding slices from second half,
- Choosing slices dated to 1960-1970 for 2,3,7,8 TCDD analysis.
- Analyzing 1960-1970 slices for 2,3,7,8 TCDD,
- Mapping TCDD in each core and over the entire stretch of river.

Details of the planning

- Sediment cores went down to refusal,
- Cores went to laboratory for splitting,
- Cores split in half and photo documented and logged for differences in strata,
- Cores sliced into 2 cm slices in both halves for age dating and future TCDD analysis,
- Age dating performed and age maps of cores generated for each slice.

Planning for dioxin analysis

Team re-unites to decide on:

- Which slices represented the 1960-1970 sediment horizon, and which slices represent the horizon below to confirm no TCDD contamination,
- Correct slices sent for Dioxin analysis,
- Dioxin analysis is performed on age dated slices.

WXYZ River results

- 2,3,7,8 TCDD found in top 1.5 ft in deep cores,
- 2,3,7,8 TCDD found in top 1 foot of shallow cores,
- Data usable to determine volume of sediment that is contaminated and would need to be removed,
- Data usable to determine how much TCDD could erode during a high flow event,
- A diverse team effort was successful in developing usable data.

PCB Landfill- Ambient air sampling

- Aroclor 1260 disposed into the landfill
- PRP collects air samples using T0-4
- Lab extracts PUF and filter,
- Analyzes extract with Aroclor analysis,
- PRP did not include EPA in scoping the project,
- PRP wants the cheapest possible cost for analysis

Air Data Review

- Data reviewed by and experienced PCB chemist,
- Report indicates Aroclor 1254 “The best match”,
- Data also reported as: “Sample exhibits altered PCB Pattern”,
- Chromatograms indicate a wide range of peaks, but no discernable PCB pattern.

Aroclor Analysis Rules

First rule of Pattern recognition analysis:

- Identify the sample Aroclor Pattern,
- Choose an Aroclor standard that matches the sample PCB pattern,
- If there is no pattern recognition then there can be no quantitation,
- If standard Aroclor peaks are chosen the quantitative data is an approximation.

Air data use and usability

- Data used to evaluate risk to public health,
- Not all PCB peaks were evaluated,
- Data could underestimate total PCB,
- Aroclor data show air concentrations 5X below risk limits,
- Is data usable?
- Maybe! But not without confirmation by congener analysis,
- Project is an example where scientists were not part of the planning process.

Data Usability Conclusions

- Assessing usefulness of project data is essential to making project decisions,
- Determining data usability is a complex process,
- Site condition and contamination history is essential,
- Having the right scoping team is essential

Data usability conclusions (continued)

- Cost of usable data needs to be evaluated,
- Team must collect the best data within the project budget,
- Some projects will require several iterations to get enough usable data to completely answer all questions that need to be answered.

Mission Critical VOA Vials: Evaluation of and Protection from Compound Intrusion/Evacuation

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ABSTRACT

Typical sample collection containers for volatile organic analyses (SW846-8360, 5035/8260, et al) consist of a 40ml glass vial and open top closure with a silicone/Teflon septa. Examination into the undesirable presence of compounds considered "contaminants" led to review of the efficacy of these containers.

This paper presents analytical data from the simulated contamination of VOA vials sealed with various septa types, and comments regarding measures to take when participating in "mission critical" sampling events.

INTRODUCTION

In February 2006, Columbia Analytical Instruments began development of a "5035 Soil Sampling Kit." It had been brought to our attention that some types of 5035 kits had an expiration date listed on them. A review of the methanol vial weights showed the reason for the expiration date. These vials typically consist of a 40ml glass vial with an open top, Teflon/ silicone liner (specified in the US EPA Method 5035, see Reference 1 below). While the methanol did not "degrade", it was determined that the loss in the net weight of the vial exceeded 0.1g. Physical properties of methanol are indicated in Table I below. Loss of this amount could cause significant inaccuracy in the determination of compound concentrations found in the collected soil samples.

Table 1: Physical Properties of Methanol

Compound Name	Boiling Point	Formula Weight	Density	CAS#
Methanol	65C	32.04	0.791	67-56-1

It was determined that a typical Teflon/silicone septa may not be the best choice of closure for this kind of use.

A review of different kinds of materials available from the septa manufacturer was done, and a septa containing additional material was chosen for evaluation. Four 40ml vials were filled with 5.0ml of purge and trap grade methanol and weighed. A time study was begun to determine the rate of loss of methanol from the vials. Several months elapsed and no methanol loss had been

measured. Columbia Analytical Instruments (CAI) selected and placed in use the specially designed septa for its 5035 Soil Sampling Kits.

EXAMINATION INTO UNWANTED COMPOUND INTRUSION

In April of 2007, Columbia Analytical Instruments desired to add a new product line to compliment the SmartBlock COD and Trace Metals block digesters, and COD tubes. An agreement was reached with Daniels Scientific (Greenville, SC) to offer pre-cleaned sample collection containers to the established client base of CAI.

During discussions of various technical issues facing environmental laboratories today, a survey was performed to attempt to quantify some of the problems. It was noted that, unless and even if strict controls were in place, compound intrusion of VOA vials was uncomfortably common. Field blanks and trip blanks were used to indicate transportation contamination. "Refrigerator blanks" and "Laboratory Blanks" were tools used to attempt to identify and quantitate unwanted vial contamination. No type of blank was used to identify compound loss.

It was determined that the special septa devised by CAI for its methanol vials might be useful in evaluating VOA vial performance. Time studies show no *loss* or *gain* in net weight of the methanol vials. In addition, a new type of septa was found which might offer an effective barrier, and evaluation was needed.

Therefore, in May of 2007, a test chamber was devised. The chamber consisted of a 14 gallon Rubbermaid storage tub with a sealed lid. The chamber was loaded with two types of test vials, one with a typical Teflon/silicone liner, and one with CAI's special "low bleed" methanol liner. Both vials were filled with 5.0ml of DI water, and placed into the chamber. Approximately 50ml of unleaded gasoline was placed into a 60ml bottle, and the bottle was placed uncapped into the chamber, along with the test VOA vials. The chamber was placed outside into ambient conditions, and left for four days.

After four days, the vials were removed, and sent to Access Analytical (data generated by Gulf Coast Analytical Laboratories) for "BTEX" analysis (USEPA Method 5035/8260B, see reference 2 below). The results are found in Appendix I- Analytical Report.

RESULTS AND CONCLUSIONS

The summary results are quite remarkable. Distinct compound intrusion of all "BTEX" analytes was noted, some in the hundreds of parts per billion. In the special protected vial, only a trace of "BTEX" compounds was noted. While the test chamber conditions are quite exaggerated, it can be noted that the typical Teflon/silicone layer septa do not offer an effective barrier for these compounds. On occasion, VOC vial users have noted the presence of some compounds, typically toluene, in VOC vials which were certified "clean" when departing the manufacturing facility.

Also, laboratories taking advantage of "Refrigerator Blank" and "Laboratory Blank" information, have noted occasional contamination of samples from the lab or storage area. Since these studies were not controlled, the ability and experience of the analyst was called upon to either invalidate expensive data, or recollect samples, neither of which are desired outcomes. However, these studies do show that effective barriers do exist to protect samples which we call "Mission Critical".

Additional studies are currently underway to evaluate the septa performance when challenged with additional 8260 compounds. Other packaging options are also being challenged to better quantitative and control compound migration.

REFERENCES

1. *Method 5035 Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples* (USEPA 6/20/2003).

2. *Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)* (USEPA 6/20/2003).

APPENDIX I

1. Analytical report: *CAI VOA Vial Integrity Study*, 5/25/2007, Laboratory Report Number 207051507.

Using Data from Diverse Sources –Quality Control Procedures in Database Management

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ABSTRACT

Environmental managers are often interested in using pre-existing (secondary) data to support management decisions. This makes sense from both schedule and financial perspectives. Large environmental databases are often placed on the Internet and are readily available for inspection and downloading. Their use reduces the need for the cost and scheduling of new field sampling. However, the compilation of data held in a variety of sources is often not straightforward and must be conducted systematically with appropriate planning and management oversight. Quality control procedures must be designed and implemented to ensure that the data are standardized and usable. Queries made against a non-standardized database can result in inaccurate data summaries, incorrect conclusions, improper protection of the environment, or legal challenges.

INTRODUCTION

Large environmental databases that are readily available for downloading are often placed on the Internet by federal and state agencies, non-government organizations, and universities. The use of these pre-existing (secondary) data have become essential for establishing fish advisories and total daily maximum loads (TMDL), preparing environmental impact statements (EIS), and conducting long-term monitoring studies because (1) collecting environmental data is expensive, and (2) a lot of data are already being collected for a host of studies and purposes. However, if data are downloaded for use without proper review, systemization, and standardization, then queries made against the resulting database can result in inaccurate data summaries and incorrect conclusions. This paper describes processes and quality control (QC) procedures we have successfully implemented to create large, multi-source databases that enable accurate data analysis and interpretation.

DATABASE DESIGN

Data quality objectives (DQO) are used as the basis for data screening criteria. The structure of the study database can be defined once the study DQOs are established, keeping in mind the end use (e.g., potential decisions, risk process, or criteria development) and end user. Using a database established for another project and purpose may not be appropriate. The database table structure should be adequate to retain the pertinent study fields but not be overly complicated. Include fields to capture the "who, what, where, when, and how" and begin development of a data dictionary. Best practices during the initial planning stage include documenting the DQOs and critical information in a Quality Assurance Project Plan (QAPP); defining key fields so that data from the various tables can be joined; naming and formatting fields consistently across data

tables; and including fields for the source data file name and data source so that data are traceable for future reference.

DATA SCREENING

The screening criteria established in the QAPP are used to judge the adequacy of each potential data set. Obvious initial screening criteria include data matrix, parameters, and temporal/spatial boundaries. For instance, screening criteria could be 1996-2000 Gulf of Mexico Sediment Metals. Less obvious, but critical criteria could include collection and analysis procedures and method detection limits. In order to assess data quality, determine the existence and extent of the quality assurance (QA)/QC program implemented for the study. The study QAPP and existence of validation qualifiers help to assess the QA/QC program.

The initial screen is followed by a detailed screen to confirm that the relevant details are available with sufficient documentation and metadata. Execute an initial data assessment with simple queries to confirm that the database includes all data pertinent to the study database. In addition, review the database structure, data dictionary, and primary keys to understand the database contents and linkages. If key information is missing from a relevant data set, contact the principle investigator for the missing information.

Best practices during the data screening stage include obtaining data from the primary data source rather than from a secondary source to ensure that the data set is current; reviewing the potential source database to ensure that it is the most recent version – more than one version may be available at different locations on a web page; verifying that the data set contains unique data records and identifying overlap or duplicate records; testing linkages across database tables to ensure that they are complete and that no nulls exist in any key fields or fields used to join tables; and avoiding the use of a data set that does not define analytical method detection or reporting limits.

DATA STANDARDIZATION

Data sets that pass the screening process are loaded into a "working" database for preliminary data processing and standardization. The working database uses the same structure as the final study database. Map the database fields from the source database to the working database. Review the structure and contents of the source database fields to correctly link data to the working database and to confirm that the field includes all data within the defined boundaries (e.g., a sediment matrix may be identified as 'S,' 'Sed,' 'Sediment,' or 'Sediment Core'). Review data in the working files for completeness and accuracy and identify updates or modifications required to standardize the data set.

Data standardization is an exacting and time-consuming process but is key to a dependable database. The study QAPP should guide the standardization process by defining critical requirements such as parameters and reporting units. These reporting requirements can be captured in the database. For example, the Code_List table can define parameter class analytical units:

Field_Name	Code	Descr
CLASS	PCB	Polychlorinated Biphenyls reported as nanogram per gram dry weight

Standardization is performed both before and after data are compiled into a centralized database. Examples of the former include filling data gaps, unifying upper case values, and moving text out of number fields. Examples of the latter include standardizing parameter codes, units, and fixing spelling errors. Once the data are loaded, run "select" queries to identify needs for further standardization and updating. Some examples are discussed below.

Select statements for standardization. A series of "Select count(*)" or "Select distinct" statements can identify inconsistencies in the data set which will cause errors when data are queried for analysis:

SQL>select param_code, count(*) from analytical_results group by param_code;	
Param_code	**Count(*)**
Diss Oxygen	17
Diss O	4
Dissolvved Oxygen	1
DISSOLVED OXYGEN	25
Etc.	

SQL> select distinct param_code, units from analytical_results;	
Param_code	**Units**
Nitrate	mg/L
Nitrate	µMol
Total PCBs	ng/g
Total PCBs	µg/g
Benzene	ppm
Benzene	ppb

Parameter codes should be standardized if inconsistencies exist. If parameter results are reported in different units then data conversions or transformations are needed. Parameters should be standardized by parameter class. Analysis methods may be referenced to standardize the analytical data and parameters.

Data gaps. Data gaps in key fields must be filled in order to perform accurate data analysis. For example, collection date gaps can be filled using a conservative default of the 1st study day; non-unique sample IDs can be created by using a combined primary key of sample ID and collection date:

STUDY	SAMPLE_ID	COLLECT_DATE
BEACH_2005	SA01	03-FEB-05
BEACH_2006	SA01	12-APR-06

Update Sample_ID to

SAMPLE_ID
SA01_03FEB05
SA01_12APR06

Duplicate records. Duplicate records within a data set can create bias or interpretive error. Further, duplicate data records may be replicates (field duplicates), QC samples (laboratory replicates), or the result of re-extracted samples, dilutions, or multiple analyses (e.g., naphthalene by EPA methods 8260 and 8270). Determine the reason for the duplicate records by either examining the data or contacting the data source. Flag the duplicate records (e.g., QC codes DU, QADU) so that queries can extract data appropriately for analysis. Update the data record to explain the duplicate (e.g., re-extract field, lab QC code).

Summed parameters. Data for some parameters may be pre-summed (e.g., Total PCB). Investigate the parameters being summed and determine if/how non-detected parameters are included in the totals. Double counting may occur if, for instance, data are reported for PCB congeners, Aroclors, and total PCBs. During analysis, re-sum the individual results for the desired totals if the summed parameters cannot be defined. The method for summing parameters may be defined by the intended use (e.g., risk process or criteria development).

Laboratory spreadsheets. Ideally, an electronic data deliverable (EDD) format is provided to analytical laboratories at the beginning of the study. If the EDD cannot be dictated to the laboratory then data spreadsheets may not contain required analytical details (e.g., analytical method and date) or, even less likely, field details (collection dates, sampling depths, coordinates). Review the data carefully to determine if missing data are reported elsewhere in the spreadsheet and confirm any assumptions with the data provider. For example, Sample IDs may contain depth data (SA01-2.5) that can be used to populate the Depth field.

SAMPLE_ID	DEPTH
SA01-2.5	

Update Depth to

DEPTH
2.5

Lack of adequate version control may lead to receipt of an outdated spreadsheet and the need for rework by the database professional. Confirm the spreadsheet date/time stamp with the supplier.

Data Qualifiers and Sample Codes. Data qualifiers contain valuable information about the data, particularly data quality, but the definitions are often organization-specific. Qualifier definitions should be obtained and stored in the code list table; multiple definitions for the same qualifier can be separated by semicolons in the description.

Field_Name	Code	Descr
LAB_QUAL	B	For Study X, B = analyte detected in blank; For Study Y, B = analyte in blank at 5X detection Limit.

Ideally, the data set will distinguish between field samples (SA) and field or laboratory QC samples (EB, DU, MS). However, if no sample code field exists, the sample collection and analysis table dates and units should be carefully examined to identify QC samples that may be included in the dataset. These should be confirmed with the person responsible for the data.

Hand-entered data. Valuable data may be identified in reports or journal articles. Every attempt should be made to obtain the data electronically to avoid transcription errors. If data must be

hand-entered into the database from a report, the entries should undergo a 100% transcription check to ensure accuracy.

Best practices during this phase include acquiring metadata associated with a data set and saving it in the database; loading data into working tables until initial standardization is complete; and maintaining the traceability of any calculations or conversions by keeping the original values in the working file and adding fields to the study database to store new calculated data. For example, the data table fields could include original_result, calc_result, and original_param, standardized_param.

DATA LOAD AND VERIFICATION

After the working file is reviewed and the initial updates are performed, load the data into a centralized relational database (e.g., Oracle, MS Access, etc). Map the database fields from the working database to the final study database. Use scripts to ensure documentation and traceability. Insert scripts can be reused for future data sets. Complete the metadata tables. Review the uploaded data for completeness and accuracy. Confirm that (1) the correct number of records was loaded by comparing the number of records in the source file to the number of records loaded; (2) the database fields were mapped accurately during the upload; and (3) the data fields are not truncated. Check a few records for accuracy by comparing database records to the source data.

QUALITY CONTROL CHECKS

After the data are loaded into the centralized database, a final QC review will ensure data completeness and accuracy. Review a few random values to ensure loading accuracy. Map coordinates to ensure the sampling locations appear reasonable. A final QC check script should be used to review the data and confirm that all data were successfully uploaded. The QC Check script should include:

- Record counts, to verify completeness of the download
- Completeness checks, to ensure all data are loaded
- Filename review, to ensure data traceability to the source file
- Sample IDs, to ensure that they are unique
- Coded fields, to ensure standardized data sets
- Duplicate check, to ensure data records are unique
- Select Distinct on most database fields, to ensure standardization
- Select Counts(*) on appropriate database fields, to determine if nulls exist
- Misc. format checks, to ensure quality data (spaces in 'Null' fields, O vs. 0, etc.)
- Right and Left Trim SQL statements (to remove leading or trailing spaces)
- Widow and orphan checks, to identify any samples without data or data without samples, etc.
- Zeros check, to determine whether a zero value is a true zero, a rounded value, or a non-detect

- Qualifiers vs Code List, to ensure that all qualifiers are included in the code table with definitions
- Qualifier use checks, to ensure values are qualified appropriately
- Reasonableness checks, to review data ranges and minimum and maximum values for reasonableness

The final QC check may identify additional data gaps that can be filled using a script that provides documentation for the modified data set. Contact the person responsible for the data or review the metadata to obtain any missing data. The final QC checks listed above will identify common errors and inconsistencies across multiple data sets. Examples include the following:

- Species identified as common name or group rather than scientific name
- Measurements without units or units without a measurement
- Coded fields identified without codes or codes not included in the code list table
- Inaccurate dates e.g., 1901 or analysis dates prior to collection data
- Obviously incorrect coordinates, units based on the result, or exceedingly high or low values.

If errors are identified, determine if errors are global or isolated. If an error is global, review the entire database for the error and communicate the error to the data source and study team because it may affect other data sets.

DATABASE QUERIES AND REPORTS

Once the database is verified as accurate and complete, report tables or figures are often generated using database queries and data exports. Database queries must be constructed with full understanding of the database structure and content to ensure that the right data are extracted. Particularly in large databases, it is difficult to detect missing data if the query is inaccurate. The data boundaries for a given report table must be clearly defined and documented so that queries select the data of interest. Best practices include confirming that all key fields are used in the query design; all data boundary fields are included; and that the correct number of records is selected. Perform a final check of the selected data by comparing a selected set of records vs. the database to ensure accuracy of the data represented in the report table.

CASE STUDIES

Two case studies will be used to demonstrate a systematic, high-quality approach to data management and the importance of performing these quality control procedures. These cases will be contrasted with examples of erroneous conclusions drawn from a database developed without rigorous quality control procedures.

Case Study 1: The Northern Gulf Nutrient Database

In February 2003, Battelle was tasked by the EPA Gulf of Mexico Program Office (GMP) to identify and compile existing water quality data from the northern Gulf region to support the

development of nutrient criteria in Alabama, Mississippi, and Louisiana. Battelle identified data sources, solicited and collected data, and compiled them into what is called the Northern Gulf Nutrient database. A database was constructed using Oracle's database management system software. The central database was a simple design, containing a few fundamental and ancillary tables. Data sets were reformatted and processed in a variety of environments including Excel, Access, and Oracle. A specialized application was used to rearrange data provided in cross-tabular spreadsheets. Over the duration of this project, 36 datasets, representing 30 studies, were loaded into the database. The loaded data comprise over 2.1 million results from 2,441 stations over the temporal span of 1905 to 2003.

Data from disparate, though well-constructed sources required standardization. At the simplest level, temperature was reported in units of both °F and in °C. Other standardizations were much more difficult to achieve. Data standardization required domain knowledge (an understanding of nutrient chemistry methods), and additional facts about sample collection, storage, preparation, or analysis. The data standardization process combined the various data sets into a unified database resulted in the reduction of the number of distinct parameter names from 678 to 58.

During the data loading process, data gaps were evaluated and filled, if possible, using metadata, conversations with the data source, or best professional judgment. In several instances, an input field name contained information that belonged in several fields. For example, a parameter description field would contain the field name and the analysis method, the fraction (total, dissolved, filtered unfiltered), the matrix (water, sediment), and the units. Method, fraction, matrix, and units were key fields in the database schema, so this information was parsed and entered into the appropriate field to fill in the gaps. To ensure traceability of the data, any parameter names, units, or values that were changed in the standardization process were not changed in place (i.e., both the original and standardized values are maintained in the database). Instead, database tables included appropriate fields for the standardized data.

All data qualifiers and flags provided with the original data sets were loaded into the database and taken into consideration during reasonableness checking. The database included a flag called "Reportable_YN" which indicated a use warning to the end-users for the following reasons: (1) the data are duplicates, (2) there are unreasonable negative values, or (3) the data in the original data sets are flagged with fatal qualifiers.

Case Study 2: Massachusetts Water Resources Authority

The Massachusetts Water Resources Authority (MWRA) is responsible for the operation and monitoring of wastewater treatment plant effluent that is regulated under a National Pollutant Discharge Elimination System (NPDES) permit program. Since 1990, water column, benthos, fish and shellfish, and effluent characteristics have been monitored and stored in a centralized Oracle database. The procedures used to manage these data are an example of using technology to maximize efficiency and meet the demand for near-real time data reporting.

Field sample collection and *in situ* data are collected electronically during field operations and uploaded to the Oracle database. A data management professional populates a separate MS Access database for each laboratory data deliverable. The MS Access database is part of a

customized data loading application and contains the Sample IDs and analysis protocols extracted from the Oracle database. The loading application is transferred to the appropriate laboratory. Laboratory personnel open the loading application and enter the results and other supporting information, such as qualifiers, using a data entry form that already contains the Sample IDs and analyte list for their data submittal. All entries are constrained by the database rules. Quality control checks built into the process allow error detection and resolution by the laboratory. Primary keys are in place so duplication cannot occur. When data entry is complete, the loading application is returned to Battelle where a data transfer form is used to upload the data. Data are truly loaded into the central database with the click of a button. Data values are automatically checked for threshold violations during loading. This approach has cut data delivery times by more than half while reducing costs.

Consequences of Poor Data Management

Consequences for poor data management range from frustration and wasted time and money to reporting inaccurate data and drawing incorrect conclusions. Three simple examples suffice:

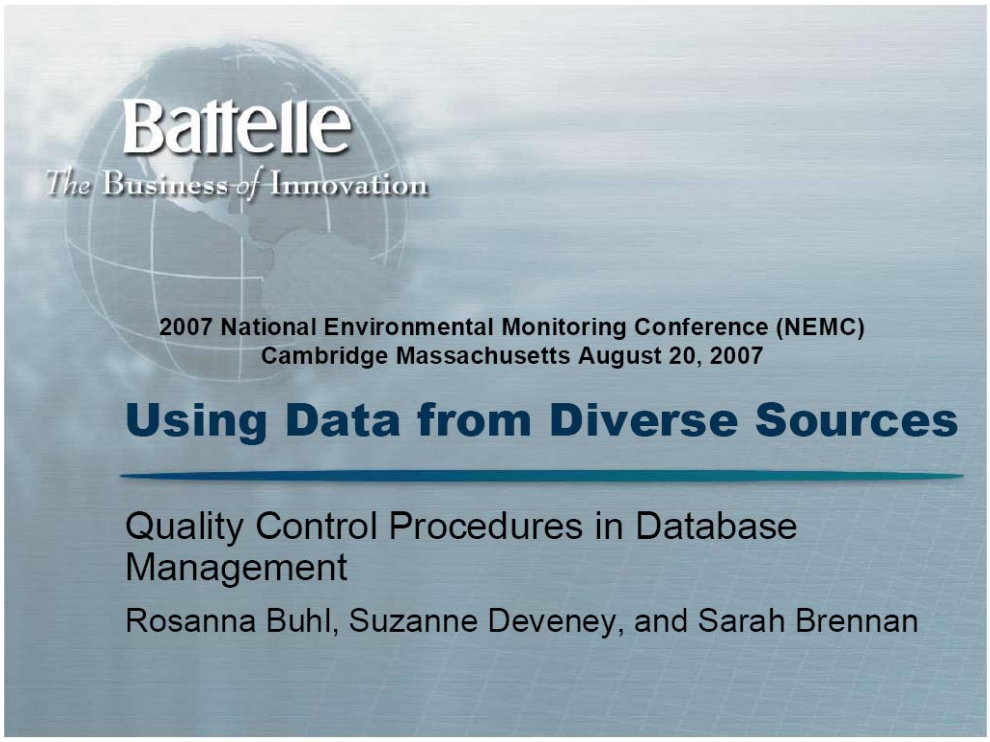
- For a current Superfund site, an existing project database was inherited from the client. Metals sample data were not properly classified as dissolved and total results. Data appeared as duplicate results and the distinction was only obvious in the sample ID.

- In a current Superfund site, a project database managed by the prime contractor was updated to standardize trace metals units, resulting in data errors. All units were assumed to be ppb without regard to the analytical method. The result was that AVS/SEM metals concentrations were reported 10^3 times the actual values.

- For a current Superfund site, an existing project database was inherited from the client. Parameters identified as LMW (Low Molecular Weight) PAH and HMW (High Molecular Weight) PAH were reported in the database but the LMW PAH and HMW PAH values did not agree with the Total PAH values. It was determined that the parameter lists used to calculate LMW and HMW values were not consistent between samples and studies in the data set.

CONCLUSION

Using pre-existing (secondary) data to support management decisions makes sense from both schedule and financial perspectives. The compilation of data held in large environmental databases from a variety of sources must be conducted systematically with appropriate planning and management oversight. Queries made against a non-standardized database can result in inaccurate data summaries, incorrect conclusions, improper protection of the environment, or legal challenges. Quality control procedures incorporated into the data acquisition, loading, and query phases of a project ensure that the data are standardized and usable. QC check scripts, data standardization, database codes, and duplicate record elimination are key examples of data management best practices and ensure successful merging of data sets from multiple sources into a useable centralized project database.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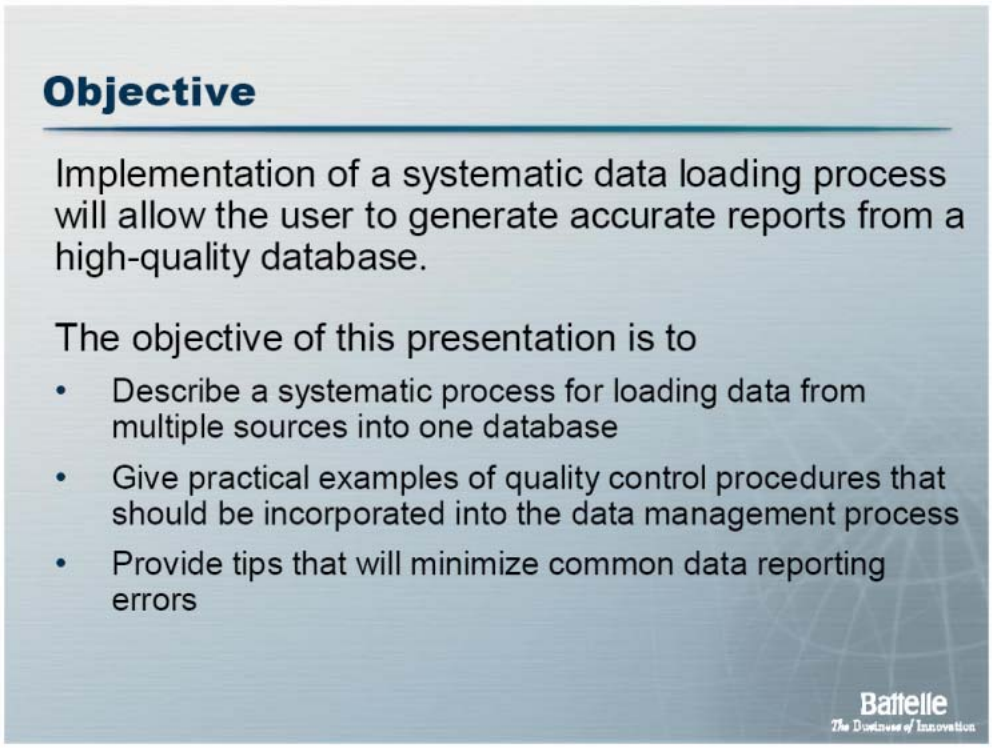
2007 National Environmental Monitoring Conference (NEMC)
Cambridge Massachusetts August 20, 2007
Using Data from Diverse Sources
Quality Control Procedures in Database Management
Rosanna Buhl, Suzanne Deveney, and Sarah Brennan


Objective
Implementation of a systematic data loading process will allow the user to generate accurate reports from a high-quality database.
The objective of this presentation is to
• Describe a systematic process for loading data from multiple sources into one database
• Give practical examples of quality control procedures that should be incorporated into the data management process
• Provide tips that will minimize common data reporting errors
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Overview

1. Database Design
2. Data Screening
3. Data Standardization
4. Data Load and Verification
5. Quality Control Checks
6. Database Queries and Reports
7. Case Studies

   Consequences of Database Errors

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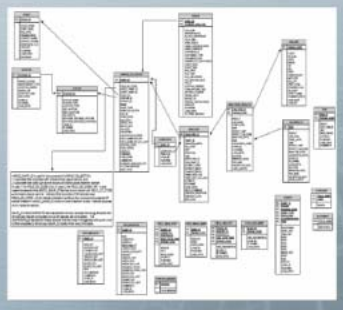
1. Database design

- Start with the end use
- Use DQOs to define required information
- Design useful relational tables
- Create database constraints
- Create formats and rules for the data



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2. Data Screening

- Define information that is critical to data use (e.g., collection date, sampling locations, methods)
- Define data quality limits or requirements
- Confirm that the database includes all pertinent data
- Review database structure, data dictionary, and primary keys
- Review metadata
- Contact data generators for missing data

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3. Data Standardization

- Use separate database schemas to store data at various stages of the project
- Expect several iterations of changes
- Maintain traceable documentation
- Identify inconsistencies that could result in errors when analyzing compiled data from multiple laboratories

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Data Standardization: Hints

- Use scripts to make database changes
- Use loading forms to standardize database procedures
- Use database codes to simplify storage and retrieval
- Review results, methods, detection limits, units, and qualifiers to ensure data appear comparable (from multiple laboratories)
- Never replace original results or units; create new columns to store modifications

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Data Standardization: Reporting Units

- Sample data and detection limits must be same units; avoid use of ppm and ppb.
- Text in database is case sensitive: NG/G, Ng/G, ng/g will be treated as separate units
- Units should be standardized by parameter class

```
SQL> select param_code, units, count(*) from
analytical_results group by param_code, units;

Param_code      units     count(*)
--------------- --------  -----------
Total PCBs      ng/g          118
Total PCBs      ug/g          117
```

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Data Standardization: Fix Units

- QAPP guides standardization process by defining critical requirements such as parameters and reporting units
- Data are standardized using the QAPP requirements
- Code_List table defines reporting requirements

Field_Name	Code	Descr
CLASS	PCB	Polychlorinated Biphenyls reported as nanogram per gram dry weight

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Data Standardization: Find Inconsistencies

- Use select queries to identify non-standard data (i.e., param codes, matrices, units)

```
SQL>
select param_code, count(*) from analytical_results
group by param_code;

PARAM_CODE                Count(*)
------------------------- ----------
Diss Oxygen               17
Diss O                    4
Dissolvved Oxygen         1
DISSOLVED OXYGEN          25
```

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Data Standardization: Fix Inconsistencies

- Use update queries to standardize a parameter

```
SQL>
update analytical_results set param_code = 'DO'
where param_code =    'Diss Oxygen';
17 records updated
SQL>
update analytical_results set param_code = 'DO'
where param_code = 'Diss O';
4 records updates
Etc.
```

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Data Standardization: Non-Unique Data

- Key database fields must be unique and not null
- Use select statement to identify non-unique fields
  - E.g., Sample ids below are not unique

```
SQL>
select sample_id, collection_date, count(*)
from sample_collection
group by sample_id, collection_date;

SAMPLE_ID  COLLECTION_DATE   count(*)
---------------------------------------------
SA01       03-FEB-05          1
SA01       04-FEB-05          1
SA01       12-APR-06          1
```

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Data Standardization: Fix Unique Records

- Create unique records by concatenating information that will make the record unique

```
SQL>
update sample_collection
set sample_id = 'SA01-03FEB05'
where sample_id = 'SA01' and collect_date = '03-FEB-05';
1 record updated
SAMPLE_ID        COLLECT_DATE       Count(*)
---------------- ------------------ ----------
SA01-03FEB05     03-FEB-05                   1
```

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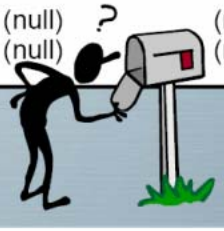
Data Standardization: Find Data Gaps

- Missing data may exist as part of another field
  - E.g., Collection dates, sampling depths, coordinates may be included as part of the sample ID, meta data, or comments:

```
SQL>
select sample_id, depth, depth_unit, count(*) from sample_collection
 group by sample_id, depth, depth unit;
SAMPLE_ID        DEPTH        DEPTH_UNIT     Count(*)
---------------- ------------ -------------- ------------
SA01-2.5         (null)       (null)                  1
SA01-2.8         (null)       (null)                  1
```



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Data Standardization: Fix Data Gaps

- Use update scripts to fill in data gaps when information is available as part of data from another column

```
SQL>
update sample_collection set depth to 2.5, depth_unit = 'm'
where sample_id = SA01-2.5;
1 record updated
```

SAMPLE_ID	DEPTH	DEPTH_UNIT	Count(*)
SA01-2.5	2.5	m	1

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Data Standardization: Duplicates or Redundant Data?

- Duplicate data records may not be true duplicates
- Simple dup check select statements help identify potential duplicates
  - E.g., Dup check shows 2 records exist per sample_id, lab_sample_id, analysis_meth:

```
SQL> select sample_id, lab_sample_id, analysis_meth, count(*) from
analysis group by sample_id, lab_sample_id, analysis_meth having
count(*) >1;
```

sample_id	lab_sample_id	analysis_meth	count(*)
SA01	B123	EPA8086	2
SA02	B124	EPA8086	2

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Data Standardization: Fix Duplicates or Redundant Data

- Use collection records, analysis dates, laboratory codes, etc. to determine if duplicate samples are actually re-extracts, dilutions, field duplicates or analytical replicates
  - E.g., If sample records are actually replicates, add rep to primary key in analysis and analytical_results

SQL> select sample_id, rep, lab_sample_id, analysis_meth, count(*) from analysis group by sample_id, rep, lab_sample_id, analysis_meth;

sample_id	rep	lab_sample_id	analysis_meth	count(*)
SA01	1	B123	EPA8086	1
SA01	2	B123	EPA8086	1
SA02	1	B124	EPA8086	1
SA02	2	B124	EPA8086	1

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Data Standardization: Null Records?

- If a column has no value, then the column is **null**
- Oracle will ignore nulls unless the “is null” or “is not null” is used
- Nulls appear in columns not restricted by NOT NULL or PRIMARY KEY constraints
- For numeric data, a zero is not equivalent to a null

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Data Standardization: Null Usage

- Use a null when the actual value is not known
- Establish default values rather than nulls in character (text) data type columns
- Use a 'UNK' code rather than a null in character data type columns (if value is unknown)
- Use the "nvl" function to replace null values with a number when selecting data using SQL scripts

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Data Standardization: Qualifiers

- Data qualifiers contain valuable data quality information
- Definitions are often organization-specific
- Qualifier definitions should be obtained and stored in the Code_List table

Field_Name	Code	Descr
LAB_QUAL	B	For Study X, B = analyte detected in blank; For Study Y, B = analyte in blank at 5X detection Limit; etc.

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4. Data Load and Verification

- Standardize and document loading procedures
- Use upload scripts (can be reused)
- Develop a verification checklist
  - Confirm number of records loaded
  - Confirm accurate mapping from source database
  - Check for truncated data
  - Check for data completeness
  - Check a few random values for loading accuracy
  - Capture source filename in database

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5. Quality Control Checks

- Develop QC check scripts
- Continually update as new issues are identified
- QC check scripts should be run on individual data sets and on the entire database
- Include all previous standardization and loading checks
- QC Check script should include:
  - Record counts, to verify completeness of the download
  - Completeness checks, to ensure all data are loaded
  - Filename review, to ensure data traceability to the source file
  - Sample IDs, to ensure that they are unique
  - Coded fields, to ensure standardized data sets
  - Duplicate check, to ensure data records are unique

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5. Quality Control Checks – cont...

- Select Distinct on most database fields, to ensure standardization
- Select Counts(*) on appropriate database fields, to determine if nulls exist
- Misc. format checks, to ensure quality data (spaces in 'Null' fields, O vs. 0, etc.)
- Right and Left Trim SQL statements (to remove leading or trailing spaces)
- Widow and orphan checks, to identify any samples without data or data without samples, etc.
- Zeros check, to determine whether a zero value is a true zero, a rounded value, or a non-detect
- Qualifiers vs Code List, to ensure that all qualifiers are included in the code table with definitions
- Qualifier use checks, to ensure values are qualified appropriately
- Reasonableness checks, to review data ranges and minimum and maximum values for reasonableness

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Quality Control Checks – Example Script

```
SELECT 'Script run on: ', to_char(sysdate,'DD-Mon-YYYY hh24:mi'),
      'USER is: ', USER FROM dual, user_users;
SET HEADING ON
SET ECHO ON
rem **REM Enter Login ID in 'Quotes'
accept login prompt 'Enter the LOGIN_ID: ';
/*****************************/
-- look at Analysis
desc analysis;
select count(*) ANALYSIS_records
from analysis where login_id in (&login);
  --select distincts
select distinct SAMPLE_ID, LAB_SAMPLE_ID from analysis
where login_id in (&login);
select distinct ANALYSIS_METH, INSTR_CODE from analysis
where login_id in (&login);
select distinct LAB, BATCH_ID, count (*) from analysis
where login_id in (&login)
group by LAB, BATCH_ID;
-- For QADU, MSD, and LCSD (lab replicate) samples the REP will be reported as '2'.
-- For QATP samples the REP will be reported as '3'.
select distinct LAB_QC_CODE, REP, count (*) from analysis
where login_id in (&login)
group by LAB_QC_CODE, REP;
```

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6. Database Queries and Reports

- Create complete and accurate queries
- Understand the database structure
- Understand the data set
- Include primary keys
- Review query output for reasonableness
- Include critical information in reports
- Compare selected data vs. database
- Ensure accuracy of data represented in report

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7. Case Studies

- Two case studies will be used to demonstrate a systematic, high-quality approach to data management and the importance of performing these quality control procedures.

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Case Study 1: Northern Gulf of Mexico Nutrients

- Compiled existing water quality data from 30 studies into one database
- 2.1 million records; 2441 stations; 1905 – 2003
- Team expertise: nutrient chemistry & data management
- Standardization
  - 678 distinct parameters reduced to 58
  - Significant data gaps filled
  - Data from the same study or source processed together
  - Questionable data identified via reportable column (Y or N)

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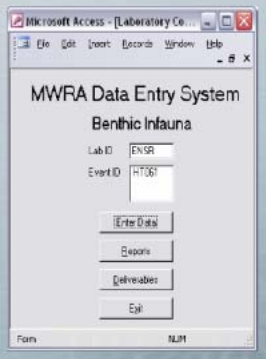
Case Study 2: Massachusetts Water Resources Authority

- Centralized database with > 2M data results
- Chemistry, nutrients, biology, remote sensing, nutrient flux, and productivity data
- Technology maximizes efficiency:
  - **Data Entry application contain sample IDs and database rules**
  - **Local QA/QC checks must pass before uploading**
  - **Check scripts run nightly ensure ongoing consistency**
  - **NPDES permit exceedences automatically identified**
  - **Efficiencies have reduced delivery times and costs**



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Consequences of Data Management Errors

- Metals data appeared to be duplicates but were actually total and dissolved results
  - "D" and T" incorporated into Sample ID but Sample Fraction column was null
- Metals data units standardized incorrectly
  - All Units assumed to be ppb resulting in data reported 10^3 times too high
- Total PAH concentrations didn't correlate with sums of LMW and HMW PAH
  - PAH sums calculated inconsistently across samples or studies

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Summary

1. Ensure database design includes the columns needed to distinguish critical data characteristics
2. Standardize, standardize, standardize!
3. Look for critical sample information within the sample IDs or units
4. Perform QC checks with every data set and on the entire database
5. Establish a documented process for data management and quality control procedures

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The Triad Approach and Sampling Program Design

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ABSTRACT

This paper discusses the complexities of sampling heterogeneous environmental media and how Triad concepts can be applied to make sure decisions are technically defensible. The following scientific issues are discussed:

- Contaminant heterogeneity can have a tremendous impact on data quality.
- Uncontrolled sampling variability can produce misleading data leading to incorrect or inefficient decisions.
- Triad relies on dynamic work strategies and state-of-the-art real-time sampling and analytical tools to reduce variability and improve data quality.
- The Ingersoll uncertainty calculator aids identification and quantification of the sources of data uncertainty.
- Collaborative data sets are used to manage both sampling and analytical uncertainties.

INTRODUCTION

It seems quite obvious why samples for chemical analysis are collected during cleanup of contaminated sites. After all, the point of collected samples is to perform tests on them in order to gather information about the presence and degree of contamination due to anthropogenic release. At a high operation level, it is a simple model: TAKE SAMPLE → TEST SAMPLE → GET DATA → MAKE DECISION. That model makes it is easy for program managers and many practitioners to assume that collecting and interpreting environmental contaminant data is a straightforward process. Just take some samples, send them to a lab for testing, get data numbers, then compare the numbers against the criteria we use to make the decision. How hard can it be?

From the inception of contaminated site cleanup programs, practitioners assumed that tiny samples could be taken from vast volumes of matrix, analyzed, the sample results directly extrapolated back to represent the contaminant concentrations in the bulk matrix from whence the sample came. Yet science, technology and experience have provided ample evidence that contaminated matrices do not conform to those expectations. Despite that, the cleanup community continues to rely on the original data model that focuses nearly all of its attention on overseeing the laboratory analysis. Data uncertainties introduced by other components, such as matrix heterogeneity and interference effects, the enormous mismatch between decision and sampling scales, and inappropriate interpretation of data results, are finally beginning to permeate the community's awareness, albeit with little programmatic change thus far. The Triad approach is focused on increasing awareness of the issues and of the tools to actively measure and control data uncertainties that reduce confidence in the correctness of cleanup decisions.

DATA USABILITY INSEPARABLE FROM INTENDED DECISIONS

Data results are influenced by much more than the analysis. Most of this influence stems from some form of matrix heterogeneity. Identifying and controlling the impact of these other influences on data quality requires that they be linked into the decision framework. Under current paradigms, the relationship between extra-analytical influences and the intended decisions are seldom identified, much less controlled in a way that reduces decision uncertainty. Unless appropriate questions are asked and answered satisfactorily, data results cannot be interpreted properly. In other words, direct comparison of lab numbers to regulatory thresholds is fraught with danger, with the decision as likely to be incorrect as correct.

Regulatory frameworks are not yet shifting away from the old data model that assumed contaminant homogeneity. Therefore, regulatory frameworks are out of sync with current science, making it difficult to construct data designs the put cleanup decisions on a firm scientific basis. For example, single threshold values are commonly provided in regulation (such as 400 ppm for lead in soil). The question arises, how should this threshold value be interpreted? Current regulatory practice nearly always treats such values as a "not-to-exceed" value. That means that any single data result from a grab sample that is higher than the threshold is interpreted to mean that unacceptable contamination exists. As will be discussed below, this approach is easily shown to be scientifically indefensible. For heterogeneous matrices, numerical "bright-line" criteria are meaningless unless the matrix volume over which the threshold applies is also provided. In other words, just saying "400 ppm lead in soil" is not sufficient. The threshold also needs to describe the "decision unit" over which the threshold applies. Following up on the previous example, the language would look something like, "400 ppm soil lead averaged over a 500 sq. yd. area to a depth of 6 inches," or "the 90^{th} percentile of sample results data set must be less than 600 ppm when collected from a 500 sq. yd. area by 6-inch depth."

The matrix volume making up a decision unit is known as the "decision support." Controlling for the effects of matrix heterogeneity requires the regulator to provide, in addition to the regulatory threshold, the decision support over which the regulatory threshold should be applied. However, this is seldom done, so interpreting data results to defensively support regulatory decision-making becomes difficult from a scientific standpoint. It also makes it difficult to identify the variables that must be controlled by a properly constructed appropriate sampling design.

In theory, the best way to get data that represents the decision unit is to analyze its entire soil volume (the decision support, say 10 yd x 10 yd x 1/6 yd, or 17 yd^3) in a single analysis. Of course, this is impossible from a sample handling and analysis perspective. However, the thought experiment is instructive because it tells us that we want to somehow collect data that represents the soil lead concentration in the 17 yd^3 soil volume (26 tons), but on sample and analytical scales that our equipment can accommodate.

Figure 1 illustrates the vast difference in spatial scale between the bulk mass of the decision unit and the mass of a two-gram soil sample. When sampling design and handling (such as homogenization) are inadequate, there is no difference between taking a two-gram sample from a

jarred sample in the lab vs. taking two grams directly from the field for digestion/extraction and analysis. When the matrix is known to be heterogeneous, it is apparent that the idea of taking such a tiny sample and extrapolating the result to represent such a large volume of matrix is ridiculous. But that is what is regularly done in environmental cleanup.

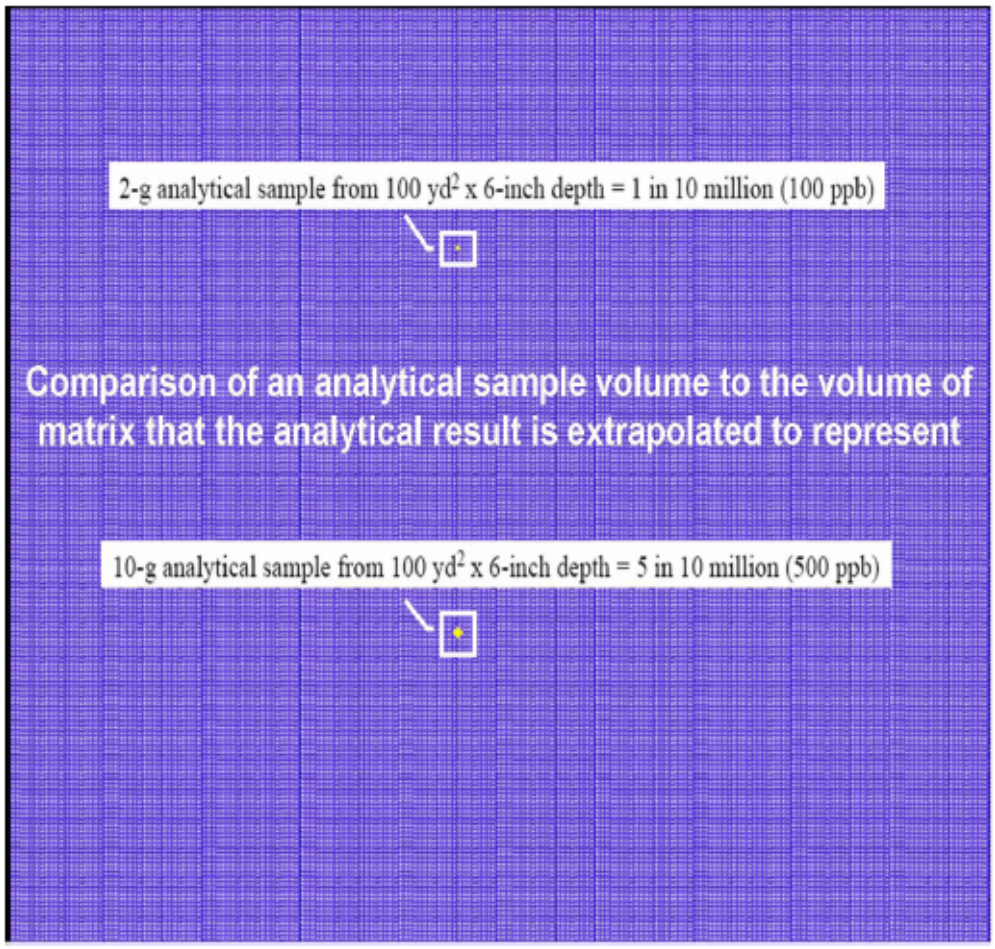

Figure 1: Spatial scale difference between decision unit and analytical sample unit

MICRO-SCALE (WITHIN-SAMPLE) HETEROGENEITY

Another challenge that soil analysis poses is illustrated with actual data from a military firing range site, presented in Table 1. Collected soil was passed through a graded series of sieves and fractionated into six particle size fractions and each fraction was analyzed separately for lead. The relationship between particle size and lead concentration is plain to see: the smaller the soil particle, the more lead associated with it. This relationship is due to the large surface area and mineral makeup of very small soil particles which causes higher adsorption of contaminants onto their surfaces.

Contaminants are not distributed randomly across a site because of release and migration influences. They are also not distributed randomly within a single jar of soil. This phenomenon has important ramifications for subsampling and sample preparation in the laboratory. Lab sampling techniques, the equipment used, and procedural consistency influence whether the reported result is high (techniques tend to select for finer particles), low (technique selected coarser particles), or medium (a mix was selected), as well as the repeatability of the analysis on samples taken from the same jar (will the same mix be selected with another subsampling of the jar?).

Firing Range Soil Grain Size (Std Sieve Mesh Size)	Pb Concentration in fraction by AA (mg/kg)
Greater than 3/8" (0.375")	**10**
Between 3/8 and 4-mesh"	**50**
Between 4- and 10-mesh	**108**
Between 10- and 50-mesh	**165**
Between 50- and 200-mesh	**836**
Less than 200-mesh	**1,970**
Bulk Total	**927 (wt-averaged)**

Table 1: Within-sample variability—Interaction between contaminant & matrix materials; adapted from ITRC (3)

Another question is: Which sample preparation method is correct? As discussed above, that is directly determined by the decision. Is the decision about risk to children exposed to fugitive dust escaping from the site into their homes? Such a decision points to analyzing the particle populations that comprise the **dust** to which a child might be exposed. On the other hand, compliance decisions might be based on the **bulk** soil average, in which case the sample would need to be thoroughly homogenized by grinding to a uniform particle size before subsampling for analysis. [This is a case where the regulator must interpret their regulation to determine whether the threshold applies to the bulk average, since it is unlikely there is any discussion of the decision unit (i.e., population of interest) in the promulgated rule.] In yet another scenario, such as a soil washing remedial decision, it is desirable to know the lead concentration of the remaining **larger particle sizes** after the finer, more highly contaminated particles have been flushed away.

CONTROLLING SAMPLE HANDLING PROCEDURES

Collection and preparation of samples has a great deal of influence on the result. Portions (samples and subsamples) must be collected from the decision unit in such a way that the data result is equivalent to (i.e., represents) the data result that would have been obtained by analyzing all the material (and only that material) falling within the population of interest to the decision. Documenting the analytics is not enough. Sampling and sample handling procedures must be documented and reproducible to support data of known and documented quality. Only then can it be known that data results are usable for the intended decision. That is why we need "representative" sampling and analysis designs.

To recap so far, it is impossible to collect "representative" samples or data unless the decision unit that the data are to represent is also known. The decision unit is defined by the nature of the decision, which could be a compliance decision, a risk decision, or a choice of remedial design. In statistical terms, the decision support is the same as the population of interest to the decision. Populations can take the form of

- general categories of contamination, such as high, medium, background, and low concentrations;
- between-sample spatial patterns of contaminant concentrations due to release or migration mechanisms (local spills, regional atmospheric deposition from a tall stack, movement of contamination by water flow, etc.);
- within-sample contaminant distributions resulting from interactions with matrix constituents (such as particle size, organic content, mineralogy, etc.) that determine migration, transformation, and adherence to the matrix components.

CALCULATING DATA UNCERTAINTY

Environmental heterogeneity produces true variability in samples; in other words, the actual concentration in one analytical sample is truly different from the concentration in a different analytical sample. It has long been recognized that variability due to sampling-related factors is usually much larger than that from analytical(1). But how can we determine how strongly sampling variability is influencing data results in any particular project? The "Ingersoll Uncertainty Calculator" is a very helpful tool that can help(2).

The Calculator is a preprogrammed Excel spreadsheet that can partition sources of variability among different aspects of sampling and analysis, IF the needed replicate quality control analyses have been performed. It also can compute the quantitative statistical uncertainty around a single measurement result. Figure 2 shows an example of the output of the spreadsheet for data generated during an uranium investigation using a field-portable x-ray fluorescence instrument. Based on the degree of variability as determined through quality control, the point measurement of 56 ppm is more appropriately reported as 41 – 71 ppm (if uncertainty around that data point is considered at the 99% statistical confidence level). Bias can also be corrected, adjusting the uncertainty interval to 45 – 78 ppm. This provides the data user with more valuable information than a single value, although the user must be taught how to use it.

Reporting the uncertainty associated with an analytical result is a much more honest way of reporting results to data users. It is an extremely helpful way to report data such that the quality is known quantitatively. It is then up to the data user to determine if the quantitative quality is "good enough" to support quality decisions (i.e., confident decisions).

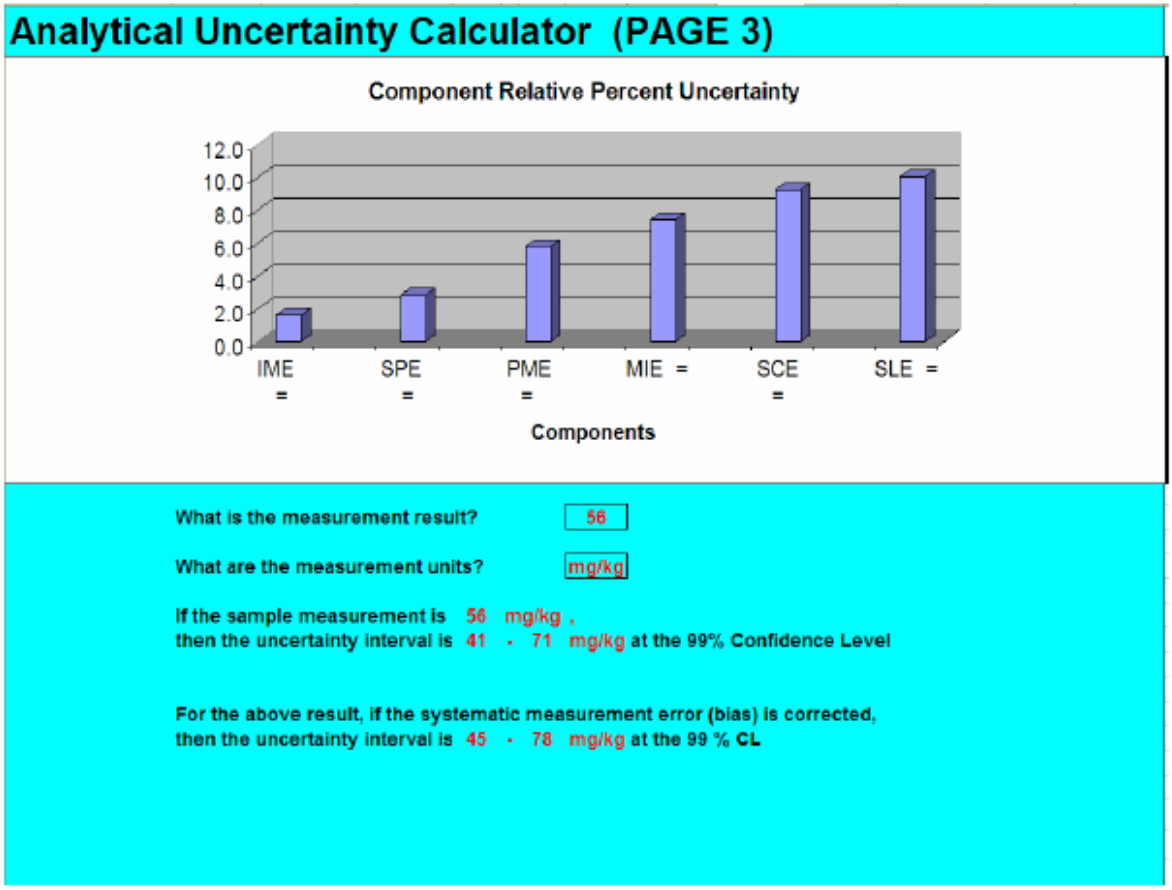

Figure 2. Uncertainty Calculation from an actual XRF Uranium Data Set

As illustrated by the uranium data set, determining measurement uncertainty is actually easier with cheaper, rapid analyses, such as field analytical methods. The number of replicates required at each of the various steps of sampling and analysis is more economically feasible with less expensive methods. When these rapid turnaround methods are used in conjunction with an adaptive, dynamic work strategy, the economics of generating quantitative estimates of data quality become even more favorable. Changes in the behavior of both the matrix and the measurement process are detected while it is possible to track down the source of the problem and take corrective actions.

The Triad approach improves the cost-effectiveness and efficiency of the entire cleanup process. But even for those interested in only the data generation aspect of site cleanup, the Triad framework of best practices fosters objective improvements in data quality and data's value to

the data user. Some of the mechanisms used in Triad projects to achieve high data and project quality include:

- A detailed systematic planning that clarifies and documents the decisions to be made, which must include consideration of the decision unit associated with each project decision.
- Using a conceptual site model (CSM) to understand potential contaminant distributions at different spatial (and temporal, if relevant) scales, and develop a sampling design that corrects the mismatch between sample unit and decision unit.
- A demonstration of methods applicability (DMA) that pretests proposed sampling and analytic procedures to ensure compatibility with the site's particular issues and matrices. The DMA will guide selection and possible modification of methods, the kind and amount of quality controls, and the relationship between rapid, non-specific analytical methods and analyte-specific, more expensive methods.
- The site- and project-specific relationship between these two classes of analytics is described in terms of a collaborative data set.

The collaborative relationship between methods analyzing for the same basic constituents can be constructed in a variety of ways. Many practitioners automatically rely on classical statistical regression, but the regression model often cannot capture the predictive relationships in a way more suitable to the project's decision-making structure. Non-parametric data analysis methods are often more suitable. Non-parametric analysis can directly calculate the false positive and negative decision error rates. In contrast, regression analysis predicts those rates indirectly based on the assumption that a mathematical distribution model can be fitted to the data set. That assumption is frequently proved erroneous in the case of real environmental data.

Each member of a collaborative method pair uses its strengths to control for the weaknesses of the other in the pair. Thus, real-time, high density analytics controls for sampling variability, while traditional lab analyses control for any analytical limitations in the other. Used together collaboratively, both major sources of data uncertainty (sampling and analytic) are controlled so that the data user can be confident that his interpretation is correct.

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2. Ingersoll, William S. 2001. Environmental Analytical Measurement Uncertainty Estimation: Nested Hierarchical Approach. Defense Technical Information Center # ADA 396946. www.navylabs.navy.mil/Archive/Uncertainty-SOP.pdf

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The Triad Approach & Sampling Program Design

NEMC, Cambridge, MA August 19, 2007

Deana Crumbling, OSRTI TIFSD, crumbling.deana@epa.gov

XRF Analysis

In situ readings or bagged samples

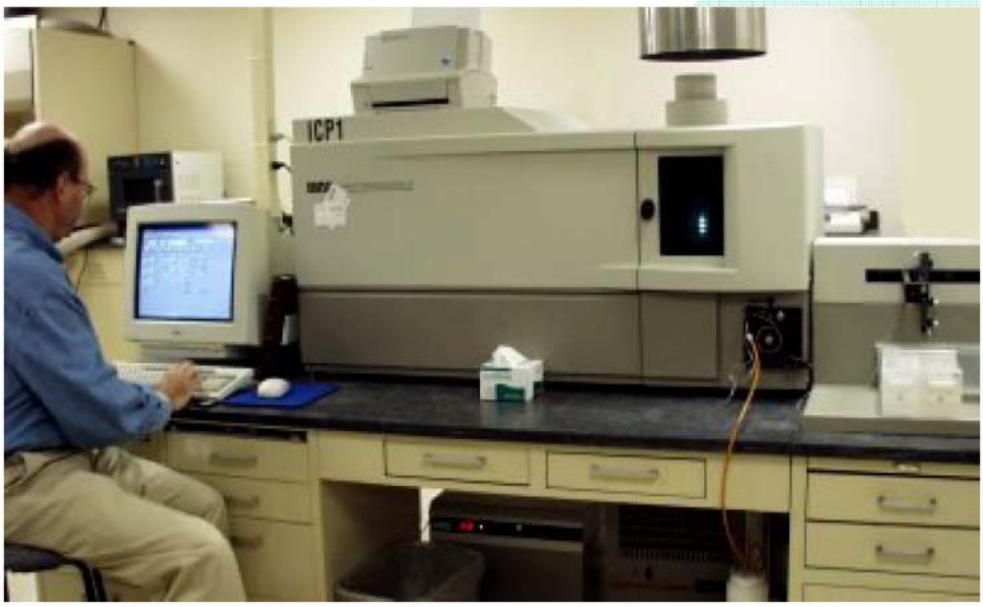
08/19/2007 2007 NEMC 2

Taking readings bagged & cupped samples

Older & newer XRF instrument design

08/19/2007 2007 NEMC 3

ICP Instrumentation

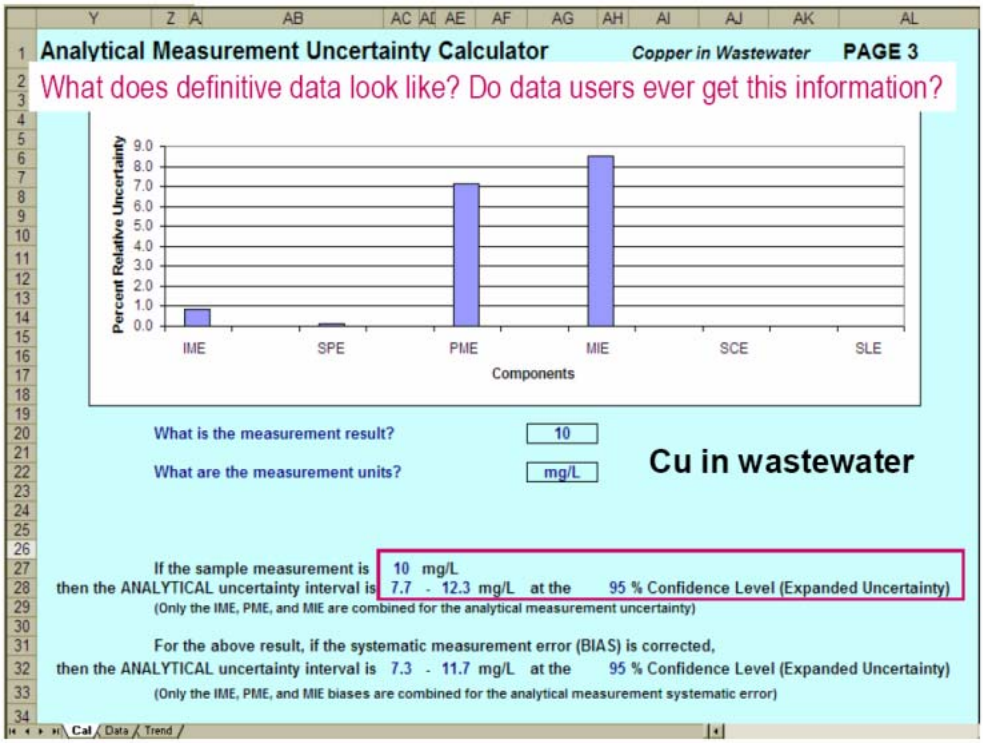


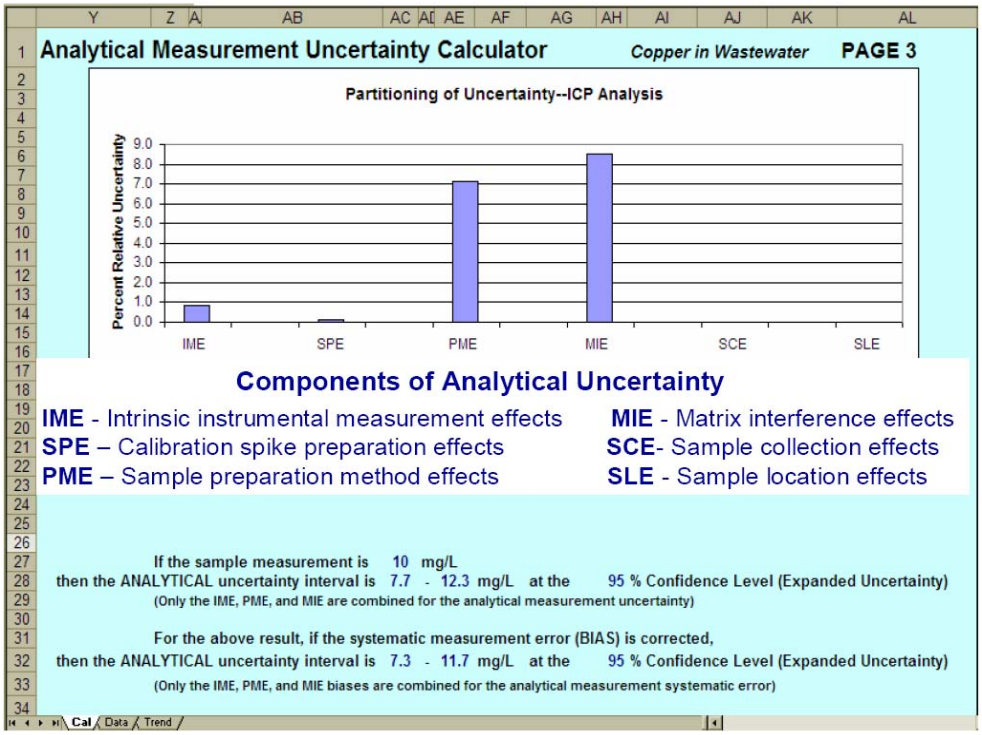
Data Quality & Heterogeneous Matrices

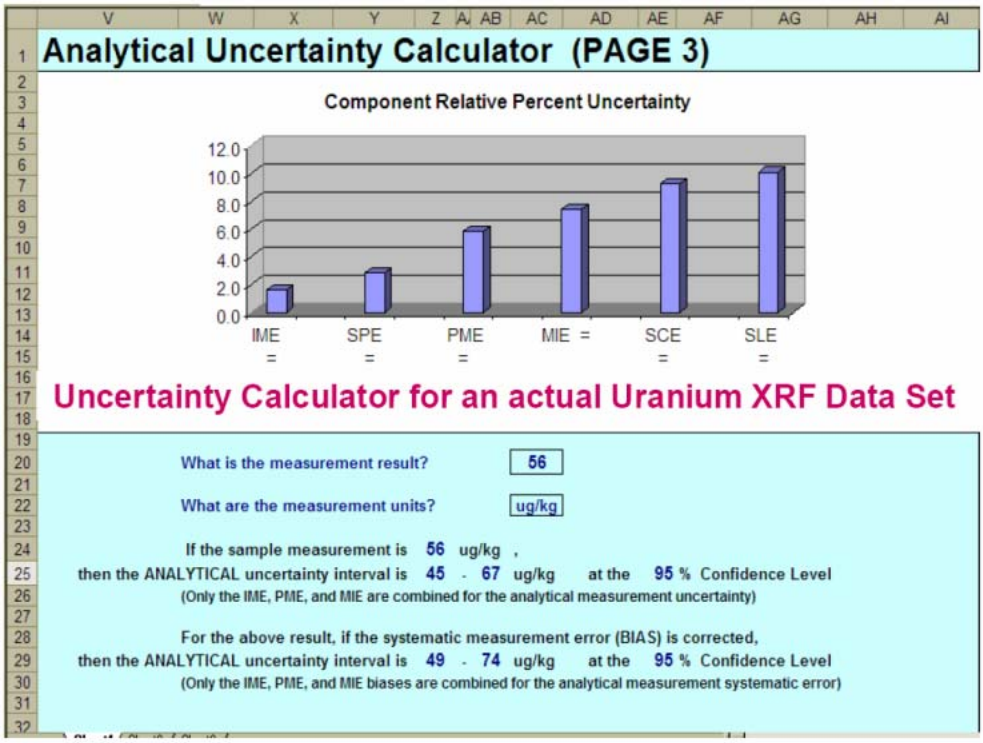
Definitive Data

"DQOs for Superfund," Page 43

"For the data to be definitive, either analytical or total measurement error must be determined."


Analytical Measurement Uncertainty Calculator
Copper in Wastewater
PAGE 3
What does definitive data look like? Do data users ever get this information?
Percent Relative Uncertainty
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
IME
SPE
PME
MIE
SCE
SLE
Components
What is the measurement result?
10
What are the measurement units?
mg/L
Cu in wastewater
If the sample measurement is 10 mg/L
then the ANALYTICAL uncertainty interval is 7.7 - 12.3 mg/L at the 95 % Confidence Level (Expanded Uncertainty)
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)
For the above result, if the systematic measurement error (BIAS) is corrected,
then the ANALYTICAL uncertainty interval is 7.3 - 11.7 mg/L at the 95 % Confidence Level (Expanded Uncertainty)
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)
Cal
Data
Trend


Analytical Measurement Uncertainty Calculator
Copper in Wastewater
PAGE 3
Partitioning of Uncertainty--ICP Analysis
Percent Relative Uncertainty
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
IME
SPE
PME
MIE
SCE
SLE
Components of Analytical Uncertainty
IME - Intrinsic instrumental measurement effects
SPE – Calibration spike preparation effects
PME – Sample preparation method effects
MIE - Matrix interference effects
SCE- Sample collection effects
SLE - Sample location effects
If the sample measurement is 10 mg/L
then the ANALYTICAL uncertainty interval is 7.7 - 12.3 mg/L at the 95 % Confidence Level (Expanded Uncertainty)
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)
For the above result, if the systematic measurement error (BIAS) is corrected,
then the ANALYTICAL uncertainty interval is 7.3 - 11.7 mg/L at the 95 % Confidence Level (Expanded Uncertainty)
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)
Cal
Data
Trend



Analytical Uncertainty Calculator (PAGE 3)

Component Relative Percent Uncertainty

Uncertainty Calculator for an actual Uranium XRF Data Set

What is the measurement result? 56

What are the measurement units? ug/kg

If the sample measurement is 56 ug/kg ,
then the ANALYTICAL uncertainty interval is 45 - 67 ug/kg at the 95 % Confidence Level
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)

For the above result, if the systematic measurement error (BIAS) is corrected,
then the ANALYTICAL uncertainty interval is 49 - 74 ug/kg at the 95 % Confidence Level
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)

Project X's ICP Data Quality (Data Usability) for Pb

Lab duplicates (2 subsamples from same jar)

- Lab acceptance limits = +/- 35%
- All ICP lab dups in data pkg exceeded 35% (40.5, 38.1 & 85.8%)
- Protocol required data validator to J-flag all associated results as "estimated."
- Protocol does not require any corrective action to determine or resolve unacceptable uncertainty

What is data quality?

USEPA OEI definition
(http://www.epa.gov/quality/glossary.htm

- ***"A measure of the degree of acceptability or utility of information for its intended use."***

08/19/2007 2007 NEMC 11

Project X's Pb Samples: Lab Dup Results

Duplicates effect on decision-making ability at AL = 500 ppm

Lab dup done on NW10-B-0-2; RPD = 38.1%

Sample Location	Lab ID	Sample Date		RESULT	Q
NW10-B-0-2	825068	4/24/2007		453	J

Lab Dup = 666; they straddle AL

Lab dup on NW14-C-0-2; RPD = 40.5%

NW14-C-0-2	824107	4/24/2007		1040	J

Lab Dup = 688

Lab dup on SWNW2-D-0-2; RPD = 85.8%

SWNW2-D-0-2	828869	4/26/2007		874	J

Lab Dup = 2187

08/19/2007 2007 NEMC 12

Even with acceptable QC at <35% RPD, variability can cause project decision uncertainty

						-35%	+35%
NW10-C-0-2	825070	4/24/2007		560	J	393	798
NW10-D-0-2	825071	4/24/2007		1160	J	814	1652
NW06-A-0-2	825072	4/24/2007		148	J	104	211
NW06-B-0-2	825073	4/24/2007		884	J	621	1259
NW06-C-0-2	825074	4/24/2007		990	J	695	1410
NW06-D-0-2	825075	4/24/2007		1590	J	1116	2265
NW05-A-0-2	825076	4/24/2007		972	J	682	1384
NW05-B-0-2	825077	4/24/2007		332	J	233	473
NW05-B-0-2D	825078	4/24/2007	FD of NW05-B-0-2	412	J	289	587
NW05-C-0-2	825079	4/24/2007		680	J	477	968

Are data users aware of the relationship between heterogeneity, data variability & site decisions?

08/19/2007 2007 NEMC 13

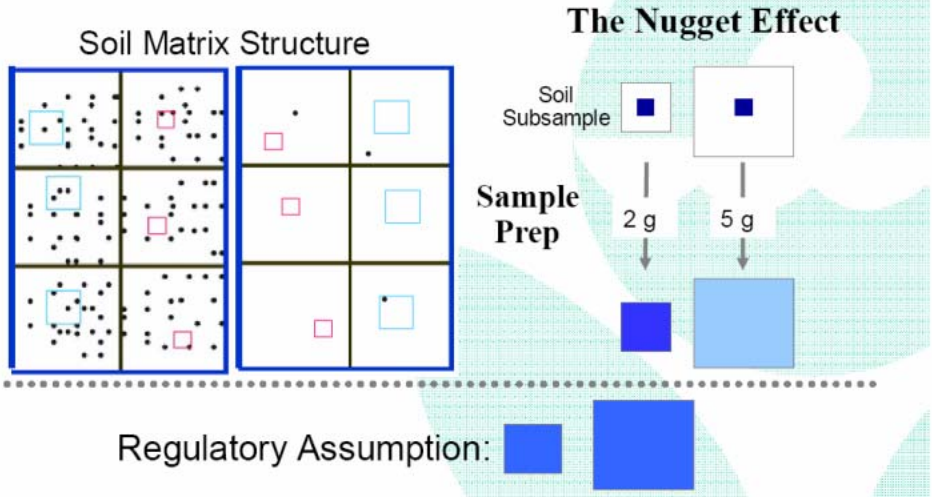
Important Cause of Poor Precision: Within-Sample Heterogeneity

Firing Range Soil Grain Size (Std Sieve Mesh Size)	Pb Concentration in fraction by AA (mg/kg)
Greater than 3/8" (0.375")	**10**
Between 3/8 and 4-mesh"	**50**
Between 4- and 10-mesh	**108**
Between 10- and 50-mesh	**165**
Between 50- and 200-mesh	**836**
Less than 200-mesh	**1,970**
Bulk Total	**927 (wt-averaged)**

Adapted from ITRC (2003)

08/19/2007 2007 NEMC 14

Concentrated Particles within Less Concentrated Matrix = "Nugget Effect"



08/19/2007 2007 NEMC 15

Micro-scale Heterogeneity Causes Highly Variable Results

Subsample Support (dried, ball-milled, sieved to <10-mesh)	Range of Results [for 20 individual subsamples (ppm)]	Coeff of Var. (CV)	Number of subsamples req'd to estimate true sample mean within a range of…	
			…± 25%* [ex: 193 ± 25% = 145 - 241 ppm]	…± 10%* [ex: 193 ± 10% = 174 - 212 ppm]
1 g	101 - 800	0.79	39	240

True mean known to be 193 ppm

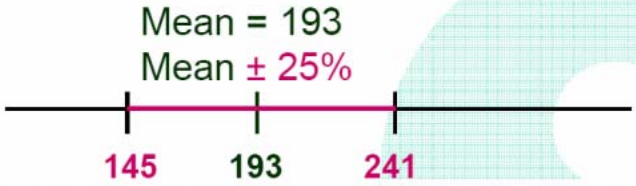
Adapted from DOE (1978)

At 95% statistical confidence

How much confidence should be placed in any single result?

08/19/2007 2007 NEMC 16

Data Variability & Decision-Making



Cannot claim at 95% statistical confidence that values between 145 & 241 are different.

If AL = 230, and you get 193, can you have 95% statistical confidence that the result is below the AL? **No**

If AL = 150, and you get 193, can you be confident the result is above the AL? **No**

If AL = 300, and you get 193, can you be confident the result is below the AL? **Yes**

17

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

- Additional replicates to increase confidence in a reported result or perform statistical estimate of "error" to produce "definitive data" (by SF definition)
- Adapt sample processing to reduce heterogeneity
- "Data validator" J-flags include indication of
  - how bad the imprecision is;
  - what effect it has on data usability, or
  - how might data user resolve the problem if causes usability problems

08/19/2007 2007 NEMC 18

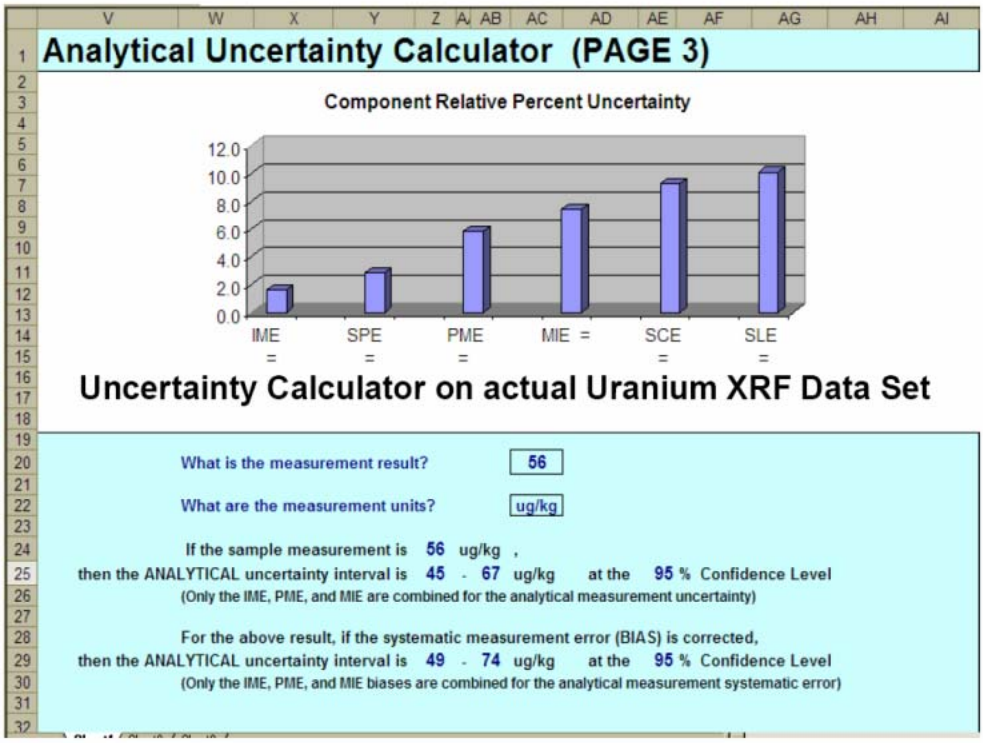
Improving Data Quality By Real-time Analysis (the Triad Approach)

Real-time Data-Decision Uncertainty Management

- Real-time availability of results allows
  - instantly recognize data-decision uncertainty
  - adaptively increase replicates to calculate "error"
  - adapt sample processing & analysis to improve data quality
  - document statistical decision confidence

Adaptive decision strategies ensure
DATA QUALITY MEETS DECISION NEEDS
as well as
meeting SF's requirement for providing
ESTIMATES OF DATA VARIABILITY
to the data user as component of definitive data

08/19/2007 2007 NEMC 21



A Second-Generation Data Quality Model (for Heterogeneous Matrices)

Cheaper/rapid (lab? field? std? non-std?) **analytical methods**

Costlier/rigorous (lab? field? std? non-std?) **analytical methods**

↓

Targeted high density sampling

Low DL + analyte specificity

↓

Manages CSM & sampling uncertainty

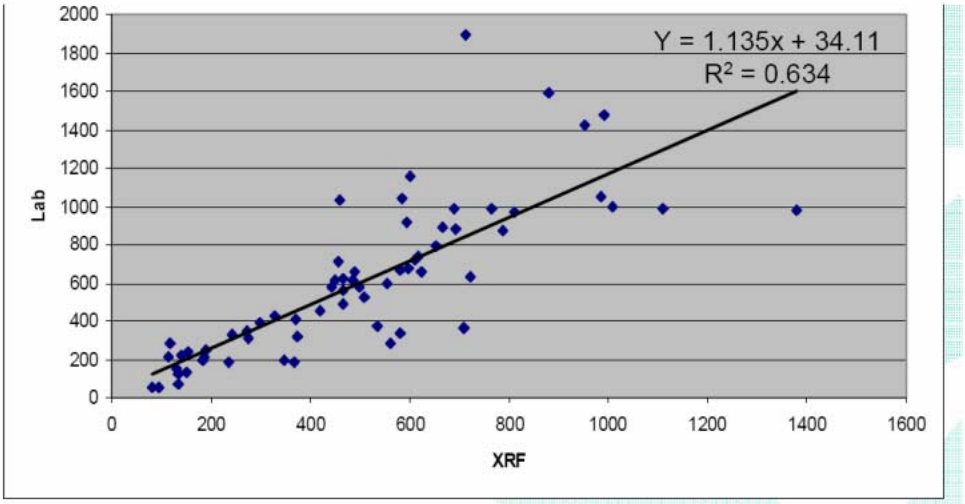
Manages analytical uncertainty

Collaborative Data Sets

Collaborative data sets complement each other so all sources of data uncertainty are managed. Using either kind of data alone will not produce reliable information.

23

Establishing Comparability between Different Data Sets for Project X: Contribution of Poor Lab Sampling Precision?



08/19/2007 2007 NEMC 24

So, How Does this Affect Labs?

As clients become educated about dangers of using uncertain data…

- Labs & data validators asked to report uncertainty
- Labs can't currently change routine sample prep unless client asks & pays for it
  - Clients may start asking; labs need equipment & SOPs
- Labs don't know how client will use data
  - Clients need to begin collaborating closer w/ labs to define data needs & ways to get it
- Triad approach catching on—spurs such changes
  - Labs may be asked to provide adaptive, rapid turnaround

08/19/2007 2007 NEMC 25

EMERGING CONTAMINANTS

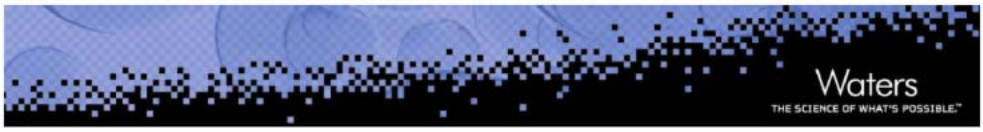
Analysis and Quantification of Perfluorinated Compounds in Environmental Matrices by UPLC®MS/MS

Aisling O'Connor
Waters Corporation

ABSTRACT

In recent years there has been much concern regarding the occurrence of perfluorinated compounds (PFCs) in the environment. PFCs are persistent pollutants and some of these compounds have been found in remote locations such as the Artic. In addition, the toxicity of these compounds is still under investigation. Studies have found that perflourinated compounds may interfere with intercellular communication, metabolism and reproduction. PFCs are widely used in products such as non-stick coatings, surfactants, fire-fighting foams, and in the production of plastics.

This presentation describes a new method for the analysis of PFCs. Drinking and surface water samples were extracted using Waters Oasis® WAX solid phase extraction (SPE) cartridges. Quantitative analysis was performed using UPLC/MS/MS on a Waters ACQUITY/TQD™ system. A total of twelve PFCs were analyzed in less than ten minutes using UPLC. The use of UPLC provides faster, higher resolution separation of these compounds compared with traditional HPLC. Contamination is a known problem when analyzing for PFCs at sub-ppb levels. Various methods for the reduction of contamination levels were investigated.



Analysis and Quantification of Perfluorinated Compounds by UPLC/MS/MS

NEMC 2007, Cambridge MA
August 22, 2007

Aisling M. O'Connor, Claude Mallet & Joe Romano

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- Introduction
- Sample preparation
- UPLC/MS/MS analysis
- Strategies for contamination reduction / elimination

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Perfluorinated Compounds

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- Widespread use in non-stick coatings, surfactants, firefighting foam, cleaning materials etc..
- Environmental concerns: persistent, very stable and mobile
- Most studies focus on PFOA and PFOS
- Found in artic polar bears to giant pandas
- Bioaccumulative
- Toxicity studies in animals and humans are ongoing
- Worldwide interest in PFC analysis

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Sample Preparation

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- Oasis WAX, 3 cc cartridge (mixed-mode weak anion exchange)
- Condition:2 mL methanol / 2 mL water
- Load: Water or centrifuged plasma / blood supernatant
- Wash:2 mL of 40% methanol in water
- Elute:1 mL 2% ammonium hydroxide in methanol
- Evaporate / reconstitute in mobile phase

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UPLC/MS/MS Conditions

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- UPLC Method
  - ***A:*** 95% 2mM Aq. Ammonium Acetate / 5% Water
  - ***B:*** MeOH + 2mM Ammonium Acetate
  - ***Column:*** ACQUITY BEH C18 2.1 x 50 mm, 1.7 µm
  - ***Column Temperature:*** 50ºC
  - ***Flow Rate:*** 0.4 mL/min
  - ***Gradient:*** 75/25 A/B to 0/100 A/B in 5 mins, Re-equilibrate 75/25 A/B
- MS Method
  - Electrospray mode, negative polarity
  - 2 MRM transitions per compound with CV and CE optimized

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MS/MS Conditions

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PFC	RT (min)	MRM Transitions	Dwell time (s)	Cone Voltage (V)	Collision Energy (eV)
PFBuS	1.97	299 > 80 299 > 99		45	30 30
PFHxA	2.60	313 > 269 313 > 119		16	7 18
PFHpA	3.22	363 > 319 363 > 169		15	7 18
PFHxS	3.29	399 > 80 399 > 99		60	35 35
PFOA	3.69	413 > 369 413 > 169		16	8 18
PFNA	4.08	463 > 419 463 > 169		20	8 18
PFOS	4.10	499 > 80 499 > 99		65	40 40

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MS/MS Conditions (2)

Waters
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PFC	RT (min)	MRM Transitions	Dwell time (s)	Cone Voltage (V)	Collision Energy (eV)
PFDA	4.40	513 > 469 513 > 219		22	8 16
PFUnA	4.68	563 > 519 563 > 319		22	9 16
PFDoA	4.92	613 > 569 613 > 169		22	8 20

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Chromatogram: 1pg/µL Standard

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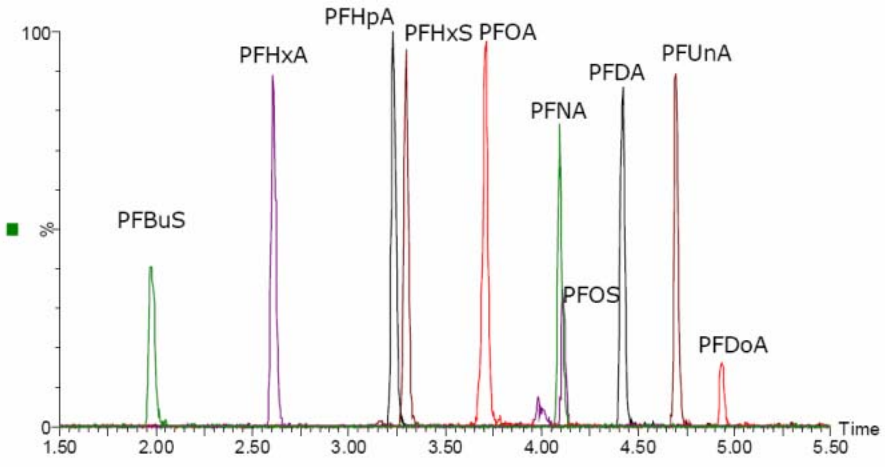

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Blank Contamination

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- Mobile Phase: Methanol & Water
- Instrument: Teflon components, mostly pre-injector (solvent lines, degasser, pump seals)
- Other Sources: IS, bottle caps etc.
- Contaminants: PFOA, PFNA, PFDA & PFUnA
- Reduction/Elimination of Contamination:
  - Replace Teflon components with PEEK
  - Use MPRT (Mobile Phase Residue Trap)
  - Use PP for making & storing samples etc.

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Replacement of Solvent Lines

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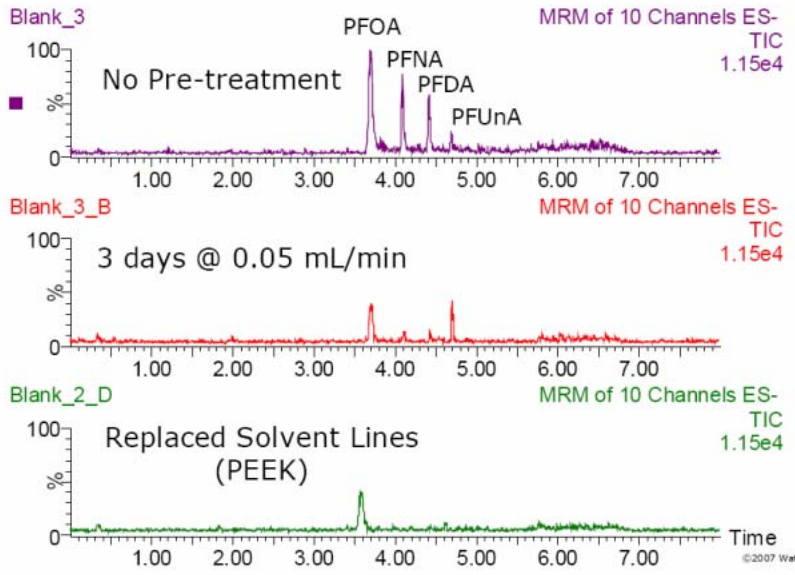

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Blank vs 1pg PFOA on Column: No Hold Up Column

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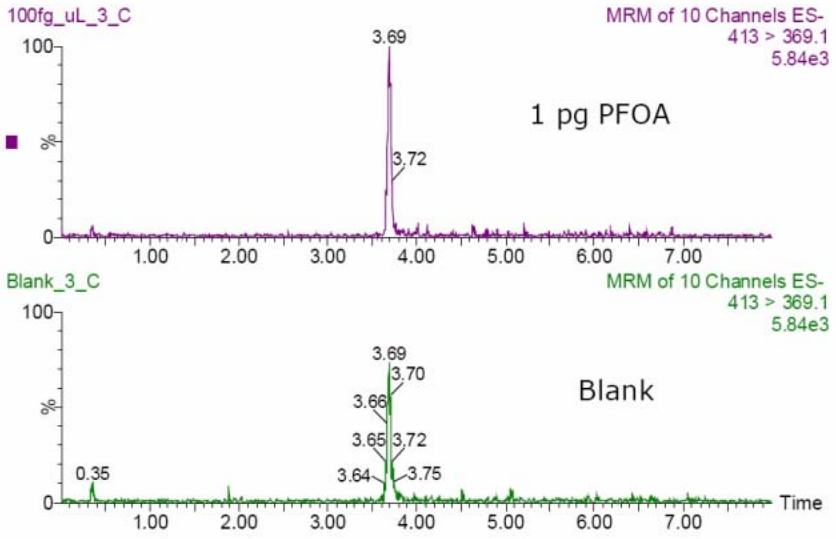

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Mobile Phase Residue Trap (MPRT)

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- Demonstrated with HPLC column
- Column at system pressure, approx. 7,500 psi
- 2 UPLC columns in series not workable, P > 15,000 psi
- Currently developing column chemistries for MPRT

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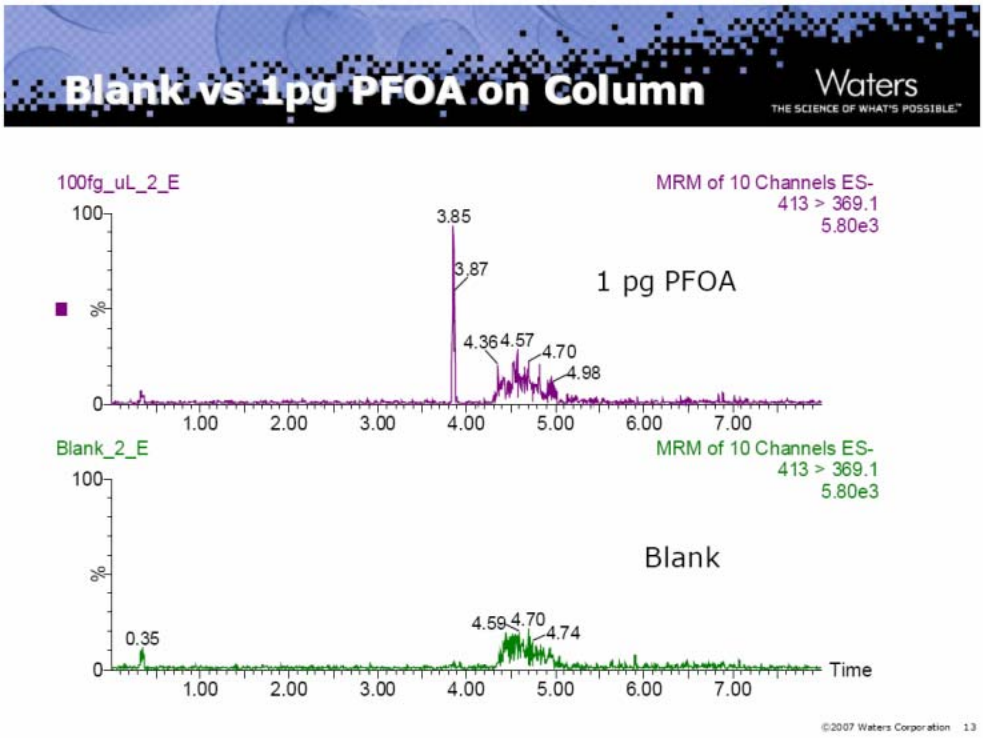
Blank vs 1pg PFOA on Column
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
100fg_uL_2_E
MRM of 10 Channels ES-
413 > 369.1
5.80e3
3.85
3.87
1 pg PFOA
4.36
4.57
4.70
4.98
Blank_2_E
MRM of 10 Channels ES-
413 > 369.1
5.80e3
Blank
0.35
4.59
4.70
4.74
Time
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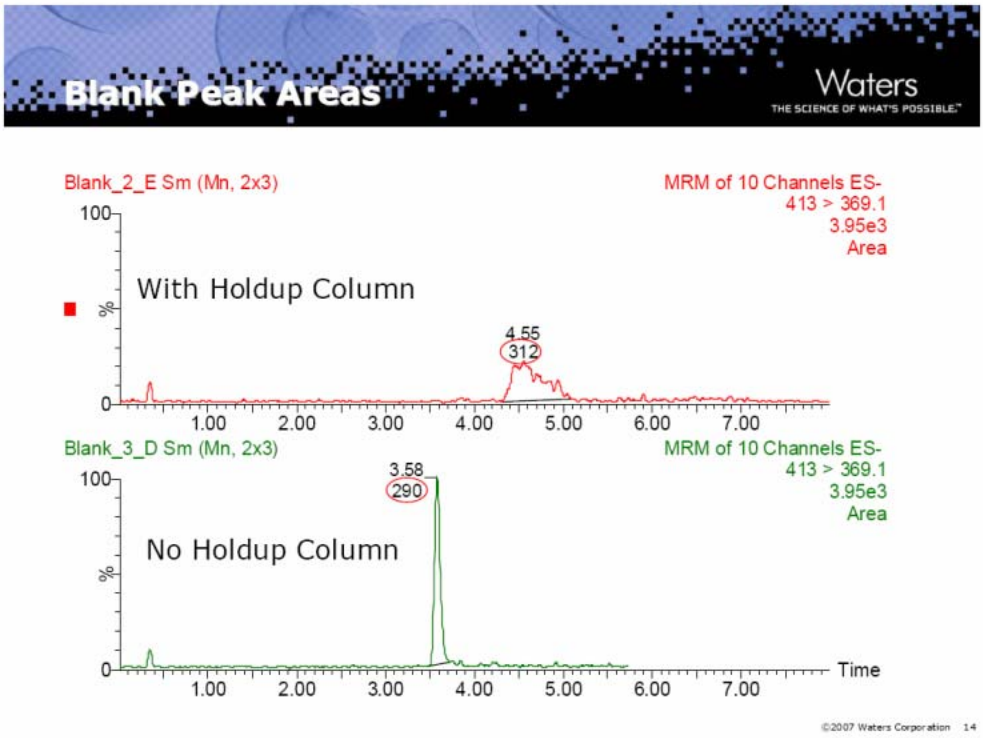
Blank Peak Areas
Waters
THE SCIENCE OF WHAT'S POSSIBLE.
Blank_2_E Sm (Mn, 2x3)
MRM of 10 Channels ES-
413 > 369.1
3.95e3
Area
With Holdup Column
4.55
312
Blank_3_D Sm (Mn, 2x3)
MRM of 10 Channels ES-
413 > 369.1
3.95e3
Area
3.58
290
No Holdup Column
Time
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Blank with Holdup Column

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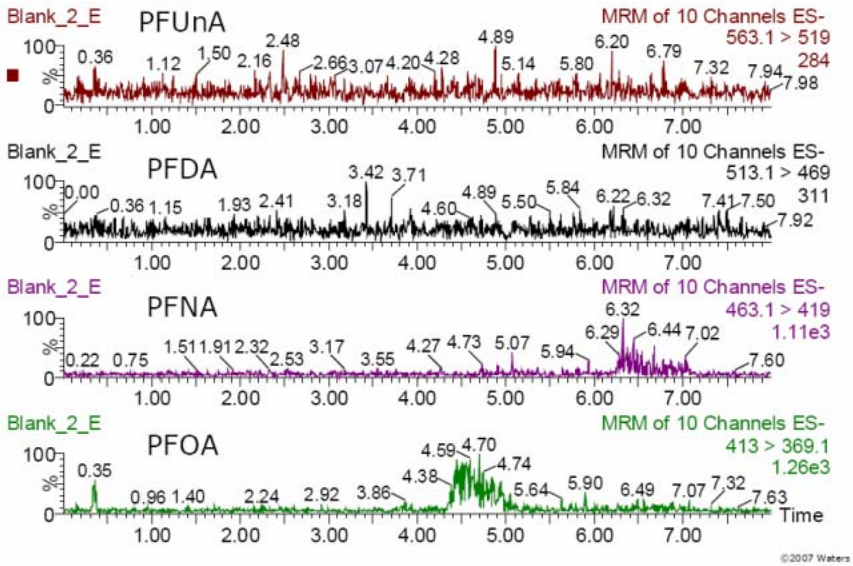

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Reproducibility / Stability of Holdup Column

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- Testing was carried out on a HPLC column
- 1,200 gradients run on holdup column at system pressure, approx. 10,000 psi with holdup and analytical column in series (7,000 psi without holdup column in-line)
- No appreciable increase in system pressure

  Inj #1 10,045 psi

  Inj #1200 10,184 psi
- No negative effects on chromatography

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1pg PFOA on column

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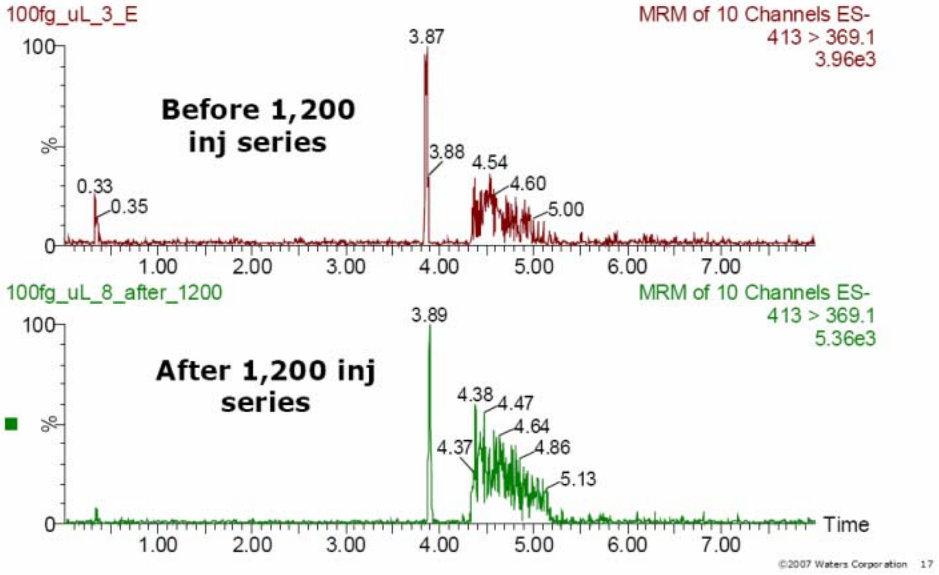

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Summary

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- A sample preparation method suitable for water and plasma / blood samples was presented
- A rapid UPLC/MS/MS method allows for the analysis of 10 PFCs in 5 minutes with a total cycle time of 7.5 minutes
- Contamination was dramatically reduced by the use of PEEK solvent lines without the need for extensive flushing
- A mobile phase residue holdup column was used to successfully delay pre-injector contaminants from analytical peaks

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Analysis of Selected Poly Brominated Diphenyl Ether (PBDE) Congeners in Tissues and Sediments by Electron Ionization Low-Resolution GC/MS

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ABSTRACT

PBDEs, a class of additive flame retardants, are of concern due to their environmental persistence, bioaccumulation and enrichment throughout the food chain, and potential adverse effects on ecological and human health. An analytical method was employed that would ensure sensitive and specific analysis of a large suite of PBDEs in challenging sample matrices. Sample processing included Accelerated Solvent Extraction (ASE) and two cleanup procedures. Low-Resolution GC/MS-EI analysis of fourteen commonly occurring PBDE congeners (tri- to deca-brominated) was achieved in one analytical run in less than fifteen minutes. Excellent results were achieved for both tissue and sediment NIST SRM samples. Using selected ion monitoring (SIM) mode, detection limit (MDL) values between 0.006 and 0.063 ng/g for sediments (dry) and between 0.021 and 0.408 ng/g for tissues (wet) were obtained. While not as sensitive as GC/ECD, LR GC/MS-NCI, or HR GC/MS for PBDE analysis, the LR GC/MS-EI offers the benefit of greater selectivity as compared to LR GC/MS-NCI and GC/ECD at a lower cost per sample than HR GC/MS.

INTRODUCTION

Brominated flame retardants, including poly brominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and polybrominated biphenyls (PBB), are the second largest group of the four major groups of flame retardant agents (inorganic, halogenated organic, organophosphorus, and nitrogen based) currently in use, and the largest group of the halogenated flame retardants [1]. PBDEs are considered additive flame retardants due to the fact that they are mixed directly with polymers and do not react with plastics or other materials.

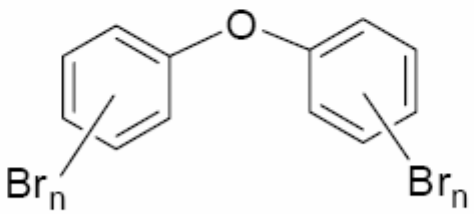


Figure 1: PBDE Structure, n can be up to 5 for each phenyl ring

PBDE mixtures are used in various products including consumer electronic equipment, textiles, polyurethane foam (used in furniture padding and cars), and other resins and

polymers. These additive PBDE congeners are released to the environment through various pathways, including leaching from products disposed of in landfills, directly into the air through evaporation and during incineration, or from chemical plants during the manufacturing of products containing PBDE additives.

PBDEs have undoubtedly saved numerous lives since they were first introduced as flame retardants. Growing concern over the possible effects on the environment as well as human health have driven the need for analytical procedures to accurately identify and quantify the presence of PBDE congeners in complex sample matrices at trace level detection limits.

There are six commercial mixtures of PBDE congeners that are currently in use, or have been used, as flame retardant mixtures. These mixtures include DE-71, Bromkal 70-5DE (both penta formulations), DE-79, Bromkal 79-8DE (both octa formulations), Saytex 102E, and Bromkal 82-0DE (both deca formulations) [3]. The penta formulations are comprised mostly of tri, tetra, penta, and hexa brominated congeners – the major congeners found in the penta formulations include 47, 85, 99, 100, 153, and 154 [3]. The two octa formulations, while different, are composed mainly of hepta and hexa brominated congeners including153, 175/186, 196, 197, 206, 207, and 209. The octa formulations are the least used of the three types of mixtures. The two deca mixtures are comprised mainly of 209 (~97%) with some nona congeners present [4]. The deca product is considered the safest of the mixtures; however evidence exists to indicate that it can degrade into less brominated congeners [5,6].

PBDE congeners have been found in environmental air, sediment, sludge, and biota samples [1,7,8,9] as well as in human tissue and breast milk [10]. Concentrations of PBDE congeners have been steadily increasing over the past two decades. In Europe, concentrations of the congeners found in the penta and octa formulations have peaked and declined significantly in recent years, most likely due to the voluntary ban on these formulations [2]. Concentrations in the United States are still continuing to climb, even after the primary manufacturer discontinued the production of the penta and octa formulations [11]; the measured PBDE concentrations are also higher than those found in Europe before concentrations there peaked. The California State Assembly has passed laws banning the use of the penta and octa PBDE formulations in products by the year 2008 [2]. It is important to note that even though sediment and sludge samples tend to show the same congener distribution as the commercially available products, the congener distribution is generally different in biological samples [2]. Differences in congener patterns are most likely due to the higher bioavailability of the lower congeners (tetra and penta) [2] and the enzymatic debromination of the higher level congeners [7]. This realization supports the expansion of current PBDE congener lists analyzed by most laboratories.

There are four analytical techniques currently in use for the detection of PBDE congeners. These methods are GC/ECD, low resolution GC/MS-EI, low resolution GC/MS-NCI, and high resolution GC/MS. The LR GC/MS-EI was chosen for this study based on higher selectivity as compared to both the GC/ECD and the LR GC/MS-NCI [14], and lower cost as compared to the HR GC/MS.

MATERIAL AND METHODS

Chemicals

PBDE congener mixes were purchased from Wellington laboratories (Ontario Canada). A second source mix and additional congeners used for surrogate internal standards were purchased from AccuStandard (New Haven CT). Polychlorinated biphenyl internal standards were purchased from Ultra Scientific (North Kingstown RI). Organic solvents (hexane, methylene chloride, and acetone) were HPLC grade or equivalent (Mallinckrodt Baker, Phillipsburg NJ). Davisil grade 634 silica gel, 100 – 200 mesh size (Sigma-Aldrich, St Louis MO) was acidified using ACS grade sulfuric acid (Mallinckrodt Baker, Phillipsburg NJ) in a ratio of 44 g of acid to every100 g silica gel.

Equipment

Sample extractions were performed using an Accelerated Solvent Extractor (ASE) model 200 (Dionex, Sunnyvale CA). HPLC cleanup was performed using Waters Breeze HPLC systems (Waters Corp, Milford MA) equipped with two Waters Envirogel columns (19 mm x 150 mm and 19 mm x 300 mm in series). GC/MS analysis was performed using a 6890N gas chromatograph (Agilent, Santa Clara CA) with a 5973 mass spectrophotometer (Agilent) operated using an electron ionization (IE) source. A 15 m x 0.25 mm ID x 0.10 µm film thickness ZB-5 Zebron column (Phenomenex, Torrance CA) was used for the analysis of all fourteen PBDE congeners.

Reference Material

NIST 1944, New York / New Jersey waterway sediment, and NIST 1946, Lake Superior Fish tissue, were purchased from the National Institute of Standards and Technology. Both reference materials were stored frozen and thawed just prior to extraction. Certified values for both were provided by NIST [12,13].

Sample Preparation

Extraction

Approximately 1.5 g of well homogenized, dry NIST 1944 sediment sample was mixed with 5 g of Hydromatrix. For the tissue sample, approximately 5 g of NIST 1946 was mixed with 5 g of Hydromatrix™. Samples were transferred to prepared 33 mL extraction cells containing two glass fiber filters and approximately 5 g of pre-muffled white quartz sand. The samples were then fortified with surrogates (TeBDE 50 and HxBDE 181); the additional cell volume was filled using more white quartz sand. In addition to the SRM samples, one procedural blank (PB) consisting of only Hydromatrix, one laboratory control spike (LCS) sample consisting of 10 g of sand or 5 g of store bought tilapia, and eight method detection limit (MDL) samples using the same background as the LCS samples, were processed for each matrix.

Samples were ASE extracted at 100°C under 2000 PSI for 10 minutes per static cycle using 1:1 hexane/methylene chloride. Three static cycles were performed on each sample with a 50% flush volume and a 200 s purge time.

Cleanup

Two separate cleanup procedures were performed on the sample extracts from both the sediment and tissue samples. After extraction, sample extracts were dried with anhydrous sodium sulfate and transferred to a 250 mL Teflon bottle. 20 g of acidified silica gel was added to each extract and then shaken on an orbital shaker table for one hour. Extracts were then transferred and concentrated. Concentrated extracts were then fractionated using size exclusion HPLC; the collected fraction was further concentrated, fortified with internal standard, and transferred for GC/MS analysis.

GC/MS Analysis

Selected PBDE congeners (Table 1) were analyzed using GC/MS-EI operated in selected ion monitoring (SIM) mode. The surrogate compounds were chosen as congeners not found in commercial mixes and not typically found in nature. For future analyses, HxBDE 181 may be substituted with a different surrogate compound as it has been found in biological samples [2]. Two PCB congeners not found in aroclor mixtures where chosen as internal standards.

GC conditions used were as follows: the injection port was set to a constant temperature of 270°C, the transfer line was set to 280°C, the MS source and quadrupoles were set to 230 °C and 150°C respectively. The initial oven temperature was set to 100°C and held for 0.5 minutes. The first ramp was set to 30°C/minute to a temperature of 209°C; the second ramp was set to 40°C/minute to a temperature of 350°C and held for 5 minutes. The carrier gas, helium, was set to a constant flow of 1 mL/minute.

Table 1: Selected Congeners and Their Associated Quant Masses

Congener	Quant Ion (Confirmation)	Comments
TrBDE 17	406, (408, 248, 246)	Do not quant using [M-2Br], this is same as mass for DDE congeners.
TrBDE 28	406, (408, 248, 246)	
TeBDE 47	486, (484, 326, 328)	Do not quant using [M-2Br], this is same as mass for Cl_5 PCB congeners.
TeBDE 66	486, (484, 326, 328)	
TeBDE 71	486, (484, 326, 328)	
PeBDE 85	564, (566)	
PeBDE 99	564, (566)	
PeBDE 100	564, (566)	
HxBDE 138	484, (486)	Quant using [M-2Br]
HxBDE 153	484, (486)	Quant using [M-2Br]
HxBDE 154	484, (486)	Quant using [M-2Br]
HpBDE 183	562, (564, 561, 563)	Quant using [M-2Br]
HpBDE 190	562, (564, 561, 563)	Quant using [M-2Br]

Congener	Quant Ion (Confirmation)	Comments
DeBDE 209	232, (799, 797)	Confirmation ion is [M-2Br]
TeBDE 50 (surrogate)	486, (484, 326, 328)	
HpBDE 181 (surrogate)	562, (564, 561, 563)	Quant using [M-2Br]
Cl5(96) (PCB IS)	326, (324)	
Cl6(161) (PCB IS)	360, (362)	

Calibration standards were run prior to each analytical sequence. The calibration range for individual PBDE congeners ranged from 0.005 to 0.4 ng/µL (0.025 to 2.0 ng/µL for DeBDE 209) over seven calibration levels. Congeners were calibrated using a quadratic curve fitting with passing criteria of 0.995 or better. Continuing calibration verification (CCV) standards were run every 10 samples or twelve hours, whichever is shorter. Analytes in the CCV samples must meet percent difference criteria of 25% from the actual concentration of the CCV in order for the bracketed samples to be used.

RESULTS AND DISCUSSIONS

The three main things to consider while choosing an analytical method are sensitivity, selectivity, and cost. The Electron Capture Detector (ECD) is cost effective and one of the most sensitive detectors currently available for halogenated compounds; however ECD is also the least selective of the three methods. With the GC/ECD it is not possible to distinguish between chlorinated and brominated compounds which can lead to false positive results. When possible, analytes of interest should be separated during sample preparation. Initial attempts to analyze environmental sample extracts using the above preparation techniques on the GC/ECD were not successful due to the high level of interferences from other non-target compounds (see Figure 2). Dual column analysis is frequently employed with GC/ECD analysis, but is time consuming and would not help in this situation. High resolution GC/MS is both sensitive and selective, but is an expensive capital investment for a laboratory and is costly and time consuming to operate. Low resolution GC/MS run in both the Electron Ionization (EI) mode and the Negative Chemical Ionization (NCI) mode are sensitive, selective, and cost effective methods for the analysis of PBDE congeners in environmental samples. In general, the NCI mode is more sensitive than the EI mode, however, the selectivity is not as good as using HR GC/MS and slightly less sensitive than LR GC/MS-EI when scanning for only the bromine mass ions (m/z 79 and m/z 81) as other brominated compounds may interfere if not removed during the sample preparation process. These bromide ions are not present in the EI spectra [6,14].

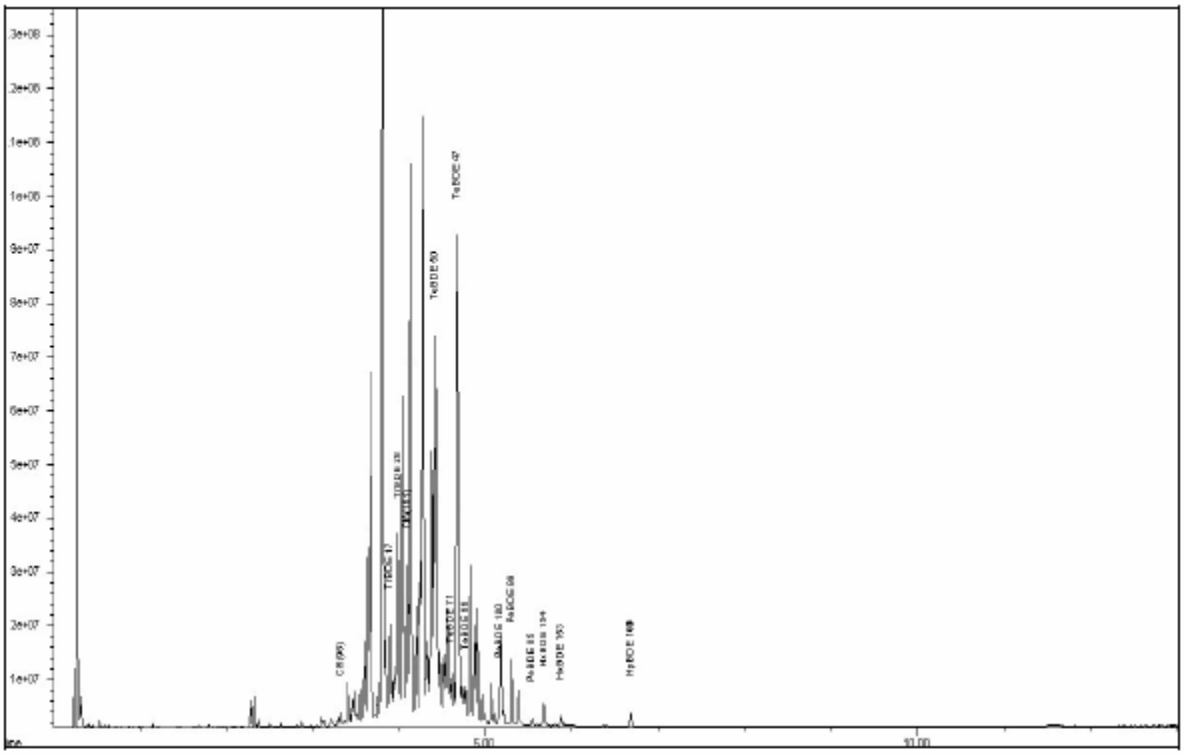


Figure 2: GC/ECD Chromatogram of NIST 1946

Using the GC/MS-EI, good results can be achieved for both sediment and tissue standard reference materials (Tables 2a and 2b) with an analytical runtime of less than fifteen minutes per sample.. Analysis of selected PBDE congeners, ranging from tri-brominated to deca-brominated, can be achieved in one analytical run with excellent resolution (Figures 3a, 3b, and 3c). It is important to point out that while the total ion chromatogram (TIC) for the NIST 1944 shown in Figure 2c appears to have high amounts of interference in the first five minutes, the actual quant ions used for the PBDE congeners are resolved (Figures 4a and 4b). The interferences seen are due to the presence of PCB congeners present in the extract that were not removed in sample preparation, this interference seemed to be related only to sediments and can be removed by additional sample preparation work and will result in cleaner extracts for analysis.

Table 2a: NIST 1946 Tissue SRM results

Client ID	051122-09: SRM 1946					
Battelle ID	BI656SRM-P					
Sample Type	SRM					
Collection Date	03/27/2006					
Extraction Date	03/27/2006					
Analysis Date	04/03/2006					
Analytical Instrument	MS					
% Moisture	71.40					
% Lipid	NA					
Matrix	TISSUE					
Sample Size	5.30					
Size Unit-Basis	G_WET	**Certified Value**	**+/-**	**Passing %Difference**	**Actual %Difference**	**Qual**
Units	NG/G_WET					
TrBDE 17	U					
TrBDE 28	0.493	0.74	0.03	33.64	33.6	
TeBDE 47	24.444	29.90	2.30	37.69	18.2	
TeBDE 66	1.211	1.35	0.16	41.85	10.3	
TeBDE 71	U					
PeBDE 85	U					
PeBDE 99	22.162	18.50	2.10	41.35	19.8	
PeBDE 100	10.820	8.57	0.52	36.07	26.3	
HxBDE 138	U					
HxBDE 153	3.079	2.81	0.41	44.59	9.6	
HxBDE 154	6.937	5.77	0.80	43.86	20.2	
HpBDE 183	U					
HpBDE 190	U					
DeBDE 209	U					
Surrogate Recoveries (%)						
TeBDE 50	96					
HpBDE 181	62					

Higher brominated congeners (octa, nona, and deca) are analyzed using quant ions from fragments only as the mass ions for these levels are above the limit of the 5973 detector (newer detectors have higher ranges up to 1050 amu). Low method detection limits were achieved for both sediment and tissue matrices (Tables 3a and 3b). High RSD values in the replicate analyses for two hepta congeners and the Decabromodiphenyl ether (especially HpBDE 190) indicate that the spike values used for these congeners, or the background levels used should be evaluated prior to the next MDL study. The same is true for PeBDE 99 in the sediment MDL study. The high RSD value related to HpBDE 190 is likely due to the partial co-elution with the surrogate HpBDE 181 and the difference in the spiked concentration of the MDL versus the surrogate. The method presented in this paper offers a low cost, rapid turn around solution for the analysis of PBDE congeners in both soil/sediment and biological samples.

Table 2b: NIST 1944 Sediment SRM results

Client ID	020111-01: SRM 1944					
Battelle ID	BI652SRM-P					
Sample Type	SRM					
Collection Date	03/27/2006					
Extraction Date	03/27/2006					
Analysis Date	04/04/2006					
Analytical Instrument	MS					
% Moisture	1.25					
% Lipid	NA					
Matrix	SEDIMENT					
Sample Size	2.77					
Size Unit-Basis	G_DRY	**Certified**		**Passing**	**Actual**	
Units	NG/G_DRY	**Value**	**+/-**	**%Difference**	**%Difference**	**Qual**
TrBDE 17	U					
TrBDE 28	0.173 J	0.32	0.22	100.09	46.1	
TeBDE 47	1.696	1.68	0.28	46.38	1.0	
TeBDE 66	U					
TeBDE 71	U					
PeBDE 85	0.090 J					
PeBDE 99	1.899	1.83	0.25	43.64	4.0	
PeBDE 100	0.392 J	0.48	0.09	48.74	17.5	
HxBDE 138	0.983 J					
HxBDE 153	6.168	6.66	0.89	43.29	7.4	
HxBDE 154	0.965	1.34	0.42	61.31	27.7	
HpBDE 183	32.555	33.08	5.33	46.13	1.6	
HpBDE 190	1.783					
DeBDE 209	195.030	250.84	276.12	140.08	22.2	
Surrogate Recoveries (%)						
TeBDE 50	122 N					
HpBDE 181	85					

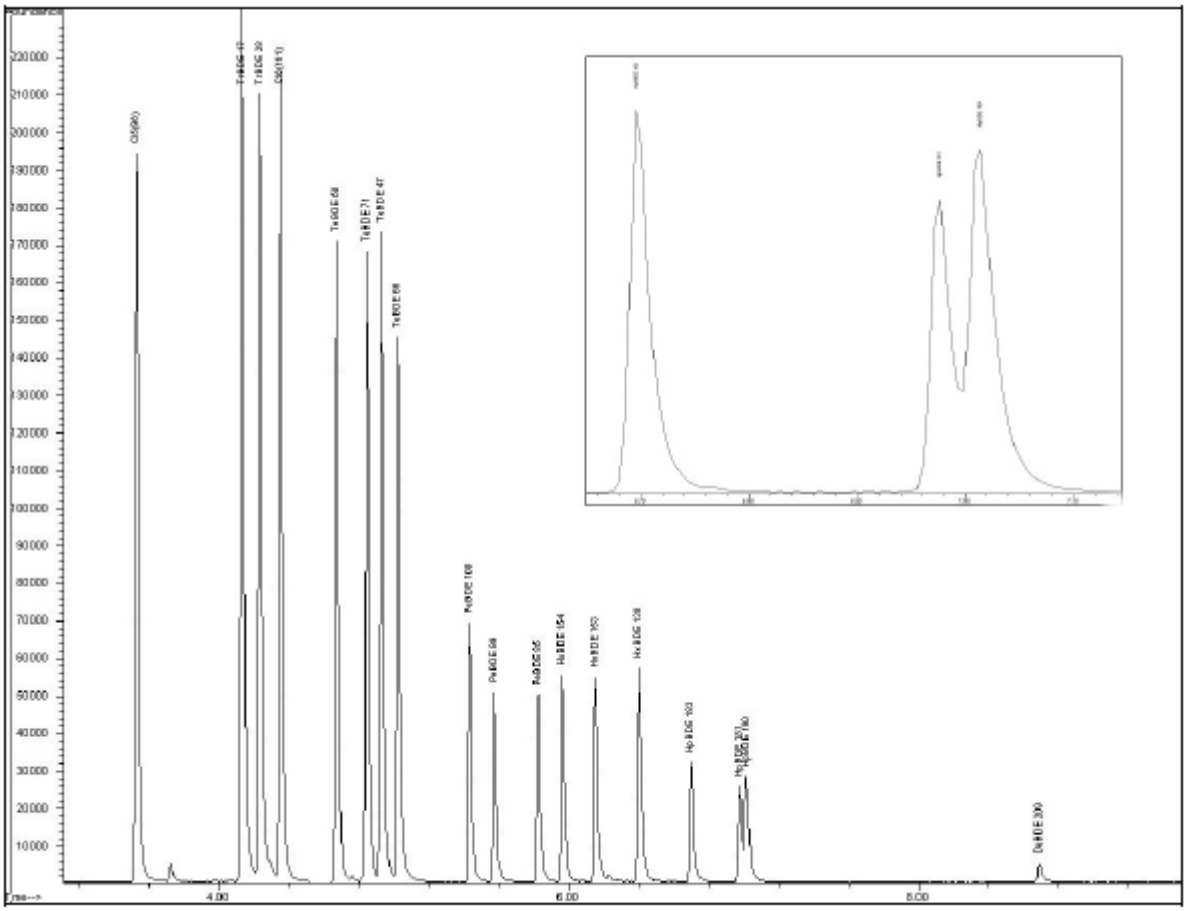


Figure 3a: Total Ion Chromatogram of GC/MS Calibration Standard

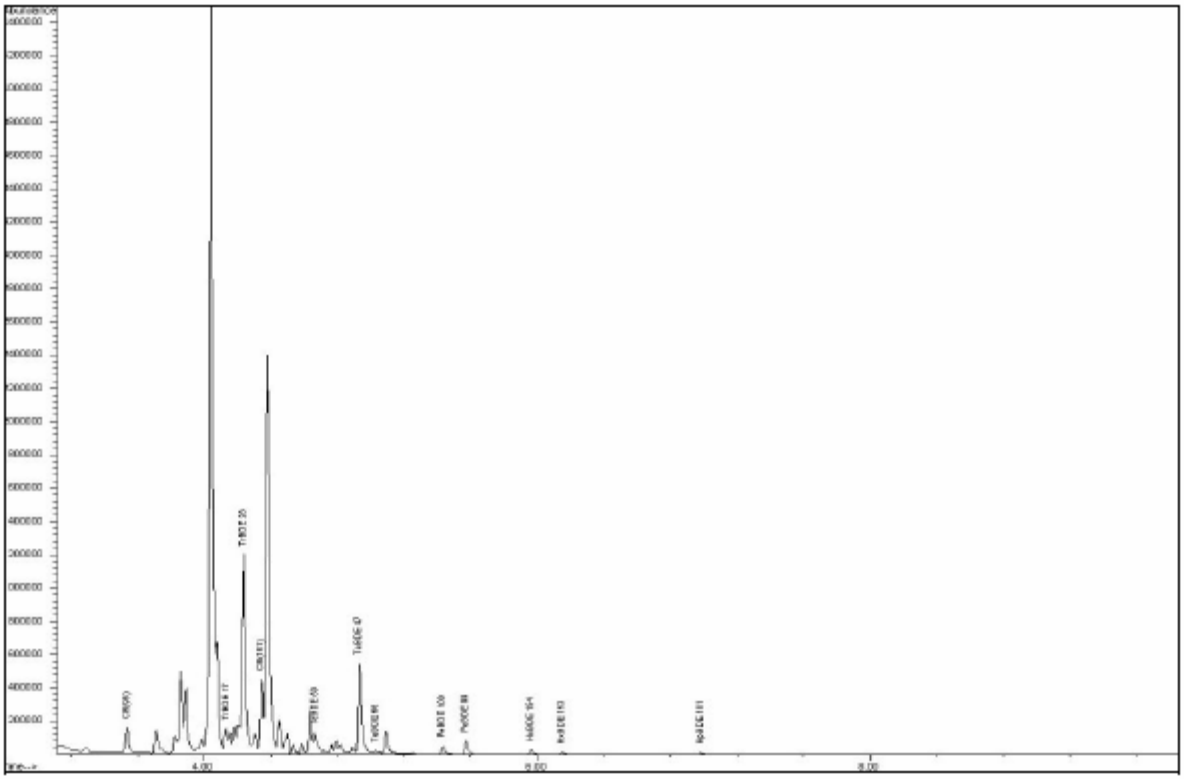


Figure 3b: NIST 1946

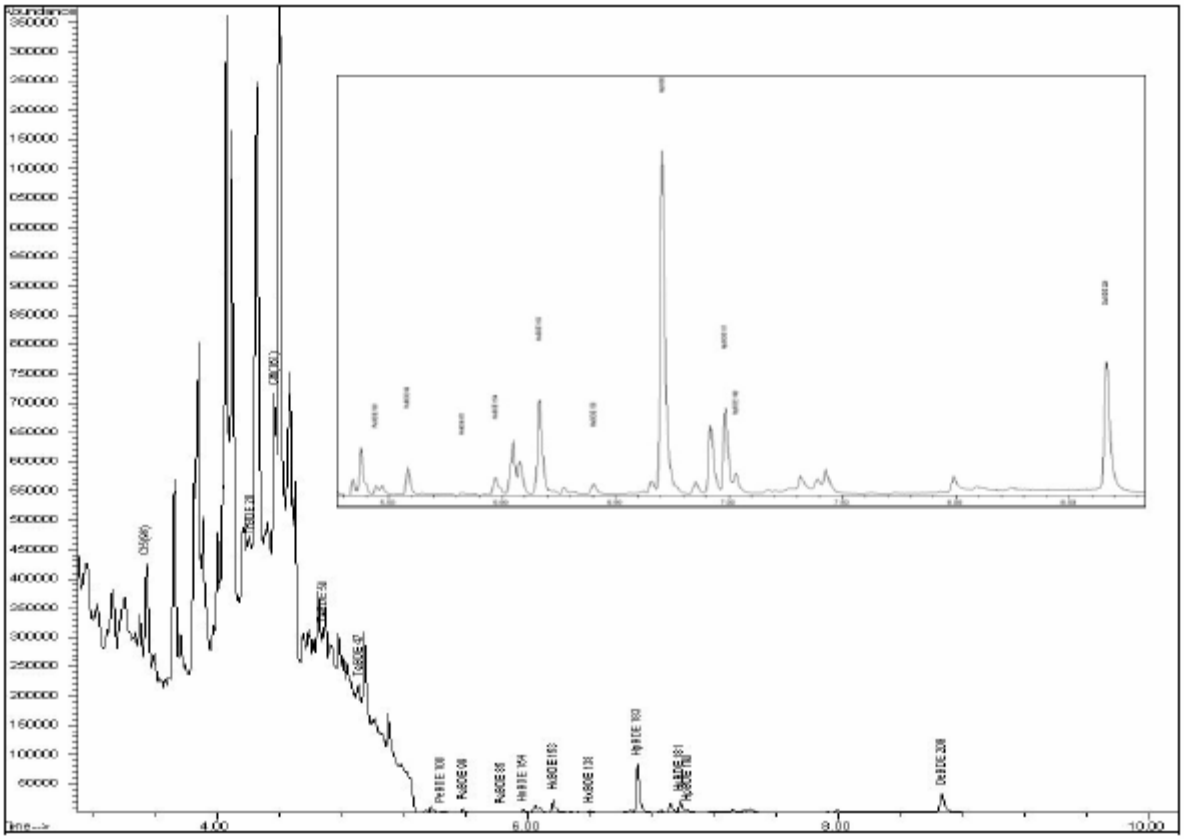


Figure 3c: TIC of NIST 1944

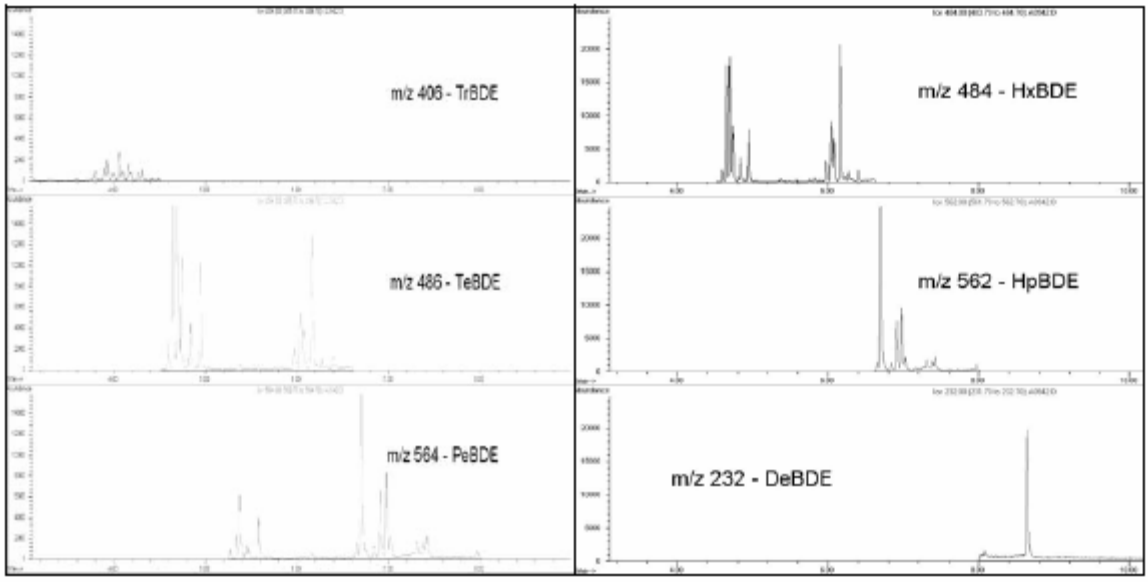
Table 3a: Tissue MDL Values

		Average	Std Dev	%RSD	MDL(ng/g)
TrBDE 17		0.12	0.008	6.897	0.024
TrBDE 28		0.11	0.007	6.195	0.021
TeBDE 47		0.24	0.040	16.529	0.120
TeBDE 66		0.10	0.008	7.921	0.024
TeBDE 71		0.12	0.012	10.345	0.036
PeBDE 85		0.10	0.011	11.579	0.033
PeBDE 99		0.16	0.035	21.605	0.105
PeBDE 100		0.11	0.018	15.929	0.054
HxBDE 138		0.21	0.040	19.324	0.120
HxBDE 153		0.08	0.017	21.519	0.051
HxBDE 154		0.10	0.018	18.182	0.054
HpBDE 183		0.07	0.022	32.353	0.066
HpBDE 190		0.15	0.136	90.066	0.408
DeBDE 209		0.17	0.053	31.928	0.159

Table 3b: Sediment MDL Values

		Average	Std Dev	%RSD	MDL(ng/g)
TrBDE 17		0.05	0.004	7.692	0.012
TrBDE 28		0.05	0.005	9.804	0.015
TeBDE 47		0.12	0.028	23.333	0.084
TeBDE 66		0.05	0.006	12.000	0.018
TeBDE 71		0.06	0.006	10.526	0.018
PeBDE 85		0.04	0.006	15.789	0.018
PeBDE 99		0.06	0.021	32.813	0.063
PeBDE 100		0.04	0.005	12.195	0.015
HxBDE 138		0.10	0.017	16.505	0.051
HxBDE 153		0.03	0.003	9.677	0.009
HxBDE 154		0.04	0.002	5.000	0.006
HpBDE 183		0.03	0.003	10.345	0.009
HpBDE 190		0.03	0.007	24.138	0.021
DeBDE 209		0.09	0.014	16.279	0.042

As newer instrumentation becomes available, more sensitive EI methods can be developed. Newer models of the Agilent LR MSD detectors have higher mass ranges than previous models (up to 1050 amu). Additional studies should be conducted to determine the extent of additional congeners that should be monitored due to the degradation of higher brominated compounds and not just the congeners present in the commercially available mixes, and to ensure that selective bioaccumulation and other biological and environmental processes are considered.



Figures 4b and 4c: Extracted ion profiles NIST 1944 using the PBDE quant masses from Table 1

ACKNOWLEGEMENTS

Special thanks to Gregory Durell and William Steinhauer for reviewing this document. Thanks to Denise Thompson for excellent sample preparation work on both MDL studies.

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Determination of Haloacetic Acids and Dalapon Using a Direct-Inject Ion Chromatography/Tandem Mass Spectrometry

Alan Zaffiro
Shaw Environmental, Inc.

ABSTRACT

The US Environmental Protection Agency (EPA) regulates five haloacetic acids (HAAs) in drinking water. The three analytical methods currently approved for compliance monitoring require sample extraction followed by derivatization of the analytes using either diazomethane or acidic methanol. The EPA is collaborating with Dionex Corporation to develop a direct-injection ion chromatography tandem mass spectrometry (IC/MS/MS) method for HAAs that eliminates the need for sample extraction and derivatization. A new anion exchange column has been developed by Dionex to separate the target HAAs from common interfering anions found in drinking water matrices. Chromatography has been optimized to divert the common anions (post column) thereby preventing matrix suppression of target compounds and improving method robustness. Several isotopically labeled HAA internal standards have been carefully selected for inclusion in the new method. Preliminary assessment of sensitivity as well as method precision and accuracy are encouraging.

EPA Method 536: A New Direct Injection Liquid Chromatography Tandem Mass Spectrometry Method for the Determination of Triazine Herbicides and their Degradates in Drinking Water

Glynda Smith
Shaw Environmental, Inc.

ABSTRACT

Atrazine and related chloro-s-triazines are a class of broadleaf herbicides that prevent the growth of target weeds by interfering with the normal function of photosynthesis. Widespread agricultural application of these herbicides has resulted in an increased presence of these compounds along with their degradation products in both surface and ground waters. The chloro-s-triazines have been evaluated using gas chromatography/mass spectrometry (GC/MS) in conjunction with solid phase extraction (SPE) methods. The polar nature of the degradates complicate the SPE procedures and the low volatility and thermal instability of the target compounds challenge the analytical technique. Thus, liquid chromatography/mass spectrometry (LC/MS) represents a more attractive analytical alternative. Advances in MS/MS detection, which improves selectivity and sensitivity through background rejection, offered the possibility of a direct injection technique. To develop a suitably robust method, however, this approach required careful selection of internal standards to avoid matrix enhancement/suppression. Finally, while occurrence studies have been conducted for this family of contaminants for over a decade, none of the researchers have reported suitable conditions for storing drinking water samples despite literature reports that these compounds are subject to hydrolysis, photolysis and microbial degradation.

Data presented herein demonstrate that the triazines, and in particular their degradation products, are rapidly lost during storage in drinking waters that contain modest levels of free available chlorine. Preservation conditions developed for Method 536 indicated adequate stability for all targets in finished drinking waters from chlorinated municipalities for twenty-eight days. Method precision and accuracy appear to be adequate to support both occurrence monitoring studies and/or compliance monitoring, though the method has not yet been approved by EPA for these purposes.

Innovative EPA Methods for the Analysis of Emerging Contaminants in Drinking Water

Barry Pepich
Shaw Environmental, Inc.

ABSTRACT

The Safe Drinking Water Act (SDWA), as amended in 1996, required the United States Environmental Protection Agency (EPA) to establish criteria for a program to monitor unregulated contaminants, and to identify thirty contaminants that would be monitored over five-year cycles. The SDWA led to the development of both the Contaminant Candidate List and the Agency's Unregulated Contaminant Monitoring Rule (UCMR), which are now in their second cycles. Together, they constitute the EPA's approach for identifying emerging contaminants in drinking water. The intended use of data collected in conjunction with the UCMR places stringent requirements on methods and data reporting since false negative and false positive results both have serious ramifications, and since data must be of known quality. In addition, the intended widespread use of these methods requires that they be easily implemented and robust. The EPA has addressed these challenges by utilizing cutting-edge technologies, by working closely with partner laboratories whenever possible, and by introducing appropriate flexibility into its methods.

This paper describes the methods that the EPA has developed in conjunction with the UCMR for emerging contaminants in drinking water. It also highlights some of the method development projects that are currently underway for emerging contaminants that may be considered by the EPA for inclusion in the next UCMR cycle.

Introducing a New ASTM Standard D 7065-06 for the Analysis Alkylphenols and Their Ethoxylates

Lawrence Zintek
US Environmental Protection Agency

ABSTRACT

Alkylphenol ethoxylates are ubiquitous in municipal, industrial effluents, surface and ground waters and degrade into octylphenol (OP), nonylphenol (NP) and short chain ethoxylates and carboxylates. Some of these degradation products act as endocrine disruptors. The United States Environmental Protection Agency (EPA) is concerned about the presence and amounts of these compounds in water. Analytical standards were made commercially available and methods were developed that could be easily implemented by environmental laboratories.

LC/MS and GC/MS analytical methods will be discussed for the analysis of nonylphenol, octylphenol and their ethoxylates and certain carboxylates. The validation of a new ASTM Standard for alkylphenol analysis will be discussed. Data from airport sewage treatment, POTW's and environmental waters will be reported.

Marine Environmental Monitoring, Changing the Game with Advanced Technologies.

Justin Manley
Battelle Applied Coastal and Environmental Service

ABSTRACT

The marine environment presents many challenges to effective environmental monitoring. Sampling programs typically require the use of vessels, a costly element, followed by analysis of samples in shore based labs. Thus marine environmental monitoring usually does not provide real time results. The costs of operating at sea also reduces the number of samples that can be collected in any one campaign. New technologies may improve the pace, efficiency and scope of marine environmental monitoring.

Battelle's Applied Coastal and Environmental Services (ACES) Product Line in Duxbury, MA is a leader in marine environmental monitoring. With a long heritage and a full complement of vessels, labs, and staff, ACES has been delivering high quality marine environmental monitoring for a variety of clients. Now, through Battelle sponsored IR&D, ACES is working to develop and deploy new technologies for marine environmental monitoring. Specifically ACES aims to develop an integrated suite including an autonomous underwater vehicle (AUV) and water analysis payloads for the vehicle.

AUVs, undersea robots, offer the promise of reduced vessel and labor costs while also increasing spatial and temporal density of data from the marine environment. AUVs have proven their value in deep ocean survey for offshore oil and military mine hunting in the Persian Gulf. Battelle ACES is working to bring online an AUV dedicated to environmental monitoring. The design specifications of this AUV and its expected benefits will be described in this paper.

To accompany the AUV, Battelle ACES is working to develop a water sampling system that will allow the AUV to bring back laboratory quality water samples. The program also aims to include a comprehensive water quality analysis package on the vehicle. Currently available sensors for conductivity, dissolved oxygen, and the like will be complemented by a new system intended to measure a broad array of chemical properties in the marine environment. The final sensor technology is still being analyzed. The paper will describe the research into this sensor and the plans for its construction and testing.

By using a case study of a previous project executed for Battelle clients, this paper will present a concept analysis for the value of AUVs and in situ sensors. Potential reductions in cost and increase in data quality or quantity will be discussed. While the technology development and deployment program at Battelle is in its early phases this paper will provide a valuable introduction to the potential improvements new technology will bring to environmental monitoring. Subsequent papers will provide the opportunity to revisit this subject and quantitatively evaluate the conceptual analysis that will be offered.

Measurement of Haloacetic Acids in Drinking Water by IC-MS/MS

Richard Jack
Dionex Corporation

ABSTRACT

Haloacetic acids (HAAs) are among disinfection by-products that are produced during chlorination of water containing natural organic matter and bromide. Five HAAs are currently regulated in finished drinking water by the US Environmental Protection Agency (EPA). The methods that are approved for compliance monitoring include EPA Method 552.1, 552.2, 552.3 and Standard Method 6251B. These methods are fairly challenging and time consuming as each requires an extraction and derivatization procedure which is followed by gas chromatography (GC) with electron capture detection (ECD) using a procedural calibration technique. Ion chromatography-mass spectrometry (IC-MS and IC-MS/MS) offers a sensitive and selective alternative that does not require sample pre-treatment or procedural calibration. Water samples are directly injected into an ion chromatograph coupled to a triple quadrupole mass spectrometer. The separation of all nine HAAs addressed in the EPA methods is achieved on either a 2 x 250 mm or 1 x 250 mm high-capacity ion exchange column using simple hydroxide gradients.

Excellent peak resolution and linearity are achieved for analyte concentrations that range between 0.4 µg/L and 100 µg/L in a matrix containing up to 250 mg/L each of chloride and sulfate, and 30 mg/L of nitrate. Using 13CClH2COOH as an internal standard, the detection limit is less than 0.4 µg/L for each of the five regulated HAAs and less than 1µg/L for the other four. No significant matrix effects are observed in the synthetic matrix and recoveries of all nine HAAs are greater than 90%. Due to its higher total capacity the 2 x 250 mm column format can handle higher injection volumes than the 1 x 250 mm format; however, the separation time can be significantly shortened to less than thirty-five minutes using the 1 x 250 mm column. This method is currently being evaluated by the EPA at the Office of Ground Water and Drinking Water's laboratory in Cincinnati, Ohio.

PFOS / PFOA and Beyond by On-line SPE Coupled with HPLC – MS/MS

Ali Haghani
MWH Laboratories

ABSTRACT

An integrated on-line SPE-HPLC-MS/MS system has been developed for rapid analysis of various groups of Perfluorinated compounds in surface and drinking water. Seventeen PFCs were included in this study, with various carboxylic, sulfonate, and sulfonamide species among them. Use of Lower Pressure Turbulent-flow chromatography columns LP-TFC as solid phase extraction cartridges enables fast on-line SPE at high sampling flow-rate (3-5 ml/min). Polymeric Oasis HLB LPTFC column allow complete extraction with good recoveries from preserved water samples. On-line coupling to HPLC is performed with re-mixing of the organic LPTFC eluate with water in front of the analytical column to ensure efficient band focusing or a rapid increase and decrease of organic solvent gradient can be used instead for efficient band focusing. For fast HPLC analysis, a short C18 column with 1.8 µm particle size is applied in combination with highly selective API-MS/MS detection. Matrix effects on Electro spray ES-MS-/MS signal were found to be adequately corrected by using isotopic labeled standards. Limits of detection, determined for 1-ml sample were in the range between 1 to 5ng/L typically for carboxylic and sulfonate PFC groups with chain length of C4-C9, and about 20ng/L for sulfonamide and C10-C14 PFCs. At an enriched water volume of 1 ml, the whole SPE-HPLC-MS/MS procedure requires less than ten minutes. The method was successfully applied to the analysis of drinking and source water samples for most of PFCs, the longer chain PFCs C10-C14 needs further refinements.

INTRODUCTION

Organic fluorochemicals (PFCs) are known as one of the 20th century marvels of modern chemistry. In 2001 more than 3000 tons were produced in the U.S. alone. PFCs have many applications including lubricants, paints, food packaging, fire retarding foams, pesticides and carpets.

The PFCs groups of compounds are characterized by chains of carbon atoms of various lengths, to which fluorine atoms are strongly bonded, making some of the indestructible chemicals that until recent years were thought to be biologically inert. However, based on the new studies, on January 30, 2007, EPA posted its outside expert panel's draft report calling PFOA a "likely" human carcinogen, an elevation from the prior "suggested" human carcinogen classification. Initially, researchers focused on PFOA and PFOS only, but more recently interest has increased into other groups of PFCs, which might also be ubiquitous contaminants. There is much published literature discussing analytical methods for PFOS/PFOA in clinical samples, but almost none of the methods cover all of the C4 through C14 PFCs in the same method. PFCs are considered to be emerging contaminants due to possible severe health effects.

In this context, high-performance analytical methods are of essential importance for the precise monitoring of trace level PFCs in the aquatic environment. In most cases, an enrichment step, for instance solid-phase extraction (SPE), has to be performed because of the low concentration level of PFCs in natural waters.

Analysis of SPE extracts obtained from water samples has commonly been performed by HPLC-MS for these polar and ionic compounds. This is reflected by numerous publications reporting on the HPLC-MS analysis of a broad variety of PFCs. Tandem-mass spectrometric detection results in further improved performance, providing additional selectivity and consequently, enhanced sensitivity.

Steadily growing numbers of samples to be analyzed cause the need of higher sample throughput. This requirement may be met to a certain extent by automation of all parts of analytical methods, including sample preparation. With a further significant time benefit, accompanied by increased sensitivity by reducing matrix effect with an on-line sample clean up compared to direct injection, in addition to decreased amounts of sample and solvent required, compared to external sample preparation procedures.

To further reduce the analysis time, integration of high-speed LC column into on-line SPE-HPLC system is recommended. For this reason a C18 4.6-50 mm with 1.8 µm particle size column was used in this study.

EXPERIMENTAL APPROACH

The following compounds were included in this study:

Table 1: Compounds Included in Method and Source

Compound	Name	Vendor
PFBA	Perfluoro-n-butanoic acid	Wellington (Canada)
PFPA	Perfluropentnoic acid	Aldrich
PFHxA	Perfluoro-n-hexanoic acid	Wellington (Canada)
PFHpA	Perfluoro-n-heptanoic acid	Aldrich
PFOA	Perfluoro-n-octanoic acid	Wellington (Canada)
PFNA	Perfluoro-n-nonanoic acid	Wellington (Canada)
PFDA	Perfluoro-n-decanoic acid	Wellington (Canada)
PFUnA	Perfluror-n-undecanoic acid	Aldrich
PFDoA	Perfluoro-n-dodecanoic acid	Wellington (Canada)
PFTrA	Perfluoro-n-tridecanoic acid	Aldrich
PFTA	Perfluoro-n-tetradecanoic acid	Aldrich
LPFBS	Sodium perfluoro-1-butanesulfonate	Wellington (Canada)
PFHxS	Sodium perfluoro-1-hexanesulfonate	Wellington (Canada)
PFHpS	Sodium perfluoro-1-heptanesulfonate	Wellington (Canada)
PFOS	Sodium perfluoro-1-octanesulfonate	Wellington (Canada)
FOSA	perfluoro-1-octanesulfonamide	Wellington (Canada)

Chemicals

Acetonitrile pesticide grade was obtained from Sigma Aldrich. Ultra PFC clean water was prepared in the lab using HPLC grade water (EM) slightly acidified with a few drops of formic acid and run through an Acclaim 4.0- 250 mm column (Dionex, Sunnyvale, CA) and an Atlantis C18 2.1-150 mm 3 um column (Waters, Corp, USA) at 0.3 ml/min and collected in a glass bottle that was baked at 600 °C prior to use. Ammonium acetate salt 98% purity was supplied from Sigma Aldrich. Formic acid ultra pure was obtained from (EM) and ascorbic acid purchased from Sigma/Aldrich. Standards were obtained from Wellington and Aldrich as listed in Table 1.

Sample Materials, Preservation and Pre-Treatment

Water samples were collected in high density polyethylene 150 ml containers. 5.25 mg of Ascorbic acid as a chlorine quencher was added to sampling bottle prior to sampling. Samples collected for determination of PFCs were stored at <6°C prior to analysis only as precautionary step. No investigation has yet been done of the stability of the compounds without refrigeration. Prior to analysis 5.0% (v/v) of Acetonitrile was added to the water samples to prevent analyte losses due to adsorption in the instrument system.

LPTFC Column

A polymer based Oasis HLB column was used for this study.

On-Line SPE-HPLC Coupling

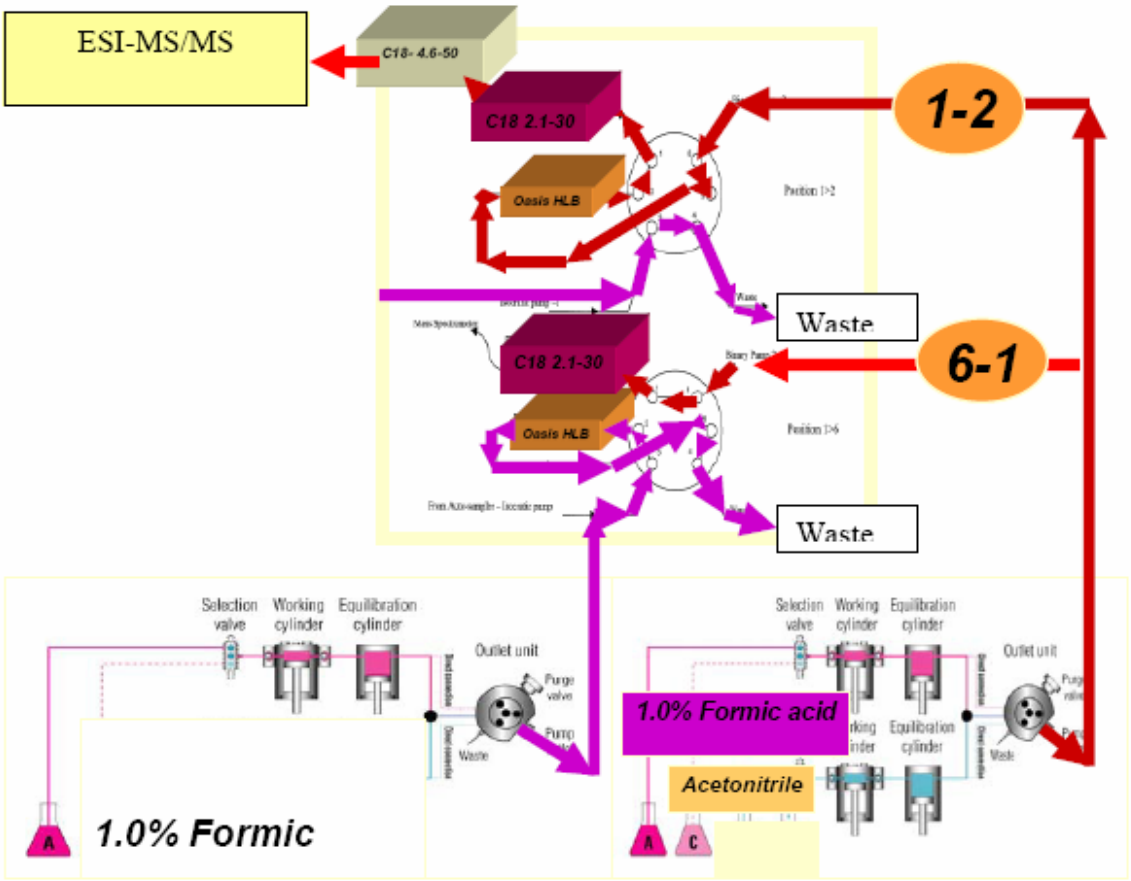
Two binary high performance liquid chromatography HPLC systems were used. An Agilent 1200 SL was used to create LPTFC and a Dionex UL3000 HPLC for gradient chromatography. A Dionex Column heater equipped with a six port valve was used for column switching technique (Figure. 1). Commonly, problems arise from the fact that optimum conditions of SPE elution are in conflict with the requirements of subsequent HPLC gradient analysis. A high organic content of the SPE eluent is desirable to achieve a narrow elution profile, while the contrary is optimum for starting the gradient HPLC. To manage this conflict, our approach includes re-mixing of the organic SPE eluate with water before entering the analytical LC column. Therefore, a T configuration of a mixing chamber was placed between the SPE organic eluate and the analytical column mixing water and the organic eluate to refocus the analytes on the analytical column to be separated by the binary gradient HPLC. The other technique (also performance based) was to increase the organic phase after column switching to 100% just long enough to achieve elution of the PFCs from SPE and immediately drop to 100% aqueous eluent and start the gradient elution after equilibration by the binary HPLC. Since the SPE columns chosen had < 0.1 µl column volume the focusing of the PFCs in conjunction of an acid such as Formic acid could be accomplished in a short time interval. Both techniques results in efficient analyte trapping on the HPLC column and thus, allows starting the subsequent gradient LC analysis under quasi-optimum conditions. The HPLC guard column used prior to the analytical column was a 2.1-30mm C18 Agilent to assist in refocusing prior to the C18 4.6-50mm 1.8 µm Agilent reverse phase analytical column.

API 4000 -MS/MS Conditions

The mass spectrometer used was an API 4000 triple quadrupole (SCIEX) equipped with both ESI (Turbospray) and APCI source (Heated nebulizer). However, the ESI was chosen to do the study since low sensitivity was observed when using APCI. Interface setting and collision gas pressure were manually optimized. Parameter tuning for maximum sensitivity of multi reaction mode MRM detection in negative ion mode was carried out by means of the optimization algorithm supported by the analyst 1.4 software using the Turboionspray interface and a syringe diffusion pump continuously supplying a PFC standard (20 µl/min, C=10 µg/L each compound). The resulting instrument values were then cross-checked for their validity under ESI conditions by flow injection MS/MS analysis (FIA-MS/MS) of the standard mixture and manual variation of the settings.

Experiments on MS/MS optimization, characterization of LPTFC columns and optimization of on-line SPE conditions, experiments, and real sample analyses were performed using the ESI interface.

Figure 1: Flow Diagram for System



RESULTS AND DISCUSSION

Instrumental and Reagent Blanks

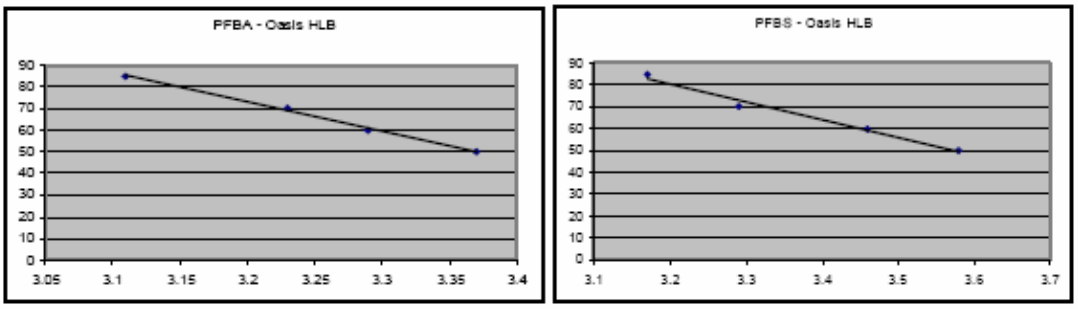
Prior to the analysis of samples, several modifications to the HPLC and experiments on the reagents and columns were conducted to reduce contamination by target PFCs. The HPLC tubing, internal fluoropolymer parts, and autosampler vial septum were identified as possible source of systematic contamination. Therefore, the HPLC tubing's, made up of polytetrafluoroethylene, were replaced with stainless steel and polyetheretherketone (PEEK) tubing. Degasser and solvent selection valves, which have fluoropolymer coatings and seals, were isolated from the HPLC system. Solvent inlet filters were replaced with stainless steel filters or none used. The autosampler vials caps were eliminated from the experiment since most caps contain PFCs. Aluminum foils was used to seal the autosampler vials.

Characterization of LPTFC Column

Breakthrough Experiments

A simplified instrumental setup was used for these investigations leaving out the column switching setup and connecting the SPE to the MS interface directly. First, breakthrough volumes (BTV) were approximated by means of elution chromatographic analyses injecting 10 µL of a 1ppb standard PFCs mixture on the LPTFC column at various eluent compositions (some examples are shown in Figure 2).

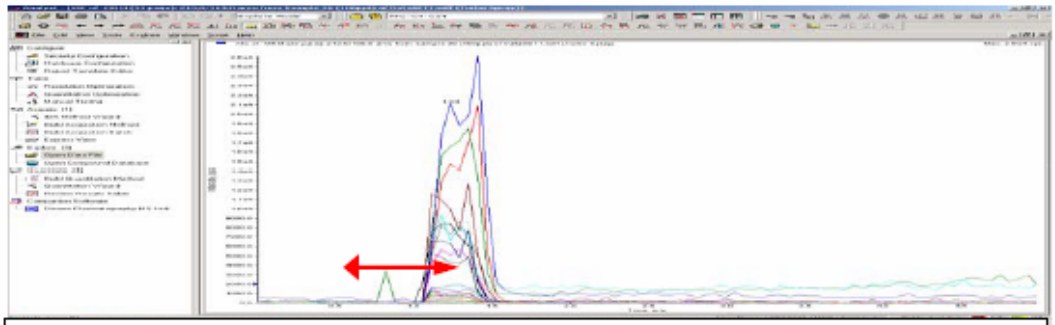
Figure 2: Example Breakthrough volume for the analyte vs. percent acetonitrile used



LPTFC Elution Profiles and Elution Efficiencies

To evaluate the shape of elution profiles obtained from Oasis HLB column 2.1-20mm 30µm particle size, 1 ml samples of ultra PFC clean water spiked with a PFCs standard mixture of 200 ng/L concentration of each PFC were enriched at flow rate of 3-5ml/min using Agilent 1200 SL, and subsequently eluted with 100% acetonitrile into the ESI interface at a flow rate of 0.8 ml/min. Figure. 3 shows the elution peaks obtained from LPTFC column Oasis HLB. A volume of approximately 400 µL of acetonitrile eluent is sufficient to remove all compounds completely.

Figure 3: Elution profile (total ion current 17 MRM) obtained



Oasis HLB O.5 min /0.8ml/min = 400 uL

Performance of the On-Line SPE-HPLC-MS/MS System

In the result of optimization of all parts of the method and equipments, a method program was developed for the enrichment of 1 ml sample.

A "washing" step subsequently to the extraction as introduced to remove matrix compounds from the LPTFC surface, for instance salts and humic substances. About 10-17X column volume was washed with 1% Formic acid containing 2% Acetonitrile prior to elution to the analytical column.

LPTFC elution in back flush mode is performed at a flow rate of 0.8 ml/min of 0.1% Formic for 0.1 ml and a rapid 200 µL of 100% acetonitrile eluent, which is then mixed with 90:10% Formic and acetonitrile eluents at 0.8 ml/min to the C18 2.1-30 mm 20um Agilent guard column and subsequently to the analytical C18 4.6-50 mm 1.8 µm column. To demonstrate the final performance of the system, Figure 4 contains a direct comparison of total ion chromatograms (17 MRM for 17 compounds) obtained from on-line HPLC-SPME-MS/MS of 1ml ultra PFC clean sample spiked at 100ppt and HPLC-MS/MS, respectively. Differences between the resulting traces are minor confirming the efficiency of analyte trapping on the analytical column. The separation quality is good enough to have the retention times as another identification criterion, supplementing the specificity of the precursor and product ion masses. At a sample volume of 1 ml, the on-line SPE-HPLC-MS/MS method requires less than 7 minutes.

Fig 4: Comparison chromatographs of direct/indirect injection

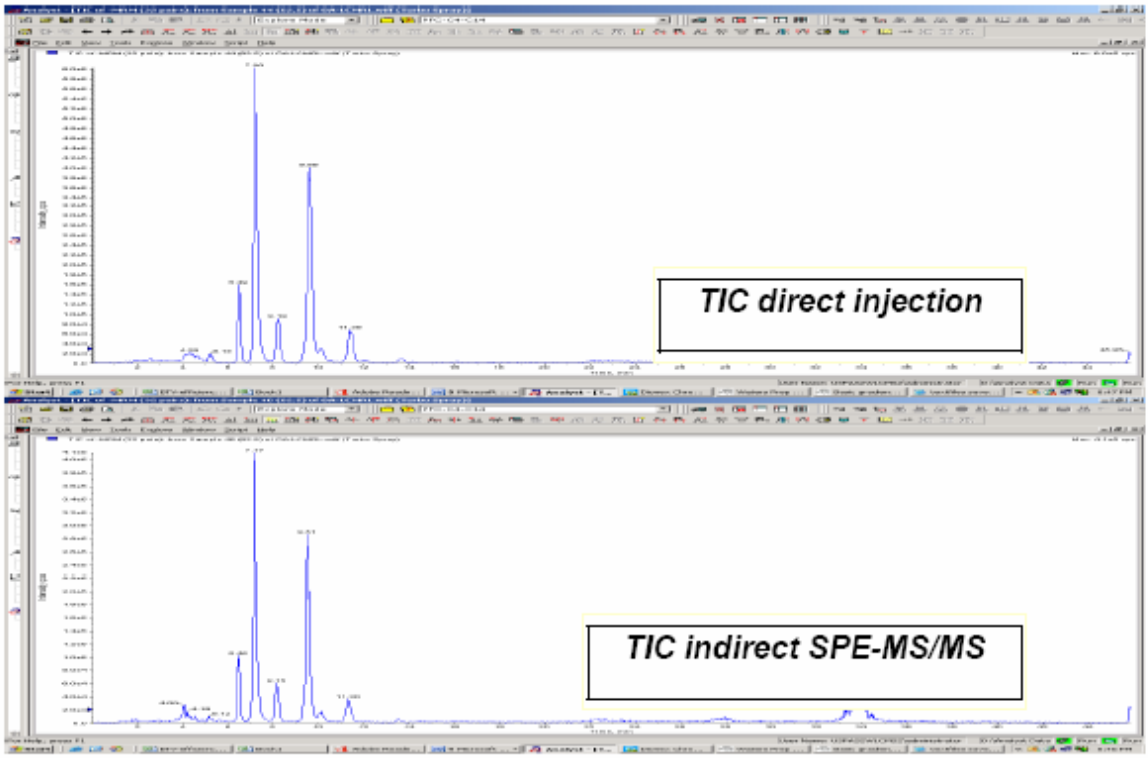


Table 2 and Figure 5 contains validation data of the on-line HPLC-SPE-ESI-MS/MS method, including recoveries, %RSD and standard deviation values (c = 20 ng/L; n = 7), quadratic correlation coefficients of calibration plots and minimum reporting limit. All data were determined for 1 ml samples of spiked ultra PFC clean water in 5% acetonitrile with 50 mg/L ascorbic acid to mimic the field samples collection protocol and sample pre-treatment.

Table 2: LCS recoveries for the indicated MRM and standard deviation (n=7)

Compound PFCs	MRM Q1 – Q3	%Rec. C= 20 ng/L	STDEV (n=7)	% RSD	Quadratic Coefficient	MRL ng/L
PFBA	213/169	85%	0.9361	6%	> 0.990	1
PFPA	263/219	103%	0.7904	4%	> 0.990	2.5
LPFBS	299/80	86%	0.9155	5%	> 0.990	2.5
PFHxA	313/269	85%	0.6256	4%	> 0.990	1.3
PFHpA	363/319	83%	1.3388	8%	> 0.990	4.4
PFHxS	399/80	91%	0.8674	5%	> 0.990	2.6
PFOA	413/369	95%	0.8426	4%	> 0.990	4.4
PFHpS	449/80	77%	1.6881	11%	> 0.990	4.7
PFNA	463/419	92%	1.6277	9%	> 0.990	3.2
FOSA	498/78	92%	6.0827	33%	> 0.990	10
PFOS	499/80	98%	1.4944	8%	> 0.990	6.3
PFDA	513/469	83%	2.2992	14%	> 0.990	5.1
PFUnA	562.9/519	NA	NA	NA	> 0.990	15
PFDoA	613.0/569	NA	NA	NA	> 0.970	25
PFTrA	663/619	96%	5.2344	27%	> 0.980	25
PFTA	713/669	166%	8.7663	26%	> 0.980	25

Figure 5: LCS recovery +/- standard deviation of the recoveries - indirect injection

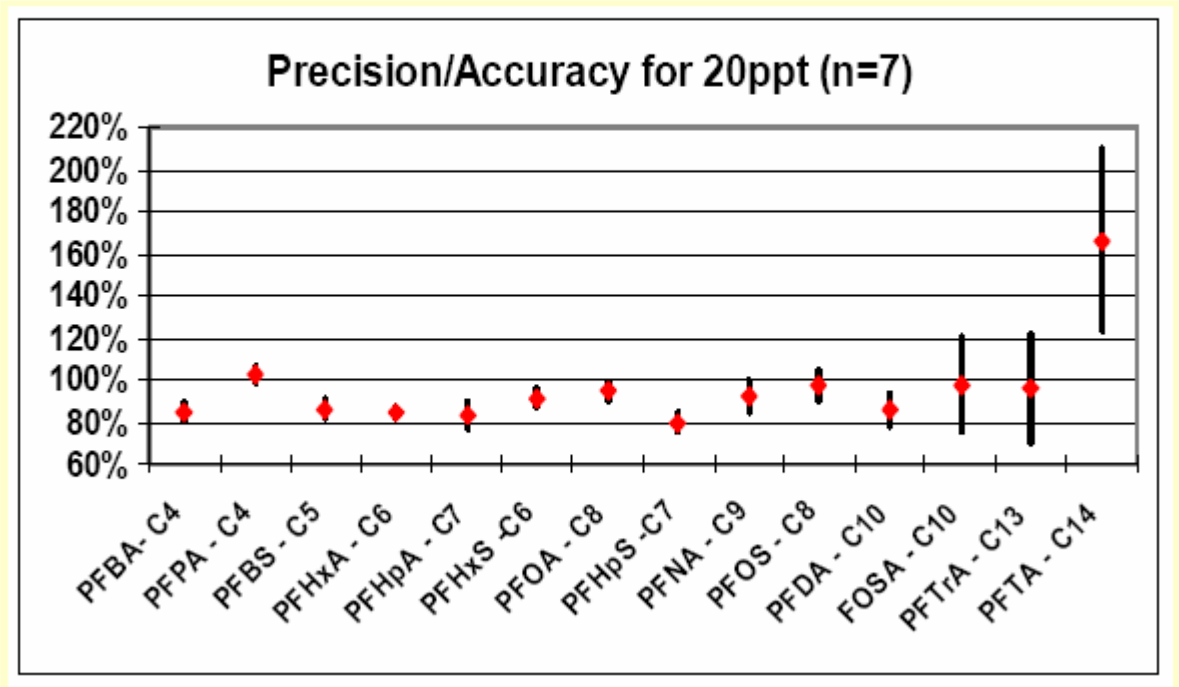
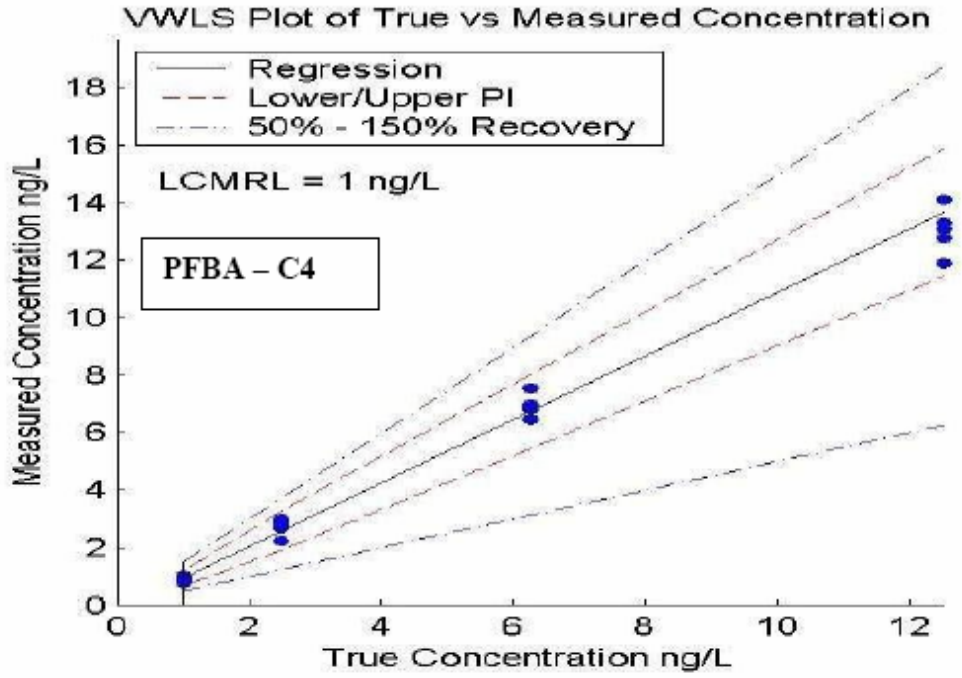


Table 3: Contains the LCMRL obtained analyzing 4 concentrations bracketing the minimum reporting limit at seven replicates.

PFBA	c = 1.25 ppt	c = 2.5 ppt	c = 6.25 ppt	c = 12.5 ppt
Rep 1	0.791	2.80	6.83	14.1
Rep 2	0.933	2.24	7.55	13.1
Rep 3	0.868	2.99	7.53	12.8
Rep 4	0.860	2.67	6.87	13.1
Rep 5	1.04	2.87	6.46	14.1
Rep 6	0.871	2.85	6.45	13.3
Rep 7	1.01	2.85	6.98	11.9



Investigation of Matrix Effects

A set of experiments was performed to evaluate the robustness of the instrumental setup against matrix effects. Special attention was paid to the influence of the water matrix to the MS against intensity (suppression or enhancement effects), which is known to be a serious problem in LC-MS/MS. The experiments were based on comparative analyses of ultra PFC clean and real water sample spiked.

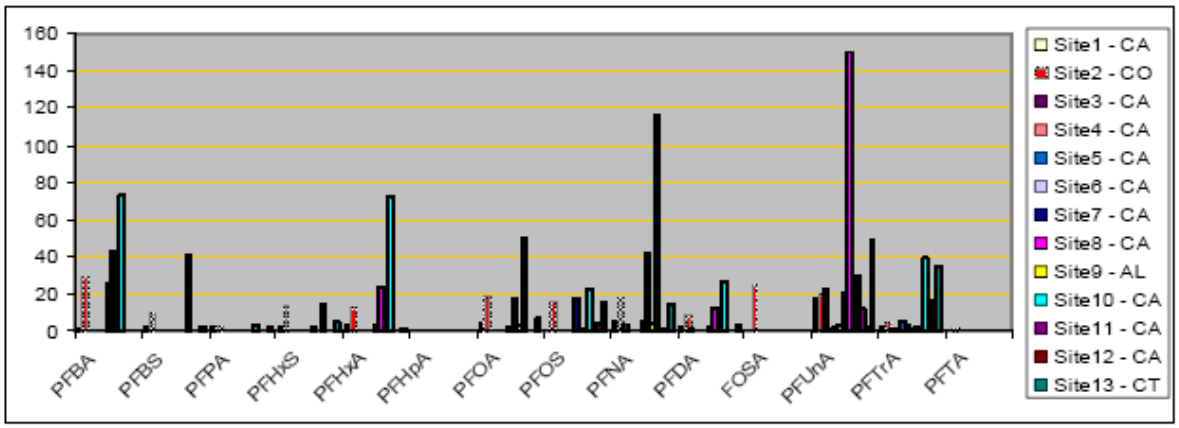
Table 4: Contains back calculation of the source water recoveries for 12, 30 and 60ppt spike amount vs. the recovery of the spiked ultra PFC clean water.

Compound	C = 12	C = 30	C = 60	UCPFCW
PFBA	90%	106%	99%	116%
PFPA	98%	101%	100%	94%
PFBS	109%	96%	101%	90%
PFHxA	111%	94%	101%	88%
PFHpA	98%	101%	100%	82%
PFHxS	110%	96%	101%	82%
PFOA	104%	98%	100%	82%
PFHpS	120%	112%	104%	84%
PFNA	110%	95%	101%	77%
FOSA	101%	100%	100%	93%
PFOS	97%	101%	100%	121%
PFDA	87%	106%	99%	86%
PFTrA	<MRL	105%	100%	53%
PFTA	<MRL	75%	102%	140%
PFDoA	<MRL	105%	100%	43%
PFUnA	<MRL	112%	99%	44%

The recoveries for C4-C9 are within acceptable 70-130% range. However, the recoveries for C10-1C14 showed severe matrix effect, as shown in Table 4

The newly developed method was applied to thirteen source water samples using external calibration and isotopic labeled standard when available. The field sample results are shown in Figure 6.

Figure 6: PFCs results for 13 sites are shown



Next, all 13 samples were spiked at 100 ng/L with a mix standard and analyzed. The recovery and the standard deviation for each spiked compound are shown in table 6 and also shown in Figure 7 & 8.

Table 6: Spiked recoveries of 13 source waters at 100ng/L are tabulated.

Compound	Average recovery	Standard deviation n=13	Compound	Average recovery	Standard deviation n=13
PFBA –ID	89	12.6	PFOS-ID	104	8.5
PFBS	78	8.1	PFNA	98	37
PFPA	91	11.5	PFDA-ID	72	7.1
PFHxS	98	8.5	FOSA	120	38
PFHxA-ID	115	8.9	PFUNA	127	26.3
PFHpA	135	22.6	PFTrA	63	54
PFOA-ID	99	13	PFTA	25	28

Figure 7: Average spike recovery of source waters and the standard deviation (n=13)

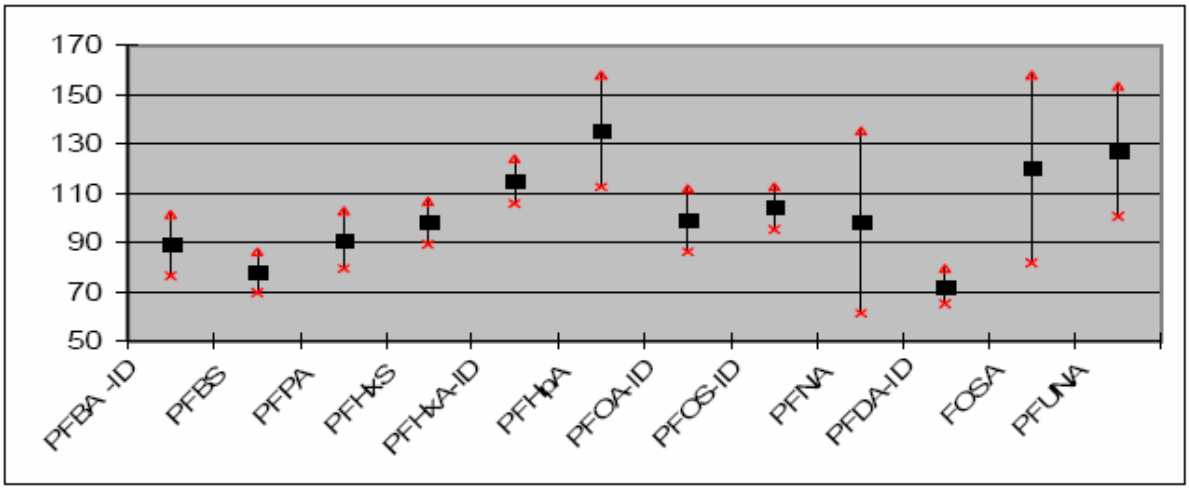
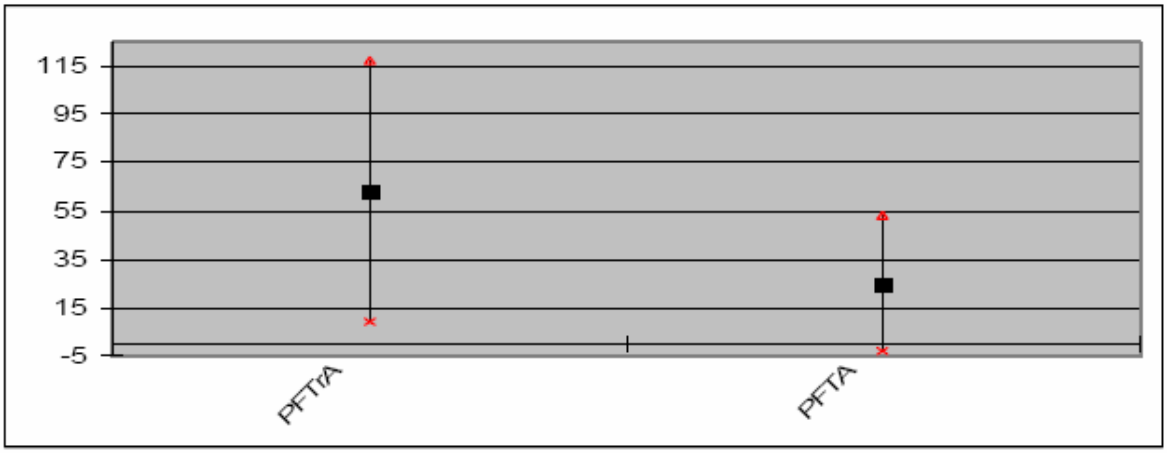


Figure 8: Average spike recovery of source waters and the standard deviation (n=13)



CONCLUSION

A new method for integrated on-line SPE-HPLC-MS/MS system was developed for rapid analysis of PFCs.

With combination of isotopic labeled standards and LPTFC reliable data can be achieved for C4-C9 of PFC groups in ground and clean source waters at low ppt levels. Further method refinements are needed for C10-C14 chains of PFCs.

Currently a new column is being tested and the preliminary results show an overall improvement for the C4-C14 PFCs, which will be discussed and presented during the oral section of this presentation at the NEMC conference.

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Quantitation and Confirmation of Endocrine Disrupting Compounds and Pharmaceuticals and Personal Care Products

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ABSTRACT

Endocrine disrupting compounds (EDC) and Pharmaceuticals and Personal Care Products (PPCP) are environmental contaminants of growing concern. In order to properly assess the effects of such compounds on our environment, it is necessary to accurately monitor their presence in the environment. The diversity of chemical properties of these compounds makes method development challenging. Presented in this work is a method which enables the quantitation of these compounds using Multiple Reaction Monitoring (MRM) and their confirmation using Enhanced Product Ion (EPI) scanning with mass spectral library searching using a 4000 Q TRAP LC/MS/MS system. Automatic software tools were used to generate the library.

Water samples collected in the inlet and outlet of water treatment plants were prepared using Solid Phase Extraction (SPE) and then analyzed in a single injection into an LC/MS/MS system. Up to 100 endocrine disrupting compounds have been analyzed using this developed method. Detection and quantitation of all compounds was achieved down to low part per billion levels (µg/L). In addition, mass spectral library searching was used to confirm the presence of detected contaminants.

Rapid Method Development for BDEs in Human Exposure Assessment Media

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Battelle

ABSTRACT

To assess human exposures to brominated diphenyl ethers (BDEs) in the residential environment, analytical methods are required for diverse matrices for all routes of exposure - inhalation, dermal penetration, dietary and non-dietary ingestion. Development of individualized analytical methods is time-consuming and costly. Since many matrices share common co-extractants, we used the concept of core analytical cleanup methods and a single instrumental method so that only the extraction method needed to be adapted for each matrix.

We developed and validated methods for BDEs 47, 99, 100, 153, 154, 181, 183, 190 and 209 in 12 matrices in three months, with 75-100% recoveries at ppb and sub-ppb fortification levels. Media/matrices included filter/XAD (inhalation); dermal dosimeter suits and socks (dermal penetration); low fat and high fat composite solid foods, infant formula, milk, juice and water (dietary ingestion); house dust, soil, surface wipes and cheese slices (non-dietary ingestion). Core analytical cleanup steps used an acidic silica wash, an acidic/basic silica column, and an alumina SPE cartridge. For a given matrix, 1-3 of these steps was combined with NCI GC/MS, EI GC/MS or GC/ECD; NCI GC/MS was the most sensitive and selective.

Precision and accuracy of methods will be discussed, together with advantages of the cleanup steps and the three instrumental analysis methods.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

Trace Level Analysis of Pesticides Residue in Drinking Water Using ON-Line SPE LC/MS/MS

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Waters Corporation

ABSTRACT

Many countries around the world have strict regulatory guide lines for drinking water quality. To satisfy legislative requirements, analytical methods have been developed to monitor a wide range of contaminants at trace levels using analytical techniques such as gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/tandem quadrupole mass spectrometry (LC/MS/MS).

In order to achieve trace level analysis, large sample volumes are usually extracted using various OFF-Line extraction methods (ex: solid-phase extraction (SPE), liquid-liquid, etc.) and are concentrated into a smaller volume. As an example, a typical extraction method usually starts with a 500 mL of sample and ends up with a final volume of a 100 µL (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. Obviously, manual extraction protocols have reached the end of their limited range. A few years ago, SPE cartridges were reformatted into an extraction column. By combining the extraction column, liquid chromatograph, analytical separation column, tandem mass spectrometer and software, a system is created known as "ON-Line SPE/LC/MS/MS." A major advantage of this integrated platform is the elimination of the labor intense evaporation and reconstitution steps in favor of a direct elution into the mass spectrometer.

This presentation will discuss the performance of ON-line SPE/LC/MS/MS for the analysis of pesticides residues in drinking water. One major advantage is the reduction of sample volume from 1 liter to a 20 mL sample. With a 10,000:1 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 three to five hours to less than five minutes.

ENSURING DATA QUALITY

Quality-in-Depth for Data Integrity

Jeffrey Worthington
US Environmental Protection Agency, Office of Environmental Information

ABSTRACT

Environmental measurements gain value through each process step: planning, sampling, storage, preparation, laboratory quality controls, analyses methodology, and verification and validation. This type of value can be represented by Michael Porter's "value-chain" model framework. Each step in the chain, properly implemented adds value to the resulting environmental measure.

Environmental measures are also information and as such are often stored in databases and used for the project at hand or for other unintended users to demonstrate trends or track historical measurements. As information, there are two key areas that managers should address to ensure the integrity of environmental measurement data during data production and during data storage, transfer, and archival. These two areas may not be accounted for in a typical value chain because the data may ultimately reside in a larger system. The two areas are:

- Information Assurance (i.e., information security) and
- Information Quality.

Information assurance is the process to ensure the confidentiality, integrity, and availability of information services. Quality assurance is the means by which managers plan and ensure the quality of products and services.

A key concept in information assurance is to ensure security through a defense-in-depth approach. Defense-in-depth identifies various perspectives in the overall information system and encourages establishing specific protocols at each level. Quality professionals typically focus on the overall management system and the project planning components. Quality activities include: 1) assuring the quality of processes which impact the product and service quality, and 2) establishing the capability to measure and understand the quality of the products and services.

Quality professionals may benefit from the information assurance defense-in-depth model. Because information is one of the enterprise's critical resources, information presentation and availability can be just as important as the program and project processes which established initial information content quality. Once that content has entered a system, a new model can be applied, a quality-in-depth approach. This suggested approach requires recognition that there are various levels, disciplines, and distinct processes which ensure quality.

This presentation provides a framework for applying quality-in-depth techniques to the overall enterprise's information process including environmental measurements resulting from project and program activities as well as the management of large data collections.

Quality Control for Environmental Contaminant Data Collection – Top Ten Pet Peeves with Traditional Analysis Practices

Ann Bailey
EcoChem, Inc.

ABSTRACT

Over the past thirty years, traditional approaches to the collection and analysis of samples for contaminant concentrations have been developed. Some of the routine methods and quality control criteria have sound scientific bases. Other methods and criteria are remnants from past programmatic requirements, and reasons for their use are no longer (or never were) appropriate or relevant. From a perspective of forty-six years of combined experience in laboratory work, field and lab audits, and data review, the authors have put together their top ten pet peeves with current sample collection and analysis practices (one pet peeve being years of experience being combined for a group of professionals).

Items reviewed will be based on experience with data collected for routine soil and water investigations using standard SW-846 metals and organic methods, as well as experience with projects involving performance-based methods on sediment and tissue samples. Discussion will include arbitrary holding time requirements, collection/analysis of rinsate blanks, prescribed analyte lists, varying qualifier codes, methods of reporting detection limits, twenty digit field identification codes, quality assurance plan preparation/distribution, etc. Attendees will be invited to provide additional nominees for the list.

Integrated Data Management in the New Bedford Harbor Superfund Remediation

Paul Dragos
Battelle

ABSTRACT

Large environmental remediation efforts generate a significant volume of data in a wide range of disciplines including chemistry, toxicology, biology, geophysics, and health science among others. These data may be generated in a range of environmental investigations including site investigations, environmental monitoring programs, and risk assessments all of which frequently require monitoring of both short-term and long-term changes within the environment. Ultimately, data need to be synthesized into focused information products such as trend analyses, fate and transport analyses, biological abundance, and habitat maps, to name a few. The effectiveness of these investigations depends on the system of data management implemented to assimilate, quality assure, manage, archive, and disseminate the environmental data and information. A remediation project case studies is presented for the New Bedford Harbor Massachusetts Superfund Remediation which demonstrate the use of integrated data management methods and lessons learned.

Proficiency Testing, Accreditation and Environmental Laboratory Data Quality

Ken Middlebrook
Canadian Association for Environmental Analytical Laboratories

ABSTRACT

Laboratory accreditation and proficiency testing are important tools used by laboratories to demonstrate competence and performance. Although it is generally accepted that accreditation and proficiency testing (PT) have helped improve the quality of testing data, there have been few studies that have objectively demonstrated this. The Canadian Association for Environmental Analytical Laboratories (CAEAL), because it operates both an accreditation program and a proficiency testing program, has long-term data that can be used to examine these issues. This paper uses long-term PT data to demonstrate that both PT participation and laboratory accreditation have a positive effect on laboratory performance. Because the CAEAL accreditation program relies on volunteer assessors from participant laboratories, an attempt is also made to determine if there is a beneficial impact to a laboratory of having a trained and active assessor on staff. Finally, a preliminary examination of an international PT study (APLAC T055 metals in water) is presented, with an emphasis on the relationship between the level of PT participation (i.e., frequency) and performance.

INTRODUCTION

In general, accreditation is a demonstration of conformance to a relevant international standard (e.g., ISO/IEC 17025) through periodic site assessments, and demonstrated testing performance through appropriate proficiency testing. Accreditation of environmental testing laboratories to an international standard has been available for over twenty years.

Prior to the availability of laboratory accreditation, it was up to laboratory clients and government regulators to develop, implement and monitor a laboratory's compliance to defined specifications. This approach resulted in specifications that varied geographically and often within the same laboratory.

In many Canadian jurisdictions, the detailed specifications in regulations and legislation have been simplified to this statement,

> "***The laboratory shall be accredited to ISO/IEC 17025 by a body that is signatory to the ILAC mutual recognition agreement.***"

Although there is abundant anecdotal evidence that accreditation is linked to an improvement in the quality of testing data, there are very few studies that have looked at this objectively. In large part this is due to the scarcity of long-term objective measures of laboratory performance that can be unequivocally associated with a laboratory's accreditation status. One of the most

prevalent measures of laboratory performance, proficiency testing, is generally operated at arms length from accreditation programs and, therefore, it is difficult to link PT and accreditation records in a single data set. The Canadian Association for Environmental Analytical Laboratories (CAEAL) is one of a few organizations that operate both a proficiency testing program and an accreditation program. As such, it has long-term data on both laboratory performance and accreditation. This paper will use this data to examine the effects of both proficiency testing and accreditation on analytical performance.

BENEFITS OF PROFICIENCY TESTING

The CAEAL PT program maintains a database that is ideal for examining performance trending. This is because laboratory participation is ongoing, not on an as-requested basis, and unique registration codes are assigned to each lab/method/analyte combination. Whenever a laboratory makes a significant change to their method a new registration code is assigned. This results in long-term performance data for specific laboratory/method/analyte combinations.

The relationship between proficiency testing and laboratory performance was examined by compiling all of the CAEAL PT data from 1995 to 2004 (eighteen studies) for laboratories that participated in at least ten consecutive studies. To eliminate the effect of PT participation prior to 1995, all laboratory/method/analyte combinations that participated in the first study of this data set were removed. The remaining data were arranged in an array such that the first participation for any laboratory/method/analyte combination was set to study 1 (Figure 1). There was no effort to separate accredited and non-accredited laboratories because the accreditation status would often change during the examined timeframe.

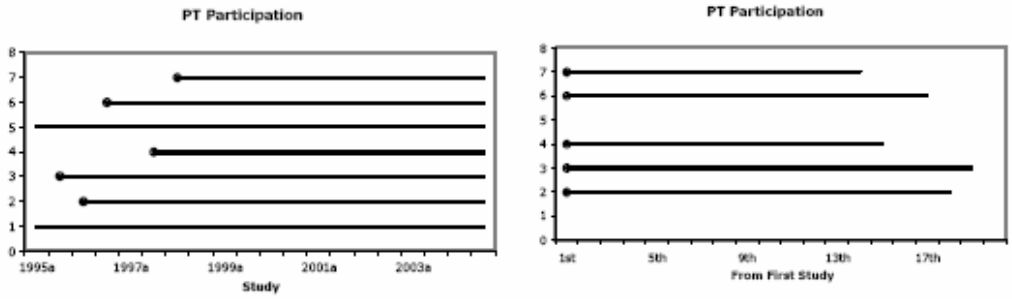

Figure 1: Chart on left depicts the series of laboratory/method/analyte participation. Chart on right depicts the normalized laboratory/method/analyte participation aligned by first participation. Circles indicate the first participation.

After the data were extracted and normalized, a total of eighty-four analytes were included in the data set with a total of 2948 laboratory/method/analyte combinations. The average PT score for all combinations is shown in Figure 2. In general, PT performance increases over the first several studies and then levels off. When separated by test group or by analyte, a similar trend was observed. However, a few analytes did not display an improvement in performance from the first participation; notable amongst these are PCBs in oil, VOCs in water and microbiology.

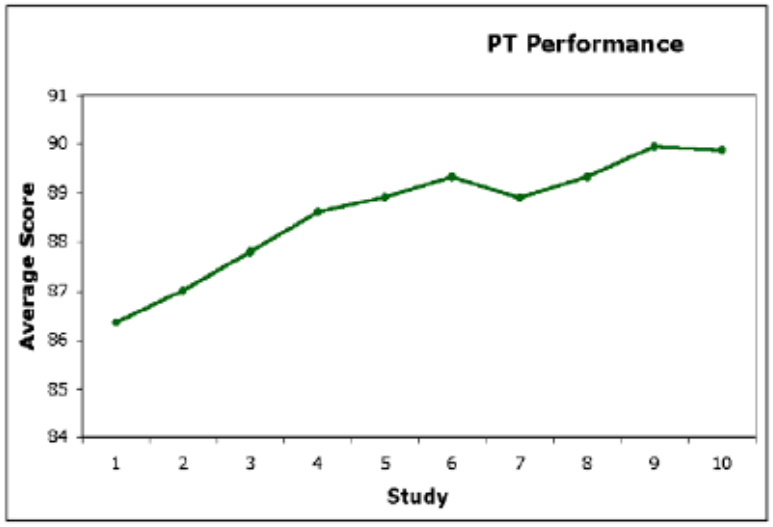

Figure 2: Average PT performance from the first participation.

As the data is a mix of accredited laboratories, non-accredited laboratories and laboratories that obtained accreditation sometime during the timeframe of the data set, the improvement can be attributed to the entire PT exercise. Since the submission and review of corrective action reports for PT failures is integral to the CAEAL program, it can not be discerned whether the improvement is due to PT participation alone or due to the extra level of scrutiny that laboratories go through when they receive an unsatisfactory evaluation.

Similar observations have been made for PT participation in the clinical laboratory industry. Taylor and Fulford (1981), using PT performance as a measure, observed that many clinical tests demonstrated an improvement in performance over time. Hassemer (1996) examined clinical PT performance from 1993 to 1996 (eleven PT rounds) and observed that the percentage of labs with acceptable scores dropped in 1994, due to the influx of a large number of newly participating laboratories (PT participation became mandatory in 1994), followed by a gradual improvement during the next few rounds. These studies further support the conclusion that PT participation has a direct and measurable impact on laboratory performance.

A factor that was not looked at in this paper, but one that is likely significant, is the effect of regulations on PT performance. In areas where the consequences of unsatisfactory PT performance are high, it is reasonable to assume that PT participation will result in disproportionate improvements in quality as compared to areas where the consequences of poor PT performance are low. Again, this is likely the result of laboratories taking a more proactive approach to the investigations of non-conformances and "near misses" than to the act of participation itself.

EFFECTS OF PT FREQUENCY

One of the more controversial issues related to proficiency testing is the optimal frequency at which PT should be run. ILAC P9 indicates a minimum frequency of one study every four years per field of testing. For many fields of testing, this is generally considered to be inadequate, however, there is no consensus on what frequency is appropriate. The reasons for the lack of consensus are many and include the high cost of PT, the lack of availability in some areas and the lack of objective evidence that PT frequency has an effect on data quality.

In October 2006, CAEAL coordinated an international PT study for metals in water for the Asia Pacific Laboratory Accreditation Cooperation (APLAC). There were 114 participants in 33 countries. A simultaneous study using the same samples was also conducted with Canadian laboratories (CAEAL C02B, 58 participants). To see if there was a difference between intra-economy variation and inter-economy variation, we looked at how the estimated assigned values compared between the two studies. As expected, the consensus means were very similar for all of the metals (Figure 3).

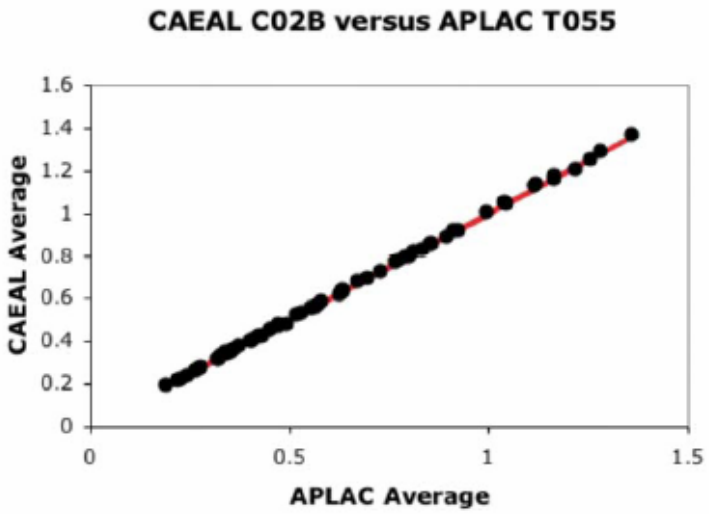

Figure 3: Plot of consensus means for the CAEAL study versus the consensus means for the APLAC T055 study. Means were calculated using the robust procedures detailed in ISO 13528. The line indicates unity.

However, when the consensus deviations were compared it was observed that most of the deviations observed for the CAEAL study were lower than the deviations observed for the APLAC T055 study (Figure 4). There are several possible explanations for this observation, many of which can not be quantified.

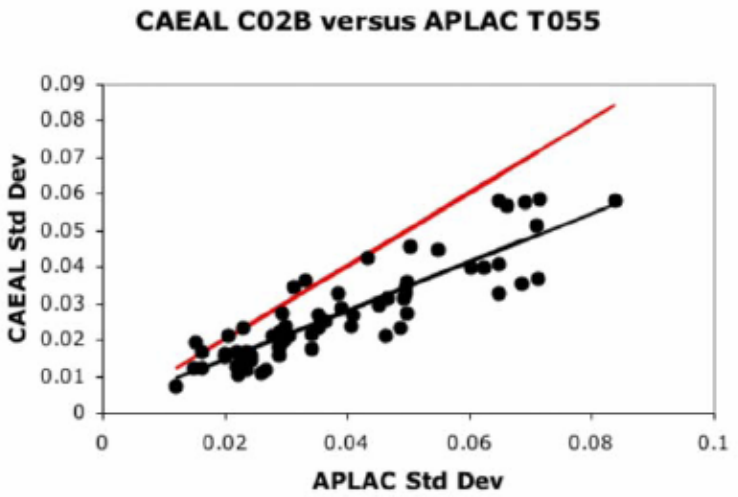

Figure 4: Plot of consensus standard deviation for the CAEAL study versus the standard deviation for the APLAC T055 study. Standard deviations were calculated using the robust procedures detailed in ISO 13528. The top line indicates unity and the bottom line is the regression line (slope = 0.668 ± 0.09).

Familiarity with the PT Scheme

Most participants in the CAEAL study have participated in previous studies from the same scheme. This may provide a comfort level to the Canadian laboratories that was not enjoyed by the other APLAC participants. Although this is a very distinct possibility, it is not one that can be easily examined with the existing data.

The Effect of Developing Economies on Data Variation

It was suggested that this observation may be due to the fact that the CAEAL study is largely restricted to Canadian laboratories that have ready access to supplies, equipment and educated and trained staff whereas the APLAC study also includes a large number of developing economies whose laboratories face challenges that laboratories in developed economies do not. To examine if this was a factor, the APLAC data was separated into data from developed economies and data from developing economies based on the lists available through the World Bank (web.worldbank.org). Figure 5 shows the plot of standard deviations from developing economies against the standard deviations from developed economies. This shows that, in general, the variation in results for developing economies is a little higher than in developed economies but does not account for the differences seen between the CAEAL study and the APLAC study.

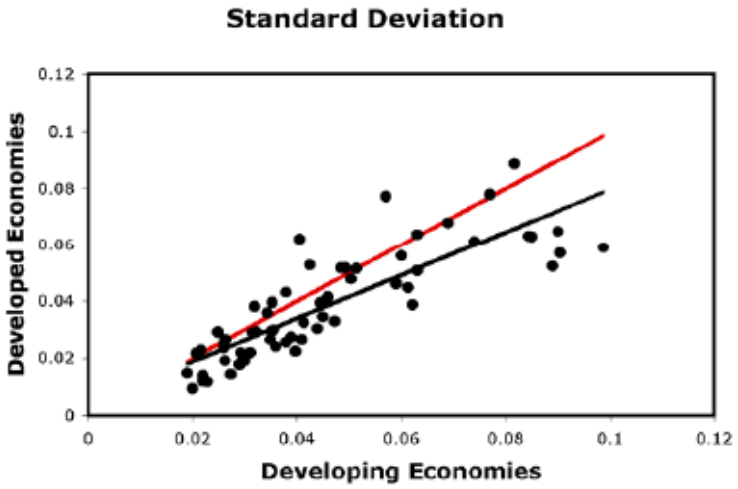

Figure 5: Plot of consensus standard deviation for laboratories from developing economies versus the standard deviation for laboratories from developed economies. Standard deviations were calculated using the robust procedures detailed in ISO 13528 (Slope = 0.763 ± 0.12).

Level of Historic PT Participation

The only other variable that could account for this observation is the historic level of PT participation of the participants. We have already demonstrated that continuous PT participation tends to result in an improvement in performance and that this improvement continues over several studies. Therefore, it is logical to assume that performance is also affected by the intensity (frequency) of the PT participation. The CAEAL PT program has two scheduled studies per year and many of the CAEAL participants have been participating in this test group from its implementation in March 2004 (six studies to date). To try to examine this in greater detail, the APLAC T055 participants were subsequently requested to provide information on the number of metals in water PT studies that they have participated in over the previous four years, excluding the APLAC study.

The data for participants were divided into those that had a high level of PT participation (≥ 2 per year) and those with a low level of participation (< 2 per year). Robust means and standard deviations were estimated for the two groups, excluding any sample/analyte combination with fewer than eleven reported results in either group. Figure 6 shows that the estimated deviations for laboratories with a high level of PT participation were lower than laboratories with a low level of PT participation. The estimated slope for the relationship between high and low level PT participation (0.366 ± 0.07) is lower than the slope between CAEAL and APLAC T055 studies (0.668 ± 0.09), strongly suggesting that PT frequency has a greater impact on laboratory performance than familiarity with the scheme.

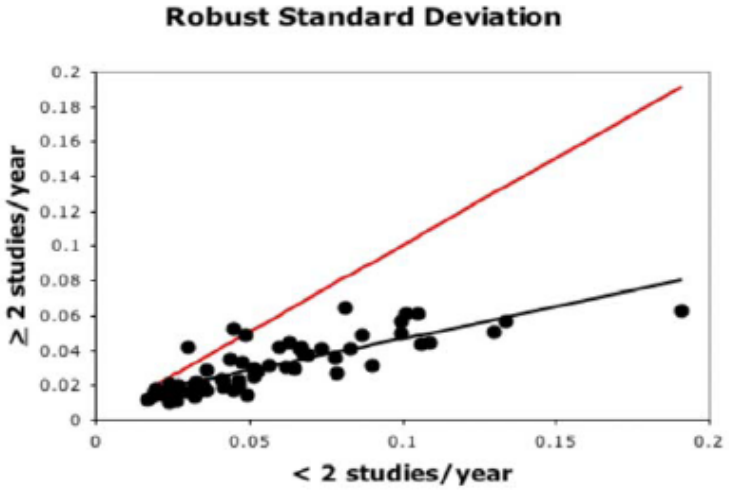

Figure 6: Plot of consensus standard deviation for APLAC participants with a high level of PT participation versus laboratories with a low level of PT participation. The top line indicates unity and the bottom line is the regression line (slope = 0.366 ± 0.07).

The only published paper that has examined the impact of PT study frequency on performance could not detect a measured improvement in performance with an increase in PT frequency from three to six studies per year (Thompson and Lowthian, 1998). The present study, however, clearly demonstrates that higher levels of PT participation have a measurable benefit. One of the reasons for the discrepancy between the two studies is likely that the Thompson and Lowthian study looked at a doubling of PT frequency whereas the current study included PT frequencies ranging from zero per year to ten per year. Unfortunately, there was an insufficient number of participants in the APLAC study to divide the participation levels into a larger number of categories.

BENEFITS OF ACCREDITATION

The CAEAL database contains performance data for both accredited and non-accredited laboratories. Since 2003, CAEAL has been summarizing the performance data for accredited and non-accredited laboratories for each study (www.caeal.ca/pt_accred_vs_nonaccred.html). In all examinations PT performance, as measured by the percentage of unsatisfactory PT scores, was better for accredited laboratories than for non-accredited laboratories (Figure 7).

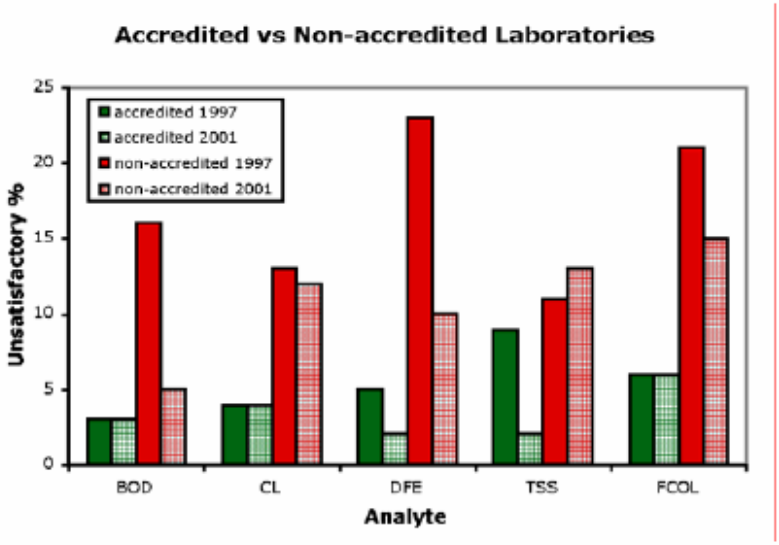

Figure 7: Frequency of unsatisfactory PT scores for accredited and non-accredited laboratories for two years (Morris and Macey, 2004).

COMMITMENT TO ISO/IEC 17025

Although accreditation is a demonstration of conformance to the requirements of ISO/IEC 17025, the process does not guarantee equivalence. It is well known to accreditation bodies that some laboratories take a proactive approach and go above and beyond the requirements of the standard; others do the bare minimum to demonstrate compliance to the standard. Although this is generally understood, there have been no attempts to quantify this difference.

CAEAL's accreditation program relies on the use of volunteer assessors that are made available from the laboratory community. These assessors are trained by CAEAL and must commit to at least two assessments per year over a three year period. The assumption made in this examination is that laboratories that make staff available to CAEAL as assessors are, on average, more proactive in their approach to ISO/IEC 17025 than laboratories that do not. Supporting this assumption is the fact that there is a real cost to laboratories that provide assessors; the laboratory must make these people available to CAEAL for up to two weeks per year. Although CAEAL covers expenses, their salaries are still covered by the laboratory.

PT performance was compared between accredited laboratories with active assessors and accredited laboratories that do not have active assessors. Because of the difficulty in compiling information about active assessors during the time of past studies, only data from the March 2006 study was examined. Figure 8 shows that accredited laboratories with active assessors tend to perform better in the PT program than accredited laboratories without active assessors. There may be several reasons for this observation. One is that, on average, laboratories with active assessors probably have a better understanding and appreciation of quality management systems

due to the training and experience of the assessor on staff. Another is that the laboratory benefits from the technology transfer inherent in laboratory staff visiting other laboratories. Even though assessors must maintain confidential anything observed in a laboratory that they assess, it is unreasonable to assume that they do not adopt practices from assessed laboratories that they perceive to be better than those currently employed in their own laboratories.

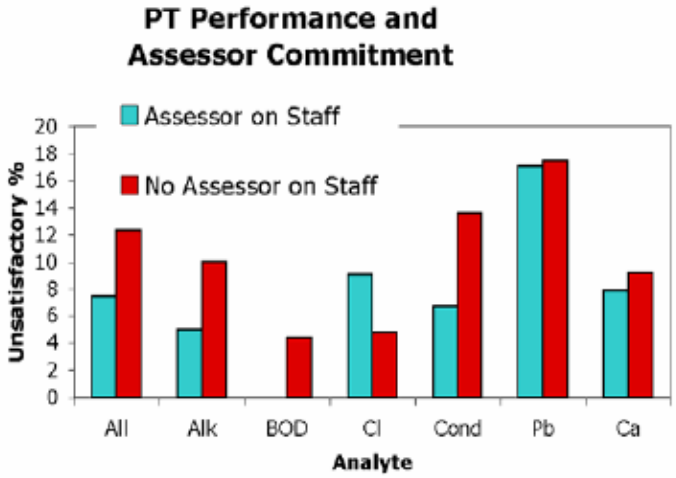

Figure 8: Frequency of unsatisfactory PT scores for accredited laboratories with active assessors and accredited laboratories that do not have active assessors.

CONCLUSIONS

From the data presented in this paper it can be concluded that the benefits laboratories obtain from participation in proficiency testing are real and measurable, and that this benefit can be maximized by selecting an appropriate frequency of PT participation. Further to this, it can be shown that, as a group, laboratories accredited to ISO/IEC 17025 perform better than laboratories that are not, and that these benefits are maximized by laboratory management being proactive and committed to the accreditation process.

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Proficiency Testing, Accreditation and Environmental Laboratory Data Quality

Ken Middlebrook
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Canadian Association for Environmental Analytical Laboratories (CAEAL)

1

OVERVIEW

- Background of CAEAL
- Benefits of Proficiency Testing
- Optimal Frequency for Proficiency Testing
- Benefits of Accreditation
- Differences Between Accredited Laboratories

2

CAEAL

Organization

- Not-for-profit laboratory association established in 1989.
- ISO/IEC 17025 accreditation body.
- ILAC:G13 Accredited Proficiency Testing Provider.
- Training services.

3

CAEAL

Accreditation

- ~200 accredited laboratories, primarily in Canada.
- Signatory to APLAC MRA.
- Signatory to ILAC MRA.

4

CAEAL

Proficiency Testing

- ~350 participants worldwide.
- 40 sample types, >200 analytes.
- Two studies per year per analyte. Four samples per study.

5

PROFICIENCY TESTING

"The accreditation body shall establish procedures to take into account.... the laboratory's participation and performance in proficiency testing."

ISO/IEC 17011:2004

6

PROFICIENCY TESTING

ACLAE CAEAL

Problems with Proficiency Testing

- Not always available.
- Often the most costly part of accreditation.
- Not always appropriate for methodology.
- Labs do not treat PT as routine.
- Method detection limit poorly handled.
- Consensus based deviation does not reflect "fitness for purpose" requirements.

7

PROFICIENCY TESTING

ACLAE CAEAL

Strengths of Proficiency Testing

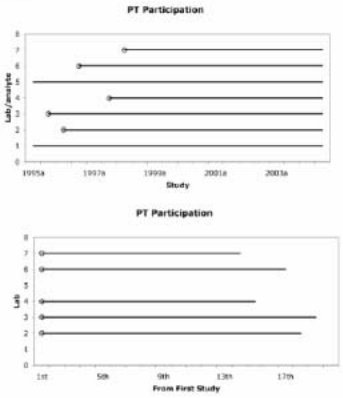
- Is an objective measure of performance.
- PT costs do not contribute to competitive disadvantage for laboratory.
- PT "near-failures" often point to opportunities for improvement.
- Provides confidence in data quality.
- Well designed PT programs are responsive to participant concerns.

8

PROFICIENCY TESTING

Does PT Benefit Laboratories?

- Examined CAEAL PT data from 1994 to 2004.
- Arranged data relative to first participation of lab/method/analyte combination
- 29,840 data points (2,840 lab/method/analyte records).

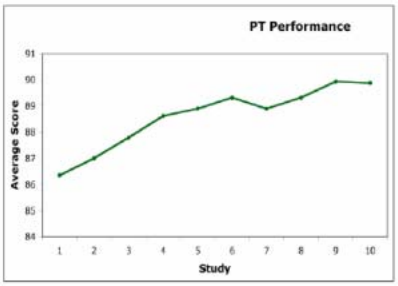


9

PROFICIENCY TESTING

Does PT Benefit Laboratories?

- Most analytes show improved performance over first few studies.
- Similar observations made by Taylor and Fulford (1981) and Hassemer (1996).

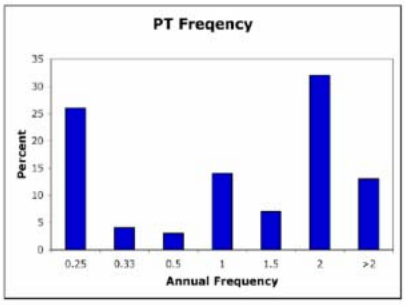


10

PROFICIENCY TESTING

What is the Optimal Frequency for PT?

- ILAC P9 requires a minimum of one PT event every four years per field of testing.
- AB requirements have modes at once every four years and twice per year.
- ILAC P9 is currently being revised to provide clearer direction.



11

PROFICIENCY TESTING

What is the Optimal Frequency for PT?

- Used an international PT study to further examine this.
- APLAC T055 Metals in water PT study (114 participants).
- Run concurrently with CAEAL PT study (50 participants). Using the same samples.

- Compared robust standard deviations between CAEAL data and APLAC data.

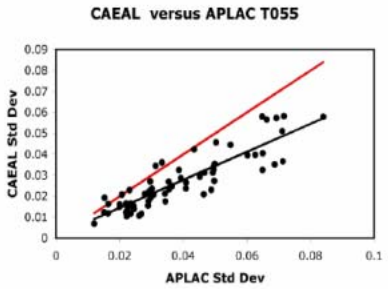
12

PROFICIENCY TESTING

ACLAE
CAEAL

What is the Optimal Frequency for PT?

- Robust deviations consistently lower for CAEAL data. **WHY?**
  - ✓ CAEAL assessments more rigorous than average?
  - ✓ Familiarity with PT Scheme?
  - ✓ Difference between developed and developing economies?
  - ✓ Differences in level of historic PT participation?



13

PROFICIENCY TESTING

ACLAE
CAEAL

What is the Optimal Frequency for PT?

Can the CAEAL assessment process explain the observation?

- CAEAL is signatory to APLAC and ILAC MRAs. Peer evaluated as equivalent to other signatories.
- 60% of the CAEAL participants were not accredited.

ilac-MRA

ACLAE
CAEAL

14

PROFICIENCY TESTING

ACLAE CAEAL

What is the Optimal Frequency for PT?

Can familiarity with the CAEAL PT scheme explain the observation?

- Familiarity with the PT scheme undoubtedly explains some of the data.
- No study has examined the impact of familiarity on PT performance.

15

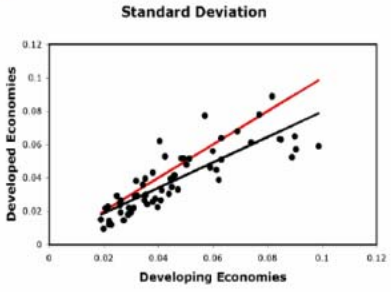
PROFICIENCY TESTING

ACLAE CAEAL

What is the Optimal Frequency for PT?

Can the difference between developed and developing economies explain the observation?

- Separated APLAC data based on World Bank designations of developing economies.
- Spread of results for labs from developing economies may be slightly greater than spread of data from developed economies (Slope = 0.763).



16

PROFICIENCY TESTING

ACLAE CAEAL

What is the Optimal Frequency for PT?

Can level of PT participation explain the observation?

- 80% of CAEAL participants have participated in two PT studies per year for the last two years.
- Only 41% of T055 participants have participated in two or more PT studies per year.
- Can not distinguish impact of familiarity from impact of the level of PT.

17

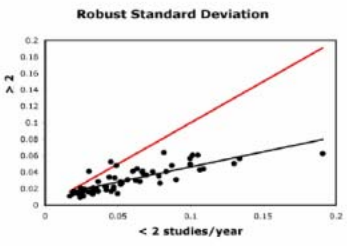
PROFICIENCY TESTING

ACLAE CAEAL

What is the Optimal Frequency for PT?

Can level of PT participation explain the observation?

- Separated APLAC data into labs that participated in < 2 studies/yr and ≥ 2/yr.
- Robust deviation for labs with low level PT higher than deviation for labs with high level PT (slope = 0.366).
- Difference is greater than that observed for CAEAL vs APLAC deviation (slope = 0.668).



- Strongly suggests that level of PT participation has a significant impact on laboratory performance.

18

ACCREDITATION

What Are the Benefits of Accreditation?

- Increased productivity
- Ability to compete in some markets
- Decreases in the cost of liability insurance.
- Greater user satisfaction
- Improved performance
- Increased morale of staff

19

ACCREDITATION

What Are the Benefits of Accreditation?

Increased productivity

- Proper root cause analysis of non-conformances will reduce frequency of non-conformances and repeat testing (i.e., improved productivity).
- Ineffective root cause analysis requires effort and does not reduce frequency of non-conformances (i.e., reduced productivity).

20

ACCREDITATION

What Are the Benefits of Accreditation?

Ability to compete in some markets

- Accreditation mandated in many jurisdictions.
- Increasing requirement for accreditation by customers.
- In areas where accreditation is not specified, perceived benefits of accreditation must outweigh costs before laboratories will adopt it.

21

ACCREDITATION

What Are the Benefits of Accreditation?

Decreases in the cost of liability insurance

- Liability premiums are often lower for accredited laboratories.
- Some regulations that specify accreditation, also specify the level of insurance coverage.

22

ACCREDITATION

What Are the Benefits of Accreditation?

Greater user satisfaction

- Increasing number of users are specifying accreditation.

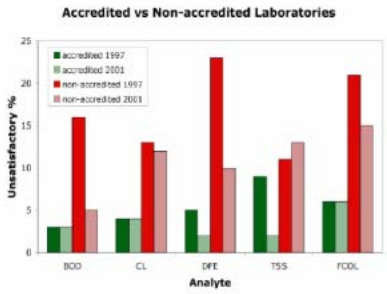
23

ACCREDITATION

What Are the Benefits of Accreditation?

Improved performance

- Accredited labs consistently perform better on PT than non-accredited labs. (*http://www.caeal.ca/pt_accred_vs_nonaccred.html*)



24

ACCREDITATION

ACLAE CAEAL

What Are the Benefits of Accreditation?

Increased morale of staff

- Depends on motivation and attitude of management.
- Seeking accreditation will decrease morale if management think that accreditation is simply a bureaucratic exercise.

25

ACCREDITATION

ACLAE CAEAL

Are All Accredited Laboratories Equal?

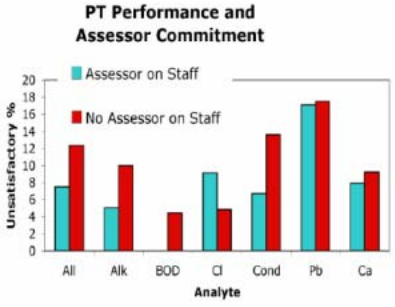
- Fact 1: CAEAL has ~ 150 volunteer assessors, donated from participant laboratories.
- Fact 2: Assessors get extensive training in ISO/IEC 17025 and assessment skills (six day training session).
- Assumption: Laboratories that provide assessors have a high level of commitment to QM systems.
- Prediction: On average, laboratories with active assessors will perform better than laboratories with no active assessors.

26

ACCREDITATION

Are All Accredited Laboratories Equal?

- Observation: In general, accredited labs with active assessors perform better than labs with no assessors.
- Reasons: Labs benefit from training received by assessors? Labs benefit from technology transfer associated with performing assessments?



27

CONCLUSIONS

- Laboratories benefit from proficiency testing.
- PT frequency plays an important role in performance.
- Laboratories benefit from accreditation.
- Not all accredited labs are equal.

28

Analytical Data Validation – Opening Up the Black Box

Anand Mudambi
U.S. Environmental Protection Agency

ABSTRACT

Analytical data produced by laboratories provide a critical foundation for environmental response activities and cleanup decisions. Each year federal agencies spend significant resources to ensure that such data can support its intended use. The review and validation of analytical data generated by laboratories is typically done by parties external to the laboratory. However, there is little consistency in how the external parties describe the nature of the reviews conducted or the procedures used to review and validate the data. These circumstances make it difficult for decision makers to appreciate the quality of the information on which site decisions must be based.

The U.S. Environmental Protection Agency (EPA) Superfund program is considering the use of consistent labels to inform Superfund data recipients about the nature of the review and the procedures used by external parties for analytical data validation. This will also let data recipients know the strengths and limitations of the validated analytical data sets.

The labels are based on general steps (completeness, compliance, recalculations, and review of laboratory instrument outputs) and procedures (electronic, manual, or a combination) used by the EPA and other agencies for analytical data review and validation.

Analytical Data Validation – Opening up the Black Box

Anand Mudambi
US Environmental Protection Agency

NEMC
August 2007

OR

- Tell me what you did when you validated my data AND don't take all day about it!!!

Presentation Outline

- Analytical Data Validation
  - Place in the general flow of project data
  - General basis of data validation
  - Processes used for data validation
- How to convey validation basis and process
- Benefits of conveying this information

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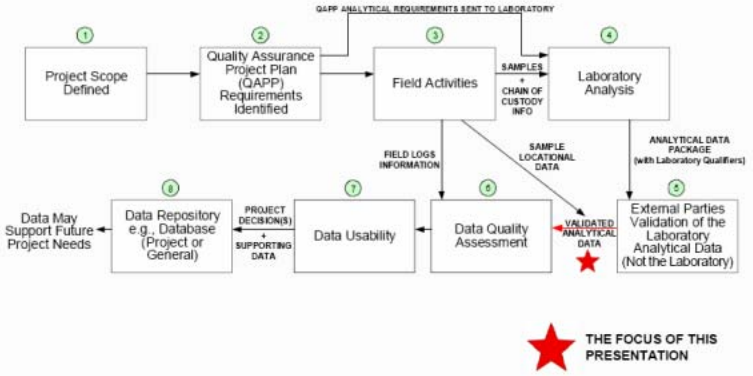
General Data Flow for a Project

FIGURE 1: SUPERFUND DATA GENERATION AND REVIEW



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The Analytical Data Validation "Black Box"

- Each year Federal Programs spend considerable resources to validate laboratory analytical data.
- Validation guidelines vary from program to program.
- No consistent mechanism to indicate what was actually checked during the validation process.

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General Basis for Analytical Data Validation

- Completeness Checks
- Compliance Checks
- Recalculation Checks
- Instrument Output Checks

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Completeness Checks

- This consists of ensuring that all requested data are present and consistent (based on hardcopy and/or electronic reporting requirements).

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Compliance Checks

- This is followed by a *compliance* check which consists of comparing the analytical Quality Control (QC) results in the data package to project specific Quality Assurance Project Plan (QAPP), method, contract, or program validation requirements or guidelines
- The analytical QC results are of two types:
  - Method related QC results
  - Instrument related QC results

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Recalculation Checks

- This is followed by checking laboratory reported values (e.g., sample results) by *recalculating* them using the instrument output data (reported by the laboratory).

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Instrument Output Checks

- This is followed by a review of the *actual instrument outputs* to ensure that the laboratory reported analytes have been correctly identified.

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Processes Used for Analytical Data Validation

- Manual
- Electronic
- Combination of Manual and Electronic

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How to convey validation basis and process

- Provide labels for validated analytical data
- Base labels on the checks and process used for validation

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Label for Validation Based on Completeness Checks

- Stage 1 Validation
- Example Checks include:
  - Completeness of the data package which may include hardcopy, electronic or both
  - Ensure that the data present are consistent within the hardcopy summary tables and instrument outputs as well as between the hardcopy and electronic deliverables, if present

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Label for Validation Based on Completeness & Compliance Checks

- Stage 2a Validation

  if based on Sample-Related Quality Control results
  - Example checks include review of method blanks, Laboratory Control Samples, Surrogates, Matrix Spikes, and Post Digestion Spikes.

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Label for Validation Based on Completeness & Compliance Checks

- Stage 2b Validation
  if based on Sample-Related Quality Control AND Instrument-Related Quality Control results
  - Example checks include review of initial calibrations, continuing calibration verifications, tunes and instrument performance checks.

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Label for Validation Based on Completeness, Compliance & Recalculation Checks

- Stage 3 Validation
  - Example checks include re-calculating laboratory reported sample results using instrument output results, dilution factors, calibration factors, percent moisture (for solid samples).

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Label for Validation Based on Completeness, Compliance, Recalculation & Instrument Output Checks

- Stage 4 Validation
  - Example checks include a review of instrument outputs like chromatograms, mass spectra, and ICP spectra.

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Labels for Process used in Data Validation

- Manual (done on hardcopy by experienced personnel using Professional Judgment).
- Manual and Electronic (done on hardcopy and electronic deliverable by experienced personnel using Professional Judgment).
- Electronic Only (done on electronic deliverable using automated tools)

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Conveying the Basis of and Processes Used in Analytical Data Validation

- All validated analytical data will have a label attached
- Label indicates the basis of and process used for validating the analytical data

Examples of Proposed Labels for Validated Analytical Data

- Stage 1 Validation Electronic Only
- Stage 2a Validation Manual
- Stage 2b Validation Manual and Electronic
- Stage 3 Validation Electronic Only
- Stage 4 Validation Manual

Benefits of Providing Validation Labels

- Opens up the "Validation Black Box" by telling data recipients and users in a short and succinct manner:
  - Checks used to validate the data
  - Process used to validate the data

Benefits of Providing Validation Labels

- Allows for automation of some stages of the data validation process (e.g., use of electronic tools for compliance checks and recalculations)
- Helps integrate manual and electronic processes used for data validation

Next Steps

- Provide guidance on which label to report with the validated data package (based on existing data validation procedures).
  - Currently undergoing an internal EPA review.
- After guidance is finalized, recommend reporting of these validation labels for all validated Superfund analytical data.

Contact Information

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Automated Data Validation – The Good, the Bad, and the Ugly or Why Should a Chemist be Reviewing Your Data?

Pamela Wehrmann
USACE

ABSTRACT

One of the challenges facing professionals in the environmental arena today is the collection and assessment of huge amounts of environmental analytical data. Multi-million dollar decisions for federal projects are made based on those analytical results. Critical to sustaining those potentially expensive decisions are evaluation of the reliability and quality of the data. Data users need to know the both strengths and limitations of the analytical data sets. That knowledge can be gained only from some level of data review or validation.

The validation of analytical data is not a consistent process and the unfortunate reality is that in many cases no one may be looking at the quality of the data at all. This can increase the uncertainty in the decisions being made especially for crucial decisions where life and health can directly be affected. The level of review should be consistent with the nature of the decisions being made with the data.

As we know, all data is not created equal. Electronic software tools are available from many sources to provide at least some minimal level of review for 100% of the data used for site decisions. Automated data review software can provide that first level of validation and allow the professional chemist to focus time, effort, and resources on the specific issues that may develop based on electronic review. Electronic review can provide documentation that some level of validation was done for the site data. What it can't do is provide the in depth knowledge and professional judgment that only the professional chemist can impart. Automated data review is a powerful tool to get that review process started.

Automated Data Validation – The Good, the Bad, and the Ugly or Why Should a Chemist be Reviewing Your Data?

Pamela Wehrmann
USACE, Sacramento District

US Army Corps of Engineers®

Introduction

A rose by any other name…what is analytical data validation, data review, data verification?

- Terms validation, verification, and data review have come to be used synonymously
- Defined as evaluating:
  - completeness,
  - correctness,
  - consistency, and
  - compliance of a data package against an established standard

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Data Validation Standards - Examples

- EPA Regional or National Functional Guidelines
- Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM) Appendix B Summary Tables
- Project-specific requirements as defined in a project Quality Assurance Project Plan (QAPP)

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Data Validation Process - Ideal

- Would be dependent on the use of the data and decided before data is collected
- Processes used would be consistent, data quality indicators to be reviewed would be consistent, and data flagging would be defined
- After data validation, data users would know the both strengths and limitations of the analytical data sets in order to make informed decisions

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Data Validation Process - Reality

- Generally not dependent on data use
- Processes are often not consistent
- Unfortunate reality is that in many cases no one may be looking at the quality of the data prior to its use

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Common Data Validation Issues

- Level of review is directly related to:
  - budget
  - schedule
- Data validation is frequently seen as an unnecessary cost and /or schedule delay
- Tight schedules and budgets can push data review to a limited sub-set of the overall data collected
- Data users or decision makers need to be aware of the added uncertainty in making project decisions on data with limited review or un-verified data

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No Surprises!

- Critical - if the data is to be used for site decisions then the quality of the data supporting those decisions should be known

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Three Types of Analytical Data Validation Processes

- Manual with professional judgment,
- Electronic (automated software) only, and
- A combination of electronic and manual with professional judgment.

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Manual Validation with Professional Judgment

- Minimum - review of the content of the hard copy, data package completeness
- Maximum – includes assessment at the level of detail such as raw instrument output
- "Manual validation" can consist of every imaginable combination of data elements between the two extremes noted above

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Manual Data Validation Issues

- Costly
- Not all data quality elements can be reviewed in a timely manner
- Leads to "partial validation" of data sets
- Data may need to be used before validation is completed

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Electronic Data Review - Benefits

- Allows for 100% review of project data
- Standardizes routine review of many data quality elements
- Saves the time that would be needed to review the same elements in large data sets by manual methods
- Saving time = Saving money
- Reviewer can focus time, effort, and resources on the specific issues that may develop based on the electronic review and / or review additional data quality elements

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Manual Validation Still Necessary

- A number of data elements require the skills of a data reviewer
  - review is not easily automated or
  - data element is not captured simply in an electronic deliverable
- Some examples:
  - Chain of Custody
  - Calculations
  - Carryover
  - Retention Time Shifts / Retention Time Windows
  - Compound Identification (false positives or false negatives)
  - Compound Confirmation (second column or detector)
  - Internal Standards
  - Data Usability / Legal Defensibility

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Benefits of Combining Electronic & Manual Validation

- Automated data review software can provide that first level of validation for routine analytical method quality elements
- The professional data reviewer can be free to focus time, effort, and resources on the specific data quality issues and perform a reality check on the results of the electronic review
- Electronic data sets allow for easy data reporting and sharing among project stakeholders

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Electronic Data Review Software

- Allows project laboratories to verify electronic data deliverable (EDD) completeness and contract compliance
- Allows data users to perform the data review against program specific, method specific and/or project specific criteria

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Data Elements Reviewed Electronically

- Technical holding times
- Instrument tune and system performance
- Calibration (IC and CCV)
- Blank contamination
- Laboratory control sample (LCS/LCSD) %R
- LCS/LCSD RPD
- Surrogate spike percent recoveries
- Field duplicate RPDs
- Matrix spike (MS/MSD) %R
- MS/MSD RPD
- Detection Limit / Reporting Limit verification
- Target analyte list verification

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Benefits & Limitations of Electronic Review

- Benefits:
  - 100% of the data can be reviewed quickly and efficiently
  - standardizes normal method review elements
- Limitations:
  - software can't replace the professional judgment of a qualified data reviewer
  - automated software is intended to be a tool for data review and still needs a reality check

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The Good, the Bad, & the Ugly

- Electronic software can review 100% of even large data sets for routine method quality elements saving both budget and schedule
- However after electronic review the data is often mistakenly thought to be usable without the assessment of a data professional, increasing the risk of poor or incorrect project decisions
- In many instances data maybe used for project decisions without the benefit of any technical quality assessment.

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Summary

- There hasn't been a software program written that can review all data quality elements in a typical data package, thus some elements must be reviewed manually, primarily because they aren't captured electronically.
- Electronic review out put needs a reality check and usability assessment.
- Electronic review software used as a tool by the data review professional can be an efficient cost saving first step in assuring data quality for informed project decisions.

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FIELD MEASUREMENTS

Accreditation Requirements for Organizations Performing Field Sampling and Measurement: An Overview and Update of the TNI Field Activities Standard

David Speis
Accutest Laboratories

ABSTRACT

It is well understood that the quality of environmental laboratory data can only be assured if minimum performance standards exist for field sampling and measurement activities – the "front-end" of the environmental data generation process. The control of environmental laboratory analytical processes and field sampling and measurement processes are of equal and significant importance in assuring the production of scientifically valid environmental data that can be used with a high degree of confidence by the end-user.

Accreditation standards have been developed and implemented by many State accrediting bodies for environmental laboratories that foster the generation of environmental laboratory data of known and documented quality through the development a national performance standard. However, data quality cannot be assured until standards for field sampling and measurement organizations are developed to close the quality loop for the generation of known quality environmental data.

The NELAC Institute (TNI) Field Activities Committee (FAC) has developed accreditation standards for field sampling and measurement organizations (FSMO) that assures field processes are conducted under a control system that is consistent with the needs of environmental data users and international standards. These standards have been developed as a separate sector within the TNI standards development framework. Standards development under a separate sector provides the opportunity to develop a standard that accommodates the unique operational style of the FSMO community without incorporating unnecessary requirements specific to laboratory organizations that operate differently than FSMOs.

The FSMO standard follows the requirements and format of ISO 17025 and ISO 17011, including additional specifications and clarifications of existing specifications, while eliminating requirements that are not applicable to FSMOs. Although the standards development process has essentially been completed, policies and procedures are under development to resolve several applications dilemmas including multi-facility accreditation, conduct of field assessments, development of media-specific requirements, conduct of proficiency testing and in-line monitoring accreditation.

Key elements of the FSMO accreditation standard will be described, focusing on the application of the TNI standards development philosophy. An overview and update on the standard's status, consortium application policies, unresolved issues, and the next steps towards adoption and implementation will also be discussed.


ACCUTEST Laboratories
IT'S ALL IN THE CHEMISTRY
Accreditation Standards For Organizations Performing Field Sampling And Measurement
National Environmental Monitoring Conference
Cambridge, Massachusetts
August 2007
David N. Speis
Director, Corporate Quality Assurance
Accutest Laboratories, Dayton, New Jersey
1958 - 2008
50
YEARS OF EXCELLENCE
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IT'S ALL IN THE CHEMISTRY
Field Sampling & Measurement Organization (FSMO) Standards Development
* The Sampling and Analysis Dichotomy
* FSMO Accreditation Standard Philosophy
* FSMO Accreditation Standard Elements
* FSMO Accreditation Policy
* Implementation for Accreditation
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Field Sampling and Measurement Organization

"FSMO"

Organizations engaged in environmental sampling for laboratory analysis and/or field measurement (analysis) using field based analytical technologies performed in the field outside of a fixed-laboratory or outside of an enclosed structure which meets the requirements of a mobile laboratory .

LabLink™
REAL-TIME ACCESS TO YOUR TEST DATA

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IT'S ALL IN THE CHEMISTRY

The Sampling & Analysis Dichotomy

* **Laboratory Operation & Accreditation Requirements**
  - Accreditation Required to Produce Regulatory Data
    - License to Conduct Business
  - Quality System (ISO 17025)
    - Specific Operational Elements
  - Internal and External Assessment
  - Proficiency Testing

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The Sampling & Analysis Dichotomy

* **FSMO Requirements**
  - Absence of Regulatory Oversight for Accreditation
  - Accreditation Unnecessary (No Licensing)
  - Quality System Not Required for General Operations
  - Assessments Rarely Performed for Field Operations
  - Less Rigorous Standards for Field Data Generation

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IT'S ALL IN THE CHEMISTRY

Environmental Data Quality Cannot Be Guaranteed Unless There Are Quality Standards for All Steps of the Sample Collection and Analysis Process.

"The Quality of the Data Can Only be as Good as the Quality of the Sample"

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IT'S ALL IN THE CHEMISTRY

FSMO Accreditation
Standard Development Philosophy

* Broad Scoped Standard
  - Limited Specificity-Compliance Flexibility
  - Applicability for Wide Range of FSMOs
* ISO Foundation - TNI Consistency
  - ISO 17025 (FSMO Competency)
  - ISO 17011 (Conformity Assessment – AB)
* Employs a "Less is Better" Approach

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ACCUTEST Laboratories

IT'S ALL IN THE CHEMISTRY

FSMO Accreditation
Standard Development Philosophy
The "Less is Better" Approach

* FSMOs Inexperienced in System Accreditation
  - High Entry Barriers Increase Participation Opposition
* Does Not Duplicate the Laboratory Standard
  - Documentation Intensive
  - Parochial Requirements
  - Evaluate Necessity of NELAC & ISO Elements
* Minimal Prescriptiveness
  * Flexibility Facilitates Implementation

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ACCUTEST Laboratories

IT'S ALL IN THE CHEMISTRY

FSMO Accreditation
Standard Development Philosophy
Advantages of The "Less is Better" Approach

* Increased FSMO Buy-In
  - Implementation Simplification
* Increased Accrediting Body Buy-In
  - Manageable Program Administration
  - Auditable Specifications
  - Manageable Resource Requirements
    - *Requires Knowledgeable Assessors*!!

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ACCUTEST Laboratories

IT'S ALL IN THE CHEMISTRY

FSMO Accreditation Standard Elements

* Generic Application of ISO 17025 and ISO 17011
* Borrowed Applicable Language from Existing Laboratory Standard
  - Non-Applicable Requirements Eliminated
  - Administrative Requirements Stripped
  - Added Requirements Specific to FSMOs
* Removal of AB Accreditation Policy
* Applied TNI ISO Standards Development Model

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ACCUTEST Laboratories

IT'S ALL IN THE CHEMISTRY

FSMO Accreditation Standard Elements
Field Activities as a Sector

* Volume 1: General Requirements for Field Sampling and Measurement Organizations

"FSMO Competency Standard"

- Management System
- Technical Requirements
  - Quality System Fundamentals Included
  - Specifications Less Prescriptive - Flexibility
  - Specifications Designed for FSMO Applications

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FSMO Accreditation Standard Elements
Field Activities as a Sector

* Volume 2: General Requirements for Accrediting Bodies Accrediting Field Sampling & Measurement Organizations

- Accreditation Body
  - System Recognition Required
  - Program Manual Specifications Detailed
  - Defined Program Organization Specified
  - Personnel and Training Requirements Detailed
  - Assessment Performance Documentation Specified

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FSMO Accreditation Standard Elements
Field Activities as a Sector

* Volume 2: General Requirements for Accrediting Bodies Accrediting Field Sampling & Measurement Organizations

- Accreditation Process
  - FSMO Specific Accreditation Process
  - Matrix Specific Accreditation Award – Broad Basis
  - Detailed Application Specifications
  - Allowances for Third Party Assessments
  - Assessment Conduct Specified

LabLink™ REAL-TIME ACCESS TO YOUR TEST DATA

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Accreditation Policy

* Accreditation Process
  - Accreditation Award
    - Employs The Umbrella Concept
  - Compliance Verification - Assessment

* Assessment Procedure
  - Common Organizational Quality System
  - Selected Facilities by Organization
  - Field Assessments of Quality System

* Media Specific Requirements
  - No Media Specificity –Generic Requirements
  - Granting of Accreditations by Abs
    - Awarded Based on Matrix, Minimizes Bureaucracy

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Future of the Field Activities Standard
"Implementation for Accreditation"

* TNI Board Approval of Accreditation Policy
* Standard Has Been Finalized
  - Commercially Availability - Late Summer
* Accrediting Body Buy-In
  - Resources Required
  - Potential Revenue Stream
* FSMO Buy-In
  - Reasonable & Achievable

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FSMO Competency Standard (Vol. I)
Application in a Commercial Setting

* Commercial Entities Do Not Accredit FSMOs
  - Commercial Entities Assess FSMO Competency
* Conformity Assessment (AB) Standard Not Needed for FSMO Qualification.
* Conformity Assessment Policies Unnecessary in Commercial Settings
  - Competency Standard as Contractual Specifications
  - Qualify Organizations Based on Compliance
  - Conduct Evaluations as Necessary

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Contact Information

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Vice-Chair, TNI Board of Directors : David Speis

732.329.0200

davids@accutest.com

Executive Director, TNI: Jerry Parr

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In-Situ Analysis of Soil and Groundwater Using a High Temperature Membrane Interface Probe: Proof of Concept and Performance Testing

Albert Robbat
Tufts University

ABSTRACT

A paucity of effective methods is available to quantify and characterize the presence of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) in soil and groundwater. Conventional subsurface sampling and analytical techniques are usually selected because of user familiarity, availability, and regulatory acceptance. Even so, data quality provided by conventional sampling and analysis techniques is typically limited by human subjectivity and bias throughout the life cycle of a conventional sampling program, with data density low due to the cost of acquiring and analyzing samples in the laboratory. As a result there is a natural market demand for methods and techniques that can increase the subsurface resolution (contaminant profile) of chemical data and decrease the time and cost associated with obtaining this information so that decision making in the field is facilitated.

To support the dynamic workplan process a new tool, the High Temperature Membrane Interface Probe (HT-MIP) was developed. The HT-MIP uses a heated membrane (130°C) and a heated sample transfer line (300°C). The MIP has been successfully used and acknowledged by the U.S. Environmental Protection Agency (EPA) as an acceptable tool for in-situ analysis for VOCs. The HT-MIP makes possible the in-situ thermal extraction of organics bound to soil, with real-time detection of pollutants by photoionization detection (PID) of polycyclic aromatic hydrocarbons (PAHs) and other organic compounds in soil and groundwater. Gas chromatography/mass spectrometry (GC/MS) is coupled to the HT-MIP to speciate and quantify PAH in the sample, with correlation between the PID and GC/MS > 0.92. The use of the HT-MIP should facilitate onsite sample collection and analysis using modified SW-846 GC/MS methods optimized to meet field conditions.

Results of the bench study and field performance tests will be presented. Results indicate that the HT-MIP can detect and quantify PAH in MGP-impacted materials in close to real-time. Field and verification sample data demonstrate onsite instrument performance versus conventional sample collection and analytical methods, and comparison of the qualitative performance of the innovative equipment versus conventional technologies. Strengths and limitations will be discussed to further refine technology performance, establish appropriate technology performance benchmarks, and to facilitate acceptance by practitioners, regulatory agencies, and remediators.

Overview of the ITRC's Latest Publication: Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Ground Water

Dee O'Neill
Columbia Analytical Services, Inc.

ABSTRACT

Because of the growing interest in the field of passive sampling, there are a number of devices that have been identified as viable passive sampling tools. The ITRC's Passive Diffusion Team furthered their technology review of twelve passive sampling devices to investigate the five most commercially viable samplers. They are the Snap Sampler®, The Hydrasleeve®, the regenerated cellulose dialysis membrane sampler, the Rigid Porous Polyethylene samplers and the Gore Sorber®.

A quick overview of passive sampling and a discussion of each of the samplers will be given. Copies of the document will be made available for those wanting to study the protocols in more depth.

Potential Limitations of Immunoassay Screening for Site Characterization: How to Make It Work at Your Site

Gregory Durell
Battelle

ABSTRACT

Immunoassay (IA) analysis is increasingly used in environmental investigations, including for rapid sediment screening (RSS). The benefits include cost savings, rapid turnaround time, and the ability to analyze more samples and thus more thoroughly characterize the study area than with standard laboratory analysis. It has, however, become clear that there are also some important possible limitations of RSS that are often overlooked. These limitations may result in considerably over- or under-estimating the contaminant concentrations if they are not identified and addressed, possibly having significant adverse consequences on environmental decision making. Results will be presented from sites where both RSS and state-of-the-art laboratory analysis was performed on a large number of sediment samples to detect polychlorinated biphenyls (PCBs), the pesticide DDT, and polycyclic aromatic hydrocarbons. This presentation will describe potential issues with RSS and how to confidently apply the technique.

A data set was generated from RSS and detailed PCB congener analysis of fifty-four sediment samples from the Hunters Point Naval Shipyard on the western shore of San Francisco Bay. The contaminant distribution and concentrations were similarly characterized by the two methods; the highest concentrations were in historically deposited sediments at a depth of about one foot and the sediment below four feet had little or no detectable PCB. The RSS to laboratory data regression yielded a slope of 1.10 and a correlation coefficient (r2) greater than 0.9; the RSS data were predictably ~10% higher than the lab data. The slightly over-estimated Total PCB results using the RSS is likely due to contributions from Aroclor 1260; Aroclor 1260 responds slightly more in the IA test than Aroclor 1254 which is the reference formulation for the test, and the samples have about equal proportion of Aroclor 1254 and 1260. Simulations were performed using other Aroclor mixtures and also contamination consisting of partially weathered and dechlorinated PCB; unpredictable and unreliable RSS data were obtained, until the composition was well characterized and addressed through composition-specific calibration or post-analysis data correction.

Marine Corps Base Quantico is located along the Potomac River south of Washington, D.C. Sediment core samples were collected in the River adjacent to the Base, to determine concentrations of the pesticide DDT and its degradation products DDD and DDE (DDx), using both RSS and laboratory analysis. The RSS to laboratory to RSS regression yielded a slope of 3.2 and a correlation coefficient of (r2) of less than 0.4; the RSS data estimated the concentrations to, on average, be about three times higher than the accurate laboratory data and there was poor precision in the data. The variability and poor fit can be attributed to variable DDx compound composition. The base RSS analysis was developed based on the compound 4,4' DDT, but most of the DDx contamination consisted of DDT degradation products (e.g., DDD, DDE, DDA, and DDMU); the relative response of these DDx compounds in the RRS analysis varies by more than a factor of ten.

For instance, the frequently abundant 4,4'-DDD responds four times as much as 4,4'DDT in the RSS test. The DDx compound response factors may be applied to the RSS data to generate "4,4'-DDT equivalent" concentrations for samples with known composition, to more accurately represent the concentrations; other approaches can also be taken to reliably compare results.

A thorough understanding of the contaminant composition is critical to ensure that immunoassay techniques and data are used appropriately. This is particularly important for multi-component methods (e.g., PCB and PAH), but often also for "single" compound analyses, such as selected pesticides, because the kit may respond to non-target analytes present in the sample. The degree of the response often varies widely for different compounds.

Sensors: Are They a New Way to Collect Environmental Data for Regulatory Decision-Making?

Stuart Nagourney
New Jersey Department of Environmental Protection

ABSTRACT

A sensor is any device that collects environmental data for air, water or soil in situ without the need to obtain a discrete sample. Sensors collect large amounts of data on a continuous basis over time, with the sensor often placed in one location. With a variety of new technologies that can acquire environmental data as simple as pH or as complex as metals, VOCs and PAHs in media ranging from air to soils, capability now exists to collect vastly more information on the environment that traditional monitoring protocols now obtain.

However, utilization of this type of technology raises as many questions as potentially answers, among them are the following:

- Can the data quality provided by sensors be adequately assured?
- Can State and Federal regulatory agencies handle such vast amounts of information?
- Do we need such volumes of data in all cases; if not, what are the best situations to apply sensor technologies?

The Interstate Technology Regulatory Council (ITRC) is a state-led coalition working together with industry and stakeholders to achieve regulatory acceptance of environmental technologies. ITRC consists of forty-seven states, the District of Columbia, multiple federal partners, industry participants, and other stakeholders, cooperating to break down barriers and reduce compliance costs, making it easier to use new technologies, and helping states maximize resources. The ITRCs Sampling Monitoring and Characterization Team is currently working with State regulatory agencies, The Army Corps of Engineers, EPA, the Woodrow Wilson International Center for Scholars and selected academics on this issue. The goal is to describe the range of sensor applications, identify potential regulatory barriers to their use and suggest ways to incorporate sensors into current environmental monitoring regimes.

The status of ITRCs efforts in implementing sensor technologies will be discussed.

SENSORS: A NEW WAY TO COLLECT DATA FOR ENVIRONMENTAL DECISON-MAKING?

Stuart J. Nagourney, Research Scientist
New Jersey Department of Environmental Protection
Office of Quality Assurance
stu.nagourney@dep.state.nj.us
609-292-4945

HOW IS ENVIRONMENTAL DATA CURRENTLY OBTAINED?

☒Process

- Define where discrete samples are collected
- Collect samples
- Take samples to lab. for analysis
- Wait for results
- Validate results
- Evaluate results

☒Problems

- Limited amount of data
- Limited spatial coverage
- No short or long-term temporal trends are possible

WHAT IF?

- ☒ it was possible to get real-time, continuous environmental data without having to physically obtain a sample
- ☒ What are the benefits of this type of data?
- ☒ What types of applications would this type of information be useful for?
- ☒ If the technology exists, what are some of the issues with the use of sensors?

CURRENT SENSOR ACTIVITY

- ☒ Commercial marketplace is booming
- ☒ Extensive academic and commercial research
- ☒ EPA
  - Strategic Plan 2006-2011: Goal 4
- ☒ NSF
  - National Ecological Observatory Network (NEON)
  - Sensors for Environmental Observatories report: 2006
- ☒ Interstate Technology Regulatory Council (ITRC)

ITRC – Shaping the Future of Regulatory Acceptance

- **Documents**
  - Technical and regulatory guidance documents
  - Technology overviews
  - Case studies
- **Training**
  - Internet-based
  - Classroom
- **Network**
  - State regulators
  - Federal government
  - Industry
  - Consultants
  - Academia
  - Community stakeholders

Host Organization: ECOS

ITRC State Members

ITRC Member State

Federal Partners: DOE, EPA, DOD

WHAT DO I MEAN BY "SENSOR"?

- A sensor is any device that collects environmental data on water or soil in situ without the need to obtain a discrete sample. Sensors collect large amounts of data on a continuous basis over time, with the sensor often placed in one location.

- We are not considering applications for
  - Air
  - Homeland Security

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

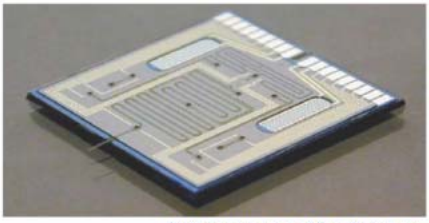
Examples of environmental sensors: cost (NA=Not Available). (From: Distributed Sensing Systems for Water Quality Assessment and Management, WWC &CENS)

EXAMPLES OF SENSORS: PHYSICAL & CHEMICAL

Physical Sensors

Chemical Sensors

Lab. On a Chip



With permission of the Woodrow International Center for Scholars

EXAMPLES OF SENSORS: RADIATION

- Active In Situ Monitoring: Reuter-Stokes
  - Used in nuclear power plant monitoring
  - Can quickly discriminate low radiation levels with an extended range of 0-10R/hr
  - Extremely reliable with a lifetime of 20 years or more for most units; operates in all conditions
  - Stores more than 20,000 data points

- Field-Portable Gamma Spectrometry
- Passive Radiation Monitoring: TLD
  - Personal radiation monitor
  - Like a film badge, A TLD is worn for a period of time (usually 3 months or less)
  - TLDs have a precision of approximately 15% for low doses.

BENEFITS TO SENSOR DATA COLLECTION

- Real time data availability
- Lower analytical cost
- Ability to evaluate trends
- Timely response to public concerns
- Transparency to data presentations

AREAS OF APPLICATION: SEPTIC SYSTEMS

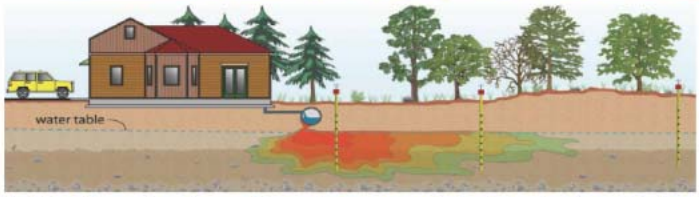


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Illustration of a sensing system used to monitor aqueous contaminants in soil and groundwater. Sensors embedded in the soil and groundwater monitor a chemical plume spreading from a source, such as a septic tank. If concentrations become too high, the system generates an alert. *Illustration: J. Fisher, UC Merced.*

- Septic Systems
  - Malfunctions are unpredictable & detrimental effects slow to accumulate
  - Temporal data provides info. on wastewater composition
  - "Meter Readers" could monitor septic systems

AREAS OF APPLICATION: NON-POINT SOURCE RUNOFF

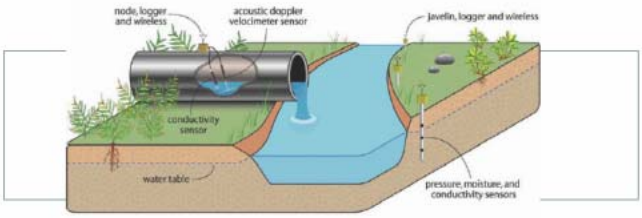

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Figure 4.2 Illustration of a hypothetical non-point source runoff drain and javeline-based monitoring system.
Illustration: J. Fisher, UC Merced.

- Non-Point Source Runoff
  - Malfunctions are unpredictable; detrimental effects are slow to accumulate
  - Temporal data provides info. on wastewater composition

AREAS OF APPLICATION: NON-POINT SOURCE RUNOFF

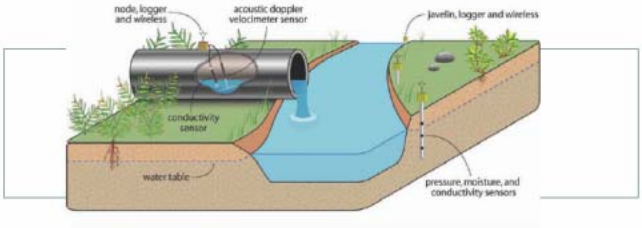

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Figure 4.2 Illustration of a hypothetical non-point source runoff drain and javeline-based monitoring system.
Illustration: J. Fisher, UC Merced.

- Non-Point Source Runoff
  - Malfunctions are unpredictable; detrimental effects are slow to accumulate
  - Temporal data provides info. on wastewater composition

AREAS OF APPLICATION: COMBINED SEWER OVERFLOWS

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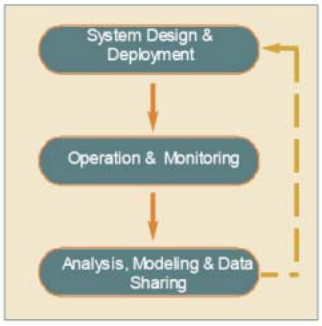
Photo © Stockphoto.com/JacobH

- Combined Sewer Overflows
  - Characterize effluent distribution
  - Actuation to minimize/avoid overflows

OPERATIONAL ISSUES

- Where to deploy?
- Durability
- Reliability



DATA QUALITY ISSUES

- Data Acceptability
- Data Comparability
- Data Quality
  - Accuracy
  - Precision
  - Decision-quality vs. screening
- Quality Assurance
- Certification

REGULATORY ISSUES

- Do state and/or federal regulations allow the use of sensor data? If so, which program areas?
- Do regulatory agencies have the computer infrastructure to accept the large amounts of data that sensors can provide?
- Sensor data can be real-time, transparent and thus uncensored; is this OK with regulators?

HOW CAN THE LAB. COMMUNITY BENEFIT FROM SENSORS ?

- Use of sensors will identify many more areas of regulatory concern ⇒ more samples
- Any regulatory decision will always require data from EPA methods done by certified labs.
- If sensors are certified, the lab. community would become involved in their deployment, calibration (QA) and maintenance

WHERE DO WE GO FROM HERE?

- Continue to publicize the interest in sensors by regulatory agencies; they drive the market!!
- ID regulatory barriers and propose solutions: see ITRC
- Provide training on sensors: see ITRC
- Conduct pilots where sensors are directly compared to traditional data acquisition systems
- Highlight numerous advantages to sensor use
- Fund research on complex chemical sensor systems

HOMELAND SECURITY

EPA's National Homeland Security Research Center (NHSRC) Role in the Development of the eLRN

Oba Vincent
National Homeland Security Research Center

ABSTRACT

This presentation discusses the NHSRC role in supporting the development of the technical underpinnings of the eLRN. NHSRC, as a component of the US Environmental Protection Agency's (EPA) Office of Research and Development, is responsible for the development and validation of methods to support the restoration of an area following a terrorist act or other incident of national significance.

This presentation provides a brief overview of the national network system, discusses the development and usage of EPA's Standardized Analytical Methods for Environmental Restoration following Homeland Security Events, provides updates on major environmental laboratory activities of possible interest, and lays out the framework for collaborative work with other internal/external organizations. Time will be provided for a discussion of the technical issues surrounding the development of eLRN, as well as other laboratory-related activities.

NHSRC Role in the Development of the Environmental Laboratory Response Network (eLRN)

Laboratory Networks

National Reference Laboratories

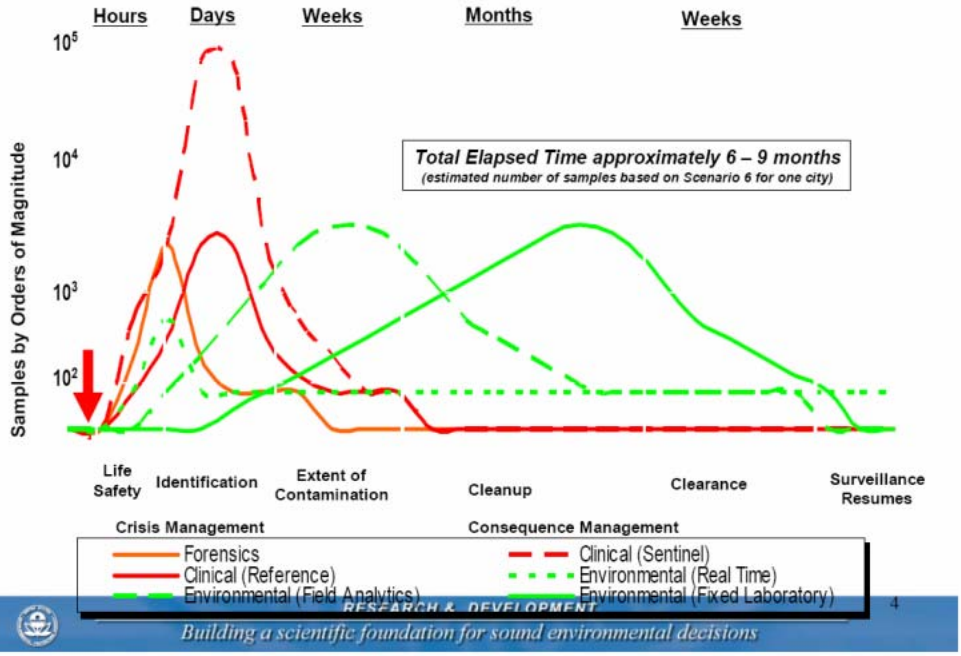
Projects of Interest

Homeland Security Presidential Directives

- **HSPD-7** Critical Infrastructure Identification, Prioritization and Protection: designates EPA as the sector-specific lead agency for critical water infrastructure safety and security
- **HSPD-9** Defense of US Agriculture and Food: directs EPA to develop a full-coordinated surveillance and monitoring program to provide early detection. Also requires EPA to develop nationwide lab network to support the routine monitoring and response requirements
- **HSPD-10** Biodefense in the 21st Century (classified): reaffirms EPA's role adding a clear directive for the Agency's lead in decon efforts including laboratory response activities
- **HSPD-??** Chemical Defense: In draft, addressed laboratory preparedness and response directly

RESEARCH & DEVELOPMENT 3
Building a scientific foundation for sound environmental decisions

Generic Anatomy of a Response



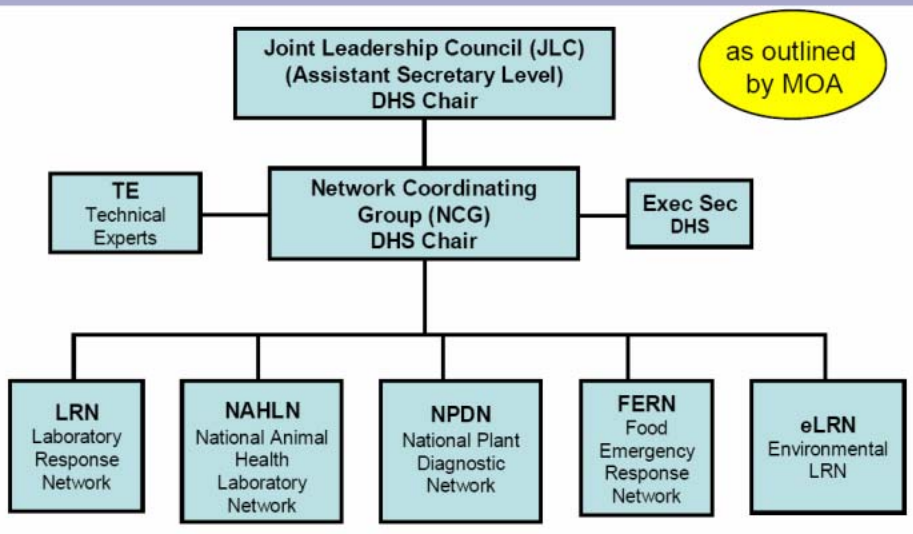
RESEARCH & DEVELOPMENT 4
Building a scientific foundation for sound environmental decisions

National Homeland Security Laboratory Network

Integrated Consortium of Laboratory Networks (ICLN)

Environmental Laboratory Response Network (eLRN)

Lab Consortium Organizational Structure



ICLN Response Matrix

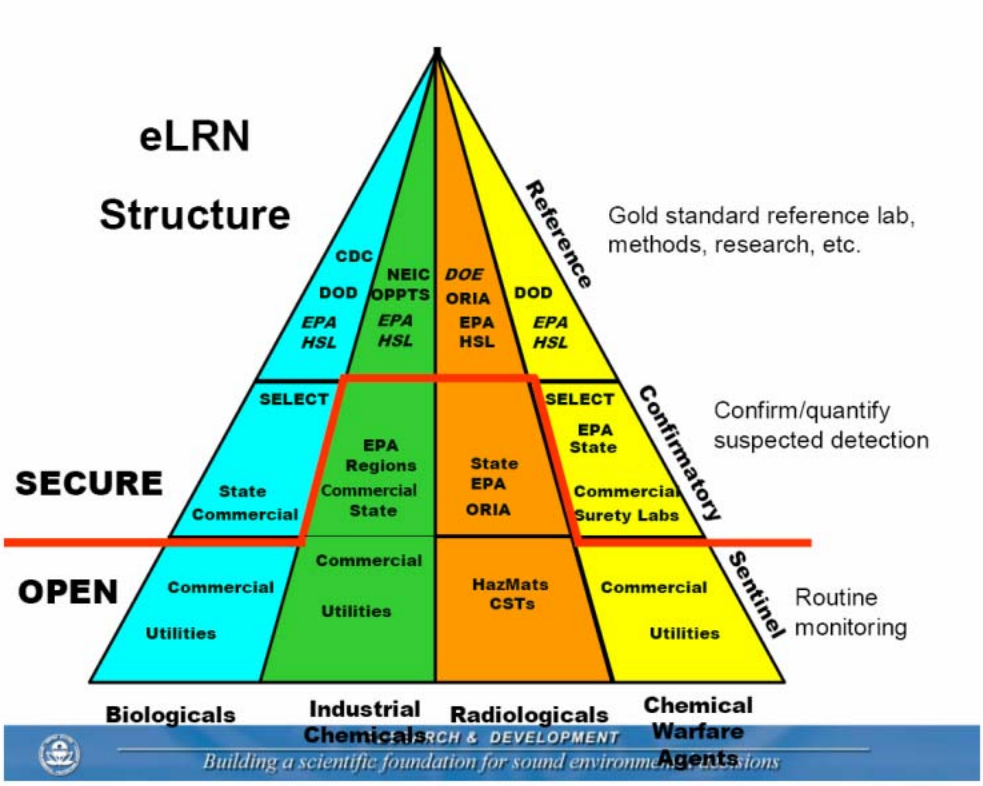
	Chemical					Biological			
	Lab Support to Phase of Response					Lab Support to Phase of Response			
	Monitoring/surveillance	Incident Response	Remediation	Forensics		Monitoring/surveillance	Incident Response	Remediation	Forensics
Human Clinical	HHS	HHS	HHS	FBI	**Human Clinical**	HHS	HHS	HHS	FBI
Environmental	EPA	EPA	EPA	FBI	**Environmental**	HHS	HHS	EPA	FBI
Food	USDA/ HHS	USDA/ HHS	USDA/ HHS	FBI	**Food**	USDA/ HHS	HHS/ USDA	USDA/ HHS	FBI
Animal	USDA	USDA	USDA	FBI	**Animal**	USDA	USDA	USDA	FBI
Plant	USDA	USDA	USDA	FBI	**Plant**	USDA	USDA	USDA	FBI
Drinking									FBI

*JLC agreed to Responsible Federal Agencies (RFAs) identified for each phase of response

ICLN Response Matrix continued

	Radiological			
	Lab Support to Phase of Response			
	Monitoring/surveillance	Incident Response	Remediation	Forensics
Human Clinical	HHS	HHS	HHS	FBI
Environmental	EPA	DOE/ EPA	EPA	FBI
Food	USDA/ HHS	USDA/ HHS	USDA/ HHS	FBI
Animal	USDA	USDA	USDA	FBI
Plant	USDA	USDA	USDA	FBI
Water	EPA	EPA	EPA	FBI

- RFAs have been identified at Dept level
- Identified agency responsible for ensuring capability exists, though actual capability may exist in another Dept



National Reference Laboratories: ORD/NHSRC – Virtual Approach

Chemical/Chemical Agent

- National Laboratories

Biological

- Cincinnati (2012), National Laboratories
- CDC, BSL-4 Agents

Radiological

- Montgomery/Las Vegas Forensic

Reference Lab Role

Methods

Training

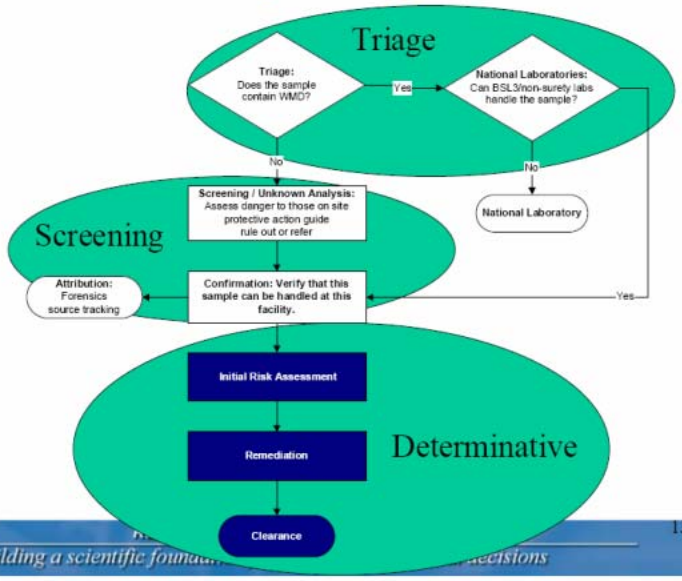
Technical Support

- Provide mechanism to obtain CWA

Surge Capacity - Future

Projects

Laboratory Sample Phases



Standardized Analytical Methods for Environmental Restoration following Homeland Security Events (SAM) Document

Cornerstone of Laboratory Response Program

Second version issued September 29, 2005

SAM III published: 28 Feb 2007

- Released for comment December 2006
- Incorporated Science Advisory Board comments
- Update analyte list and methods based on research
- Resolve "To Be Determined" methods

Past vs. Current SAM Revisions

SAM 1.0	SAM 2.0	SAM 3.0
Chemical Methods 82 analytes (10 biotoxins) 4 matrices	Chemical Methods 93 analytes 5 matrices	Chemical Methods 122 analytes 5 matrices
Biological Methods 27 analytes (5 BSL-4 Agents) 3 matrices	Biological Methods 33 analytes (6 BSL-4 Agents) 4 matrices 2 types (identification and viability)	Pathogen Methods 37 analytes 5 matrices 2 types (identification and viability)
	Radiochemical Methods 12 analytes 5 matrices 2 types (gross determination and confirmatory)	Radiochemical Methods 15 analytes 5 matrices 2 types (gross determination and confirmatory)
	Biotoxin Methods 12 analytes 5 matrices	Biotoxin Methods 17 analytes 4 matrices

Document Accessibility (as of 24 April 2007)

Located on EPA Website:
http://www.epa.gov/nhsrc/pubs

SAM 1 Downloads: 29,099
SAM 2 Downloads: 12,881
SAM 3 Downloads: 6,121

Total: **48,101** downloads

Standard Analytical Protocols (SAPs)

Provides details on procedures needed to analyze samples with SAM identified method

- Chemical: SVOC, VOC, HPLC, IC, ICP drafted – SVOC, VOC validation ongoing
- Biological: Shigella, Salmonella Typhi, Vibrio Cholera, Escherichia Coli drafted
- Sample collection: Bio-toxin – water soluble (e.g. ricin, botulinum toxin), Anthrax drafted – Radioisotopes – Pending release

Additional SAM based Support Documents

Sample Collection Information Document – Draft March 2007

Sample Disposition Document – Pending

Lab Screening Methods Document – Draft Pending

Field Equipment Cross Reference Guide - Pending

Method Collaborations

NIOSH: LCMS methods for air/wipes
FDA: Biotoxin methods for water
EPA Region 5: LCMS methods for water
EPA Region 7: ICP method validation
EPA Region 1, 3: CWA method validation
EPA Regions 1, 5, 6, 7, 9,10: VOC method validation
EPA Region 10: Laboratory support – multiple methods
Oregon: CWA degradation method development

Process established for Collaborators to propose projects/roles

All Hazard Receipt Facility Status

DHS led project, jointly funded with EPA
DoD, CDC, FBI, States involved
AHRF Protocol on APHL website
Both prototypes delivered
- EPA Region 1
- New York State Laboratory

Evaluation scheduled this year
- Began week of May 7, expected completion Aug 2007

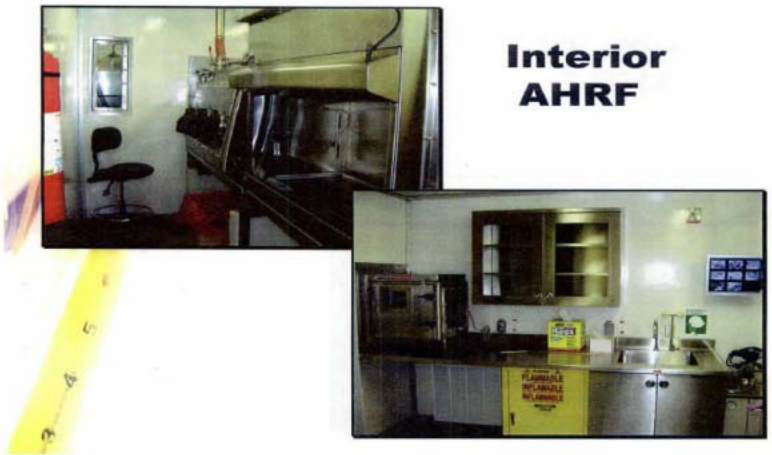
Draft Unknown Sample Collection Document pending issuance by DHS/DoD

Selected Detection Projects

All Hazard Receipt Facility

Selected Detection Projects

All Hazard Receipt Facility



Chemical Warfare Agent (CWA) activities

Negotiated and funded Interagency agreement with DoD to obtain CWA for use at contractor laboratories – includes agent for calibration purposes in emergency situations

Negotiated agreement to obtain ultradilute CWA for calibration purposes at eLRN laboratories (Regional, State or Commercial)

Ultradilute Chemical Warfare Agent (uCWA)

Defined in draft EPA/DoD MOU

- 10 ppm of Agent (G, V, H, L) in 1 ml vials with no more than 10ml total/agent
- Level slightly above drinking water standards
- Hazard driven by solvent (eg. Hexane)

Development of CWA degradation product procedures

- State of Oregon validating GC/MS methods
- NEMC developing validating LC/MS methods
  - NIOSH – AIR/Wipes
  - Region 5 – Water/Library Development
  - NERL – Water/Soil
  - Region 10 - Validation
- Developing "tool kit" for regional use

CWA Degradation Products

Degradation Product	Original Agent	CAS Number
Dimethylphosphoramidic Acid	GA	33876-51-6
Isopropyl methylphosphonate	GB	1445-75-6
Isopropyl methylphosphonic Acid (IMPA)	GB	1832-54-8
1,2-Dichloroethane	HD	107-06-2
1,4-Dithiane	HD	505-29-3
Thiodiglycol	HD	111-48-8
1,4-Thioxane	HD	15980-15-1
2-Chlorovinyl Arsonous Acid	Lewisite	85090-33-1
Lewisite Oxide	Lewisite	1306-02-1
EA2192	VX	73207-98-4
Ethyl methylphosphonate	VX	1832-53-7
MethylPhosphonic Acid	VX, GB, GD	993-13-5

Plans for 2007

Validate, validate, validate

- Joint FDA/EPA biotoxin (Ricin/ botulism) method
- Joint NIOSH/EPA LC/MS method validation

SAM III, Support Documents, AHRF Testing, Receipt of uCWA, CWA degradation product methods

Budget increased from approximately $3m to $5m

Other projects

Sampling process validation support (in response to GAO report)

Airport decontamination projects

Thank You… Questions???

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Health Risk-Based Criteria for Validating Chemical Analytical Methods

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ABSTRACT

This paper summarizes a report under preparation by the U.S. Environmental Protection Agency (EPA) National Homeland Security Research Center (NHSRC) that is compiling and developing potential health risk-based detection criteria from existing ambient air and drinking water health benchmarks. The resulting estimates of compound-specific air and water concentrations are intended to assist development of analytical detection criteria for use in homeland security preparedness planning. Current focus is on existing benchmarks for chronic exposures to the general public as a means of identifying potential detection goals that analytical methods may need to attain during decontamination certification. However, detection limits for shorter exposure durations are also relevant in many cases, notably for contaminants that do not persist in environmental media. In addition, many chemicals will degrade to form other products within minutes to hours or days. Hence, a sound validation program should consider breakdown products as well as product toxicity, relevant exposure routes, and persistence to ensure that detection efforts address the potential presence of relevant fate products in the environment. To this end, the current analyses identified more than 200 risk-based detection criteria as potential detection method certification targets across nearly 130 contaminant and fate products in both drinking water and air. Relevant health benchmarks for these compounds were also evaluated and summarized when possible. This paper summarizes results for two priority compounds (chloropicrin and methyl parathion) and their degradation products.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) National Homeland Security Research Center (NHSRC) has identified priority compounds and radionuclides as possible homeland security threats to public drinking water supplies and ambient air. In order to support validation of analytical methods for use in identifying threat compounds, NHSRC has developed health risk based detection criteria for more than 100 chemicals and radionuclides as support for the analytical method validation program. Existing exposure benchmarks and information on environmental fate in water and air were evaluated in the development of these risk based detection criteria. While the current focus has been on chronic benchmark exposures for the general public as a means of identifying potential detection goals that analytical methods may need to attain during decontamination certification, it is understood that guideline levels for shorter exposure durations are equally relevant, particularly for nonpersistent compounds. Examples of relevant short-duration guidelines include those developed by the Acute Exposure Guideline (AEGL) program of the Office of Pollution Prevention and Toxic Substances [1] and those under development by the Provisional Advisory Level (PAL) program of the NHSRC [2].

It is further understood that fate and removal processes such as hydrolysis and photolysis, as well as biodegradation and sedimentation, will limit potential for long-term exposures to the "parent" material. This assessment strongly supports development of operational (detection) criteria values based on realistic exposure estimates following release of any threat compound. The criteria values presented in this summary and provided in the "parent" report [3] are taken from available benchmarks without assessing underlying toxicological interpretations and extrapolations conducted by the authoring organizations that originally developed and published each chronic exposure benchmark. It is also important to emphasize that the compiled detection criteria presented here are not intended to be used directly as health-based advisory levels to guide homeland security responses; the user is directed to the parent organization responsible for developing the benchmark of interest as well as other organizations with specific responsibility for developing such advisories.

METHOD

The Threat and Consequence Division (TCAD) of the NHSRC provided a starter list of compounds and radionuclides selected as possible threats to public drinking water supplies or air; obtaining health risk-based detection concentrations as validation criteria was the driver for the current analysis.

A three-step process was applied to analysis of the threat materials:

1. Assess the fate and persistence of each threat material.
2. Identify concentration benchmarks relevant to general public exposure for threat compounds and degradation products, emphasizing chronic exposure.
3. Identify dose benchmarks or reference values, and derive detection criteria values by applying standard estimation techniques.

These steps are highlighted in the subsections below.

Fate and Persistence Assessment

Many primary threat materials do not persist if released to water or air, and transform to various reaction products often within minutes to hours by the processes of hydrolysis, oxidation, photolysis, biodegradation and radiological decay [4-6]. While details of the resulting fate and persistence findings are summarized in the parent document, the current paper provides detection criteria for degradation products of several "parent' compounds selected from the priority list for method validation established by NHSRC for developing standardized analytical methods [7].

It is noted that consideration of persistence in selecting appropriate and reasonable detection criteria for homeland security planning should be driven by the chemical, physical and toxicological characteristics of the material of concern as well as specifics of site, release and available exposure routes. For example, solid reaction products are not likely to pose an inhalation hazard. Additional aspects of persistence important to appropriate detection criteria selection include degradation reaction yields and the transient presence of intermediates. When evaluating homeland security events involving non-persistent compounds with persistent degradates, detection capability for degradates can have significant forensic value.

For homeland security planning purposes, it is acknowledged that the residence time of threat materials or fate products in drinking water or urban air would not typically extend to 30 years or a lifetime given the dynamic nature of water and air flow. Similarly, if threat materials were released to a surface water supply source such as a reservoir and were not hydrolyzed, there is a possibility that they could enter water treatment or distribution systems over a period of time. Nevertheless, fate processes such as hydrolysis and photolysis as well as biodegradation would be expected to limit the potential for long-term (lifetime) exposures. The detection criteria estimated in this report should be considered a point of departure for advance planning and are not intended to be applied proscriptively. Operational criteria values that reflect practical exposure durations and compound-specific characteristics are expected to be higher.

Benchmark Evaluation

More than 20 different categories of benchmarks were evaluated for relevance to developing analytical method detection goals. Categories ranged from chronic to shorter-duration concentration limits established by EPA for the general public and subgroups (such as children), to standard EPA reference toxicity values for both cancer and noncancer endpoints, to health-based screening goals and exposure guides developed by other organizations such as state agencies and international scientific bodies.

Toxicity values were assessed according to the following EPA-recommended hierarchy [8]:

1. EPA Integrated Risk Information System (IRIS) values *(the primary source for air and water concentration benchmarks).*
2. EPA provisional peer-reviewed toxicity values (PPRTVs) *(for direct chronic benchmarks).*
3. All other values, including from regional, state, and international sources.

Emphasis is on EPA inhalation and ingestion benchmarks that reflect the most recent analyses; when multiple benchmarks were found, alternate values have also been identified to offer further context. Where the value accounts for additional exposure routes such as dermal, those contributions are incorporated into the presented detection criteria.

Derivation of Criteria Values for Chemicals

Standard EPA methods and procedures [9] were followed in the calculation of potential detection criteria values. For benchmarks given as doses rather than concentrations, the derivation involved combining an estimate of intake or dose from the assumed repeated exposures over an extended time with an estimate of the associated toxicity for that chemical by the given route of exposure. At present, inhalation toxicity values are expressed as concentrations (e.g., mg or µg per m^3 air). The reference concentration (RfC) represents the criteria for non-cancer effects; the inhalation unit risk (IUR) corresponding to an incremental risk of 10^{-6} is used in this analysis for all routes of exposure. To derive criteria values for water from oral RfDs (mg/kg-d), the following calculational protocol was followed:

1. Multiply the RfD by 70 kg.
2. Divide by 2 L/d.
3. To convert mg/L to µg/L, multiply by 1,000.

To derive criteria water values from oral SF (risk per mg/kg-d), for a 10^{-6} risk level:

1. Multiply 10^{-6} (the target risk level) by 70 kg.
2. Divide by SF, 2 L/d.
   (Where a risk-specific concentration is given for a 10^{-6} risk, that level is used directly.)
3. To convert mg/L to µg/L, multiply by 1,000.

To convert an RfC or reference concentration to an RfD:

1. Divide by 70 kg.
2. Multiply by 20 m^3/d.

To provide context for method validation, additional benchmarks and other data were pursued when a chronic exposure benchmark for the general public was not found.

Derivation of Criteria Values for Radionuclides

Health risk-based detection criteria for air and drinking water are being derived for each of the following 15 radionuclides: americium-241 (Am-241), californium-252 (Cf-252), cesium-137 (Cs-137), cobalt-60 (Co-60), curium-244 (Cm-244), europium-154 (Eu-154), iridium-192 (Ir-192), plutonium-238 (Pu-238), plutonium-239 (Pu-239), polonium-210 (Po-210), radium-226 (Ra-226), ruthenium-103 (Ru-103), ruthenium-106 (Ru-106), strontium-90 (Sr-90), and uranium-238 (U-238). These are identified radionuclides of concern for potential homeland security incidents [7].

Detection criteria for air are being based on a maximum annual dose of 10 mrem, which is the EPA's limit for the air pathway identified in the National Emissions Standard for Hazardous Air Pollutants (NESHAPS) [10]. Detection criteria for drinking water are being based on the maximum annual doses (mrem) or concentrations (pCi/L) established as MCLs [11]. Current International Commission on Radiological Protection (ICRP) [4] dose coefficients are being applied to develop radionuclide-specific detection criteria consistent with radiation dosimetry provided in the most recent federal guidance report on intake of radionuclides [12] and recent procedural rules for nuclear radiation protection promulgated by the Department of Energy [13] (June 2007). The goal is to ensure harmonization of health risk based detection criteria values for air and water with existing EPA limits as well as current national and international guidance regarding estimation of dose from intake of radionuclides. Ingestion standards and detection criteria for polonium-210 are of particular concern in light of recent documentation and news reports regarding the highly toxic nature of small oral doses [14]; a low detection criterion for polonium-210 seems justified.

RESULTS

For the 23 priority threat chemicals examined, health risk detection criteria are available or can be derived for nearly all (N = 21) chemicals in water and approximately two-thirds (N = 15) in air. Coverage "gaps" are primarily due to unavailable chronic exposure guidelines for compounds that are either nonpersistent or better known for acute toxicity characteristics; in some cases the "gap" is due to the fact that the compound is airborne but not water-borne, or vice versa. More than 60% of the detection criteria reflect EPA benchmarks, with most based on exposures assumed to continue for decades. Where multiple relevant benchmarks exist, EPA values have been given priority, with emphasis on values reflecting recent studies. Example evaluations for 2 compounds (chloropicrin and methyl parathion) from the initial priority list are presented in Tables 1 (criteria in air) and 2 (criteria in water). These examples exhibit both air and water benchmarks for the parent + degradates. The variety of benchmarks evaluated and prioritized (e.g., Cal/EPA CRELs, ARELs and action levels; EPA RfCs, MCLs, DWLOCs and NAAQS values, state-specific acceptable ambient levels and drinking water guidelines, etc.) is also illustrated. All known degradates with existing benchmarks are compiled. It is acknowledged that not all degradates are of operational interest due to their low reaction yields, physical properties (reducing biological availability), presence as transient reaction intermediates or low toxicity. Nevertheless, information on these compounds allows designation of analytical goals to be prioritized according to need. Forensic applications are also served by this analysis.

Table 1: Health Risk-based Detection Criteria in Air for Selected Initial Priority Compounds and Key Degradation Products

Compounds (CAS No.)		Proposed Air Concentration ($\mu g/m^3$)	Basis	Authority
Chloropicrin (76-06-2)		0.4	CREL[a]	Cal/EPA
	Degradation Products			
	Phosgene (75-44-5)	0.3	RfC of 0.0003 mg/m^3	EPA/IRIS
	Hydrogen chloride (7647-01-0)	20.0	RfC of 0.02 mg/m^3	EPA/IRIS
	Ozone (10028-15-6)	160.0	NAAQS[b], 0.08 ppm	EPA/OAQPS[c]
	Nitrogen dioxide (10102-44-0)	100.0	NAAQS	EPA/OAQPS[c]
	Nitric acid (7697-37-2)	(86.0)	Acute value only; AREL[d]	Cal/EPA
Methyl parathion (298-00-0)		0.001	RfC of 0.001 to 0.008 $\mu g/m^3$ for sensitive populations and assumed mixture with paraoxon	Cal/EPA
	Degradation Products			
	ρ-Nitrophenol (100-02-7)	0.1	Proposed Rhode Island (2004) and NY acceptable ambient level; annual limit	NYSDEC and State of Rhode Island
	Methyl paraoxon (950-35-6)	(0.001)	As for parent methyl parathion and assumed mixture of parathion and paraoxon in field	Cal/EPA
	Methanol (67-56-1)	4,000	CREL	Cal/EPA
	Phosphoric acid (7664-38-2)	7	CREL	Cal/EPA

Except as indicated, these concentrations represent long-term repeated or continuous exposure durations.
Parentheses identify derived concentrations.

[a]CREL = Chronic reference exposure level, inhalation (Cal/EPA, OEHHA)
[b]NAAQS = National Ambient Air Quality Standards (EPA)
[c]OAQPS = Office of Air Quality Planning and Standards (EPA)
[d]AREL = Acute reference exposure level (CAL/EPA, OEHHA)

Table 2: Health Risk-based Detection Criteria in Water for Selected Initial Priority Compounds and Key Degradation Products				
Compounds (CAS No.)		**Proposed Water Concentration (µg/L)**	**Basis**	**Authority**
Chloropicrin (76-06-2)		50	From archived action level of 0.05 mg/L	CA Dept. Health Services Drinking Water Program
	Degradation Products			
	Nitrate (NO_3) as N (14797-55-8)	10,000	MCL of 10 mg/L	EPA Office of Water
	Nitrite (NO_2) as N (14797-65-0)	1,000	MCL of 1 mg/L	EPA Office of Water
Methyl parathion (298-00-0)		8.8	From RfD of 0.00025 mg/kg/d[a]	EPA/IRIS
	Degradation Products			
	ρ-Nitrophenol (100-02-7)	60	From lifetime HA of 0.06 mg/L	EPA Office of Water
	Methyl paraoxon (950-35-6)	(8.8)	From RfD for parent methyl parathion	EPA/IRIS
	Methanol (67-56-1)	18,000	From RfD of 0.5 mg/kg/d	EPA/IRIS
	Phosphoric acid (7664-38-2)	12,000	From drinking water guideline of 12 ppm	Dept of Water Supply for Maui County, HI

Except as indicated, these concentrations represent long-term repeated or continuous exposure durations. Parentheses identify derived concentrations.

[a]Assumed body mass of 70 kg and drinking water consumption of 2 L/d.
[b]DWLOC = Drinking water level of comparison

Tissue doses from intake of accompanying radioactive progeny have been evaluated and found to be relatively unimportant except for certain members of the uranium-238 chain and, in some situations, members of the radium-226 chain. On the other hand, generation of radioactive progeny of strontium-90, cesium-137, ruthenium-106, and other radionuclides inside the body contribute significantly to risk from intake of the parent radionuclide.

CONCLUSIONS

This paper was derived from the much larger and more detailed parent report [3] being prepared by the NHSRC which includes comparison of proposed detection criteria with current analytical

limits, evaluation of persistence durations, fate processes, physical properties, etc. Examples are provided for chloropicrin and methyl parathion and their degradation products in air and water.

Health-based detection criteria developed in the present analysis provide a foundation for analytical method validation. Combining fate and benchmark information provides the backbone for this validation effort and other NHSRC research activities designed to guide health protection. It is noted that Compilation of proposed detection criteria for persistent degradation products has considerable forensic value. Gaps identified in this study can help frame research and development to address critical method needs as well as those for fate and toxicity data to strengthen preparation for potential homeland security events.

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Health Risk-Based Criteria for Validating Chemical Analytical Methods

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August 17, 2007

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PROJECT OVERVIEW

- **PURPOSE**: Compiled and developed health risk-based detection criteria for potential threat chemicals and radionuclides to support analytical method validation for homeland security preparedness planning. Focused on air and water exposure routes.
- **METHODS:** Identified compound-specific inhalation/ingestion toxicity values (benchmarks) for chronic (and short-term) exposures. Applied standard exposure assumptions to derive target concentrations.
- **RESULTS:** Identified and/or derived approximately 200 risk-based criteria from health benchmarks for contaminant and fate products in water and air. These criteria are to be used as validation targets for standardized analytical methods (SAM). Details are presented in EPA's draft report: *Risk Based Concentrations to Support Method Validation for Drinking Water and Air.* (In review).

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1

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OBJECTIVE AND SCOPE

- Objective: Address critical homeland security need for contaminant releases
  - scenario: contaminants released to drinking water or air
  - priority: ensure analytical methods can detect levels considered safe
  - time frame: from release through final decontamination/recovery
- Scope: Focus on final detection needs post-release; >120 threat agents
  - toxic industrial chemicals *(~50)*
  - chemical agents *(~30)*
  - radionuclides *(15)*
  - other contaminants *(including agent precursors and byproducts)*

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METHODS

- *What happens to the threat agents after release to drinking water or air?*
  - identify other chemicals likely to form, & when, if the parent is released
- *Do relevant health-based benchmarks exist for validation concentrations?*
  - emphasis: general public, chronic exposures
  - important: must also address transformation products
- *How can dose benchmarks be used?*
  - deriving concentrations using standard calculations *(intake, endpoints)*

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ASSESSED ENVIRONMENTAL FATE & PERSISTENCE

- Peer-reviewed information was evaluated to provide:
  - structure, chemical formula, molecular weight *(parents and products)*
  - fate and persistence data *(organized by water and air)*
  - toxicity data from sources *(e.g., NCEA, OPP, TOXNET, journal articles)*
  - main fate processes *(e.g., hydrolysis, photolysis, oxidation, volatilization)*
  - persistence *(half lives)* and time interval indicators *(sec-hr, d-wk, wk-mo, mo-yr)*

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EVALUATED EXPOSURE BENCHMARKS

- Evaluated >20 different categories of chronic exposure levels
  (this is the focus of the detection targets)

  ➔Applied hierarchy of toxicity information in descending order:

  - reference doses & concentrations *(IRIS)*
  - cancer unit risks, slope factors *(IRIS)*
  - provisional peer-reviewed toxicity values (PPRTVs)
  - health advisories *(OW)*
  - minimal risk levels *(ATSDR)*
  - reference exposure levels *(Cal EPA)*
  - others *(including regional, state, and international sources)*

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DERIVED TARGET CONCENTRATIONS FOR CHEMICALS

- *Applied standard EPA risk assessment method as follows:*

1. Intake: $I_i = \frac{C_i \times IR \times EF \times ED}{BW \times AT}$ *(may apply CF where needed to adjust mass units)*

- I_i = intake of chemical *i* (mg/kg-d)
- C_i = concentration of chemical *i* in water (µg/L), or air (µg/m^3)
- IR = intake (ingestion or inhalation) rate, assumed to be 2 L water/d, or 20 m^3 air/d
- EF = exposure frequency, assumed to be 365 d/yr
- ED = exposure duration, assumed to be 30 yr
- BW = body weight (kg), assumed to be 70 kg (adult)
- AT = averaging time (in d): 10,950 d for noncancer effects; 25,550 d for cancer risk
- CF = conversion factor, as indicated for a given calculation (e.g., 10^3 µg/mg)

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6

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DERIVED TARGET CONCENTRATIONS FOR CHEMICALS (cont'd)

2. Cancer endpoint: target incremental risk level of 10^{-6}

- Cancer risk = Intake × Slope factor, or I × SF

- Unit risk values and risk-specific levels (for 10^{-6} risk) were applied

3. Noncancer endpoint: target hazard quotient (index) of 1

- Noncancer hazard quotient (HQ) = $\frac{\text{Intake or I/RfD}}{\text{Reference dose}}$

- For oral exposure; inhalation reference concentrations were used directly

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7

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DERIVED TARGET CONCENTRATIONS FOR RADIONUCLIDES

- Applied current ICRP models for ingestion or inhalation of radionuclides by an adult member of the public.
- Detection criteria values for 15 radionuclides in air are based on a maximum annual dose of 10 mrem (EPA, NESHAPS).
- Derived all risk-based criteria values for drinking water on the basis of an annual dose limit of 4 mrem. This yields risk-based concentrations that are consistent with EPA standards for radium and uranium.

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RESULTS OVERVIEW

- Identified and/or derived approximately 200 risk-based criteria values from health benchmarks for contaminants and fate products in water and air. Criteria to be used for validating standardized analytical methods (SAM). Details are presented in EPA's *Risk Based Criteria to Support Detection Validation for Drinking Water and Air (*in review).
- Majority of the detection criteria reflect EPA benchmarks; i.e., assumed life-time chronic exposure scenarios
- Compiled all known degradation products with existing benchmarks. However, not all degradates are of operational interest due to:
  - low-reaction yields; physical properties (reducing biological availability)
  - present as transient reaction intermediates
  - low toxicity

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EXAMPLE: CHLOROPICRIN

CRITERIA VALUES FOR AIR		Basis	Reference
Chloropicrin in Air	0.4 µg/m³	Chronic Reference Exposure Level	Cal/EPA
Degradates in Air			
Phosgene	0.3 µg/m³	RfC of 0.0003 mg/m³	EPA/IRIS
Hydrogen chloride	20.0 µg/m³	RfC of 0.02 mg/m³	EPA/IRIS
Ozone	160.0 µg/m³	National Ambient Air Quality Standard (0.08 ppm)	EPA/OAQPS
Nitrogen dioxide	100.0 µg/m³	National Ambient Air Quality Standard	EPA/OAQPS
CRITERIA VALUES FOR WATER		**Basis**	**Reference**
Chloropicrin in Water	50 µg/L	Archived Action level of 0.05 mg/L	Cal DHSDWP
Degradates in Water			
Nitrate (as N)	10,000 µg/L	MCL of 10 mg/L	EPA/Office of Water
Nitrite (as N)	1,000 µg/L	MCL of 1 mg/L	EPA/Office of Water

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10

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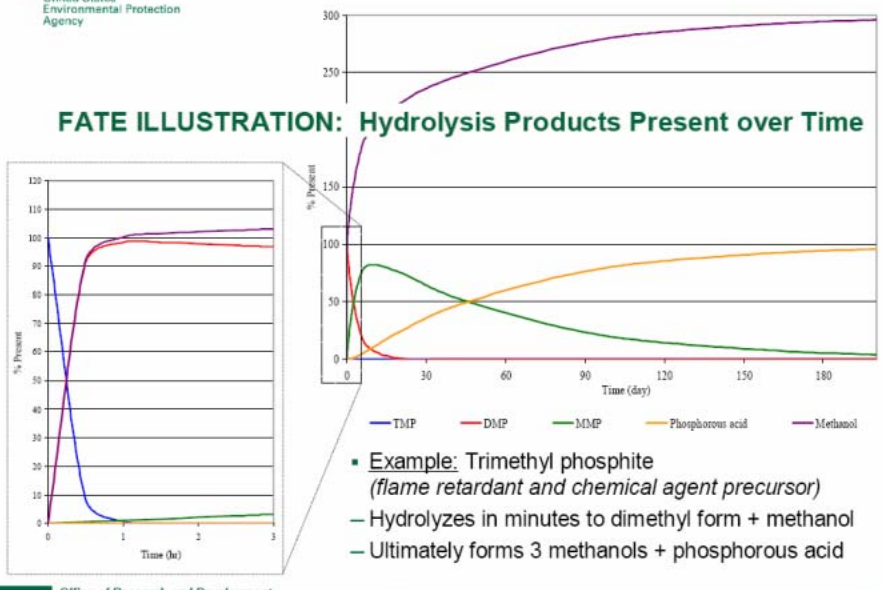
FATE ILLUSTRATION: Hydrolysis Products Present over Time



- Example: Trimethyl phosphite
  (flame retardant and chemical agent precursor)
  - Hydrolyzes in minutes to dimethyl form + methanol
  - Ultimately forms 3 methanols + phosphorous acid

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11

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CONCLUSIONS

- Health-based detection criteria developed in the present analysis provide a solid foundation for validating standard analytical methods. Combining fate and benchmark information provides the backbone for this validation effort and has considerable forensic value.
- More than 200 health risk-based criteria values are identified for validating standardized analytical methods to support a critical need for homeland security preparedness.
- Gaps identified in this study can help frame future research and development of analytical methods. They also point to the need for fate and toxicity information to effectively respond to homeland security threats.

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  - Oak Ridge colleagues: Annetta Watson, Richard Leggett, and Dennis M. Opresko

(The technical document, *Risk-Based Concentrations to Support Method Validation for Drinking Water and Air*, is to be published in 2008)

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Any Questions?

GC/MS Determination of Hydrolysis Products of the Chemical Warfare Agents Listed in the EPA's Standardized Analytical Methods for Environmental Restoration Following Homeland Security Events (SAM)

Ted Haigh
Oregon Department of Environmental Quality

ABSTRACT

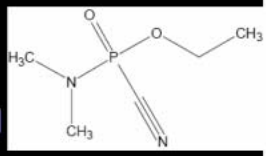
Using EPA Method 8270D and Solid Phase Extraction (SPE) the hydrolysis products from the chemical warfare agent GA, GB, GD, VX, and HD listed in the EPA Standard Analytical Methods (SAM) have been quantified in water samples. The water samples are passed through SPE cartridges to extract the hydrolysis products. The hydrolysis products are eluted from the SPE cartridges and derivatized with N-Methyl-N-(t-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) and analyzed on the GC/MS.

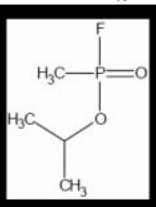
GC/MS Determination of Hydrolysis Products of the Chemical Warfare Agents Listed in the EPA Standardized Analytical Methods

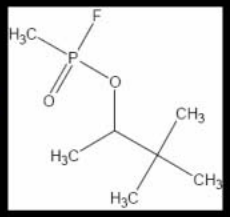
Theodore A. Haigh, M.S.
Oregon Department of Environmental Quality

Short History of Nerve Agents

- December 1936 – Dr. Gerhard Schrader prepares Tabun (N,N-dimethylphosphoramidocyanidic acid, ethyl ester)
  - Large scale production begins 1939
- 1938 Sarin discovered (isopropylmethylphosphonofluoridoate)
  - Named after its discoverers: Schrader, Ambros, Rödriger, and van der Linde
- Spring 1944 – Richard Kuhn discovers Soman (Pinacolylmethylphosphonofluoroidate)

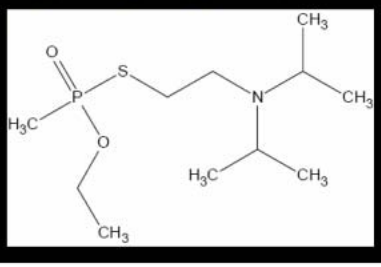






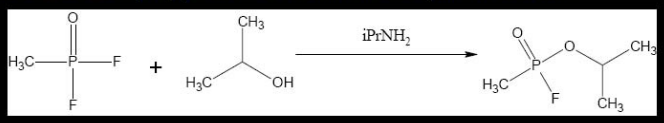
After WWII

- During the early 50's several chemical companies and independent scientists discovered the potency of substituted 2-Aminoethanethiol Organophosphate Esters.
- 1954 ICI, Bayer, and the Swedes produce many of these compounds
- British CW lab at Porton notifies US CW lab at Edgewood of the anticholinesterase activity of these compounds, and the US begins systematic investigation of these compounds.
- 1958 US selects VX → (S-[2-[bis(1-methylethyl)amino]ethyl]-O-ethyl methylphosphonothiolate for manufacture.
- 1959-1968 VX produced in the US.

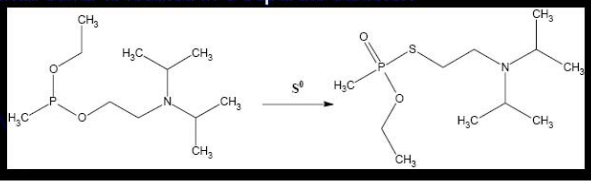


Weapons

- Binary Weapons
  - Binary chemical weapons mix two, separate and relatively non-toxic chemicals in flight to create the toxic chemical agent.
- Sarin Binary
  - Methylphosphonyl difluoride (DF) is initially located in one canister, while a mixture of isopropyl alcohol and isopropyl amine is located in a separate canister.



- VX Binary
  - O-Ethyl O-2-diisopropylaminoethyl methylphosphonite (QL) is initially located in one canister, while elemental sulfur is located in a separate canister.

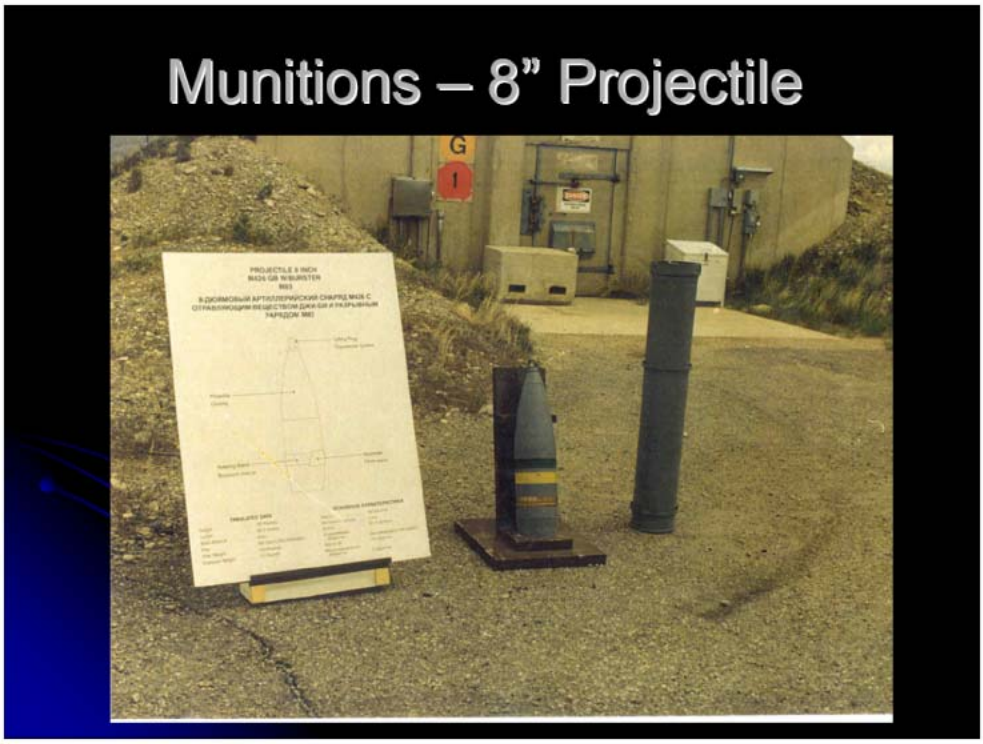


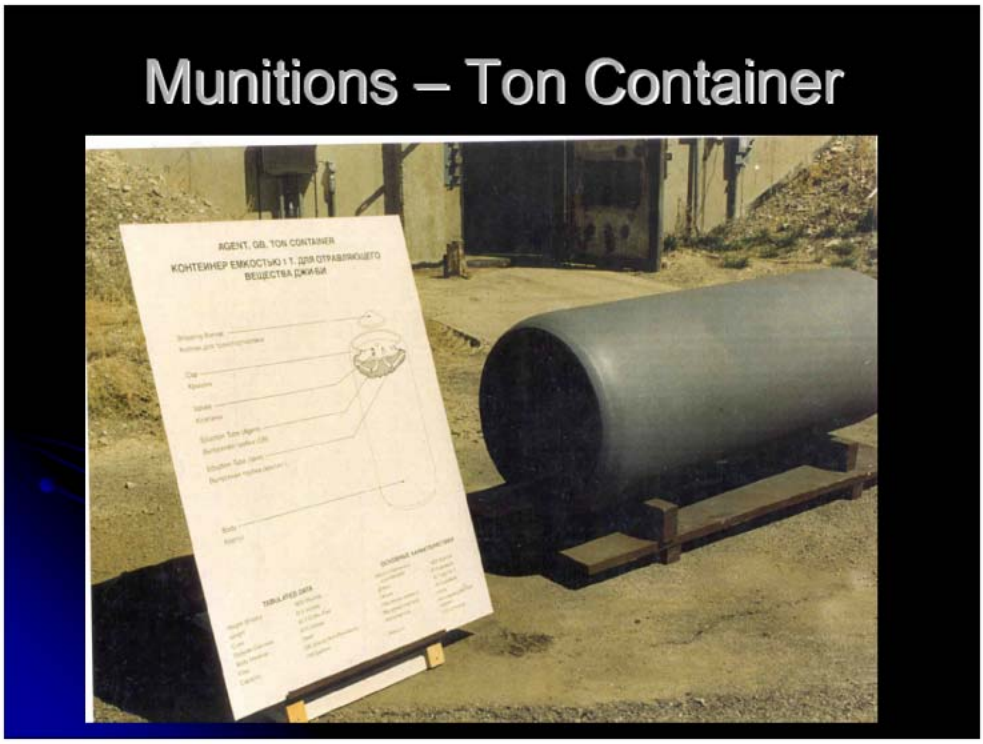

Munitions – Land Mine


Munitions – Spray Tank


Munitions – M55 Rocket


Munitions – 155mm Projectile
PROJECTILE, CHEMICAL AGENT GB
M121A1, 155mm


Munitions – 8” Projectile


Munitions – Ton Container
AGENT, GB, TON CONTAINER
КОНТЕЙНЕР ЕМКОСТЬЮ 1 Т. ДЛЯ ОТРАВЛЯЮЩЕГО ВЕЩЕСТВА ДЖИ-БИ

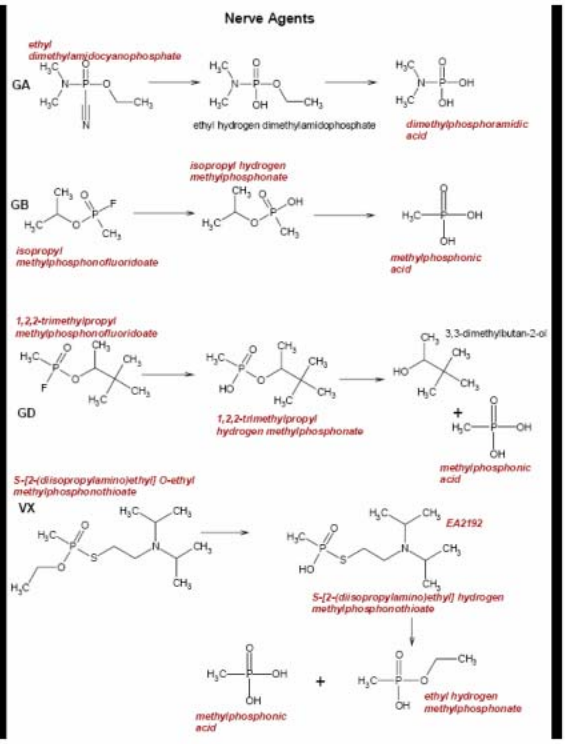
Nerve Agent Hydrolysis

GA=Tabun

GB=Sarin

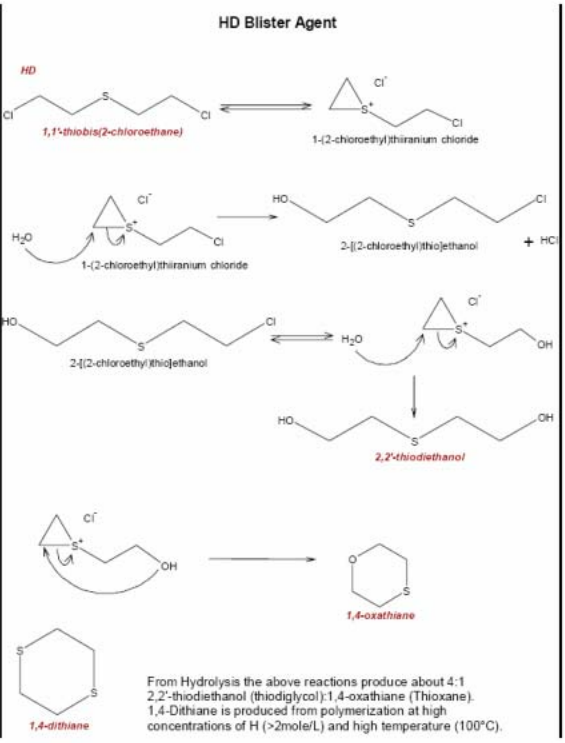
GD=Soman

Target Compounds Highlighted in Red



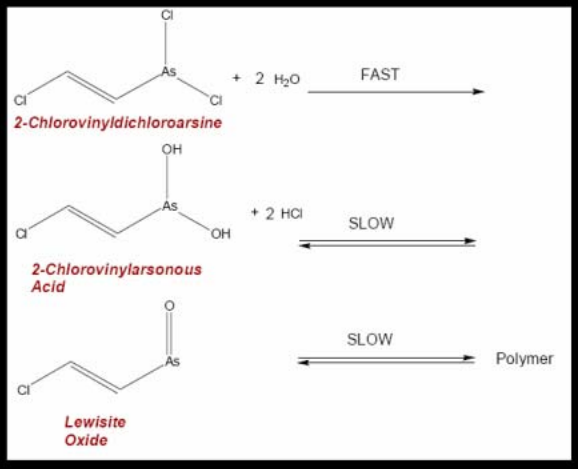
HD Hydrolysis

Target Compounds Highlighted in Red



Lewisite Hydrolysis

- Lewisite (L),
  - CAS#: 541-25-3
  - Hydrolysis
  - Polymerization



Target Compounds Highlighted in Red

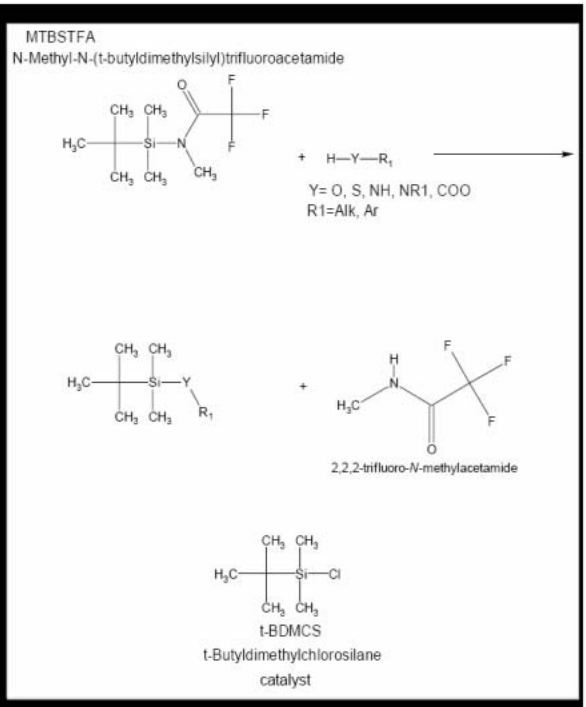
Degradation Products

Degradation Product	Original Agent	CAS Number
Dimethylphosphoramidic Acid	GA	33876-51-6
Diisopropyl methylphosphonate	GB	1445-75-6
Isopropyl methylphosphonic Acid (IMPA)	GB	1832-54-8
1,2-Dichloroethane	HD	107-06-2
1,4-Dithiane	HD	505-29-3
Thiodiglycol	HD	111-48-8
1,4-Thioxane	HD	15980-15-1
2-Chlorovinyl Arsonous Acid	Lewisite	85090-33-1
Lewisite Oxide	Lewisite	1306-02-1
EA2192	VX	73207-98-4
Ethyl methylphosphonate	VX	1832-53-7
MethylPhosphonic Acid	VX, GB, GD	993-13-5
Pinacolyl methyl phosphonate	GD	616-52-4

Yellow Cells = Not Commercially Available

OP Derivatization

- Replaces Active hydrogen's to form t-BDMS derivatives.
- Exceptionally Strong yet mild silylating agent.
- ~10,000 times more resistant to hydrolysis than TMS derivatives.
- Produces easily interpreted mass spectra for GC/MS.
- This technique has worked for all degradation products of interest in this project.



GC/MS Methods

- Scan mode
  - Injector: 300°C; Oven: 40°C(4min), 10°C/min to 270°C (8min); Column: HP-5MS 30m x 250µm with 0.25µm film; Flow 1.0mL/min He, 7.07psi, 36cm/sec; Mass range 35-500amu
- SIM Mode
  - Tuned to each compound
- Combined SIM/SCAN?
  - Not all equipment has the ability
  - Lower signal to noise ratio
  - No plans to use this on the Agilent 5975

Sample Preparation

- Extract Agent/Degradation Products
- React MTBSTFA/1%TBMCS with extracted Degradation Products
- Dilute and add Internal Standards
- Analyze

Extraction

- Extract Agent/Degradation Products
  - OP's Quaternary Amine SPE Cartridge
    - Extract from SPE with Acidic Methanol
  - HD – Mustard, C18 SPE Cartridge
    - Extract from SPE with Ethyl Acetate

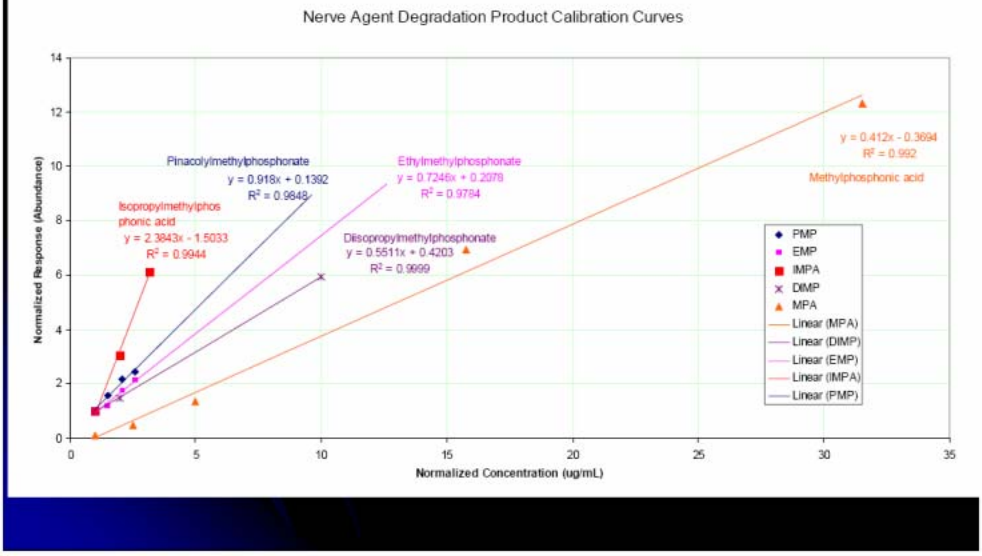
Sample Reaction

- React MTBSTFA/1%TBMCS with extracted Degradation Products
  - 60°C ± 2°C for 4 Hours

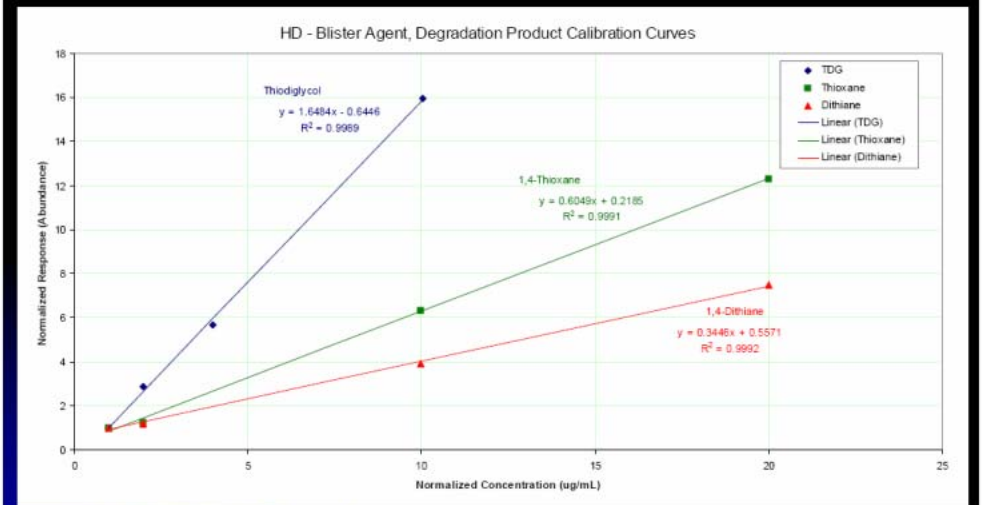
Mass Spec Results

Degradation Hydrolysis Product	Parent	Predominant Masses from Most to Least Abundant									
Diisopropyl Methyl Phosphonate	180	97	123	79	43	45	41	27	80	139	121
Isopropyl Methyl Phosphonic Acid	252	153	75	41	154	39	73	121	27	195	155
1,4-Dithiane	120	120	61	46	45	60	92	64	59	73	27
Thiodiglycol	122	61	45	104	91	47	60	31	46	27	44
1,4-Thioxane	104	46	28	61	104	45	27	26	74	76	47
Ethyl Methyl Phosphonate	238	153	181	75	41	39	56	27	29	154	182
Methyl Phosphonic Acid	324	267	73	268	135	195	133	153	269	75	212
Pinacolyl Methyl Phosphonate	294	153	154	237	41	75	211	73	43	69	121
	Highlighted Masses are MTBSTFA derivatives										

Calibration Curves



Calibration Curves



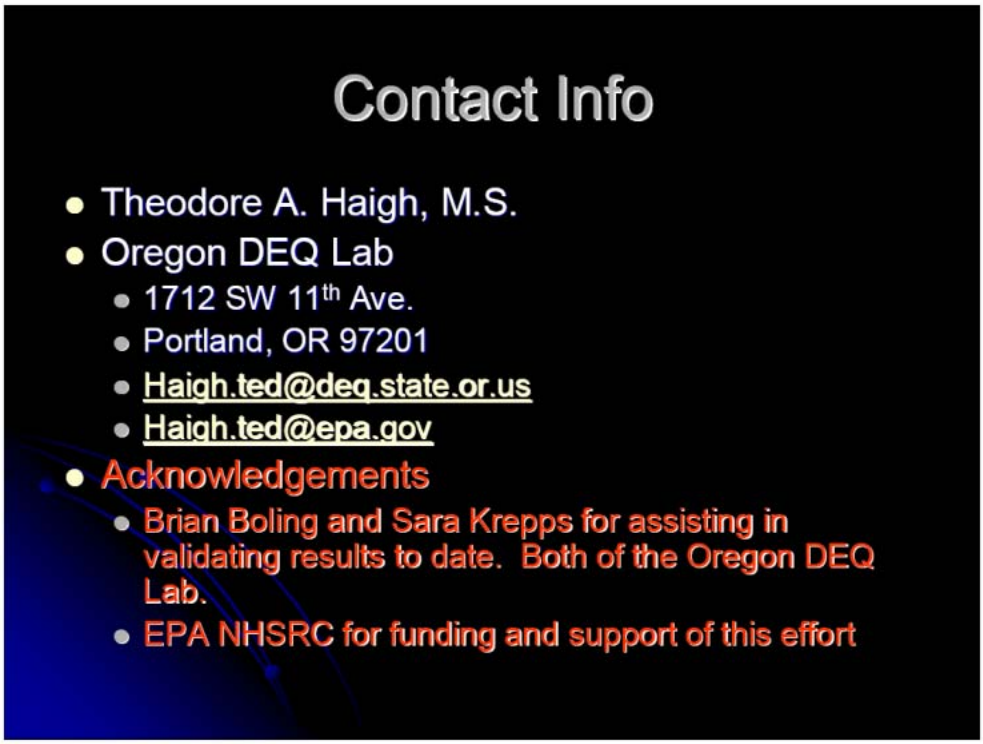
Status

- Method calibrated for all compounds.
  - Linear to about 1ppm (TDG ~2ppm)
- MTBSTFA works well
  - Working on most simplistic procedure
- SIM method in place
  - Masses of derivatized compounds added

Status

- Detection Limits with the SIM method currently being validated.
  - ppb=ng/mL
- Water extraction efficiencies underway.
- Results will be published.

Compound	Theoretical Concentration Producing a 5:1 S:N ratio (ppb or ng/mL)
1,4-Thioxane	273.6
1,4-Dithiane	51.8
Thiodiglycol	1545.7
Pinacolyl Methyl Phosphonate	1.7
Methyl Phosphonic Acid	0.5
Ethyl Methyl Phosphonic Acid	0.8
Isopropyl Methyl Phosphonic Acid	37.5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Brian Boling and Sara Krepps for assisting in validating results to date. Both of the Oregon DEQ Lab.
EPA NHSRC for funding and support of this effort

Validation of Standard Analytical Protocol for Semi-Volatile Organic Compounds

Brian Schumacher
U.S. Environmental Protection Agency/National Exposure Research Lab

ABSTRACT

There is a growing concern with the potential for terrorist use of chemical weapons to cause civilian harm. In the event of an actual or suspected outdoor release of chemically hazardous material in a large area, the extent of contamination must be determined. This requires a system with the ability to prepare and quickly analyze a large number of contaminated samples for the traditional chemical agents, as well as numerous toxic industrial chemicals. Liquid samples (both aqueous and organic), solid samples (e.g., soil), vapor samples (e.g., air) and mixed state samples, all ranging from household items to deceased animals, may require some level of analyses. To meet this challenge, the U.S. Environmental Protection Agency (EPA) National Homeland Security Research Center, in collaboration with experts from across the EPA and other Federal Agencies, initiated an effort to identify analytical methods for the chemical and biological agents that could be used to respond to a terrorist attack or a homeland security incident. The EPA began development of standard analytical protocols (SAPs) for laboratory identification and measurement of target agents in case of a contamination threat. These methods will be used to help assist in the identification of existing contamination, and the effectiveness of decontamination as well as clearance for the affected population to reoccupy previously contaminated areas. One of the first SAPs developed was for the determination and measurement of the semi-volatile organic compounds (SVOCs). The SAP was based on EPA SW-846 Methods 3520C, 3535A, 3540C/3541, 3545A, and 3580A for the sample preparation and Method 8270D for analysis. The matrices of concern for these methods include soil/sediment, wipes, and drinking water samples. To address the potential for contamination via air, the air toxic method Task Order 13-A (TO) was selected.

The primary objective of this research is to provide validation of several sample preparation and analysis methodologies for selected semi-volatile organic compounds (SVOCs) in four matrices (drinking water, soil, air, wipes). The evaluation of sample preparation and analytical methodological study was conducted to address the following questions:

(1) What are the responses (definitive, questionable, none) of various chemicals based on initial evaluation of Method 8270?

(2) What are the responses (definitive, questionable, none) of various chemicals based on initial evaluation of Method 525.2?

(3) What are the limits of quantitation (LOQ) for chemical analytes?

(4) What are the recoveries of the selected chemicals from various matrices by using the above mentioned methods?

(5) What are the recoveries of the selected chemical from various matrices by using micro-extraction technique?

(6) Are there any method modifications needed to include maximum number of analytes in a single injection? If so, what kinds of modification(s) are needed?

The research is nearing completion and the results will be presented at the conference.

NOTICE: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

Laboratory Preparation and Concept of Operation for Detection of Chemical Warfare Agents and Degradation Products in Environmental Samples

Robert Maxfield, Michael Kenyon, Daniel Boudreau, and Jeremy O'Kelly
U.S. EPA Region 1 New England Regional Laboratory

ABSTRACT

Post 9/11 the US Environmental Protection Agency (EPA) has had to take a more expansive view of what may be required from an environmental laboratory when addressing decontamination following an intentional release of a hazardous material. A range of particularly toxic chemicals known as chemical warfare agents (CWAs) has been identified as a particular concern due to the very limited testing capacity for these materials within the environmental laboratory community. DHS and EPA have developed a pilot program to expand the nation's capacity for CWAs and their environmental degradation products.

The nature of these agents necessitates administrative controls limiting access to CWA materials. Implementation of these controls presents some unique challenges to an environmental laboratory considering adding CWA analytical capability to its range of services.

The first part of the presentation will discuss a range of preparatory activities that will be necessary in order to establish an analytical capability for chemical warfare agents within an environmental laboratory. The presentation will cover communications strategies, laboratory infrastructure improvements, health and safety procedures, agent accountability measures and facility security requirements. The speaker will also describe a concept of operations for the Regional Laboratory that builds in strategies for limiting hazard exposure, dual use of instruments and laboratory space, and surge capacity for major incident response.

Laboratory Preparation for Detection of Chemical Warfare Agents (CWAs) in Environmental Matrices

Rob Maxfield
EPA New England
August 20, 2007

Roadmap

- Project Context and Concept of Operations
- Communications
- Health and Safety
- Infrastructure
- Accountability
- Security

Context

- Federal Government Laboratory
- Modern Laboratory with Engineering Controls for Toxic Chemicals
- Goal: Confirmatory CWA/TIC Laboratory within environmental Laboratory Response Network (eLRN)
- Ultra-dilute CWA Calibration Materials
- Current Status: Infrastructure Improvement Progress

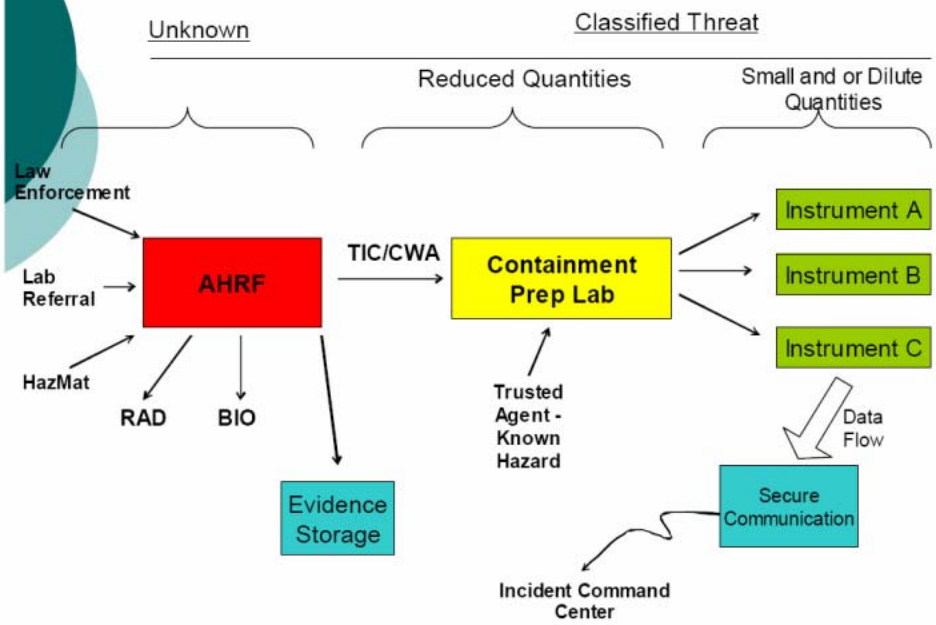
Considerations

- Environmental Samples w CWA vs Ultra-Dilute Standards
- Dedicated vs Dual-Use
- Capability vs Capacity
- Operational Modes - PTs>Small Event>Large Event
- Decontamination and Return to Routine Use

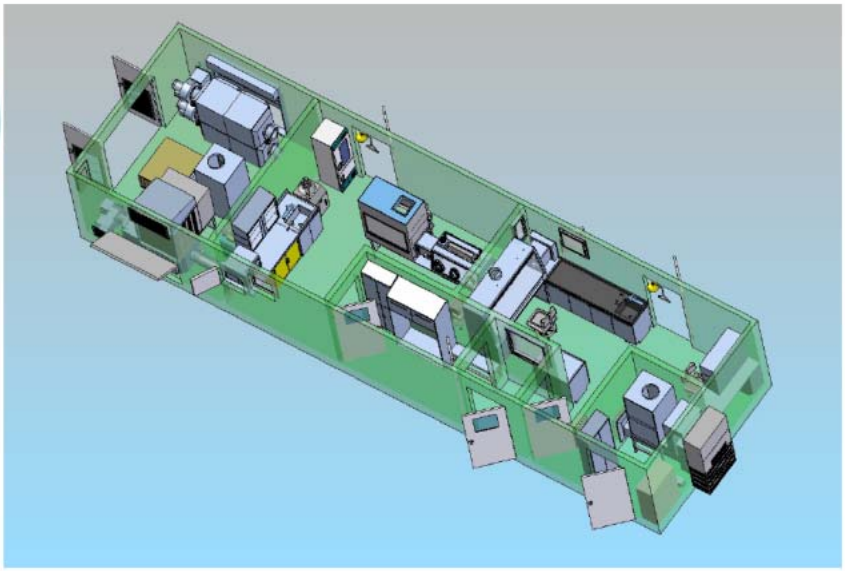
Risk Management

- Hazard Assessment
- Reduce Volume
- Reduce Concentration
- Control Personnel Access
- Administrative Exclusion Zones

Concept of Operations



All Hazard Receipt Facility (AHRF)



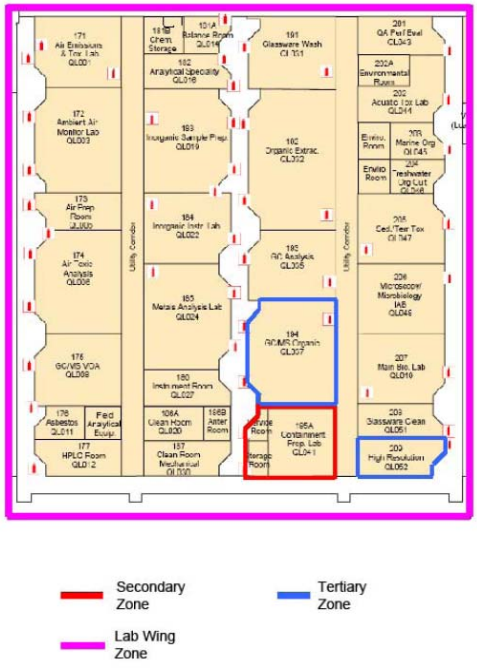
Exclusion Zone Concept

Primary Zone
AHRF - high hazard, dedicated use, limited access

Secondary Zone
Containment Prep Lab - moderate hazard, limited volume samples, dedicated use, limited access

Tertiary Zone
Instrument Labs - moderate hazard, sealed and or reduced volume extracts, dual use, limited access based on use

Lab Wing Zone
Laboratory Wing - moderate hazard, dual use, surge capacity only, limited access based on use



Communications

- Essential!
- Different Audiences
- Professional Assistance
- Planning
  - Sequence of notification
  - Timing
  - Regular updates
- National Environmental Policy Act

Health and Safety

- Addendums to Existing SOPs
  - Chemical Hygiene
  - Medical Monitoring
  - Laboratory Safety
  - PPE
- Medical Response
- Antidotes

Building Infrastructure

- Engineering Controls
  - Hoods
  - Exhaust filters
- Safety Equipment
  - Eye wash and shower locations
  - Sinks
- Laboratory Space
  - Floors
  - Controlled Access
  - Administrative Exclusion Zones

Accountability

- Management of Controlled Materials
- Assigned Custodian
- Weekly Inventory
- Use, destruction, and return
- Reporting to Program

Security

- Facility
  - Locks
  - Lighting
  - Key control
  - Security Plan
- Storage Area and Refrigerator

Acknowledgement

- Department of Homeland Security
  Directorate for Science and Technology
  Chemical and Biological Division
- U.S. Environmental Protection Agency
  Office of Solid Waste and Emergency Response
  Office of Emergency Management
- U.S. Environmental Protection Agency
  Office of Research and Development
  National Homeland Security Research Center
- Midwest Research Institute

References

- Army Regulation 50-6 "Chemical Surety" (AR 50-6) Chapter 6, 26 June 2001
- Edgewood Chemical Biological Center (ECBC) "Guidelines for Managing a Research Development Testing Evaluation (RTDE) Dilute Solution Laboratory", September 2005
- Interagency Agreement between the USEPA and Department of Defense (DoD), November 22, 2006, for use of ultra-dilute chemical weapons agent (CWA) solutions
- Initial Assessment of the New England Regional Laboratory Function for Chemical Warfare Agent (CWA) Analysis, June 18, 2007

For more information on EPA New England's Regional Laboratory, go to:
www.epa.gov/ne/lab

INORGANIC METHODS

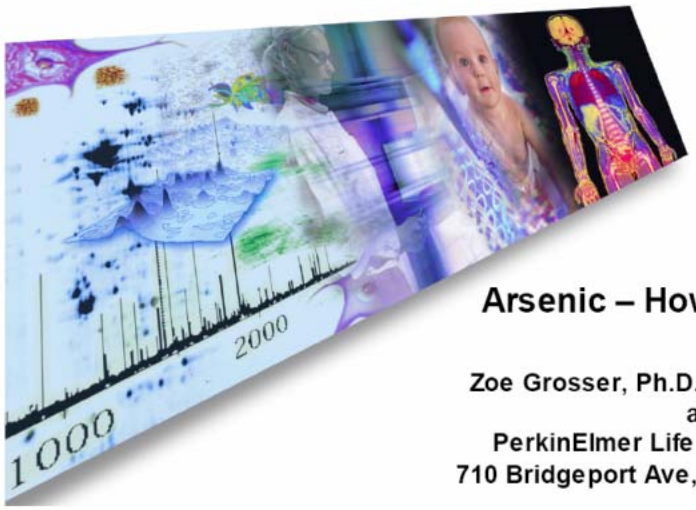
Arsenic Measurements – How Low Can You Go?

Zoe Grosser
PerkinElmer, Inc.

ABSTRACT

Arsenic is a toxic element of interest in many environmental programs. In the US drinking water program the regulated limit was recently lowered from 50 µg/L to 10 µg/L. This ruled out traditional ICP-OES from measuring the required limit because of detection limit constraints. Furthermore, California has considered implementing regulations requiring limits lower than the federal level, perhaps as low as 4 ppt! How can lower levels of arsenic be measured? What are the lowest levels that can be measured and what issues must be considered to make adequate measurements at ultratrace levels? These questions will be considered and data presented from a variety of approaches.

PerkinElmer®
precisely.



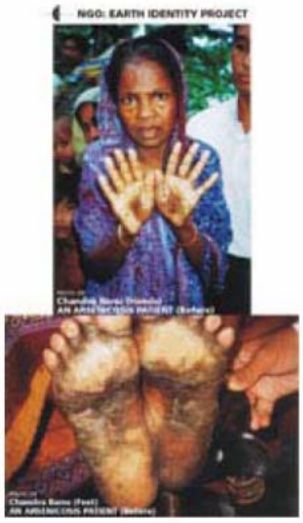
Arsenic – How Low Can you Go?

Zoe Grosser, Ph.D., Lee Davidowski, Ph.D.,
and Ken Neubauer, Ph.D.
PerkinElmer Life and Analytical Sciences
710 Bridgeport Ave, Shelton, CT 06484 USA

Arsenic Background

PerkinElmer®
precisely.

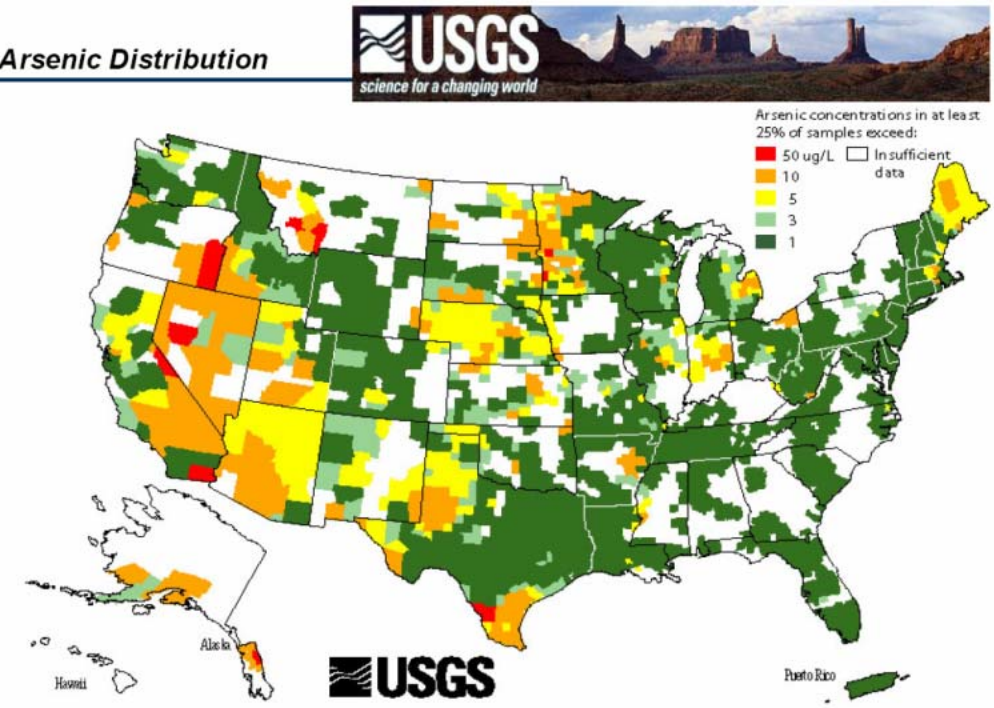
- As is obviously toxic at high (mg/L) levels
- Chronic exposure to As can cause
  - Skin lesions
  - Skin cancer
  - Internal cancers of the bladder, kidney, and lung
  - Neurological effects
  - Hypertension and cardiovascular disease
  - Pulmonary disease
  - Peripheral vascular disease
  - Diabetes mellitus
- As may be toxic at very low (ug/L) levels



Source: *Bulletin of the World Health Organization, 2000, 78 (9).*

Page 2

Arsenic Distribution



http://nationalatlas.gov/arsenicm.html

Page 3

Arsenic in Drinking Water Background

- Regulated in the US under the US Safe Drinking Water Act since 1974.
- World Health Organization (WHO) limit:
  - 1958 – 0.20 mg/L
  - 1963 – 0.05 mg/L
  - 1993 – 0.01 mg/L established as a provisional guideline because of measurement limitations at concentrations below 10 ppb

Page 4

The Arsenic Rule for US Drinking Water

- Federal Register / Vol. 66, No. 14 / Monday, January 22, 2001 / Rules and Regulations
- Maximum Contaminant Level Goal (MCLG) for arsenic of zero
  - Health-based, non-enforceable
- Maximum Contaminant Level (MCL) for arsenic of 0.01 mg/L
  - Enforceable
  - This regulation will apply to non-transient non-community water systems, which are not presently subject to standards on arsenic in drinking water, and to community water systems.
- Water systems must comply with the new 10 ppb standard by January 23, 2006.

Page 5

Los Angeles Daily News — Friday, March 07, 2003

State EPA recommends lowering arsenic levels

Jennifer Coleman Associated Press

SACRAMENTO -- State environmental officials released a preliminary public health goal for arsenic in drinking water Friday, recommending a level that's far below the federal standard. The draft public health goal will be used by state officials in creating a drinking water standard for arsenic, a naturally occurring carcinogen. The standard will set the maximum allowable level of arsenic in drinking water.

The California Environmental Protection Agency, through the Office of Environmental Health Hazard Assessment, proposed a limit of 4 parts per trillion for arsenic in drinking water. At that level, there wouldn't be more than one additional cancer case in a population of one million people, the department said.

"Arsenic is a naturally occurring element, but it is also one of the most toxic substances commonly found in drinking water," said Joan E. Denton, the director of OEA. The proposed goal is about 2,500-fold lower than the incoming federal standard for arsenic in drinking water, which will be 10 parts per billion in 2006, said Dr. Gina Solomon, a senior scientist with the Natural Resources Defense Council. ...

States can set their own goals that meet or exceed the federal standard.

Page 6

California Update

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

NEWS RELEASE

OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT

FOR IMMEDIATE RELEASE:
Release No. 04- 02
April 23, 2004

CONTACT: Allan Hirsch
(916) 324-0955
www.oehha.ca.gov

OEHHA Publishes Health Goal for Arsenic in Drinking Water

SACRAMENTO – The California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) today announced the publication of a final Public Health Goal (PHG) for arsenic in drinking water.

The PHG identifies 4 parts per trillion as a level of arsenic in drinking water that would not be expected to pose a significant human health risk.

"Our public health goal establishes a long-term objective for the reduction of arsenic in California's drinking water," OEHHA Director Dr. Joan E. Denton said. "Arsenic is one of the most toxic substances commonly found in drinking water, and it occurs naturally in many parts of the world, including California."

Page 7

US EPA Water Quality Criteria

EPA's compilation of national recommended water quality criteria is presented as a summary table containing recommended water quality criteria for the protection of aquatic life and human health in surface water for approximately 150 pollutants. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and tribes to use in adopting water quality standards.

Priority Pollutants

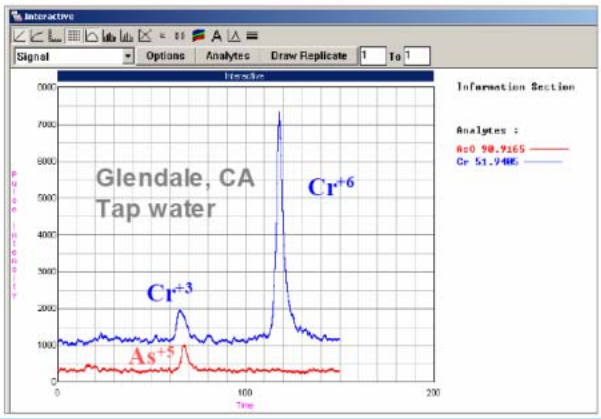
			Freshwater		Saltwater		Human Health for the consumption of		
	Priority Pollutant	CAS Number	CMC[1] (acute) (µg/L)	CCC[1] (chronic) (µg/L)	CMC[1] (acute) (µg/L)	CCC[1] (chronic) (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)	FR Cite/ Source
1	Antimony	7440360					5.6 B	640 B	65FR66443
2	Arsenic	7440382	340 A,D,K	150 A,D,K	69 A,D,bb	36 A,D,bb	0.018 C,M,S	0.14 C,M,S	65FR31682 57FR60848

Page 8

Speciation

- Toxicity of the different forms of arsenic are very different.
- Bioavailability of different species may be different
- Environmental mobility may depend on the form
- Future regulations may be species-based

- Lower concentration measurements desirable since element is spread among several peaks



Page 9

Arsenic Detection Limits in Literature

Species	Preconcentration/ separation	Detection	LoD (µg/L)	Reference
As (III)	FI-KR	ICP-MS	0.021	X-P. Yan, R. Kerrich, MJ. Hendry, Anal. Chem. (70) (1998) 4736
As (V)		ICP-MS	0.029	
As (V)	SPE	ICP-MS	0.008	C. Yu, Q. Cai, Z-X Guo, Z. Yang, S.B. Khoo, Spectrochim. Acta B 58 (2003) 1335
As (III)	HG	ICP-MS	0.003	M-F. Huang, S-J. Jiang, C-J. Hwang, J.A.A.S. 10 (1995) 31
As (III)	HG-GF	ICP-MS	0.002	I. Marawi, J. Wang, J.A. Caruso, Anal. Chim. Acta 291 (1994) 127
As (III)	HPLC	ICP-MS	0.02	B.S. Sheppard, W.L. Shen, J.A. Caruso, D.T. Heitkemper, F.L. Fricke, J.A.A.S. 5 (1990) 431
As (III)	HPLC	ICP-MS	0.06	A. Shraim, N.C. Sekaran, C.D. Anuradha, S. Hirano, Appl. Organomet. Chem 16 (2002) 202

D.Q. Hung, O. Nekrassova, R.G. Compton, *Analytical Methods for Inorganic Arsenic in Water: a Review*, Talanta 64 (2004) 269.

Page 10

How to get Lower Detection Capabilities

- Use technology with lower detection limits
- Optimize the method for the element of interest exclusively
- Use sample preparation to optimize sample introduction
- Preconcentrate the element of interest before analysis

Page 11

Arsenic Method Detection Limits – Typical AS Techniques

Technique	MDL (μg/L)
Flame AA	150
GFAA	0.13
Axial ICP-OES	2.2
ICP-MS	0.03

- ICP-MS provides the lowest detection limit
- As a multielement technique, it also provides the ability to run may elements at once

Page 12

Optimization of Instrumental Analysis Conditions

- ICP-MS chosen for optimization
- Optimize conditions for arsenic
- Integration time
- Dwell time

Page 13

Detection Limit Improvement – ICP-MS

- Power: 1500W
- Integration time: 1 and 2 seconds evaluated
- Oxygen added to shift analyte to AsO 91

Integration Time	MDL (ppt)
1 sec	2.6
2 sec	1.3

Page 14

What Interferes with Arsenic Analysis?

- Chlorides
  - $ArCl^+$
  - $CaCl^+$
- Examples of chloride or calcium containing matrices
  - Environmental
    - Waters, soil digests
  - Clinical
    - Urine
  - Semiconductor
    - High purity HCl
- Isobaric Correction Equation for Standard ICP-MS

  As = As75 - 3.127*{ArCl77 – (0.815*Se82)}

Page 15

Collisional Focusing

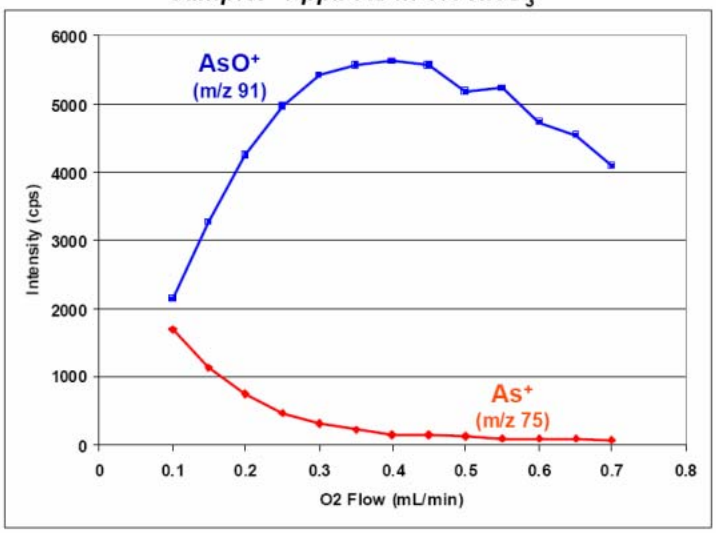
- There are two ways to use the Dynamic Reaction Cell (DRC) to correct for isobaric interferences.
  - Remove the interference before the analyte enters the analytical quadrupole
- Move analyte away from the interference
  - Lower backgrounds
  - Possible because of controlled chemistry

Page 16

Reaction of As^+ with O_2: Moving the Analyte

PerkinElmer

Sample: 1 ppb As in 1% HNO_3



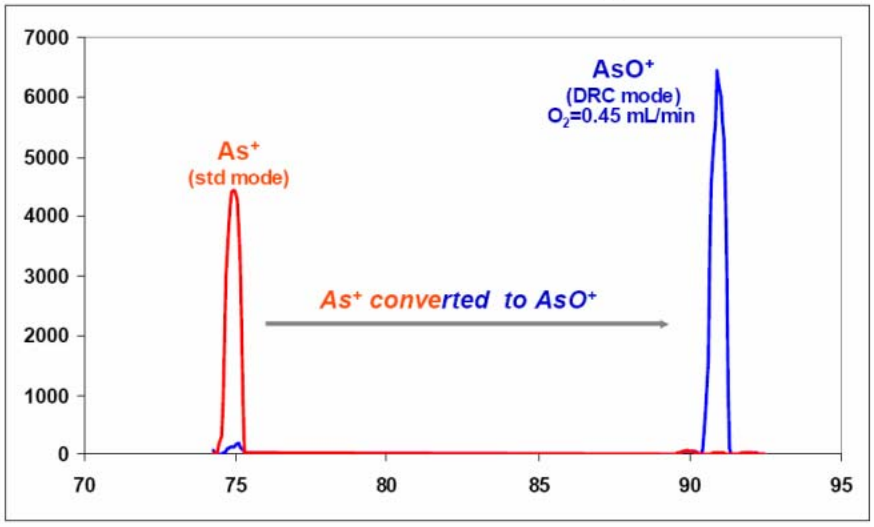
AsO^+ forms while As^+ disappears

Page 17

Conversion of As^+ to AsO^+

PerkinElmer

Sample: 1 ppb As in 1% HNO_3



Page 18

As in the presence of Matrices

Y. Kishi, K. Kawabata *"Analysis of Semiconductor-Grade HCl with the ELAN DRC ICP-MS: Elimination of Chloride-Based Interferences"* ***Atomic Spectroscopy*** 23, 5 (2002) 165.

Matrix	DL (ppt)	BEC (ppt)
20% HCl	3.0	13

(AsO 91 in DRC mode)

Page 19

Hydride Generation Sample Introduction

- Hydride generation provides a gaseous sample

$$As^{+3} + 6H \longrightarrow AsH_3 + 3H^+$$

- That is introduced into the analytical system as a plug
- Cleaned of the matrix

Page 20

Hydride Generation Sample Introduction

- Hydride generation provides a gaseous sample

$$As^{+3} + 6H \longrightarrow AsH_3 + 3H^+$$

- That is introduced into the analytical system as a plug
- Cleaned of the matrix

Page 20

Hydride Generation Detection Limits

- Hydride generation with atomic fluorescence detection
  B. Chen, M. Krachler, Z. I. Gonzalez, W. Shotyk, J.A.A.S. 2005, 20, 95-102. *Improved Determination of Arsenic in Environmental and Geological Specimens using HG-AFS*

  Detection limit measured As (III): 6 ng/L (3 σ)

Page 22

Clean Room Effects

- Help to minimize the introduction of elements found in air and dust, such as Al, Zn, Na
- Arsenic is not common, but when you get to ultratrace concentrations everything becomes an easy contaminant
- Clean acids and water are a minimum requirement

Page 23

Clean Room Detection Limit

- In a clean room arsenic detection limits can be further lowered
- 1% Nitric Acid Matrix
- 8 Readings
- IDL = 3*Standard Deviation

Spike Level (ppt)	^{75} As IDL (ppt) (DRC Mode)
0	0.6
1	1.8
5	1.7

Page 24

What if we Combine Hydride generation and Best Conditions?

- Hydride generation continuous flow, not batch
- Clean reagents necessary for good results
- Integration time 4 seconds
- O_2 added to remove any further interfering species
- No clean room

Detection Limits (ng/L)

Trial 1	1.5
Trial 2	1.9

Page 25

Preconcentration

- EPA Method 1638 combines preconcentration with ICP-MS to meet water quality criteria for 4 elements
  - Publication by Canadian National Research Council describes a similar method for 8 elements,

  Determination of Cu, Ni, Zn, Mn, Co, Pb, Cd, and V in Seawater Using Flow Injection ICP-MS, S.N. Willie, Y. Iida , and J.W. McLaren, Atomic Spec. 19 (3) 67 (1998).

- Arsenic forms AsO^+ so a different approach required

- Potential to further reduce detection limits possible

Page 26

Evaluation Criteria – ICP-MS Procedures

- Detection limit performance
  - Careful optimization for one element good
  - Hydride also has advantages
  - DRC to remove interferences
- Time for measurement
  - Hydride has more set-up
- Possibility for automation
  - The more complicated the procedure, the harder to automate
- Capital investment
  - Clean room can be expensive

Page 27

Summary

- Lower arsenic compliance levels may be required in the future
- A number of techniques are available for consideration
- As in any situation where low detection limits are to be measured, extra care will be required to purchase clean reagents and avoid contamination of samples at any point along the analysis path

Page 28

Metrohm-Peak Ion Chromatography

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Bromide and Bromate by Suppressed Conductivity, UV/VIS and tandem Mass Spectrometry

Jay Gandhi, Technical Manager
Metrohm-Peak, LLC
Houston TX

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Outline

- History and Background
- Current Analytical method for regulations
- Emerging technologies
- Conclusion

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US EPA method 300.0 & 300.1

Bromide and Bromate By Suppressed Conductivity

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Current Analytical Methods

- USEPA Method 300.0 Part B
- Dual Column Approach
- Dual Loop injection
- Method Detection Limit is 10 parts per billion for BrO_3
- USEPA MCGL is 0 ppb for Bromate
- Needs another method to achieve MCGL

- USEPA Method 300.1 Part B (DCA as surrogate)
- Dual Column Approach
- Dual Loop injection
- Method Detection Limit is 10 parts per billion
- USEPA MCGL is 0 ppb for Bromate
- Needs another method to achieve MCGL

Here are the results we achieved in collaboration with USEPA region-6 Lab since 2003

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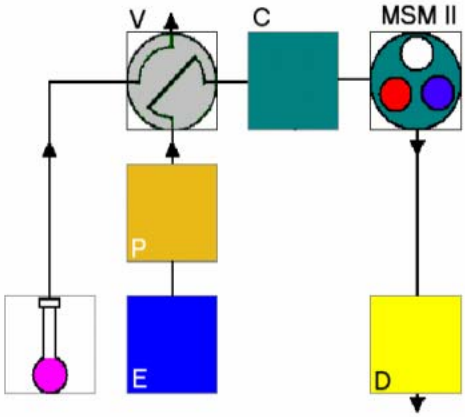
USEPA method 300.0 and 300.1

Professional IC	
E	Eluent
P	Pump
V	Valve with loop
C	Column
MSM II	Metrohm Suppressor Module «MSM»
D	Detector



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Equipment Used/Setup

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Experimental Conditions

- **Metrohm Professional IC**
  - 50 uL loop injection
  - Column: Metrosep ASUPP-7 (4mm x 250mm)
  - Column Temp: 45 °C
  - Eluent: 3.5mM Na_2CO_3 + 15% Acetonitrile
  - Flow rate: 0.8 ml/min

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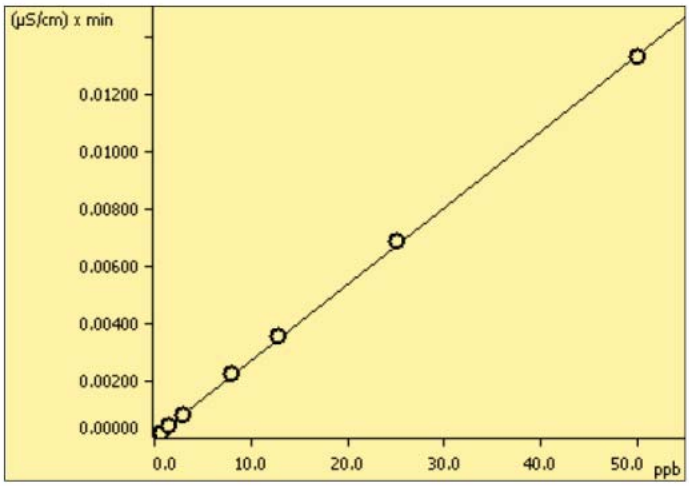
Calibration Curves for Bromate (cond)



Curve Type: Linear
R^2 = 0.99989
RSD %: 2.437

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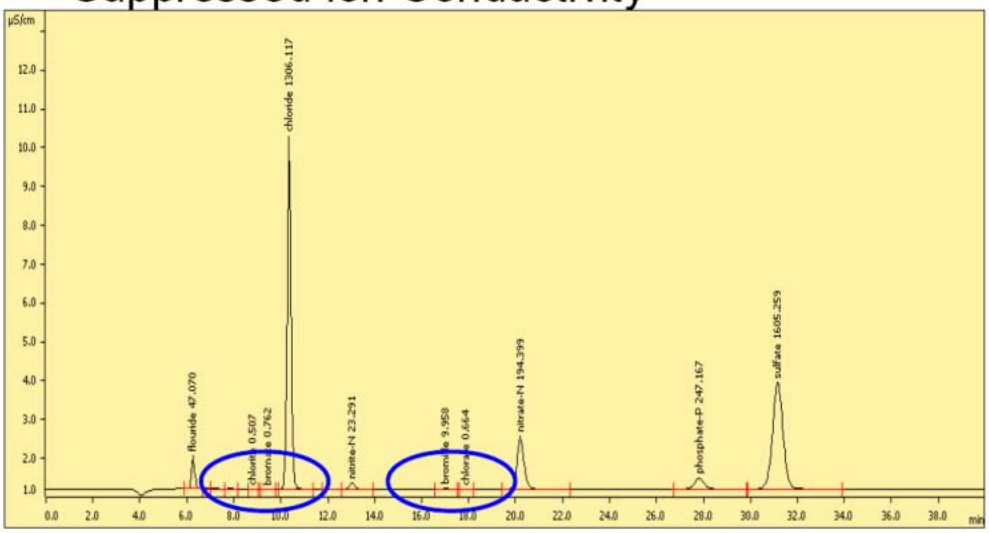
USEPA Method 300.0 and 300.1 part B

- Suppressed Ion Conductivity



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Metrohm-Peak Ion Chromatography

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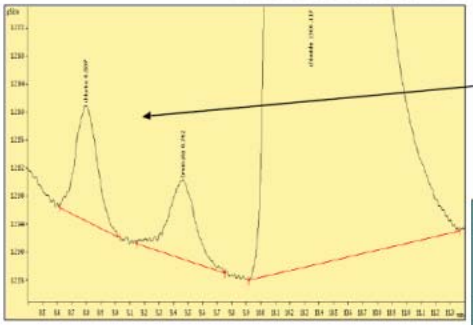
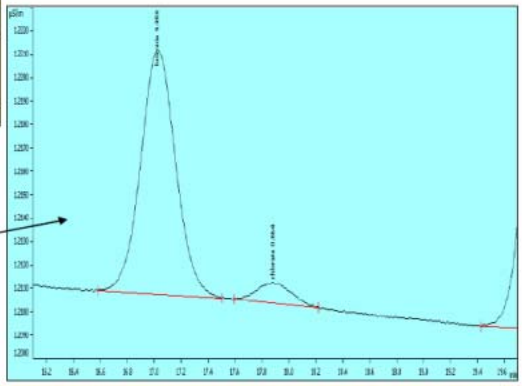
Zoomed Chromatogram



Chlorite and Bromate



Bromide and Chlorate

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US EPA method 317.0 & 326.0

Bromate by UV/PCR

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Ozonation

- Drinking water disinfection technique preferred by consumers
- Frequently utilized in desalination treatment for drinking water
- Increasingly utilized by water treatment facilities
- Used by many bottled water companies
- Forms disinfection byproducts

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Bromate

- Ozonation disinfection forms bromate in waters containing bromide
- Bromide is found in seawater
- Bromate causes cancer in animals
- Bromate has been classified by the International Agency for the Research on Cancer as a possible carcinogen

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Bromate Regulations

- World Health Organization
  - 25 parts per billion exposure limit
  - Lifetime cancer risk of 1:100,000 for 3 parts per billion
- United States Environmental Protection Agency
  - Maximum contaminant level for bromate in drinking water is 10 parts per billion
  - Maximum contaminant level goal of zero parts per billion of bromate in drinking water
- European Community
  - Maximum contaminant level for bromate in drinking water is 10 parts per billion. June 2008, MCL will be at 3 parts per billion

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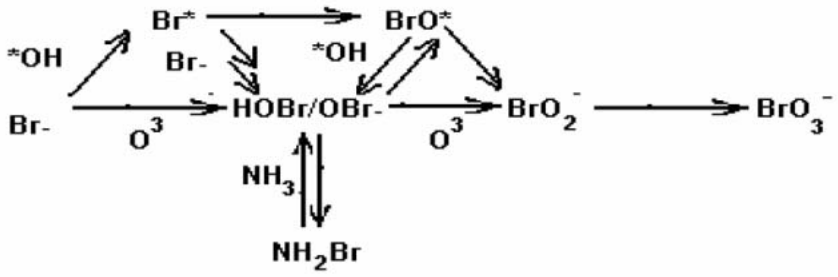
Mechanism of bromate formation

- Complicated mechanism (Pinkernell and von Gunten)
  - Formed by ozonation of bromide containing waters
  - Multi-step reaction
  - Bromide reacts with ozone and hydroxyl radicals
  - Hypobromous acid and hypobromite ions are key intermediates



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Reaction rates

$$O_3 + Br^- \xrightarrow{k_1} O_2 + OBr$$

$$O_3 + OBr^- \xrightarrow{k_2} 2O_2 + Br^-$$

$$2O_3 + OBr^- \xrightarrow{k_3} 2O_2 + BrO_3^-$$

- Where Where $k_1 = 160\ M^{-1}s^{-1}$ (+/- 20)
- $k_2 = 330\ M^{-1}s^{-1}$ (+/- 20)
- $k_3 = 100\ M^{-1}s^{-1}$ (+/- 20) at 20 °C

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Bromate analysis techniques and methods

- Several methods have been used to detect bromate
- Documentation of bromate detection was done prior to information on bromate carcinogenicity
- Modern instrument method detection limits are below USEPA limit of 10 ppb

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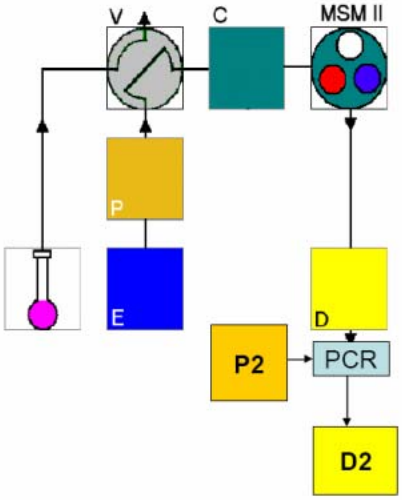
USEPA method 317.0 or 326.0

Professional IC	
E	Eluent
P1	Pump
V	Valve with loop
C	Column
MSM II	Metrohm Suppressor Module «MSM»
D1	Conductivity Detector
P2	Reagent Pump
D2	UV Detector



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USEPA Method 317.0 or 326.0

- USEPA Method 317.0
- Tandem Post Column Reaction for Bromate (Oxyhalide)
- USEPA Method 317 – o-Anisidine as PCR

- USEPA Method 326.0
- Tandem Post Column Reaction for Bromate (Oxyhalide)
- USEPA Method 326.0 – KI as PCR (tri-iodide)

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(1) Influence of temperature

(2) Influence of molybdate concentration

(3) Influence of iodide concentration

(4) Influence of sulfuric acid concentration

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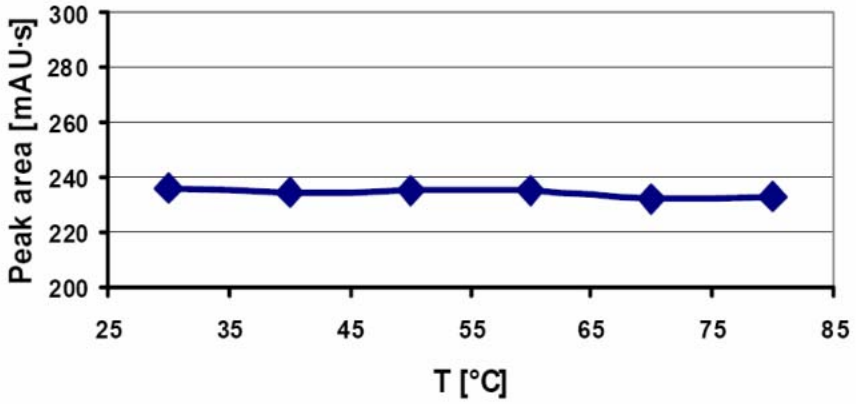
(1) Influence of temperature (of PCR)



→ *No temperature influence !*

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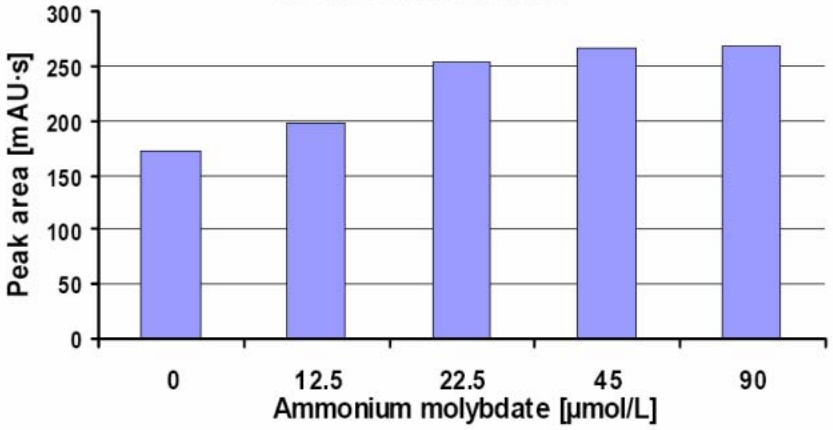
(2) Influence of Molybdate concentration



→ *Without Molybdate 70 % response !*

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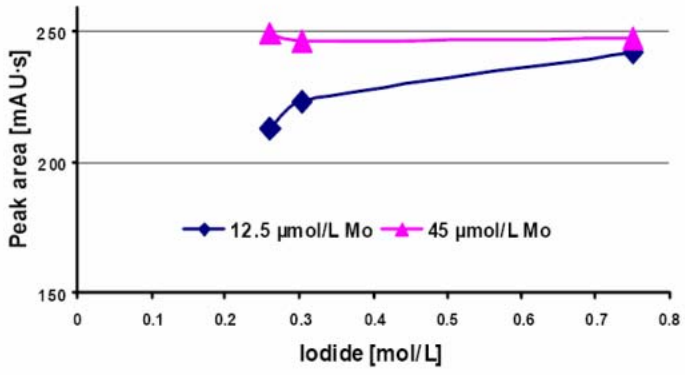
(3) Influence of iodide concentration



→ *With these conditions no influence of Iodide conc.!*

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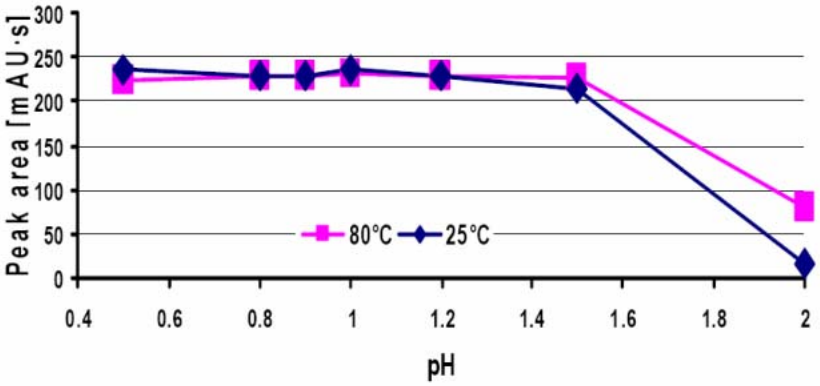
(4) Influence of sulfuric acid concentration



→ At pH > 1.3 decrease of bromate response !

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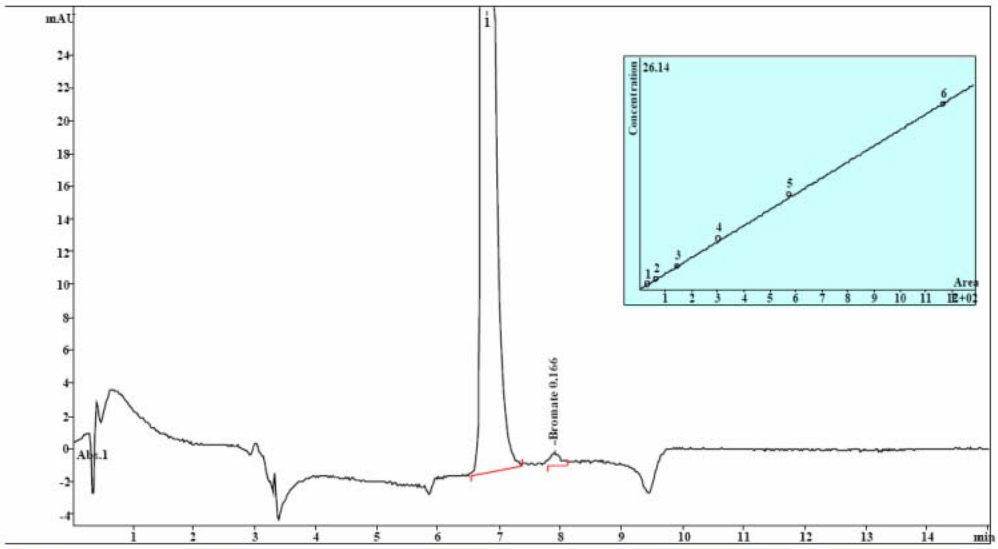
USEPA Method 326 – Triiodide method



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Bromate/Bromide By ICMS

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Objectives

- Optimize ICMS for bromate / bromide analysis
  - Mobile phase optimization
  - Temperature
  - Injection volume
  - Fragmentation optimization / gain
  - Fast Injection Analysis
  - Proper column selection
- Low level calibration
- Method Detection Limit Study

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Ion Chromatography Mass Spectrometry

- Instrument becoming widely used in modern water quality laboratory
- Mass specific detector
- Utilize a high efficiency ion exchange column for bromate and bromide separation
- Using Selective Ion Monitoring (SIM mode)
  - 79 amu for bromide, 129 amu for bromate
  - Eliminates many interferences
  - Improves detection limits

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Method for bromide and bromate analysis by ICMS

- Objectives
  - Measure bromide and bromate of drinking waters below USEPA detection limit of 10 ppb
  - Produce detection limit below 1 ppb
  - Require no special sample preparation or preconcentration steps

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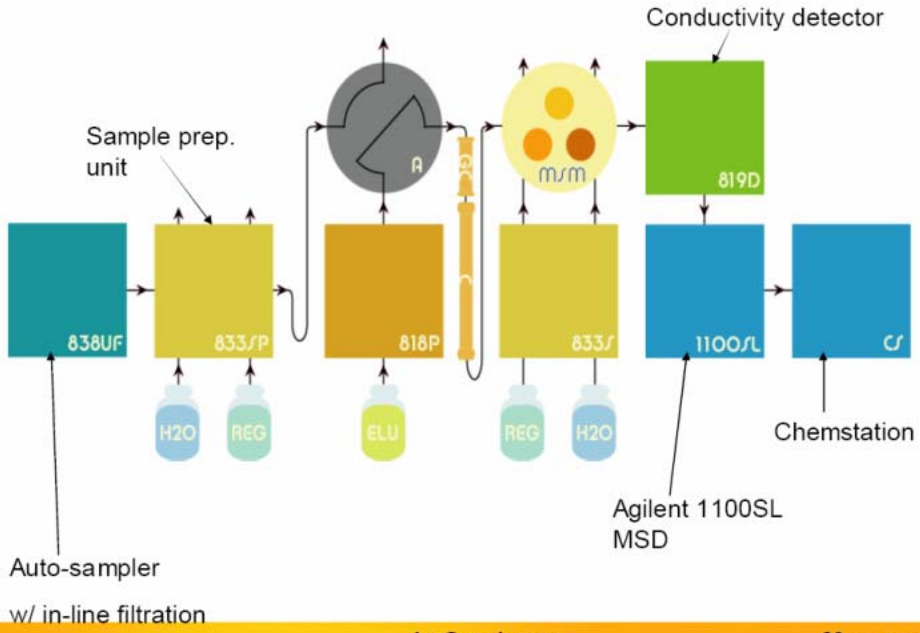
Metrohm-Peak Ion Chromatography — Professional IC



Metrohm-Peak Ion Chromatography — Professional IC

Experimental Conditions

- **Metrohm Advanced IC**
  - 50 uL loop injection
  - Column: Metrosep ASUPP-7 (4mm x 250mm)
  - Column Temp: 45 °C
  - Eluent: 3.5mM Na_2CO_3 + 15% Acetonitrile
  - Flow rate: 0.8 ml/min with NO Matrix Diversion.
- **Agilent 1100 SL LC/MSD ESI**
  - Negative mode "auto-tune"
  - V_{cap} = 1750V, Drying Gas = 10L/minute @ 350 °C.
  - Dominick Hunter Nitrogen Generator applied for continuous drying gas flow
  - Nebulizer Pressure=50 psig.
  - Fragmentor = Variable.

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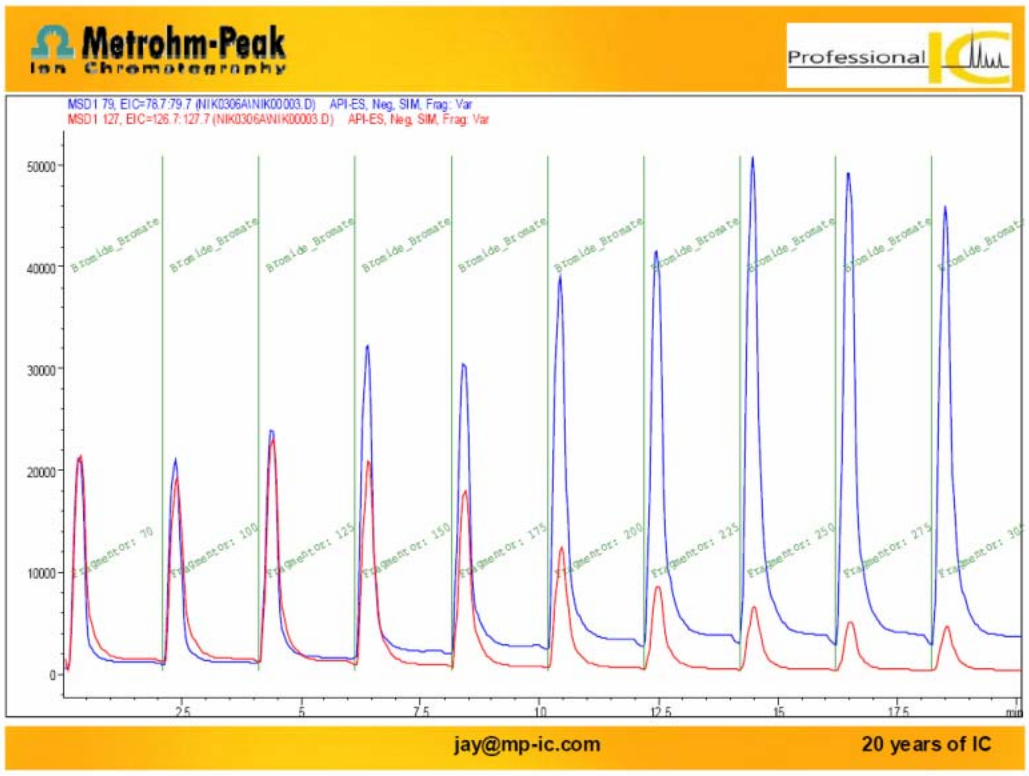
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Ion Chromatography
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MSD1 79, EIC=78.7:79.7 (NIK0306A\NIK00003.D) API-ES, Neg, SIM, Frag: Var
MSD1 127, EIC=126.7:127.7 (NIK0306A\NIK00003.D) API-ES, Neg, SIM, Frag: Var
Bromide_Bromate
Fragmentor: 70
Fragmentor: 100
Fragmentor: 125
Fragmentor: 150
Fragmentor: 175
Fragmentor: 200
Fragmentor: 225
Fragmentor: 250
Fragmentor: 275
jay@mp-ic.com
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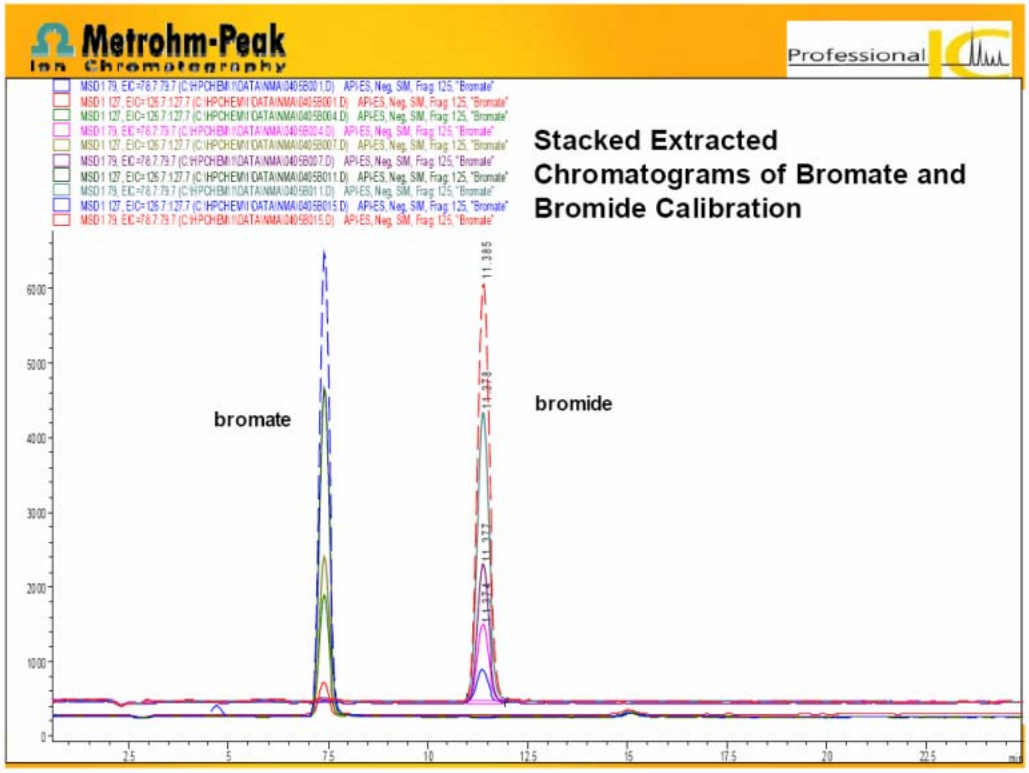
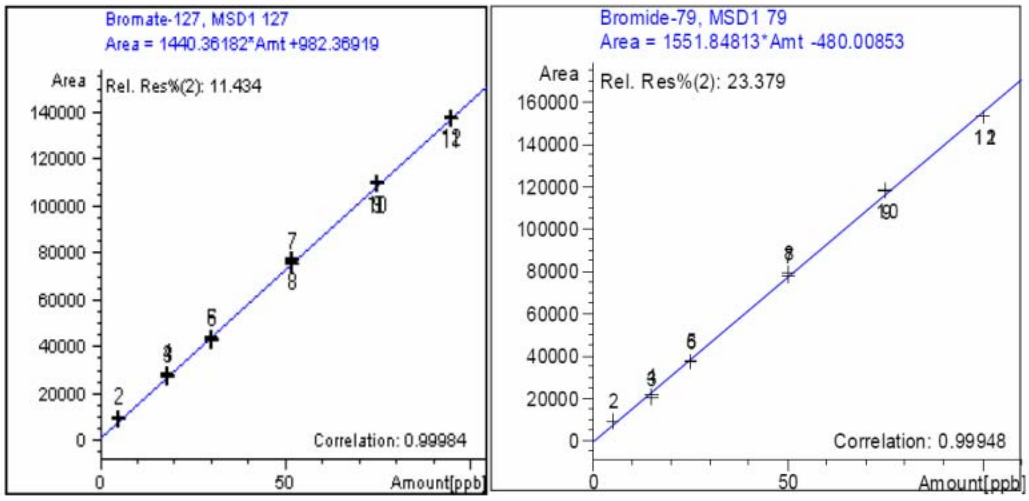

Metrohm-Peak
Ion Chromatography
Professional IC
Stacked Extracted Chromatograms of Bromate and Bromide Calibration
bromate
bromide
11.385
11.328

Metrohm-Peak Ion Chromatography

Professional IC

6 point calibration with 3 replicates per point

Calibration curves of bromate and bromide



Metrohm-Peak Ion Chromatography

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Method Detection Limit Study

- USEPA defines as the minimum concentration measured and reported with 99% confidence that the analyte concentration is greater than zero
- Consists of 7 replicates
- MDL = s x t (n-1, 1-α = 0.99)
  - n = number of replicate spike determinations at 1 to 5 times the estimated detection limit
  - s = standard deviation of measured concentrations of n spike determinations
  - t = t value at n-1 degrees of freedom and 1-α (99 percent) confidence level
  - α = level of significance

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Method detection limit study

	bromide					bromate			
	5 ppb	15 ppb	25 ppb	50 ppb		5 ppb	15 ppb	25 ppb	50 ppb
	5.03	14.77	25.03	50.67		4.61	15.00	24.92	51.01
	4.89	14.69	24.67	50.08		5.19	15.11	24.16	50.81
	5.17	15.09	24.79	50.69		4.49	15.07	24.74	50.49
	4.64	14.78	24.81	49.72		4.78	15.00	24.85	50.06
	5.17	14.90	25.02	49.10		5.20	15.29	24.97	50.00
	4.96	14.93	24.72	49.97		5.23	15.96	24.99	51.16
	5.16	15.16	25.42	49.94		4.93	15.15	24.63	49.96
avg.	5.00	14.90	24.92	50.03	avg.	4.92	15.23	24.75	50.50
std.dev	0.019	0.017	0.26	0.55	std.dev	0.030	0.034	0.029	0.051
RSD%	0.386	0.116	0.104	0.110	RSD%	0.514	0.122	0.118	0.600
MDL*	0.161	0.154			MDL*	0.195	0.206	0.192	0.159
* = SD x 3.14 (3.14= t95 value for 7 replicates)									

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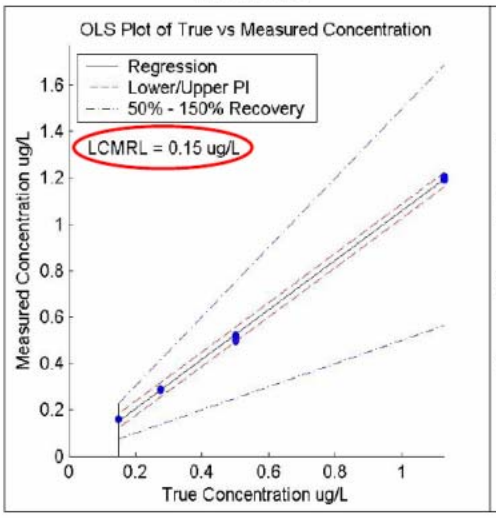
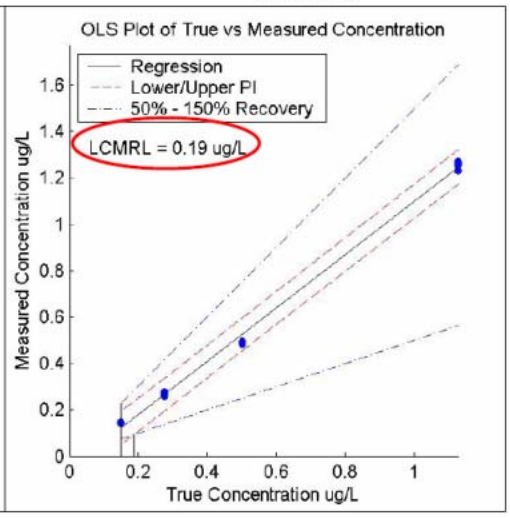
Metrohm-Peak Ion Chromatography — Professional IC

LCMRL data

Bromate



Bromide



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Metrohm-Peak Ion Chromatography

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Drinking water sample testing

- Bottled water samples
- Tap water samples
- Spiked samples

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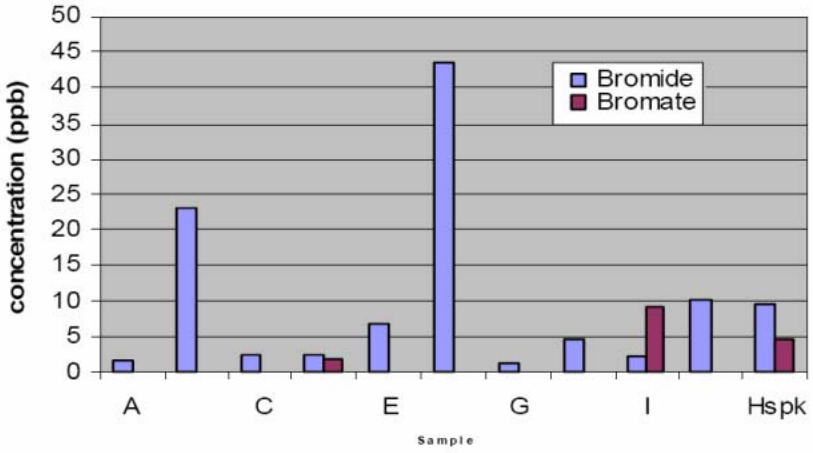
Bottled water samples



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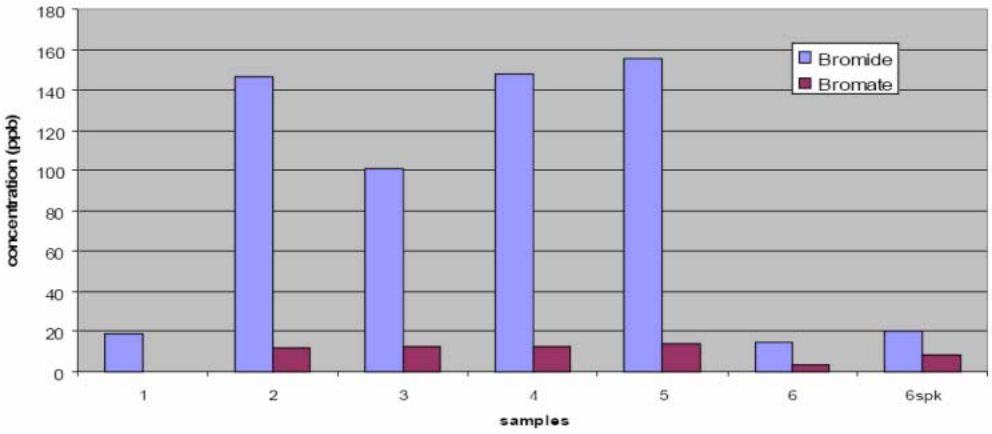
Tap water samples (southeast Houston)



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Spiked sample data

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TAP WATER (HOUSTON, TX AND VICINITY)		
Sample ID	Bromide ppb	Bromate ppb
Sample-1(n=3)	19.00	0.00
Sample-2(n=3)	146.40	12.38
Sample-3(n=3)	101.13	12.77
Sample-4(n=3)	147.93	13.29
Sample-5(n=3)	155.45	14.25
Sample-6(n=3)	15.15	3.41
Sample-6spike (n=3)	**20.16**	**8.68**
True Spike Value	**5.00**	**5.00**
Spike Recovery%	**100.26**	**105.41**

OTC - BOTTLED WATER		
Sample ID	Bromide ppb	Bromate ppb
Sample-A(n=3)	1.63	0.00
Sample-B(n=3)	23.05	0.00
Sample-C(n=3)	2.57	0.00
Sample-D(n=3)	2.37	1.84
Sample-E(n=3)	6.77	0.00
Sample-F(n=3)	43.40	0.00
Sample-G(n=3)	1.17	0.00
Sample-H(n=3)	4.61	0.00
Sample-I(n=3)	2.28	9.39
Sample-J(n=3)	10.22	0.00
Sample-Hspike(n=3)	**9.61**	**4.66**
True Spike Value	5.00	5.00
Spike recovery%	**100.03**	**93.22**

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Summary
Detection Limits

Analyte	Conductivity	UV/PCR	ICMS
Bromide	2.0 ppb	n/a	0.2 ppb
Bromate	0.25 ppb	0.2ppb	0.2ppb

Metrohm-Peak Ion Chromatography

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Acknowledgements

- David Neliegh – USEPA Region-6
- Rick McMillin – USEPA Region-6
- Dr. Melvin Ritter – USEPA Region-6
- Johnson Mathew – USEPA Region-6
- Dr. David Munch and his group – USEPA Cincinnati for guidance and support
- Dr. Chunlong Zhang, University of Houston – Clear Lake
- Niklas Adams – Graduate Student University of Houston Clearlake

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Determination of Trace Arsenic and Selenium in Difficult Matrices by ICP-DRC-MS

Hakan Gürleyük
Applied Speciation and Consulting, LLC

ABSTRACT

Arsenic and selenium are elements of great environmental interest and a challenge to determine at ultratrace levels. Inductively coupled plasma mass spectrometry (ICP-MS) offers low detection limits, but the detection limits can be limited by molecular and elemental interferences. This paper explores techniques to achieve lower detection limits by the elimination of interferences introduced by difficult matrices for arsenic and selenium.

Trace Arsenic and Selenium Analysis by ICP-DRC-MS

Hakan Gürleyük

(hakan@appliedspeciation.com)

Russell Gerads

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Why are we interested in As & Se?

- Considered to be cancerogenic and Se can bioaccumulate
- NPDES permit limits on arsenic and selenium discharges are very stringent.
- Wastewaters = high concentrations of matrix components
- Low trace metal content
  - Even lower after dilution…
- Different analytical methods can generate inaccurate results for total arsenic and selenium.
- Since important treatment decisions are made using these analytical results, the ramifications of generating poor analytical data cannot be understated.

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Analytical Methods

- ICP-MS
  - Direct and HG-ICP-MS
- ICP-AES
  - Direct and HG-ICP-AES
- HG-AAS
- HG-AFS
- Voltammetry (No need to discuss!)

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HG-AAS or HG-AFS

- As(III) forms hydrides more efficiently
- DMAs and AsB can not be determined
- Only Se(IV) is capable of forming the hydride
- An off-line or on-line reduction step is necessary to first oxidize everything to Se(VI) and then reduce Se(VI) to Se(IV).

Table 1 Acid dissociation constants of some acids[7,8]

	Abbreviation	pK
$As(OH)_3$	As^{III}	$pK_1 = 9.2$
$As(O)(OH)_3$	As^{V}	$pK_1 = 2.3$
		$pK_2 = 6.8$
		$pK_3 = 11.6$
$(CH_3)As(O)(OH)_2$	MMAA	$pK_1 = 4.0$
		$pK_2 = 8.6$
$(CH_3)_2As(O)OH$	DMAA	$pK = 6.3$
$Se(O)(OH)_2$	Se^{IV}	$pK_1 = 2.5$
		$pK_2 = 7.3$
$Se(O)_2(OH)_2$	Se^{VI}	$pK_1 = -3$ (estimated)
		$pK_2 = 2.0$

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HG-AAS or HG-AFS

- Arsenic by HG-AAS is more straightforward than Se
- Multiple sample digestion techniques have been promulgated for analysis via hydride generation (7741A and 7742)
- Current promulgated digestion techniques do not require incorporation of different selenium species to monitor digestion efficiency
- Some laboratories have generated their own digestion techniques similar to Standard Method 3500 using persulfate and hydrochloric acid

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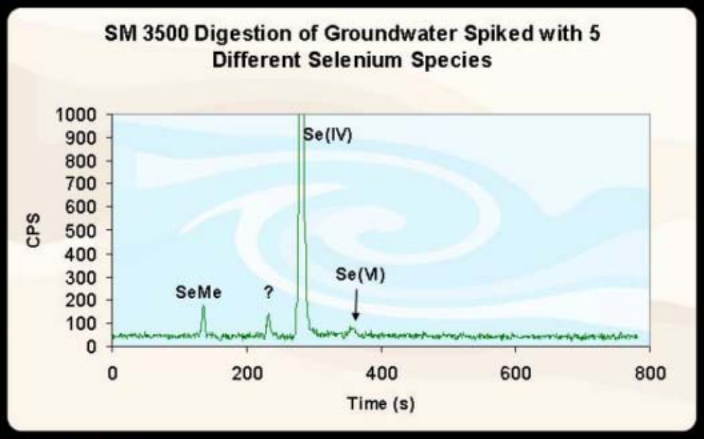
Performance of Standard Method 3500-Se

- Digestion facilitates reactions with HCl, $K_2S_2O_8$, and heat (specifics of digestion method can be acquired from Standard Methods)



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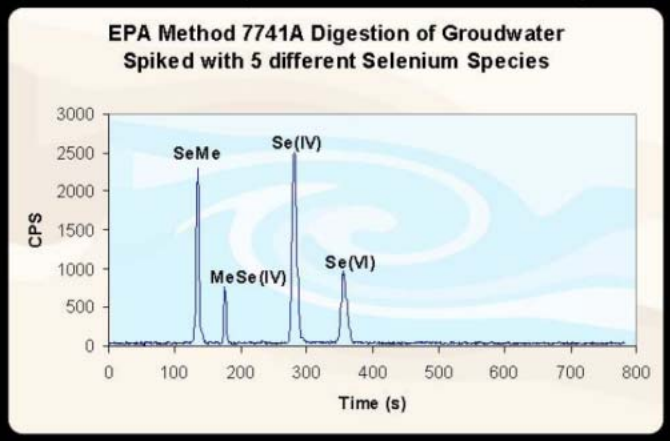
Performance of EPA Method 7741A

- Digestion facilitates reactions with HNO_3, H_2SO_4, and heat (specifics of digestion method can be acquired from Standard Methods)



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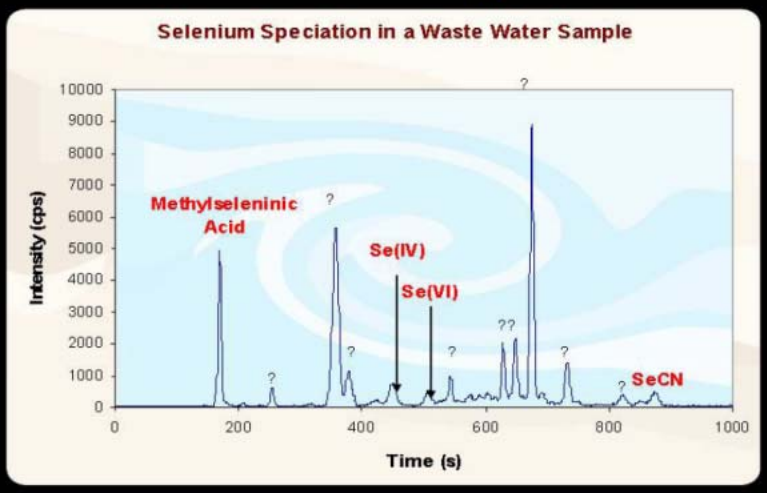
Se Speciation in FGD Wastewater

HG = False Negatives!



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Inductively Coupled Plasma-Mass Spectrometry

- Mature technique
- Almost all elements can be determined.
- Sub-ppt detection limits for most elements
- Polyatomic Interferences:
  - $^{40}Ar^{12}C$ on ^{52}Cr, $^{37}Cl^{16}O$ on ^{53}Cr,
  - $^{40}Ar^{35}Cl$ on ^{75}As,
  - $^{40}Ar^{40}Ar$ on ^{80}Se, $^{81}Br^{1}H$ on ^{82}Se
- Cell-based instruments can eliminate interferences

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Issues with Se Analysis by ICP-MS

- ^{80}Se, the most abundant isotope is isobaric w/ $^{40}Ar^{40}Ar^{+}$
- Conventional ICP-MS instruments need to use ^{77}Se, ^{78}Se, or ^{82}Se
  - $ArCl^{+}$, and BrH^{+} can result false positives
  - Also affects As since correction equations for As use m/z82
  - $ArAr^{+}$ causes high background on m/z 78
- Both Se and As have very high first ionization potentials.
  - ~ $1/10^{th}$ the sensitivity compared to other metals
- Accurate Se analyis REQUIRE the use of DRC instruments

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Se by DRC

- Bromine is a major interference on conventional ICP-MS instruments due to $^{1}H^{81}Br^{+}$.
  - Methane does not react with bromine efficiently.
  - Oxygen works well for Se at high gas flow rate
  - Ammonia reacts w/ bromine very efficiently.
- Allows multiple isotope monitoring at multiple gas conditions.
  - Conventional ICP-MS can only monitor m/z 82

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Se by Method 200.8

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1: ESTIMATED INSTRUMENT DETECTION LIMITS[1]

Element	Recommended Analytical Mass	Scanning Mode[2]	Selection Ion Monitoring Mode[3]
Aluminum	27	0.05	0.02
Antimony	123	0.08	0.008
Arsenic[(3)]	75	0.9	0.02
Barium	137	0.5	0.03
Beryllium	9	0.1	0.02
Cadmium	111	0.1	0.02
Chromium	52	0.07	0.04
Cobalt	59	0.03	0.002
Copper	63	0.03	0.004
Lead	206, 207, 208	0.08	0.015
Manganese	55	0.1	0.007
Mercury	202	n.a	0.2
Molybdenum	98	0.1	0.005
Nickel	60	0.2	0.07
Selenium[(3)]	82	5	1.3
Silver	107	0.05	0.004
Thallium	205	0.09	0.014
Thorium	232	0.03	0.005
Uranium	238	0.02	0.005
Vanadium	51	0.02	0.006
Zinc	66	0.2	0.07

Instrument detection limits (3σ) estimated from seven replicate integrations of the blank (1% v/v

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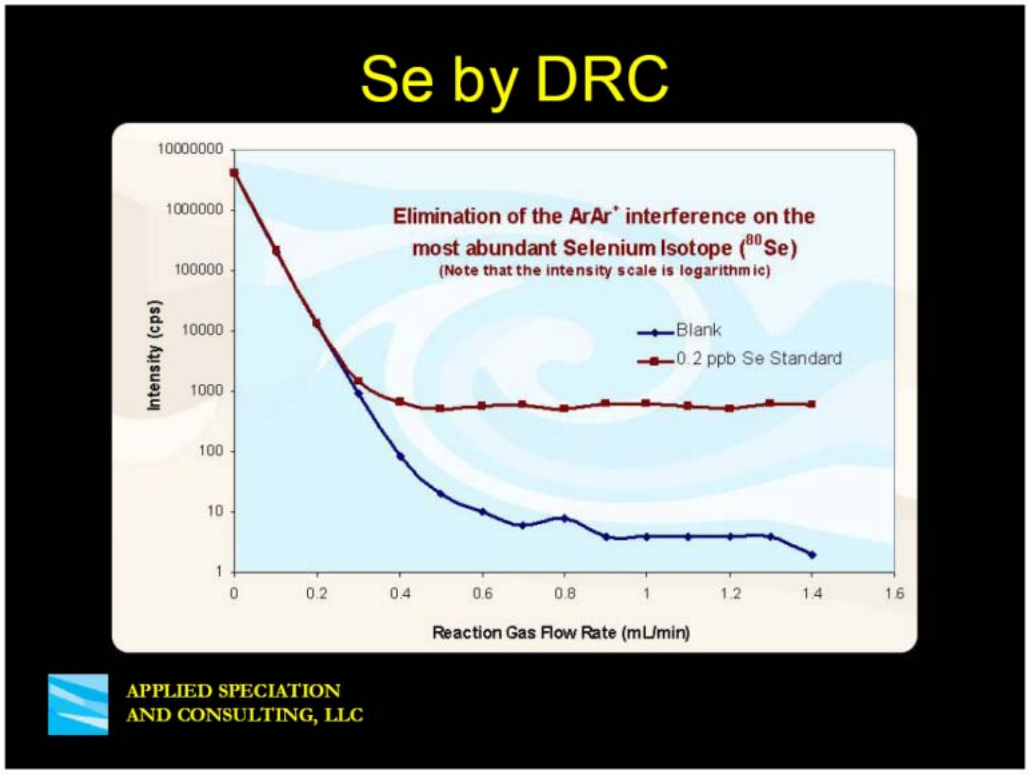
Se by DRC
Elimination of the ArAr+ interference on the most abundant Selenium Isotope (80Se)
(Note that the intensity scale is logarithmic)
Blank
0.2 ppb Se Standard
Intensity (cps)
10000000
1000000
100000
10000
1000
100
10
1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Reaction Gas Flow Rate (mL/min)
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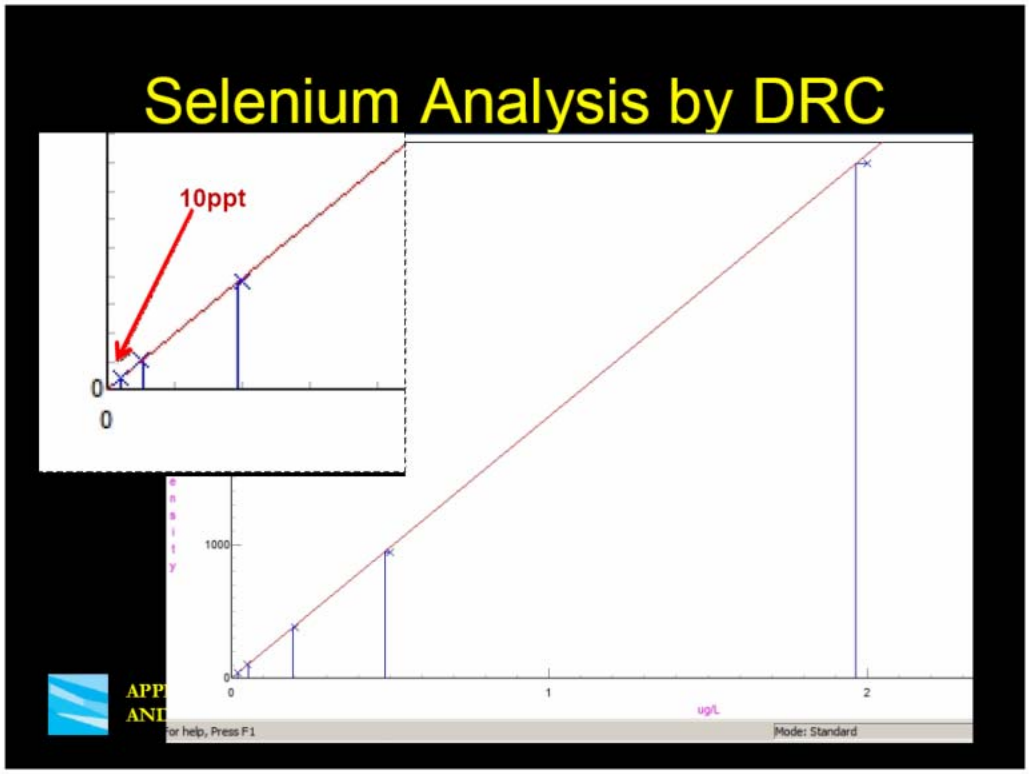
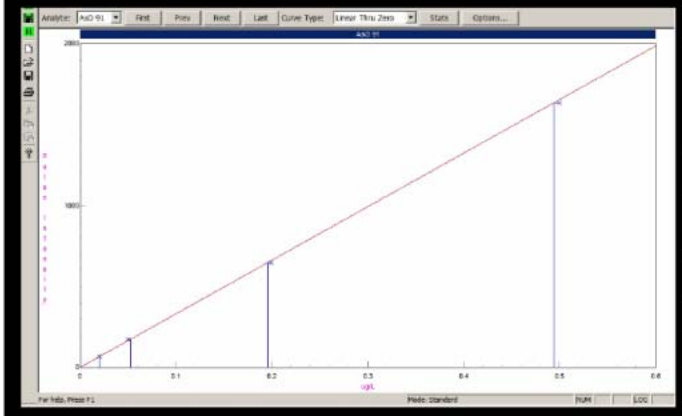

Selenium Analysis by DRC
10ppt
0
0
1000
0
1
2
ug/L
For help, Press F1
Mode: Standard

As Analysis by DRC



	5ppt Spike
1	4.8
2	4.4
3	3.8
4	4.4
5	4.1
6	4.7
7	4.0
Average=	4.3
MDL=	1.1

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Method Intercomparison Study

"A Comparison of Methods for Measuring Total Selenium and Selenium Species in Water" performed for the Nitrogen and Selenium Management Program (NSMP) Working Group

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Conventional ICP-MS Performance

	DRC and CRC ICP-MS			Conventional ICP-MS	
	DRC ASC	CRC WCAS	DRC BR	CalTest	CRG
1	3.18	3.7	3.1	4.6	5.8
2	3.32	3.1	3.1	3.9	5.7
3	3.26	3.3	3.1	4.6	5.9
4	3.24	3.3	3.1	4.0	5.6
5	3.22	3.5	3.0	3.9	5.5
6	3.37	3.2	3.1	4.1	5.8
7	3.31	3.5	3.2	4.3	6.1
% RSD	2.00	5.96	1.86	7.27	3.32

CRG Results exceed CA Toxics Rule Water Quality Objective of 5 ug/L

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Detection Limits

Lab	Method	Total Se (direct)	Selenate	Selenite
ASC	ICP-DRC-MS	0.008	0.015	0.013
WCAS	ICP-CRC-MS	0.3	0.2	0.1

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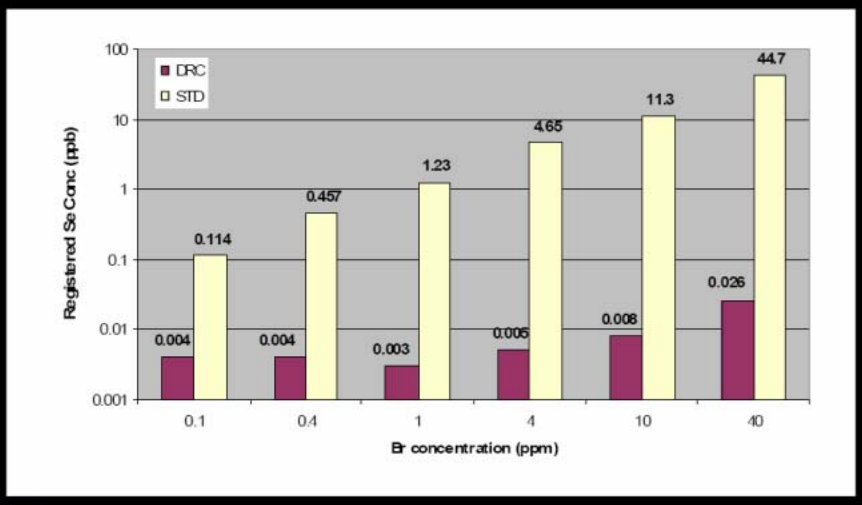
False Positives Due to Bromine



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Conv ICP-MS = False Positives

	77Se DRC	78SeDRC	82SeSTD
Sample 1	1.026	1.078	16.6
Sample 2	11.1	11.4	65.9
Sample 3	2.31	2.71	43
Sample 4	98.5	99	132

- Without the DRC, no way of finding out about these false positives
- MS/MSD can not correct for false positives
- Dilution is the only solution = higher MDLs

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Conclusions

- HG-AAS/AFS provides false negatives
  - Requires method development for each type of sample to get accurate results
  - Its use should be limited unless appropriate QA/QC is followed (spikes, etc)
- Conventional ICP-MS instruments can produce false positives
  - Use of DRC instruments are highly recommended
  - Monitoring masses such as 79Br and 81Br may help catch false positives

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Acknowledgements

Perkin Elmer

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FAST Automated Sampling System for High Throughput ICPMS Analysis of Environmental Samples Using EPA Method 200.8

Daniel Wiederin
Elemental Scientific

ABSTRACT

The majority of ICPMS sample analysis time is typically spent either bringing the sample to the instrument or rinsing out after the measurement is completed. The proportion of time spent measuring ions in a typical configuration may be as low as 15% to 25%, with the balance of time spent on non-productive activities such as sample uptake, stabilization, and rinse-out. The proportion of time spent rinsing the ICPMS instrument is often most unfavorable when analyzing environmental samples due to the wide range of analyte concentrations possible within a sample set.

A new fully-automated constant-flow ICPMS sample introduction system optimizes each aspect of sample introduction. Samples are introduced without intervening air segments at a rate of 0.3 to 0.4 ml/min. Sensitivity is increased and ICPMS memory effects are dramatically decreased, reducing sample uptake, stabilization, and rinse times. Six areas of the sample introduction system are optimized to eliminate or reduce sources of memory effects, including the ICPMS cones, sample injector, nebulizer, spray chamber, uptake tubing, and autosampler probe. A 6-port inert valve system eliminates all contact between samples and peristaltic pump tubing.

The new system increased the proportion of time spent measuring ions to between 60% and 73%. ICPMS sample throughput was increased two to three fold or more. The low, constant-flow nebulizer system reduced the frequency of cone maintenance and improved ICPMS long-term stability while making interference correction factors work accurately in normal (non-reaction/collision) mode. A novel low volume tee was used for on-line internal standard addition without compromising sample throughput.

SC-FAST Automated Sampling System for High Throughput ICPMS Analysis of Environmental Samples using EPA Method 200.8

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Elemental Scientific
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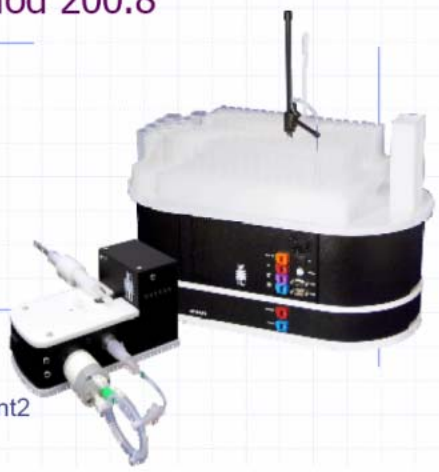
dan@icpms.com



Perkin Elmer ELAN and Thermo Element2

Overall Limiting Factors
ICPMS Throughput = Stability

- Sample analysis time
- QC Failures
- Instrument drift and maintenance

All three problems are primarily related to sample introduction.

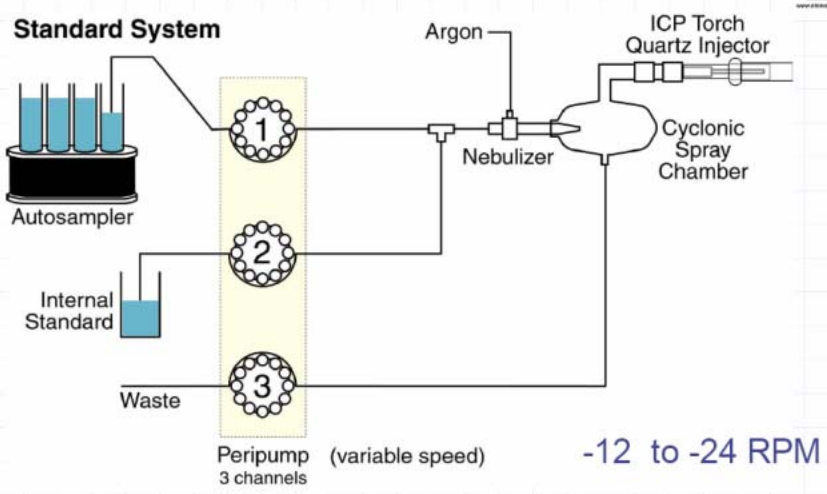
Standard ICPMS Analysis Steps

1) Autosampler Movement (up-over-down)
2) Sample Uptake Time (high speed pump)
3) Stabilization Time (measurement speed pump)
4) Measurement Time
5) Rinse Time (high speed pump)

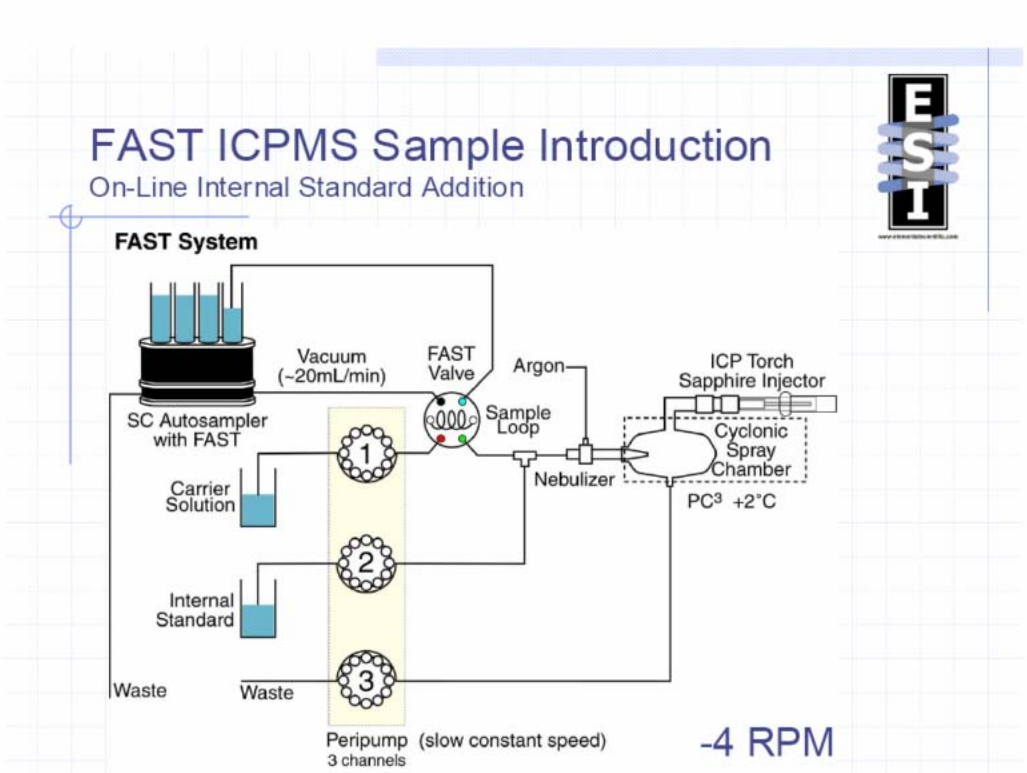
Environmental lab only ~ 20% of analysis time is actually measuring ions.

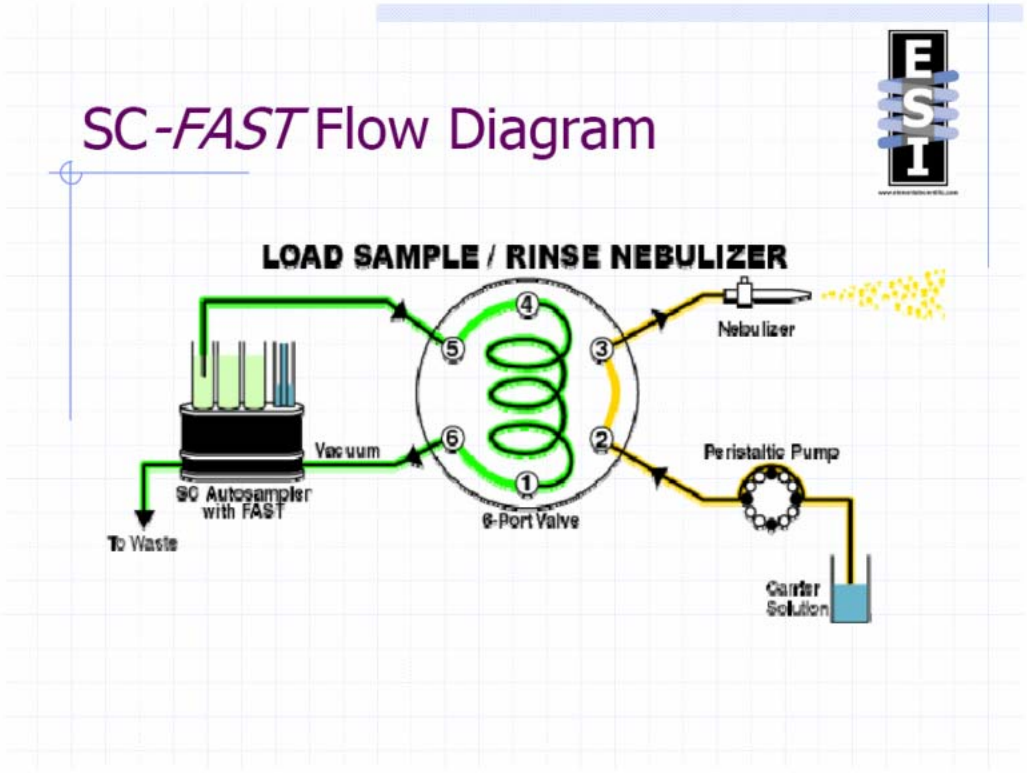
Normal ICPMS Sample Introduction

On-Line Internal Standard Addition



Sample passes through peristaltic pump tubing.


FAST ICPMS Sample Introduction
On-Line Internal Standard Addition
FAST System
Vacuum
(~20mL/min)
FAST
Valve
Argon
ICP Torch
Sapphire Injector
SC Autosampler
with FAST
Sample
Loop
Cyclonic
Spray
Chamber
Carrier
Solution
Nebulizer
PC3 +2°C
Internal
Standard
Waste
Waste
Peripump (slow constant speed)
3 channels
-4 RPM


SC-FAST Flow Diagram
LOAD SAMPLE / RINSE NEBULIZER
Nebulizer
Vacuum
Peristaltic Pump
SC Autosampler
with FAST
6-Port Valve
To Waste
Carrier
Solution

FAST ICPMS Analysis Steps

1) Autosampler Movement (1s, down only)
2) Loop Fill/Stabilize Time (20s, low speed pump)
3) Measurement Time (60s, Move Rinse, Move Next)
4) Rinse Time (5s, low speed pump)

Environmental lab ~ 60% of analysis time is actually measuring Ions.

SC-FAST Improvements

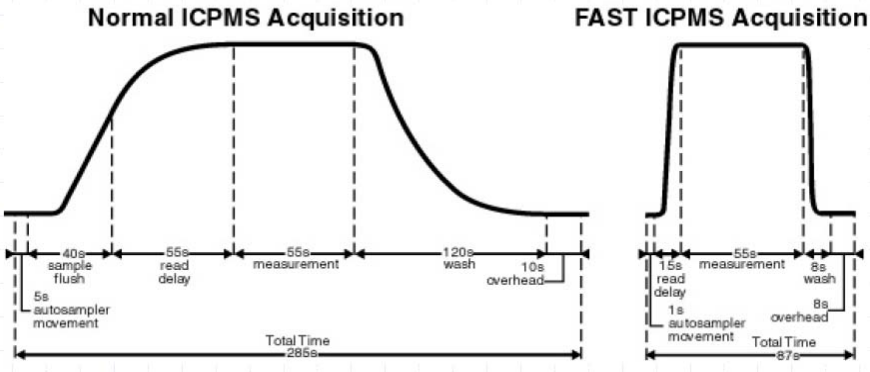
- No sample contact with peristaltic pump tubing—teflon injection valve
- No high-speed pumping
- Vacuum sample loading
- Low flow nebulizer—0.2 to 0.3 ml/min.
- Peltier-cooled cyclonic spray chamber
- Sapphire injector
- Dual flowing rinse station
- Probe retraction speed control
- Probe rinsing during analysis
- No air bubbles between samples and rinse

200.8 Analysis SC-FAST

V

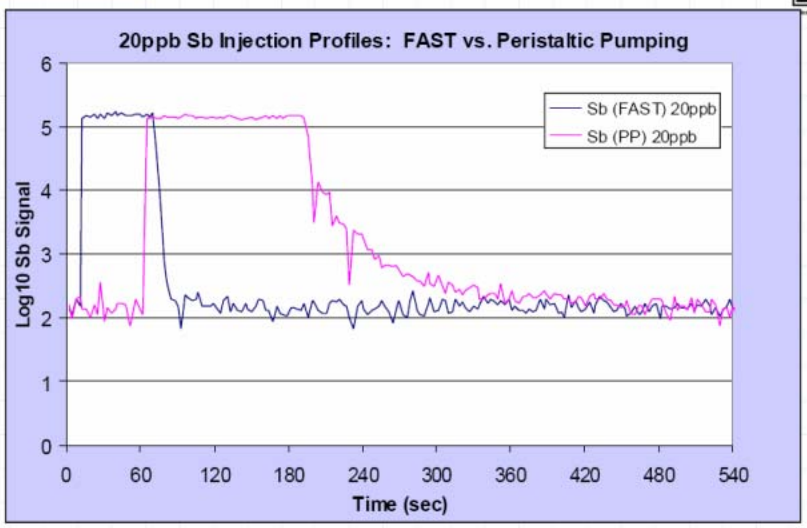
ICPMS Method 200.8 Timing Parameters

Pumped System (19% Efficient)
SC-FAST System (63% Efficient)



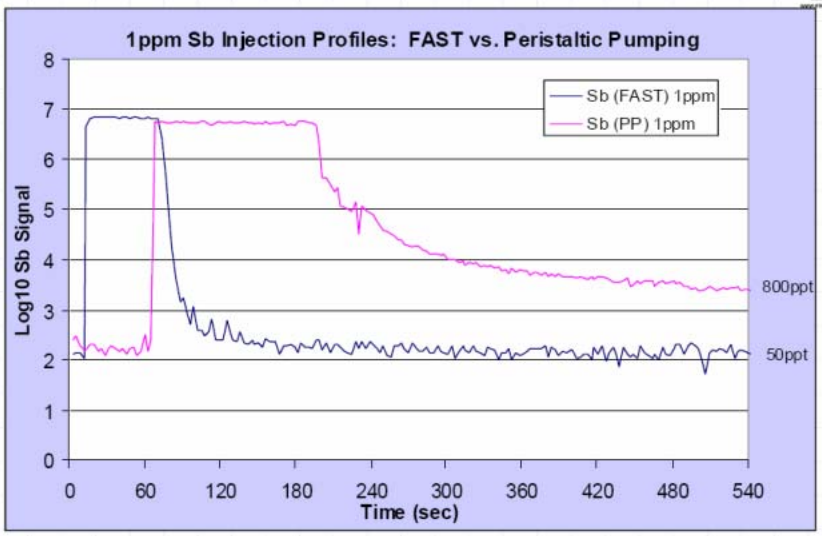
EPA Method 200.8 ELAN ICPMS

SC-FAST vs. Peristaltic Pumped Antimony Flush-in and Rinse-out

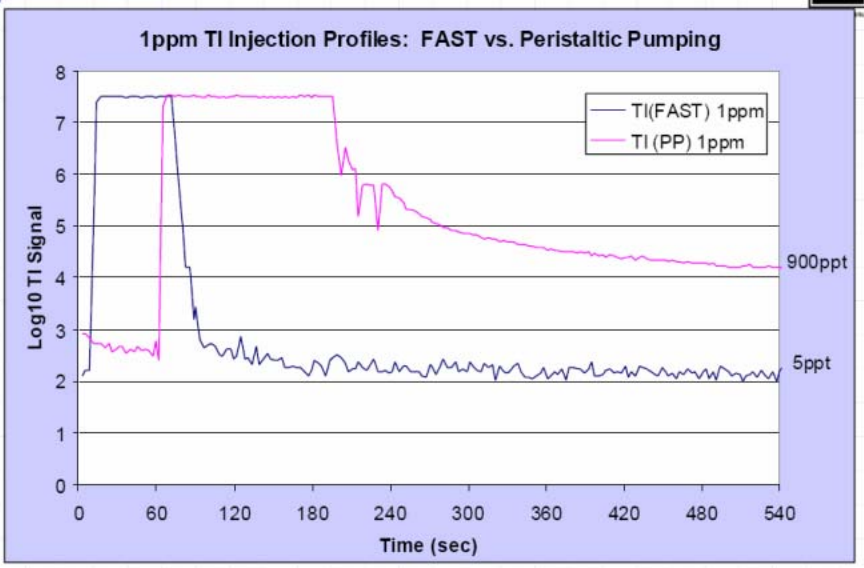


FAST analysis completed before normal measurement begins.

SC-FAST vs. Peristaltic Pumped Antimony Flush-in and Rinse-out



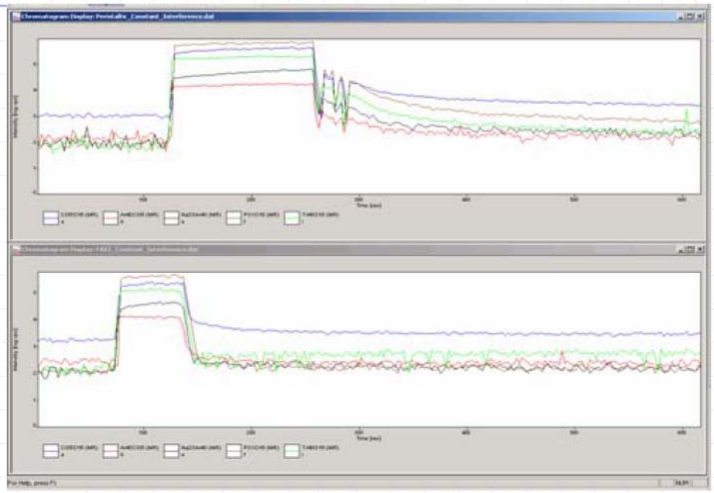
SC-FAST vs. Peristaltic Pumped Thallium Rinseout



HR-ICPMS Interference Uptake and Washout ClO^+, $ArCl^+$, $NaAr^+$, PO^+, TiO^+, (log scale) ICS Solution SC-FAST vs. Peripump

Direct Peristaltic Pumped

SC-FAST



ICS (10x diluted) sampled at time = 60 seconds.

PFA-ST nebulizer, quartz cyclonic chamber

Peltier-Cooled Spray Chamber

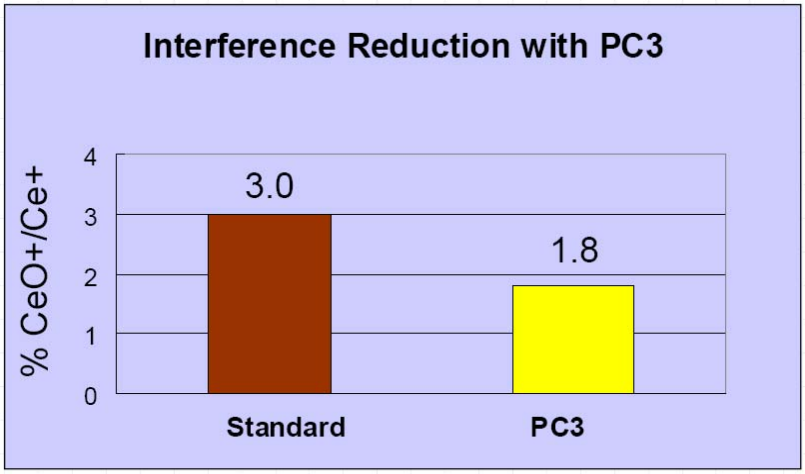
Reduced and Stable Formation of Polyatomic Interferences

PC3-FAST

Peltier cooler, injection valve, internal standard tee, PFA nebulizer, quartz cyclonic, sapphire injector

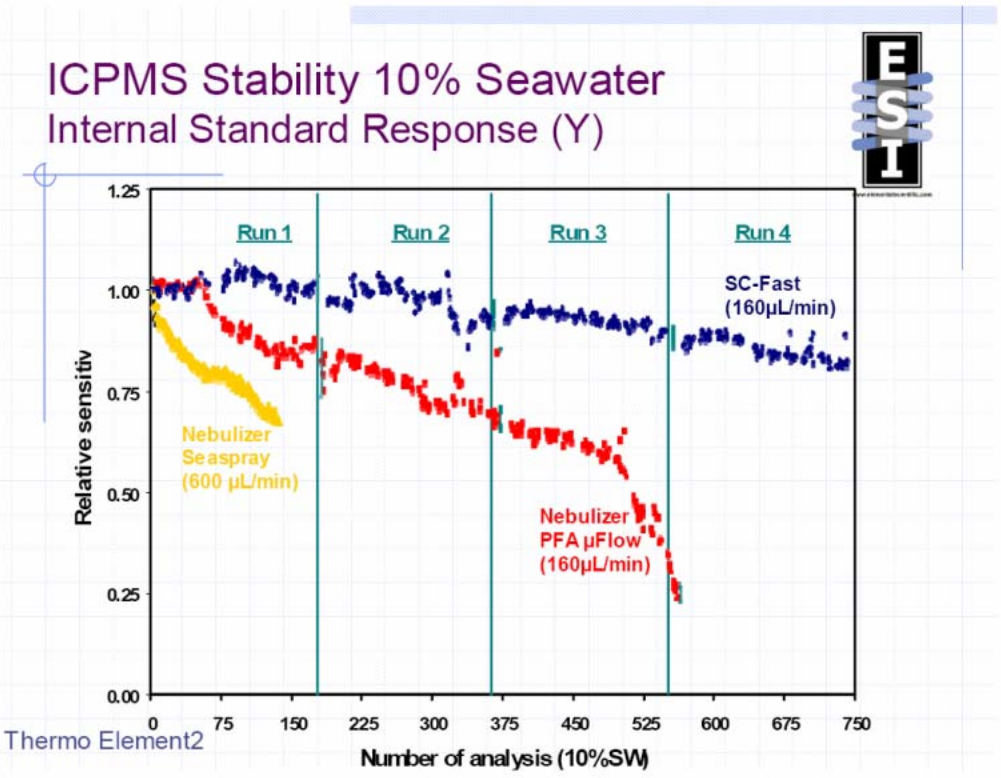
PC3 Peltier-cooled spray chamber

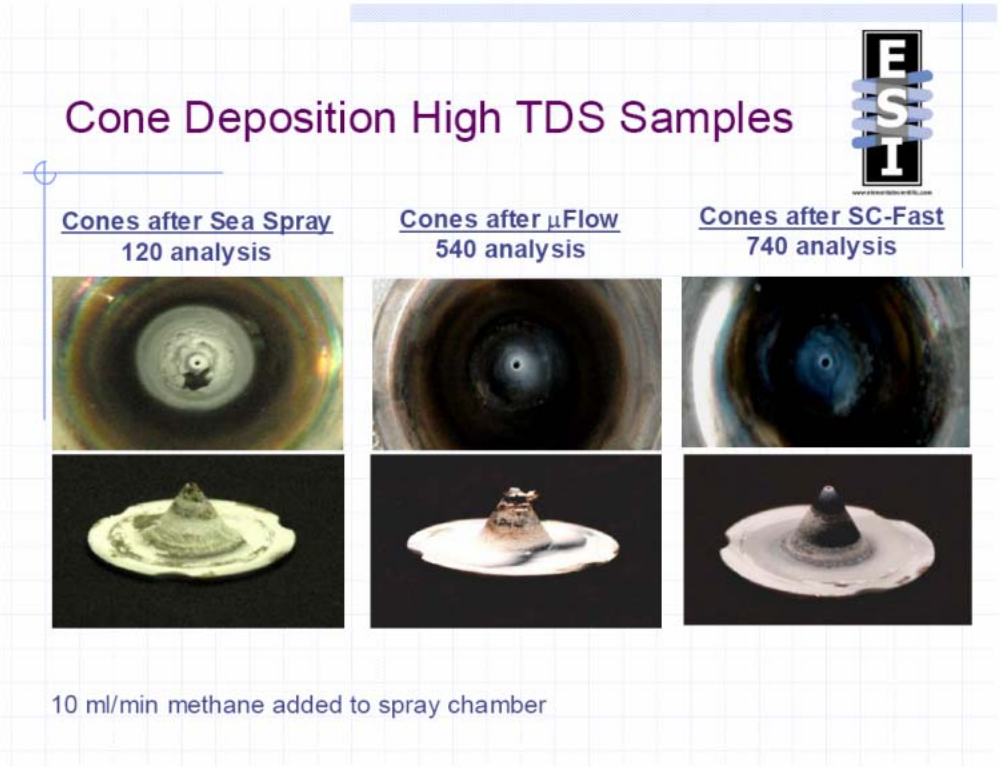
Low, stable oxides = stable interference corrections



Low Flow Nebulizers

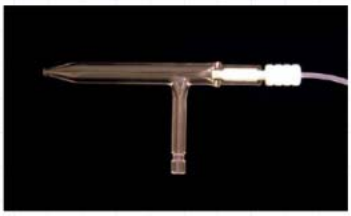
Improving ICPMS Stability


ICPMS Stability 10% Seawater
Internal Standard Response (Y)
Run 1
Run 2
Run 3
Run 4
SC-Fast
(160µL/min)
Nebulizer
Seaspray
(600 µL/min)
Nebulizer
PFA µFlow
(160µL/min)
Relative sensitiv
1.25
1.00
0.75
0.50
0.25
0.00
0
75
150
225
300
375
450
525
600
675
750
Number of analysis (10%SW)
Thermo Element2

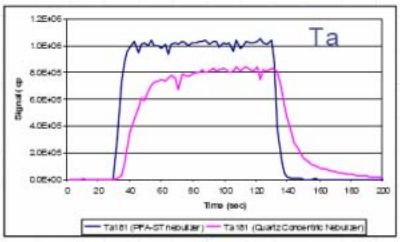

Cone Deposition High TDS Samples
Cones after Sea Spray
120 analysis
Cones after µFlow
540 analysis
Cones after SC-Fast
740 analysis
10 ml/min methane added to spray chamber

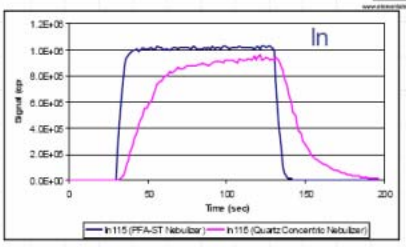
MicroFlow PFA-ST Nebulizer
Low Internal Volume

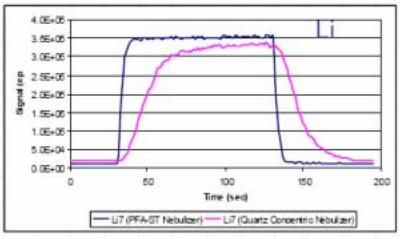
- Robust, general-purpose ICPMS nebulizer
- High TDS samples
- Zero dead volume connection
- Improves ELAN sensitivity.

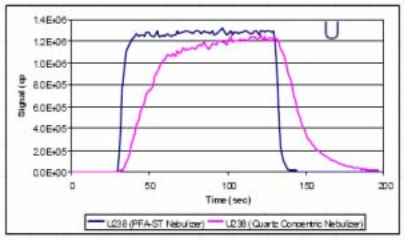


SC-FAST Injection Profiles
Low Flow PFA-ST vs. Low Flow Quartz









100 second injection 1ppb Standard Sample flow rate 200µL/min

Dual Flowing Rinse (Brown Photoresist Sample)

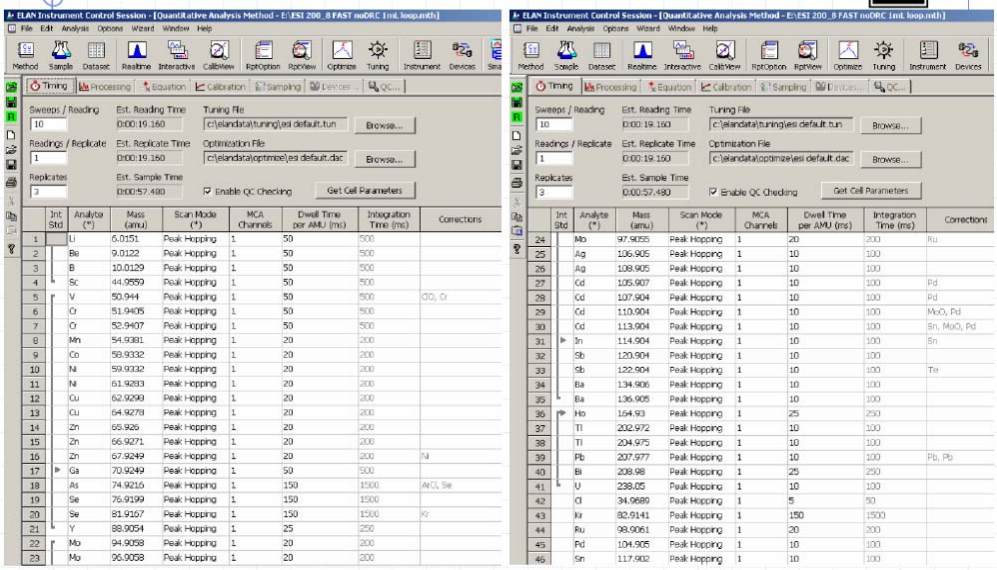
- First station collects most of probe contamination
- Second station clean—low cross-contamination

R1 R2

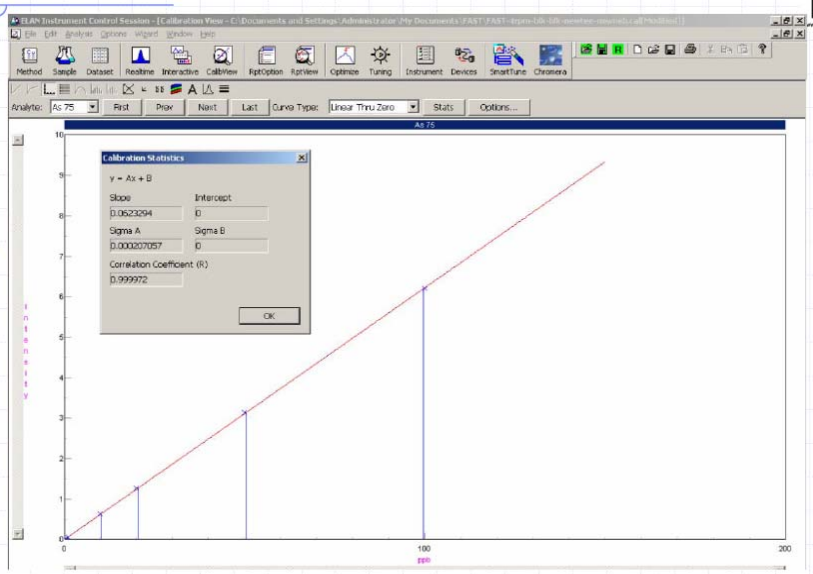
Recommended SC-FAST Isotopes for Standard Mode Analysis EPA 200.8

^{6}Li	^{44}Ca	^{59}Co	^{82}Se	^{121}Sb	^{209}Bi
^{9}Be	^{45}Sc	^{60}Ni	^{89}Y	^{137}Ba	^{232}Th
^{23}Na	^{51}V	^{65}Cu	^{98}Mo	^{165}Ho	^{238}U
^{24}Mg	^{52}Cr	^{66}Zn	^{107}Ag	^{202}Hg	
^{27}Al	^{55}Mn	^{71}Ga	^{111}Cd	^{205}Tl	
^{39}K	^{57}Fe	^{75}As	^{115}In	^{208}Pb	

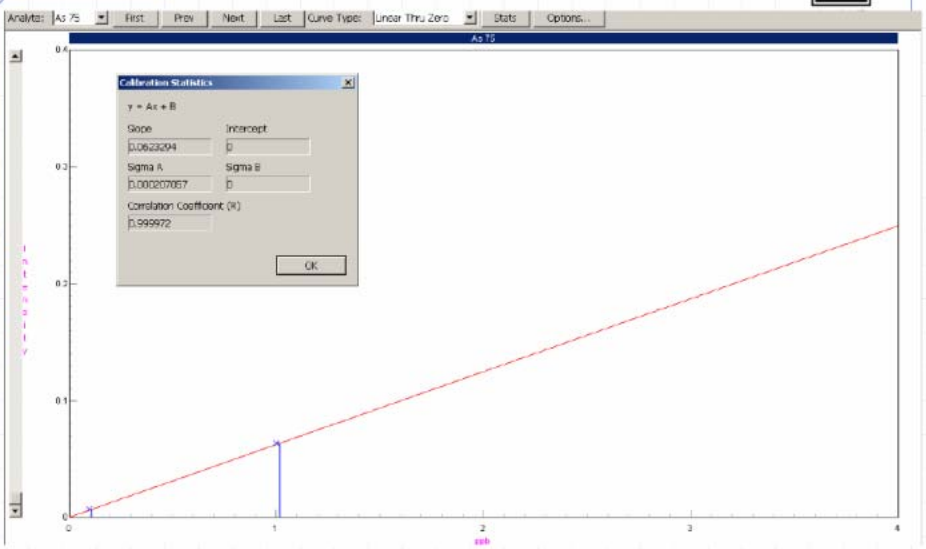
ICPMS Method SC-FAST 200.8
95 seconds per sample



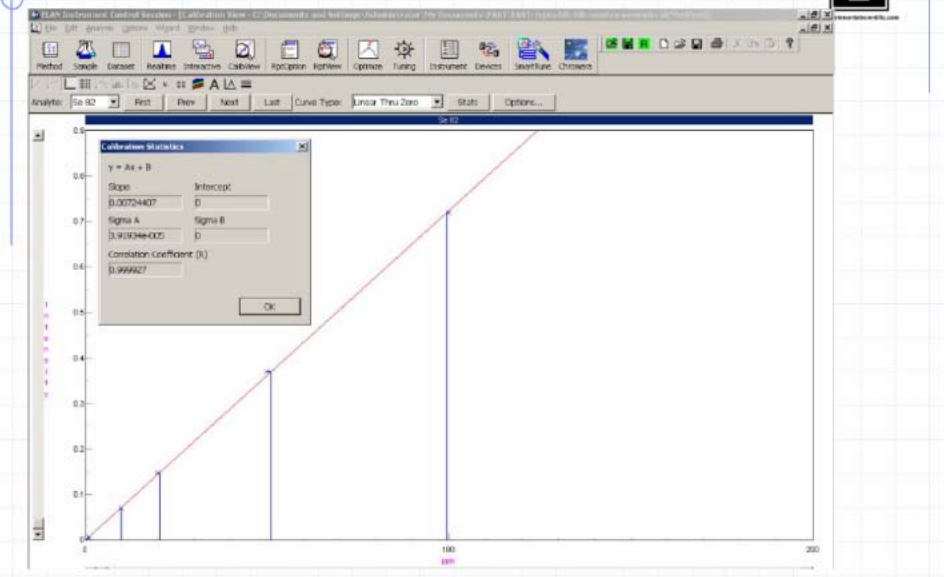
Method 200.8 As Calibration
SC-FAST ELAN 9000



Method 200.8 As Calibration SC-FAST ELAN 9000



Method 200.8 Se-82 Calibration SC-FAST ELAN 9000

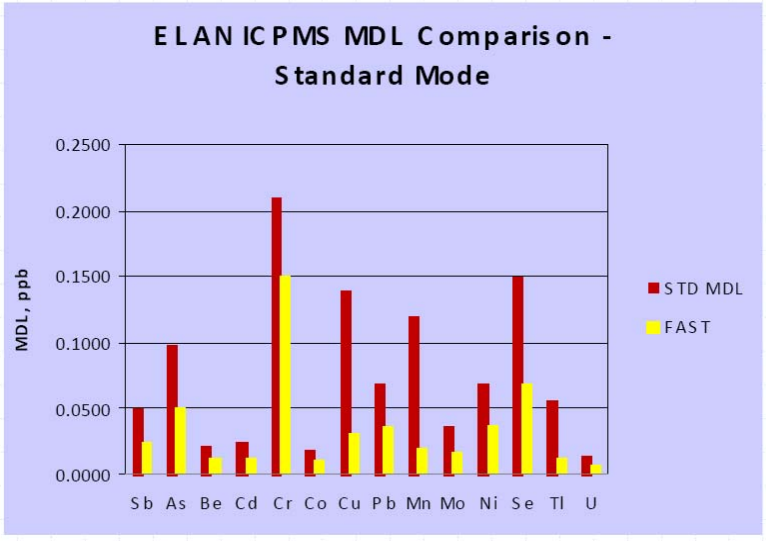


200.8 ICV
SC-FAST ELAN 9000

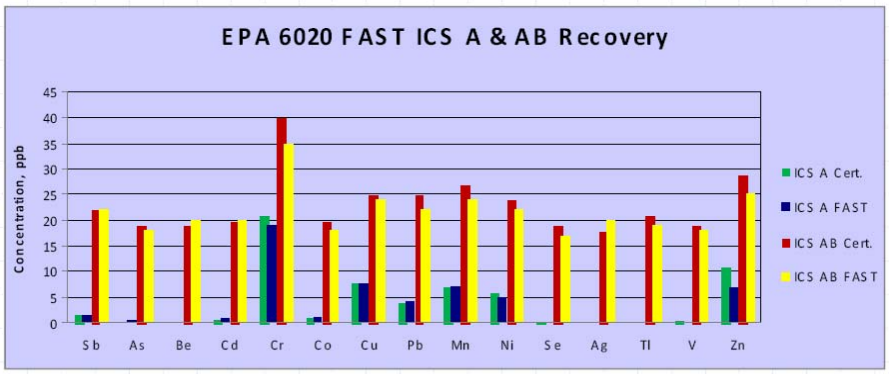
Concentration Results

	Analyte	Mass	Meas. Intens. Mean	Blank Intensity	Conc. Mean	Conc. RSD	M. Int. RSD	Sample Unit	Mode
I>	Li	6	9141.3	8848.3			2.9	ppb	Standard
I	Be	9	58606.1	44.0	49.985	6.5	2.8	ppb	Standard
I	Al	27	573020.8	21926.8	49.828	6.5	3.7	ppb	Standard
L	Sc	45	61178.8	60094.7			4.5	ppb	Standard
I	V	51	814141.2	1693.3	51.070	3.6	2.1	ppb	Standard
I	Cr	52	707460.9	5693.8	50.877	2.7	1.4	ppb	Standard
I	Cr	53	83111.7	1403.4	49.969	4.1	2.6	ppb	Standard
I	Mn	55	1077218.4	783.4	50.768	1.3	0.6	ppb	Standard
I	Co	59	933841.1	203.3	51.133	2.5	0.9	ppb	Standard
I	Ni	60	182101.3	303.3	50.505	3.7	2.1	ppb	Standard
I	Ni	62	27404.6	63.3	49.731	2.9	2.1	ppb	Standard
I	Cu	63	466762.0	975.1	50.738	1.5	1.6	ppb	Standard
I	Cu	65	221201.8	486.7	50.378	3.7	2.7	ppb	Standard
I	Zn	66	144096.7	4067.6	50.651	2.5	2.0	ppb	Standard
I	Zn	67	24083.6	668.4	50.554	5.1	4.4	ppb	Standard
I	Zn	68	107264.2	1475.1	49.963	2.8	1.5	ppb	Standard
I>	Ga	71	34369.5	33939.9			1.5	ppb	Standard
I	As	75	108627.0	-249.3	50.922	1.6	1.8	ppb	Standard
I	Se	77	9672.3	104.4	50.249	2.3	0.7	ppb	Standard
L	Se	82	12831.0	-1.9	50.750	2.0	0.4	ppb	Standard
I	Mo	95	261248.9	80.0	49.534	3.2	2.6	ppb	Standard
I	Mo	97	165936.2	199.3	49.919	3.3	2.3	ppb	Standard
I	Mo	98	417894.3	72.1	49.668	2.5	1.9	ppb	Standard
I	Ag	107	711275.4	120.0	50.436	3.2	1.9	ppb	Standard
I	Ag	109	691003.7	103.3	50.193	2.9	1.1	ppb	Standard
I	Cd	106	13995.2	-276.8	48.143	7.5	6.1	ppb	Standard
I	Cd	108	10129.8	-305.8	49.847	6.8	5.2	ppb	Standard
I	Cd	111	157528.0	54.6	49.976	5.2	3.7	ppb	Standard
I	Cd	114	376976.3	64.7	50.276	4.4	3.8	ppb	Standard
I>	In	115	117578.1	114783.9			2.4	ppb	Standard
I	Sb	121	600764.1	476.7	50.548	3.3	3.8	ppb	Standard
I	Sb	123	460188.1	365.8	49.682	3.3	3.3	ppb	Standard
I	Ba	135	159579.3	206.7	50.659	4.2	2.9	ppb	Standard
L	Ba	137	276317.6	443.4	50.450	1.9	1.5	ppb	Standard
I>	Ho	165	175411.5	169410.8			1.7	ppb	Standard
I	Tl	203	653884.7	75.7	49.498	1.7	1.2	ppb	Standard
I	Tl	205	1561799.3	126.7	49.228	0.8	1.0	ppb	Standard
I	Pb	208	2066142.5	593.4	49.289	2.6	1.6	ppb	Standard
I	Pb	208	2066142.5	593.4	49.289	2.6	1.6	ppb	Standard

SC-FAST ELAN ICPMS
Method 200.8 Detection Limits



ICS A and AB Recovery Standard Mode

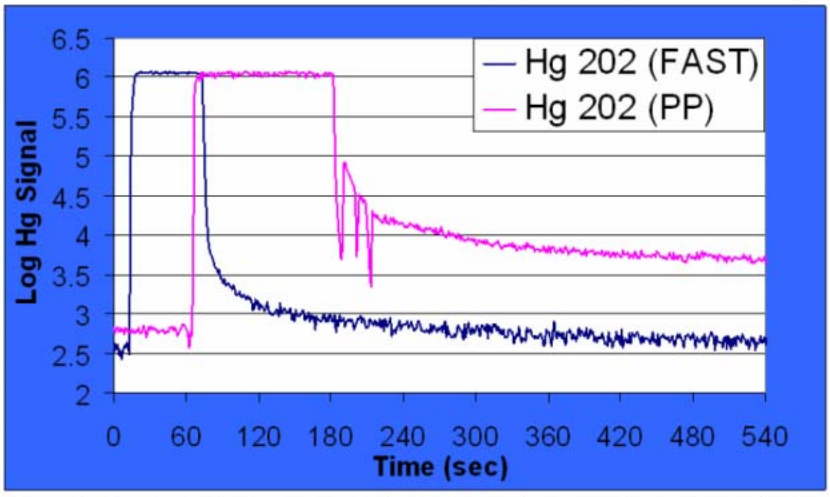


SC-*FAST* ELAN ICPMS
1 min 35 sec total sample time

High Speed Determination of Mercury by ICPMS

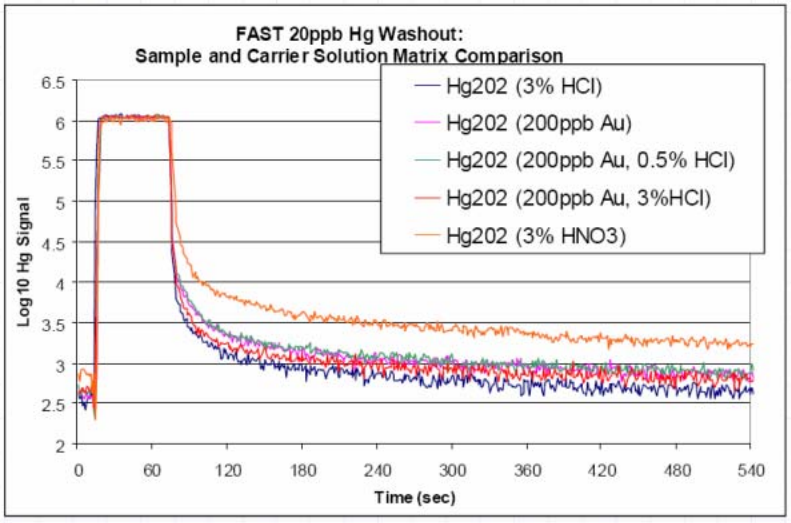
SC-*FAST*
Sample Introduction System

20 ppb Mercury Rinse-out (log scale) SC-FAST vs. Peristaltic Pumped

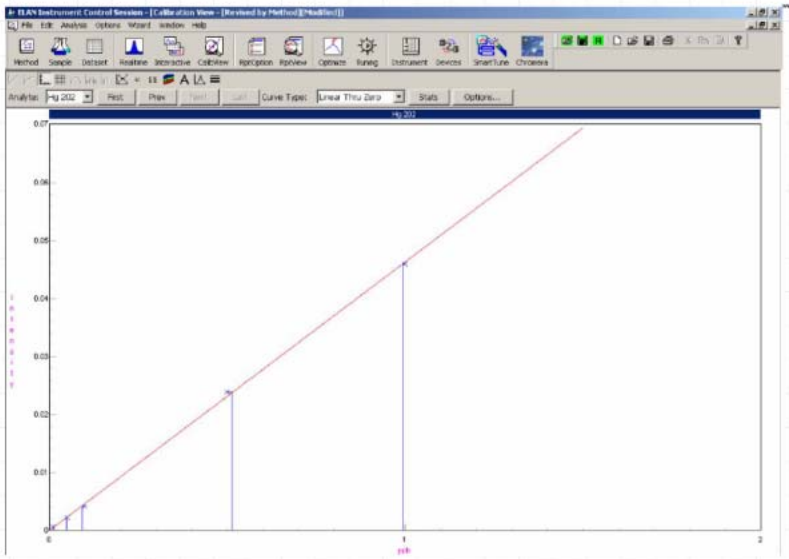


SC-FAST: 1000x rinse-out in ~ 60 seconds.
Sample and Carrier Solution Contain 3% HCl.

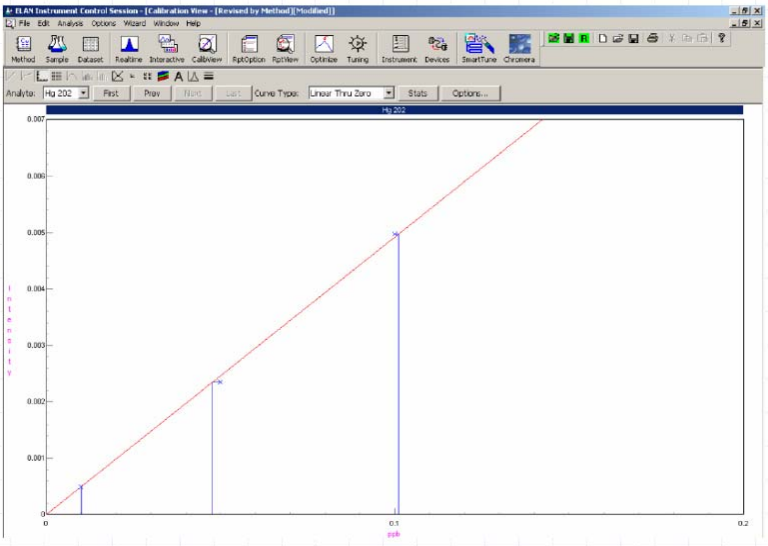
Effect of Au and HCl on Hg Washout SC-*FAST*



202 Hg Calibration
SC-FAST ELAN 9000



Low End Hg Calibration
10, 50, 100 ppt



Hg Blank (n=5) Immediately After Calibration 5 ppb Hg High Standard

	Hg 200	Hg 202
ICB 1	0.003	0.003
ICB 2	-0.002	0.000
ICB 3	0.001	0.003
ICB 4	0.000	0.001
ICB 5	-0.003	0.002
std. deviation	0.0024	0.0013
3s	**0.007 ppb**	**0.004 ppb**

Total ICPMS analysis time (from sample to sample for all elements) 1 min 45 sec
Iridium used as internal standard for Hg calibration.

Determination of Hg in Omaha Water SC-*FAST* ICPMS

Sample	Measured Concentration		Spike Recovery	
	200 Hg	202 Hg	200 Hg	202 Hg
Omaha Tap Water	17.9 ppt	16.8 ppt	--	--
100 ppt Hg Spike	119.8 ppt	118.1 ppt	102%	101%

Faucet flushed for 15 minutes before sampling

Determination of Se in Great Salt Lake Water

Reaction Cell ICPMS
SC-FAST

10 g sample evaporated

ICPMS Analysis Great Salt Lake Water
All Se Isotopes Have Spectral Interferences

- ICP Background
  - $ArAr^+$ (m/z 74, 76, 78, **80**)
  - Kr^+ (m/z 82)
- Matrix-related interferences, e.g.
  - $ArCl^+$ (m/z 77)
  - SO3+ (m/z **80**)
  - BrH+ (m/z **80**, 82)
- DRC with O2 eliminates $ArAr^+$, BrH^+, SO_3^+
- SC-FAST long-term stability and throughput

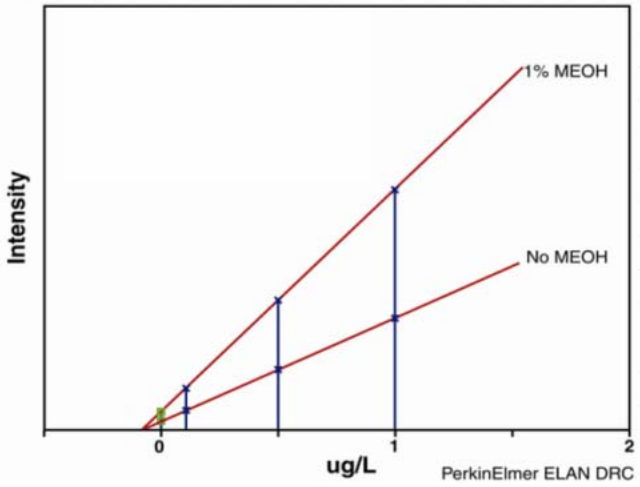
Se in Great Salt Lake Water ELAN DRC Conditions

RF Power	1600
Nebulizer	PFA-ST (SC-FAST)
Peltier cooler	PC3, 2 C
Cell Gas	Oxygen, 1.5 mL/min
RPq	0.75
m/z	80
Internal Standard	Rh, on-line addition
Sample Dilution	25x
Total Analysis Time	59 seconds/sample

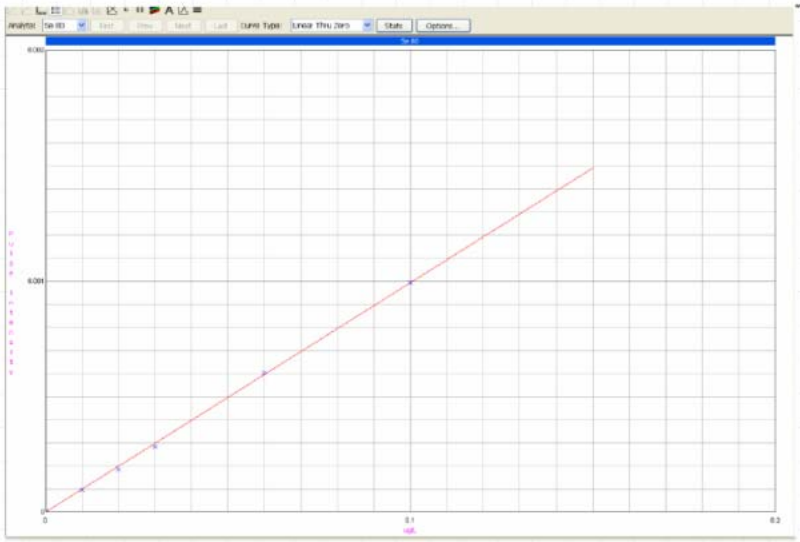
Sample Preparation

- Samples filtered 0.4 micron syringe filter.
- 2 mL GSL water + 0.5 mL methanol + 0.5 mL HNO3 diluted to 50 mL with high purity water.

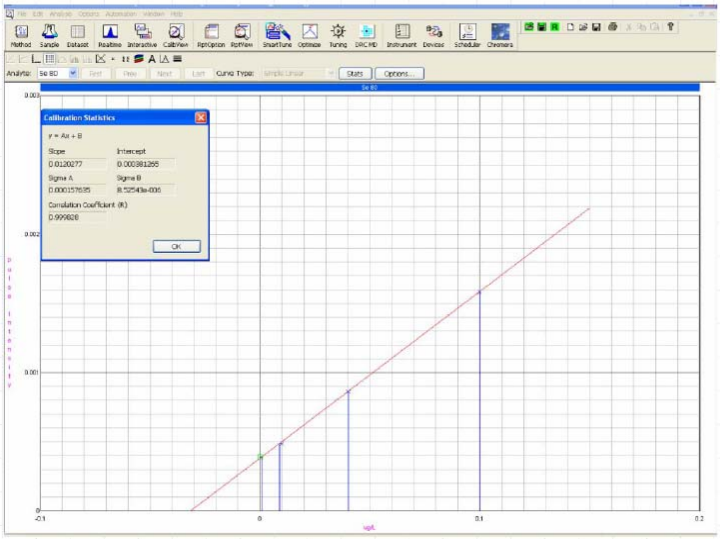
Effect of Methanol on Se Sensitivity



Se 80 Calibration 0 to 100 ppt
Matrix-Matched Standards
ELAN DRC with SC-FAST



Standard Addition Se in 25x GSL Water 0-100 ppt

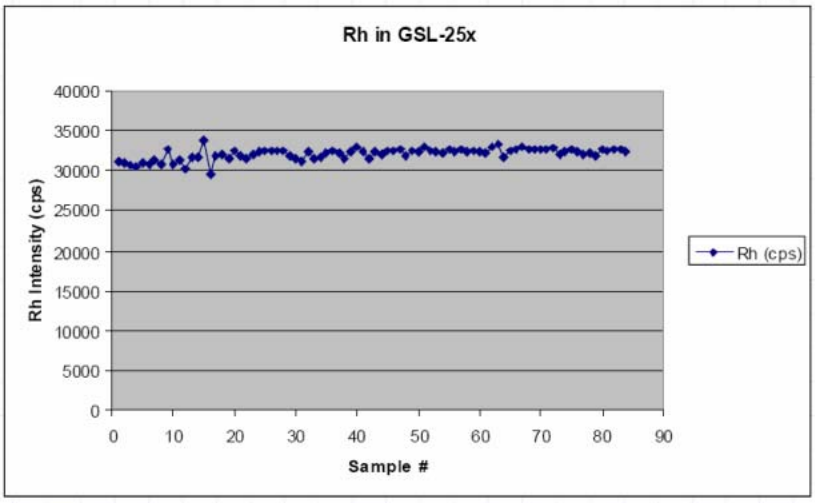


ICPMS Sampler Cone After >300 Great Salt Lake Water Samples with SC-FAST

- Long-term stability with high TDS samples
- Improved recoveries and DL
- Low instrument maintenance

Stability 0.5% TDS

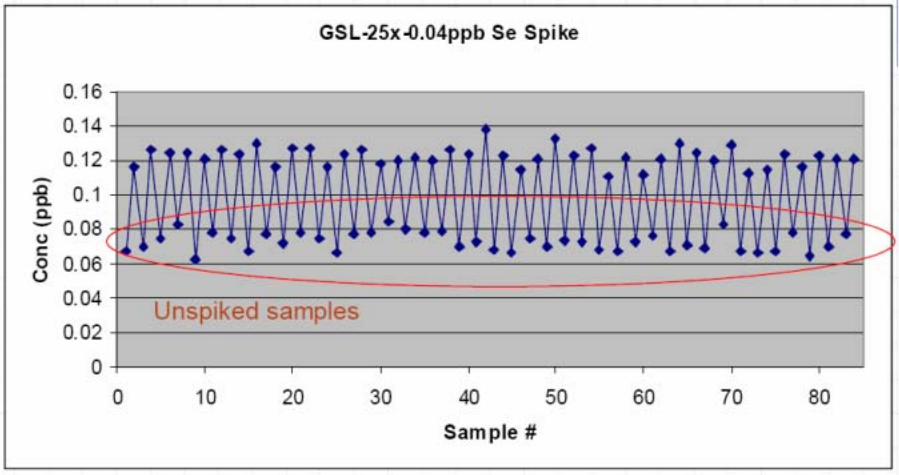
On-Line Addition Rh Internal Standard



84 replicate injections of 25x GSL water alternating unspiked and 40 ppt spike

Great Salt Lake Water

Alternating Unspiked and 40 ppt Se Spike



Spike level is 2.5x the detection limit. Total analysis time 84 minutes.

Se Detection Limit

42 replicate injections unspiked 25x GSL water

DL as Analyzed	DL in GSL Water
0.017 ppb	0.4 ppb

Selenium Spike Recovery Great Salt Lake Water

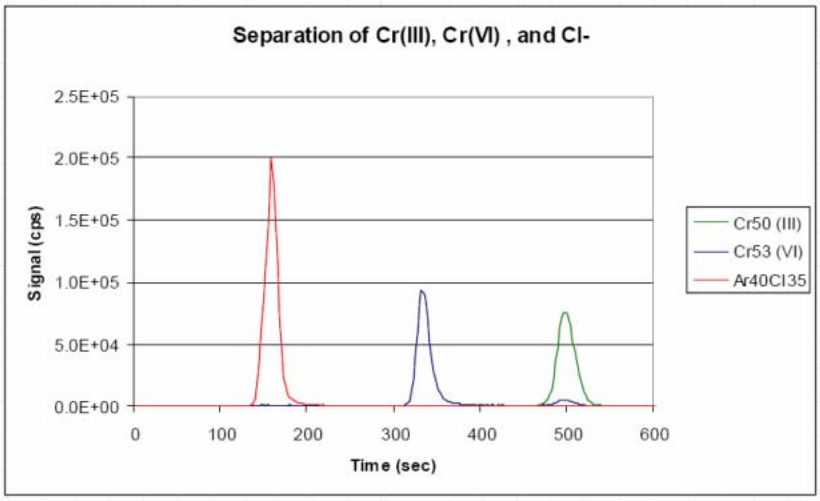
Spike Concentration	Spike as Analyzed	Recovery (%)
0.5 ppb	0.02 ppb	112%
1 ppb	0.04 ppb	103%
75 ppb	3 ppb	100%

ELAN DRC with SC-FAST Sample Introduction System

SC-FAST for Low Pressure Elemental Speciation

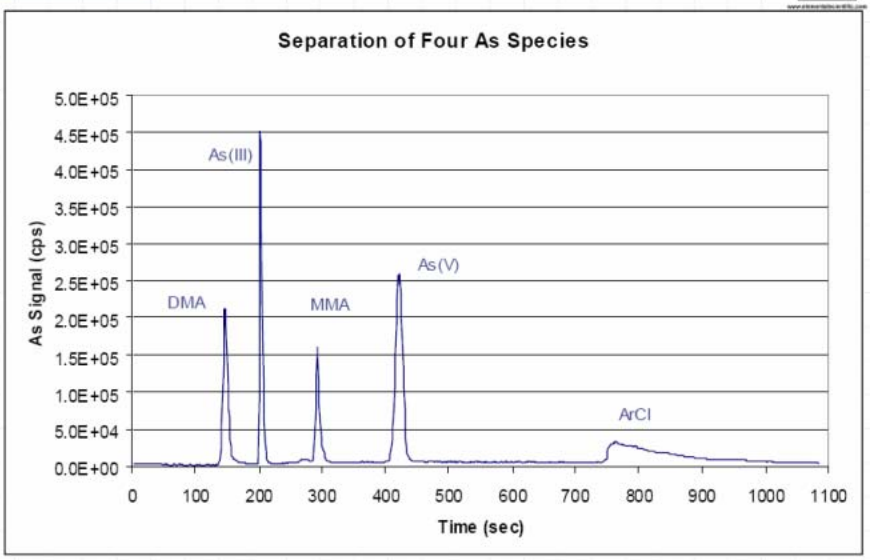
Peristaltic pump driven LC-ICPMS

Cr Speciation
2 ppb Cr in 0.5% HCl

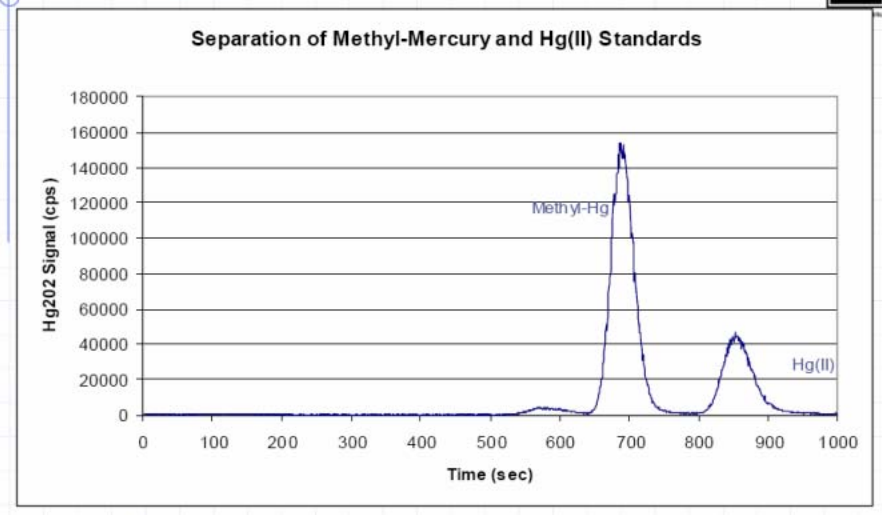


As Speciation

Low Pressure Step-Gradient Elution SC-FAST

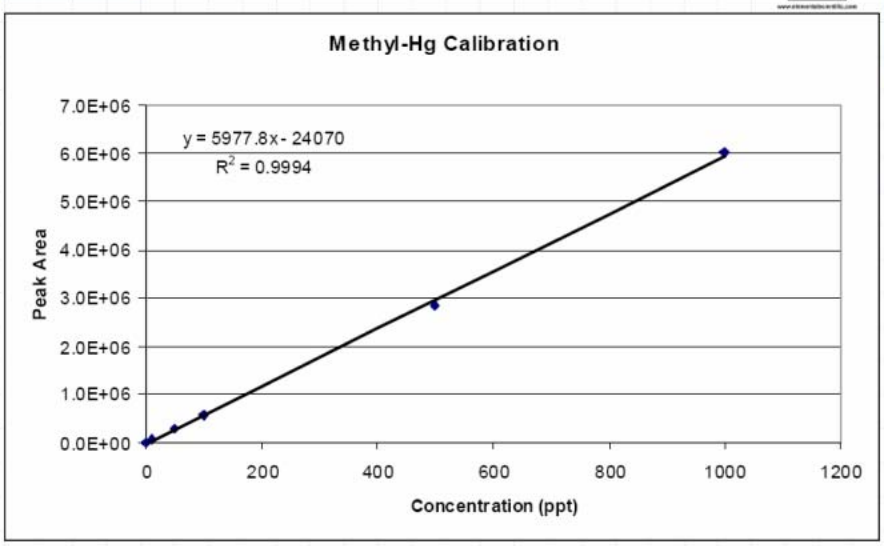


Hg Speciation

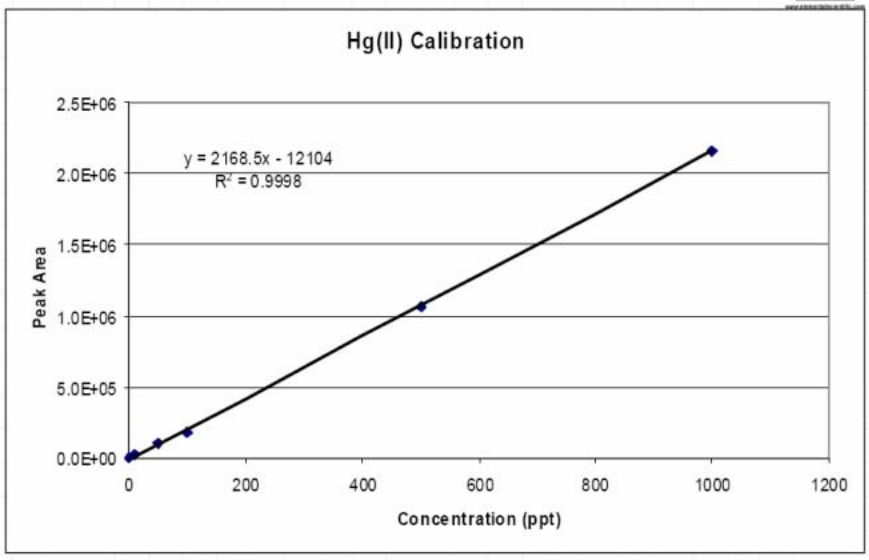


C-18 Column (30 x 4.6 mm)

Hg Speciation: Methyl Mercury Calibration



Hg Speciation: Mercury Calibration



SC-*FAST* System ICPMS and ICPAES

- Improve ICP and ICPMS efficiency by 200% to 300%.
- No contact between peristaltic pump tubing and sample solution.
- Low, constant sample delivery rate to reduce matrix effects and improve stability.
- Low pressure chromatography interface.
- Stable ICPMS Analyses

Earlier Work to Improve Throughput DIN Papers from 1991

Anal. Chem. **1991**, *63*, 219–225

Direct Injection Nebulization for Inductively Coupled Plasma Mass Spectrometry

Daniel R. Wiederin, Fred G. Smith, and R. S. Houk*
Ames Laboratory–U.S. Department of Energy and Department of Chemistry, Iowa State University, Ames, Iowa 50011

1626 *Anal. Chem.* **1991**, *63*, 1626–1631

On-Line Standard Additions with Direct Injection Nebulization for Inductively Coupled Plasma Mass Spectrometry

Daniel R. Wiederin,[1] Ronald E. Smyczek,[2] and R. S. Houk*
Ames Laboratory—U.S. Department of Energy and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Shortcomings and Resolution for SW846 Method 7199 for Hexavalent Chromium (Cr^{+6})

Jay Gandhi*, Technical Manager
Spencer Gambacurta, Applications Chemist
Metrohm-Peak, LLC
Houston TX

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Outline

- Method SW846 7199 – review
- USEPA Method 218.6 – review
- Chemistries of Eluant, Reagent and Columns for this analysis
- Suggested improvement
- Data to support improvement
- Conclusion

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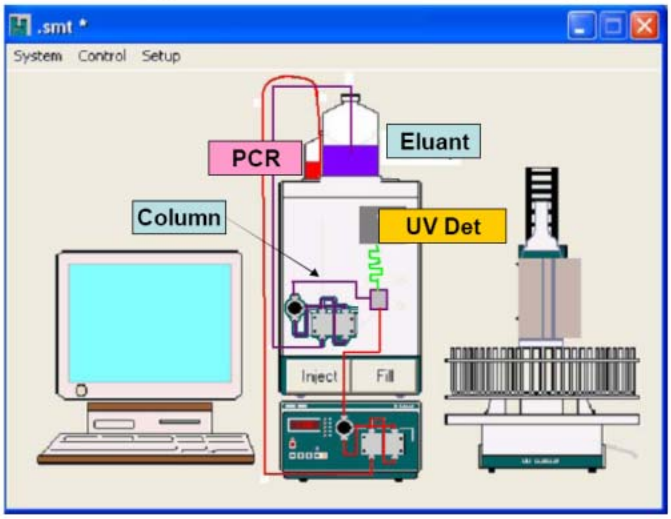
Typical Instrument Set-up



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SW 846 method 7199
Or
US EPA method 218.6
Chromium (VI) by UV/PCR

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SW Method 7199 and USEPA method 218.6

- **Uses IC-UV/PCR for detection of Cr(VI)**
  - Various loop sizes permitted to achieve results
  - Ammonium Sulfate/Ammonium Hydroxide Eluent
  - Sample Digested with high ionic strength buffer solution
  - Applicable to Soil Samples, but used for water samples as well

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Chemistries Review

5.7 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

20 g NaOH = 0.5M Strength
0.5M = 500mM NaOH
30g Na_2CO_3 = ~0.3M strength
0.3M = 300mM NaOH
Total Strength = 0.8M

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Eluant:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4 Flow Rate = 1.5 mL/min
Post-Column Reagent:	2mM Diphenylcarbohydrazide 10% v/v CH_3OH 1 N H_2SO_4 Flow rate = 0.5 mL/min

Eluent = 0.25M + 0.1M = 0.35M Strength
PCR Reagent = 0.5M (1N) H_2SO_4

Neutralizing 0.5M Acid @ 0.5mls with 1.1M Base (0.35M+0.8M digestion) @ 0.8 or 1.0mls/min

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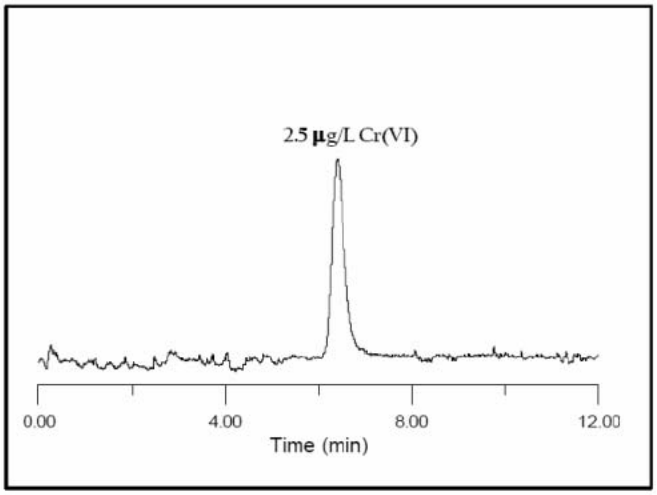

Figure 6: Chromatogram of 2.5 µg/L Cr(VI) fortified in a simulated wastewater effluent sample using a 100 mV analog output. The synthetic sample contained 100 mg/L chloride, 100 mg/L sulfate, 100 mg/L carbonate and 50 mg/L nitrate.

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Column dimensions	100 x 4.0 mm
Column body	PEEK
Standard flow	1.0 mL/min
Maximum flow	2.0 mL/min
Maximum pressure	20 MPa
Particle size	4.5 µm
Organic modifier	0...30%
pH range	0...14
Temperature range	10...70 °C
Capacity	85 µmol (Cl^-)

Important parameter

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Experimental Conditions (modified)

- **Metrohm IC**
  - 100 uL loop injection or 1000ml loop injection
  - Column: Metrosep ASUPP-10 (4mm x 250mm)
  - Column Temp: 35 °C
  - Eluent: 10mM LiOH + 5g/L $LiSO_4$
  - Flow rate: 0.8 ml/min
- **PCR Chemistry**
  - 0.5g/L Di-Phenyl Carbazide (dye)
  - Flow rate = 0.5ml/min
  - UV Detection at 530nm

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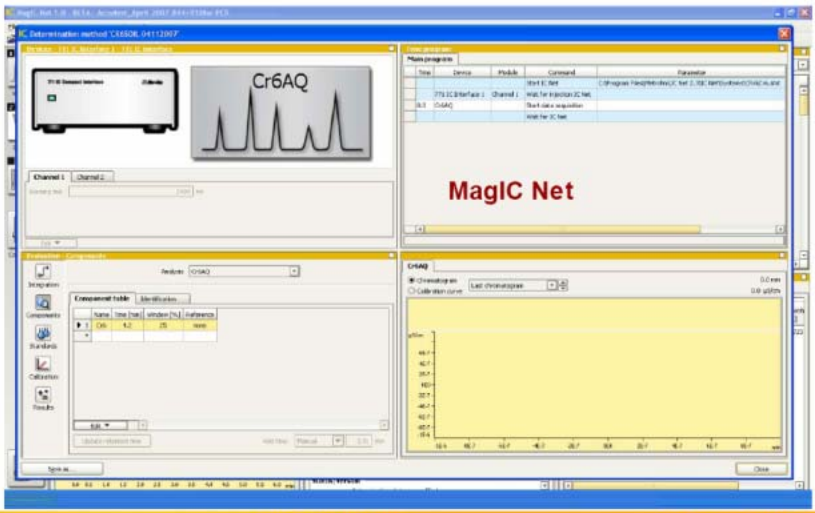
IC Net running in Background



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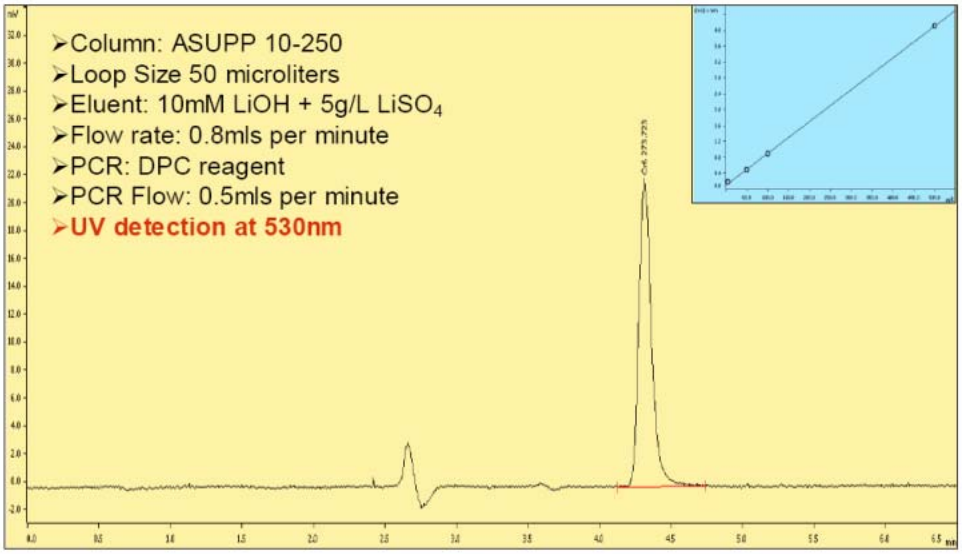
Chromatogram (Cr^{+6})

- Column: ASUPP 10-250
- Loop Size 50 microliters
- Eluent: 10mM LiOH + 5g/L $LiSO_4$
- Flow rate: 0.8mls per minute
- PCR: DPC reagent
- PCR Flow: 0.5mls per minute
- **UV detection at 530nm**



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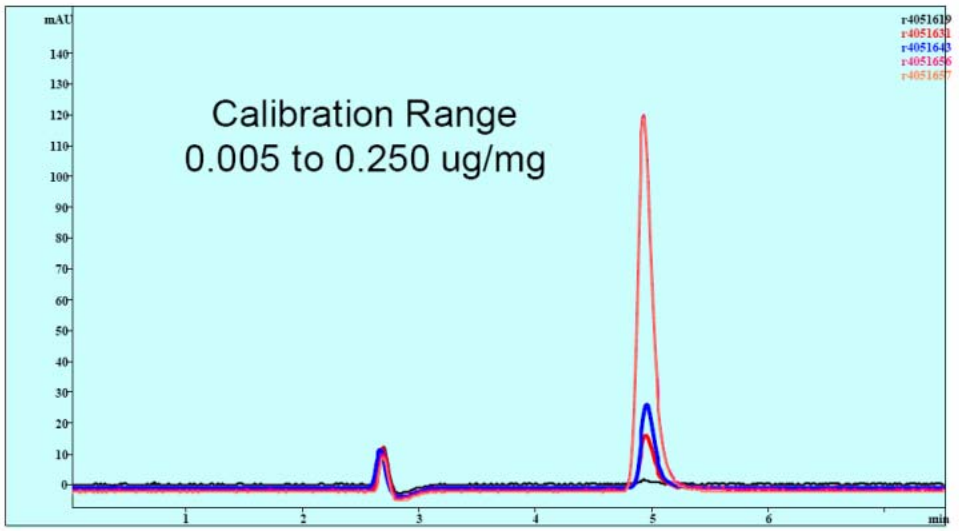
Stacked Calibration Standards



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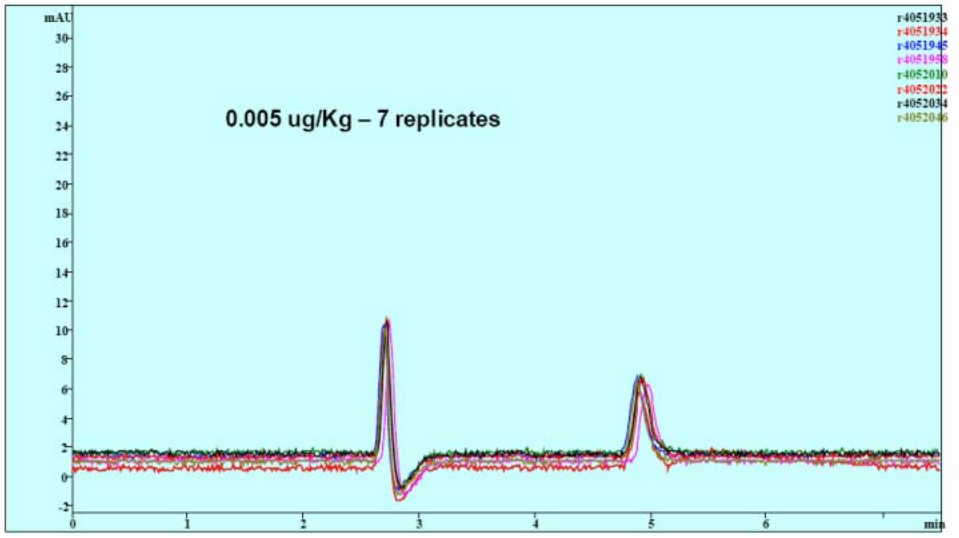
MDL - Chromatograms



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MDL - Data

Sample ID	Date/Time of injection	Amount
MDL-5 ppb-1	19/03/2007 17:05:36	5.0948
MDL-5 ppb-2	19/03/2007 17:16:45	5.0966
MDL-5 ppb-3	19/03/2007 17:27:53	4.7743
MDL-5 ppb-4	19/03/2007 17:39:02	5.1069
MDL-5 ppb-5	19/03/2007 17:50:10	4.9916
MDL-5 ppb-6	19/03/2007 18:01:18	4.7333
MDL-5 ppb-7	19/03/2007 18:12:27	4.9926
	Average	4.9700
	Std.Dev	0.156
	MDL (3.14*Std.Dev)	0.489
	%RSD	3.135

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Interferences???
Or
Other emerging analytes

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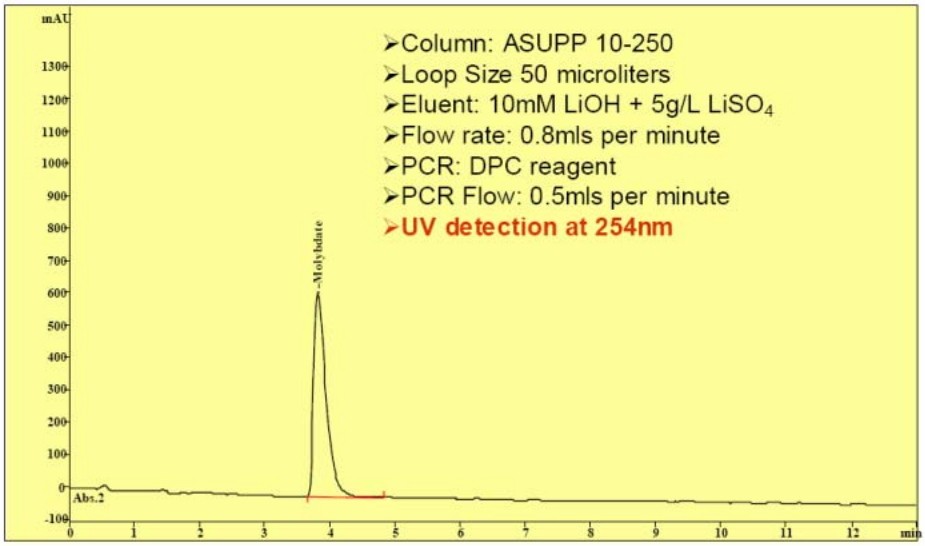
Chromatogram (Molybdenum as MoO_4^{-2})



- Column: ASUPP 10-250
- Loop Size 50 microliters
- Eluent: 10mM LiOH + 5g/L $LiSO_4$
- Flow rate: 0.8mls per minute
- PCR: DPC reagent
- PCR Flow: 0.5mls per minute
- **UV detection at 254nm**

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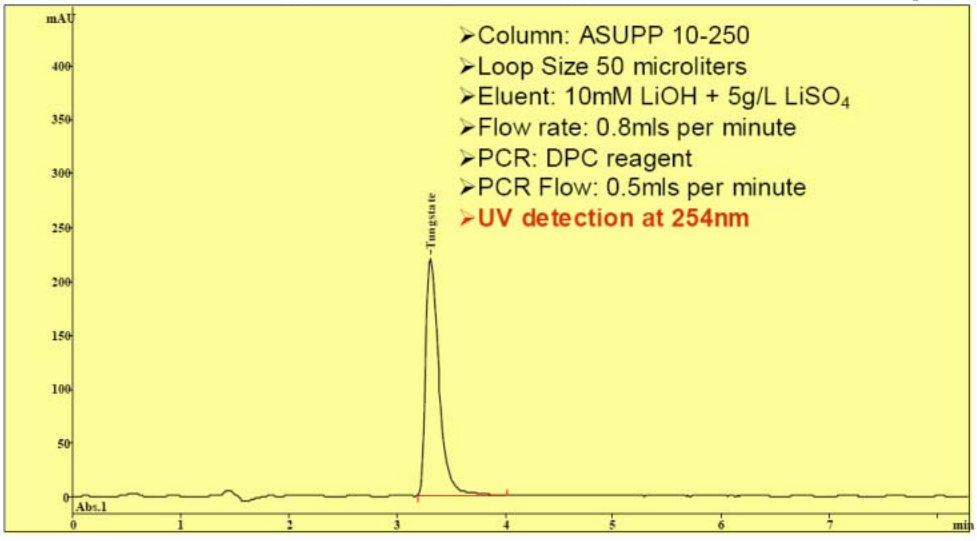
Chromatogram (Tungsten as WO_4^{-2})



- Column: ASUPP 10-250
- Loop Size 50 microliters
- Eluent: 10mM LiOH + 5g/L $LiSO_4$
- Flow rate: 0.8mls per minute
- PCR: DPC reagent
- PCR Flow: 0.5mls per minute
- **UV detection at 254nm**

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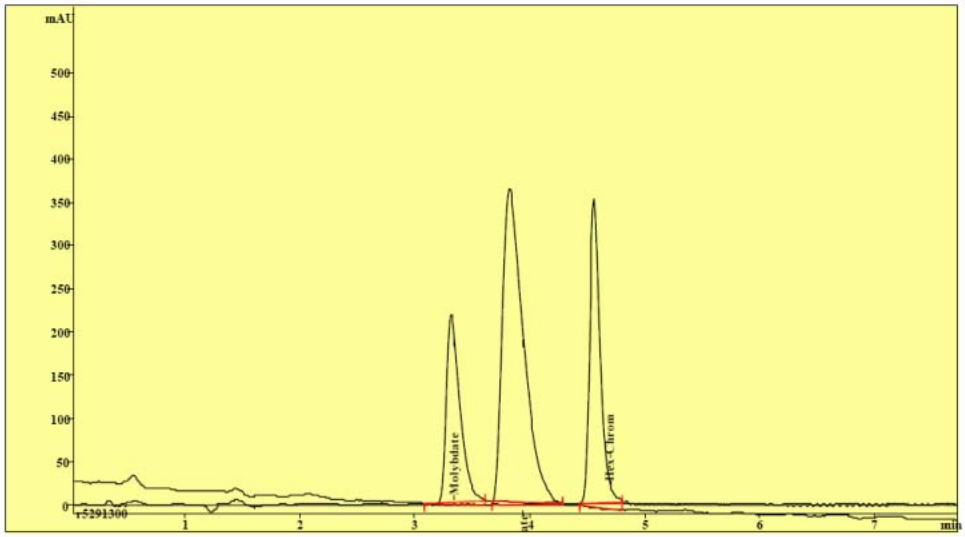
Chromate, Tungstate, Molybdate



Metrohm-Peak Ion Chromatography

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Acknowledgements

- Metrohm Competency Center, Herisau – Switzerland
- Metrohm-Peak Customers for providing samples

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Simple, Rapid Interference-Free Analysis of Elements in Environmental Samples by Collision Cell ICP-MS

Bill Spence
Thermo Fisher Scientific

ABSTRACT

Polyatomic interferences have long been an Achilles heel for ICP-MS, particularly when samples containing large quantities of dissolved matter are to be analyzed. Collision/reaction cells have been available in commercial ICP-MS instruments for ten years now, and have been proven to be effective at reducing or removing polyatomic species of various types using one of several mechanisms:

1) collision-induced dissociation of the polyatomic;
2) chemical reaction or charge exchange with the polyatomic;
3) chemical reaction with the analyte;
4) kinetic energy discrimination.

Mechanism 1 is thought not to contribute greatly. Mechanisms 2 and 3 work very effectively, but are dependent upon favourable thermodynamic and kinetic conditions for a useful reaction to proceed and therefore their use is complex in terms of the selection of the ideal gas for a particular polyatomic and the predictability of the reaction. Mechanism 4 can be efficacious under very specific instrument conditions, dependent upon the instrument design, and can uniquely offer blanket polyatomic reduction under a single set of conditions.

This presentation describes a new ion optical design incorporated into the Thermo Scientific XSERIES 2 ICP-MS, giving the third generation of collision cell technology. This design has been optimized for use with the kinetic energy discrimination approach to polyatomic removal. The presentation will give example data for the application of this mode of use to the analysis of environmental samples using USEPA Method 6020 with a focus on the removal of multiple interferences under a single set of instrument conditions illustrated by analysis of ICS solutions and presents the ability of the system to measure multiple matrices without interference under a single set of conditions. This dramatically simplifies method development and daily setup and produces an extremely rapid analysis time due to the lack of need for gas-change stabilization delays.

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The world leader in serving science

Simple, Rapid Interference-Free Analysis of Elements in Environmental Samples by Collision Cell ICP-MS

your partner for ultimate environmental analysis

Bill Spence, Julian Wills, Meike Hamester, Fergus Keenan
Thermo Fisher Scientific, Ion Path, Winsford, Cheshire, CW7 3GA, UK
Telephone: +44 1606 548100. Fax: +44 1606 552588. E-mail: bill.spence@thermo.com.

Polyatomics: The Achilles Heel of ICP-MS

Achilles statue, moment of dying, Achillion Palace, Greece

2

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Polyatomic Interferences

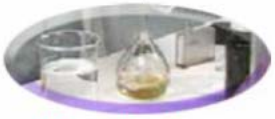
Caused by molecular species formed in plasma overlapping with analyte isotope

Ar, Air

(O, N, C)

ArAr, ArO, ArN, ArC, ArH, ArCa, ArNa, ArK, ArMg, ArCl, ClO, NO, CO, CaO, NaO, etc

H_2O, Ca, Na, K, Mg, Cl, etc



Products ← Reaction ← Reactants

3

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The consequences of polyatomic interference (1)

- Calibrate analyte in 'clean' matrix
- Measure same analyte in sample containing interfering species
  - e.g. Vanadium (m/z 51) in sample containing high chloride ($^{35}Cl^{16}O$)
- Quadrupole MS is unable to distinguish between V-51 and ClO-51
- Results in positively biased data (falsely high values):

Ref Value (ppb)	Measured Value (ppb)	Recovery (%)
10.0	52.7	527

4

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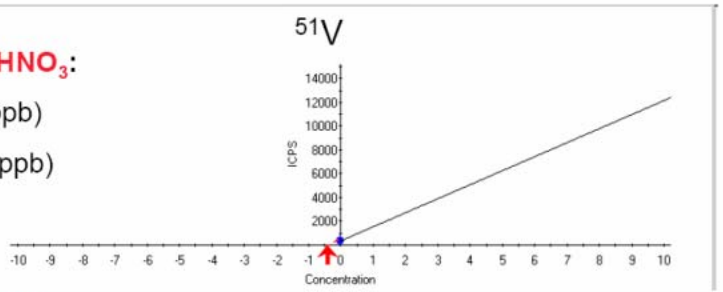
The consequences of spectral interference (2)

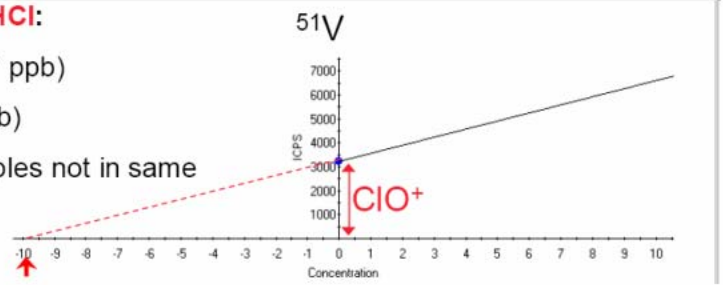
Calibrate in 1% HNO_3:

- Low BEC (0.3 ppb)
- Good DL (0.03 ppb)



Calibrate in 1% HCl:

- Higher BEC (9.7 ppb)
- Poorer DL (1 ppb)
- Also bias if samples not in same conc. of HCl



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Some Typical Spectral Interferences

Analyte	m/z	Elemental Isobaric Interferences	Gas-based Polyatomics	Matrix-based Polyatomics
V	**51**			ClO
Cr	**52**		ArO	ArC
Fe	54	54Cr	ArO, ArN	
Fe	**56**		ArO	CaO
Ni	**60**			CaO
As	**75**			ArCl
Se	**82**	82Kr		BrH
Sr	86	86Kr		
Mo	98	98Ru		
Cd	114	114Sn		(MoO)
Sb	123	123Te		
Ba	138	138La, 138Ce		

6

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How to Deal with Polyatomics?

75As = 75M - 3.1322*77ArCl & 77ArCl = 77M - 0.8260*(82M - 1.0010*83Kr - 0.9728*79BrH). Of course, the 40Ar40Ar+ dimer becomes an issue for 79BrH in most instruments as does 80Se, but this can be further corrected for 80 Se by the corrected ratio for 82Se as follows:

75As = 75M - 3.1322*77ArCl & 77ArCl = 77M - 0.8260*(82M - 1.0010*83Kr - [0.9728*79BrH - 5.683*(82M - 1.0010*83Kr - 0.9728*79BrH)].

Of course, that leaves the 40Ar40Ar+ dimer. One can correct for that by using the ratio of Ar40Ar38+ to Ar40Ar40+ as follows:

75As = 75M - 3.1322*77ArCl & 77ArCl = 77M - 0.8260*(82M - 1.0010*83Kr - [0.9728*79BrH - 5.683*(82M - 1.0010*83Kr - {0.9728*79BrH - 0.0015840Ar38Ar}]

leaving only the correction for the effect of 78 Se and 78Kr to deal with.

75As = 75M - 3.1322*77ArCl & 77ArCl = 77M - 0.8260*(82M - 1.0010*83Kr - [0.9728*79BrH - 5.683*(82M - 1.0010*83Kr - {0.9728*79BrH - (0.0015840Ar38Ar - 0.3144*0.8260*(82M - 1.0010*83Kr - [0.9728*79BrH - 5.683*(82M - 1.0010*83Kr - 0.9728*79BrH) - 0.0304*83Kr}].

Please check my math. I ran out of brackets, parentheses, and other closure marks, so it became a bit confusing. Nevertheless, assuming that you have a smooth Ar dimer signal, this can be done.

R. Steven Pappas, Ph.D.
Emergency Response & Air Toxicants Branch Centers for Disease Control & Prevention 4770 Buford Hwy. NE, M.S. F-44 Atlanta, GA 30341-3717 Phone 770-488-4661 RPappas@cdc.gov

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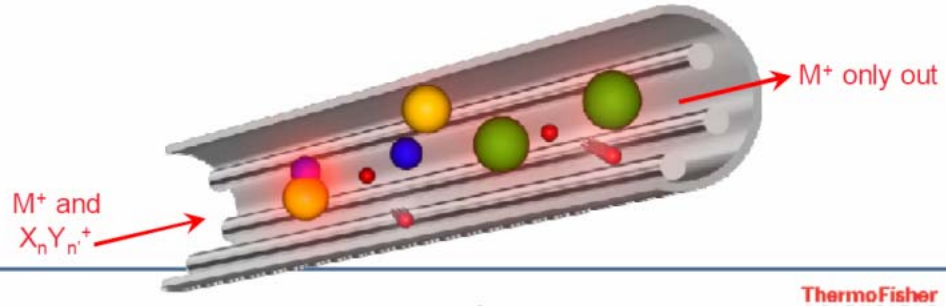
What is a CRC ?

Collision/Reaction Cell Technology

- A multipole enclosed in a cylinder
- Controlled flow of gas into the cell
- Interaction of ions with the gas
- If reactive gas used, reactions occur
- If non-reactive gas, only kinetic energy loss occurs



8

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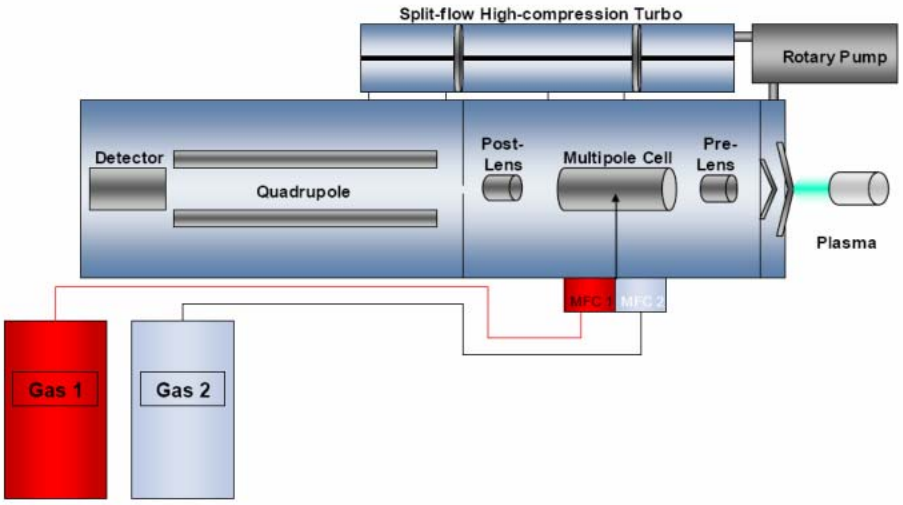
Basic Schematic of CRC ICP-MS



9

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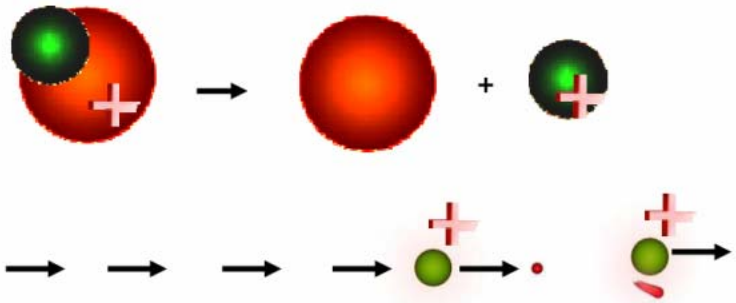
What does a CRC give me ?

Reduction / elimination of interferences…..



….whilst analytes are relatively unaffected

10

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How does it work?

4 Possible mechanisms for interference removal:

- collision-induced dissociation
- chemical reaction
- electron transfer

Require reactive gases

- collisional retardation / differential transmission (kinetic energy discrimination - KED)

11

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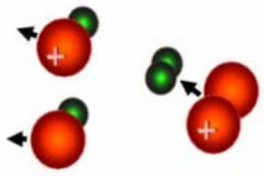
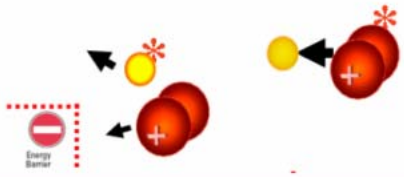
Cell Operation Approaches

- Two fundamentally different cell operation approaches have been used:
  1. Reactive removal of interferences (chemical reactions and electron transfer reactions)



  2. Collisional retardation and energy filtering (Kinetic energy discrimination, KED)



12

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Gas Selection – Some Reactive Gases

Gas	+	-
H_2	Excellent removal of ArX^+ species and many other polyatomics. No reaction with most atomic ions	No reaction with ClO^+ or refractory XO^+ species.
NH_3	Excellent removal of ClO^+ and some other polyatomics.	Reaction with many atomic ions: reduction in analyte sensitivity, e.g. As and Se; formation of new interferences
O_2	Good for 'shifting' analytes or interferences, e.g. measure as MO^+, or move XO^+ interferences to XO_2^+	Not much use for more than a small number of interferent/analyte pairs. Reaction with many analytes
CH_4	Good removal of some polyatomics, e.g. ArX^+ and some XO^+ species.	Reaction with many atomic ions: reduction in sensitivity, formation of new interferences

13

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Using Reactive Gases

- **Reactions with gases such as NH_3, O_2 and CH_4 form products**
  - e.g. NH_3 reactions can form "clusters"
  - Causes new interferences
  - Reduces reactive analyte sensitivity
  - But, can be useful for "shifting" masses
- Some elements are completely unreactive
- Others highly reactive

14

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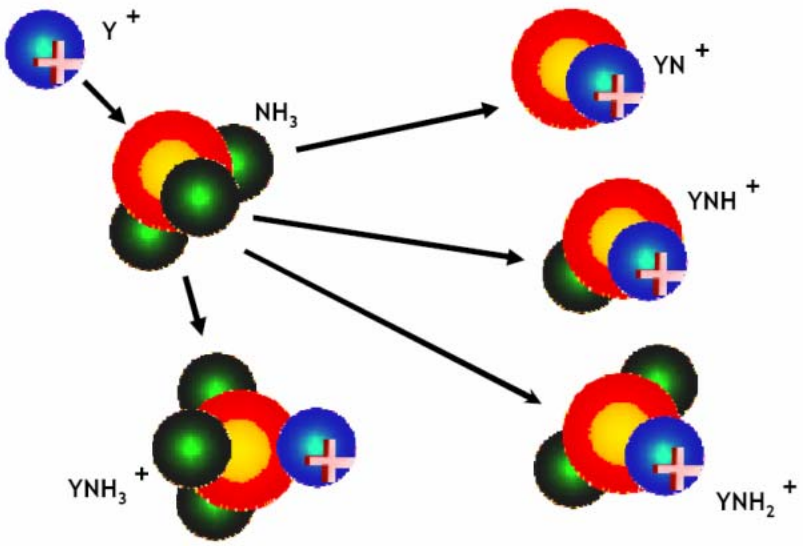
Cluster formation ($Y + NH_3$)



15

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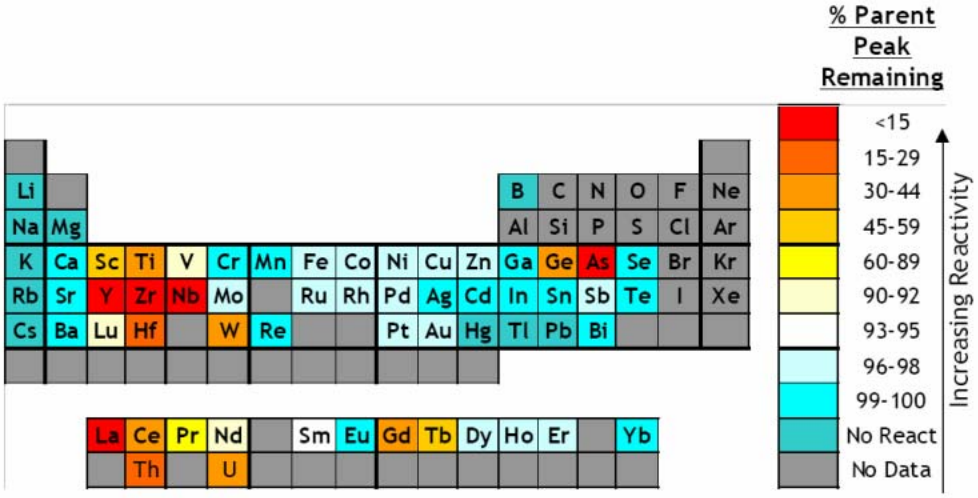
Ammonia – Reactive or Inert Analytes?



16

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Reactions or KED?

Reactive Removal	KED
+	+
▪ Very efficient at removing specific interferences	▪ Non-specific interference removal – one size fits all! ▪ Great for multi-element analyses ▪ No new interferences observed
-	-
▪ Very selective chemistry – must choose the right gas for the interference ▪ Not ideal for multi-element analyses ▪ Reaction products may cause new interferences	▪ Some loss of analyte sensitivity, esp. at low mass

17

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The Basis of KED Operation

$^{51}V^{+}$
~140 pm

$^{51}[ClO]^{+}$
~250 pm

18

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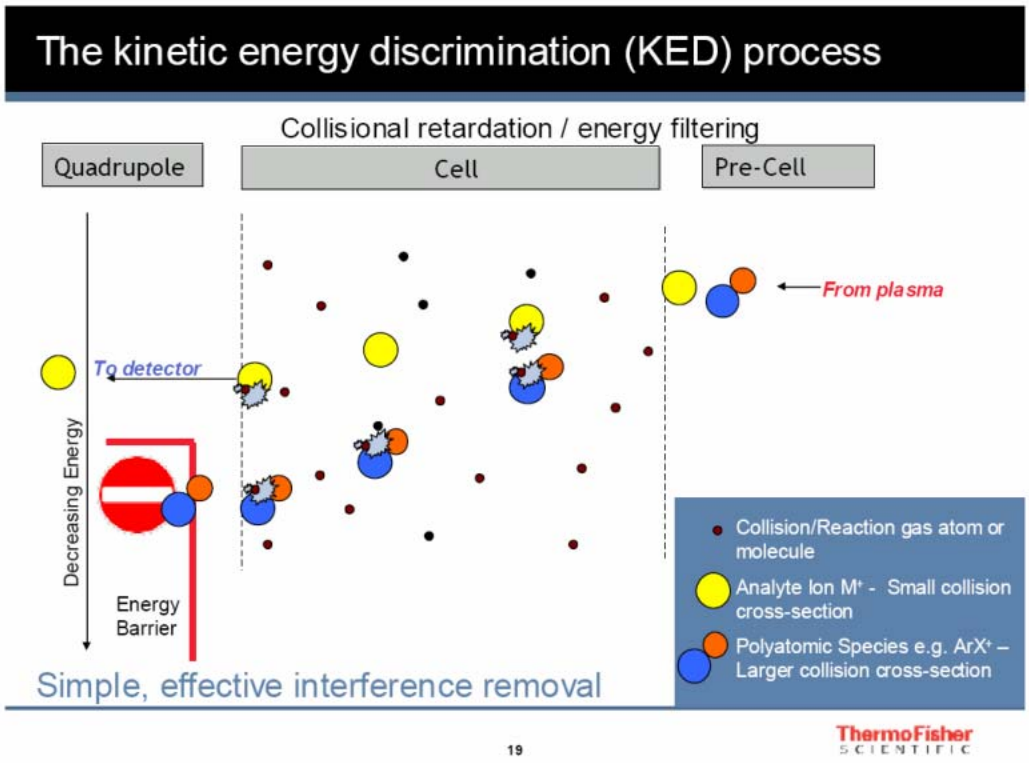
The kinetic energy discrimination (KED) process
Collisional retardation / energy filtering
Quadrupole
Cell
Pre-Cell
From plasma
To detector
Decreasing Energy
Energy Barrier
Collision/Reaction gas atom or molecule
Analyte Ion M+ - Small collision cross-section
Polyatomic Species e.g. ArX+ – Larger collision cross-section
Simple, effective interference removal
19
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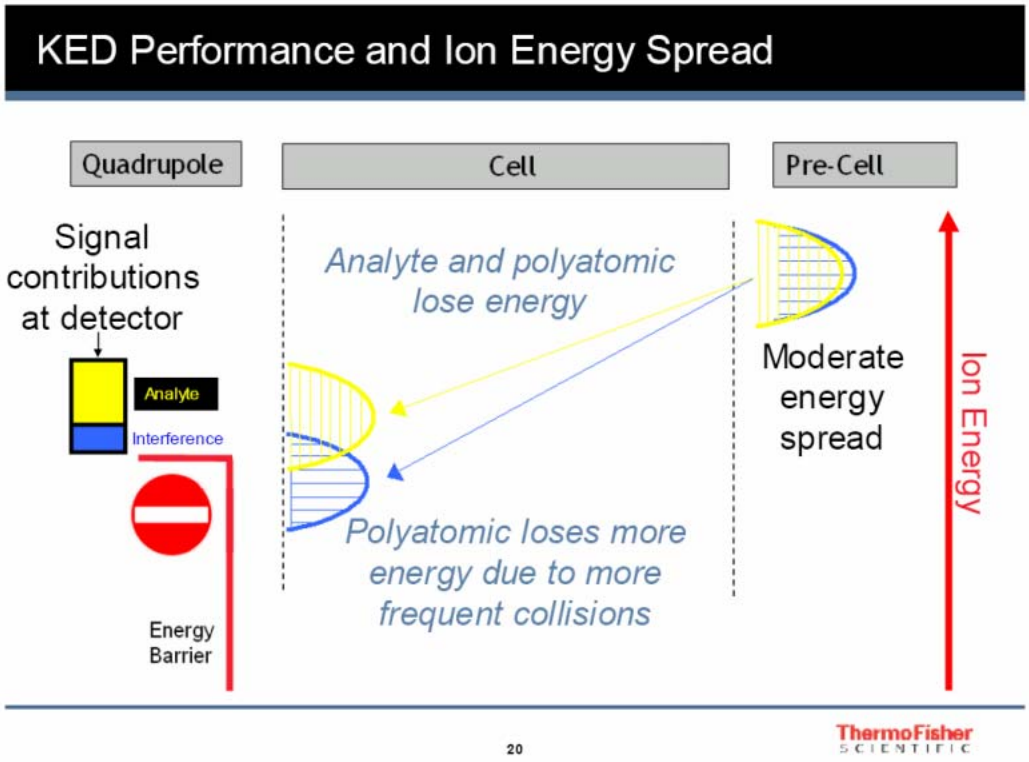
KED Performance and Ion Energy Spread
Quadrupole
Cell
Pre-Cell
Signal contributions at detector
Analyte
Interference
Energy Barrier
Analyte and polyatomic lose energy
Polyatomic loses more energy due to more frequent collisions
Moderate energy spread
Ion Energy
20
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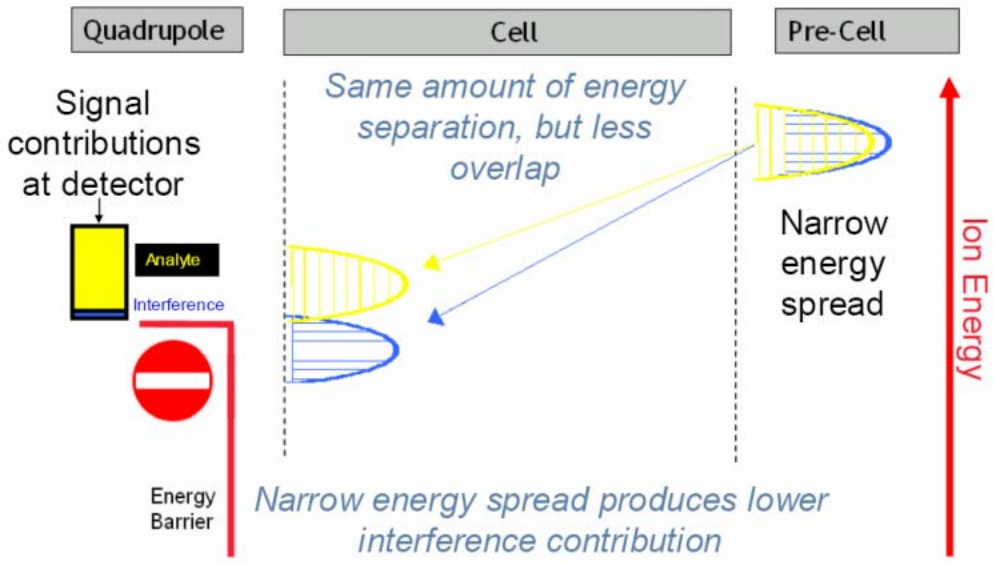
KED Performance and Ion Energy Spread



21

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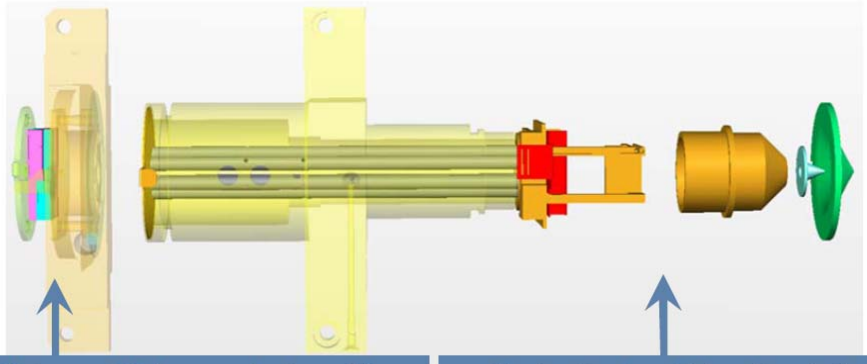
XSERIES 2: New Collision Cell Design



Chicane ED-lens redesigned for optimum Kinetic Energy Discrimination performance and uniquely set off-axis to remove cell-formed neutrals and photons

Protective Ion Extraction (π) ensures good analyte ion transmission in π extraction mode and decouples non-optimum energy ions

22

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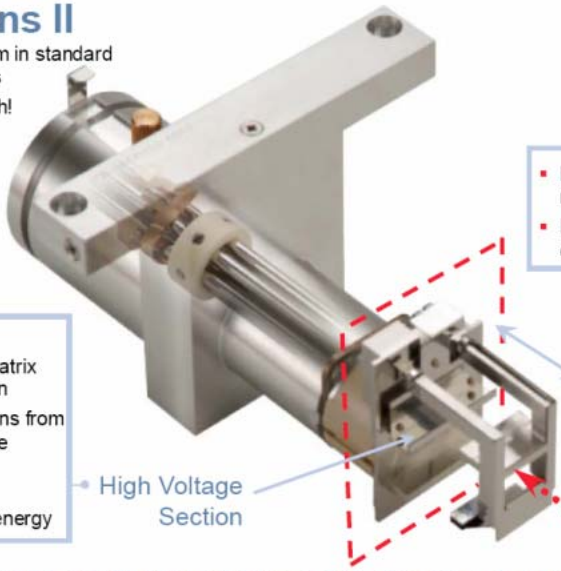
Design for Environmental Applications: Lens System

Infinity Lens II

- Identical lens system in standard and cell instruments
- Simple upgrade path!



- Low surface area for matrix material deposition
- Excellent ion transmission efficiency

Open Structure Pi-lens Region

- Resistant to field changes due to matrix material deposition
- Protected by Pi-lens from extractive interface species
- Ion transmission controlled by ion energy

High Voltage Section

Ions in

The high performance optic that requires zero user maintenance

23

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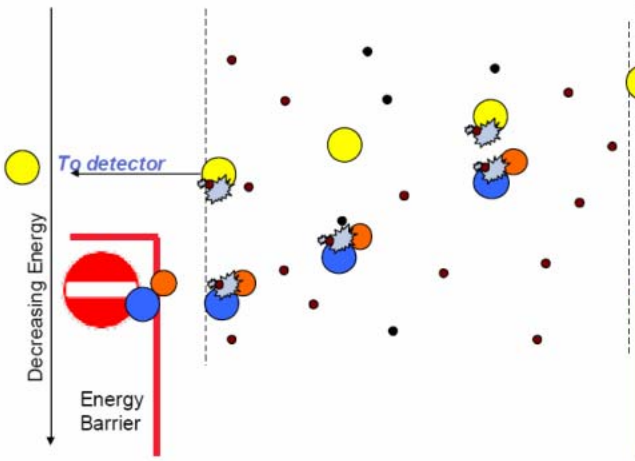
Design for Environmental Applications: Simple CCT^{ED}

Collisional retardation / energy filtering

Quadrupole | Cell | Pre-Cell



π Extraction Lens – ensures that the energy of the ions entering the cell are ideal for collisional or reactive chemistry

- Collision/Reaction gas atom or molecule
- Analyte Ion M^+ - Small collision cross-section
- Polyatomic Species e.g. ArX^+ – Larger collision cross-section

Simple, effective interference removal

24

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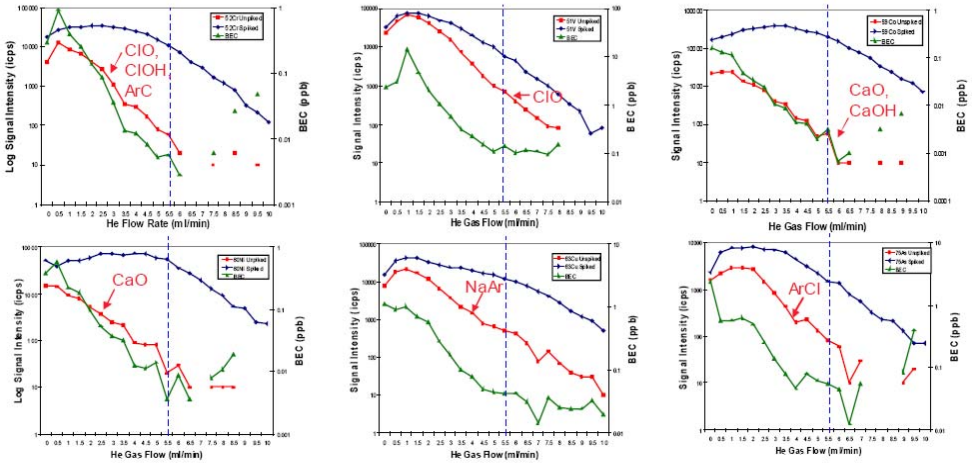
Design for Environmental Applications: Simple CCT*ED*

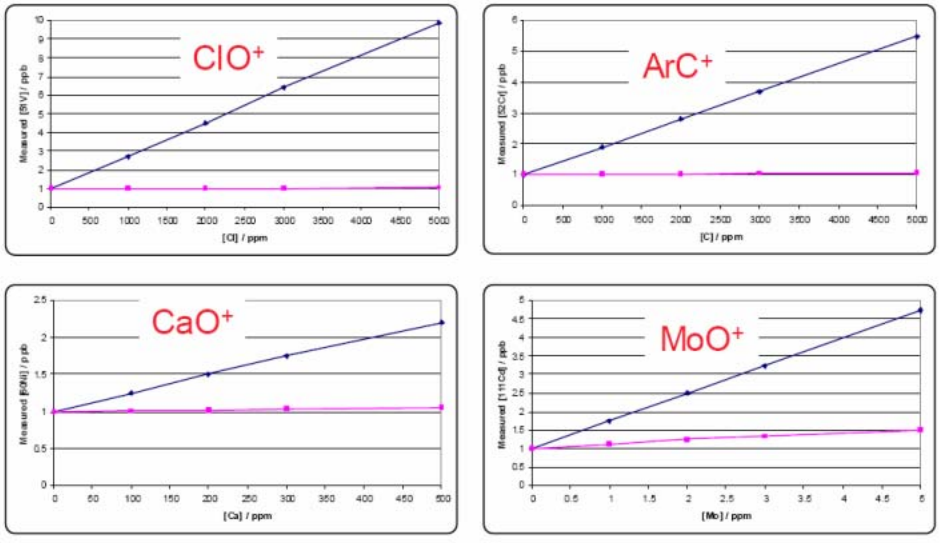
Cell gas flow optimisations performed in 1:10 diluted seawater



All interferences removed under 1 simple set of conditions!

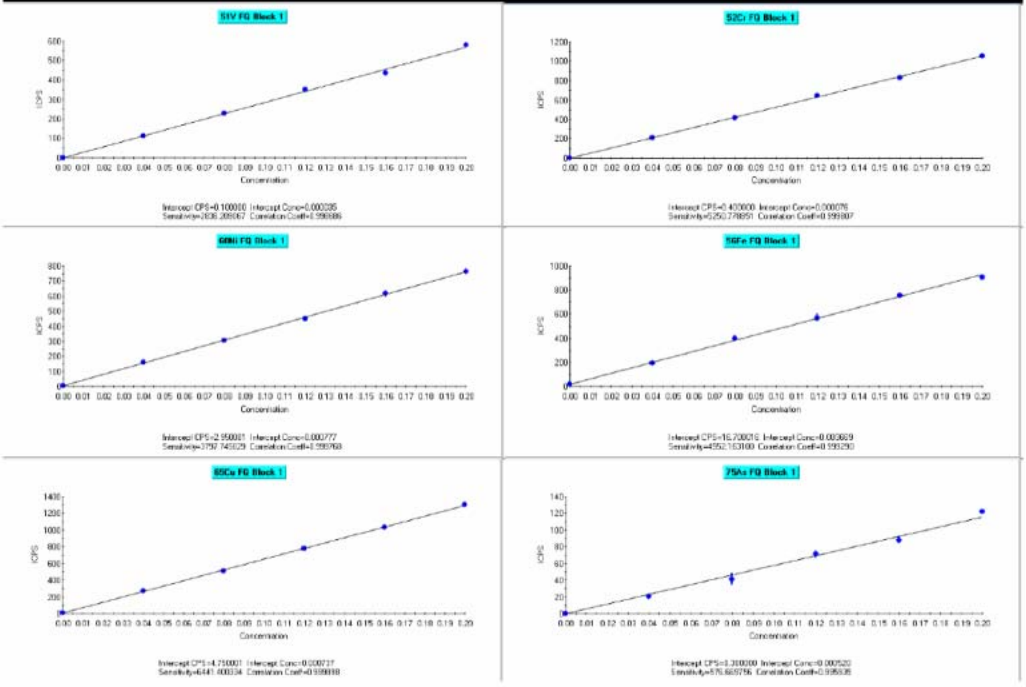
25

Non-Specific Interference Removal



26

Some Calibration Curves: 0 – 200 ppt



Performance: He KED Mode MDLs in 1% HCl

m/z	Element	MDL in 1%HCl (ppb)	LDR Tested (ppb)
9	Be	0.1	1000
23	Na	5	500000
24	Mg	1	100000
27	Al	0.5	100000
39	K	20	500000
44	Ca	10	500000
51	V	0.03	10000
52	Cr	0.02	10000
55	Mn	0.02	10000
56	Fe	0.05	500000
59	Co	0.01	10000
60	Ni	0.02	10000
65	Cu	0.01	10000
66	Zn	0.02	10000
75	As	0.02	10000

m/z	Element	MDL in 1%HCl (ppb)	LDR Tested (ppb)
78	Se	0.1	10000
88	Sr	0.01	1000
90	Zr	0.02	1000
98	Mo	0.01	10000
107	Ag	0.01	10000
111	Cd	0.005	10000
118	Sn	0.02	10000
121	Sb	0.02	10000
137	Ba	0.02	10000
202	Hg	0.05	10000
205	Tl	0.002	10000
208	Pb	0.01	10000
232	Th	0.001	10000
238	U	0.001	10000

28

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ICSA Composition and Potential Interferences

Experiment running method 6020A ICS solutions

Interferent	Concentration / ppm	Mg	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Ba
C	200	CC	CO			ArC										
Na	250										ArNa					
Mg	100											ArMg				
Al	100			AlO												
P	100															
S	100															
Cl	2000				ClO	ClOH							ArCl			
K	100						KO									
Ca	300							CaO	CaO	CaO				ArCa		
Ti	2															
Fe	250															
Mo	2														MoO	ArMo
Gas-based	---		ArH	Ar		ArN		ArO								

29

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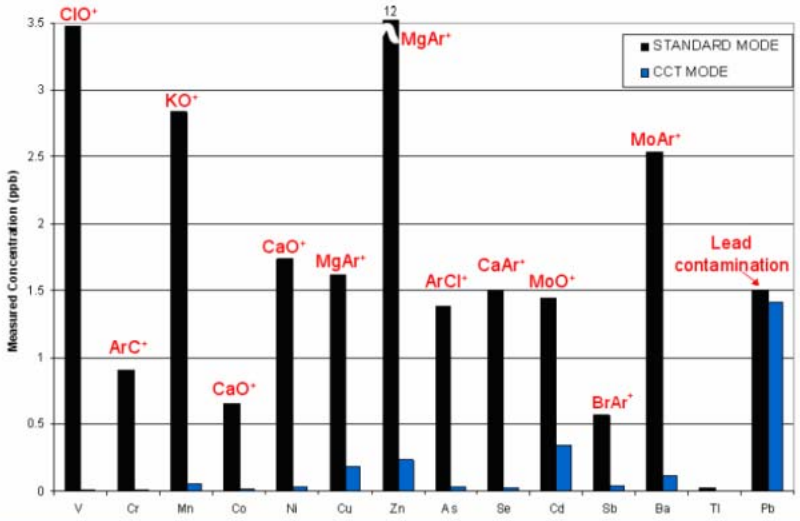
Performance: Interference Checks (ICSA Solution)

Shows measured concentrations for 6020A ICSA solution in standard mode (without interference correction) and He cell mode



30

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Accuracy (NIST 1640 River Water in 1% HCl)

m/z	Elem't	Meas'd (ppb)	Cert. (ppb)	Recovery %
9	Be	35.9	34.9	103
23	Na	28461	29350	97
24	Mg	5620	5819	97
27	Al	53.5	52	103
39	K	1046	994	105
44	Ca	6982	7045	99
51	V	13.2	13.0	102
52	Cr	36.8	38.6	95
55	Mn	120	122	99
56	Fe	35.1	34.3	102
59	Co	20.1	20.3	99
60	Ni	27.6	27.4	101

m/z	Elem't	Meas'd (ppb)	Cert. (ppb)	Recovery %
60	Ni	27.6	27.4	101
65	Cu	88.3	85.2	104
66	Zn	51.9	53.2	98
75	As	26.3	26.7	99
78	Se	21.4	22.0	98
88	Sr	128.0	124.2	103
98	Mo	46.7	46.8	100
107	Ag	8.1	7.7	105
111	Cd	23.1	22.8	101
121	Sb	13.6	13.8	99
137	Ba	148	148	100
208	Pb	27.5	27.9	99

31

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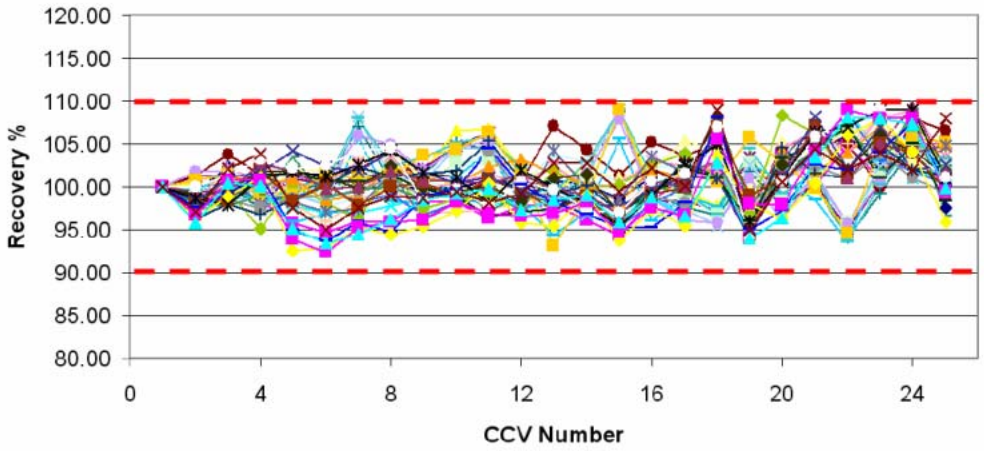
Long-Term Stability



CCV results during repeat measurement of ICSA solution

32

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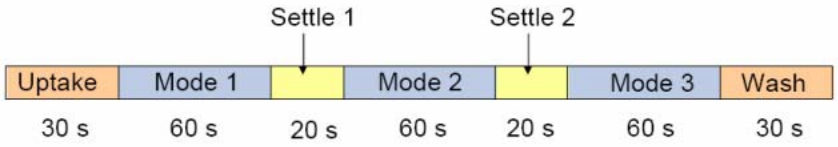
Speed Comparison

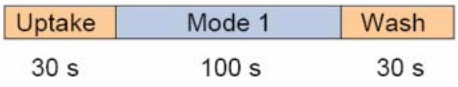
3 Mode Analysis



Total = 4 mins 40 secs

12.8 samples/hour

1 Mode Analysis



Total = 2 mins 45 secs

21.8 samples/hour

33

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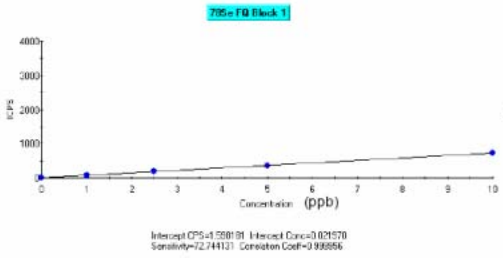
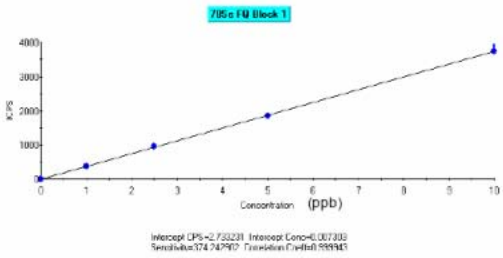
Comparison of He and H_2 Cell Gas for Selenium

Helium KED Mode



Hydrogen KED Mode



Mode	He	H_2
Sensitivity (icps/ppm)	72,000	374,000
BEC (ppt)	22	7
Est. IDL (ppt)	15	1
RSD % at 1 ppb level	8	1

34

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Conclusion

He KED mode allows:

- Simple set-up and optimization
- A single set of conditions for all analytes
- Faster analysis due to elimination of gas switch delays
- Analysis of entire TAL without interference corrections
- More accurate data in the presence of interferences
- Better DLs for analytes normally interfered by gas- or acid matrix-based polyatomics
- The use of HCl digestion procedures and with good DLs for As and V

Simple, rapid interference-free analysis

35

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Thank You

36

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The Current Status of the RCRA Inorganic Methods Development Program

Shen-yi Yang
US Environmental Protection Agency

ABSTRACT

This presentation gives an overview of the RCRA Inorganic Methods Program. This presentation will discuss the important current as well as future RCRA Inorganic Methods Program activities, including the publication of the final Methods Innovation Rule (MIR), Update IIIB, IVA, and IVB methods, and the new SW-846 methods for mercury speciation, metal cyanide complexes, and for perchlorate in various environmental matrices; and our planned activities for the 4th Edition of SW-846.

Current Status: RCRA Inorganic Methods Development Program

Shen-yi Yang
U. S. Environmental Protection Agency
Office of Solid Waste – Methods Team
1200 Pennsylvania Ave., N. W. (5307P)
Washington, D.C. 20460

National Environmental Symposium
Cambridge, MA

August 21, 2007

Topics for Discussion

- SW-846 Methods
  - Update IV to Third Edition
  - Fourth Edition
- New Methods
- On-going SRM and Methods Development Projects

2

OSW Methods Program

- Uses performance-based approach (PBMS).
- Analytical methods are published as guidance in SW-846.
- Allows flexibility in adapting SW-846 methods for RCRA applications.
- Used in other programs, e.g., Superfund and Homeland Security and used by other offices, e.g., OPPTS in support of TSCA.

3

Update IV of Third Edition

- Will be finalized as a NODA later this year.
- Combines Updates IVA and IVB.
- Revisions to Chapter Three for inorganic analytes.
- 23 new methods (12 Organic & 11 Inorganic).
- 24 revised methods (16 Organic & 8 Inorganic).
- 3 OAQPS air methods added.
- 44 methods deleted (1 Organic & 43 AA methods integrated into two methods).
- All methods in Fourth Edition format (Style Guide on Methods Team Homepage).

4

New Inorganic Methods in Update IV

- Method 1040: Test Method for Oxidizing Solids.
- Method 1050: Test Methods to Determine Substances Likely to Spontaneously Combust.
- Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.
- Method 6500: Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis.
- Method 6800: Elemental and Speciated Isotope Dilution Mass Spectrometry.
- Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry.

5

New Inorganic Methods in Update IV (Contd.)

- Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry.
- Method 7474: Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry.
- Method 9000: Determination of Water in Waste Materials by Karl Fisher Titration.
- Method 9001: Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction.
- Method 9216: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode.

6

Revised Inorganic Methods in Update IV

- Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.
- Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.
- Method 6010C: Inductively Coupled Plasma – Atomic Emission Spectrometry.
- Method 6020A: Inductively Coupled Plasma – Mass Spectrometry.
- Method 7000B: Flame Atomic Absorption Spectrophotometry.
- Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique).
- Method 9056A: Determination of Inorganic Anions by Ion Chromatography.
- Method 9210A: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode.

7

Deleted Inorganic Methods in Update IV

- 43 Individual Flame AA and Graphite Furnace Method AA methods integrated into two methods, Method 7000B- FAA and Method 7010-GFAA.

8

Fourth Edition of SW-846

- Designed for electronic format.
- Organized in two sections:
  - Methods for laboratory analysts.
  - Systematic planning, QA/QC and sampling for both project planners and laboratory analysts.
- Major revisions to Chapter One on QA/QC.
- Expansion of guidance on methods selection.
- Methods to be arranged both by series and sequential method numbers.

9

Fourth Edition of SW-846 Progress to Date

- Draft of Chapter One completed and distributed for Workgroup review.
- We prepared a new "Style Guide" for preparation of Fourth Edition methods based on EMMC format and distributed to Workgroup and posted it on Methods Team Website.
- All new method submissions will be in Fourth Edition format.

10

Fourth Edition of SW-846 Progress to Date

- All Third Edition methods currently being revised have been converted to Fourth Edition format including all Update IV methods and "New Methods".
- We plan to complete the Fourth Edition in two years, if resources are available.

11

Completed New Methods for Fourth Edition

- Posted on Website under "New Methods".
  - Method 3200: Mercury Species Fractionation and Quantification by Microwave-assisted Extraction, Selective Solvent Extraction and/or Solid Phase Extraction.
  - Method 9013A: Cyanide Extraction Procedure for Solids and Oils
  - Method 9015: Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection.

12

Completed New Methods for Fourth Edition (Contd.)

- Posted on Website under "New Methods".
  - Method 6850: Perchlorate in Water, Soils and Solid Wastes Using HPLC/Electrospray Ionization/Mass Spectrometry
  - Method 6860: Perchlorate in Water, Soils and Solid Wastes Using IC/Electrospray Ionization/Mass Spectrometry

13

New Method 3200

- An extraction procedure for mercury speciation. Extraction is accomplished with the aid of either microwave irradiation or ultrasound;
- The procedure can separate total mercury into four different fractions (extractable organic mercury, extractable inorganic mercury, semi-mobile mercury, and non-mobile mercury);
- The extracts can be analyzed by determinative methods using CVAA, ICP-MS, and HPLC-ICP-MS;
- Developed by Dr. Skip Kingston at Duquesne University;
- The method posted in July 2005 on the OSW Methods website for public use and comments.

14

Revised Method 9013

- All CN species are soluble under alkaline conditions
  - **Simple CN salts:** $ACN \xrightarrow{pH \geq 11} A^+ + CN^-$
  - **Metal CN complex salts:** $A_a[M(CN)_x] \xrightarrow{pH \geq 11} aA^+ + [M(CN)_x]^{y-}$

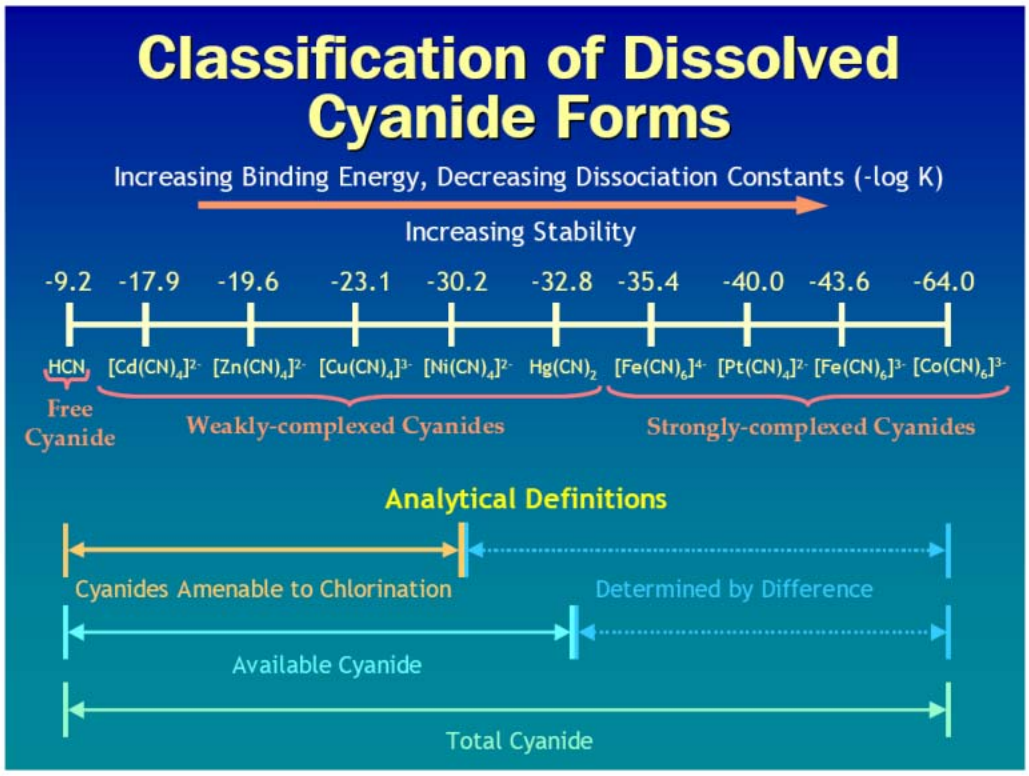
    $T_d[M(CN)_x]_b \xrightarrow{pH \geq 11} tT^+ + b[M(CN)_x]^{y-}$

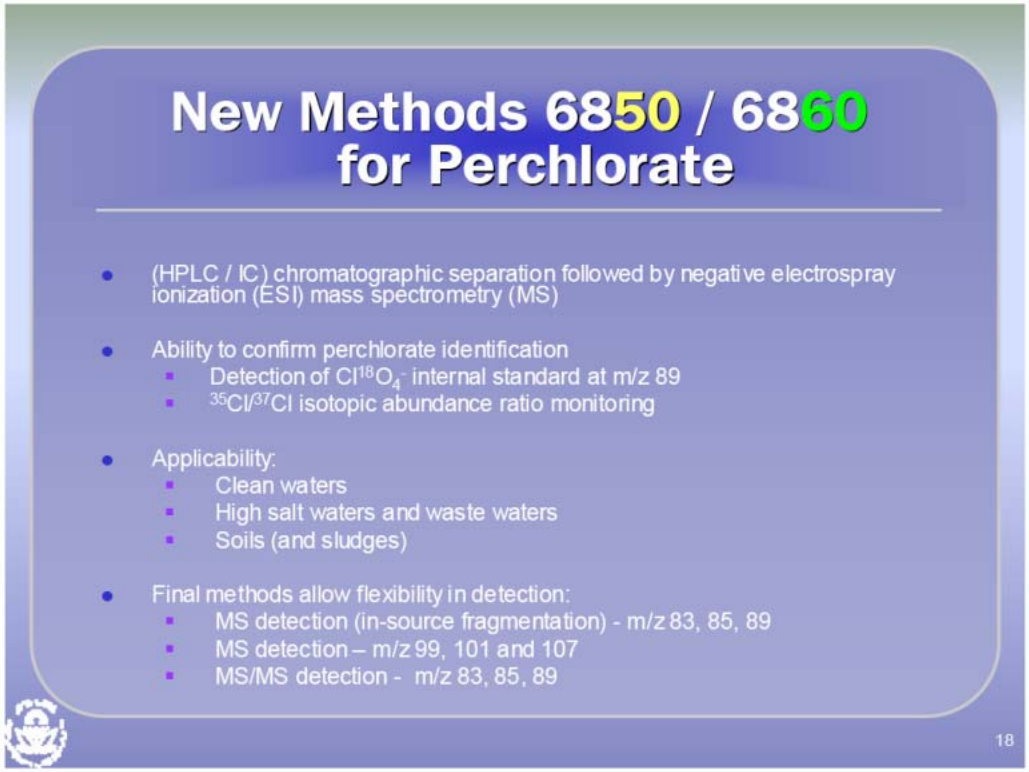
    A = alkali or alkaline earth metal
    M = transition metal
    T = transition metal
- Simple alkaline pre-extraction procedure (Method 9013) applicable for all determinative CN Methods: 9010, 9012, 9014
- Modification added to existing Method 9013 for pre-extraction prior to Method 9015 IC analysis of metal cyanide complexes
- Method 9013 posted in November 2004 on the OSW Methods website for public use and comments.

New Method 9015

- Determines metal cyanide complexes (of iron, cobalt, silver, gold, copper, and nickel) in waters and alkaline solid extracts.
- Based on ion chromatography:
  - **Anion exchange separation**
  - **UV spectroscopic detection**
- Simple alkaline pre-extraction procedure (Method 9013) for solids
- Developed and drafted by Sharon Drop of SAIC, and Dr. Rajat Ghosh of the Retec Group, Inc.
- The inter-lab studies for quantifying both low-level (ppb) and high-level (ppm) metal cyanide complexes in waters and solid matrices were completed
- Method 9015 posted in November 2004 on the OSW Methods website for public use and comments.

16


Classification of Dissolved Cyanide Forms
Increasing Binding Energy, Decreasing Dissociation Constants (-log K)
Increasing Stability
-9.2 -17.9 -19.6 -23.1 -30.2 -32.8 -35.4 -40.0 -43.6 -64.0
HCN
[Cd(CN)4]2- [Zn(CN)4]2- [Cu(CN)4]3- [Ni(CN)4]2- Hg(CN)2
[Fe(CN)6]4- [Pt(CN)4]2- [Fe(CN)6]3- [Co(CN)6]3-
Free Cyanide
Weakly-complexed Cyanides
Strongly-complexed Cyanides
Analytical Definitions
Cyanides Amenable to Chlorination
Determined by Difference
Available Cyanide
Total Cyanide


New Methods 6850 / 6860 for Perchlorate
(HPLC / IC) chromatographic separation followed by negative electrospray ionization (ESI) mass spectrometry (MS)
Ability to confirm perchlorate identification
Detection of $Cl^{18}O_4^-$ internal standard at m/z 89
$^{35}Cl/^{37}Cl$ isotopic abundance ratio monitoring
Applicability:
Clean waters
High salt waters and waste waters
Soils (and sludges)
Final methods allow flexibility in detection:
MS detection (in-source fragmentation) - m/z 83, 85, 89
MS detection – m/z 99, 101 and 107
MS/MS detection - m/z 83, 85, 89
18

Methods 6850 and 6860 Status

- **Phase I: Initial Demonstration of Proficiency (IDP)**
  - Analysis of varying levels of perchlorate in reagent water
  - ***Completed in September 2005***
- **Phase II: Method Validation**
  - Analysis of perchlorate in salt water, waste water, soil and sludge
  - Varying perchlorate and conductivity background levels
  - Evaluate aqueous extraction procedure
  - Holding time studies for high salt water, waste water and sludge
  - ***Completed in July 2006***
- Methods 6850 and 6860 were posted in January 2007 on the OSW Methods website for public use and comments.
- **Phase III: Extraction Procedure(s) for Sludge**
  - Two extraction procedures are in consideration
  - ***May start later part of 2007***

19

On-going Methods and Reference Material Development Projects

- Development of non-aqueous Cr(VI) SRM
- Method 6250 (XRF)
- Method 6300 (XRD)
- Method 68XX (As speciation in seafood)
- Method 9016 (Free cyanide in solids using micro-diffusion)

20

Development of Non-Aqueous Cr(VI) SRM

- OSW partners with:
  - NJDEP, USGS, NIST, Rutgers University
- To be used for remediation of Cr(VI) wastes on the east and west of the U.S.
- Phase I study:
  - Determines the long-term stability of the source materials
  - 10 laboratories participated
- Phase II study:
  - 35 laboratories volunteered to participate
  - Analyze Cr(VI) SRM using methods of laboratory choice

21

Method 6250

- Determines elemental concentrations in environmental matrices
- Uses laboratory X-ray fluorescence spectrometry
- Next steps:
  - Revise the draft method based on Workgroup and Agency experts comments
  - Prepare non-aqueous reference materials
  - Identify laboratories for method validation study

22

Method 6300

- Identifies crystalline materials in environmental matrices
- Uses laboratory X-ray powder diffractometer
- Next steps:
  - Revise the draft method based on Workgroup and Agency experts comments
  - Prepare non-aqueous reference materials
  - Identify laboratories for method validation study

23

Methods 3110/6870

- Method 3110: extracts arsenic species from seafood using tetramethyl ammonium hydroxide (TMOH)
- Method 6870: analyzes extracts using IC-ICPMS Next steps:
  - Can determine arsenite (As+3), arsenate (As+5), monomethyarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB)
- Next steps:
  - Revise the draft methods based on Workgroup and OSW Arsenic Speciation Focus Group comments
  - Prepare for inter-lab method validation study

24

Method 9016

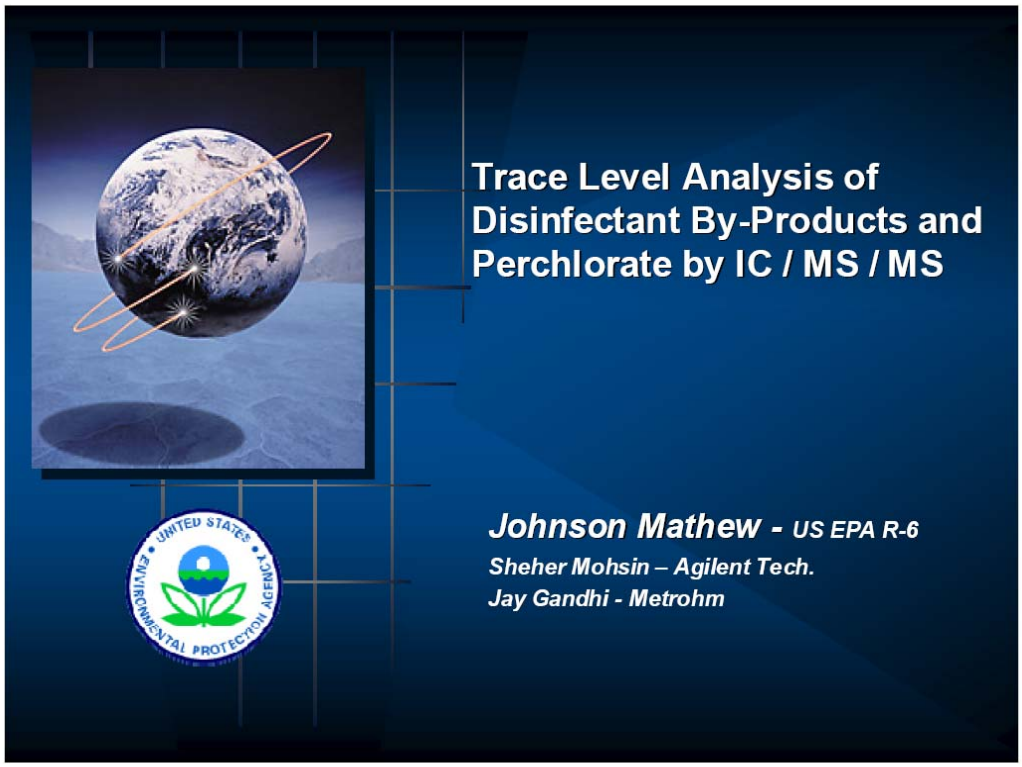
- Determines free cyanide in waters, wastewaters, and leachates using micro-diffusion
- Inter-lab method validation study starts this August
- Next steps:
  - Evaluate and statistically analyze information and data collected from the validation study

25

Relevant Contact Addresses and Phone Numbers

- Methods Team Homepage: *www.epa.gov/SW-846*
- Methods Information Communication Exchange (MICE)
  - Phone No.: (703)-676-4690
  - E-mail: *mice@cpmx.saic.com*
- Shen-yi Yang
  - Phone No.: (703)-308-0437
  - E-mail: *yang.shen-yi@epa.gov*

26


Trace Level Analysis of Disinfectant By-Products and Perchlorate by IC / MS / MS
Johnson Mathew - US EPA R-6
Sheher Mohsin – Agilent Tech.
Jay Gandhi - Metrohm


No product endorsement
*Reference herein to any specific commercial products or nonprofit organization, process, or service by trade name, trademark, manufacturer, or other-wise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government and shall not be used for advertising or product endorsement purposes.
2

Outline

- Background
- EPA Methods
- Experimental condition
- Data
- Future Work
- Conclusion

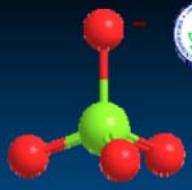
3

Background

- Disinfection Byproducts (DBPs)
  - Bromate: BrO_3^- , Chlorate ClO_3^- , Chlorite ClO_2^-
  - trihalomethanes (chloroform, bromoform, bromodichloromethane, and dibromochloromethane)
  - Halo Acetic Acids (monochloro-, dichloro-, trichloro-, monobromo-, dibromo-).
- DBPs sources
  - form when disinfectants used to treat drinking water react with naturally occurring materials in the water
- EPA has regulated DBPs since 1979
  - to address health risks posed by a potential association between chlorinated drinking water and cancer.
  - evidence available at this time raises concern about a possible link between chlorinated drinking water and reproductive and developmental effects
- To protect public health, EPA continues to strongly support both the disinfection of drinking water to reduce the risk of waterborne disease and the reduction of disinfection byproducts.

4

Background



- **Perchlorate: ClO_4^-**
  - Both manmade and naturally occurring
- **Perchlorate contamination sources**
  - Solid propellants and explosives manufacturing
  - Fireworks, highway safety flares, airbag inflators
  - Certain nitrate-based fertilizers
- **Inhibits iodine uptake by the thyroid gland, thus may**
  - Affects thyroid hormone production and thyroid regulation of metabolism
  - Impairs neurological development of fetus and newborn
  - Changes in thyroid hormone levels may result in thyroid gland tumors
- **Very mobile in aqueous systems - persistent under typical ground water and surface water conditions**

5

EPA methods for DBPs

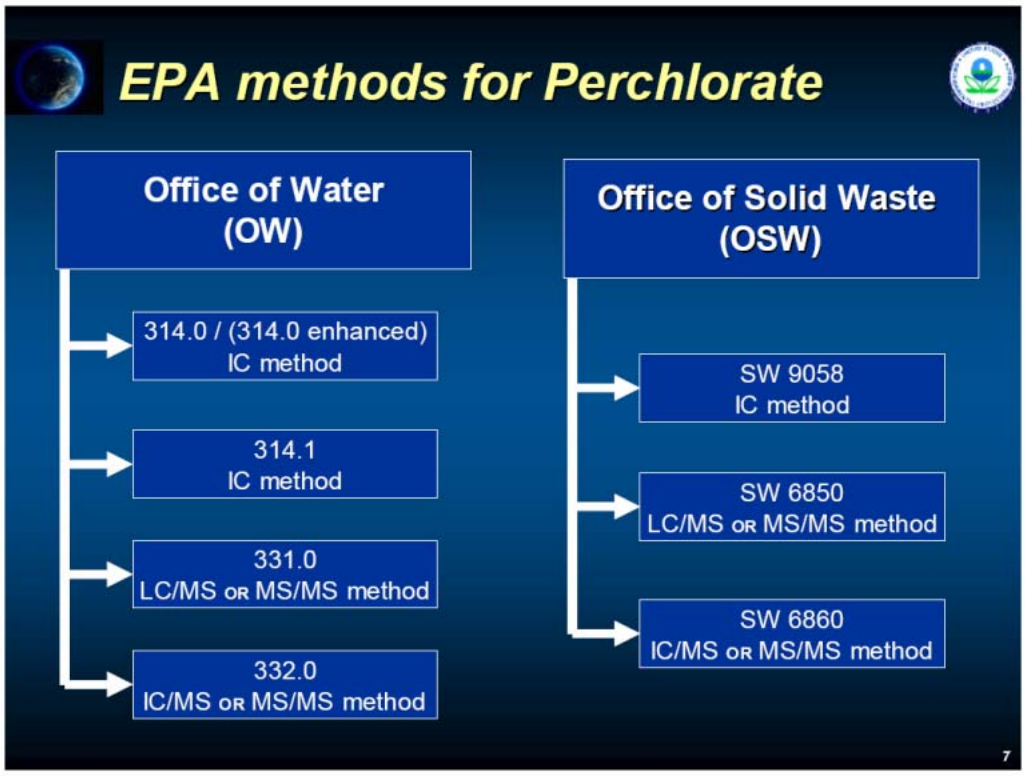
Office of Water (OW) – DBP/Bromate

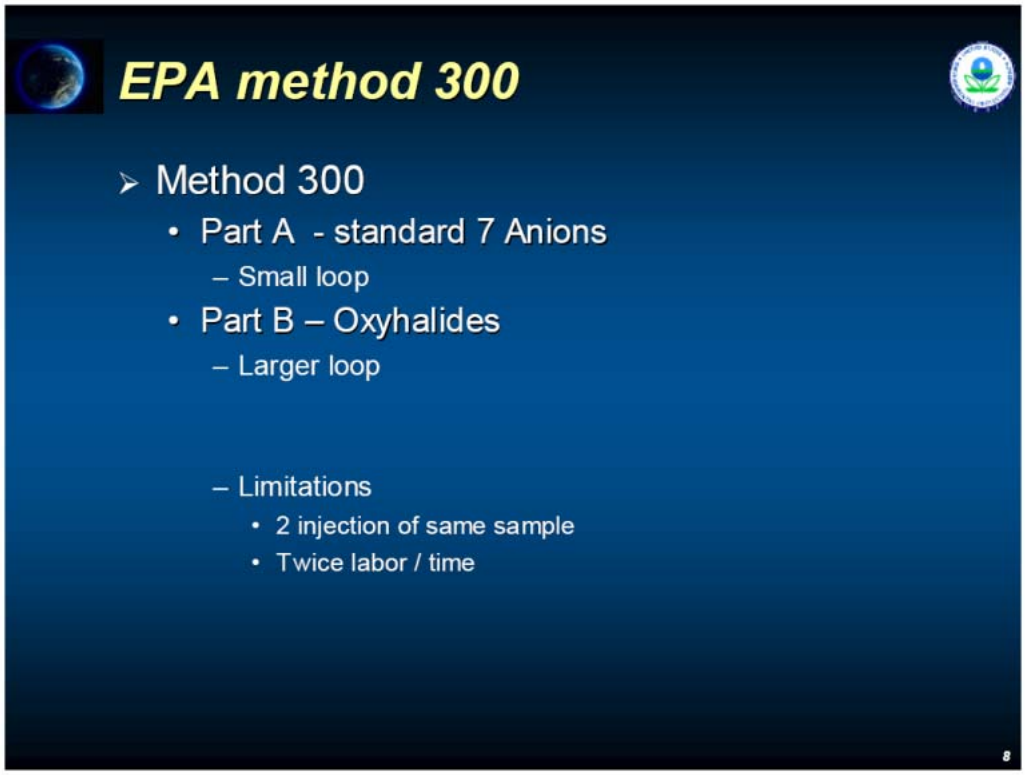
- 300.0/300.1 IC method
- 317 IC / UV / VIS method
- 326 IC / UV / VIS method

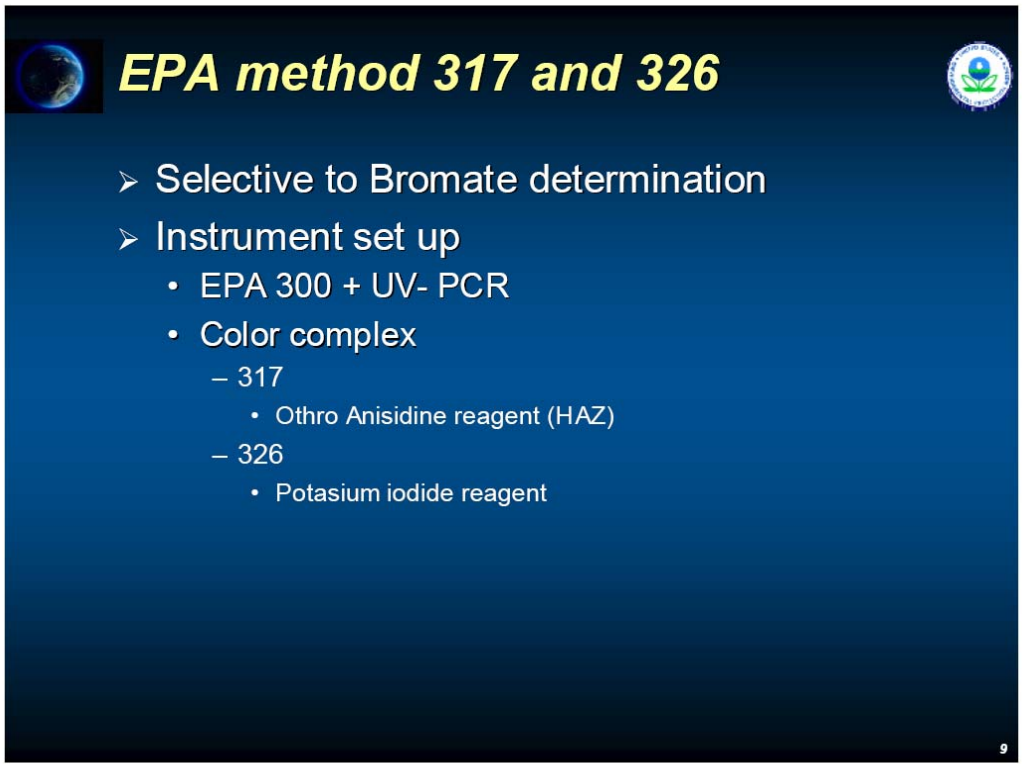
Office of Water (OW) - HAA

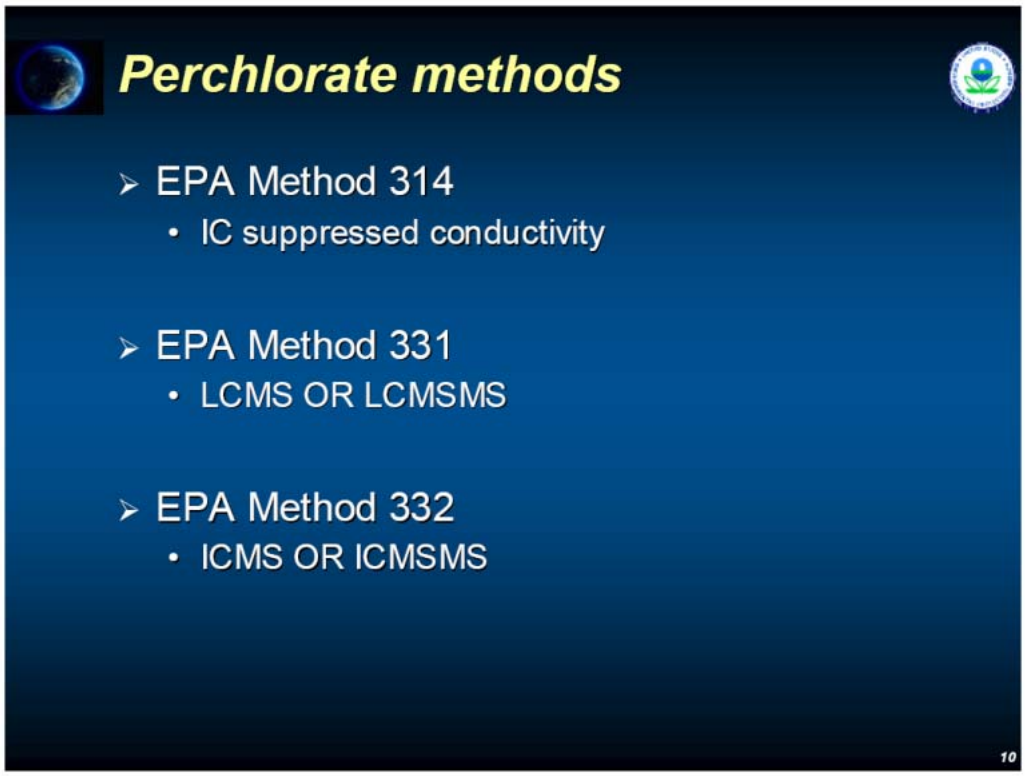
- 552 GC method
- OW - Method proposed IC/MS OR ICMS/MS
- EPA R-6 working on the method

6


EPA methods for Perchlorate
Office of Water (OW)
314.0 / (314.0 enhanced) IC method
314.1 IC method
331.0 LC/MS OR MS/MS method
332.0 IC/MS OR MS/MS method
Office of Solid Waste (OSW)
SW 9058 IC method
SW 6850 LC/MS OR MS/MS method
SW 6860 IC/MS OR MS/MS method
7


EPA method 300
Method 300
Part A - standard 7 Anions
Small loop
Part B – Oxyhalides
Larger loop
Limitations
2 injection of same sample
Twice labor / time
8


EPA method 317 and 326
Selective to Bromate determination
Instrument set up
EPA 300 + UV- PCR
Color complex
317
Othro Anisidine reagent (HAZ)
326
Potasium iodide reagent
9


Perchlorate methods
EPA Method 314
IC suppressed conductivity
EPA Method 331
LCMS OR LCMSMS
EPA Method 332
ICMS OR ICMSMS
10

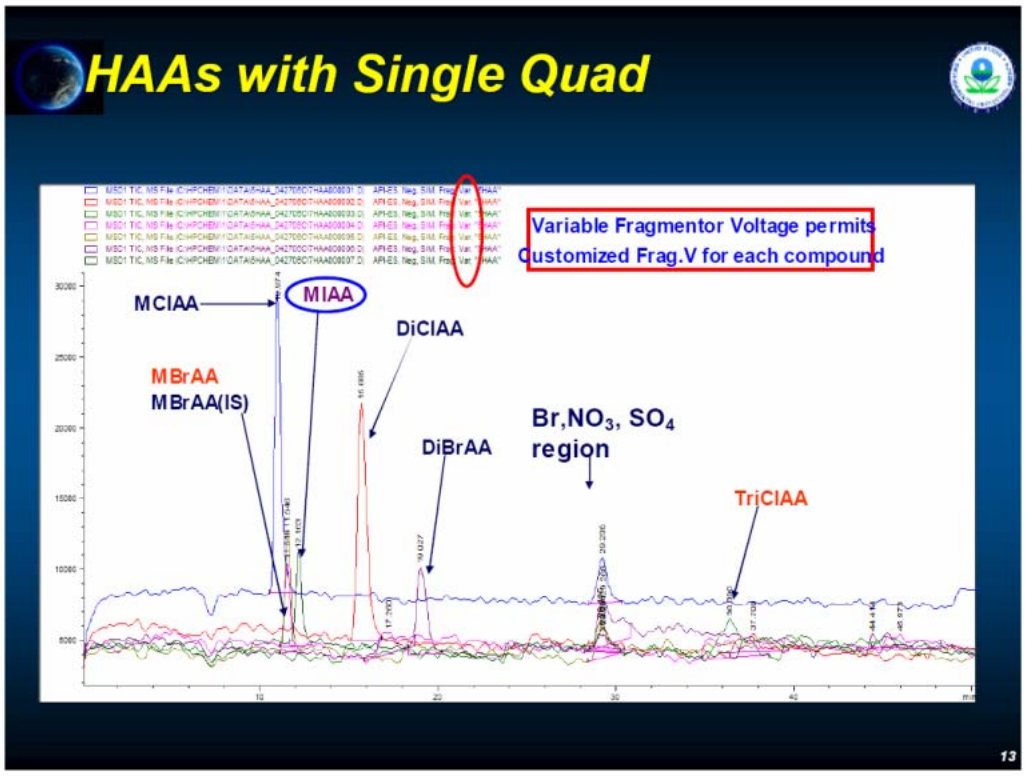
Fragmentation pattern

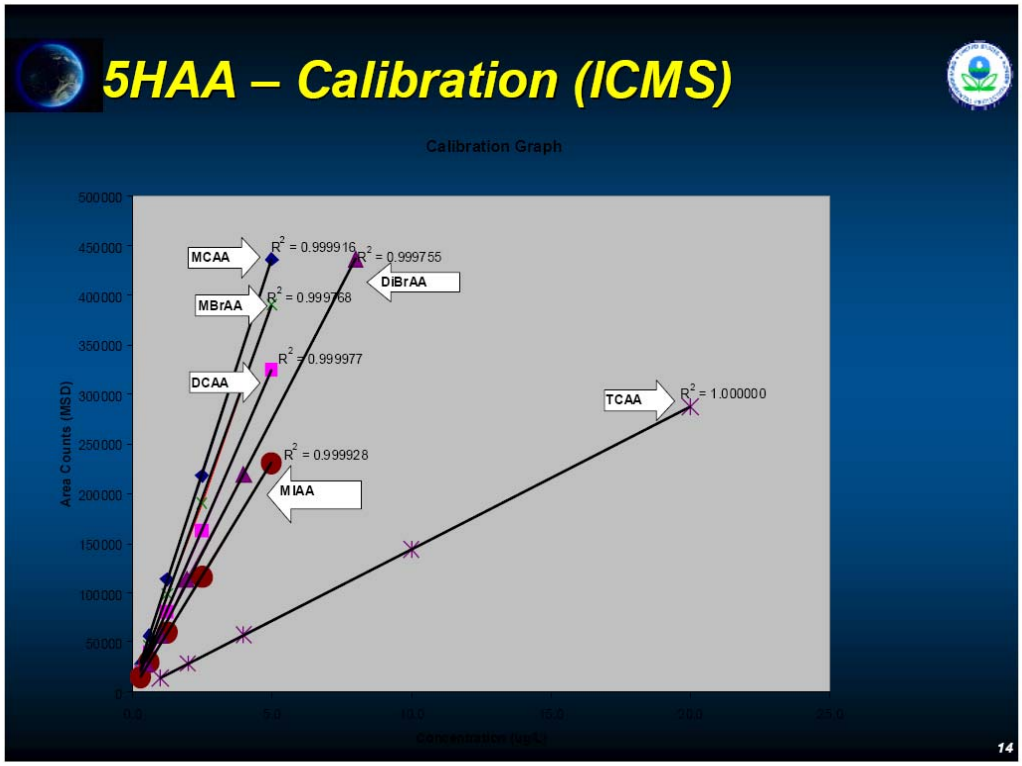
- **Bromate**
  - BrO_3^{-1} = $^{79/81}Br + ^{16}O$ = m/z 127/129, 49/51% abundance
    MSMS = 127/129 → 79/81
- **Chlorate**
  - ClO_3^{-1} = $^{35/37}Cl + ^{16}O$ = m/z 83/85, 75/25% abundance
    MSMS = 83/85 → 67/69
- **Chlorite**
  - ClO_2^{-1} = $^{35/37}Cl + ^{16}O$ = m/z 67/69, 75/25% abundance
    MSMS = 67/69 → 51/53
- **Perchlorate**
  - ClO_4^{-1} = $^{35/37}Cl + ^{16}O$ = m/z 99/101, 75/25% abundance
    MSMS = 99/101 → 83/85
  - Internal Standard
    - ClO_4^{-1} = $^{35/37}Cl + ^{18}O$ = m/z 107/105, 75/25% abundance
    - MSMS = 107→ 89

11

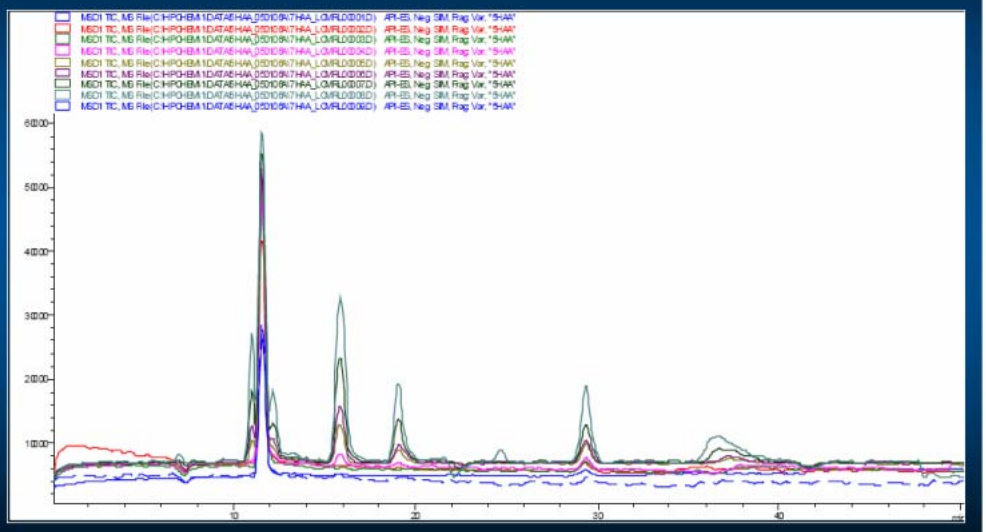
Metrohm IC / MS (Single Quad)

12


HAAs with Single Quad
Variable Fragmentor Voltage permits Customized Frag.V for each compound
MCIAA
MIAA
DiCIAA
MBrAA
MBrAA(IS)
DiBrAA
Br,NO3, SO4 region
TriCIAA
13

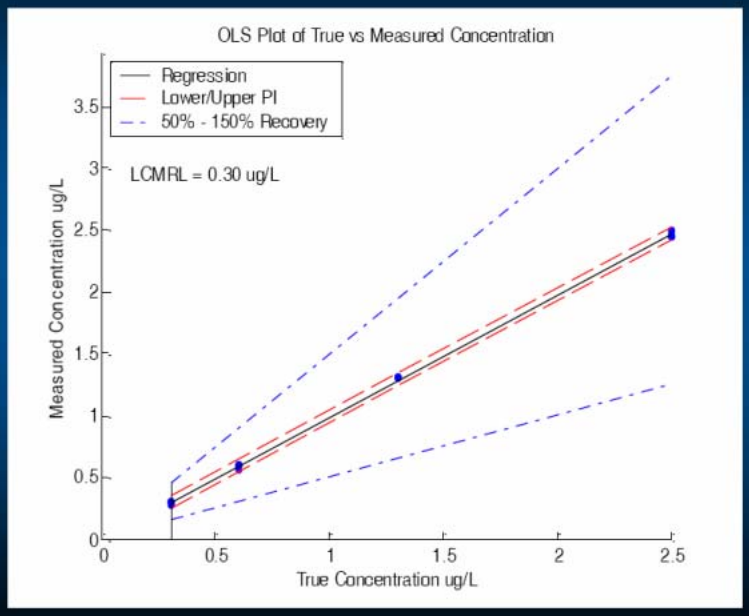

5HAA – Calibration (ICMS)
Calibration Graph
Area Counts (MSD)
MCAA
R2 = 0.999916
DiBrAA
R2 = 0.999755
MBrAA
R2 = 0.999768
DCAA
R2 = 0.999977
TCAA
R2 = 1.000000
MIAA
R2 = 0.999928
14

Stacked TIC of 5 Cal. standards



15

LCMRL – MCAA



16

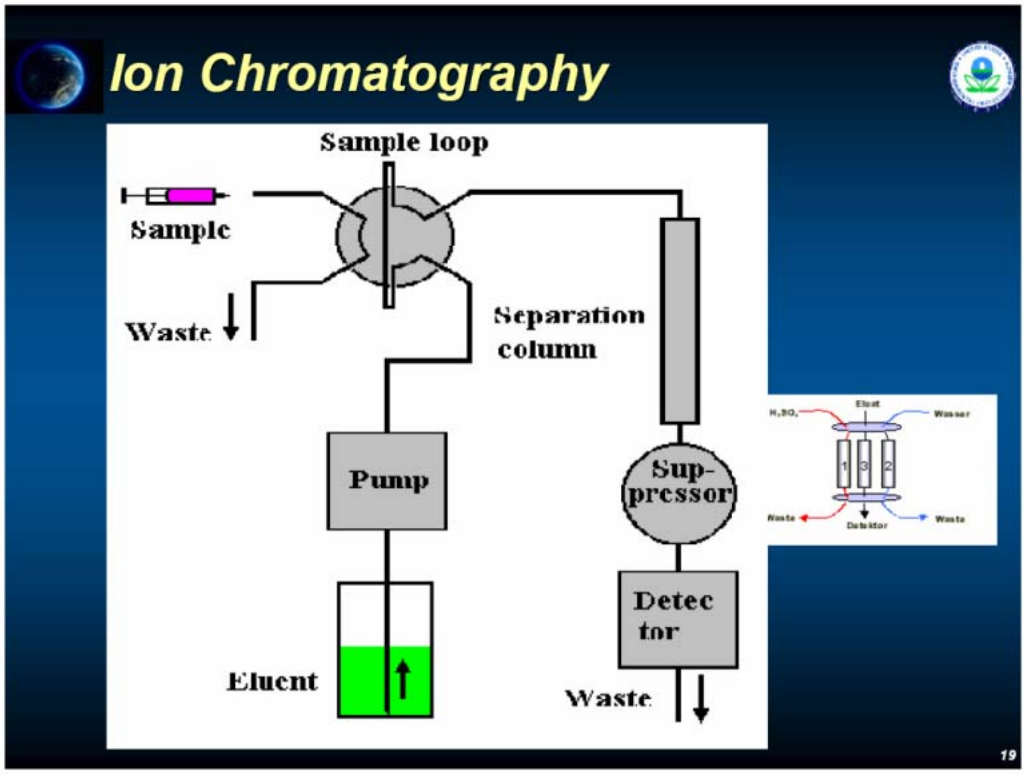
MDL Study for 5 HAAs

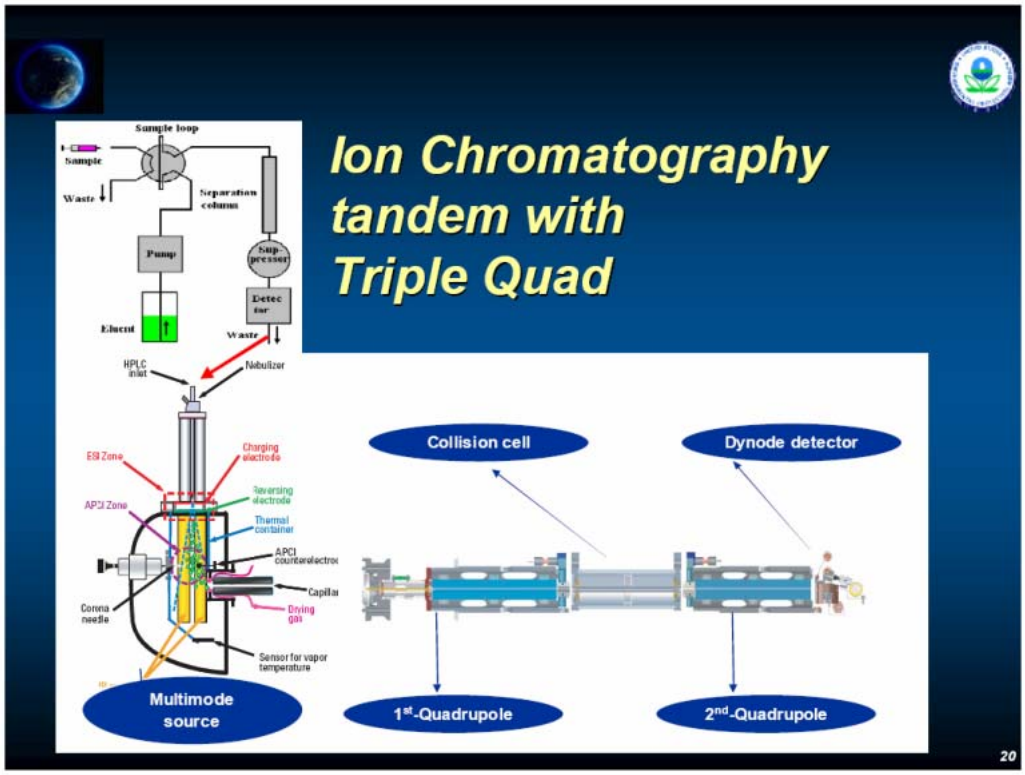
	Concentration, parts per billion							
Analysis Number	MChlAA	Bromate	MBrAA	MBrAA(ISTD)	MIAA	DiChlAA	DiBrAA	TriChlAA
1	0.250	0.109	0.250	5.00	0.250	0.200	0.250	0.750
2	0.249	0.101	0.255	5.00	0.249	0.199	0.248	0.749
3	0.234	0.099	0.260	5.00	0.250	0.189	0.244	0.755
4	0.251	0.098	0.245	5.00	0.248	0.199	0.249	0.756
5	0.245	0.102	0.250	5.00	0.249	0.203	0.255	0.751
6	0.256	0.103	0.246	5.00	0.255	0.200	0.251	0.749
7	0.249	0.095	0.239	5.00	0.239	0.201	0.235	0.751
Average	0.248	0.101	0.249	5.000	0.249	0.199	0.247	0.752
Std.Dev	0.00687	0.00443	0.00687		0.00479	0.00450	0.00640	0.00282
MDL(Calculated)	0.2158	0.1392	0.2158		0.1504	0.1413	0.2009	0.0885
RSD%	2.775%	4.391%	2.757%		1.927%	2.264%	2.586%	0.375%

17

IC / MS / MS (QQQ)

18


Ion Chromatography
Sample loop
Sample
Waste
Separation column
Pump
Sup-pressor
Detec tor
Eluent
Waste
19

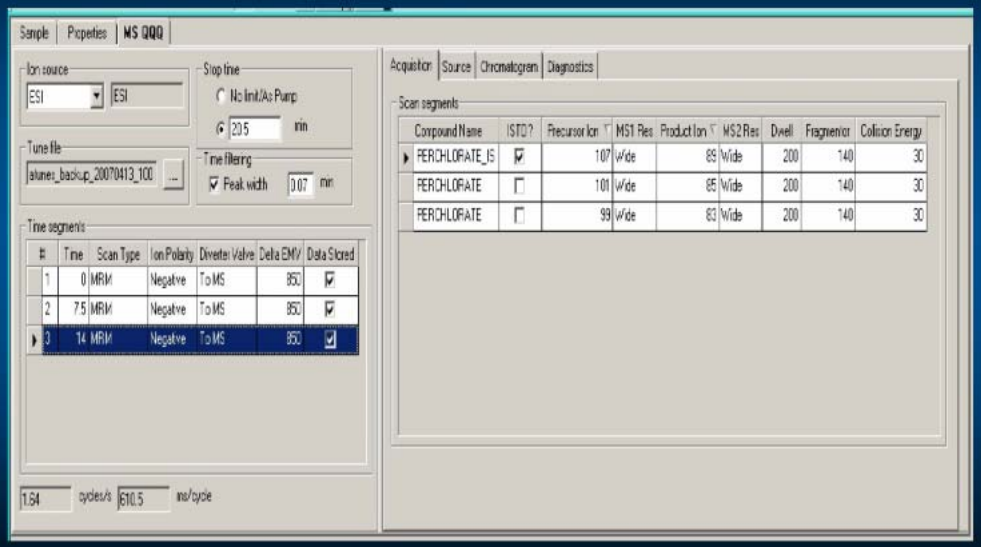

Ion Chromatography tandem with Triple Quad
Sample loop
Sample
Waste
Separation column
Pump
Sup-pressor
Detec tor
Eluent
Waste
HPLC inlet
Nebulizer
ESI Zone
Charging electrode
APCI Zone
Reversing electrode
Thermal container
Corona needle
Drying gas
Sensor for vapor temperature
Multimode source
Collision cell
Dynode detector
1st-Quadrupole
2nd-Quadrupole
20

Instrument Setup

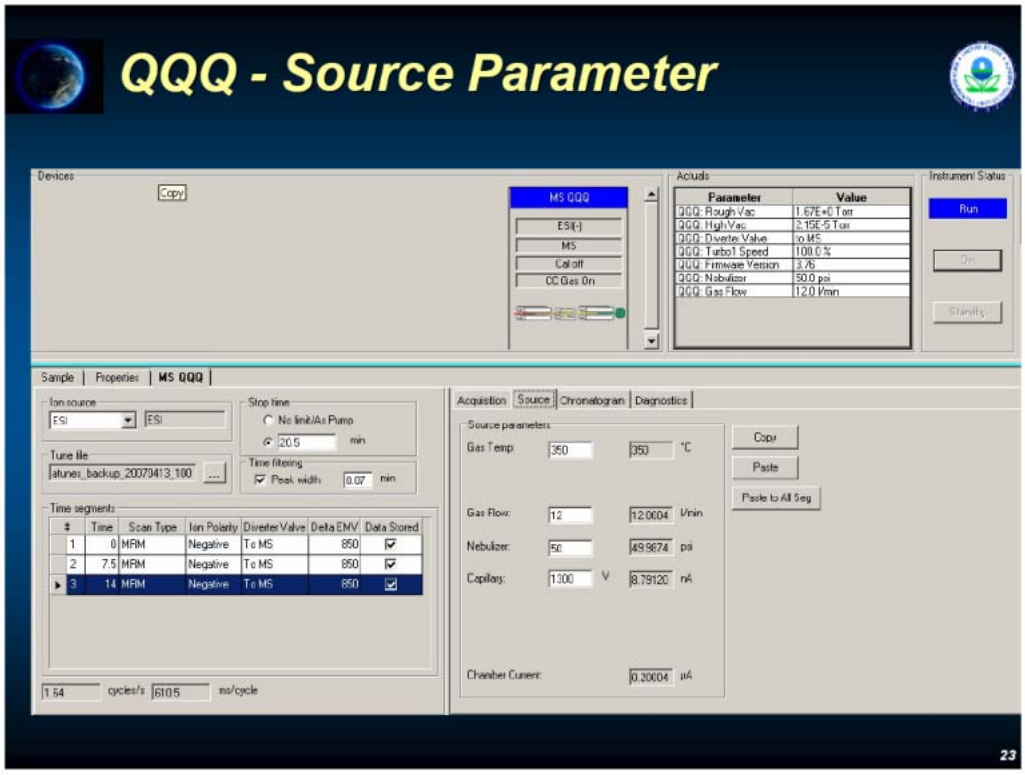
- **Metrohm Ion Chromatograph**
  - 100 uL loop injection
  - Column: Metrohm ASUPP 7 (4mm x 250mm)
  - Eluent A: 10 mM Sodium Carbonate + 45% ACN
  - Isocratic
  - Flow rate: 0.8 ml/min
- **Agilent Triple Quad**
  - Mode: Negative mode
  - Tune: "auto-tune"
  - Vcap = 1300V
  - Drying Gas = 12L/min @350° C
  - Nebulizer Pressure=50 psig.
  - Fragmentor = variable V
  - Collision Energy = variable V

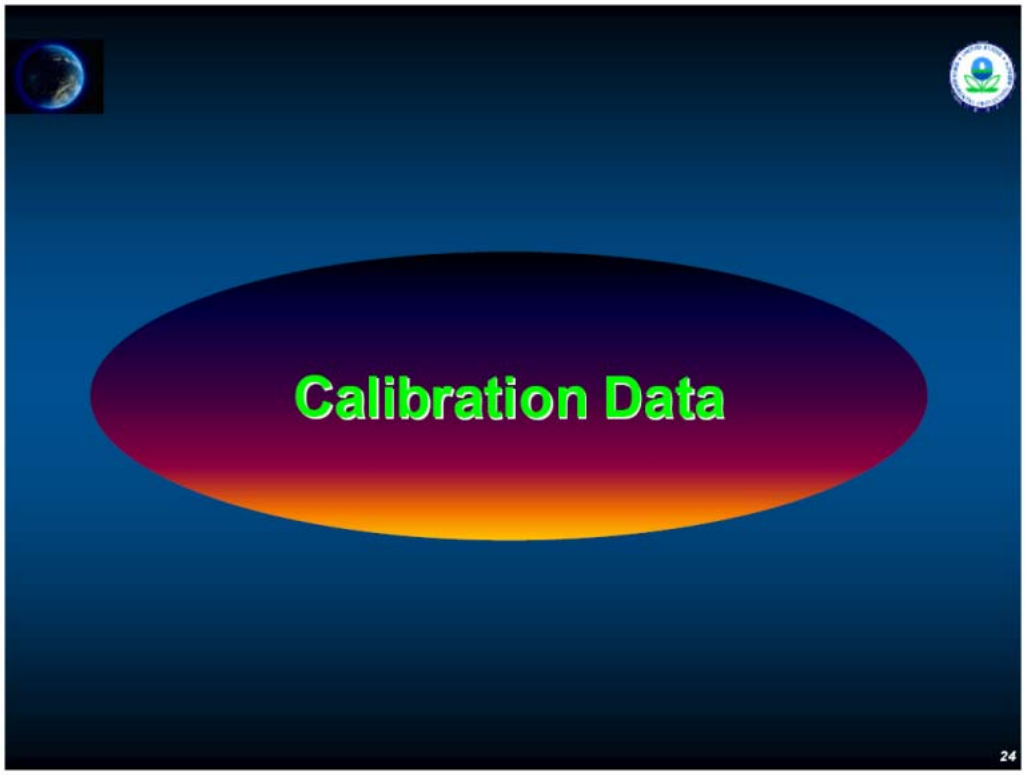
21

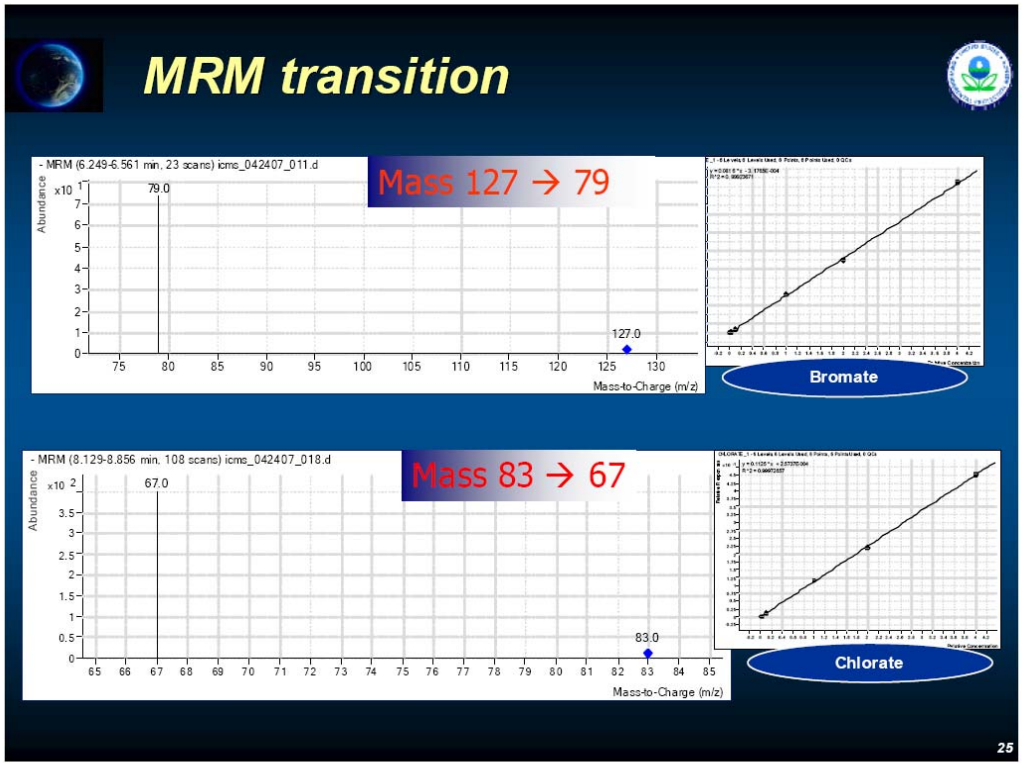
QQQ Acquisition

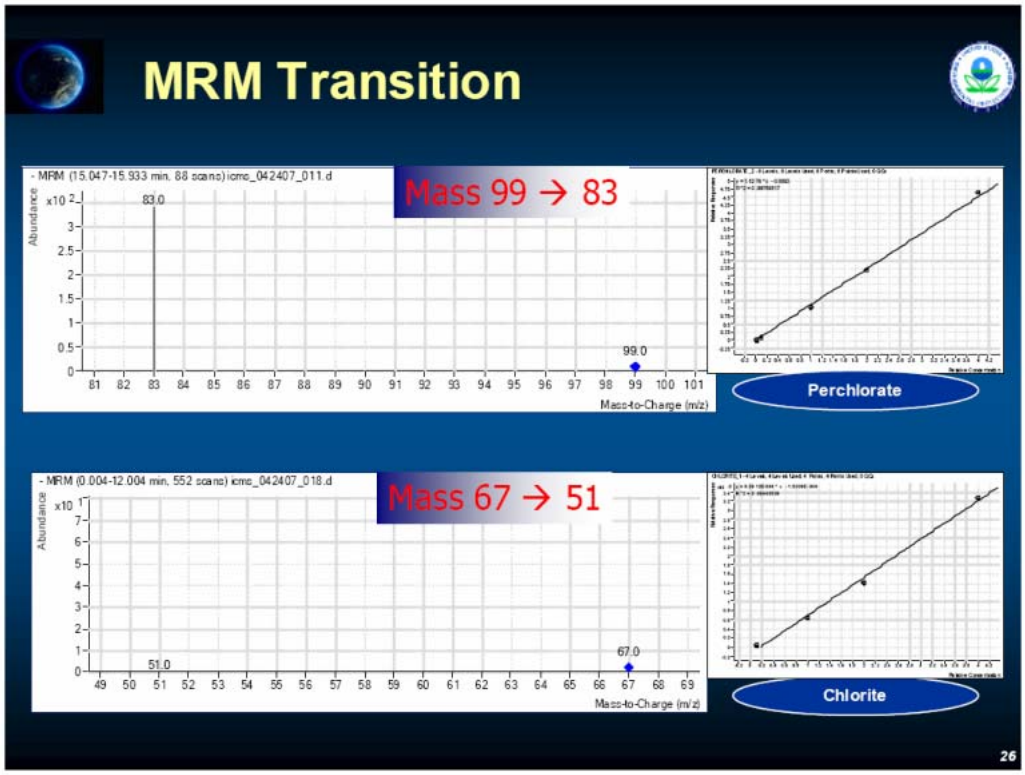


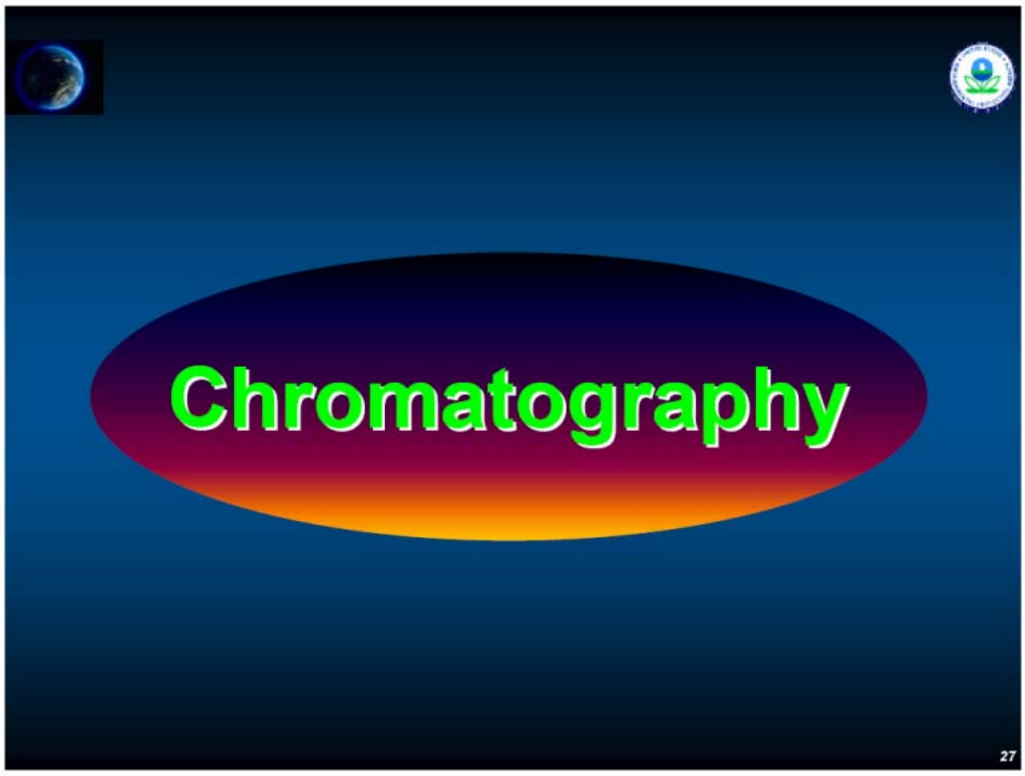
22

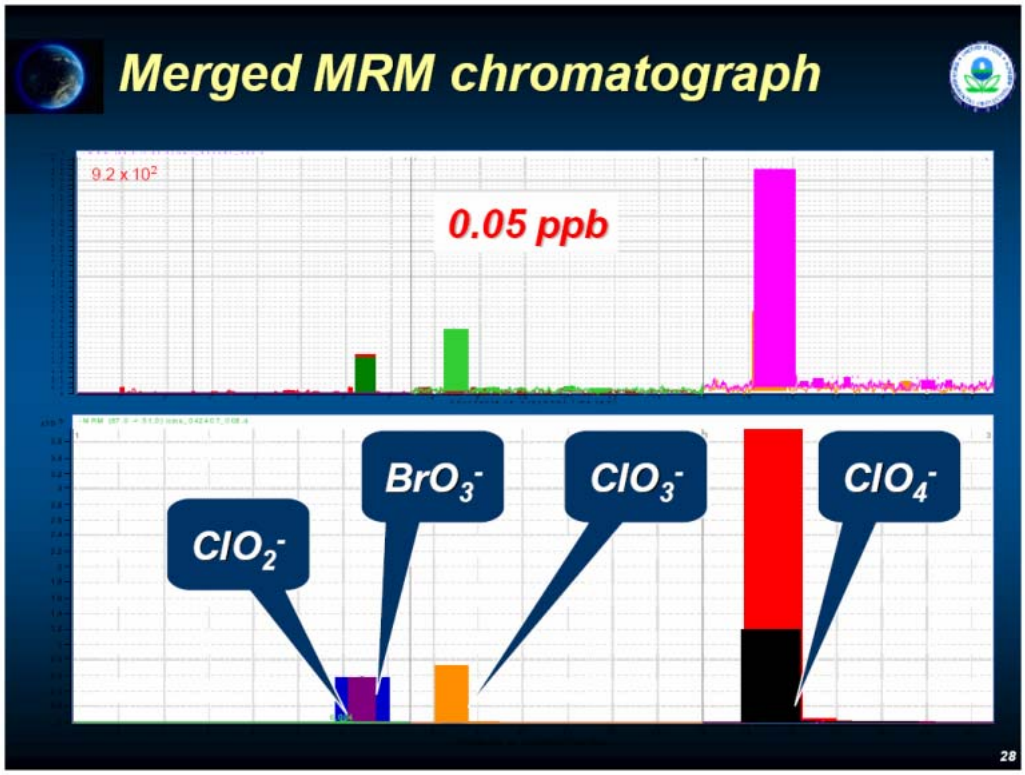

QQQ - Source Parameter
Devices
Copy
MS QQQ
ESI(-)
MS
Cal off
CC Gas On
Actuals
Parameter
Value
QQQ: Rough Vac
1.67E+0 Torr
QQQ: High Vac
3.15E-5 Torr
QQQ: Diverter Valve
to MS
QQQ: Turbo1 Speed
100.0 %
QQQ: Firmware Version
3.76
QQQ: Nebulizer
50.0 psi
QQQ: Gas Flow
12.0 l/min
Instrument Status
Run
On
Standby
Sample | Properties | MS QQQ
Ion source
ESI
Stop time
No limit/As Pump
20.5 min
Tune file
atunes_backup_20070413_100
Time filtering
Peak width 0.07 min
Time segments
Time Scan Type Ion Polarity Diverter Valve Delta EMV Data Stored
1 0 MRM Negative To MS 850
2 7.5 MRM Negative To MS 850
3 14 MRM Negative To MS 850
1.64 cycles/s 610.5 ms/cycle
Acquisition Source Chromatogram Diagnostics
Source parameters
Gas Temp: 350 350 °C
Gas Flow: 12 12.0004 l/min
Nebulizer: 50 49.9874 psi
Capillary: 1300 V 8.79120 nA
Chamber Current: 0.20004 µA
Copy
Paste
Paste to All Seg
23

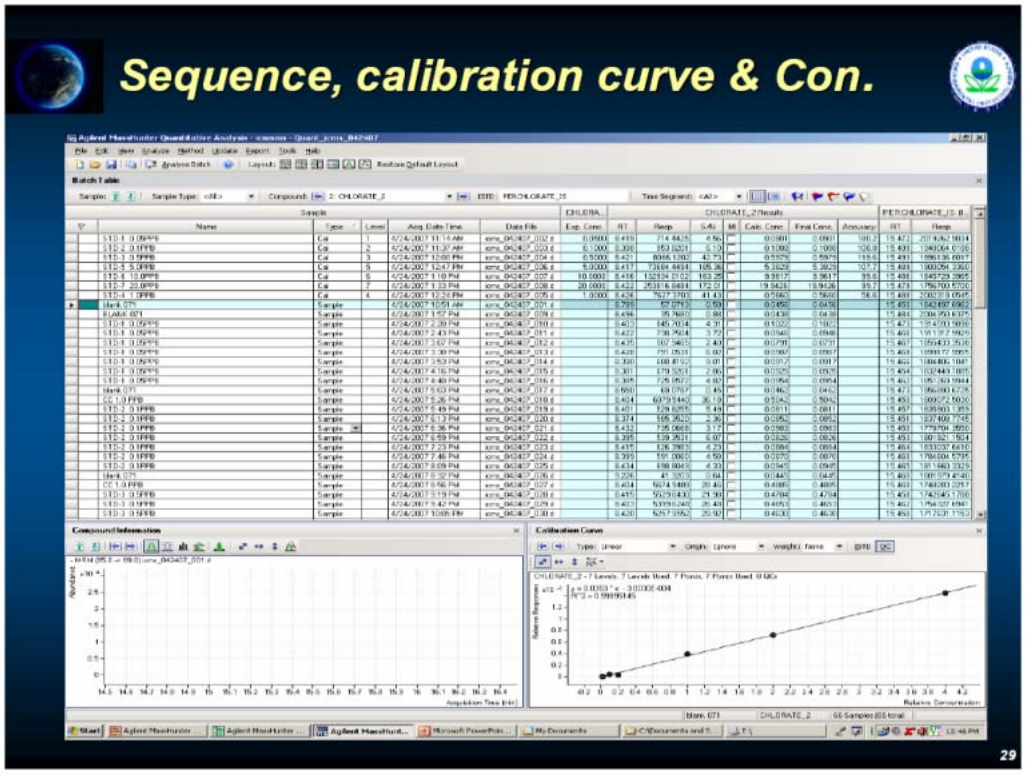

Calibration Data
24


MRM transition
- MRM (6.249-6.561 min, 23 scans) icms_042407_011.d
Mass 127 → 79
Abundance
79.0
127.0
Mass-to-Charge (m/z)
Bromate
- MRM (8.129-8.856 min, 108 scans) icms_042407_018.d
Mass 83 → 67
67.0
83.0
Chlorate
25


MRM Transition
- MRM (15.047-15.933 min, 88 scans) icms_042407_011.d
Mass 99 → 83
Abundance
83.0
99.0
Mass-to-Charge (m/z)
Perchlorate
- MRM (0.004-12.004 min, 552 scans) icms_042407_018.d
Mass 67 → 51
51.0
67.0
Chlorite
26


Chromatography
27


Merged MRM chromatograph
9.2 x 10²
0.05 ppb
ClO2-
BrO3-
ClO3-
ClO4-
28


Sequence, calibration curve & Con.
29


RECOVERY RESULTS
30

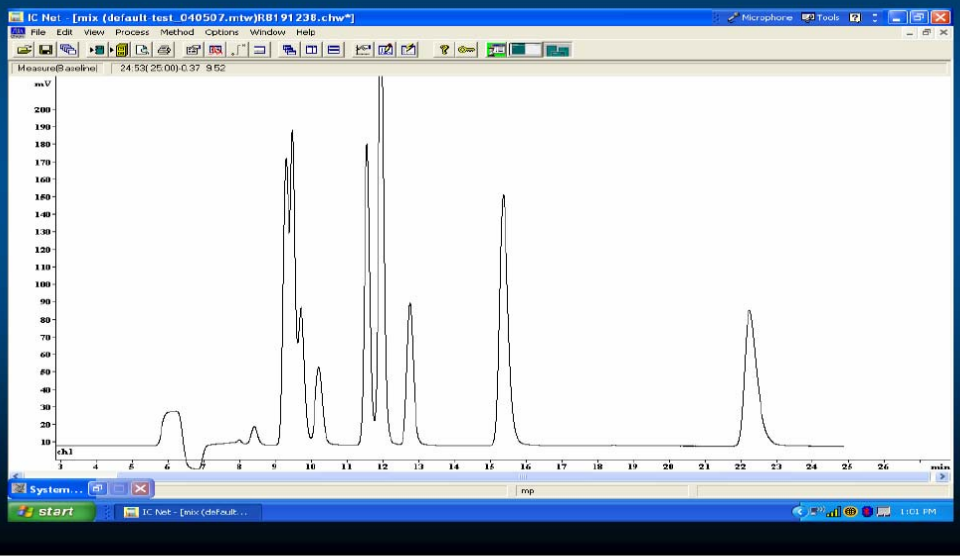
Recovery

Analyte	Concentration (ppb)	% Recoveries
Bromate	0.05	92-102
Bromate	0.1	94-104
Chlorite	10	88-103
Chlorate	0.05	92-101
Chlorate	0.1	90-104
Perchlorate	0.05	89-103
Perchlorate	0.1	90-102

Spike Recovery from tap and various bottle water

31

Ion Chromatogram for Dalapone, Bromate, Chlorate, Perchlorate and Halo Acetic Acid in single run



32

Future work

- Optimizing MS/MS for HAA compounds
- Front end separation – if possible
- Investigating in narrow bore column
  - –Better S/N, sharper peaks
  - –Better sensitivity
  - –Lower flow rate

33

Conclusion

- Using emerging technology like Ion Chromatography hyphenated with single Quadrople, Triple Quadropole and Time of Flight are advantages to measure low molecular weight anions, Disinfection By-Products, Halo Acetic Acid (HAA) and other emerging target compounds in single analysis

34


Acknowledgements
David Neleigh
Branch Chief - US EPA
Rick McMillin
Deputy Branch Chief – US EPA
Dr Melvin Ritter
Team Lead - US EPA
35

Two New SW 846 Methods for The Analysis of Perchlorate in Various Environmental Media

Shen-yi Yang

U. S. Environmental Protection Agency
Office of Solid Waste (OSW)
1200 Pennsylvania Ave., N. W. (5307P)
Washington, D.C. 20460

Enviromental Measurement Symposium

August 21, 2007
Cambridge, MA

Background

- Perchlorate: ClO_4^-
  - Both manmade and naturally occurring
- Perchlorate contamination sources
  - Manufacturing of solid propellants and explosives
  - Production and improper disposal of fireworks, highway safety flares, and airbag inflators
  - Production and use of certain nitrate-based fertilizers
- Perchlorate inhibits iodine uptake by the thyroid gland, thus
  - Affects thyroid hormone production and thyroid regulation of metabolism
  - Impairs neurological development of fetus and newborn
  - Changes in thyroid hormone levels may result in thyroid gland tumors

Environmental Measurement Symposium

August 21, 2007

Perchlorate in The Environment

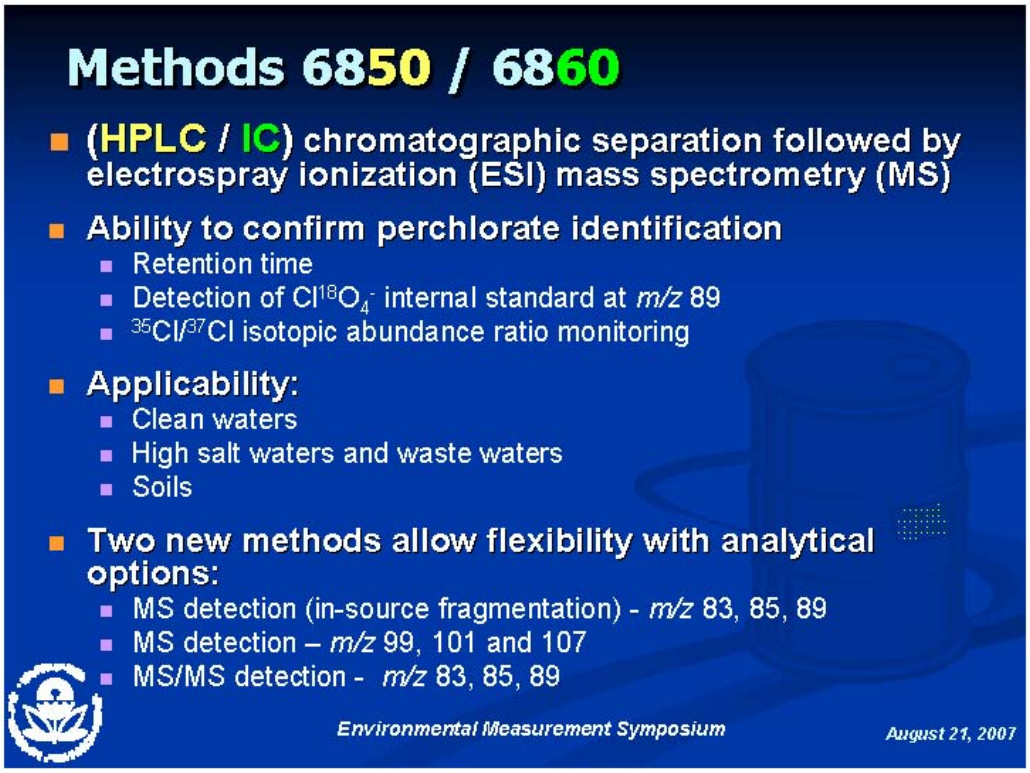
- Very mobile in aqueous systems - persistent under typical ground water and surface water conditions
- Absorbs weakly to most soil minerals
- Factors that may affect perchlorate degradation:
  1. The presence of Perchlorate reducing bacteria (PRB), and
  2. Conditions that favor PRB growth
     - Anaerobic conditions
     - Carbon source (electron donor)
     - Alternate electron acceptors
     - Low salinity level
- Perchlorate has been detected in thirty five (35) states in the U.S. and Puerto Rico in various aquifers, crops, and milk

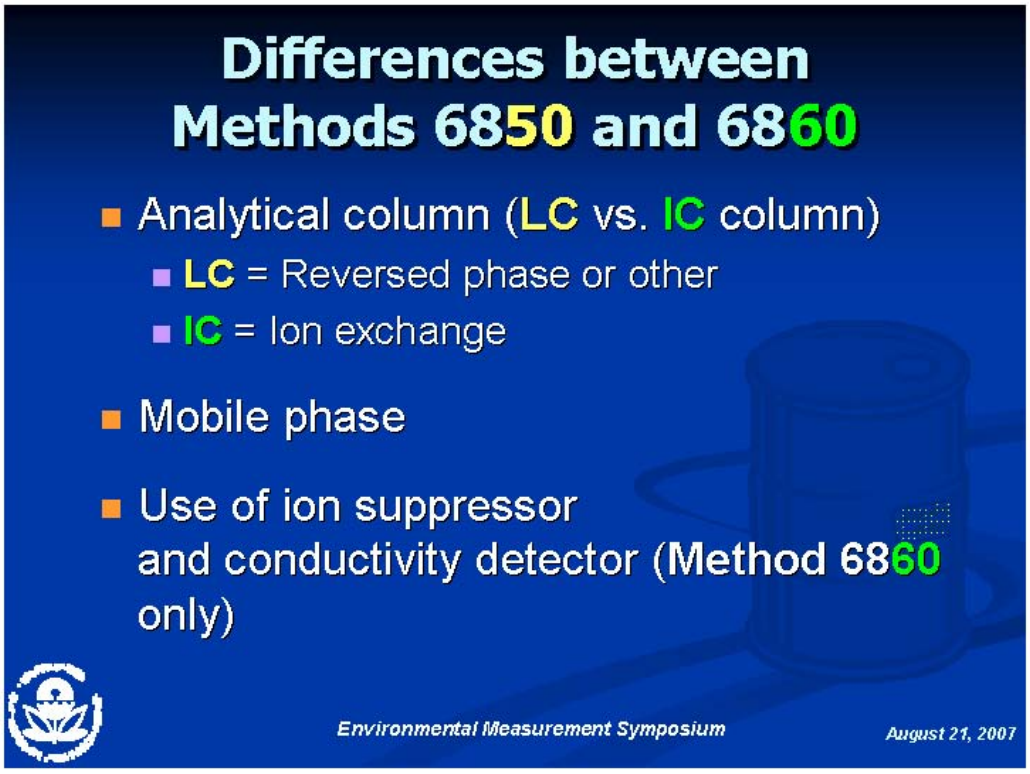
Environmental Measurement Symposium *August 21, 2007*

The EPA OSW Perchlorate Task Force

- Lead by OSW - Members include:
  - EPA Office of Research and Development (ORD)
  - EPA Regional Laboratories
  - Department of Defense (DOD)
  - Instrument vendors
  - Commercial laboratories
- Objectives
  - Refine existing procedure – **Method 9058**
  - Develop two new improved methods
    - Provide better identification and quantification of perchlorate
    - Applicable to groundwater, surface water, high salt water and soil

Environmental Measurement Symposium *August 21, 2007*


Methods 6850 / 6860
(HPLC / IC) chromatographic separation followed by electrospray ionization (ESI) mass spectrometry (MS)
Ability to confirm perchlorate identification
Retention time
Detection of $Cl^{18}O_4^-$ internal standard at m/z 89
$^{35}Cl/^{37}Cl$ isotopic abundance ratio monitoring
Applicability:
Clean waters
High salt waters and waste waters
Soils
Two new methods allow flexibility with analytical options:
MS detection (in-source fragmentation) - m/z 83, 85, 89
MS detection – m/z 99, 101 and 107
MS/MS detection - m/z 83, 85, 89
Environmental Measurement Symposium
August 21, 2007


Differences between Methods 6850 and 6860
Analytical column (LC vs. IC column)
LC = Reversed phase or other
IC = Ion exchange
Mobile phase
Use of ion suppressor and conductivity detector (Method 6860 only)
Environmental Measurement Symposium
August 21, 2007

Examples of Methods 6850 and 6860 Analytical Conditions under Evaluation

	Column	Mobile Phase	Detection	Quantitation Ions (m/z)
6850	■ K'(Prime) RP	- 9.6 M CH_3CN - 0.035 mM CH_3COOH	LC/MS	83, 85, 89
	■ IC Pak™ Anion HR	- 25 mM NH_4HCO_3 - 9.6 M CH_3CN (pH 10)	LC/MS/MS	83, 85, 89
	■ 2 Alltech GA-1 guard cartridges in series	- 0.8 mM $CH_3CO_2NH_4$ - 20% CH_3OH	LC/MS/MS	83, 85, 89
6860	■ MetroSep ASUPP 5	-12.8 mM Na_2CO_3 - 4mM $NaHCO_3$ - 8.6 mM CH_3CN	IC/MS	99, 101, 107
	■ IonPac® AS16	- 45 mM KOH	IC/MS	99, 101, 107
	■ IonPac® AS16	- 45 mM KOH	IC/MS/MS	83, 85, 89

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SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- Collect water samples in clean, 125-mL polyethylene bottles
  - Whenever possible, water samples should be sterilely filtered in the field at the time of collection using 0.2-µm PTFE membrane to remove potentially PRB
- Collect solid samples in clean, 4-oz amber glass bottles
  - Extract solids within 28 days of sample acquisition
- Store all samples and extracts with headspace to reduce potential anaerobic biodegradation
- Analyze water samples and extracts of solid samples within 28 days of collection or preparation, respectively
- Care should be taken to avoid temperature extremes during shipment and storage

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6850/6860 Sample Preparation

- Aqueous samples
  - 0.2 (or 0.45) µm membrane filtration
- Soils
  - Aqueous extraction procedure
    - 1 g sample/ 10 mL reagent water
    - Vortexing
    - Centrifuge for 5 minutes at 4000 rpm
    - 0.2 µm (or 0.45 µm) filtration
    - C^{18} or other cleanup if necessary

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Soil Extract Chromatogram
LC/MS With Fragmentation

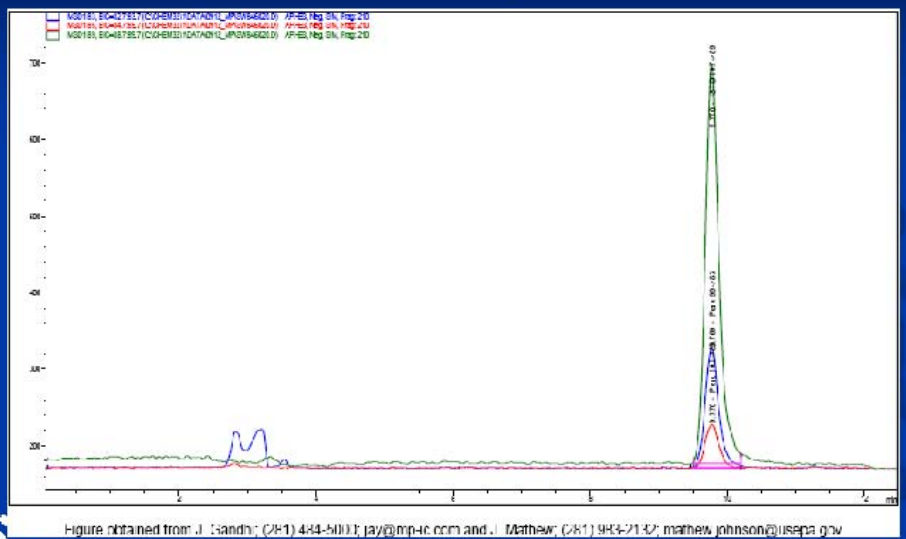

Figure obtained from J. Gandhi; (281) 484-5000; jay@mp-ic.com and J. Mathew; (281) 983-2132; mathew.johnson@usepa.gov

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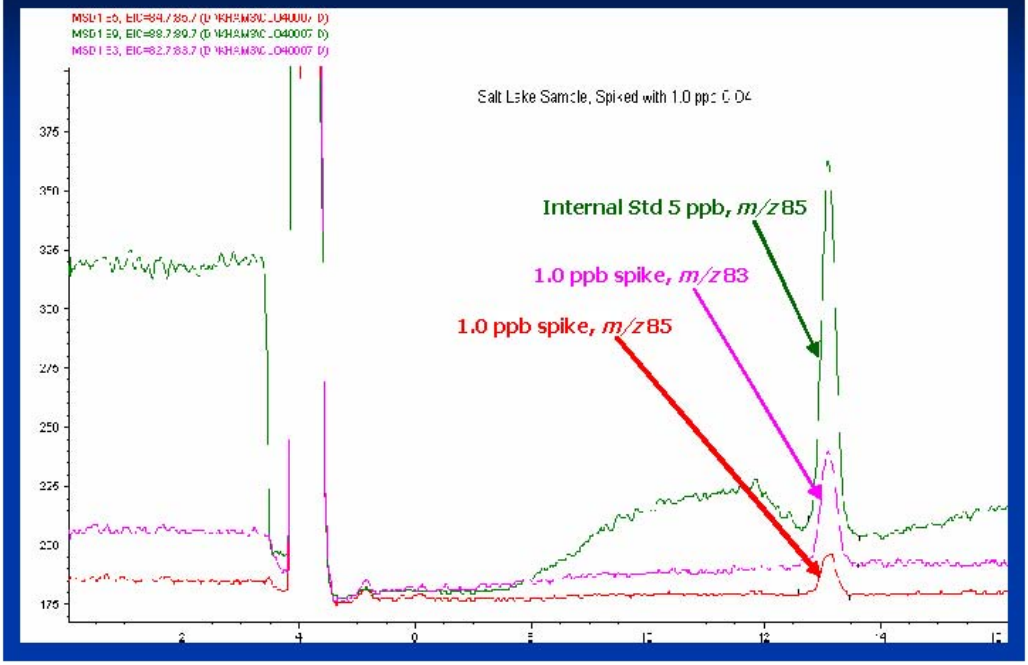
Method 6850: Great Salt Lake Water



Reporting Limits

- Removed MDLs from all SW 846 methods
- Uses the lowest calibration standard as the Lower Level of Quantitation (LLOQ) for data reporting
- LLOQs
  - water samples: 0.2 µg/L
  - solid samples: 2 µg/kg

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Methods 6850 and 6860 Status

- Voluntary inter-lab method validation studies

Phase I: Initial Demonstration of Proficiency (IDP)

- Analysis of varying levels of perchlorate in reagent water
- ***Completed in September 2005***

Phase II: Method Validation

- Analysis of perchlorate in salt water, waste water, soil and sludge
- Varying perchlorate and conductivity background levels
- Evaluate aqueous extraction procedure
- Holding time studies for high salt water, waste water and sludge
- ***Completed in July 2006***

Phase III: Extraction Procedure(s) for Sludge

- Two extraction procedures are in consideration
- May start later part of 2007

- Two methods were issued in January 2007 and posted on the OSW Methods website for public use and comments

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Phase II Validation Study Objectives

- **Evaluate method performance characteristics**
  - ***Bias***
    - Difference between the analysis result and the "true" or assigned concentration value
  - ***Precision***
    - Consistency between repeated measurements of the same sample
      - Determine extract vs. analysis precision
  - ***Robustness***
    - Ability to perform high quality measurements over time and/or in challenging matrices
      - Week-to-week method performance
      - Challenging study matrices
- **Evaluate perchlorate holding time and appropriate storage protocol**

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Method 6850
Validation Study Results

	Phase I: Initial Demonstration of Proficiency		Phase II: Real world Matrices							
Matrix	Reagent Water		Salt Water		PCTW Waste Water		Soil			
ID	1	2	1	2	1	2	1	2	3	QC Standard[b]
Selected Matrix Characterization Data										
Conductivity[c]	< 1 µS/cm	< 1 µS/cm	44,600 µS/cm	44,600 µS/cm	d	d	243 µS/cm	243 µS/cm	3200 µS/cm	d
Aluminum			d	d	d	d	3700 mg/kg	3700 mg/kg	3700 mg/kg	d
Calcium	---	---	200 g/L	200 g/L	d	d	8900 mg/kg	8900 mg/kg	8900 mg/kg	d
Iron	---	---	d	d	d	d	3070 mg/kg	3070 mg/kg	3070 mg/kg	d
Magnesium	---	---	1050 g/L	1050 g/L	d	d	288 mg/kg	288 mg/kg	288 mg/kg	d
Potassium	---	---	332 g/L	332 g/L	d	d	138 mg/kg	138 mg/kg	138 mg/kg	d
Sodium	< 5 µg/L	< 5 µg/L	9910 g/L	9910 g/L	d	d	e	e	e	d
TOC	< 60 µg/L	< 60 µg/L	d	d	d	d	670 mg/kg	670 mg/kg	670 mg/kg	d
Round Robin Testing Results										
Number of Laboratories	12	12	12	12	1	1	11	11	10	12
Perchlorate True Value	1.75 µg/L	47.0 µg/L	1.70 µg/L	0.30 µg/L	1.70 µg/L	0.30 µg/L	16.0 µg/kg	150 µg/kg	63.0 µg/kg	564 µg/kg
Relative Bias	-0.58%	-0.16%	-6.06%	-8.11%	1.16%	3.47%	-13.0%	-12.2%	-7.6%	-14.1%
Repeatability[f] (RSD)	2.99%	4.30%	3.75%	6.06%	4.85%	1.92%	8.00%	4.20%	8.33%	9.1%
Reproducibility[g] (RSD)	6.33%	8.46%	26.0%	12.6%			16.0%	13.7%	16.0%	16.2%

[a]Samples were prepared and analyzed using the conditions described in the test method.
[b]Soil and Hazardous Waste QC Standard, Wilbby™ Environmenta., Inc., Golden, Colorado.
[c]For solids, the conductivity values were based on a 1 g/10 mL extraction solution.
[d]Not determined
[e]Not calculated
[f]Intralaboratory precision
[g]Interlaboratory precision

Comparative Study Results
Reagent Water vs. 50% Acetonitrile

Matrix ID	Soil 1[d]		Soil 2[d]		Soil 3[d]		Soil QC Standard[d,e]	
Comparative Testing Results								
Extraction Solvent	Reagent Water	50% CH_3CN	Reagent Water	50% CH_3CN	Reagent Water	50% CH_3CN	Reagent Water	50% CH_3CN
Measured Perchlorate Concentration	13.0 mg/kg	12.6 mg/kg	122 mg/kg	117 mg/kg	62.8 mg/kg	60.6 mg/kg	109 mg/kg	110 mg/kg
Repeatability (RSD)	2.13%	2.09%	5.22%	2.00%	4.29%	1.73%	19.1%	[f]

Matrix ID	Sludge 1	Sludge 2	Sludge 3
Selected Matrix Characterization Data			
Conductivity[g]	5100 µS/cm	5100 µS/cm	26000 µS/cm
Aluminum	3220 mg/kg	3220 mg/kg	3220 mg/kg
Calcium	42.4 g/kg	42.4 g/kg	42.4 g/kg
Iron	17.3 g/kg	17.3 g/kg	17.3 g/kg
Magnesium	6390 mg/kg	6390 mg/kg	6390 mg/kg
Potassium	3100 mg/kg	3100 mg/kg	3100 mg/kg
Sodium	4620 mg/kg	4620 mg/kg	4620 mg/kg
TOC	4680 mg/kg	4680 mg/kg	4680 mg/kg
Comparative Testing Results			
Extraction Solvent	Reagent Water / 50% CH_3CN	Reagent Water / 50% CH_3CN	Reagent Water / 50% CH_3CN
Measured Perchlorate Concentration	3.53 mg/kg / 20.6 mg/kg	6.46 mg/kg / 27.6 mg/kg	41.9 mg/kg / 60.5 mg/kg
Repeatability (RSD)	7.18% / 5.61%	3.37% / 0.788%	5.17% / 5.61%

[a]Reagent water extracts were prepared as described in the test method.
[b]50% (v/v) acetonitrile extracts were were prepared as described in Ref. 5.
[c]All sample extracts were analyzed by HPLC/MS/MS using a Waters IC-Pak™ Anion HR column with 100 mM $CH_3CO_2NH_4$, 9.0 M CH_3CN mobile phase.
[d]See Table 3 for soil matrix true values and characterization data.
[e]Soil and Hazardous Waste QC Standard, Wilbby™ Environmenta., Inc., Golden, Colorado.
[f]Result based on a single analysis.
[g]Based on a 1 g/10 mL extraction solution.

Data taken from Reference 6. These data are provided for guidance purposes only.

Study Findings to Date

- Perchlorate appears to be fairly stable in salt water and soil
- Perchlorate may be anaerobically degraded in certain wastewaters and sludges by bacteria
- Perchlorate was recovered poorly using reagent water
  - Phase III study is planned for late 2007 to compare different reagents using extraction procedures (developed by FDA and Metrohmn Peak) for soil and sludge
  - May amend the methods to be applicable for sludge

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Method 9058 (IC)

- **Proposed in November 2000**
- **Current version has limited scope and applicability**
  - 4 µg/L sensitivity for reagent waters
  - Performs adequately on waters ≤ 1000 µS/cm EC
  - ECs >1000 µS/cm have not been rigorously tested
  - Potential for false positive/negative results due to matrix interferences
    - Co-eluents
    - High total dissolved solids (TDS)
  - No written procedure for extracting perchlorate in solids

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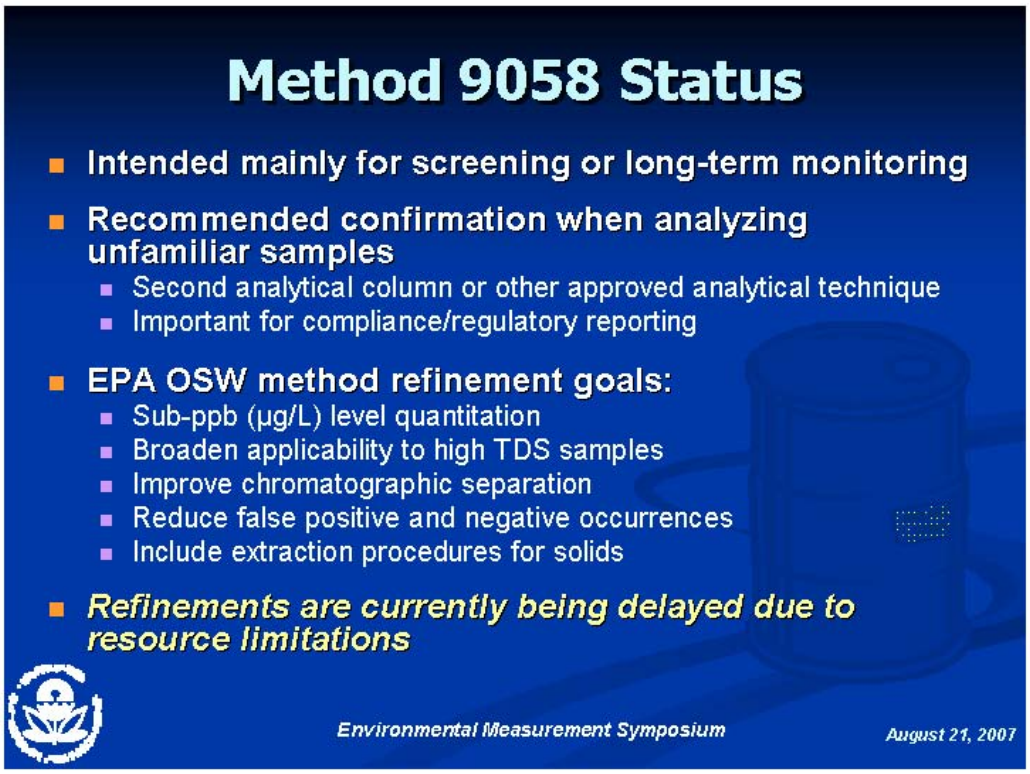
Method 9058 Status
Intended mainly for screening or long-term monitoring
Recommended confirmation when analyzing unfamiliar samples
Second analytical column or other approved analytical technique
Important for compliance/regulatory reporting
EPA OSW method refinement goals:
Sub-ppb (µg/L) level quantitation
Broaden applicability to high TDS samples
Improve chromatographic separation
Reduce false positive and negative occurrences
Include extraction procedures for solids
Refinements are currently being delayed due to resource limitations
Environmental Measurement Symposium
August 21, 2007


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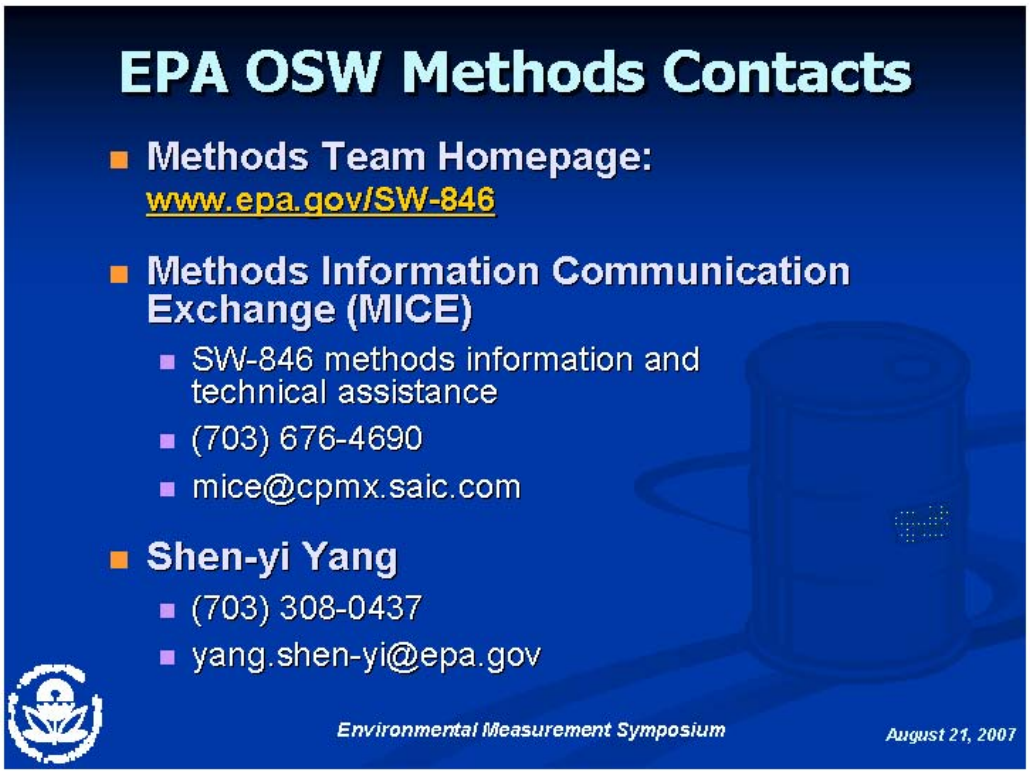
USACE Deborah Walker, Denise MacMillan
Access Ralph Hindle
Alpha Analytical Labs Scott McLean
Battelle Raj Mangaraj, Pernell Horton
Columbia Analytical Services Dee O'Neill, Lisa Reyes, Lee Wolf
Del Mar Analytical David Dawes
EPA Region VI Johnson Mathew
ES Babcock & Sons Larry Chrystal
FDA Alex Krynitsky
GEL Bob Pullano
MDS Sciex Houssain El Aribi, Takeo Sakuma
Southern Nevada Water Authority Rebecca Colgate, Stan Van Wagenen
Waters Jim Krol
WCAS Mike Shelton


EPA OSW Methods Contacts
Methods Team Homepage:
www.epa.gov/SW-846
Methods Information Communication Exchange (MICE)
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ORGANIC METHODS

Accelerated Solvent Extraction (ASE) as a Innovative Sample Preparation Technique for Analytical Determination of Conventional Contaminates in Environmental Samples

Sheldon Henderson
Dionex Engineering

ABSTRACT

Accelerated solvent extraction (ASE) is an innovative approach to liquid-solid extraction. It is accepted under USEPA Method 3545A for the extraction of conventional environmental toxins such as PCBs, dioxins, PAHs, diesel range organics and chlorinated pesticides. This technique uses elevated temperatures and pressures to achieve analyte extractions from solid or semi-solid matrices in about fifteen minutes and with small volumes of solvents. For example, a 10-g sample can be extracted in about twelve minutes and with about 15 mL of solvent.

Traditional methods such as Soxhlet or sonication horns have been used to extract solid samples containing environmental contaminates. These methods require long periods of time (sixteen hours) and large volumes of solvent or aqueous buffers (300 mL) and large amounts of manual sample handling and manipulation in preparation for analysis. ASE can perform these extractions in short periods of time and with small amounts of solvent.

This presentation will discuss the use of ASE and ASE-compatible techniques such as in cell clean-up for the effective sample preparation of several environmental matrices, including soils, sediments, plant or animal tissues, for analysis of various conventional contaminates. Comparisons of analyte recovery to traditional methods of extraction will be presented for Dioxins, Organochlorine pesticides, Polychlorinated biphenyls, and Polybrominated Diphenyl Ethers.

Analysis of EPA Method 8081A Chlorinated Pesticides Using Two New Improved GC Column Phases

Kory Kelly
Phenomenex

ABSTRACT

The current work demonstrates the use of two new and unique phases, which have been optimized for the analysis of all classes of pesticides. The phase chemistry improves separation and peak shape for the more polar pesticide compounds when compared to standard 5% phenyl columns. Selectivity data is compared between a 5ms type phase and the two new columns.

Multi-pesticide residue screening is evaluated over 250 different pesticides commonly analyzed from fruits and vegetables. The unique selectivity offered by the two phases improves resolution for multi-component analytes providing a more unique elution pattern, which can be used to identify closely eluting analytes.

Since the phases have orthogonal selectivity, they are also a good choice for dual column methods. Some data is presented for EPA specified testing procedures.

Analysis of EPA Method 8081A Chlorinated Pesticides Using Two New Improved GC Column Phases

Kory Kelly, Sky Countryman

Overview

1. EPA Method 8081A Overview
2. Developing A New GC Column
3. Method Performance
4. Other Methods

1. EPA Method 8081A Overview

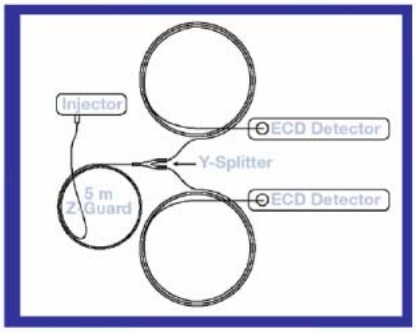
- Organochlorine Pesticides by GC/ECD
  - Full Method
    - 26 compounds
    - Chlordane & Toxaphene
    - 24 additional compounds that may also be determined
  - Standard Method:
    - 20 compounds + 2 surrogates
    - Other compounds are commonly added

EPA Method 8081A Overview Cont.

- Dual column option
- Co-elutions require two mix calibration
- Internal standards are optional
- System activity for certain compounds – inlet deactivation is critical

Dual Column Analysis

- ECD has no spectral confirmation
- Using two columns reduces the chance of co-elutions
- Phases must be "sufficiently dissimilar"
  - Two elution order changes
- Difficult to separate all compounds using the same oven program



EPA Performance Requirements

- Calibration
  - RSD for all target analytes must be <20 %
  - Performance check every 12 hours or 20 samples: calibration difference must be <15%
- Breakdown
  - Endrin & DDT must be <15 %
- Resolution
  - Must resolve all compounds on both columns
  - If not, must run separate mixes to avoid co-elutions

2. Developing A New GC Column

- Most column pairs have co-elutions
- Co-elutions increase as additional compounds are added
- Poor resolution limits method optimization
  - Long analysis times
  - Poor quantitation
  - Short column lifetime

Common Critical Pairs

5% Phenyl
- Endosulfan I/α-Chlordane
- 4,4'-DDT/Endosulfan Sulfate
- 4,4'-DDE/Dieldrin

50% Phenyl
- γ–Chlordane/Endosulfan I
- 4,4'-DDD/Endrin

1701
- 4,4'-DDE/Dieldrin
- γ–Chlordane/Endosulfan I
- Endosulfan Sulfate/Methoxychlor
- Endosulfan II/4,4'-DDT

608
- Endosulfan I/α-Chlordane
- 4,4'-DDD/Endrin

Designing a Better Solution

- Started with specific objectives
  - Baseline resolution of the 20 common pesticides in <15 minutes
  - Low activity for DDT/Endrin
  - MS certified bleed levels
  - High temperature limits 320/340 °C
  - No-cyanopropyl chemistry

The Stationary Phase

- No commercially available phases provided enough selectivity for pesticides
- Variations in phenyl or other chemistries didn't offer enough selectivity
  - Or had undesirable drawbacks: bleed, activity, etc
- New polymer chemistries were developed for the general pesticide chemistry

A Pesticide Solution

- We looked at the selectivity multiple classes of pesticides
- The result: two new phases with optimized resolution for multiple classes of pesticides

ZB-MultiResidue™-1	ZB-MultiResidue™-2
• Low-mid polarity	• Mid-high polarity
• Polarity* is between a ZB-5ms and a ZB-35	• Polarity* is between a ZB-35 and a ZB-50

* Polarity ≠ Selectivity

3. Method Performance

Analysis Conditions:

Column:	Zebron MultiResidue-1 Zebron MultiResidue-2
Dimensions:	30 meter x 0.32 mm x 0.50 µm 30 meter x 0.32 mm x 0.25 µm
Injection:	Splitless @ 250 °C, 1 µL
Carrier Gas:	Helium @ 3.4 mL/min (constant flow)
Oven Profile:	100 °C for 0.5 min to 220 °C @ 35 °C/min to 340 °C at 20 °C/min for 2min
Detector:	ECD @ 350 °C

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Analytes

1. TCMX (surr)
2. 1-Bromo-2-nitrobenzene (IS)
3. a-BHC
4. γ-BHC (Lindane)
5. β-BHC
6. δ-BHC
7. Heptachlor
8. Aldrin
9. Heptachlor epoxide
10. γ-Chlordane *(trans)*
11. α-Chlordane *(cis)*
12. Endosulfan I
13. 4,4'-DDE
14. Dieldrin
15. Endrin
16. 4,4'-DDD
17. Endosulfan II
18. Endrin aldehyde
19. 4,4'-DDT
20. Endosulfan sulfate
21. Methoxychlor
22. Endrin ketone
23. DCB (surr)

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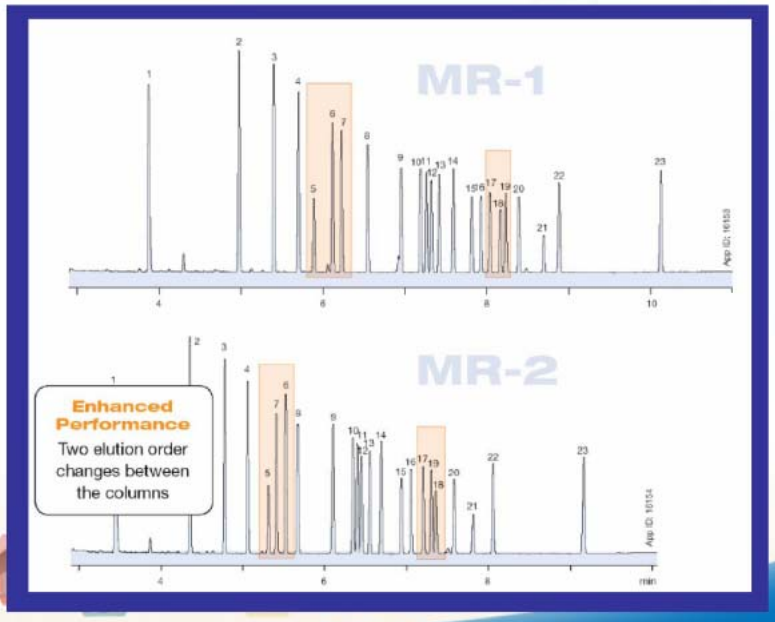
Resolution



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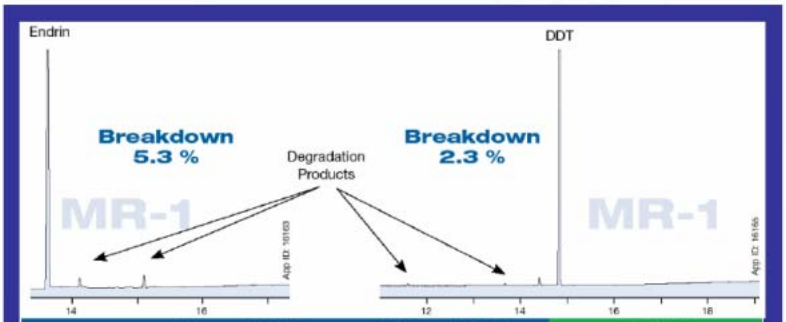
Activity



Analyte	Zebron MR-1 % Breakdown	Zebron MR-2 % Breakdown	US EPA Requirements
Endrin	5.3	7.0	< 15
DDT	2.3	2.9	< 15

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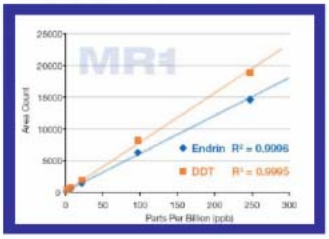
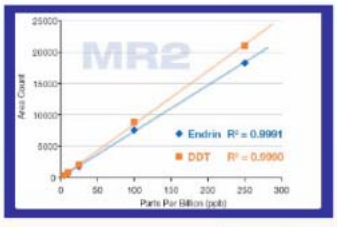
Calibration Stability

Analyte	Zebron™ MR-1 % RSD*	Zebron™ MR-2 % RSD*	US EPA Specifications
α-BHC	6.75	7.91	< 20
γ-BHC (Lindane)	5.52	5.70	< 20
β-BHC	3.57	9.21	< 20
δ-BHC	5.90	7.58	< 20
Heptachlor	4.21	5.37	< 20
Aldrin	4.34	5.25	< 20
Heptachlor epoxide	3.70	4.48	< 20
γ-Chlordane	3.68	3.61	< 20
α-Chlordane	2.91	3.39	< 20
Endosulfan I	2.93	3.91	< 20
DDE	4.56	6.77	< 20
Dieldrin	3.85	4.75	< 20
Endrin	4.17	3.84	< 20
DDD	4.79	7.36	< 20
Endosulfan II	2.63	3.53	< 20
Endrin aldehyde	4.11	4.72	< 20
DDT	3.70	5.42	< 20
Endosulfan sulfate	3.31	3.20	< 20
Methoxychlor	7.39	4.21	< 20
Endrin ketone	3.48	3.95	< 20
Average	4.28	5.21	< 20





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Low Level Repeatability

Analyte	MR-1 % RSD	MR-2 % RSD
Lindane (γ-BHC)	2.78	3.53
Heptachlor	2.83	3.60
Dieldrin	3.38	3.28
Endrin	4.34	4.54
DDT	5.92	5.14
Methoxychlor	5.21	5.96

Relative standard deviation (RSD) for five replicate injections of pesticide at 5 pg on-column concentration

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Method Optimization

- Time = money
- More samples/hour = more money
- After the resolution, accuracy, and precision have been achieved
- Run time should be as fast as possible!

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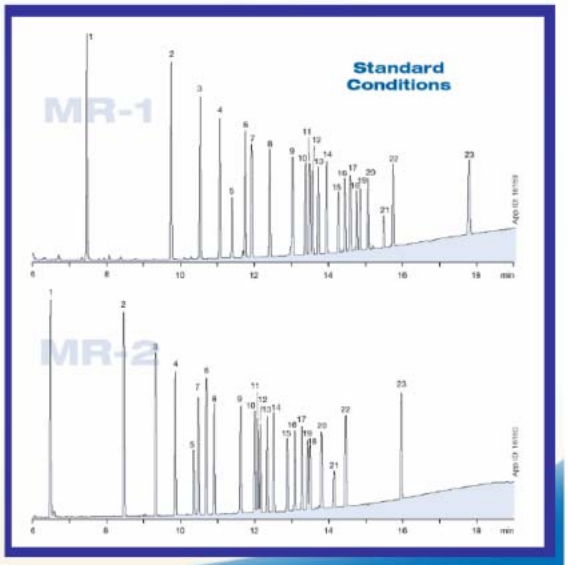
Lab Productivity

Column: Zebron MultiResidue-1 &2
Dimensions:
30 meter x 0.53 mm x 0.50
30 meter x 0.53 mm x 0.50
Injection: Splitless @ 250 °C, 1 µL
Carrier Gas: Helium @ 5.2 mL/min (constant flow)
Oven Program: 90 °C for 0.5 min to 320 °C @ 15 °C/min for 5 min
Detector: ECD @ 350 °C

18min Analysis



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Same Columns
+ Optimized Conditions
= Increased Productivity

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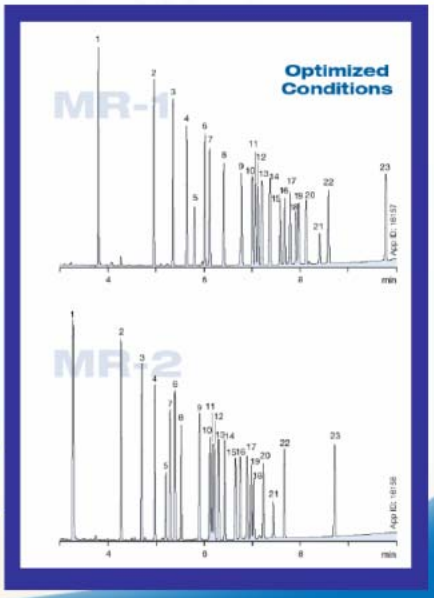
Increased Productivity

Column: Zebron MultiResidue-1 &2
Dimensions:
30 meter x 0.53 mm x 0.50
30 meter x 0.53 mm x 0.50
Injection: Splitless @ 250 °C, 1 µL
Carrier Gas: Helium @ 8 mL/min (constant flow)
Oven Program: 110 °C for 0.5 min to 250 °C @ 30 °C/min to 340 °C @ 20 °C/min for 2 min
Detector: ECD @ 350 °C

9min Analysis



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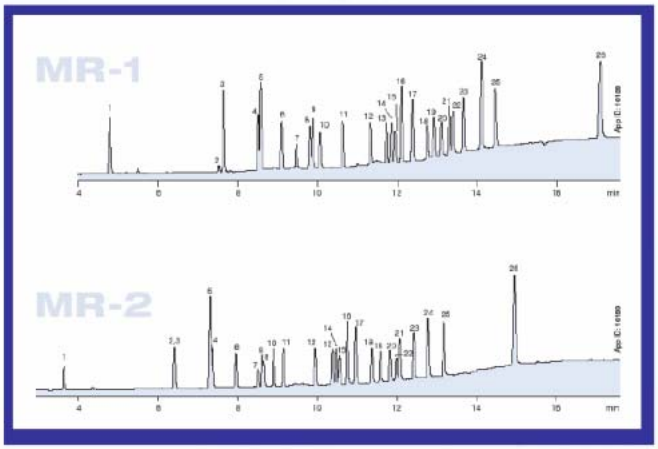
Additional Compounds – No Problem

1.Hexachlorocyclo-pentadiene
2.Propaclor
3.Tetrachloro-*m*-xylene
4.α-BHC
5.Hexachlorobenzene
6.γ-BHC (Lindane)
7.β-BHC
8.Alachlor
9.δ-BHC
10.Heptachlor
11.Aldrin



4. Other Methods

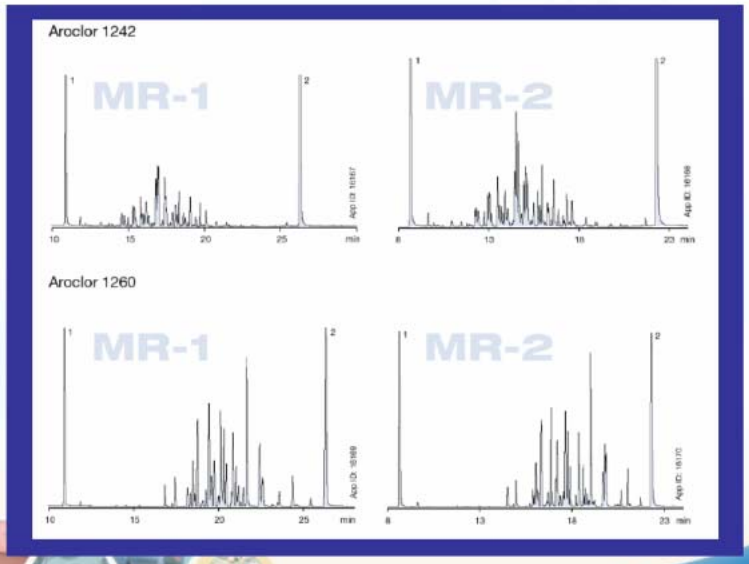
- Most labs typically run other methods on the same instruments
- Changing columns is time consuming
  - Re-conditioning
  - Re-Calibration

EPA Method 8082

Polyclorinated Biphenyls (PCBs) as Aroclors

- Aroclors mixtures are identified based on the pattern
- Certain Aroclors mixtures have similar patterns
- Samples often contain other high boiling contaminants
- ZB-MultiResidue™ have unique selectivity for PCBs
- Results in a more unique pattern

EPA Method 8082: Aroclors



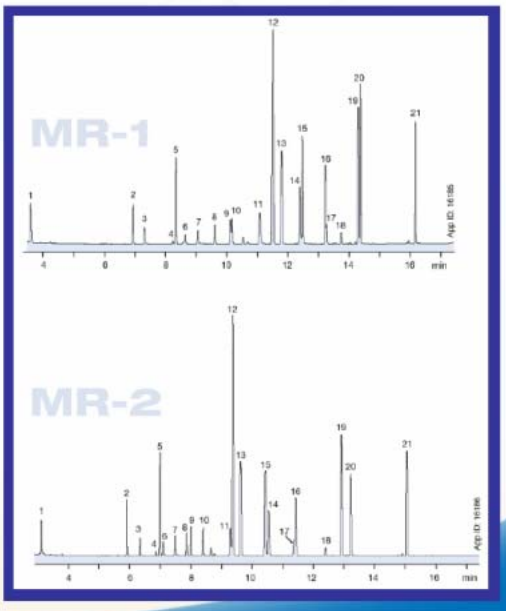
EPA Method 8151

Chlorophenoxy Acid Herbicides

- Acidic pesticides require derivatization before analysis
- Optional internal standard
  - DBOB
- Resolution is achieve for all targets

EPA Method 8151

1. Dalapon
2. 3,5-Dichlorobenzoic acid
3. 4-Nitrophenol
4. DCAA (surr)
5. Dicamba
6. MCPP
7. MCPA
8. Dichloroprop
9. Contaminant
10. 2,4-D
11. Pentachlorophenol
12. DBOB (IS)
13. Silvex
14. Chloramben
15. 2,4,5-T
16. Dinoseb
17. 2,4-DB
18. Bentazon
19. Picloram
20. DCPA
21. Acifluorfen



Summary

- The Zebron MultiResidue™ 1 & 2 column exceed EPA 8081A specifications
- Allow methods to be optimized for increased lab efficiency
- Provide good results for other commonly run EPA Methods


phenomenex
Thank You!
Questions!
Copyright 2007 Phenomenex

Determination of Explosives and Related Species in Soils by Gas Chromatography/Negative Ion Chemical Ionization Mass Spectrometry (GC/NICI-MS)

Bruce Benner, Jr.
National Institute of Standards and Technology

ABSTRACT

For over a century, explosives have been produced at many U.S. manufacturing facilities operated by the U.S. Army. A by-product of these manufacturing processes includes wastewater contaminated with explosives and other organic species that were typically pumped into unlined settling lagoons as part of the current treatment procedure. In addition to this wastewater contamination by explosives and related chemicals, aged/obsolete batches of explosives are destroyed by burning resulting in contamination of the adjacent soil with both explosive residues as well as combustion by-products. A publication in 2001 (J. A. MacDonald, Cleaning up unexploded ordinance, Environ, Sci. Technol. 35, 370A – 374A, 2001) described the magnitude of the problem of explosives contaminated soil resulting from buried unexploded ordinance (UXO). Regarding sites selected for base closings, the U.S. Environmental Protection Administration (EPA) and Defense Science Board (DSB) task force on UXO estimated that 7500 and 1500 sites, respectively, are contaminated with UXO. The environmental impact of explosives manufacture, UXO leeching, and ordinance detonations are many tons of soil contaminated with significant levels of explosives and other organics, contamination that prevents the sites from being developed by the private sector (demilitarization). Verification of the efficacy of any remediation process would require a material of similar composition. Although there are a number of vendors providing standard solutions of individual explosives and their mixtures, there is currently only one vendor that provides limited batches of soil spiked with explosives and some of their degradation products. A "natural matrix" soil standard with stated concentrations of specific explosives and some of their degradation products and assessed for the stability of these analytes would fill a void for the environmental remediation, forensics, and homeland security research communities.

In late October, 2003, a large quantity of soil was collected from craters of recent detonations at a military proving site. The bulk soil was air-dried and filtered through a coarse (10 mesh, 2 mm) sieve. A sub-sample of this soil was sieved, yielding approximately 1.5 kg of material between 70 and 170 mesh (≤ 212 μm and ≥ 90 μm). This material was mixed manually and aliquots were characterized for energetic compounds by GC/NICI-MS using stable isotope labeled-explosives as internal standards. The soil was then irradiated with cobalt-60 by a commercial facility to minimize future microbial degradation of the inherent energetic compounds. This presentation will discuss the results of stability assessments (~ 3 years) of the irradiated soil and a finer fraction soil derived from the same bulk soil. In addition, the talk will include a discussion of any differences observed in the extraction kinetics of explosives incurred by detonation versus those spiked onto soil from solutions.

Determination of Explosives and Related Species in Soil by Gas Chromatography/ Negative Ion Chemical Ionization Mass Spectrometry (GC/NICI-MS)

Bruce A. Benner, Jr. and William A. MacCrehan,
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NIST
National Institute of Standards and Technology

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Measurement of Explosives in Soil: Why?

- Environmental Concerns: Soil contamination at the Nation's Proving Grounds from over a century of production and disposal (1500 – 7500 sites). Need to verify bioremediation of soils (demilitarization).
- Strategic and Homeland Security: Leaching from landmines (unexploded ordinance), post-blast investigations, airline passenger screening.

Cleaning up Explosives Contaminated Military Sites

- USEPA and the Army Corp of Engineers reported the bioremediation of soil contaminated with explosives using composting techniques (Innovative uses of compost: composting of soils contaminated by explosives, EPA530-F-97-045, October 1997).
  - mixed sifted soil with amendments (straw, alfalfa, manure, agricultural waste, and wood chips). These materials disperse soil and provide carbon source for bacteria. Mixture spread out into long piles or windrows and mixed periodically using special windrow turning machines.
  - goals of reducing the TNT concentrations in the mixture to less than 30 µg/g (TNT < 1 µg/g after 12-40 days). Reduction in the TNT concentration was due to a combination of biodegradation and/or irreversible sorption of the TNT to the soil mixture.

Why is a Reference/Control Matrix Material Needed?

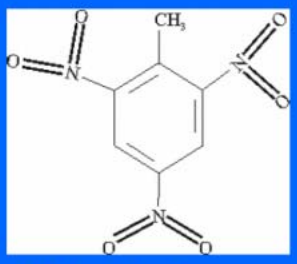
- For method verification: greater probability that the extraction and measurement methods are in control. Control material is also needed for verifying stated method detection limits as well as for use as a soil of known composition for bioremediation studies.
- Matrix versus Spiked: "naturally" incurred species better simulate analyte extraction behavior of a real-world sample (spiked analytes much easier to extract).

Two Explosives-Contaminated Soils

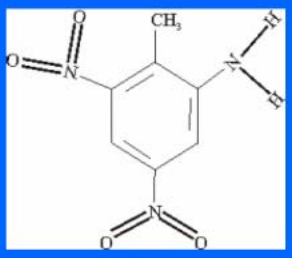
Fortified soil from commercial vendor for lab accreditation using method 8330 or comparable (sonication with acetonitrile, filtering, LC-UV). Results from participating labs (~ 40) are pooled and consensus concentration ranges are reported.

"Virginia Soil": collected by BAB and WAM on 10/30/03 (~100 lbs). Dried outside for ~4 days, then with N_2 for several hours. A sub-sample was sieved and mixed collecting ~1.5 kg of the medium fraction (90 – 212 µm) and ~ 0.7 kg of the fine fraction (≤ 90 µm).

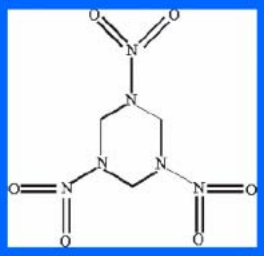
Structures of Energetic Compounds



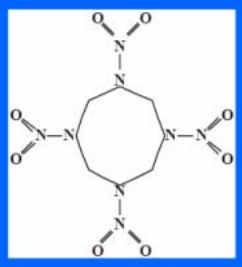
2,4,6-trinitrotoluene



2-amino-4,6-dinitrotoluene



RDX



HMX

Sample Preparation of Soils

- **Weighed samples (0.5 - 0.6 g) into 1 mL and 11 mL extraction vessels (neat and mixed with ~ 2.5 g Hydromatrix).**
- **Pressurized fluid extraction with acetone at 2000 psi and 100 °C. 5 min heat, 5 min static extraction, 90 volume % flush, 90 sec purge, for 3 cycles. Collected sequential extractions for kinetic study. Spiked with labeled energetic standards.**
- **Concentrated extracts under N_2 to approximately 0.5 – 1 mL.**

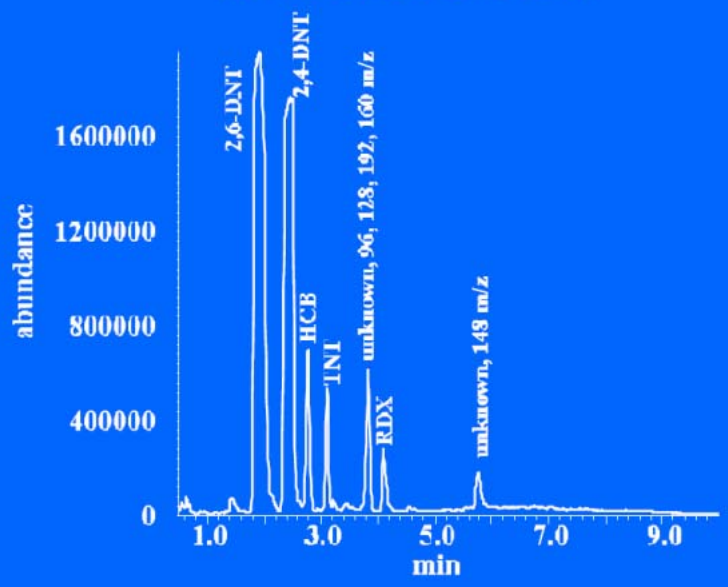
Gas Chromatography/Negative Ion Chemical Ionization Mass Spectrometry (GC/NICI-MS)

- This electron-capture mechanism most favorable Primary mechanism: $MX + e^-_{(thermal)} \Rightarrow MX^{\bullet -}$
- Selective for molecules containing heteroatoms (N, O, P, S, and Si).
- Use isotopically-labeled energetics for quantification, including 2-nitrotoluene-ring-$^{13}C_6$, 4-nitrotoluene-ring-$^{13}C_6$, 2,6-dinitrotoluene-methyl-d_3 2,6-dinitrotoluene-methyl-d_3, $^{13}C_7$-$^{15}N_3$-TNT, $^{13}C_3$-RDX, and $^{13}C_4$-$^{15}N_4$-HMX.

Gas Chromatography/Negative Ion Chemical Ionization Mass Spectrometry (GC/NICI-MS)

- 1 m retention gap, 6 and 12 m x 0.22 mm HT5 GC column, 6-14 mL/min He flow.
- Methane as CI reagent, scan 50-350 m/z.

GC/NICI-MS (TIC) of Virginia Soil, Medium Fraction



Explosives and Related Species in NSI Spiked Soil Sample (PFE and GC/NICI-MS)

(neat packed)

Compound	Mean (µg/g)	SD (µg/g)	%RSD	Spiked µg/g	Acceptance Limits (µg/g)
nitrobenzene	5.11	0.23	4.48	2.79	2.30 – 3.29
2-nitrotoluene	8.52	0.35	4.09	7.60	6.25 – 8.94
3-nitrotoluene	12.69	0.43	3.39	12.20	10.6 – 13.7
4-nitrotoluene	4.97	0.21	4.32	3.75	2.32 – 5.19
1,3-dinitrobenzene	7.71	0.73	4.09	4.33	2.38 – 6.28
2,6-dinitrotoluene	4.28	0.36	8.48	1.98	0.874 – 3.08
2,4-dinitrotoluene	8.22	1.06	12.8	5.67	4.93 – 6.41
2,4,6-trinitrotoluene	6.88	0.29	4.20	6.26	5.74 – 6.78
PETN	4.5	0.7	15.0	4.32	1.96 – 6.67
1,3,5-trinitrobenzene	3.78	0.32	8.37	3.05	1.67 – 4.43
RDX	0.02 – 0.08			0.00	0 - 0
4-amino-2,6-DNT	0.57	0.26	45.9	0.52	0.00 – 3.07
2-amino-4,6-DNT	3.17	0.48	15.1	3.82	2.11 – 5.52
HMX	23	5.7	25	6.12	5.01 – 7.24

Explosives and Related Species in NSI Spiked Soil Sample (PFE and GC/NICI-MS) (w/ Hydromatrix))

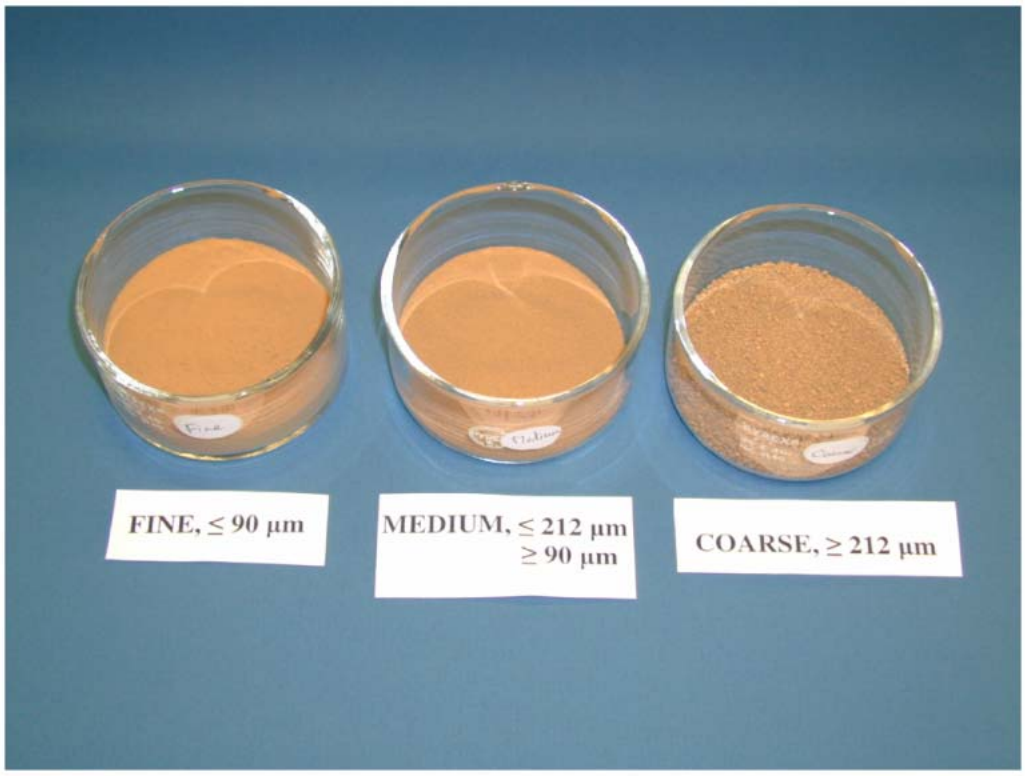
Compound	Mean (µg/g)	SD (µg/g)	%RSD	Spiked µg/g	Acceptance Limits (µg/g)
nitrobenzene	4.97	0.94	18.9	2.79	2.30 – 3.29
2-nitrotoluene	7.34	1.40	19.0	7.60	6.25 – 8.94
3-nitrotoluene	13.3	1.45	10.9	12.20	10.6 – 13.7
4-nitrotoluene	4.09	0.39	9.63	3.75	2.32 – 5.19
1,3-dinitrobenzene	10.15	1.16	11.4	4.33	2.38 – 6.28
2,6-dinitrotoluene	4.35	0.50	11.5	1.98	0.874 – 3.08
2,4-dinitrotoluene	7.58	1.16	15.3	5.67	4.93 – 6.41
2,4,6-trinitrotoluene	4.61	0.60	12.9	6.26	5.74 – 6.78
PETN	7.75	0.38	4.93	4.32	1.96 – 6.67
1,3,5-trinitrobenzene	3.98	0.43	10.8	3.05	1.67 – 4.43
RDX	0.02 – 0.08			0.00	0 - 0
4-amino-2,6-DNT	1.08	0.30	27.6	0.52	0.00 – 3.07
2-amino-4,6-DNT	5.48	0.44	8.02	3.82	2.11 – 5.52
HMX	7.96	0.30	3.72	6.12	5.01 – 7.24

1st Extraction Recoveries of Explosives from NSI Spiked Soil Sample (PFE and GC/NICI-MS) (w/ Hydromatrix))

Compound	Mean (%)	SD (%)
nitrobenzene	99.3	0.3
2-nitrotoluene	98.9	0.3
3-nitrotoluene	99.1	0.1
4-nitrotoluene	98.6	0.2
1,3-dinitrobenzene	98.9	0.2
2,6-dinitrotoluene	96.5	0.6
2,4-dinitrotoluene	90.9	2.1
2,4,6-trinitrotoluene	88.10	0.05
PETN	100	
1,3,5-trinitrobenzene	93.0	0.3
4-amino-2,6-DNT	90	3
2-amino-4,6-DNT	96.7	0.1
HMX	100	0

Candidate Soil Material

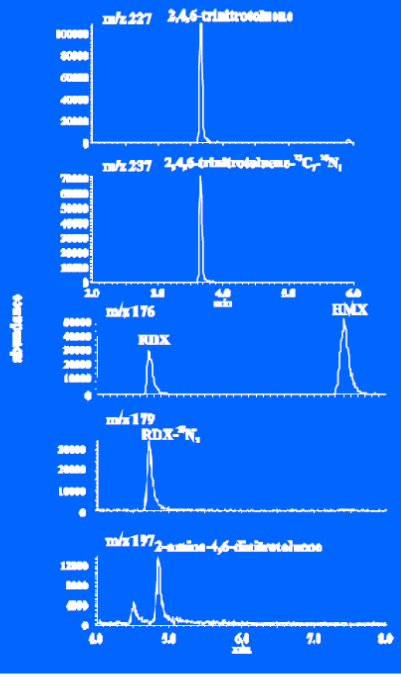
- "Virginia Soil": collected by BAB and WAM on 10/30/03 (~100 lbs). Dried outside for ~4 days, then with N_2 for several hours. A sub-sample was sieved and mixed collecting ~1.5 kg of the medium fraction (90 – 212 µm) and ~ 0.7 kg of the fine fraction (≤ 90 µm).



Irradiation of Virginia Soil (medium fraction)

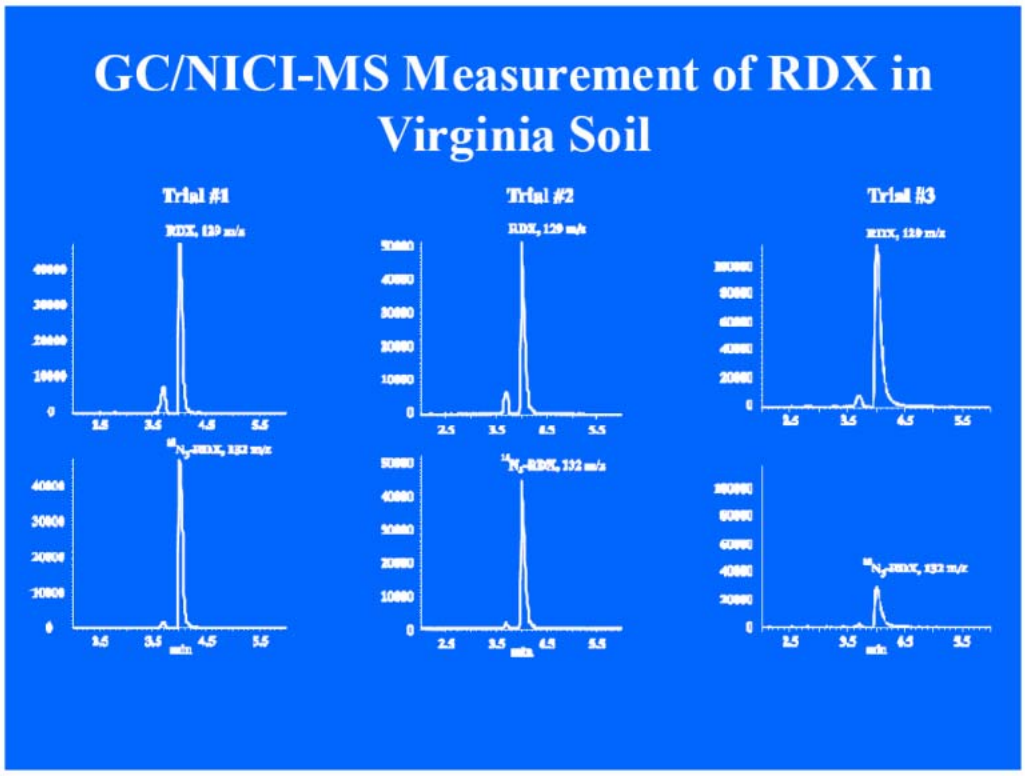
- Date of irradiation: March 11, 2004.
- Source of neutrons: ^{60}Co.
- Absorbed dose measured: 28.2 – 37.0 kilograys (kGy).
- Stored at room temperature in same 1 gallon amber bottle in which it was irradiated.

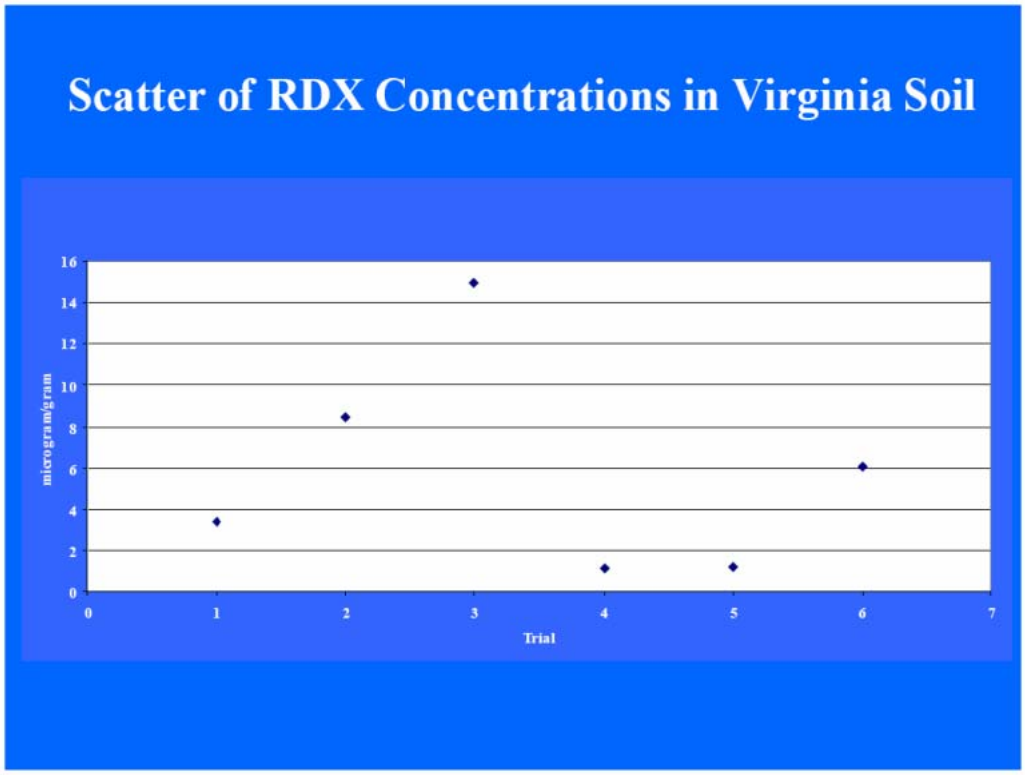
Reconstructed GC/NICI-MS of Soil



Energetic Concentrations in Medium Size Fraction of Virginia Soil (before ^{60}Co irradiation)

Energetic	Mean (µg/g)	SD (µg/g)	RSD, %
4-NT	0.30	0.01	4.0
2,6-DNT	> 150		
2,4-DNT	> 250		
1,3,5-TNB	0.042	0.004	10.4
TNT	1.51	0.07	4.8
RDX	1 - 15		
4-A-2,6-DNT	0.11	0.01	8.7
2-A-4,6-DNT	.043	0.006	15
HMX	0.08	0.05	60


GC/NICI-MS Measurement of RDX in Virginia Soil
Trial #1
Trial #2
Trial #3


Scatter of RDX Concentrations in Virginia Soil
microgram/gram
Trial
0
2
4
6
8
10
12
14
16
0
1
2
3
4
5
6
7

Energetic Concentrations in Fine Size Fraction of Virginia Soil (before ^{60}Co irradiation)

Energetic	Mean (µg/g)	SD (µg/g)	RSD, %
4-NT	0.47	0.003	6.5
2,6-DNT	> 200		
2,4-DNT	> 350		
1,3,5-TNB	0.041	0.005	11.1
TNT	1.76	0.02	1.3
RDX	3.6	0.7	20
4-A-2,6-DNT	0.08	0.02	23
2-A-4,6-DNT	.052	0.009	18
HMX	0.04	0.01	34

Energetic Concentrations in Medium Size Fraction of Virginia Soil (after ^{60}Co irradiation)

Energetic	Mean (µg/g) t=0	Mean (µg/g) t=3 y
4-NT	0.30 ± 0.01	0.44 ± 0.01
1,3,5-TNB	0.20 ± 0.05	0.07 ± 0.01
TNT	1.38 ± 0.10	0.8 ± 0.1
4-A-2,6-DNT	0.049 ± 0.005	0.15 ± 0.06
2-A-4,6-DNT	0.018 ± 0.001	0.18 ± 0.07

1st Extraction Recoveries of Explosives from NSI and Virginia Soils (PFE and GC/NICI-MS)

(w/ Hydromatrix))

Compound	NSI	Virginia Soil (candidate)
4-nitrotoluene	98.6 ± 0.2	95 ± 1
2,4,6-trinitrotoluene	88.10 ± 0.05	92.2 ± 0.3
4-amino-2,6-DNT	90 ± 3	43 ± 3
2-amino-4,6-DNT	96.7 ± 0.1	49 ± 2

Conclusions

- A PFE and GC/NICI-MS method has been used to measure explosives in an accreditation soil with generally good agreement with consensus values reported by vendor.
- An explosives contaminated soil candidate material is currently under study to investigate the feasibility of offering a naturally incurred material with long-term stability. Material has been thoroughly characterized and will be useful for a controlled study of the stability of energetics in soil.
- Issues with material: very high concentrations of DNTs, low concentrations of HMX and PETN, and RDX heterogeneity.

Future Work

- Refine sample preparation procedure (post-extraction - SPE).
- Continue post-irradiation stability study
- Scale-up processing of material or collect additional soil. Blend with other soils to achieve desired energetic concentrations and soil composition (natural organic composition).

Acknowledgements

Many thanks to Steven Beggs, Don Robinson, Jon Girton, and Joe Kennedy of ATF&E for their cooperation and assistance in obtaining energetics-contaminated soil.

Improved Productivity in Methods 8260, 8270, and 8015 as a Result of the Application of Novel Gas Chromatograph Technology

William Goodman
PerkinElmer, Inc.

ABSTRACT

In environmental laboratories improvements in GC throughput (cycle time reductions) offer an opportunity to reduce analysis time and improve productivity. Demonstrated in this presentation will be the application of new GC oven technology and the resulting cycle time reductions. The GC cycle time reduction will be related to sample throughput in commonly used environmental methods; such as EPA 8260, EPA 8270, and EPA 8015 (DRO).

Methods 8260 and 8270 were chosen not only as a result of their popularity, but also because of the twelve hour "QC Clock" under which they operate. The ability to include additional samples in each clock will provide the laboratory not only improved productivity, but also an increase in the ratio of billable to non-billable GC runs.

Method 8015, an increasingly popular GC FID method, generates low per-sample revenue; as a result a decrease in GC cycle time will again offer an opportunity to improve productivity.

In summary, the intent of this presentation is to demonstrate the application of novel GC oven technology to common environmental methods and exhibit dramatic improvements in both GC cycle time and instrument productivity.

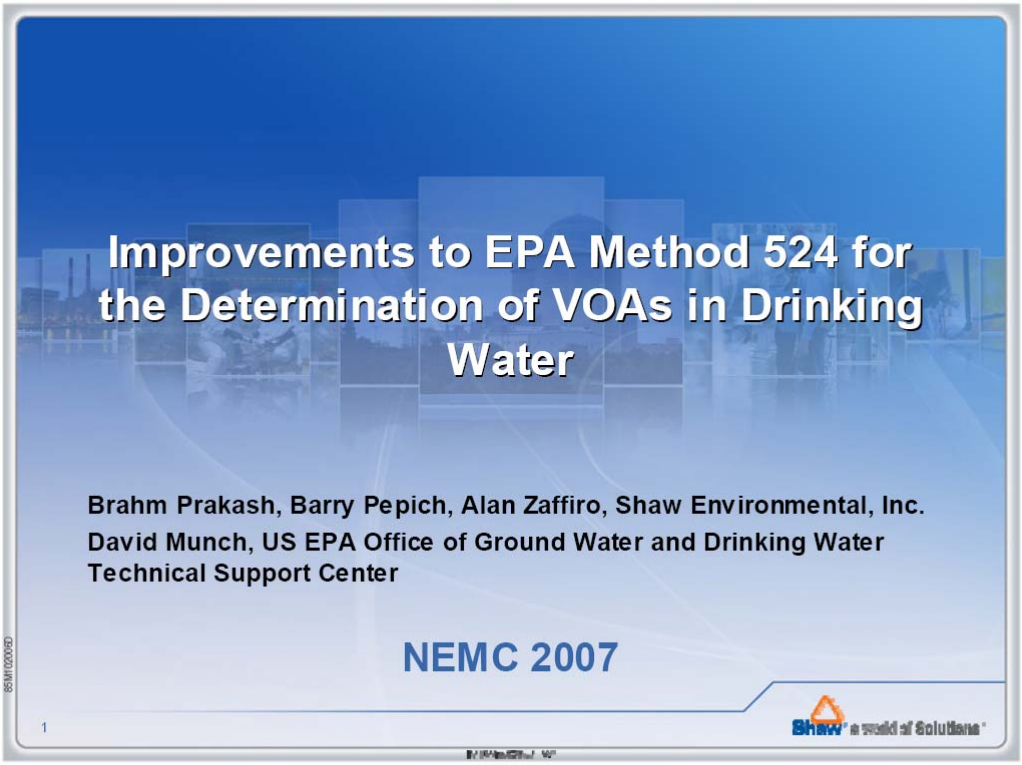
Improvements to USEPA Method 524.2 for the Determination of Volatile Organics

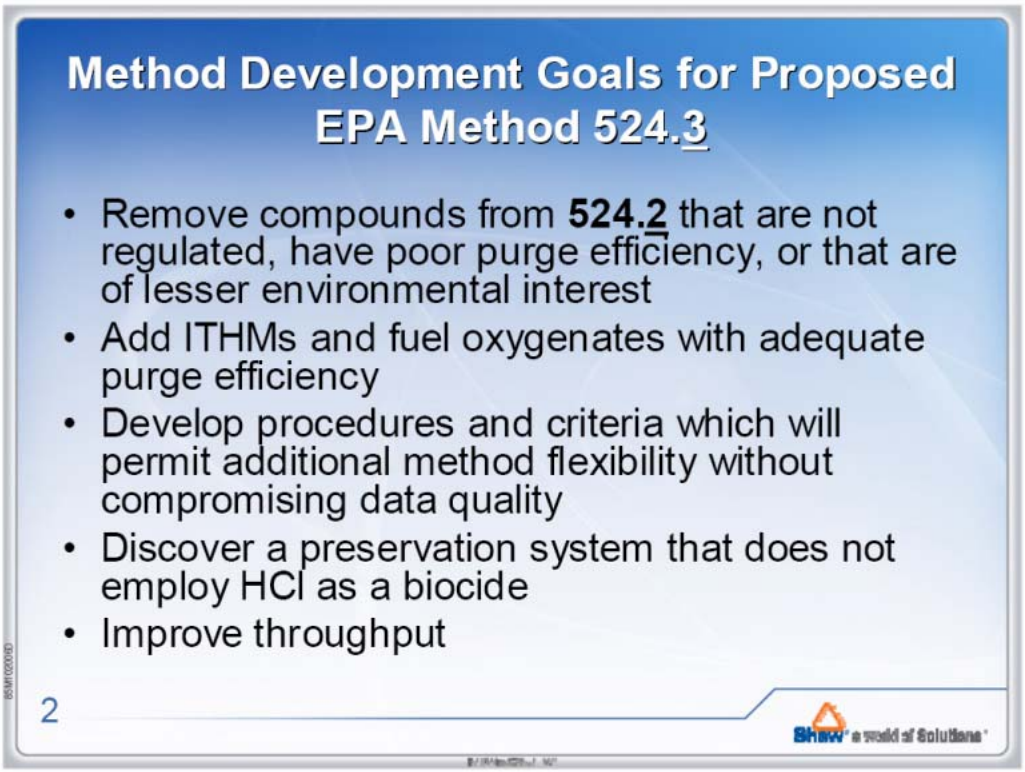
Brahm Prakash
Shaw Environmental, Inc.

ABSTRACT

The U.S. Environmental Protection Agency (EPA) is currently in the process of developing a revision to USEPA Method 524.2. This work is being conducted to revise the current list of analytes to add emerging contaminants such as the iodinated trihalomethanes (ITHMs) and fuel oxygenates. Additional goals for revising the method include: (i) developing criteria that will permit laboratories to modify currently prescriptive portions of the method while maintaining data quality, (ii) evaluating tandem purge-and-trap concentrators interfaced to a single gas chromatograph to increase sample throughput, and (iii) developing a preservation scheme that does not employ hydrochloric acid (HCl).

Purge efficiency data from studies that were conducted using the new internal standards and historical occurrence data were used to eliminate some of the current targets from Method 524.2. Appropriate ITHMs and fuel oxygenates that have acceptable purge efficiencies and method performance may be added. Initial storage stability studies demonstrated that the ITHMs were unstable under the acidic sample storage conditions employed in Method 524.2. However, they exhibit acceptable stability in a pH range of 7 to 9, and they have adequate storage stability in chlorinated waters preserved with sodium thiosulfate. Maleic acid, a solid organic acid, has also been found to yield acceptable ITHM stability even at low pH. Maleic acid in combination with ascorbic acid, which removes free available chlorine, is currently being pursued as the preservation system for the entire method target list. The presentation will summarize all method performance data available at the time of the conference and will outline the remaining objectives that must be accomplished prior to publication of the revised method.


Improvements to EPA Method 524 for the Determination of VOAs in Drinking Water
Brahm Prakash, Barry Pepich, Alan Zaffiro, Shaw Environmental, Inc.
David Munch, US EPA Office of Ground Water and Drinking Water Technical Support Center
NEMC 2007
1


Method Development Goals for Proposed EPA Method 524.3
• Remove compounds from 524.2 that are not regulated, have poor purge efficiency, or that are of lesser environmental interest
• Add ITHMs and fuel oxygenates with adequate purge efficiency
• Develop procedures and criteria which will permit additional method flexibility without compromising data quality
• Discover a preservation system that does not employ HCl as a biocide
• Improve throughput
2

Presentation Overview

- **524.2** to **524.3** comparison
- Instrumentation and GC columns
- Proposed target list
  - Deletions and additions
- Purge efficiency and overall efficiency studies
- New preservation system
- Parameter variation studies
- Remaining tasks

3

Method Comparison

524.2	524.3 (proposed)
• 0.32 to 0.75 mm i.d. columns	• 0.18 to 0.25 mm i.d. columns
• Cryogenic interface; no split; jet separator to MS	• Split injection
• 5 or 25-mL purge volume	• 5-mL purge volume
• Trap: Tenax™ – Silica Gel – Charcoal (No. 3)	• Any trap that meets method criteria
• Single concentrator	• Tandem concentrators
• 1 internal standard – fluorobenzene	• 3 internal standards – 1,4-difluorobenzene – chlorobenzene-d_5 – 1,4-difluorobenzene-d_4

4

Method Comparison (Cont.)

524.2	524.3 (proposed)
• 2 Surrogates – 4-bromofluorobenzene – 1,2-dichlorobenzene-d_4	• 3 Surrogates – MTBE-d_3 – 4-bromofluorobenzene – 1,2-dichlorobenzene-d_4
• Preservation: HCl + ascorbic acid, pH < 2	• Preservation: maleic acid + ascorbic acid, pH ~ 2
• BFB 12-hour tune criteria	• BFB w/each initial calibration
• No dry purge	• Dry purge allowed
• Water management not mentioned	• Options allowed

5

Shaw a world of Solutions

Columns and Split Ratios Evaluated

- 0.18-mm i.d. VOA columns with split ratios of 40:1 and 80:1
- 0.25-mm i.d. VOA columns with split ratios of 20:1, 25:1, 35:1, and 40:1
- Evaluation Criteria
  - Precision
  - Peak shape and signal-to-noise ratio
  - Detection limit estimates

6

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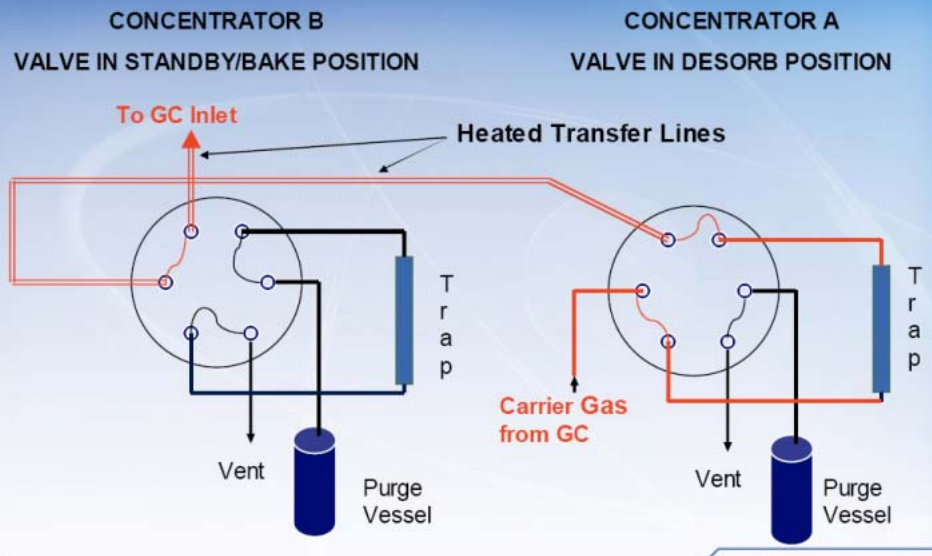
Columns and Split Ratios Selected for Method Development Activities

- 0.25-mm i.d. column
- 30:1 split ratio
- 1-mm i.d. inlet liner
- 45 ^{0}C GC start temperature
- All compounds eluted within 16 minutes
- 19-minute cycle time for tandem concentrators
- 30-minute cycle time for single concentrator

7

Tandem Concentrator Operation



8

Purge and Trap Conditions for Method Development Activities

- **Concentrator A with water management system (MCM)**
  - Purge temperature: 40 ^{0}C
  - Purge volume: 440 mL
  - Purge Flow: 40 mL/min
  - Desorb time: 1 minute
  - Desorb temp. VOCARB trap: 240 ^{0}C
  - Desorb temp. 3-phase trap:190 ^{0}C
  - Dry Purge volume: 80 mL
  - MCM temperature during desorb: 30 ^{0}C
  - Calibration: procedural w/preservatives
- **Concentrator B without water management system**
  - Purge temperature: Ambient
  - Purge volume: 440 mL
  - Purge Flow: 40 mL/min
  - Desorb time: 1 minute
  - Desorb temp. VOCARB trap: 260 ^{0}C
  - Desorb temp. 3-phase trap:190 ^{0}C
  - Dry Purge volume: 200 mL
  - MCM bypased
  - Calibration: procedural w/preservatives

9

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Proposed Deletions from 524.2 Target List and Purge Efficiencies at 35 ^{0}C and 60 ^{0}C (Reagent Water)

Analyte	Purge Efficiency, % (RSD, n=3) 35 ^{0}C	60 ^{0}C	Justification
acetone	23 (14)	65 (9.8)	non-carcinogenic
acrylonitrile	30 (19)	93 (9.1)	poor response, probable carcinogen
2-butanone	20 (12)	71 (17)	non-carcinogenic
chloroacetonitrile	8.3 (34)	27 (24)	purge efficiency, non-carcinogenic
chloroethane	170 (9.0)	170 (12)	non-carcinogenic, water and methanol interference
trans-1,4-dichloro-2-butene	56 (9.6)	100 (5.5)	non-carcinogenic
1,1-dichloropropanone	23 (12)	90 (3.9)	non-carcinogenic
2-hexanone	33 (12)	110 (7.5)	non-carcinogenic
methacrylonitrile	47 (13)	120 (3.4)	non-carcinogenic
methylacrylate	48 (8.2)	110 (12)	non-carcinogenic
methylmethacrylate	60 (6.8)	110 (5.5)	non-carcinogenic
4-methyl-2-pentanone	43 (12)	110 (5.1)	non-carcinogenic
nitrobenzene	9.4 (36)	36 (23)	purge efficiency, non-carcinogenic
2-nitropropane	30 (12)	98 (7.4)	poor response, possibly carcinogenic
proprionitrile	17 (9.9)	54 (7.3)	purge efficiency, non-carcinogenic

10

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Method 524.3 Proposed Additions to Target List and Observed Purge Efficiencies at 35 °C and 60 °C (Reagent Water)

Analyte	Purge Efficiency, % (RSD, n=3) 35 °C	60 °C	Justification
bromodiiodomethane	41 (16)	78 (7.4)	potential disinfection byproduct
bromochloroiodomethane	86 (4.2)	100 (0.3)	potential disinfection byproduct
chlorodiiodomethane	63 (7.6)	100 (2.6)	potential disinfection byproduct
dibromoiodomethane	67 (3.3)	100 (2.0)	potential disinfection byproduct
dichloroiodomethane	94 (2.6)	100 (3.5)	potential disinfection byproduct
diisopropyl ether (DIPE)	94 (2.6)	96 (3.3)	reformulated gasoline additive
iodoform	28 (16)	56 (9.3)	potential disinfection byproduct
methyl acetate	44 (11)	83 (3.0)	breakdown product of MTBE [a] (microcosm studies)
t- amyl ethyl ether (TAEE)	96 (2.9)	96 4.1)	reformulated gasoline additive
t- amyl methyl ether (TAME)	110 (1.6)	100 (1.7)	reformulated gasoline additive
t- butyl alcohol (TBA)	6.5 (24)	22 (6.5)	breakdown product of MTBE [a]
t- butyl ethyl ether (ETBE)	100 (1.1)	100 (3.8)	reformulated gasoline additive

a. MTBE = methyl-t-butyl ether

11

Compounds Evaluated and Rejected

- Ethanol (ambient purge efficiency in reagent water = 7.2%)
- Isopropyl alcohol (5.7%)
- t-Butyl formate (0%)
- t-Amyl alcohol (6.9%)

Note: t-butyl alcohol (6.3%) retained with elevated MRL due to environmental relevance

12

Purge Efficiency and Overall Efficiency Measurements

- Investigated for use as a potential demonstration of capability tool to allow flexibility for the selection of P&T conditions

Purge efficiency (PE) = extraction efficiency from the aqueous sample at a given temperature, purge volume, sample volume, and electrolyte composition

Overall Efficiency (OE) = overall analyte recovery including PE, desorb efficiency, and transfer efficiency

13

Purge Efficiency Experimental Design

- Calibration
  - Installed injection port in heated mount above purge vessel (90 ^{0}C)
  - Purged blank plus internal standards and surrogates including preservative
  - 1 uL methanol containing 100 ng all targets injected into port in mount at beginning of purge cycle using a 1-uL, plunger-in-needle syringe
- Analytical Sequence
  - Alternated calibration injections with 20 ug/L purged standards (1 uL to 5 mL H_2O using the same syringe)
  - 5 replicates each

14

Overall Efficiency Experimental Design

- Calibration
  - Installed 4-mm single goose neck GC inlet liner w/glass wool plug, 150 ^{0}C
  - Purged blank plus internal standards and surrogates including preservatives
  - 1 uL methanol containing 100 ng all targets injected into GC inlet at beginning of desorb cycle using 1-uL, plunger-in-needle syringe
- Analysis Sequence
  - Alternated GC inlet injections with 20 ug/L purged standards (1-uL to 5 mL H_2O using the same syringe)
  - 5 replicates each

15

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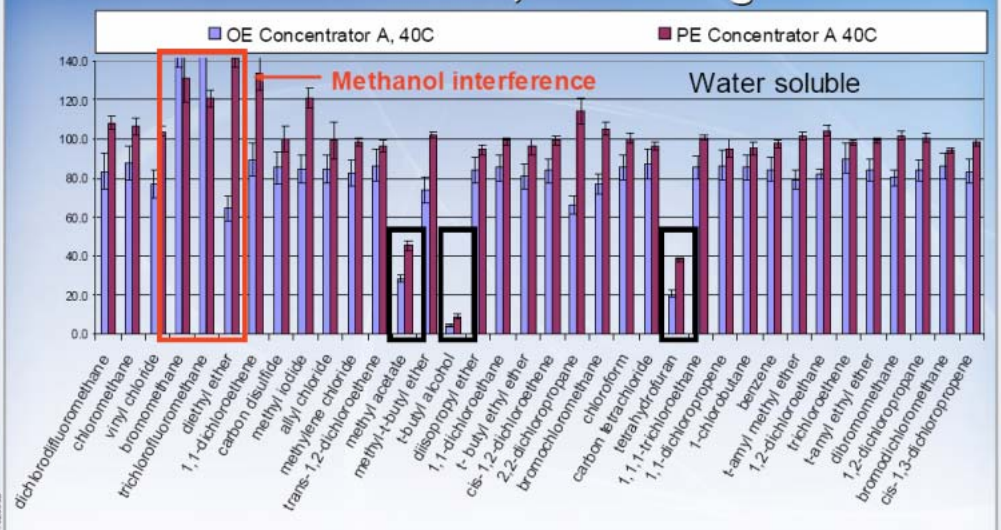
Comparison OE to PE (with preservative) Concentrator A, IS #1 Targets



16

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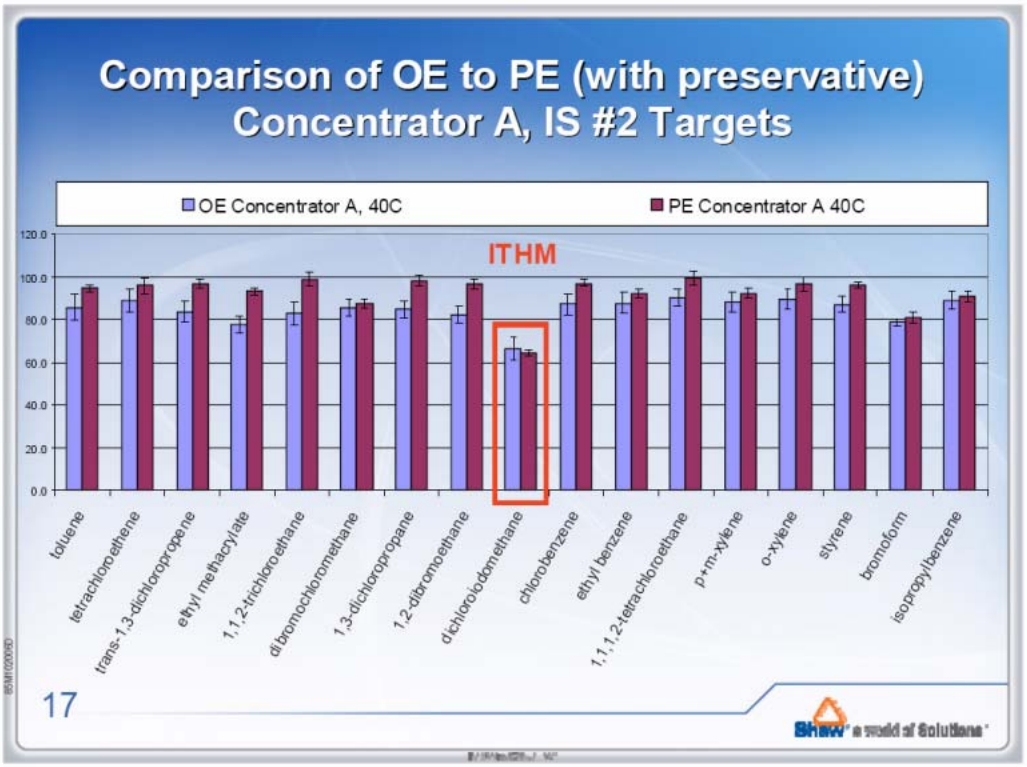
Comparison of OE to PE (with preservative)
Concentrator A, IS #2 Targets
OE Concentrator A, 40C
PE Concentrator A 40C
ITHM
120.0
100.0
80.0
60.0
40.0
20.0
0.0
toluene
tetrachloroethene
trans-1,3-dichloropropene
ethyl methacrylate
1,1,2-trichloroethane
dibromochloromethane
1,3-dichloropropane
1,2-dibromoethane
dichloroiodomethane
chlorobenzene
ethyl benzene
1,1,1,2-tetrachloroethane
p+m-xylene
o-xylene
styrene
bromoform
isopropylbenzene
17
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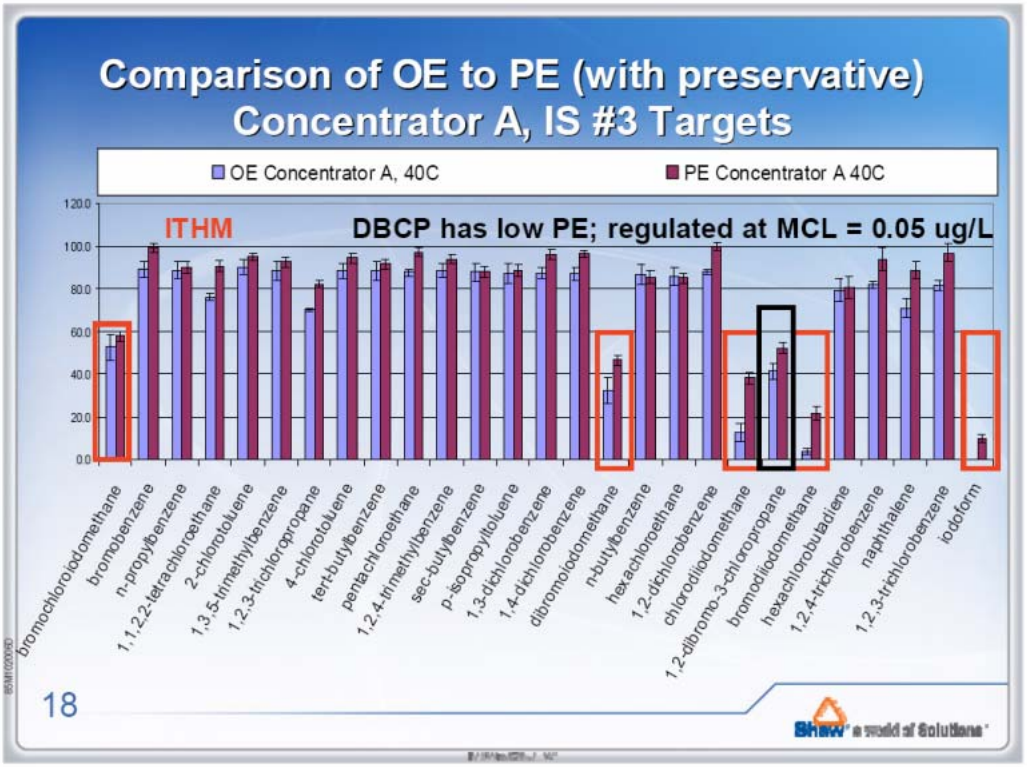
Comparison of OE to PE (with preservative)
Concentrator A, IS #3 Targets
OE Concentrator A, 40C
PE Concentrator A 40C
ITHM
DBCP has low PE; regulated at MCL = 0.05 ug/L
120.0
100.0
80.0
60.0
40.0
20.0
0.0
bromochloroiodomethane
bromobenzene
n-propylbenzene
1,1,2,2-tetrachloroethane
2-chlorotoluene
1,3,5-trimethylbenzene
1,2,3-trichloropropane
4-chlorotoluene
tert-butylbenzene
pentachloroethane
1,2,4-trimethylbenzene
sec-butylbenzene
p-isopropyltoluene
1,3-dichlorobenzene
1,4-dichlorobenzene
dibromoiodomethane
n-butylbenzene
hexachloroethane
1,2-dichlorobenzene
chlorodiiodomethane
1,2-dibromo-3-chloropropane
bromodiiodomethane
hexachlorobutadiene
1,2,4-trichlorobenzene
naphthalene
1,2,3-trichlorobenzene
iodoform
18
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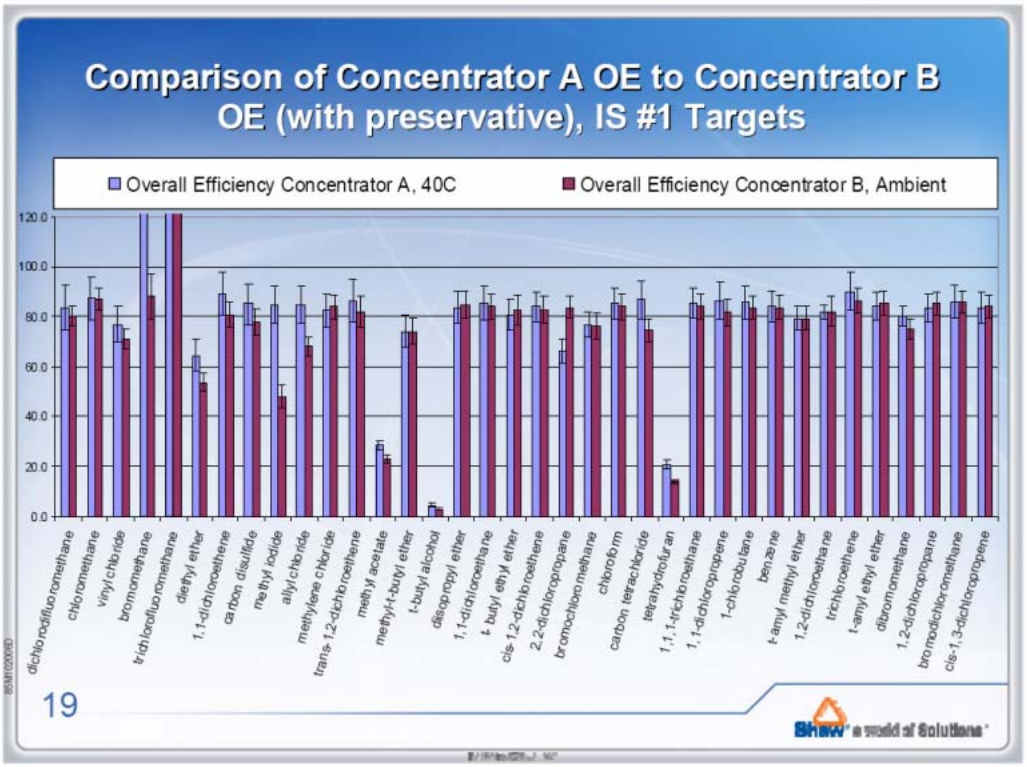
Comparison of Concentrator A OE to Concentrator B OE (with preservative), IS #1 Targets
Overall Efficiency Concentrator A, 40C
Overall Efficiency Concentrator B, Ambient
120.0
100.0
80.0
60.0
40.0
20.0
0.0
dichlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
trichlorofluoromethane
diethyl ether
1,1-dichloroethene
carbon disulfide
methyl iodide
allyl chloride
methylene chloride
trans-1,2-dichloroethene
methyl acetate
methyl-t-butyl ether
t-butyl alcohol
diisopropyl ether
1,1-dichloroethane
t- butyl ethyl ether
cis-1,2-dichloroethene
2,2-dichloropropane
bromochloromethane
chloroform
carbon tetrachloride
tetrahydrofuran
1,1,1-trichloroethane
1,1-dichloropropene
1-chlorobutane
benzene
t-amyl methyl ether
1,2-dichloroethane
trichloroethene
t-amyl ethyl ether
dibromomethane
1,2-dichloropropane
bromodichloromethane
cis-1,3-dichloropropene
19
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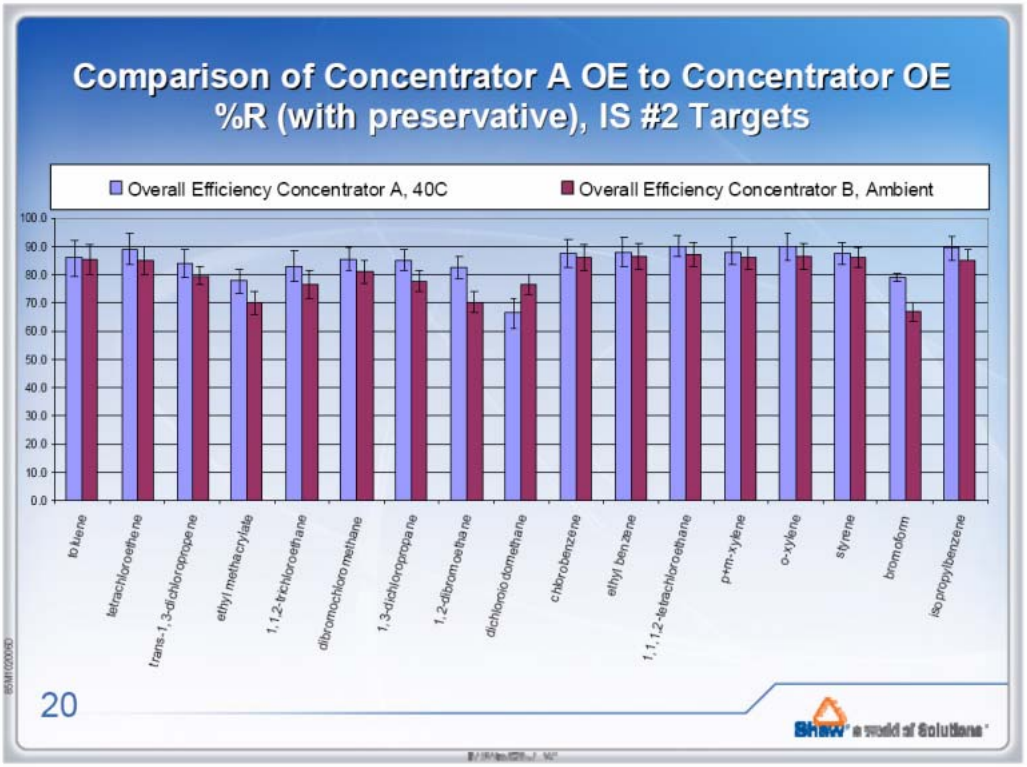
Comparison of Concentrator A OE to Concentrator OE %R (with preservative), IS #2 Targets
Overall Efficiency Concentrator A, 40C
Overall Efficiency Concentrator B, Ambient
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
toluene
tetrachloroethene
trans-1,3-dichloropropene
ethyl methacrylate
1,1,2-trichloroethane
dibromochloromethane
1,3-dichloropropane
1,2-dibromoethane
dichloroiodomethane
chlorobenzene
ethyl benzene
1,1,1,2-tetrachloroethane
p+m-xylene
o-xylene
styrene
bromoform
isopropylbenzene
20
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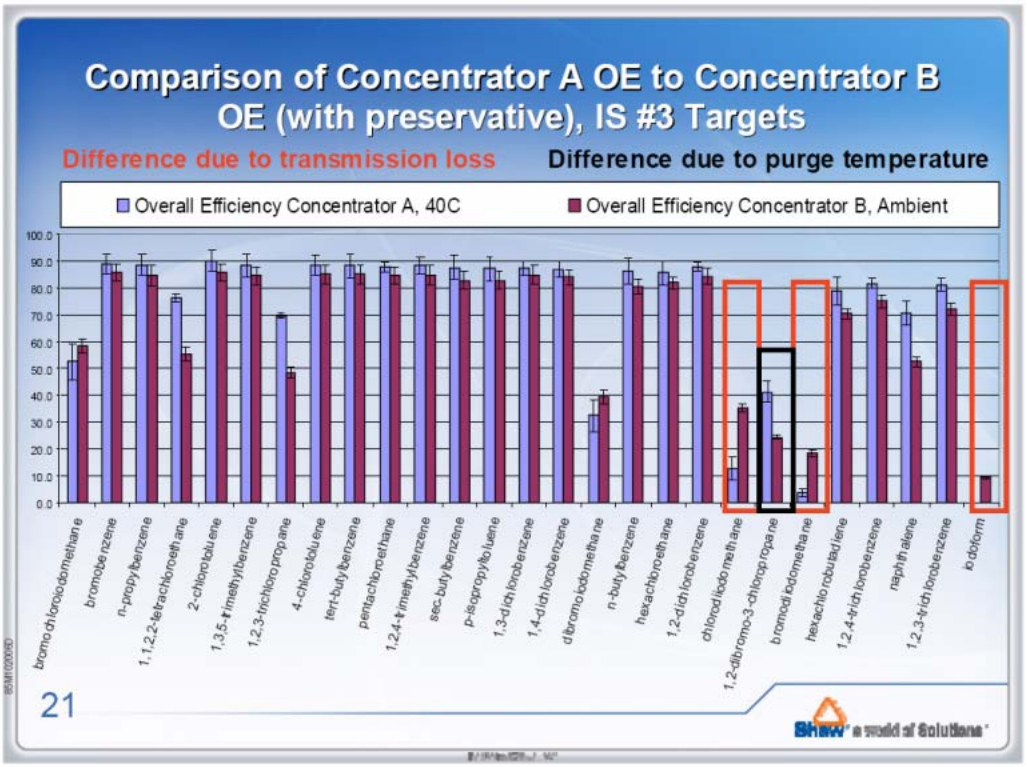
Comparison of Concentrator A OE to Concentrator B OE (with preservative), IS #3 Targets
Difference due to transmission loss
Difference due to purge temperature
Overall Efficiency Concentrator A, 40C
Overall Efficiency Concentrator B, Ambient
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
bromochloroiodomethane
bromobenzene
n-propylbenzene
1,1,2,2-tetrachloroethane
2-chlorotoluene
1,3,5-trimethylbenzene
1,2,3-trichloropropane
4-chlorotoluene
tert-butylbenzene
pentachloroethane
1,2,4-trimethylbenzene
sec-butylbenzene
p-isopropyltoluene
1,3-dichlorobenzene
1,4-dichlorobenzene
dibromoiodomethane
n-butylbenzene
hexachloroethane
1,2-dichlorobenzene
chlorodiiodomethane
1,2-dibromo-3-chloropropane
bromodiiodomethane
hexachlorobutadiene
1,2,4-trichlorobenzene
naphthalene
1,2,3-trichlorobenzene
iodoform
21
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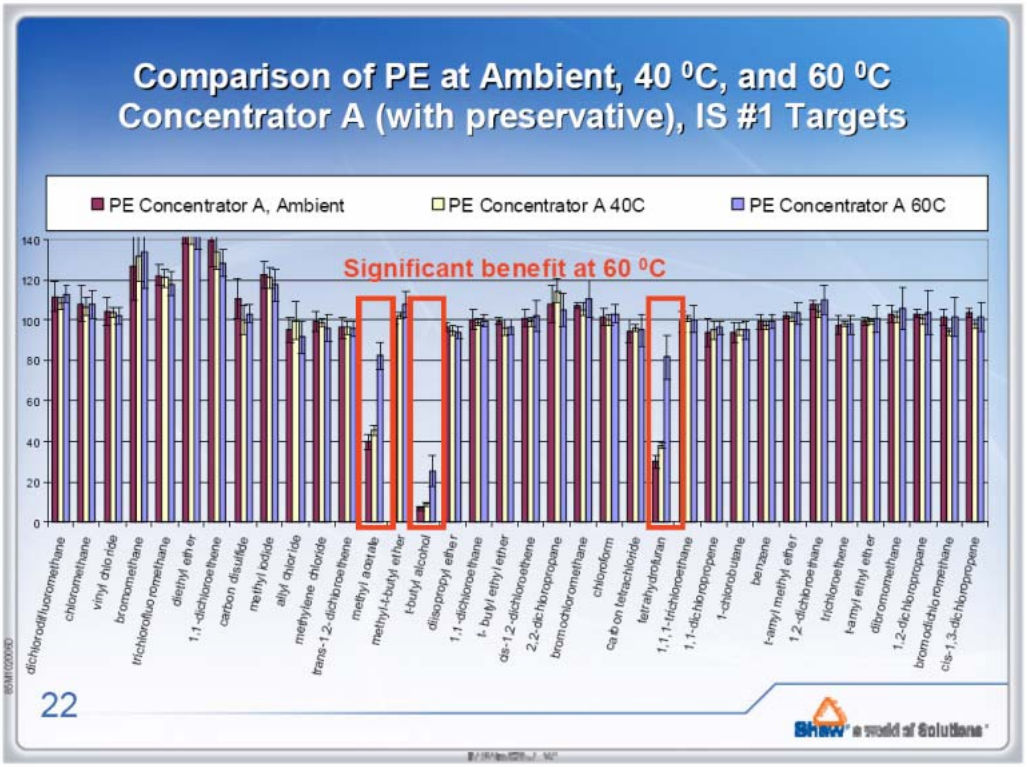
Comparison of PE at Ambient, 40 °C, and 60 °C Concentrator A (with preservative), IS #1 Targets
PE Concentrator A, Ambient
PE Concentrator A 40C
PE Concentrator A 60C
Significant benefit at 60 °C
140
120
100
80
60
40
20
0
dichlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
trichlorofluoromethane
diethyl ether
1,1-dichloroethene
carbon disulfide
methyl iodide
allyl chloride
methylene chloride
trans-1,2-dichloroethene
methyl acetate
methyl-t-butyl ether
t-butyl alcohol
diisopropyl ether
1,1-dichloroethane
t- butyl ethyl ether
cis-1,2-dichloroethene
2,2-dichloropropane
bromochloromethane
chloroform
carbon tetrachloride
tetrahydrofuran
1,1,1-trichloroethane
1,1-dichloropropene
1-chlorobutane
benzene
t-amyl methyl ether
1,2-dichloroethane
trichloroethene
t-amyl ethyl ether
dibromomethane
1,2-dichloropropane
bromodichloromethane
cis-1,3-dichloropropene
22
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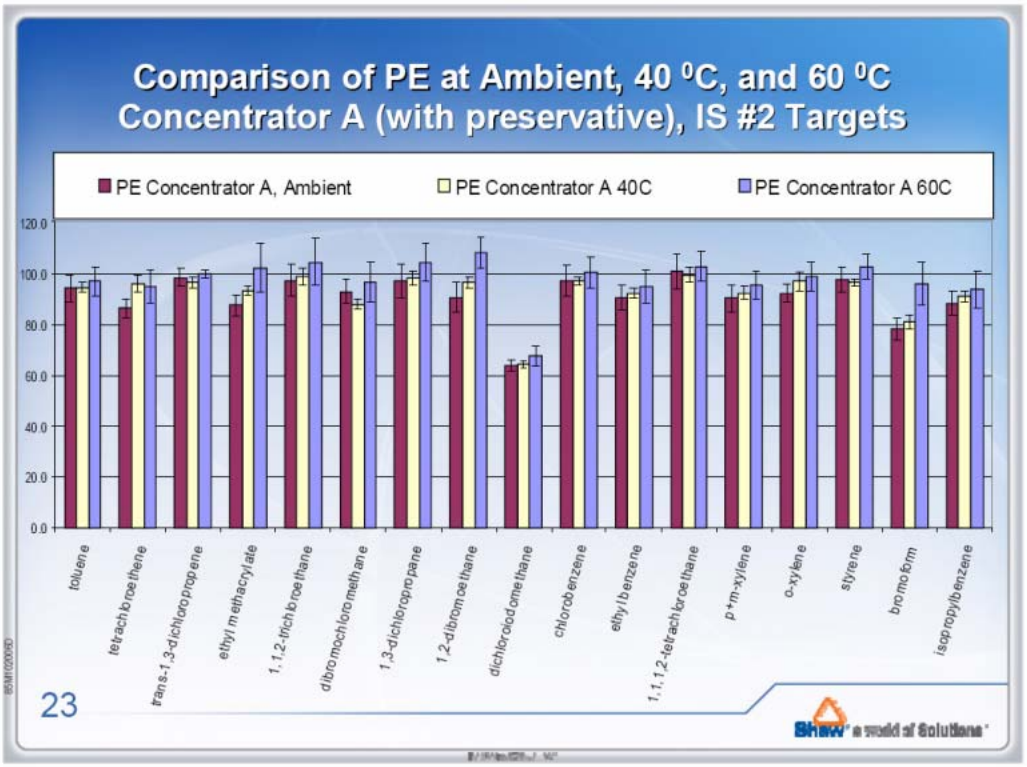
Comparison of PE at Ambient, 40 °C, and 60 °C
Concentrator A (with preservative), IS #2 Targets
PE Concentrator A, Ambient
PE Concentrator A 40C
PE Concentrator A 60C
120.0
100.0
80.0
60.0
40.0
20.0
0.0
toluene
tetrachloroethene
trans-1,3-dichloropropene
ethyl methacrylate
1,1,2-trichloroethane
dibromochloromethane
1,3-dichloropropane
1,2-dibromoethane
dichlorodiodomethane
chlorobenzene
ethylbenzene
1,1,1,2-tetrachloroethane
p+m-xylene
o-xylene
styrene
bromoform
isopropylbenzene
23
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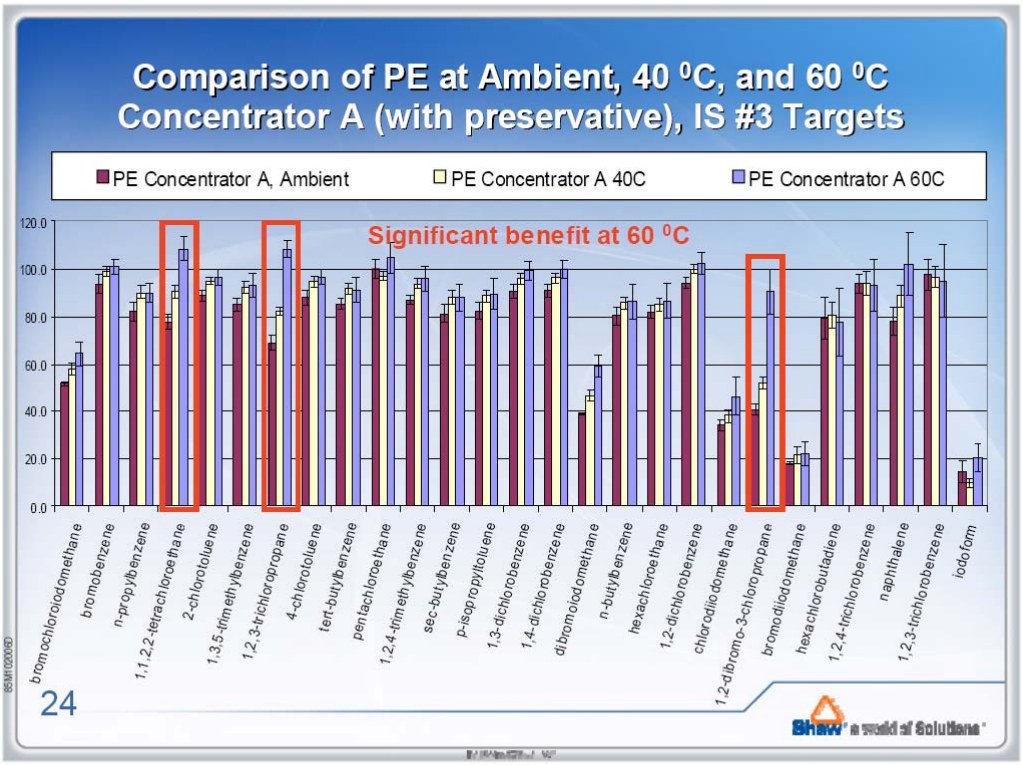
Comparison of PE at Ambient, 40 °C, and 60 °C
Concentrator A (with preservative), IS #3 Targets
PE Concentrator A, Ambient
PE Concentrator A 40C
PE Concentrator A 60C
Significant benefit at 60 °C
120.0
100.0
80.0
60.0
40.0
20.0
0.0
bromochloroiodomethane
bromobenzene
n-propylbenzene
1,1,2,2-tetrachloroethane
2-chlorotoluene
1,3,5-trimethylbenzene
1,2,3-trichloropropane
4-chlorotoluene
tert-butylbenzene
pentachloroethane
1,2,4-trimethylbenzene
sec-butylbenzene
p-isopropyltoluene
1,3-dichlorobenzene
1,4-dichlorobenzene
dibromoiodomethane
n-butylbenzene
hexachloroethane
1,2-dichlorobenzene
chlorodiiodomethane
1,2-dibromo-3-chloropropane
bromodiiodomethane
hexachlorobutadiene
1,2,4-trichlorobenzene
naphthalene
1,2,3-trichlorobenzene
iodoform
24
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Comparison of Average PE's at Ambient, 40 ^{0}C, and 60 ^{0}C for All Targets

	PE Ambient	RSD Ambient (n=5)	PE ** 40 ^{0}C	RSD 40 ^{0}C (n=5)	PE 60 ^{0}C	RSD 60 ^{0}C (n=5)
Average 77 analytes *	87.3	5.3	89.3	3.6	94.0	7.7

* Bromomethane, trichlorofluoromethane, and ethyl ether not included due to methanol bias.
** Recommended by the manufacturer.

25

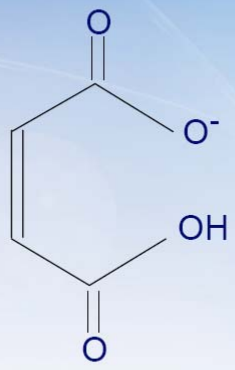
OE and PE Conclusions

- **Abandoned idea of requiring PE or OE measurements in the method because such measurements are technically difficult**
- Increase in PE for water soluble analytes at 60 ^{0}C purge temperature may not be worth the cost (increased RSD and more water)
- Observed significant differences between concentrators, and water management designs for ITHMs
- OE and PE decrease rapidly with iodo substitution
- Iodoform may require elimination from the proposed target list for 524.3

26

Preservation Studies
(Maleic Acid)

- **State:** solid
- **pKa:** Diprotic acid with values of 1.8 and 6.0
- **Application:** 200 mg Maleic acid + 25 mg ascorbic acid to 40-mL VOA vial
- **Action:** lowers pH (antimicrobial); prevents decomposition of acid sensitive targets via chelating (in theory)



Maleic Acid (mono-basic form)

27

Preliminary Storage Stability Study Results for THMs and ITHMs[a] (21 Days Refrigerated)

Target Compound	Ascorbic+HCl pH 2.2 (reagent water) Day 21 %Recovery	%RSD (n=3)	$Na_2S_2O_3$ pH 7.5 (reagent water) Day 21 %Recovery	%RSD (n=3)	Ascorbic+Maleic Acid pH 1.9 (groundwater) Day 21 %Recovery	%RSD (n=3)
Chloroform	89	9.9	98	3.4	106	13
Bromodichloromethane	89	8.1	96	3.1	111	13
Dibromochloromethane	89	5.2	94	2.7	116	11
Dichloroiodomethane	63	10	90	1.7	98	9.0
Bromoform	83	3.9	90	2.2	110	12
Bromochloroiodomethane	58	14	88	1.7	98	8.7
Dibromoiodomethhane	57	15	89	4.6	100	10
Chlorodiiodomethane	39	22	80	3.5	98	10
Bromodiiodomethane	45	20	85	6.7	99	3.9
Iodoform	42	33	76	25	93	16

[a] THM = trihalomethane, ITHM = iodinated-trihalomethane

28

Parameter Variation Studies

- **Purpose:** To identify a set of conditions against which method modifications can be compared in order to ensure acceptable method performance

- **Parameters Investigated (to date)**
  - purge volume
  - purge rate
  - dry purge volume

29

Parameter Variation Studies Experimental Design

- Fortified reagent water plus preservative with 20 ug/L all targets
- Established a reference point at typical P&T conditions (calibration conditions)
  - 440 mL purge volume
  - 40 mL/min flow rate
  - 200 mL dry purge volume Conc. B (80 mL Conc. A)
  - Vendor recommended desorb temperature
- Analyzed each set of conditions in triplicate bracketed by calibration standards at the standard conditions

30

Parameter Variation Studies
Sequence Example (w/ bracketing)

Run No.	Sequence Structure	Example
1	20 ug/L cal	440 mL purge
2	20 ug/L sample	40 mL purge, rep 1
3	20 ug/L sample	40 mL purge, rep 2
4	20 ug/L sample	40 mL purge, rep 3
5	20 ug/L cal	440 mL purge
6	20 ug/L sample	80 mL purge, rep 1
7	20 ug/L sample	80 mL purge, rep 2
8	20 ug/L sample	80 mL purge, rep 3
9	20 ug/L cal	440 mL purge

Sx Avg., Area

Cal. Avg., Area

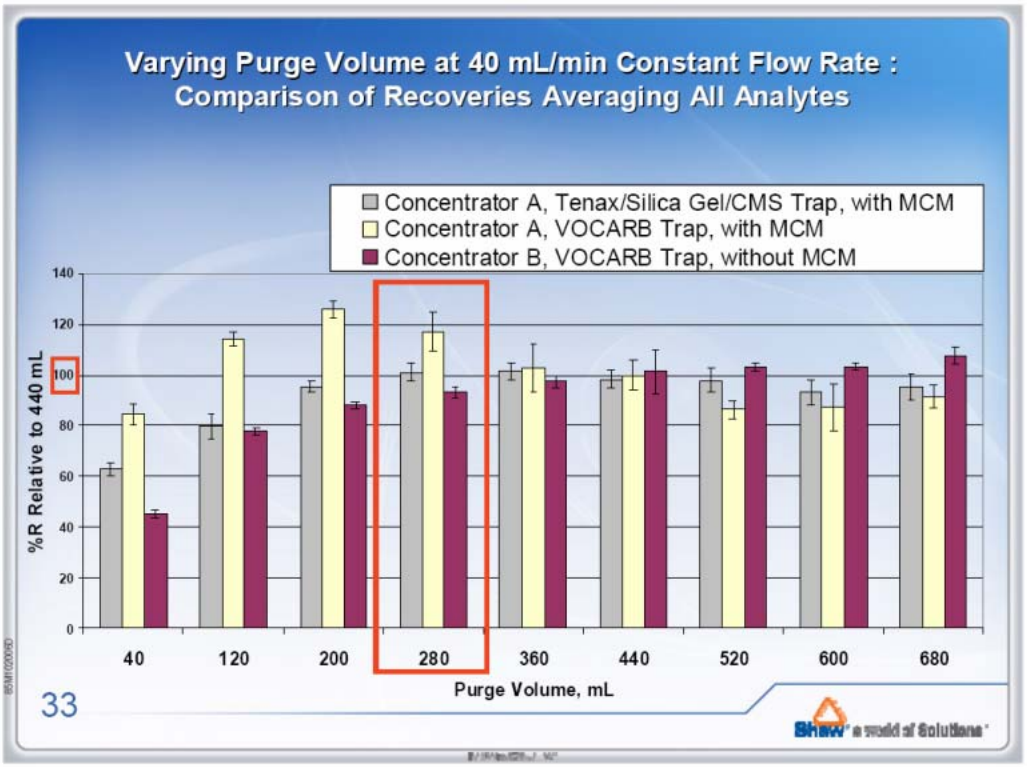
%R = Sample Avg. (n=3) / Calibration Avg. (n=2)

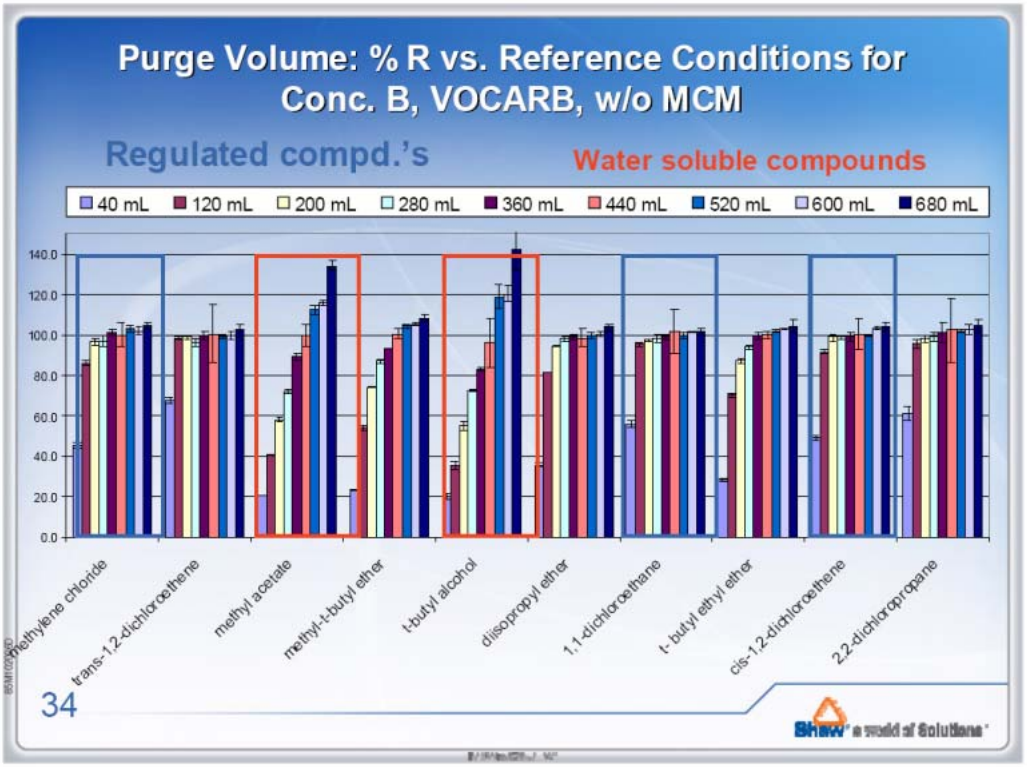
31

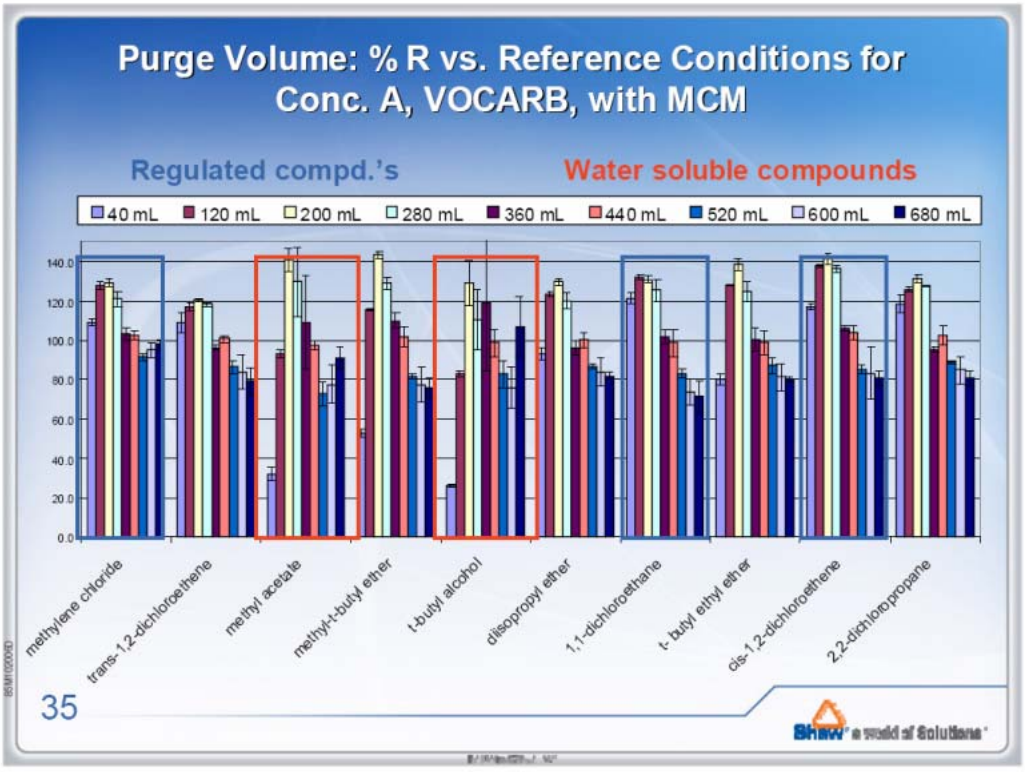
Parameter Studies
Variables Investigated

- 2 concentrators
  - with and without moisture control module (MCM)
- 3 trap designs
  - VOCARB and 3 phase (Tenax™/silica gel/charcoal, Tenax™/silica gel, CMS)
- **Purge volumes:** 40, 120, 200, 280, 360, **440**, 520, 600, 680 mL
- **Flow rates:** 20, **40**, 60, 80, 100, 120, 200 mL/min
- **Dry purge volumes:** 50, 100, 150, **200**, 250, 300, 350, 400, 800 mL
- All studies done in triplicate

32


Varying Purge Volume at 40 mL/min Constant Flow Rate :
Comparison of Recoveries Averaging All Analytes
Concentrator A, Tenax/Silica Gel/CMS Trap, with MCM
Concentrator A, VOCARB Trap, with MCM
Concentrator B, VOCARB Trap, without MCM
%R Relative to 440 mL
140
120
100
80
60
40
20
0
40
120
200
280
360
440
520
600
680
Purge Volume, mL
33


Purge Volume: % R vs. Reference Conditions for
Conc. B, VOCARB, w/o MCM
Regulated compd.'s
Water soluble compounds
40 mL
120 mL
200 mL
280 mL
360 mL
440 mL
520 mL
600 mL
680 mL
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
methylene chloride
trans-1,2-dichloroethene
methyl acetate
methyl-t-butyl ether
t-butyl alcohol
diisopropyl ether
1,1-dichloroethane
t- butyl ethyl ether
cis-1,2-dichloroethene
2,2-dichloropropane
34


Purge Volume: % R vs. Reference Conditions for Conc. A, VOCARB, with MCM
Regulated compd.'s
Water soluble compounds
40 mL
120 mL
200 mL
280 mL
360 mL
440 mL
520 mL
600 mL
680 mL
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
methylene chloride
trans-1,2-dichloroethene
methyl acetate
methyl-t-butyl ether
t-butyl alcohol
diisopropyl ether
1,1-dichloroethane
t- butyl ethyl ether
cis-1,2-dichloroethene
2,2-dichloropropane
35
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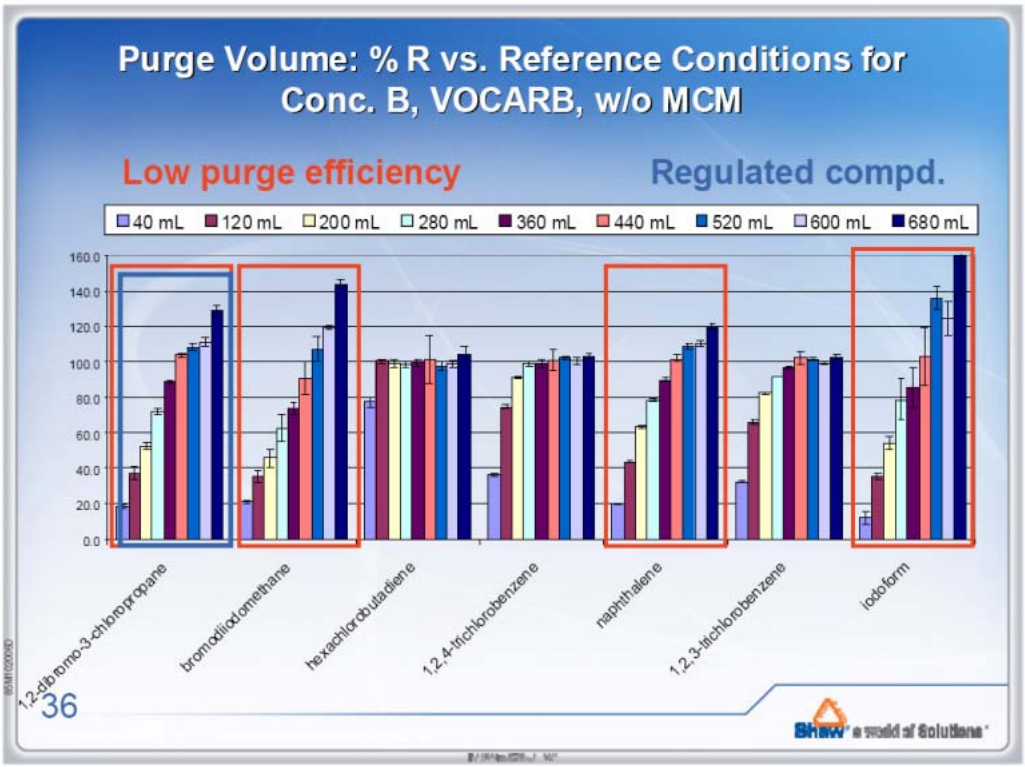
Purge Volume: % R vs. Reference Conditions for Conc. B, VOCARB, w/o MCM
Low purge efficiency
Regulated compd.
40 mL
120 mL
200 mL
280 mL
360 mL
440 mL
520 mL
600 mL
680 mL
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
1,2-dibromo-3-chloropropane
bromodichloromethane
hexachlorobutadiene
1,2,4-trichlorobenzene
naphthalene
1,2,3-trichlorobenzene
iodoform
36
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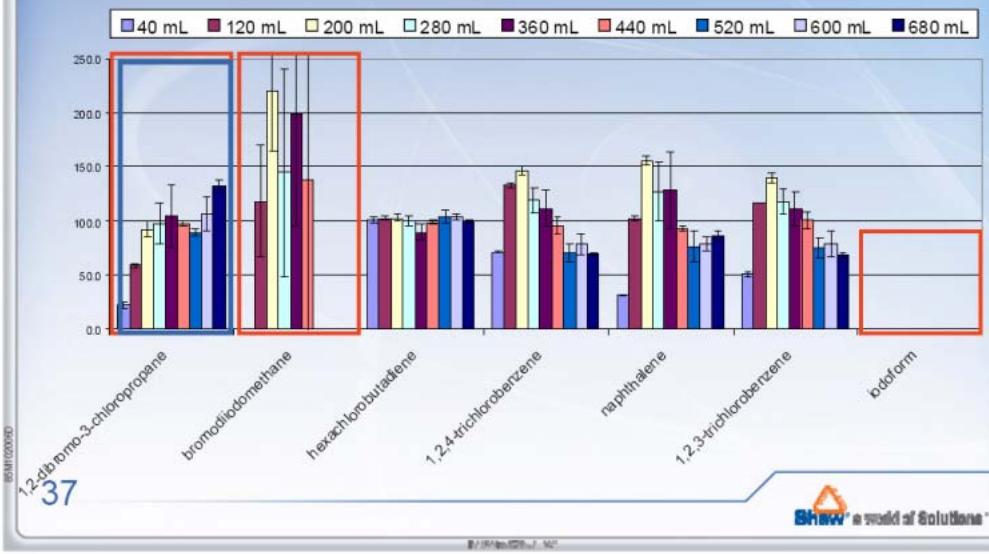
Purge Volume: % R vs. Reference Conditions for Conc. A, VOCARB, with MCM

Low purge efficiency

Regulated compd.



37

Conclusions- Varying Purge Volume

- Purge volume has a large effect on purge efficiency
- 80% of the targets are efficiently purged within 280 mL. Water soluble targets are still increasing after 680 mL
- The use of a MCM and/or breakthrough decreased precision and overall recovery for large purge volumes. This was worse on the trap not recommended by the manufacturer for use with this device.
- The MCM and/or moisture in the lines were not compatible with the anlaysis of idoform and bromodiiodomethane

38

Varying the Purge Flow Rate Studies

- These studies investigated the effect that purge gas flow rate has on PE
  - Rates from 20 mL/min to 200 mL/min were evaluated
  - Only one concentrator could achieve the highest flow rates
  - Standard/reference flow rate was 40 mL/min

39

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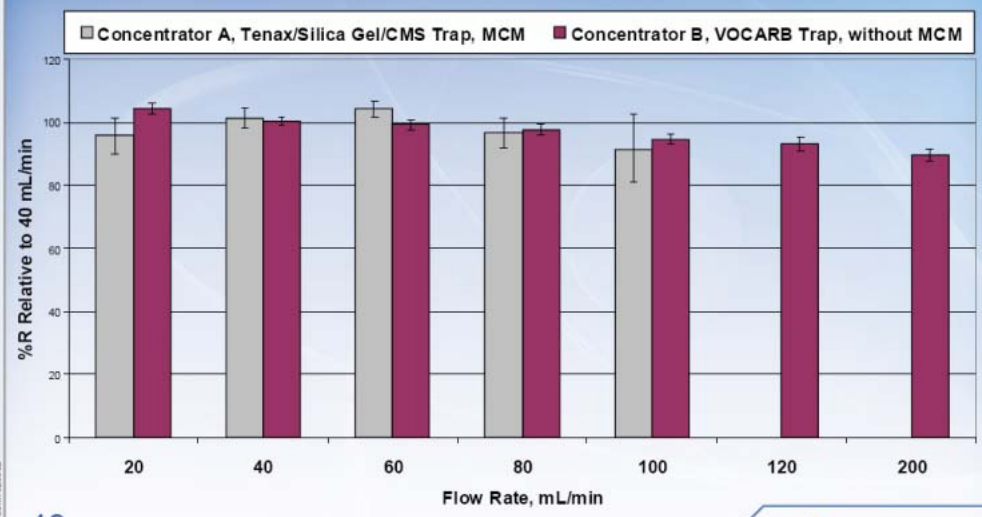
Varying the Purge Flow Rate: Comparison of Average Recoveries for 440-mL Purge Volume



40

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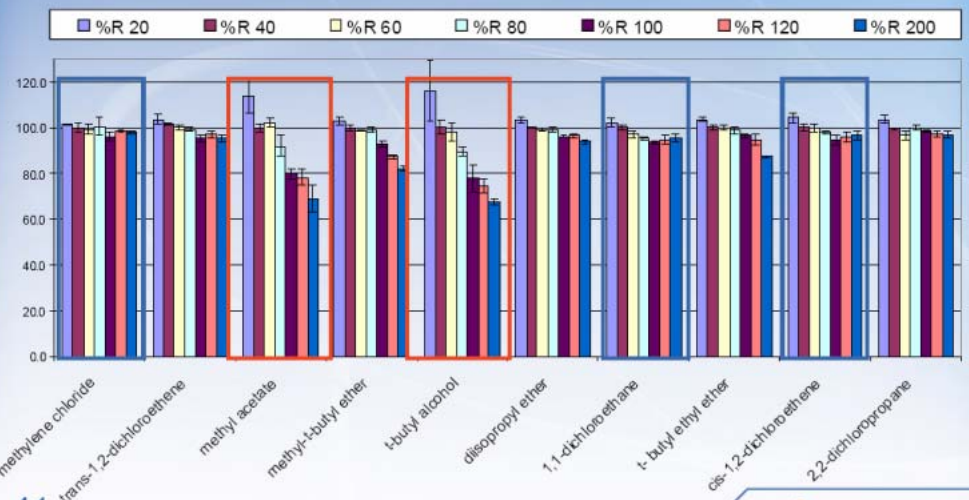
Varying Purge Flow Rate: % R vs. Reference Purge Rate (40 mL/min) for Conc. B, VOCARB, without MCM

Regulated compd.'s Water soluble compounds



41

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Varying the Purge Rate - Summary of Problem Target Compounds

Compounds with Recoveries Less Than 80% Relative to Reference Conditions

Concentrator B, VOCARB, w/o MCM	Concentrator A, 3 phase, with MCM
Methyl acetate	Methyl acetate
t-Butyl alcohol	t-Butyl alcohol
----------	2,2-dichloropropane
Tetrahydrofuran	Tetrahydrofuran
t-Amyl methyl ether	----------
Ethyl methacrylate	----------
Dichloroiodomethane	Dichloroiodomethane
Bromoform *	**Bromoform ***
Bromochloriodomethane	Bromochloriodomethane
1,1,2,2-Tetrachloroethane	1,1,2,2-Tetrachloroethane
1,2,3-Trichlorooopropane	1,2,3-Trichlorooopropane
Dibromoiodomethane	Dibromoiodomethane
Chlorodiiodomethane	Chlorodiiodomethane
1,2-Dibromo-3-chlorpropane *	**1,2-Dibromo-3-chlorpropane ***
Bromodiiodomethane	Bromodiiodomethane
Iodoform	Iodoform

42

* Regulated compounds

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Conclusions - Varying the Purge Rate

- Purge rate had a smaller effect on purge efficiency than purge volume even at very high rates (up to 200 mL/min)
- Compounds with low purging efficiency (higher water solubility) are most affected
- This effect would likely increase as purge volume is decreased (e.g., most compounds are purged at 280 mL; the study used 440 mL)
- Purge rates can probably be increased in moderation

43

Varying the Dry Purge Volume Studies

- These studies investigated the effect of dry purge volume on overall efficiency
  - VOCARB and 3-phase studied even though 3-phase traps are not usually dry purged
  - Standard/reference dry purge volume was 200 mL (concent. B), 80 mL (concent. A)
  - Dry purge volumes ranged from 50 mL to 800 mL
    - breakthrough was expected at high volumes

44

Varying Dry Purge Volume - Problem Target Compounds

Compounds with Recovery Less Than 80% Relative to Reference Condition with Dry Purge Volume of 800 mL

Conc. B, 3 phase Trap, w/o MCM	Conc. B, VOCARB Trap, w/o MCM	Conc. A, VOCARB Trap, w/ MCM
Chloromethane		
	Bromomethane	Bromomethane
Trichlorofluoromethane		
Carbon disulfide		
	Methyl iodide	Methyl iodide
Allyl chloride	Allyl chloride	Allyl chloride
	2,2-dichloropropane	
	Carbon tetrachloride	

45

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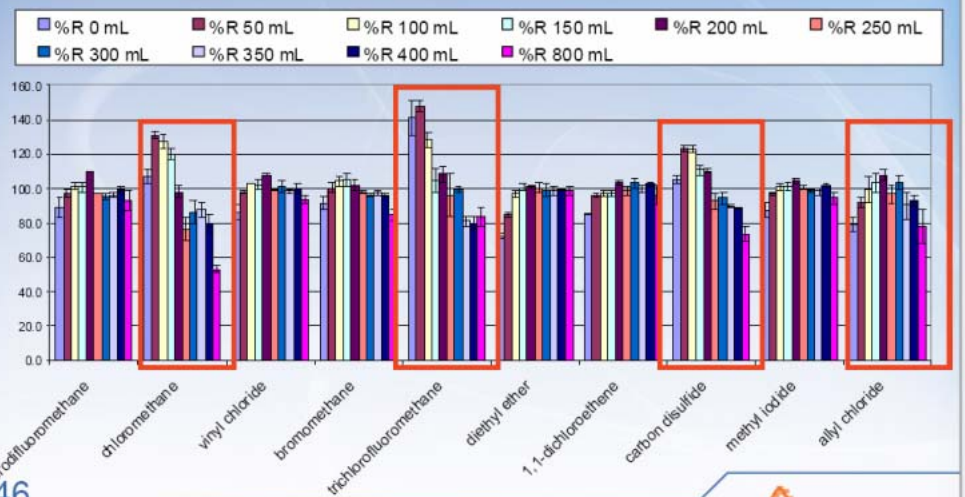
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. B, 3-Phase Trap, without MCM

Problem analytes – breakthrough



46

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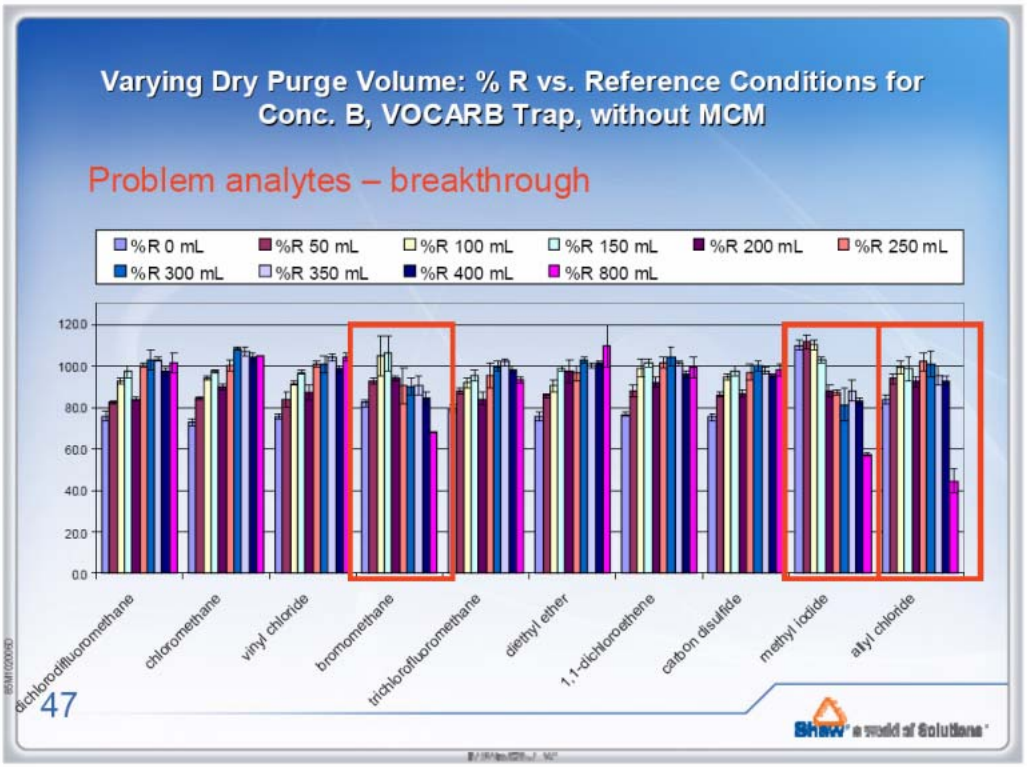
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. B, VOCARB Trap, without MCM
Problem analytes – breakthrough
%R 0 mL
%R 50 mL
%R 100 mL
%R 150 mL
%R 200 mL
%R 250 mL
%R 300 mL
%R 350 mL
%R 400 mL
%R 800 mL
1200
1000
800
600
400
200
0.0
dichlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
trichlorofluoromethane
diethyl ether
1,1-dichloroethene
carbon disulfide
methyl iodide
allyl chloride
47
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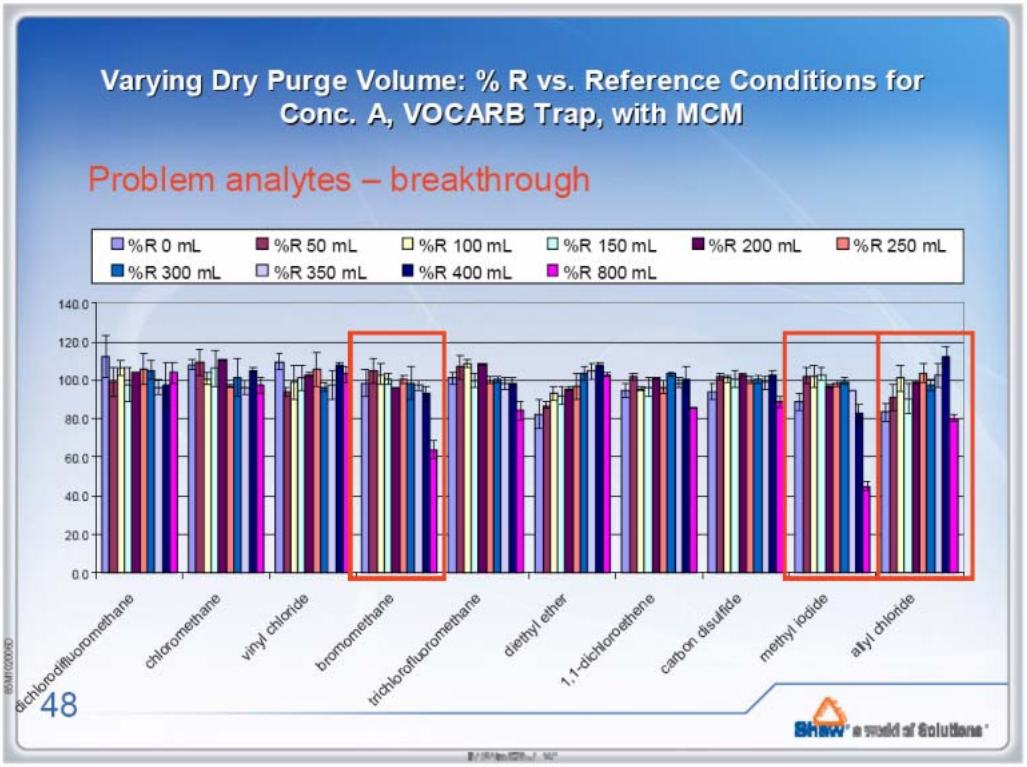
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. A, VOCARB Trap, with MCM
Problem analytes – breakthrough
%R 0 mL
%R 50 mL
%R 100 mL
%R 150 mL
%R 200 mL
%R 250 mL
%R 300 mL
%R 350 mL
%R 400 mL
%R 800 mL
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
dichlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
trichlorofluoromethane
diethyl ether
1,1-dichloroethene
carbon disulfide
methyl iodide
allyl chloride
48
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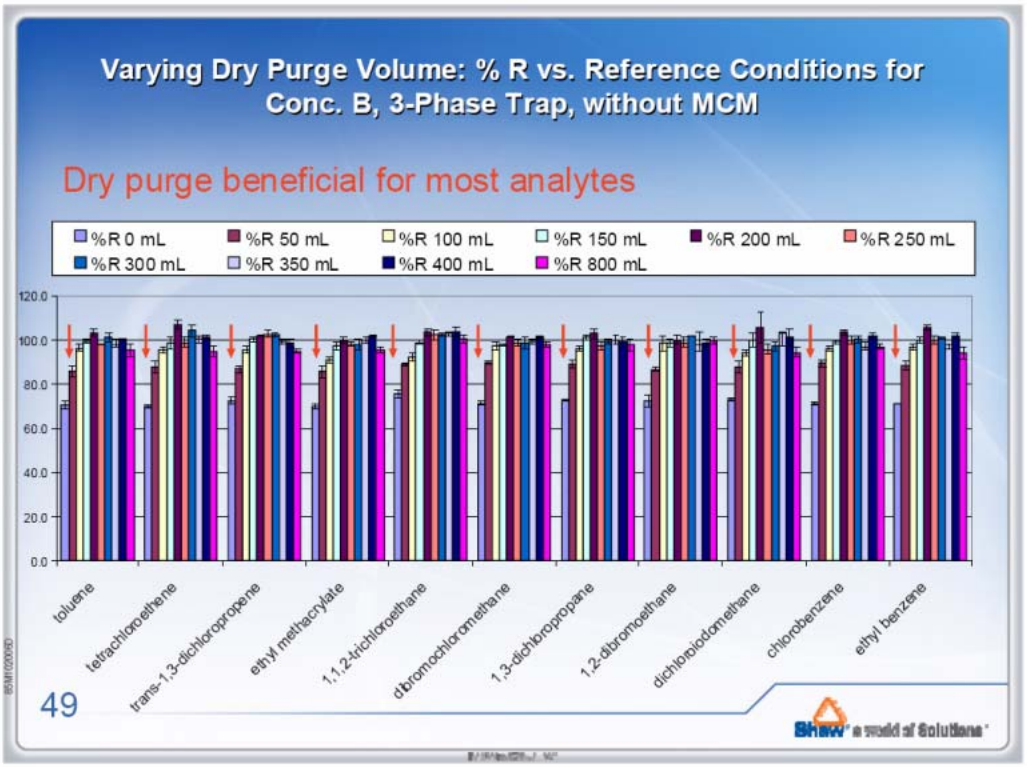
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. B, 3-Phase Trap, without MCM
Dry purge beneficial for most analytes
%R 0 mL
%R 50 mL
%R 100 mL
%R 150 mL
%R 200 mL
%R 250 mL
%R 300 mL
%R 350 mL
%R 400 mL
%R 800 mL
120.0
100.0
80.0
60.0
40.0
20.0
0.0
toluene
tetrachloroethene
trans-1,3-dichloropropene
ethyl methacrylate
1,1,2-trichloroethane
dibromochloromethane
1,3-dichloropropane
1,2-dibromoethane
dichloriodomethane
chlorobenzene
ethyl benzene
49
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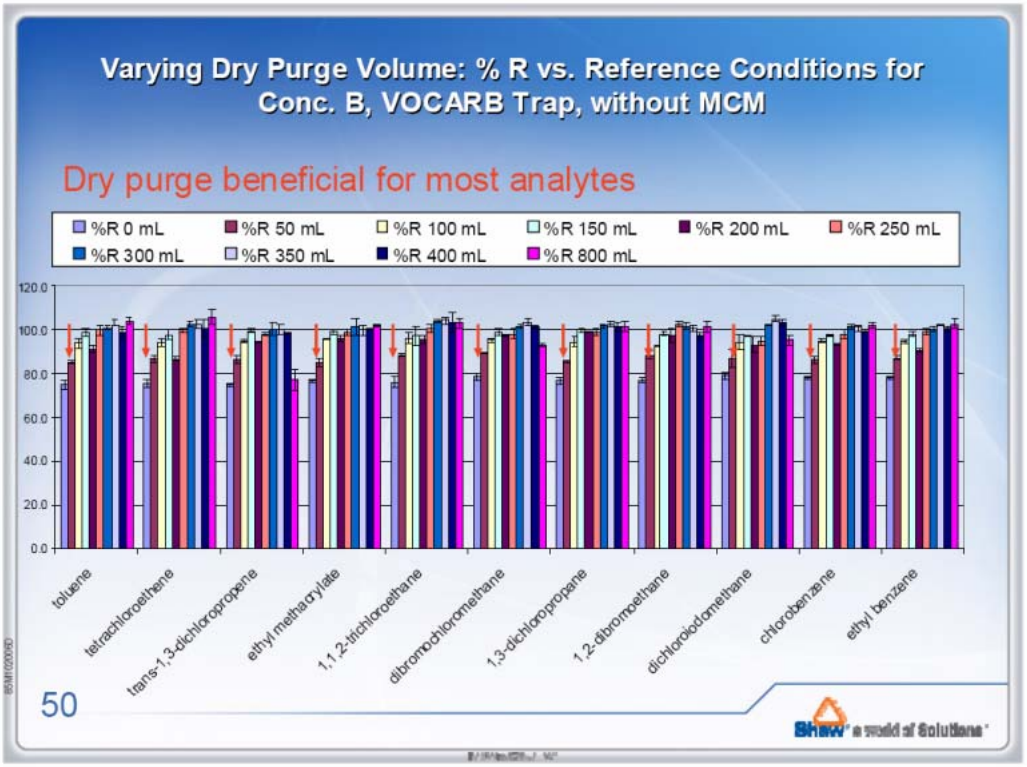
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. B, VOCARB Trap, without MCM
Dry purge beneficial for most analytes
%R 0 mL
%R 50 mL
%R 100 mL
%R 150 mL
%R 200 mL
%R 250 mL
%R 300 mL
%R 350 mL
%R 400 mL
%R 800 mL
120.0
100.0
80.0
60.0
40.0
20.0
0.0
toluene
tetrachloroethene
trans-1,3-dichloropropene
ethyl methacrylate
1,1,2-trichloroethane
dibromochloromethane
1,3-dichloropropane
1,2-dibromoethane
dichloriodomethane
chlorobenzene
ethyl benzene
50
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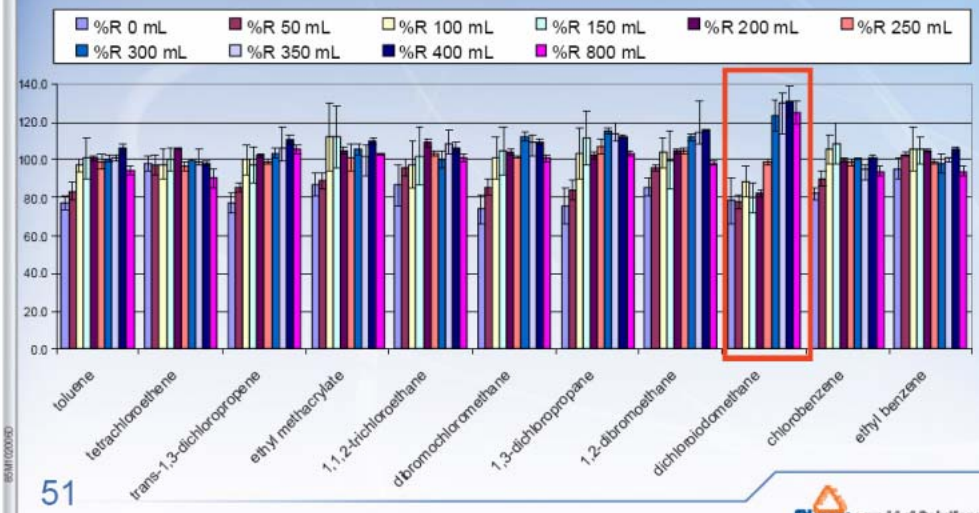
Varying Dry Purge Volume: % R vs. Reference Conditions for Conc. A, VOCARB Trap, *with MCM*

Impact of dry purge on ITHMs



51

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Conclusions – Varying Dry Purge Time

- Both concentrators and both traps exhibited improved performance with dry purging
- Eight compounds exhibited decreased recovery (breakthrough), but only at the highest dry purge volume (800 mL)
- Dry purging exhibited a larger effect on the concentrator that had a MCM

52

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Overall Conclusions

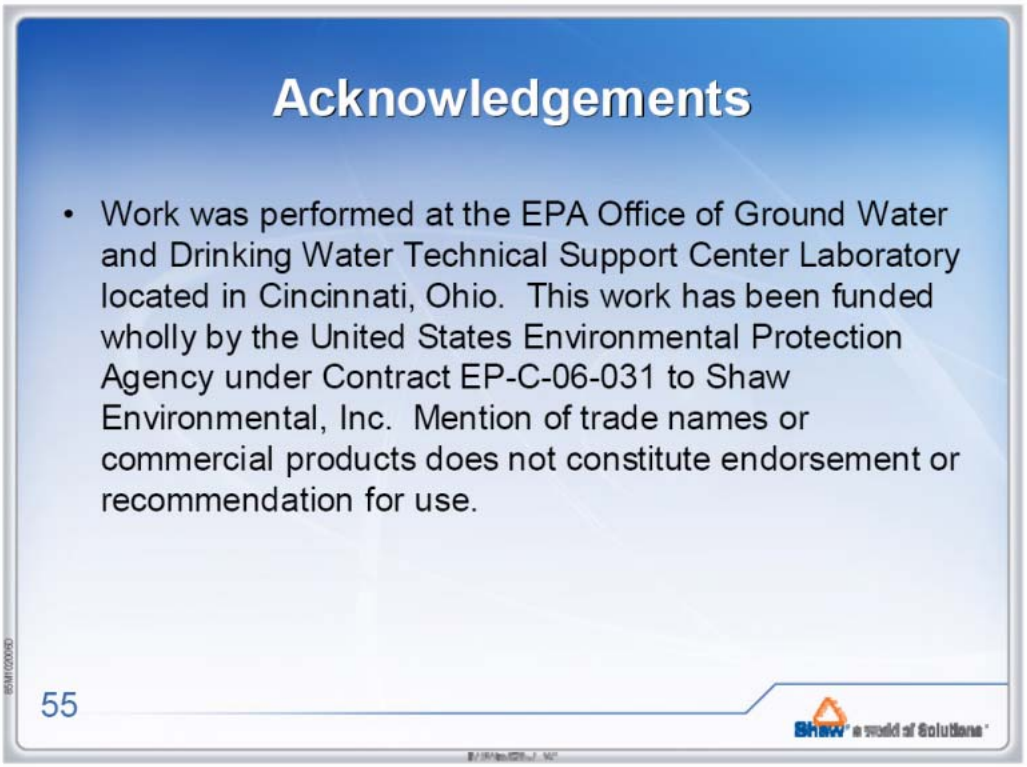
- Several method development objectives have been met
  - New preservative identified
  - Fuel oxygenates, ITHMs added
  - Poorly purged analytes removed
  - Tuning requirements minimized
  - Throughput enhanced
  - Dry purge will be allowed

53

Overall Conclusions

- A few method development objectives remain
  - Balancing method flexibility with method performance
    - Purge volume and moisture control are the key issues
  - Enhancing sensitivity for EDB, DBCP and TCE (SIM)
  - Determining LCMRL and MRL values for each analyte

54


Acknowledgements
• Work was performed at the EPA Office of Ground Water and Drinking Water Technical Support Center Laboratory located in Cincinnati, Ohio. This work has been funded wholly by the United States Environmental Protection Agency under Contract EP-C-06-031 to Shaw Environmental, Inc. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
55

Automated Solid Phase Extraction GC/MS for Analysis of Semivolatiles in Water and Sediments

David Kovacs[1], Robert G. Ford[2], Diane Gregg[2], Richard Siscanaw[2], Andy Beliveau[2]
[1]Shaw Environmental
[2]U.S. Environmental Protection Agency

ABSTRACT

Data is presented on the development of a new automated system combining solid phase extraction (SPE) with GC/MS spectrometry for the single-run analysis of water samples containing a broad range of organic compounds. The system uses commercially available automated in-line sample extraction with large volume injection and GC/MS. Two commercially available SPE sorbents used in series allow extraction of both polar and non-polar compounds. Variance in SPE extraction efficiency is directly monitored and quantitative accuracy improved through the use of "internal" deuterated and non-deuterated standards/surrogates added to calibration standards, blanks and samples prior to automated SPE concentration. System performance has been demonstrated for 92 target organic compounds, including acidic, basic and neutral semivolatile compounds as well as chlorinated and nitrogen-containing pesticides. Analyte carryover has been systematically examined for the various components in the analytical system and improvements to system hardware and operation procedures have been implemented to significantly reduce analyte carryover between sample analyses. This detection system has also been successfully applied to the analysis of a range of Method 8270 semivolatile compounds in complex matrices derived from water-isopropanol extracts of contaminated sediments, resulting in enhanced sample throughput with optimum detection limits. Preliminary work has also demonstrated the potential for quantitation of both volatile and semi-volatile compounds in a single analysis. The performance and flexibility of this system along with increases in automation and reduction in solvent usage and accompanying analyst exposure make this an attractive alternative for the analysis of volatile and semi-volatile organic compounds in aqueous samples.

Notice: This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

Automated Solid Phase Extraction GC/MS for Analysis of Semivolatiles in Water and Sediments

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USEPA Region 1, Boston, MA*

2007 NEMC, Cambridge, MA
23 August 2007

Shaw The Shaw Group Inc.

EPA

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Presentation Outline

OBJECTIVE Develop automated system for quantitation of Method 8270 target analytes in accordance with data quality and EQL guidelines, using the 8270 surrogates and internal standards.

1) System Overview
2) Sorbents & Extraction Solvents
3) Initial Demonstrations of Capability
4) Performance Improvements
5) Other Potential Applications

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System Overview

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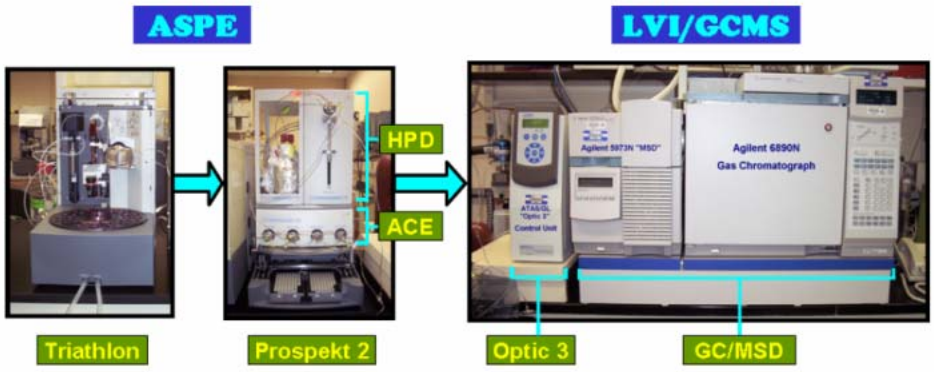
System Layout



Triathalon, Prospekt 2: Spark Holland
Optic 3: ATAS/GL International
GC/MSD: Agilent Technologies

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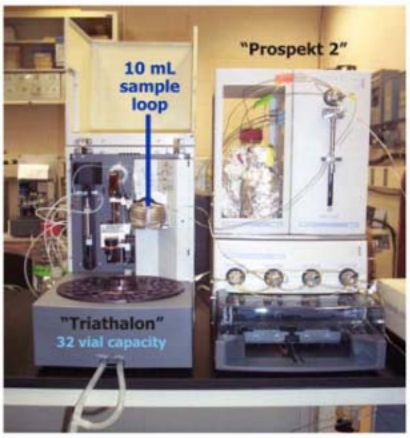
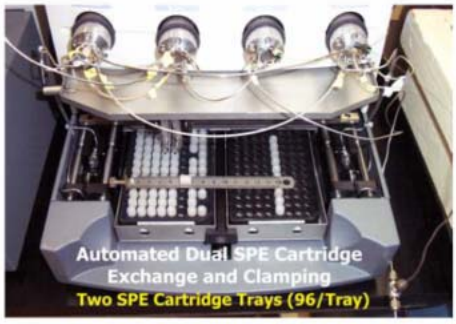
Spark Holland Autosampler and SPE





Note: "Triathlon-Prospekt 2" now marketed as "Symbiosis Environ"

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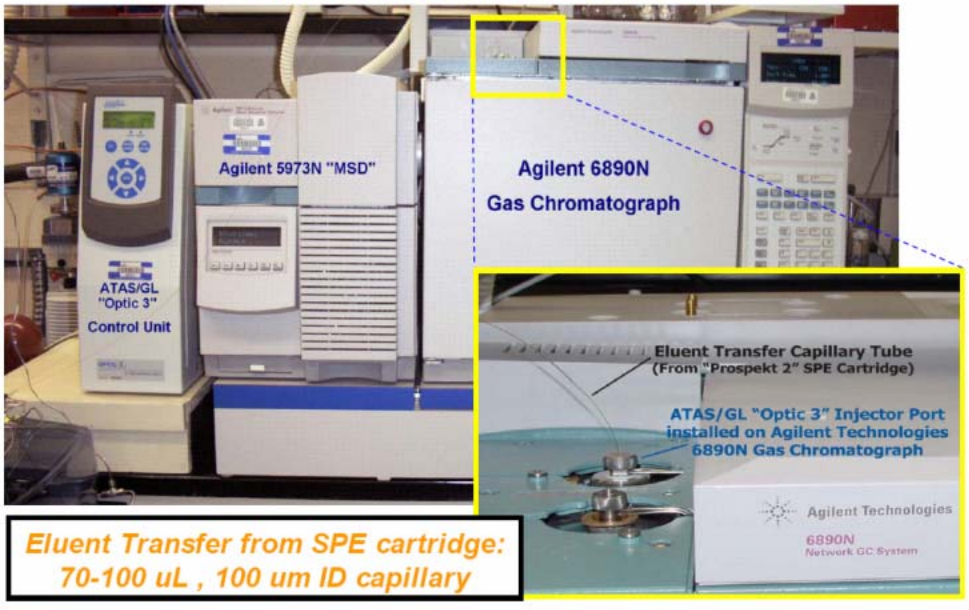
LVI Port Controller and GC-MS



Eluent Transfer from SPE cartridge:
70-100 uL , 100 um ID capillary

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Sorbents & Extraction Solvents

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System Considerations

1) Single SPE analysis per sample. No sample adjustment (e.g., pH, salt). Use 10 mL sample size.
2) Elution solvent(s) be compatible with good GC chromatography.
3) SPE sorbent(s) used must be in the Spark Prospekt cartridge format
4) Minimize total extraction solvent waste volume

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Sorbent/Eluent Selection

Spark Holland
- HySphere Resin SH
- HySphere C18 (EC)
- HySphere C2
- HySphere CN
- HySphere C8
- HySphere C8 (EC-SE)
- HySphere C18 HD
- HySphere Resin GP

Varian, Inc.
- Nexus
- Focus
- Polaris C18-A
- PLRP-s

ATAS/GL – "GL"

Phenomenex – Strata X

Waters – Oasis HLB

Serial sorbent configuration:

1. HySphere C18 HD
2. Focus

1 Least polar compounds

2 Polar compounds, acids, bases

Elution Mix 90/10 MTBE-Ethyl Ether

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Initial Demonstrations of Capability

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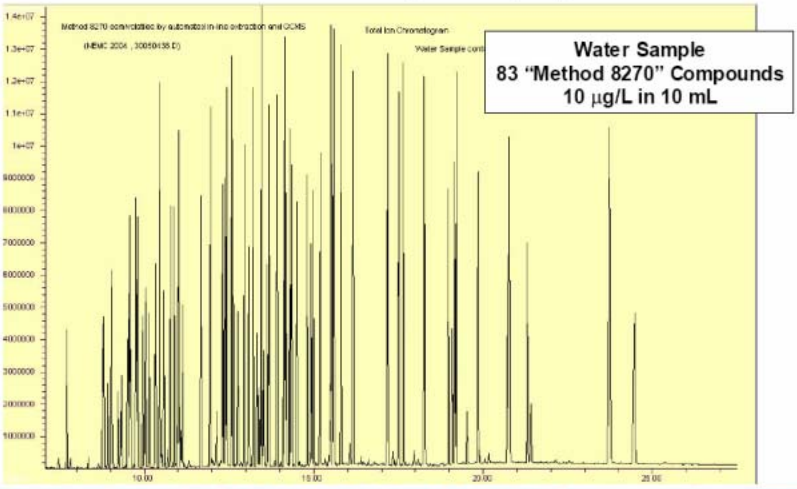
Initial Demonstration of Capability

Certified Performance Evaluation Samples
Measurement of Precision and Detection Limit
Pesticide Compounds: Chlorinated (20), Nitrogen (15)
EPA CLP OLM4.2 Semivolatile Compounds (60), Internal Standards



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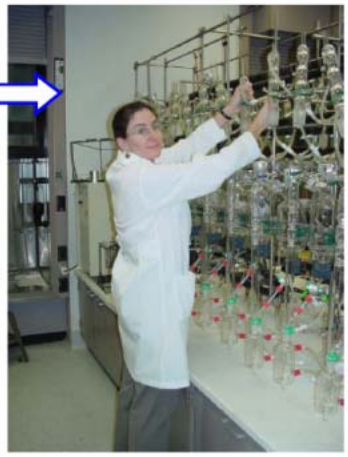
Real World Sample Comparison

Region 6 Laboratory & EPA/ORD-Ada

- 10 samples from Texas creosote site extracted by different procedures
- *SPE/LVI results from both labs compared to original continuous liquid-liquid extractions (AOS)
- SPE system at Region 6 Lab Houston, TX
  - Offline sample preparation using Horizon 4790 Solid Phase Extractors
  - JT Baker Speedisk SDVB Hydrophilic Disks with 1g of Sorbent
  - Extracts dried with Horizon DryDisk™
- Both SPE procedures add surrogates and matrix spikes to the sample prior to extraction
  - Ada Lab adds internal standards to all samples prior to SPE extraction



Note: SPE samples were analyzed past holding time

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Comparison Study
Region 6 Laboratory & EPA/ORD-Ada

Compound	AOS	R6 SPE	Ada SPE
Sample 0310002-10, ug/L			
Naphthalene	1920	1620	2160
2-MeNaph.	210	186	247
2-Methylphenol	156	156	186
2,4-Dimethylphenol	582	505	507
Pentachlorophenol	1350	910	942
Surrogate Recovery (avg. of 8)	93%	77%	92%
Sample 0310001-02, ug/L			
Naphthalene	1760	1430	2020
2-MeNaph.	393	271	346
Acenaphthene	230	228	274
Pentachlorophenol	406	225	310
Fluorene	100	108	107
Surrogate Recovery (avg. of 8)	84%	66%	92%

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Performance Improvements

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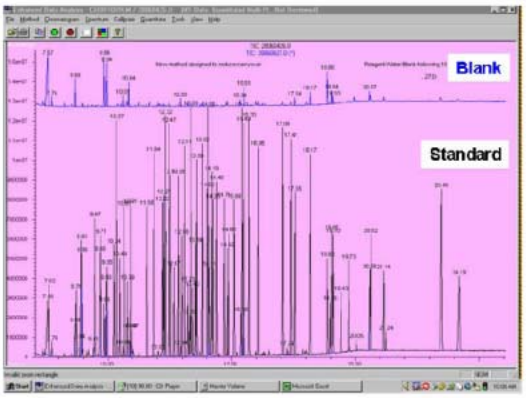
Reduction of Carryover

- Systematic analysis and correction of carryover in analytical train
- Use method automation to progressively examine sources of carryover from GCMS upstream to autosampler
- Goal to reduce carryover to <1% through method or materials modifications
- Use Method 8270 DMC list of compounds



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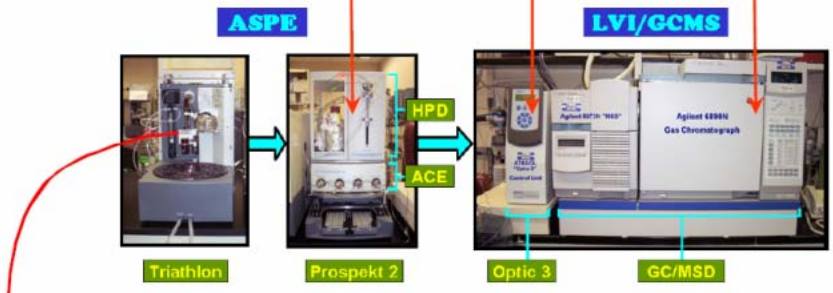
Sources of Carryover

Carryover observed in Prospekt valves, lines and transfer line

LVI – none observed

GCMS – none observed



- Adding wash steps for HPD/ACE and extract transfer line reduced carryover to 1% or less
- Carryover not yet resolved for autosampler; PAHs >>1% even with additional washing steps for Triathlon

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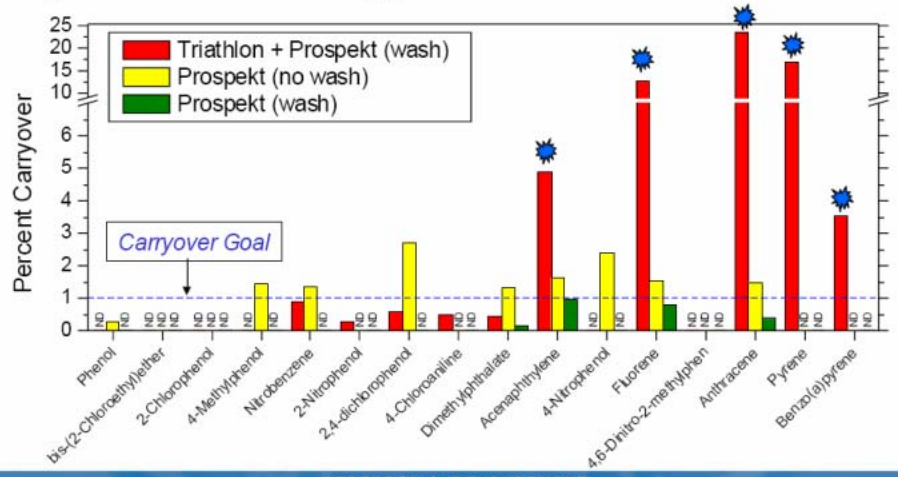
Improvements - Transfer Line Wash

Triathlon vs. Prospekt as "Autosampler"

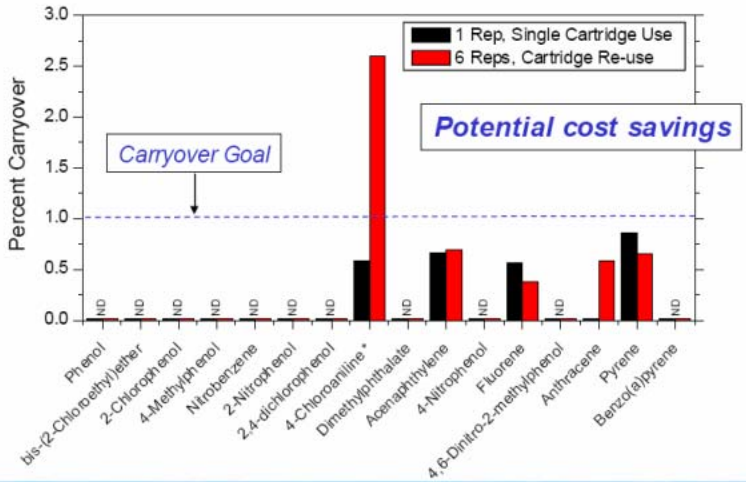
- Triathlon needs further development to address some compounds
- Carryover objective met using Prospekt as autosampler with implementation of washing procedure



Carryover – SPE Cartridge Re-use

Prospekt as "Autosampler"

- Carryover low even with multiple uses of the sorbent cartridge
- Can change wash solvent to reduce 4-chloroaniline carryover
- Solvent/Sample: 20 mL water (incl. sample), 14.7 mL organic solvent



Other Potential Applications

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Semivolatiles in Sediments (Preliminary)

- Pressurized Fluid Extraction using Dionex ASE w/ Isopropanol:Water
  - similar to USGS NWQL Method O-5433-05, Techniques and Methods 5–B2
- PFE extract dilution with water, ASPE concentration/in-line GCMS

NIST SRM 1944 (mg/kg, dry)	Certified	EPA/ORD
Napthalene	1.65 ± 0.31	2.18
Phenanthrene	5.27 ± 0.22	5.01
Anthracene	1.77 ± 0.33	1.36
Fluoranthene	8.92 ± 0.32	8.18
Pyrene	9.7 ± 0.42	8.95
Benz[a]anthracene	4.72 ± 0.11	6.41
Chrysene	4.86 ± 0.1	5.41
Beno[b+j]fluoranthene	5.96 ± 0.44	6.23
Benzo[k]fluoranthene	2.3 ± 0.2	2.83
Benzo(a)pyrene	4.3 ± 0.13	3.38
Indeno[1,2,3-cd]perylene	2.78 ± 0.1	1.93
Benzo[g,h,i]perylene	2.84 ± 0.1	1.78

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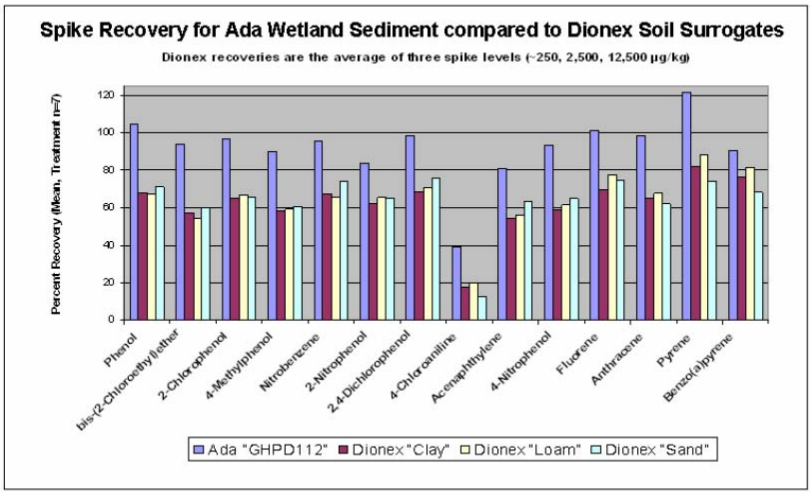
Semivolatiles in Sediments (Preliminary)

EPA/ORD-Ada PFE/(Isopropanol-Water), ASPE/GCMS
Dionex Corp. PFE/Methylene Chloride-Acetone (1:1), GCMS [1]



[1] Dionex Document #116064, B. Richter, J. Ezzel, D. Felix, "Single Laboratory Method Validation Report, Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD", 1994

RESEARCH & DEVELOPMENT
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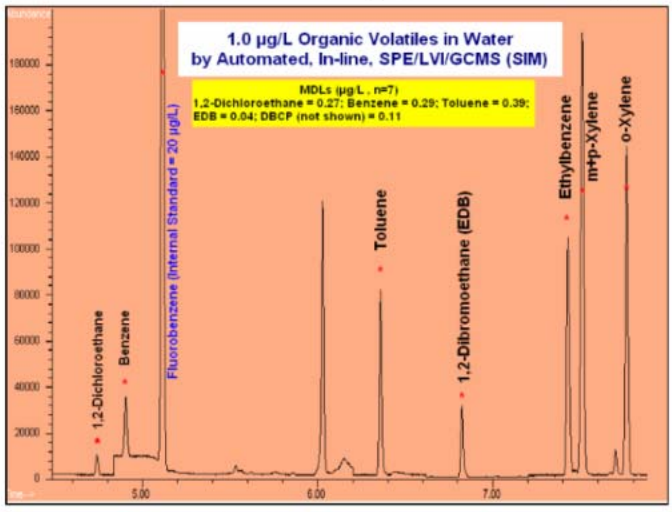
Analysis of Volatiles (Preliminary)

- Potential for single analysis of volatiles and semivolatiles
- Linear Concentration Range (µg/L, r2 > 0.999) => 100X



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Advantages

Analytical Performance

- In-line, automated, solid phase extraction and GC-MS analysis of aqueous samples for acidic, basic and neutral organic compounds (USEPA Method 8270 listed compounds tested)
- Single analysis of acid, base and neutral compounds per sample
- Lower detection limits means smaller sample size required
- More accurate, using extracted internal standards for calibration

Method Implementation

- Simplified field sample collection, with lower transportation and storage costs, due to smaller sample size
- No extract concentration step (present in previous methods)
- One analyst required, combines extraction and GC-MS
- High throughput, with little operator intervention.
- Reduces waste disposal cost, <15 mL/sample organic solvent
- Reduces solvent exposure to workers, closed in-line delivery

RESEARCH & DEVELOPMENT
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Disadvantages

- Carryover from samples not yet resolved for autosampling component – *alternative approach may be needed*
- Extraneous peaks from sorbent problematic for data reduction of tentatively identified compounds (e.g., benzaldehyde from Focus™ SPE)
- Particulates can prohibit extraction by SPE
- Higher initial capital equipment cost

RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions

Acknowledgements

- Garmon Smith, Roger Cosby & Steve Vandegrift, EPA/ORD, Ada, OK
- Alex Berhitu & Dirk Hiemstra, Spark Holland Inc.
- Rob Stubbs & David Jones, Varian Inc.
- Geert Alkema, ATAS/GL
- Greg Bedenk, AIS
- Edward Lee (Retired), Lawrence, KS, USGS
- Wes Moyers & Michael Horton, Leap Technologies
- Funding from EPA/ORD Office of Science Policy under the Regional Methods Program to EPA Regions 1 and 6
- Andy Beliveau now with Battelle

Disclaimer

Mention of trade names or commercial products does not constitute endorsement for use.

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

PERFORMANCE APPROACH

Use of the Performance Approach for Everglades R-EMAP Phase III

Charles G. Appleby, Mike A. Wasko, Michael H. Birch, and Peter I. Kalla
U.S. Environmental Protection Agency, Region 4

ABSTRACT

The US Environmental Protection Agency (EPA) occasionally performs environmental monitoring/ assessment studies such as the Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP). In-situ data were documented in the field, and eight analytical labs were contracted to perform sixty unique analyses for nutrients, anions, mercury, and physical parameters on samples of seven different matrices collected at over 250 Everglades sampling stations. Data quality in any survey study, but especially in one this size, must be part of project planning and execution from start to finish.

The development and implementation of the quality system for Everglades R-EMAP Phase III through the performance approach are presented. One goal of this study was to produce data of known and documented quality that met pre-defined project goals and data quality objectives. For this $1.6 million project, the investment in quality assurance exceeded $100,000. Out of approximately 25,000 data points generated for this study, less than 0.01% were rejected as unusable.

Performance Approach for Everglades R-EMAP

Charlie Appleby
U.S. EPA Region 4
Science and Ecosystem Support Div.
Quality Assurance Section

PROGRAM ORIGIN

- 1989: Florida panthers found dead in the Everglades with high mercury levels in their blood. Human health fish consumption advisory posted. Mercury origin unknown.
- FDEP requested EPA assistance to determine magnitude and extent of mercury contamination.
- EPA Regional Administrator initiated program in 1992.

SURVEY DESIGN

- 8 synoptic sampling events completed
  - ~125 sites per event, each in ~12 days
  - Wet and dry season 1995, 1996, 1999, 2005
  - ~ 1000 sites sampled (>100,000 data points)
  - 60 biogeochemical parameters
  - All habitats were sampled
  - Media: surface water, soil pore water, soil, periphyton, floc, macrophytes, mosquitofish, aquatic community.
  - Indicators: nutrients, mercury, physical and chemical properties, enzyme activity, species composition, vegetation mapping.

Sampling sites 1993-2005

Phase I Canal = 1993-95

Phase I Marsh = 1995-96

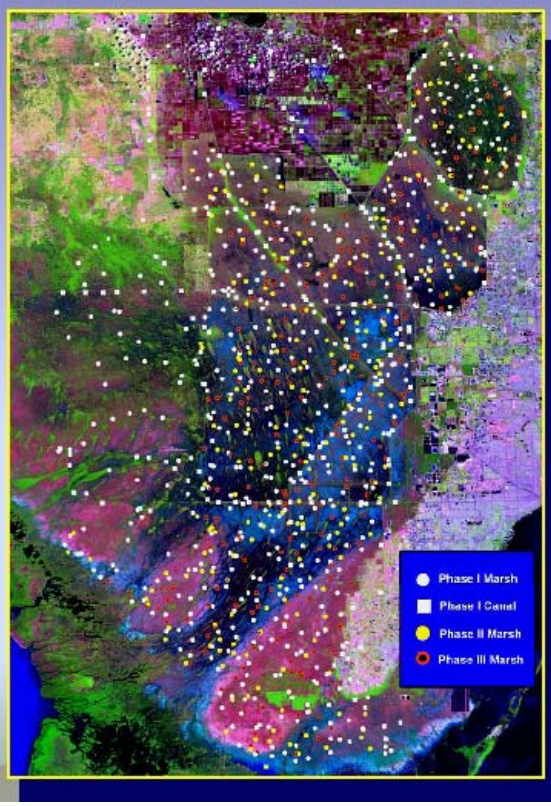
Phase II Marsh = 1999

Phase III Marsh = 2005

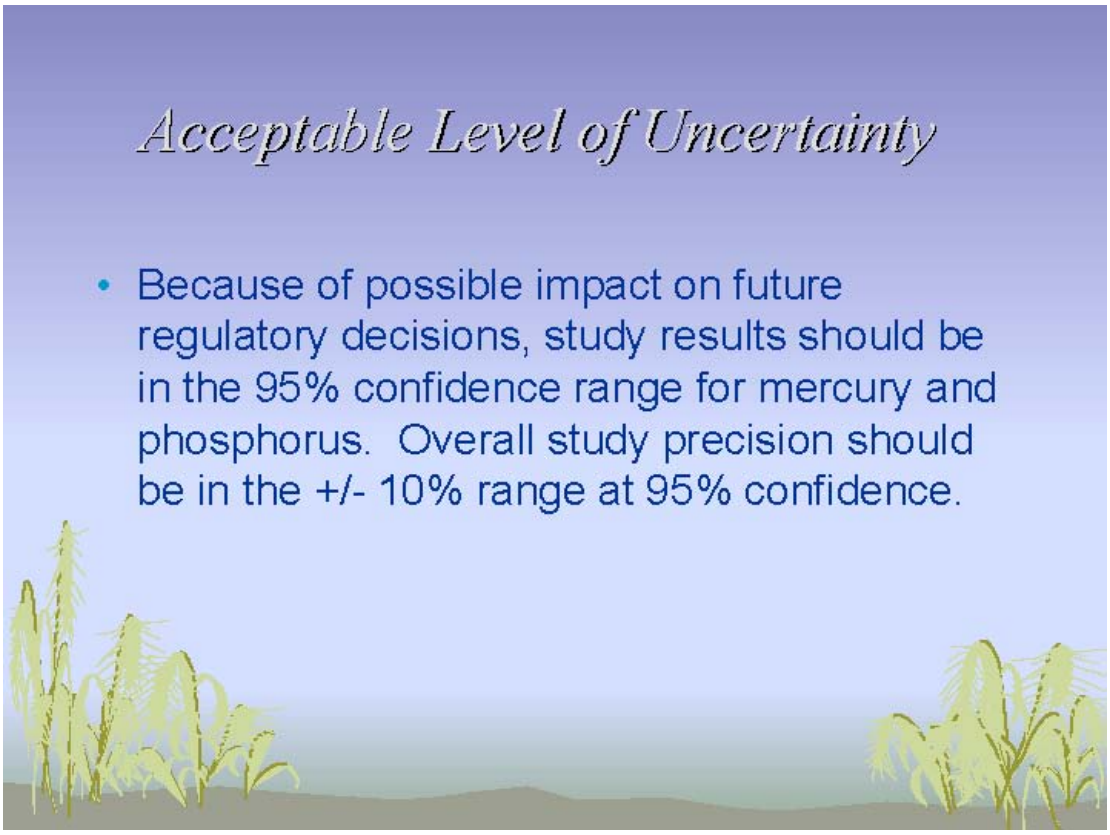
1145 Sample Sites

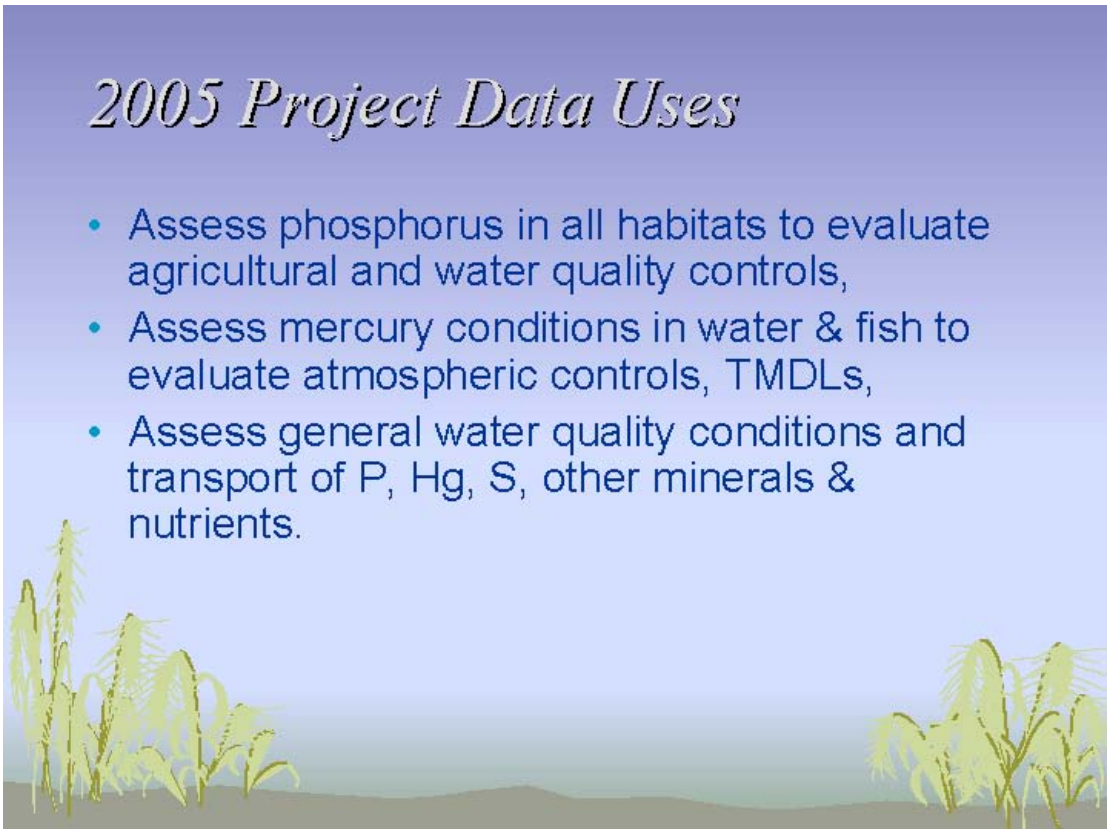
~100,000 biogeochemical data values

Largest study ever done by EPA Regional scientists




PROGRAM FOCUS
• Mercury and phosphorus contamination
• State and federal restoration efforts
• Everglades Forever Act (EFA) phosphorus control
• Mercury control
• Comprehensive Everglades Restoration Plan (CERP)
• Overall ecosystem health
• Water quality criteria
• Trends


Acceptable Level of Uncertainty
• Because of possible impact on future regulatory decisions, study results should be in the 95% confidence range for mercury and phosphorus. Overall study precision should be in the +/- 10% range at 95% confidence.


2005 Project Data Uses
• Assess phosphorus in all habitats to evaluate agricultural and water quality controls,
• Assess mercury conditions in water & fish to evaluate atmospheric controls, TMDLs,
• Assess general water quality conditions and transport of P, Hg, S, other minerals & nutrients.

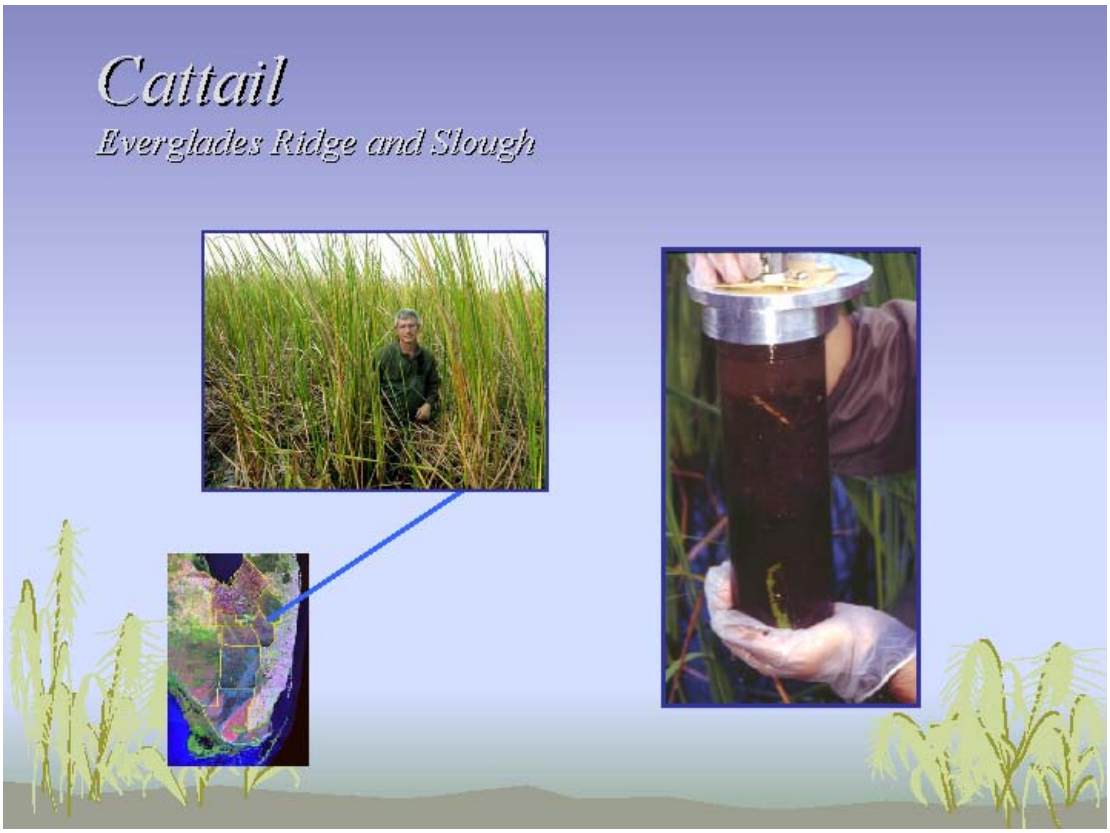

R4 Everglades R-EMAP data users to date
FLORIDA
NRCS Natural Resources Conservation Service
TETRA TECH, INC.
UNIVERSITY OF FLORIDA
Sugar Cane Growers Cooperative of Florida
UNITED STATES SUGAR CORPORATION
An Integrated Family of Agribusiness Companies

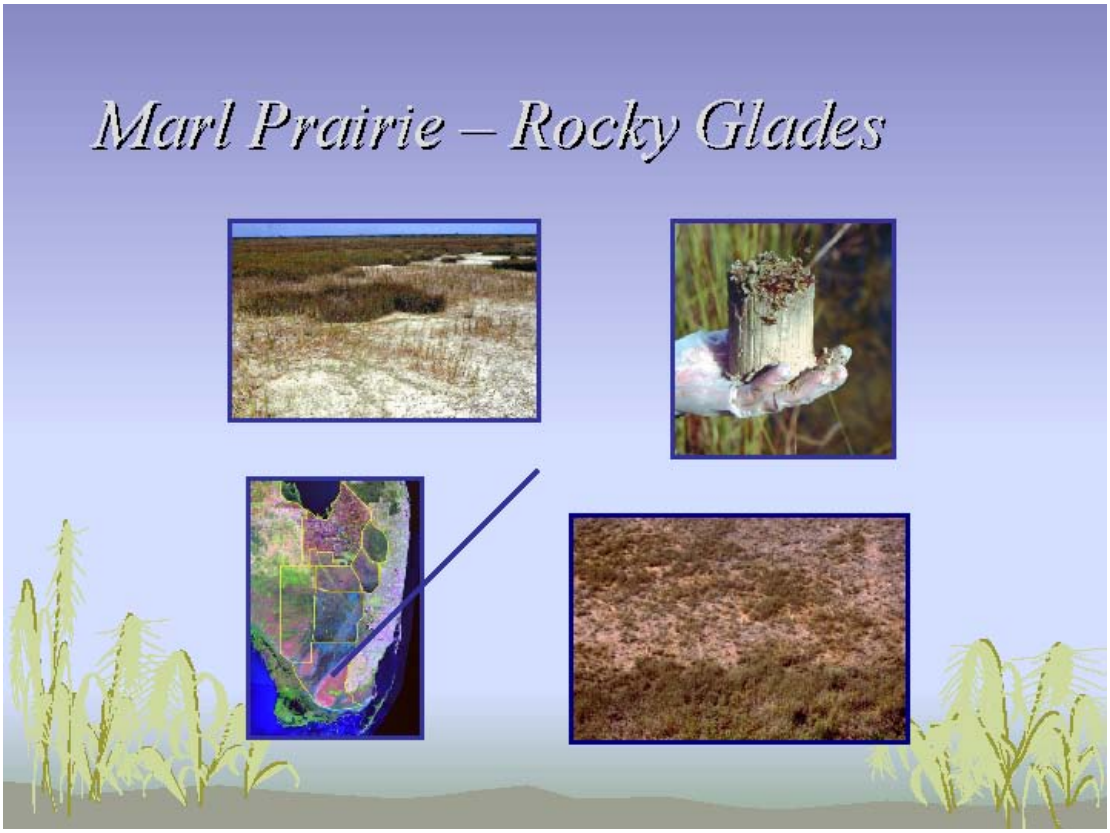
Phase III Effort

- May, November 2005 sampling
  - 228 stations, 3000 square miles, 25,000 data points, 7 field weeks, 3 helicopters
- Field crew EPA/FIU~ 30 people
- 8 analytical labs
- Extensive QA/QC

Sawgrass and Wet Prairie

Everglades Ridge and Slough


Cattail
Everglades Ridge and Slough


Marl Prairie – Rocky Glades

Sampling Everywhere

Soil Coring

Porewater Sipping

2005 R-EMAP Quality System

Basis for R-EMAP Quality System

- Clean Water Act (40 CFR, Part 136)
- U.S. EPA Information Quality Guidelines (EPA/260R-02-008)
- Agency Order 5360.1 A2
- Florida DEP QA Rule (Chap. 62-160, FAC)
- CERP Quality Assurance Systems Requirements (QASR)

R-EMAP III QA Challenges

- New techniques in common use
  - Data Comparability with Phases I & II
- Input from many stakeholders
  - Data quality for secondary uses
- 2,000 – 3,000 sample containers to 8 labs within 10-day sampling window
  - Logistics

QA Preparation

- Methods Review Phases I & II
- Laboratory Document Review
  - QA Manual, SOPs, QA/QC Data
  - Staff resumes, training
- On-site Laboratory Evaluation
  - Facilities, Sample flow, Data system
- Laboratory / Method Selection
- QAPP development

R-EMAP 2005 Parameters

Parameter	Matrix
Diss Org Carbon	SW
H_2S	SW, PW
AVS	SD
pH	SW, PW, SD
MC, AFDW, BD	SD, FC
Br^-, Cl^-, F^-, $SO4^{--}$	SW, PW

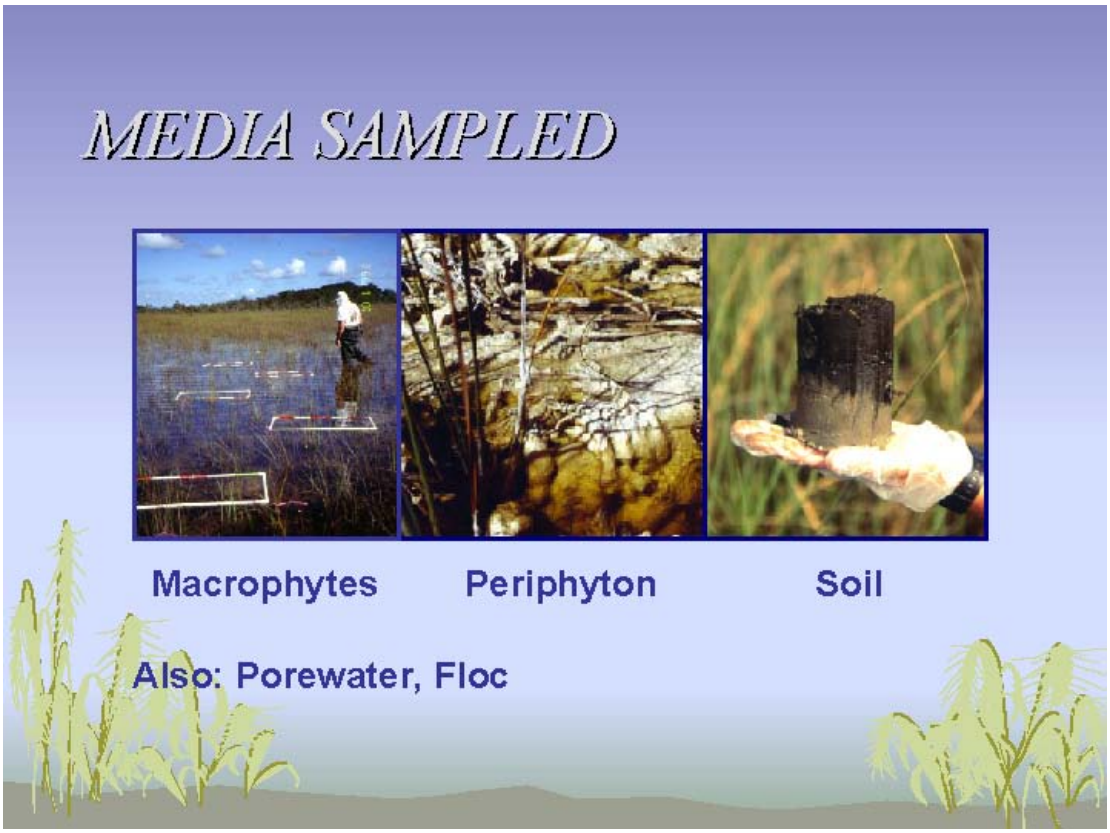
R-EMAP 2005 Parameters

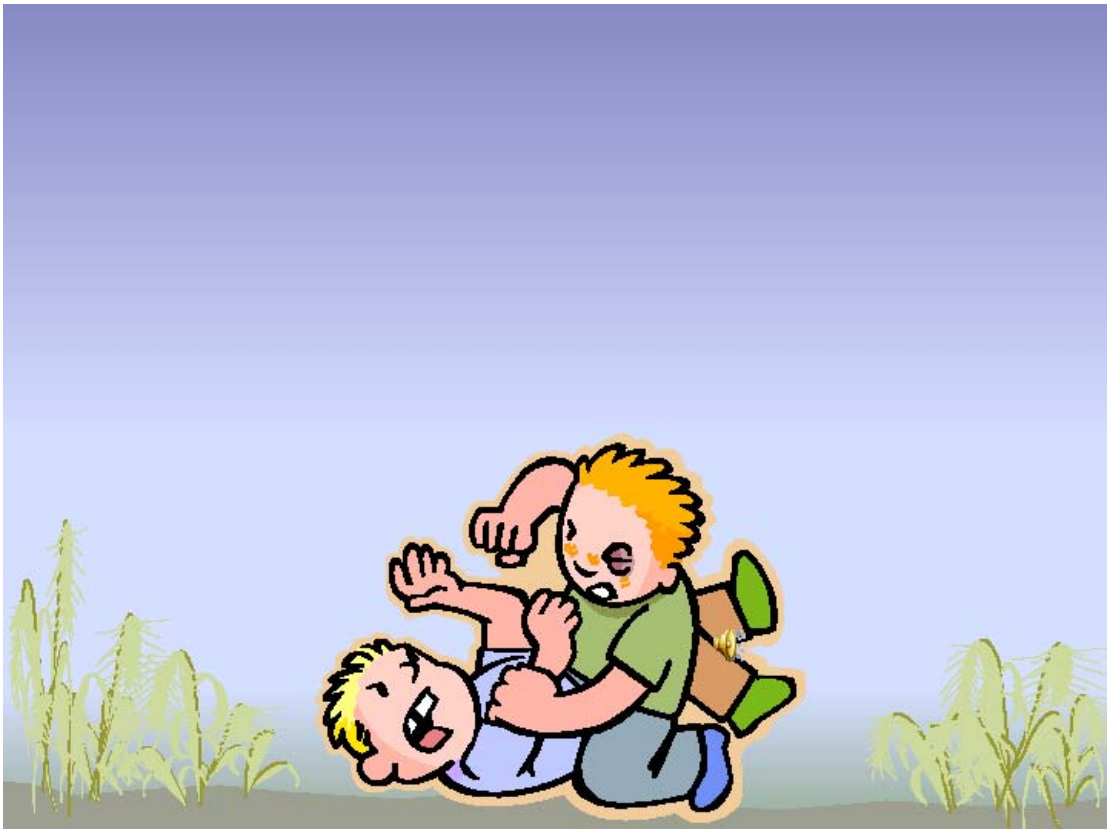
Parameter	Matrix
SRP, NO_3, NO_2, NH_3, N+N, TIN, TON	SW, PW
TP, TN, TC	SD, FC
Total Hg	SW, SD, FC, PB, PF, PE, FS
meHg	SW, SD, PU, PF, PM, FC
Chlorophyll-a	SW, FC
Alk Phosphatase	SW

MEDIA SAMPLED

Surface Water

Mosquitofish


MEDIA SAMPLED
Macrophytes
Periphyton
Soil
Also: Porewater, Floc



R-EMAP 2005 Laboratories

Lab #1	Nutrients, Chlorophyll, Phys
Lab #2	Non-aqueous THg, meHg
Lab #3	me-Hg in water
Lab #4	THg in water
Lab #5	TOC/DOC
Lab #6 (mobile)	APA, H_2S
Lab #7	Anions
Lab #8	Acid-volatile sulfide

Quality System Requirements

- **Project Documentation**
  - Quality Assurance Manual
  - Current SOPs
  - Approved QAPP
  - Analytical Services Statement of Work (SOW)

Quality System Requirements

- **Laboratory Documentation**
  - Quality Assurance Manual
  - Current SOPs
  - Training and personnel records
  - Concise data deliverables in accordance with SOW
  - Initial and continuing proficiency

Quality System Requirements

- Clear organizational structure and delineation of responsibilities / independent QAO
- Policies governing ethics, training, security, and record keeping
- Policies governing data review, verification, approval, and reporting
- Procedures for document control and data/document archiving
- Corrective action procedures and policy

Laboratory Performance Evaluation

- Round-Robin Tests
  - Conducted for all critical parameters
    - Three labs participated in aqueous total and methyl Hg RRs
    - Two labs participated in phosphorus RRs
    - One lab participated in fish tissue RR
  - Usually conducted annually

Ready for the Next Step

QA in the Field

- Overview equipment prep / loadout
- Overview training for samplers & RSCC
- Attend all trip briefings / debriefings
- Overview RSCC operations
- Overview operations at local lab
- Respond to QA/QC inquiries from field
- Progress reports to stakeholders

Samples

Laboratory Performance Evaluation

- Custom PE Samples
  - Developed for critical parameters and matrices
    - Total Hg in water, sediment, and fish
    - Methyl mercury in water, and sediment
    - SRP in water
    - Total phosphorus in sediment
  - Submitted with samples during each season

Documenting Data Quality, Data Elements

- Chain-of-Custody (COC)
  - Signed, dated by all who touched the sample
  - Courier tracking / airbill numbers, if applicable
  - All sample containers listed
  - Requested analyses specified
  - Any planned QC samples noted

Data Elements (continued)

- Sample preparation logs
  - Sample descriptions traceable back to COC
  - Including all information necessary for recreating analysis
  - And any information necessary to enable traceability of standards and reagents

Data Elements (continued)

- Instrument performance and calibration data
  - Daily performance checks on background and sensitivity
  - Initial calibration and continuing cal checks

Data Elements (continued)

- Method performance data:
  - Method Blank performance
  - Matrix Spike recovery
  - Matrix Duplicate precision
  - PT Sample performance
  - System Performance data

Data Elements (continued)

- Sample data
  - Sample results including raw data
  - Any dilutions or re-analyses
  - All manual calculations performed
  - Notes on any routine analytical problems
  - Corrective Action Reports
  - Signatures of analyst, peer reviewer, supervisor

Data Deliverable

- Hardcopy and electronic
- Level of detail
- Project narrative
- Records kept by laboratory
- Spelled out in SOW

Data Reporting

- Sample results
  - Using proper units
  - Data uncertainty quantified (when possible)
  - Significant digits consistently reported
  - Any limitations on data clearly identified
  - Documented Review/Approval Process

Data Validation / Assessment

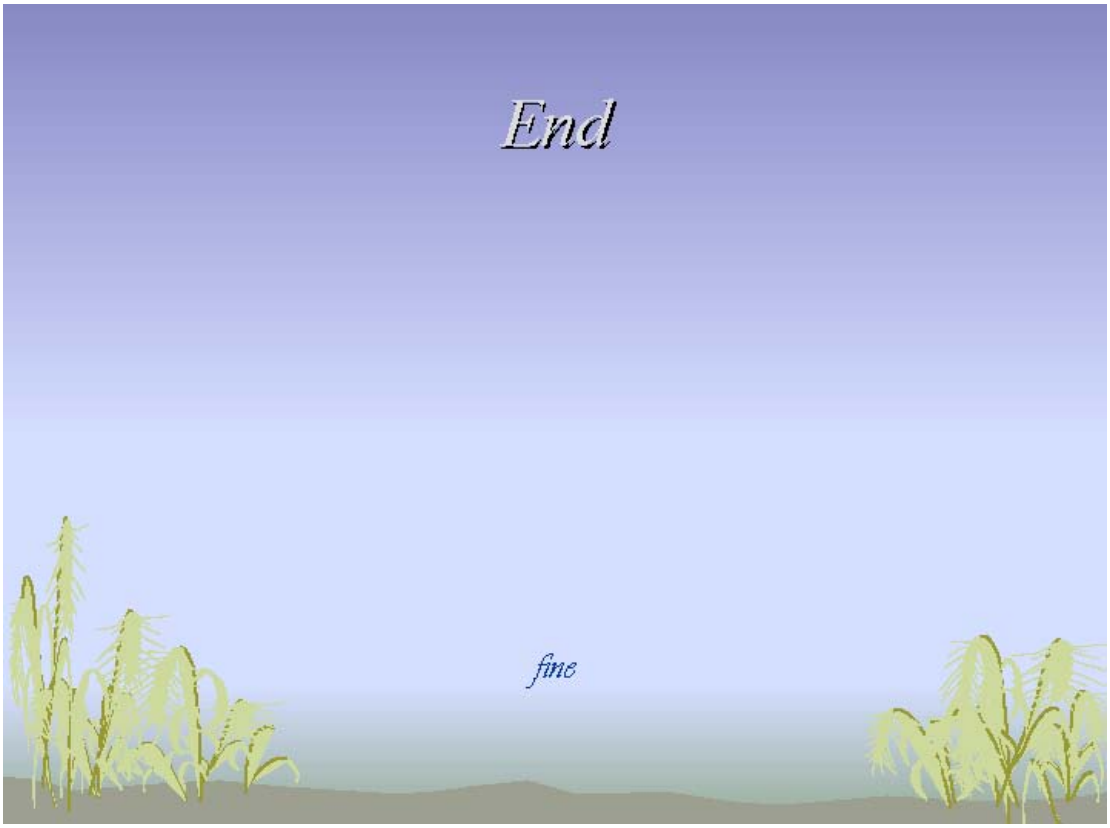
- Third-party validation of data quality
  - Reviewers Knowledgeable of Analytical Methods and Principles and with QAPP
  - Documented Procedures for Review
  - Pre-defined guidelines for data qualification
  - Established Reporting Process

Data Validation / Assessment

- Comparison of final data to project DQOs
- Evaluation of data applicability to support or reject the hypothesis or decision
- Usability of data for project reports and design of future studies

2005 QA/QC Outcomes

- Approximately 110 sample stations in May with 1970 sample containers
- Approximately 120 sample stations in November with 3110 sample containers
- Overall about 25,000 chemical results
- 100% of lab results were reviewed; 3 were rejected, others qualified
- ~ $100,000 invested in project QA, and 700 hrs by EPA QA Team, about 10% of budget


End
fine


The Guilty
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A Comparison of a PCB Homologue to Aroclor Method, a Demonstration for the Performance-Based Measure

Wayne Whipple
US Environmental Protection Agency/R5 CRL

ABSTRACT

Current regulatory methods are prescriptive and do not allow for a rapid transition into new technologies or more efficient and better analytical methodologies. Adopting a performance-based measurement approach has the advantage of being able to adapt more quickly to the new technologies, using more efficient analytical techniques to determine site specific data requirements. This approach is expected to improve data quality, reduce the analytical expenses while maintaining comparability of data.

Samples were collected in at a contaminated site, homogenized, split and sent to two different laboratories for total PCB analysis. One laboratory analyzed the sample using Method 8082 while the other used a modified Method 680. The results were comparable with a correlation coefficient of 0.98 (0.95 to the 99% confidence level) although the slope of the correlation gave a greater result for the homologue analysis. Both extractions were similar using pressurized fluid extraction although the laboratory performing the Aroclor analysis used hydromatrix drying material and a 1:1 acetone:hexane mix where the homologue laboratory dried their samples at 30ºC and extracted in hexane. Sample clean-up procedures were also different. The results were comparable suggesting that a properly planned analysis with well-defined data quality objectives and a strict quality control procedure to document the laboratory's capability is the way to ensure the success of the performance based measurement approach.

Accreditation and Assessment of Performance Based Methods Systems

Patrick Conlon
Environmental Standards

ABSTRACT

An accreditation model for Performance Based Methods Systems, due to the shear number and diversity of testing and monitoring processes, faces unique challenges. The accreditation process must be adaptable to the technologies applied, the programmatic requirements, if any, and the end user data quality objectives. Within a programmatic setting this requires attention to and definition of programmatic performance criteria and the technical expertise of the assessor in determining whether a procedure meets these performance criteria. Outside of a programmatic setting it requires attention to and definition of the data quality objectives of the end user and the technical expertise of the assessor in determining whether the procedures being evaluated are capable of meeting these data quality objectives.

This presentation will discuss a) the implication of these challenges to the current NELAC accreditation process, b) examples of how a dynamic approach to evaluating PBMS may also be applied to non-traditional accreditation arenas such as fields sampling and field monitoring activities, and c) opportunities for expansion of the TNI standards writing activities outside of the traditional programmatic FOT framework.

Setting the Standards for Innovative Environmental Solutions

ENVIRONMENTAL STANDARDS

NEMC & NELAC Combined Meeting
Cambridge Massachusetts
August 2007

By Patrick Conlon

ENVIRONMENTAL STANDARDS

- Definitions of "Performance Based" Terms.
- Comparison of Water and RCRA programs toward method flexibility.
- Comparison of how the Water and RCRA assessment and accreditation processes are impacted by the "performance based approach".
- Limitations and challenges for method assessment and accreditation.
- Additional challenges expected for Field Programs.

ENVIRONMENTAL STANDARDS

Performance Based Measurement System

Set of processes wherein the data needs, mandates, or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner.

Performance Based Approach

Framework that permits the use of any appropriate sampling and analytical technology that demonstrates the ability to meet established performance criteria and complies with specified DQOs and MQOs of the project in which the sampling and analytic technology is employed.

ENVIRONMENTAL STANDARDS

Precision – *A measure of the scatter of results obtained from the measurement of samples that are ostensibly the same*

Bias - *is the difference between the value determined using the measurement system in question and the true value; operationally, the difference between the sample mean and an accepted true value.*

Selectivity - *the ability to accurately measure the analyte in the presence of other sample matrix components or analytical process contaminants.*

Sensitivity -*Ability of the measurement system to yield valid measurements at the level of interest in the samples of concern.*

ENVIRONMENTAL STANDARDS

Data Quality Objective (DQO)

Qualitative and quantitative statements of the overall level of uncertainty that a decision-maker is willing to accept in results…derived from environmental measurements, includes….sampling location, sample handling, and sample analysis.

Measurement Quality Objective (MQO) -

Measurement quality objectives (MQO) address only uncertainty of measurements from the analytical or measurement process of the laboratory.

ENVIRONMENTAL STANDARDS

EPA Water and OSWER Milestones

- Updated the methods approval and validation process including both primary and alternative test procedure methods.
- Established guides for method flexibility for methods within these programs.
- Added many new methods and retired old methods.
  - Methods Update Rule of 40 CFR Part 136, finalized March 12, 2007

ENVIRONMENTAL STANDARDS

USEPA Water Program Methods

For SDWA and CWA:

- Methods must be EPA approved for use within these programs (list of approved reference methods and alternative methods published in 40 CFR parts 136 and 141).
- Flexibility guidelines added, and have effectively become part of the code for method use.
- Laboratory must use "approved" method within the "approved" method flexibility guidelines.

ENVIRONMENTAL STANDARDS

Water Program Methods Approval

- Validation/Approval based on comparison of precision, bias, sensitivity and selectivity of proposed alternative method vs. reference method
- Method should have standardized QC, including:
  - Calibration linearity and ongoing verification,
  - Initial and ongoing precision and recovery,
  - Blanks, matrix spike and duplicate,
  - MDL, Reference sample analysis,
  - QC acceptance criteria ≥ to reference method

ENVIRONMENTAL STANDARDS

Water Program Lab Assessment

- Does the laboratory have appropriate QA documents.
- Is the laboratory following the method requirements?
- Are method variances within the agency approved method flexibility guidelines?
- Does the laboratory perform all required QC and is this equal to or better than the method acceptance criteria?

ENVIRONMENTAL STANDARDS

OSWER Methods Innovation Rule (MIR)

- Became a Final Rule June 14, 2005.
- Removes unnecessary requirements to use only SW-846 methods for RCRA applications (excepting MDPs).
- Permits a a shift in focus toward measurement objectives rather than measurement technologies. (ie. a performance based approach)
- Allows publishing of methods as guidance, such as SW-846, without formal rule making process.

ENVIRONMENTAL STANDARDS

Consequences of the MIR

- Regulators must clearly delineate DQO's.
- Appropriate methods may include any reliable and acceptable technology that can produce data of sufficiently known and adequate quality for supporting project-specific decisions
- Enforcement must determine if method quality indicators of interest meet DQO/MQO.
- Need for comprehensive, accurate and appropriate laboratory method performance data.

ENVIRONMENTAL STANDARDS

SW-846 Laboratory Assessment

- Does the laboratory have appropriate QA documents?
- Is the laboratory following the method where requirements are clearly defined?
- Are method variances documented in the SOPs?
- Does the laboratory have the method/NELAC defined QC for all of the methods/ analytes of interest?

ENVIRONMENTAL STANDARDS

SW-846 Assessment Limitations

- Accuracy/Appropriateness of the laboratory QC data
  - Tunes, Calibrations, Precision, Bias, MDLs
- Quality of communications with client
  - Method Quality data accurately calculated and presented.
  - Communication of variance and non-conformances.
  - Project planning and SAPs.

ENVIRONMENTAL STANDARDS

NELAC ASSESSMENT
What it does well

Precision, Bias and Selectivity for Water Programs

- For water programs NELAC assessment looks for all method defined Quality indictors.
- Includes Initial and ongoing method performance demonstration.

Method Sensitivity

- For water programs NELAC assessment looks for LODs (MDLs) and/or LOQs as required in the method or by regulation.

ENVIRONMENTAL STANDARDS

NELAC ASSESSMENT
limitations

- For OSWER programs NELAC assessment performs well at the Quality Systems Level.
- There is little time for qualitative or technical review of appropriateness of data and protocols.
- Pass/Fail approach to assessment works well for compliance programs but provides limited depth of assessment for RCRA methods.
- The data user may have to scratch deeper to be sure that the laboratory performance data actually reflect measurement uncertainty.

ENVIRONMENTAL STANDARDS

Field Sampling & Monitoring Organization Considerations

- Assessment of field testing methods for compliance reporting to work similarly to lab method accreditation.
- Assessment of field testing methods for RCRA expected to have similar challenges regarding assessment limitations.
- Accreditation of field sampling methods desirable but highlights lack of consensus reference protocols.
- Accreditation extended to non-lab organizations.
- Accreditation of field samplers for sampling procedures?

ENVIRONMENTAL STANDARDS

Method Assessment Needs

- Where acceptable practices for generating method QC are not defined by method or program - these need to be established for a adequate method assessment.
  - The formulation of best practices or default good laboratory practices does not eliminate project specific flexibility
- Assessment and reporting of performance based methods may need more qualitative assessment and information in a report.

ENVIRONMENTAL STANDARDS

Method Assessment Needs

- Field Sampling Assessment would benefit from uniform consensus methods.
- Certification of Field Samplers may require a new approach to assessment (formalized third party training?)
- Field sampling organization audits should include capabilities and effectiveness for generation of project plans or SAPs.
- Field Assessments are likely to provide the first opportunity to apply accreditation to non-tradition methods/technology.

ENVIRONMENTAL STANDARDS

Tools for Assessment of a Measurement System
ASTM D6956-03

Evaluation of Precision Bias Selectivity and Sensitivity

- Compare results for a method on real samples to results an Alternate Technology.
- Standard Reference Material.
  - Best when it closely matches the project sample matrix
- Matrix spikes and sample surrogates.
  - Some techniques may generate QC that looks better than the procedure actually performs
- Use of Historical results where available.
- Best Measure of sensitivity is direct demonstration of detection at or below the required reporting level

ENVIRONMENTAL STANDARDS

http://www.epa.gov/epaoswer/hazwaste/test/pbms.htm

http://www.epa.gov/epaoswer/hazwaste/test/methdev.htm

http://www.epa.gov/epaoswer/hazwaste/test/mir.htm

ATSM D6956-03

Standard Guide for Demonstrating and Assessing Whether a Chemical Measurement System Provides Analytical Results Consistent with Their Intended Purpose

Use of a Standard Reference Material as a Tool for Ensuring Accuracy and Extraction Efficiency

Ann Shellenbarger Jones[1], Craig Hutchings[2], Ann K. Bailey[2]
[1]Industrial Economics, Incorporated, Cambridge, Massachusetts
[2]EcoChem, Inc., Seattle, Washington

ABSTRACT

Method quality objectives for laboratory analysis programs include a large suite of quality controls to ensure precision and accuracy, both within and between batches (e.g. surrogates, laboratory control samples, matrix spikes, duplicates). However, under standard protocols the determination of accuracy relies on the extraction of spiked samples. Extraction efficiency for particular compounds may vary depending on whether the chemical is spiked into the sample or was originally present in and bound to the matrix. For both biological and non-biological matrices, this binding effect may be observed and is not adequately measured by the standard quality control samples. Certified or standard reference materials can be used in an analytical program to provide a measure of both precision and accuracy in a relevant matrix. One key parameter the reference material measures is the accuracy and precision with which chemicals originally present in the matrix are extracted from the matrix. We report on a large-scale organochlorine analysis in fish tissue (>800 samples). The quality assurance plan developed for this project included a standard reference material (SRM) from the National Institute for Standards and Technology, certified for selected organochlorine compounds. Initial quality control results indicated that most method quality objectives were generally met. However, the performance criteria also specified a performance range for the SRM with each batch. Results for major constituents for the SRM, including organochlorine contaminants and lipids (as total extractable organics), were consistently outside acceptable thresholds. Further tests were conducted to evaluate the extraction and analysis procedures. Test results indicated that under-extraction was occurring in the analytical samples. The laboratory undertook a series of rigorous evaluations of the method, resulting in changes to the extraction process. Following an initial demonstration of capability, a revised method was approved and field samples were reanalyzed. We discuss the tests on the method and the resulting conclusions, compare quality control results between the initial and final methods, and report on the effects of the modified method on analytical results in field samples.

INTRODUCTION

Performance based methods provide unique challenges to both the laboratory and the data user. The laboratory must use their knowledge and experience to develop a method that extracts the analytes of interest from what is usually a non-standard matrix. The method must be cost effective, timely, and the data generated by this method must be accurate and precise over the

IEc

USE OF A STANDARD REFERENCE MATERIAL AS A TOOL FOR ENSURING ACCURACY AND EXTRACTION EFFICIENCY

Ann Shellenbarger Jones[1], Craig Hutchings[2], Ann K. Bailey[2]

1. Industrial Economics, Cambridge, Massachusetts
2. EcoChem, Inc., Seattle, Washington

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Project Overview

- Analysis of fish tissues - multiple species, mostly fillet
- Purpose of study - comprehensive data set
  - update consumption advisories
  - identify locations for restoration projects
- Multi-year collection and analysis
- Sampling and analysis plan designed with scientific advisory board
- Performance-based requirements for analysis
- MQOs set based on data needs
- On-going data validation throughout the project provided by EcoChem

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Scope of Analysis

- Target detection limits: 1.0 ppb for DDT isomers and chlordane and 0.1 ppb for PCB congeners and dieldrin. Measured 6 DDT products (2,4'- and 4,4'-DDD, DDE, and DDT) as well as 45 PCB congeners.
- Matrix types: 25 fish species or species groups from 30 locations.
- Wide range of concentrations expected, from several ppb to several ppm, for both total DDTs and total PCBs.
- Analysis by GC/MS-SIM

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QC Overview

- Value of both accuracy and precision
- Matrix effects
- Concern - most QA/QC does not evaluate extraction efficiency except from spiked samples

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Standard QC Samples

Quality Control	Description	Frequency	Properties Measured
Laboratory Control Sample	Clean matrix spiked with known concentrations of target analytes	Once per batch	Extraction efficiency under ideal conditions
Matrix Spike	Field sample spiked with known concentrations of target analytes	Once per batch	Extraction efficiency in field samples
Matrix Spike Duplicate	Duplicate of field sample spiked with known concentrations of target analytes	Once per batch	Precision of extraction
Sample Duplicate	Duplicate of field sample	Once per batch	Precision of extraction, sample homogeneity
Surrogate Compounds	Chemicals not usually found in field samples that behave similarly to target analytes	Every sample	Extraction efficiency (also used to correct data results)

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Project Criteria

Sample Type	Acceptance Criteria
Certified Reference Material (SRM1946)	Values must be within 15% of 95% confidence interval for the true or reference value
Method Blank	No analytes to exceed 3x MDL unless analyte not detected in associated sample(s) or analyte concentration > 10x blank value.
Matrix Spike	%Recovery = 50% to 125% if sample concentration is less than 4x the matrix spike concentration.
Laboratory Control Sample	%Recovery = 50% to 125%
Sample Duplicate	RPD < 30% if > 10x MDL for fillets
Surrogates	% Recovery = 60% to 110%

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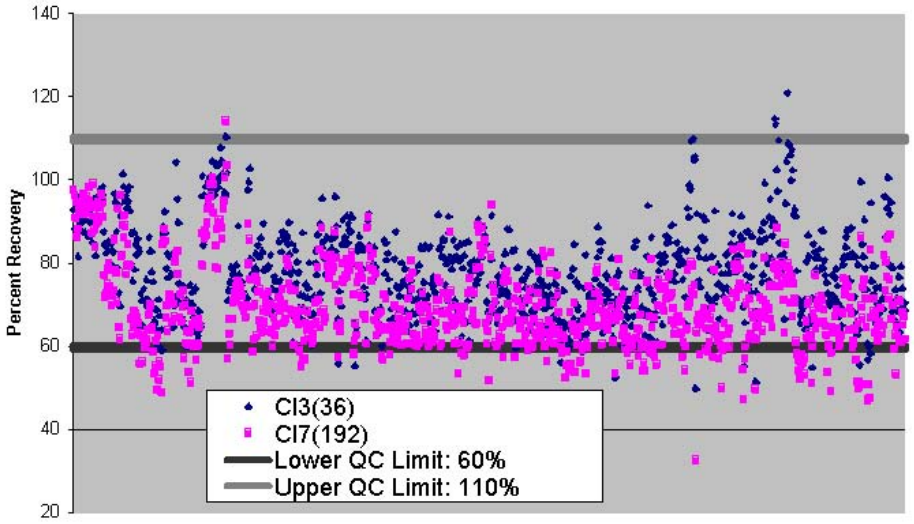
Surrogate Recovery - Initial



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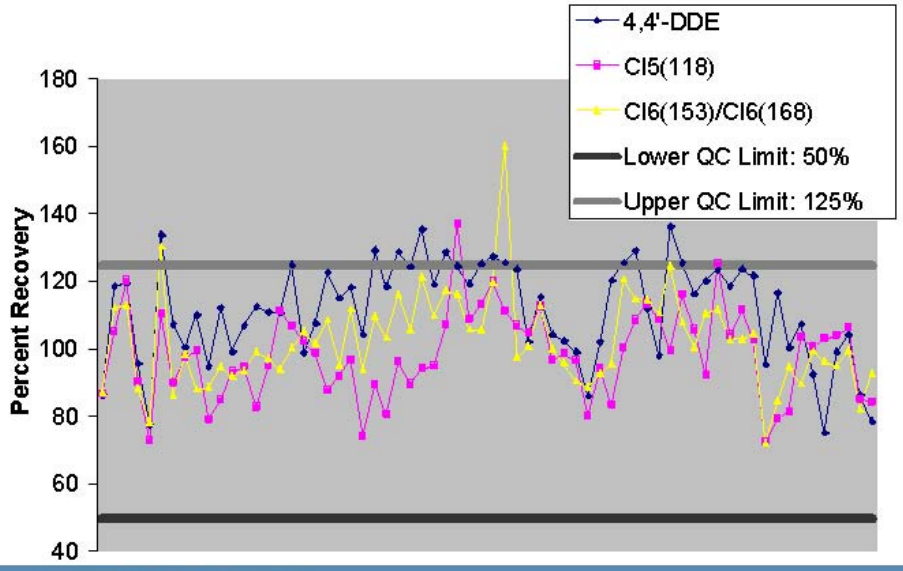
LCS Recovery - Initial



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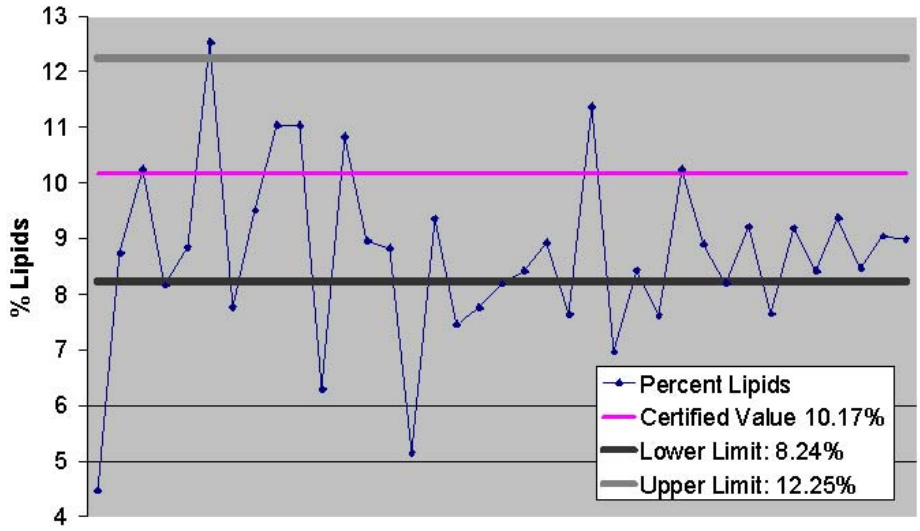
SRM 1946 % Lipids - Initial



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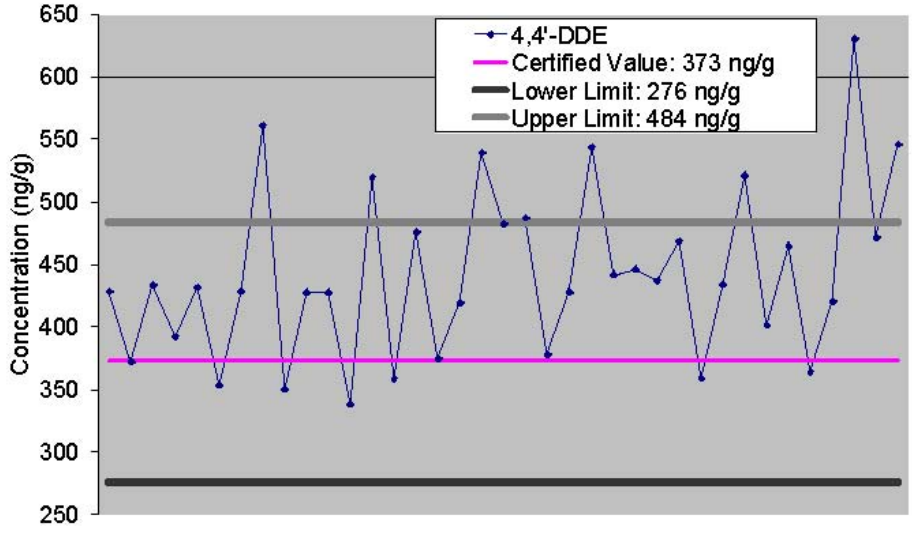
SRM 1946 4,4'-DDE - Initial



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Initial Analysis QC Results

- Surrogates: Within limits, but consistently low
- LCS: Generally within limits; low precision; inconsistent across constituents
- Matrix Spike: High levels of target analytes skewed results
- Sample Duplicate: Most analytes (96%) within limits; some issues apparent with lipids and 4,4'-DDE
- SRM: Key constituents indicate potential issues with precision and accuracy

➢Laboratory ran tests on extraction efficiency

- Decision to re-analyze samples with revised method

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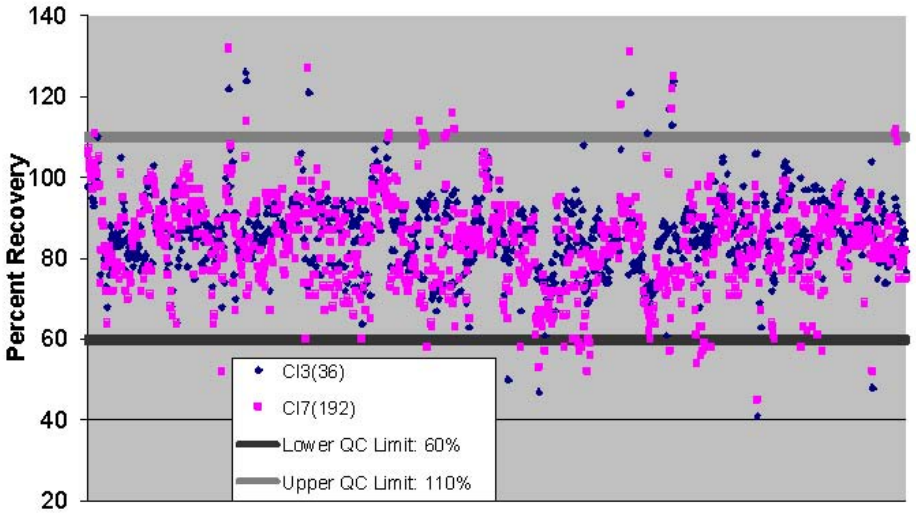
Surrogate Recovery - Re-analysis



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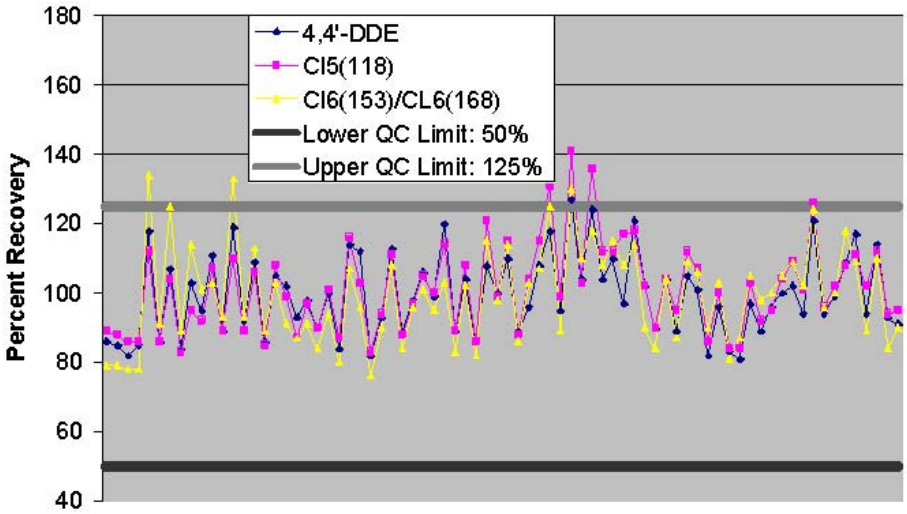
LCS Recovery - Re-analysis



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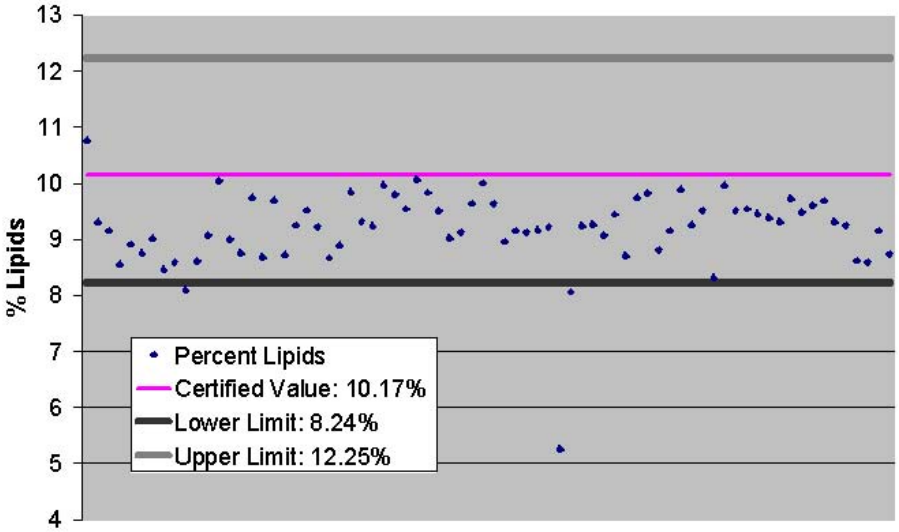
SRM 1946 % Lipids - Re-analysis



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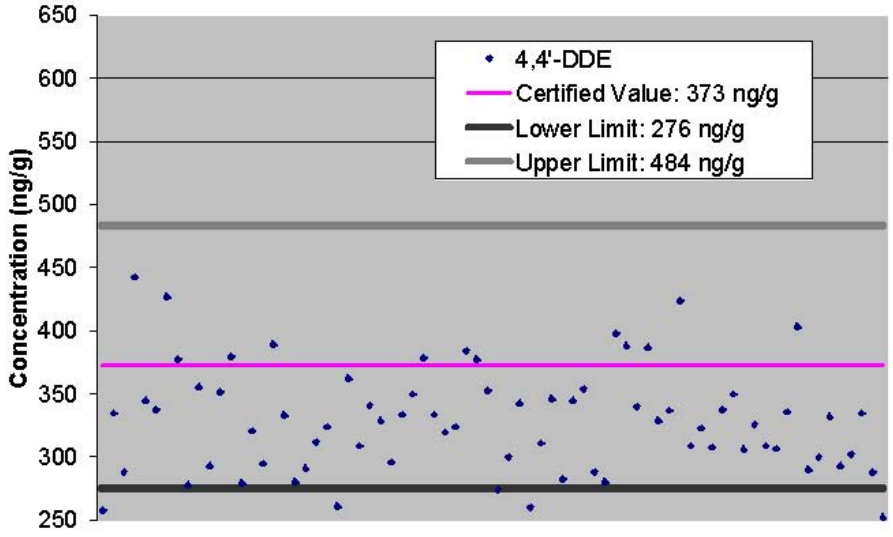
SRM 1946 4,4'-DDE- Re-analysis



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Re-analysis QC Results

- Surrogates: Within limits. Increased consistency throughout analytical run.
- LCS: Generally within limits; recovery generally near 100%
- Matrix Spike: High levels of target analytes skewed results
- Sample Duplicate: Analytes within limits except one sample
- SRM: Substantial improvements in results

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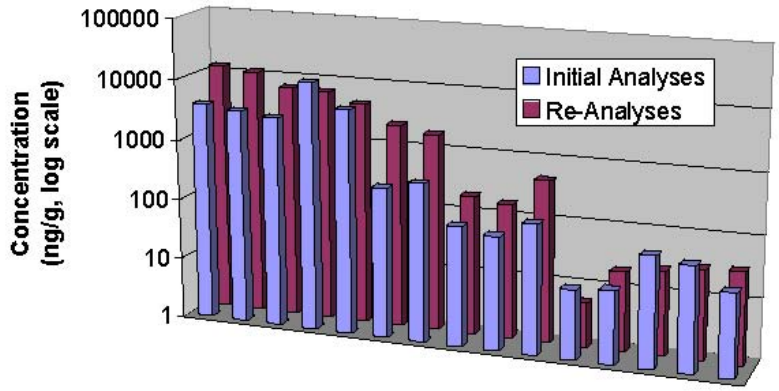
DDT Results - Field Samples



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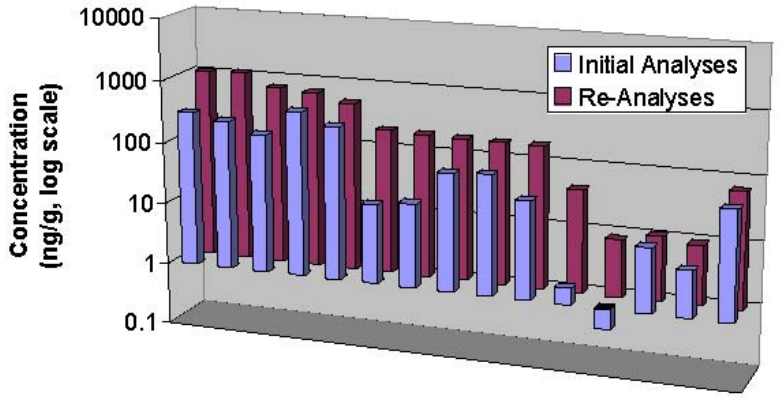
PCB Results - Field Samples



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Results

- Order of magnitude increases between initial and re-analysis values for many samples
- Decrease in total DDTs in three of the fifteen samples.
- DDTs: RPD ranged from 9% to 152%
- PCB congeners: RPD ranged from 2% to 184%
- Data from the original analysis would not have accurately assessed risk to human health - significantly understated for PCB congeners in some cases.

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Conclusions

- SRM ensures data are reliable, accurate, and precise.
- SRM measures not just accuracy but also between-batch precision
- Interim independent validation of data is critical for large datasets - Trust your instincts!

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Mass Spectrometry Quantitative Deconvolution Data Analysis Software: How Does It Fit into Performance-Based Methods and Improved Data Quality?

Albert Robbat
Tufts University

ABSTRACT

With the advent of performance-based methods, independent testing labs no longer must stick to procedures as written in the U.S. Environmental Protection Agency (EPA) SW-846 handbook of methods. In fact, independent testing labs have for a long time "pushed" to reduce sample prep and GC run-times, but do so at the risk of misidentifying target compounds or under/overestimating their concentration in complex samples. Labs routinely dilute samples that contain soil contaminated with coal tar or petroleum, while analyzing these samples under the same conditions they identify standards, but know they will miss target compounds, internal standards, and surrogates.

Because current instrument vendor software is incapable of differentiating target compound mass spectra from chemical noise, customers and regulators have learned to live with inferior data. In this paper, mass spectrometry deconvolution algorithms developed at Tufts University and commercialized by Ion Signature Technology are used to untangle target spectra from matrix noise and to quantitatively identify all target compounds in the sample. Results will show that PAH, PCBs, and chlorinated pesticides can be quantitated in 5-min in a soil contaminated with gasoline and engine oil and the complete list of 8270 compounds in 16-min without losing data quality. The Ion Signature data analysis software results in reporting limits that equal method detection limits, even for the most complex samples.

Discussion will follow to illustrate how labs can rapidly screen or quantitatively analyze samples employing a performance based methods approach.

Mass Spectrometry Quantitative Deconvolution Data Analysis Software.

How Deconvolution Fits into Performance Based Methods and Improved Data Quality.

2007 National Environmental Monitoring Conference

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Industry Trends - Analysts Want

More Sensitivity

Better Precision and Accuracy

Faster Chemical Analyses

Find Unknowns

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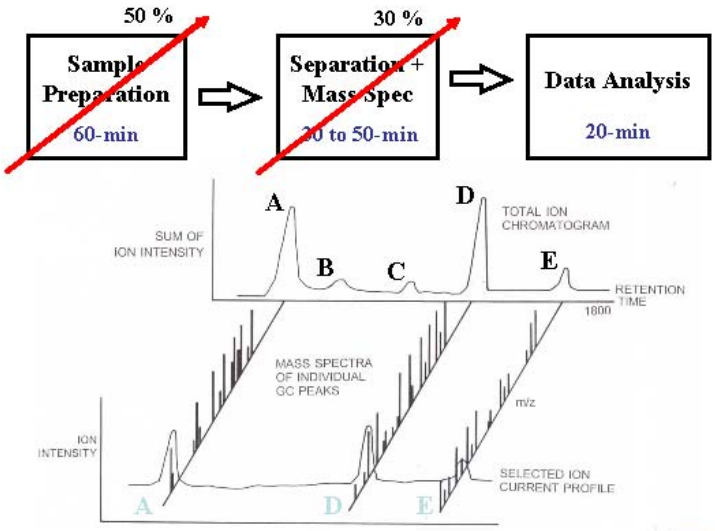
Conventional Laboratory Analysis



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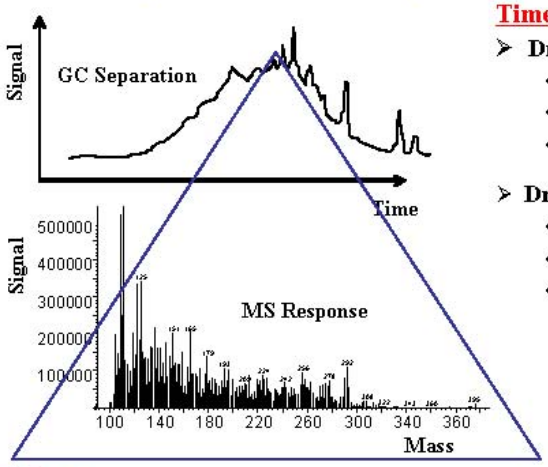
Industry Shift – Faster & Faster Analyses

Complex Mixture Analysis



Time Compression Means

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

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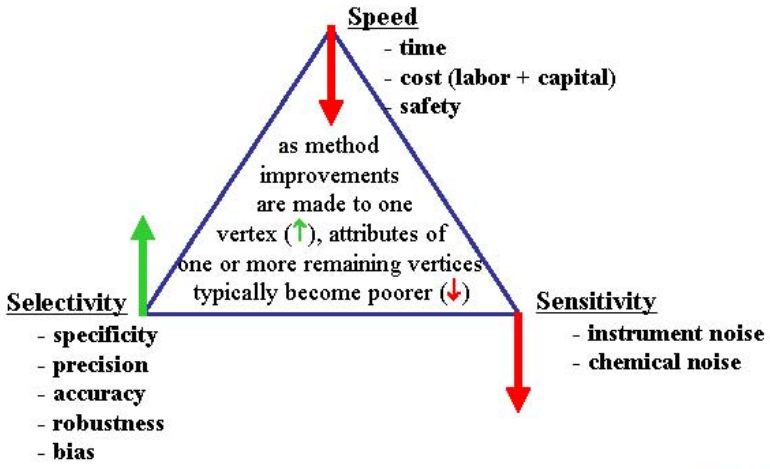
The Analytical Challenge



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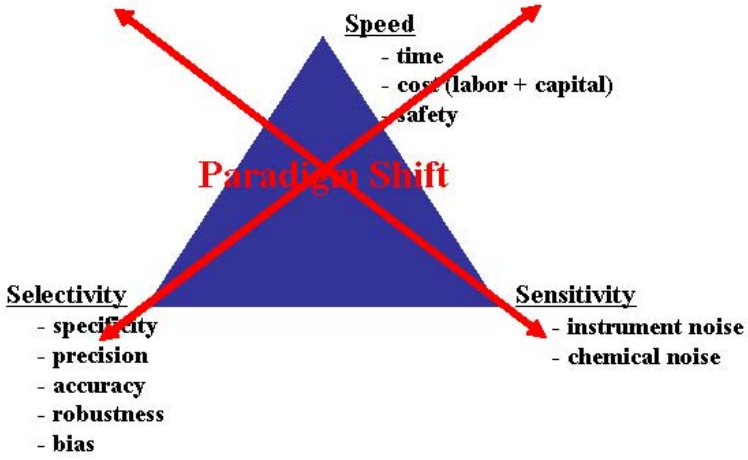
Ion Signature Quantitative Deconvolution



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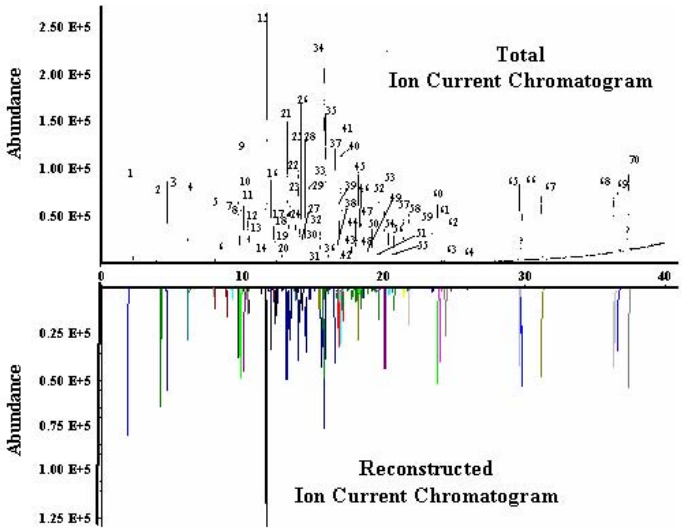
PCB, PAH, Pesticide Standard Mixture, 40-minutes



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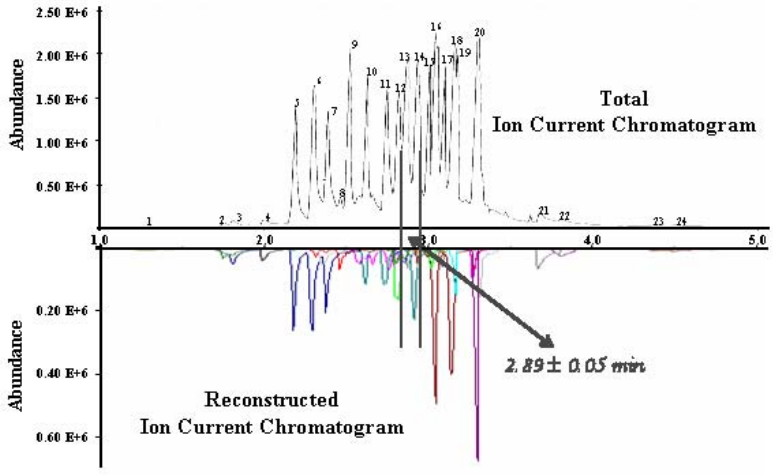
PCB, PAH, Pesticide Standard Mixture, 5-minutes



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Mass Spectrometry Algorithms

$$f_i(t) = \frac{R_i(t)}{L_i} A_m(t)$$

L_i is established library abundance ratio

R_i (t) is observed relative abundance for the i^{th} ion ($1 \le i \le N$)

A_m (t) is observed abundance of the main ion

Three Different Algorithms Used to Identify Target Compounds

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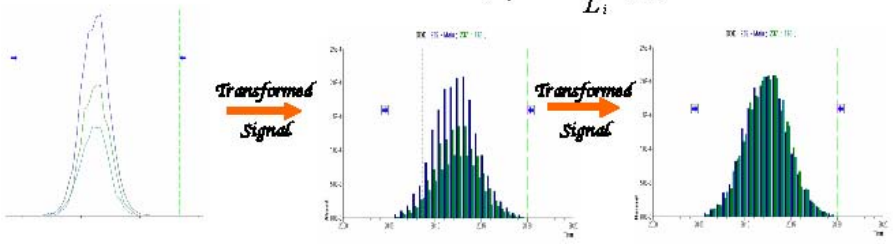
Target Compound Spectrum Matches Library Spectrum

$$f_i(t) = \frac{R_i(t)}{L_i} A_m(t)$$



When the scan-to-scan variation falls within the analyst's established error limit, confirming ions scale to the main ion, the compound is reported present in the sample and quantified.

The analyst can quickly and easily inspect the accuracy of the process at each scan.

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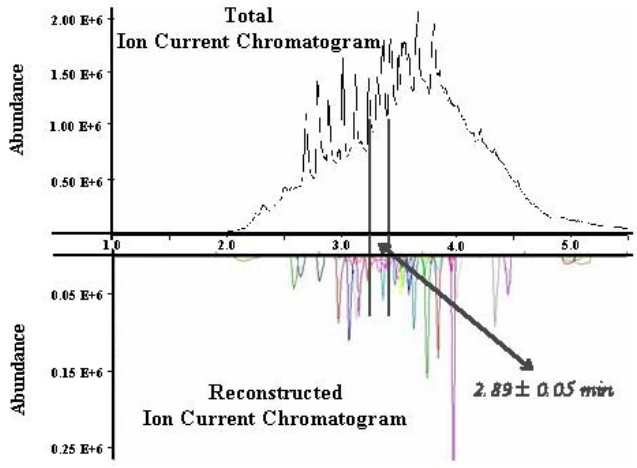
PCB, PAH, Pesticide + Gasoline/Engine Oil , 5-minutes



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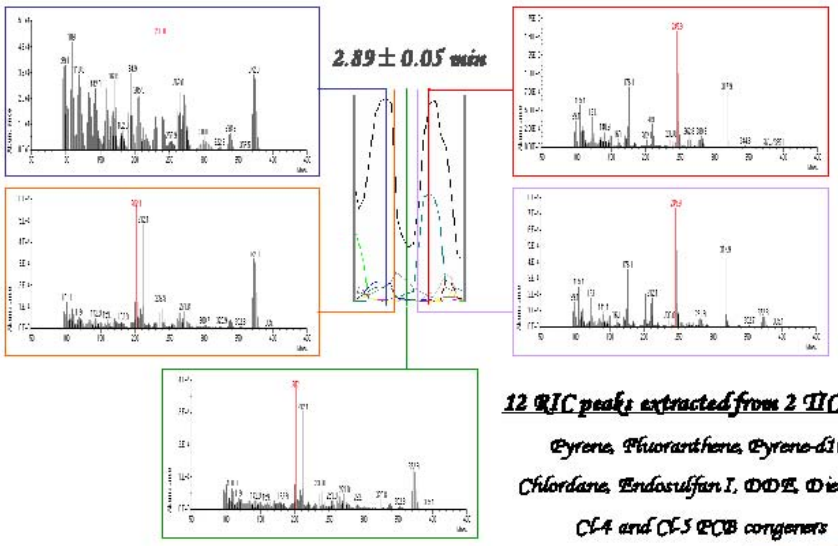
Quantitative Deconvolved Mass Spectra

PCB, PAH, Pesticide + Gasoline/Engine Oil



12 RIC peaks extracted from 2 TIC peaks

Pyrene, Fluoranthene, Pyrene-d10

Chlordane, Endosulfan I, DDE, Dieldrin

Cl-4 and Cl-5 PCB congeners

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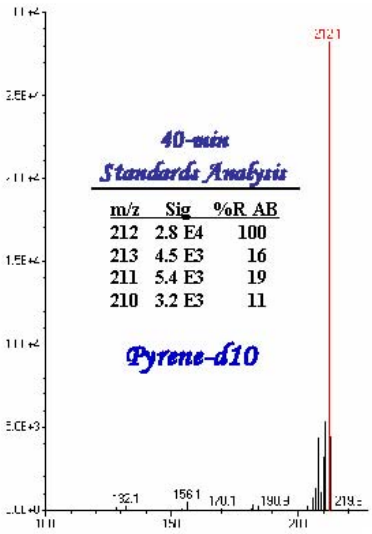
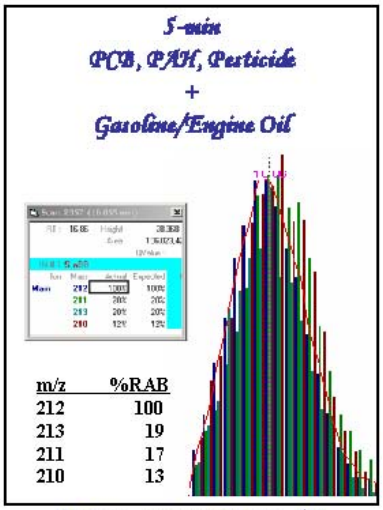
Deconvolution Provides Unambiguous Identification





20 scan average Pyrene-d10
Ion Signature

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No Statistical Difference

5 vs 40-min Data Comparison
PCB, PAH, Perticide + Gasoline/Engine Oil

Deconvolution Algorithms
Correctly Identify & Quantify
All Target Compounds in the Sample

No Sample Cleanup & Fast GC Run-times

No.	Selected Target Compounds	40 min	5 min
2, 3	Acenaphthylene, Acenaphthene	112	106
19	Aldrine	120	89
11	Benzo(a)pyrene	120	118
14	Benzo(gh,i)perylene	91	91
9	Benzo[a]anthracene/Chrysene	96	96
10	Benzo[b](k)fluoranthene	116	113
15, 16, 18	β,γ,δ-BHC	95	95
35	C1-3	96	96
36	C1-4	111	106
37	C1-5	96	92
38	C1-6	128	87
22	Chlordane	111	109
24, 26, 29	DDE, DDD, DDT	103	103
13	Dibenz(a,h)anthracene	83	87
25	Dieldrine	124	119
28, 33	Endrin aldehyde and keton	86	86
23, 27	Endosulfan1 and2	126	123
32	Endrin	124	101
6	Fluoranthene	110	110
4	Fluorene	95	95
21	Heptachlor	118	118
20	Heptaclor Epoxide	112	117
12	Indeno(1,2,3-c,d)pyrene	88	90
31	Methoxychlor	122	122
1	Naphthalene	148	128
5	Phenanthrene & Anthracene	92	96
7	Pyrene	116	116
Average Recovery(%RSD)		107 (15%)	103 (12%)

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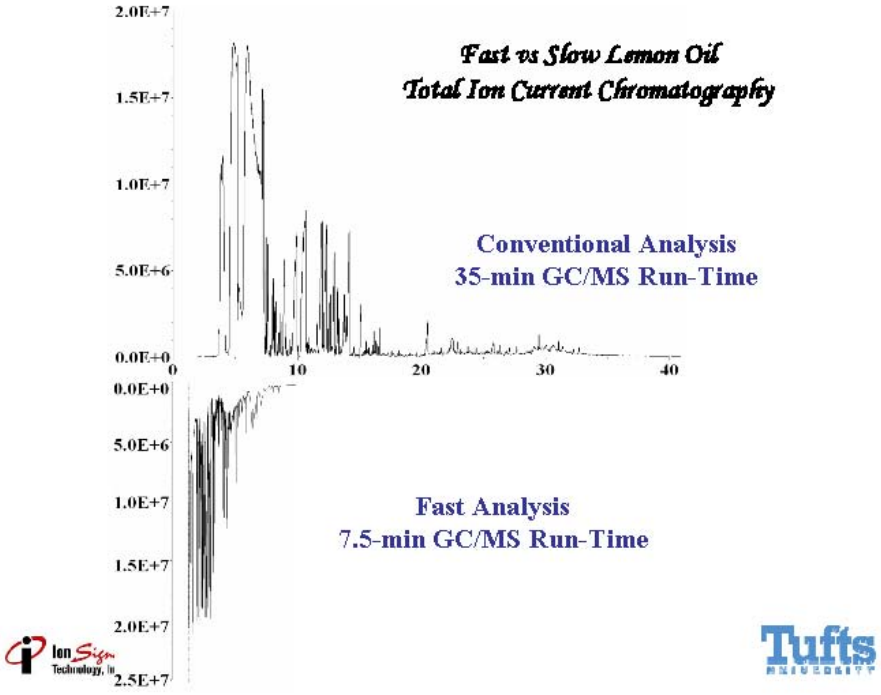
Fast vs Slow Lemon Oil
Total Ion Current Chromatography
Conventional Analysis
35-min GC/MS Run-Time
Fast Analysis
7.5-min GC/MS Run-Time
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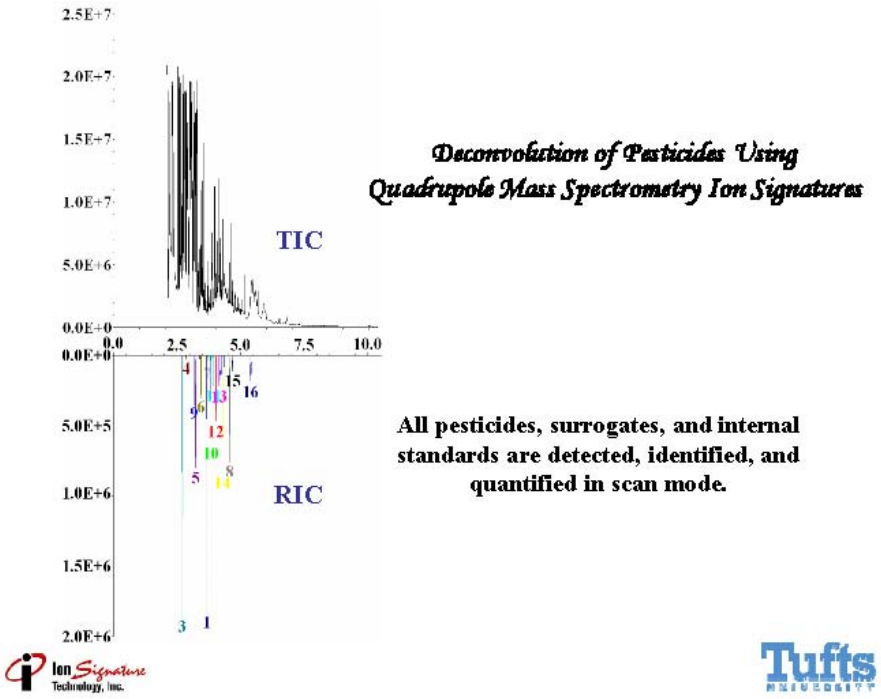
Deconvolution of Pesticides Using
Quadrupole Mass Spectrometry Ion Signatures
TIC
RIC
All pesticides, surrogates, and internal standards are detected, identified, and quantified in scan mode.
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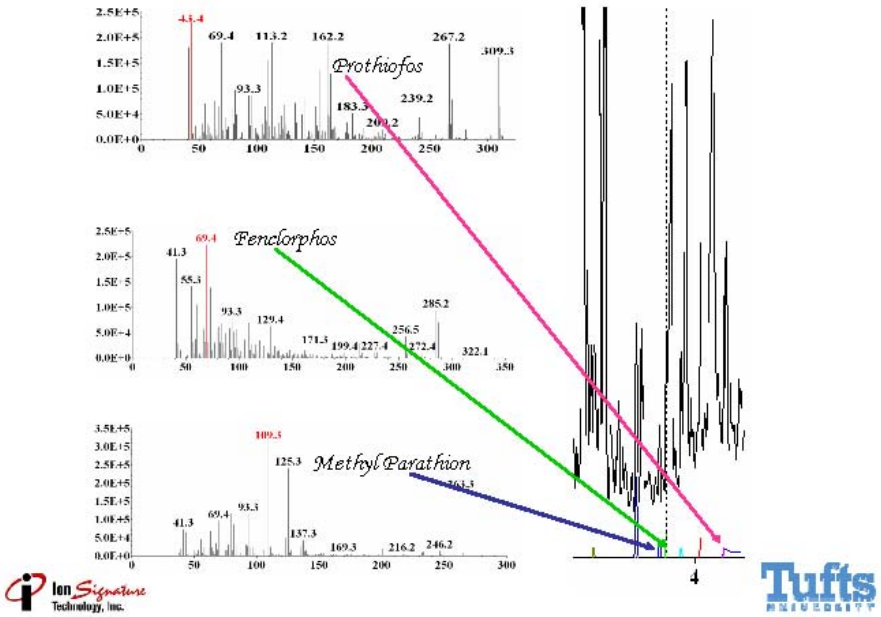
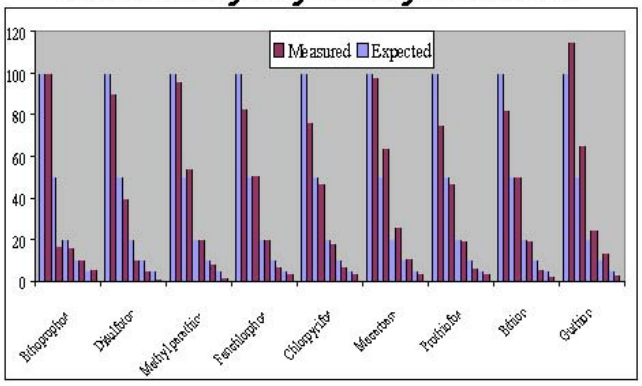
The Ion Signature quantitative deconvolution software unambiguously differentiates target compound mass spectra from chemical noise.



Pesticide recovery as a function of concentration.



Surrogates were added to each pesticide fortified lemon oil sample (100, 50, 20, 10, 5, and 2 ppm) at 20 ppm concentration.

The average surrogate recovery was 17 ± 6 ppm.

The average measured concentration for all pesticides across the concentration range of 2 ppm to 100 ppm was within 20% of the expected, fortified, concentration.

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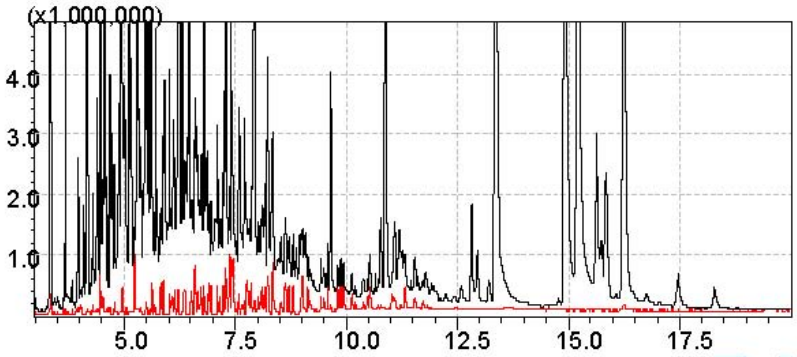
Fast GC/MS Analysis

112 fortified Japanese regulated pesticides in orange peel extract, 0.1mg/mL



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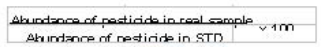
ID	Compound	GCMSsol	I ST
1	Methamidophos	120	123
2	DDVP(Dichlorvos)	115	98
3	EPTC	111	136
4	Butylate	115	118
5	Aceplate	121	131
6	MIPC(Isoprocarb)	114	110
7	BPMC(Fenobucarb)	112	97
8	Ethoprophos	115	117
9	IPC(Chlorpropham)	108	129
10	Bendiocarb	88	104
11	Cadusafos	135	114
12	alpha-BHC	119	103
13	Thiometon	118	108
14	beta-BHC	127	106
15	Dimethipin	108	132
16	gamma-BHC	118	101
17	Isofenfos	120	142
18	Diazinon	114	109
19	Isofluthrin	108	98
20	Etrimfos	111	114
21	delta-BHC	368	96
22	Pirimicarb	108	121
23	Ethiofencarb	103	117
24	Benfuresate	108	105
25	Fenitrothion-methyl	151	129
26	Tolclofos-methyl	113	117
27	NAC(Carbaryl)	74	75
28	Pirimiphos-methyl	114	107
29	MEP(Fenitrothion)	142	145
30	Methiocarb	95	95
31	DicHoflunanid	78	78
32	Esprocarb	110	109
33	Malathion	113	116
34	Metolachlor	111	108
35	Chlorpyrifos	198	104
36	Thiobencarb	105	114
37	Dimethylvinphos	112	120
38	Diethofencarb	106	110
39	MPP(Fenthion)	105	108

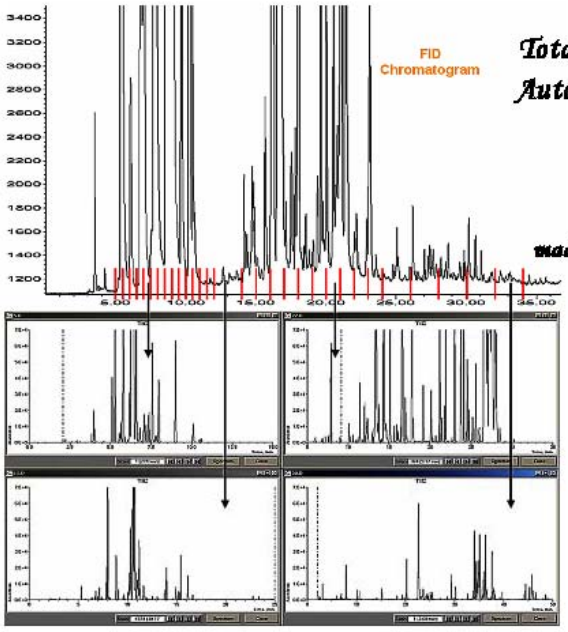
ID	Compound	GCMSsol	IS I
40	Parathion	131	120
41	Isofenphos P=O	201	119
42	dicofol deg.	124	125
43	Fosthiazate-1	156	116
44	Fosthiazate-2	100	107
45	Pendimethalin	150	123
46	CVP(Chlorfenvinphos)-E	126	113
47	Pyrifenox-Z	107	110
48	Isofenphos	121	126
49	CVP(Chlorfenvinphos)-Z	117	111
50	PAP(Phenthoate)	113	106
51	Quinalphos	101	119
52	Captan	119	131
53	Triadimenol-1	129	126
54	Triadimenol-2	154	125
55	Chlormethionat	109	102
56	Pyrifenox-E	110	108
57	Procbutrazol	136	161
58	Flutolanil	111	108
59	Prothiophos	111	109
60	Tricyclazole	113	163
61	Pretilachlor	116	126
62	pp'-DDE	112	108
63	Myclobutanil	132	175
64	Flusilazole	167	119
65	Cyproconazole	155	103
66	Chlorobenzilate	109	112
67	Fensulfothion	159	108
68	pp'-DDD	110	110
69	Mepronil	119	122
70	Propiconazole-1	179	165
71	EDDP(Edifenphos)	121	126
72	Propiconazole-2	138	136
73	Lenacil	115	139
74	Thenylchlor	122	140
75	Tebuconazole	113	141
76	Acetochlor	162	89

ID	Compound	GCMSsol	IS I
79	EPN	121	101
80	Tebufenpyrad	111	109
81	Phosalon	128	128
82	Cyhalothrin-1	109	104
83	Pyriproxyfen	112	127
84	Mefenacet	114	124
85	Cyhalothrin-2	149	130
86	Acrinathrin	80	86
87	Fenpropathrin	115	133
88	Pyraclofos	167	143
89	Bitertanol-1	220	106
90	Permethrin-1	115	127
91	Bitertanol-2	332	283
92	Permethrin-2	115	115
93	Pyridaben	122	138
94	Cyfluthrin-1	163	127
95	Cyfluthrin-2	126	144
96	Cyfluthrin-3,4	226	132
97	Cypermethrin-1	83	126
98	Halfenprox	133	115
99	Cypermethrin-2	88	115
100	Cypermethrin-3,4	134	141
101	Flucythrinate-1	121	129
102	Flucythrinate-2	150	145
103	Silafluofen	113	117
104	Pyrimidifen	148	89
105	Fenvalerate-1	83	120
106	Fluvalinate-1	147	128
107	Fluvalinate-2	153	111
108	Fenvalerate-2	150	102
109	Esfenvalerate-1	209	98
110	Esfenvalerate-2	301	97
111	Deltamethrin	116	118
112	Imibenconazole	125	102



Ion Signature Technology, Inc.

Tufts University



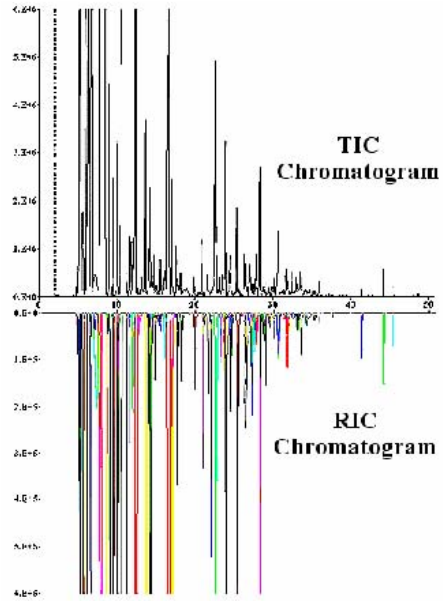
Total product Characterization by Automated Sequential 2D GC/MS

FID Trace of Gin-based Essential Oil made from 10 botanical and citrus oils

GC/MS Trace of cuts from wax to DB5 columns

Ion Signature Technology, Inc.

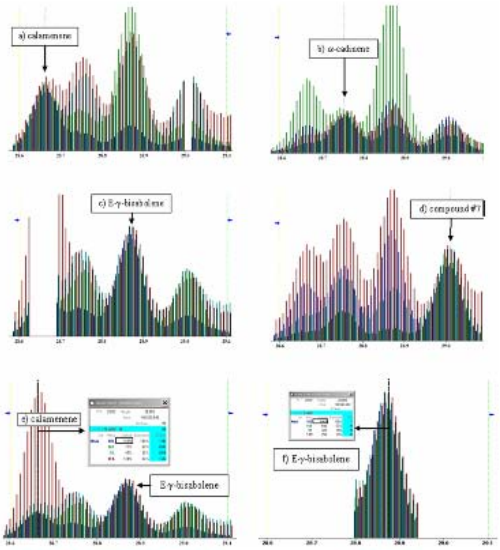
Tufts University



101 Unique Mass Spectra Identified in 1D GC/MS

Ion Signature Technology, Inc.

Tufts University



Peak Response versus Relative Error

Ion Signature Technology, Inc.

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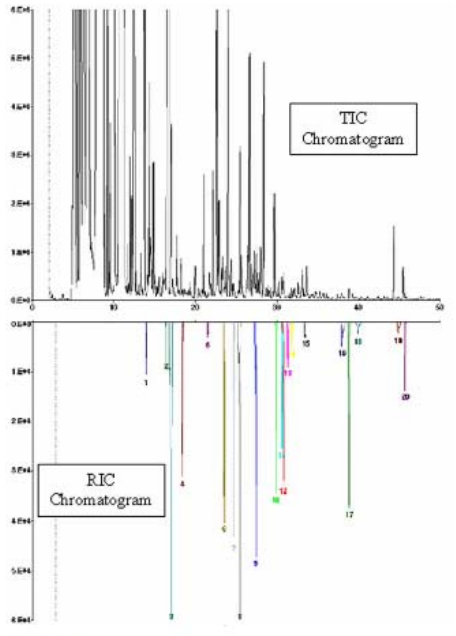

Addition of 0.7% Nutmeg OIL

Ion Signature Technology, Inc.

Tufts University

Funding Sources and Partners

- 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
- Irish Distillers

Ion Signature Technology, Inc.

Tufts University

Increase Confidence

- Finding
  - Internal Standards
  - Surrogates
  - Target Compounds
- Extending
  - Method Detection Limits
- Improvements
  - Precision and Accuracy
  - Robustness

Ion Signature Technology, Inc.

Tufts University


The Role of "Standard Methods" in a Performance Based World
Andrew Eaton, Ph.D.
Joint Editorial Board
Standard Methods for the Examination of Water and Wastewater
and
MWH Labs
Monrovia, CA 91016
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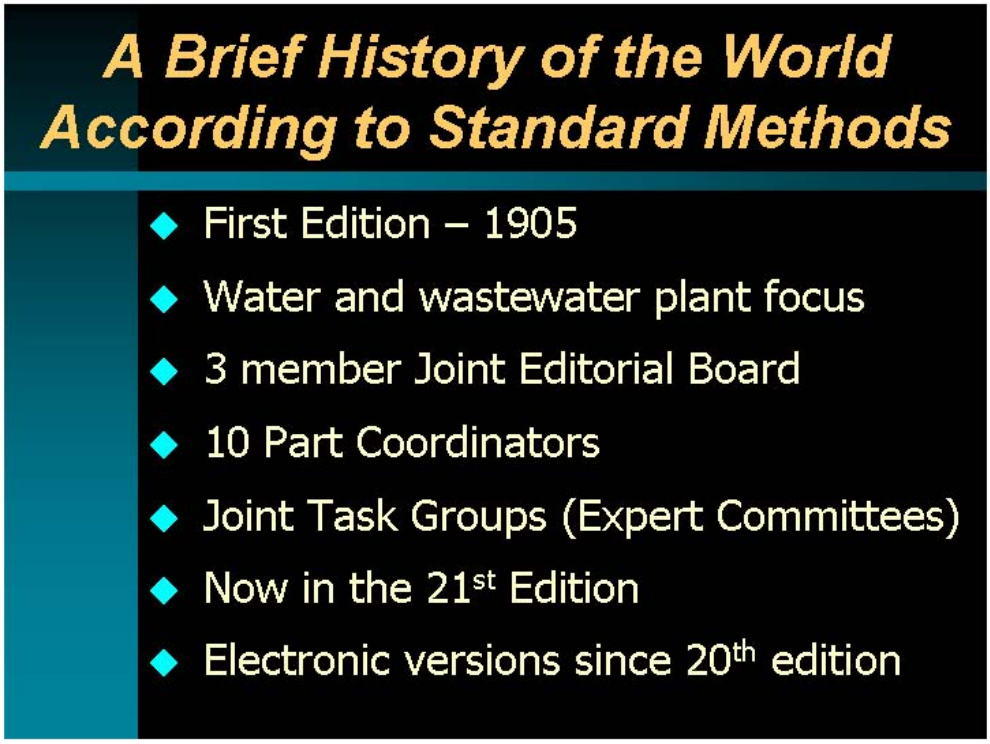
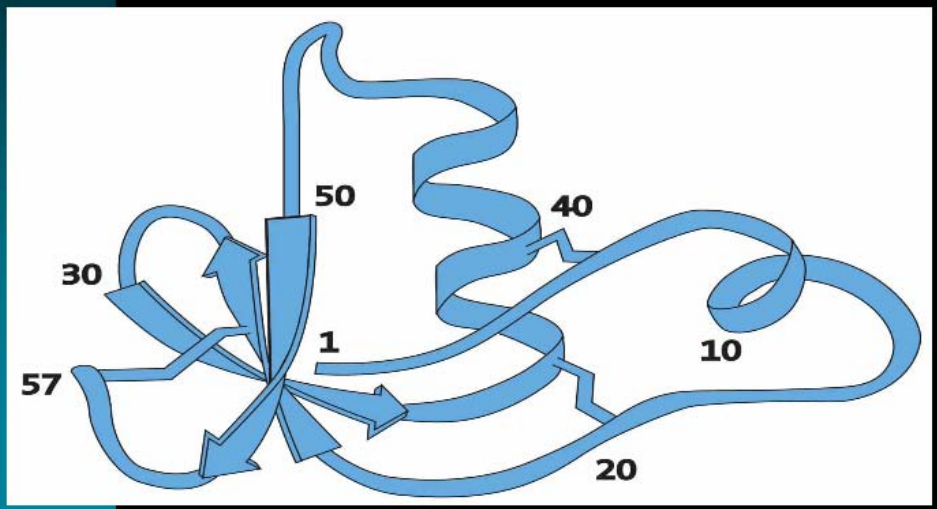
Andrew.d.eaton@mwhglobal.com
STANDARDMETHODS


A Brief History of the World According to Standard Methods
First Edition – 1905
Water and wastewater plant focus
3 member Joint Editorial Board
10 Part Coordinators
Joint Task Groups (Expert Committees)
Now in the 21st Edition
Electronic versions since 20th edition

More Historical Perspectives

- Used world-wide
- Almost all volunteer organization
- Each edition sells between 5,000 and 30,000 copies
- Interact with EPA through an EPA liaision (currently Steve Wendelken)
- True Consensus organization (all negatives must be addressed)

The Standard Methods Approval Process Is A Bit Like a Protein Structure- Very Deliberate



The Methods Approval Process Can Be Fast (or Slow)

- It can take from 3 months to 5 years to produce a method for Standard Methods
  - Motivation of the committee (JTG)
  - Quality of information in the method (validation, verification, etc)
  - Issues raised in balloting
    - Example: Nitrosamines (SM6450)-an attempt to be performance based

How Does the Approval Process Actually Work ?

- JEB or PC or External folks see a need to produce a new method for Na-baloneyate
- PC recruits experts (JTG)
- PC and JTG put together a "charge"
- JTG prepares a method
- JTG ballots a method within JTG
- JTG can't agree on details of the method or can't get validation studies done
  - Na-baloneyate method on hold

More Insights on the Approval Process

- Na-baloneyate method study completed and JTG achieves consensus
- Final JTG method goes to JEB/Editor for "wordsmithing"
- Final method balloted by full SMC
- SMC member has a specific technical objection (negative vote) backed up by details
  - Method returned to JTG for review and revision
  - Requires further testing with proposed changes

Standard Methods Process – Could this be Completed in a Performance Based Environment?

- Na-baloneyate revised method study completed and JTG achieves consensus
- Goes back to full SMC for reballot
  - You can only vote on reballot if you voted the first time
- Consensus achieved by full SMC
- Method goes to JEB Liaison, PC and (sometimes) JTG chair for post-ballot editing (to address editorial comments from SMC)
- Final method (after post ballot editing) goes to Editor
- Method goes to printer to produce pdf version

Where Might Performance Based Approaches Cause Holdups?

- At the JTG - if they don't agree on details
- At the PC/JEB - if they're not satisfied that method is rugged
- At the full SMC level - if there are specific technical objections
- At the PC/JEB level (again) - if technical objections weren't addressed adequately

The EPA Approval Process Adds Another Complexity

- Comply with Administrative Procedures Act (APA)
- All methods subject to EPA approval are reviewed by EPA staff
  - If a method is unchanged, it still must be reviewed (to verify the lack of changes)
  - SM provides strikeout/revision modes to EPA to facilitate review
  - A change in a referenced section (e.g. 3020) can impact approval of another section (e.g. 3111, 3113)
- Methods updates don't have priority within EPA so it can take awhile - but MUR changed that....

For the Record - Why does EPA Not Approve Everything in the Book?

- EPA does not approve books - they approve methods
  - Phenols (5520) is still approved ONLY from the 15th edition
    - Because SM changed the pH in the 16th to get better recoveries (a performance base)
  - EPA does not approve methods for constituents that aren't regulated - so you can use any method you want... (so you can have a "performance" method...but don't ask us to "validate" your changes)

"Standard Methods" in the pre-MUR World

- Easier to update non-regulatory methods than compliance methods
- EPA approval critical to regulatory acceptance
- EPA approval process abysmally slow
  - No incentive to update methods and lose approval (any change loses approval)
  - No opportunity to improve QA/QC or clarify protocols
  - Therefore no real chance to go "performance based"

MUR Impact on "Standard Methods"

- Suddenly SM is the only game in town for many analytes
- Many EPA methods became obsolete
- Clarification of method details became much more important
  - Particularly significant for wet chemistry
- The Catch-22 of the old approval process came home to roost

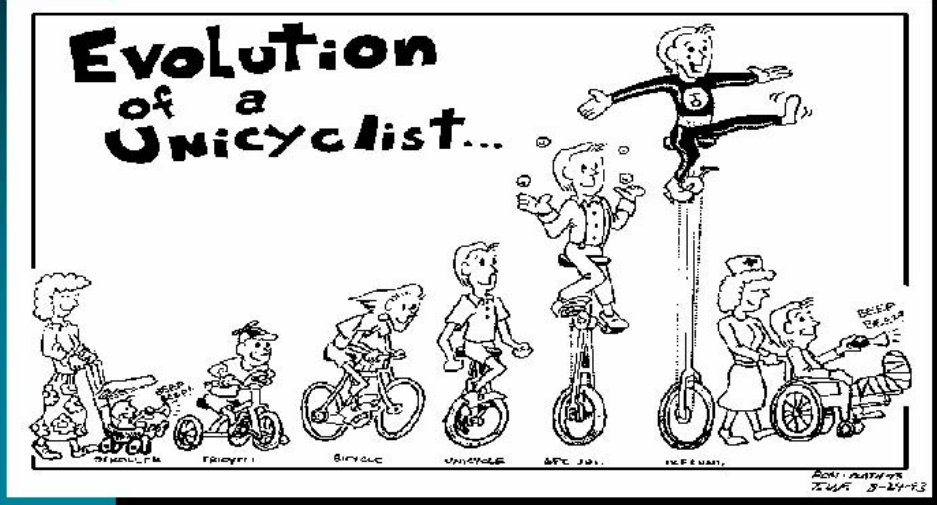
Examples of the Dilemma-TSS (2540)

- TSS – Graduated Cylinder or Pipette?
  - Process says that any technical change needs to be balloted
  - Is this a change, or an interpretation?
  - Can regulators make an interpretation vs the JEB?
  - If a regulator "allows" a change and method subsequently shown to have problems, who is responsible?
  - In this case there was "precedent"

Another Example of the Performance Dilemma - BOD

- More inquiries on BOD than any other method in Standard Methods
- Different degrees of sophistication in queries
  - Can I have a higher blank depletion?
  - For BOD meters, does Standard Methods prefer the air calibration over the Winkler Method? Is there anyone that can send some comments on why they prefer one method over the other?
- Where does "performance" criteria stop and sloppy lab practice begin?

The Potential of Too Much Flexibility Without Controls



QC in Standard Methods and the Impact on Performance Based Approaches

- Most SM QC is very generic
- QC is often not embedded in individual methods (particularly older ones)
- This makes it difficult to encourage a lot of flexibility in methods
  - Limited fixed acceptance criteria to judge the impact of changes

Standard Methods is Moving in a New Direction on QC

- With expedited EPA approval it will become easier to implement change (and retain approval)
- QA/QC definitions in 1000 (1020)
- QC protocols in 020 sections (4020)
- QC Acceptance Criteria in individual methods (4500-P)

If Someone Makes a Change to a Method Who Evaluates It?

- The essence of the Standard Methods process is balloting and consensus.
- No one person in Standard Methods has the time or expertise to "vet" a change (volunteer process).
- Who has the responsibility for ensuring the change does not have a negative impact on accuracy?
  - Wet chem methods are subject to lots of potential interferences

The Irony of a Performance Based World for "Standard Methods"

- If "we" (SM) make a change to a method, we lose EPA approval….
- But since MUR, there are accrediting authorities who are allowing certain method modifications…. (many of which do make sense)

We Will Move To More Flexibility in Some Methods, but not All

- Instrumental methods offer more room for flexibility because it's easier to use the QC as a control.
  - e.g. – 4110 (IC), 3125 (ICP-MS), 6200 (VOCs by GCMS)
- Wet chemistry methods MUST have less flexibility because one may be changing the chemistry of the reaction and bench knowledge has been lost over the years

To Really Move in a Performance Direction Takes Qualified Volunteers

- If you would like to help, let us know. We need qualified, experienced chemists willing to work hard, particularly for the organics methods.

- See John Gumpper if you want to volunteer for part 6000. His grandson wants you to help!


So Can You Have Your Cake and Eat it Too ?

SPECIATION

A New Tool to Assure the Accuracy of Cr(VI) Measurements

Stuart J. Nagourney[1], Rachel Ellis[1], Dr. Stephen Long[2], Bruce MacDonald[3], Shen-yi Yang[4], Dr. Brian Buckley[5]
[1]New Jersey Department of Environmental Protection
[2]United States Department of Commerce, National Institute for Standards and Technology (NIST)
[3]National Institute for Standards and Technology (NIST), Office of Standard Reference Materials
[4]US Environmental Protection Agency/OSW
[5]Rutgers University

ABSTRACT

The accuracy of analysis of speciated metals in non-aqueous matrices has to be a dilemma for the scientific and regulatory communities for many years. For example, most soil samples analyzed for Cr(VI) by EPA Methods 3060A (alkaline extraction) and 7196A (colorimetry) for the New Jersey Department of Environmental Protection (NJDEP) fail method-required QA because of matrix-induced interferences. Use of EPA Method 6800 (speciated isotope dilution mass spectrometry) offers a tool to diagnose problems and provide reliable Cr(VI) data; however, to date only one laboratory is certified by the NJDEP to perform this test method. While Department recommendations state that Method 6800 is to be used when definitive Cr(VI) information is needed (for example, when a "No Further Action" decision is rendered at a remedial site), the majority of future Cr(VI) tests may continue to be performed by other analytical methods. What do we do to assess the quality of those data?

To address this concern, a collaborative effort involving the NJDEP, NIST, the USEPA, and EOHSI is underway to produce a Standard Reference Material (SRM) for Cr(VI) using source material from sites contaminated with this material in Hudson County, New Jersey. This will be the first attempt by NIST to produce a speciated SRM from a natural source. A description of the sampling, sample preparation, stability testing and analysis plans as well as current analytical data will be presented.

Automated Simultaneous Analysis of Methyl and Inorganic Mercury in Biotic Tissues

Christopher Shade
Quicksilver Scientific, LLC

ABSTRACT

Hg is well-known for its bioaccumulative nature and is a toxin of great importance due to its presence in the food supply. However, most importance is typically placed on bioaccumulation of monomethylmercury (CH_3Hg^+). Inorganic mercuric mercury (HgII), though it does not accumulate in the higher levels of the food chain to the degree that CH_3Hg^+ does, has equal or greater ability to impair the biochemical functioning of organisms exposed to it. Recent studies in Spain have shown significant pathologies in livers of fish exposed to high loads of HgII. Thus, effective monitoring of the effect of mercury on ecosystem integrity requires analysis of both HgII and CH_3Hg^+.

The current benchmarks for analysis, USEPA Methods 1630 (CH_3Hg^+) and 1631 (Total Hg – HgT) set the stage for mercury speciation analysis but it has always been a difficult and expensive endeavor. It requires extensive labor by a skilled technician and two separate analyses, with HgII determined indirectly by the difference. In addition, it is not easily scalable or automatable, thus keeping the price for such analyses prohibitively high despite the passage of time.

To surmount this inherent limitation and provide a convenient and rapid method for widespread environmental biomonitoring, we developed a simple leaching procedure coupled to an automated system for liquid chromatography-based separation and atomic fluorescence quantification of both inorganic and methylmercury in a single analysis (Hg-Thiourea Complex/Ion Chromatography - CVAFS). The method works on fresh or dried tissues, features exceptional accuracy, and gives %CV's on replicates routinely below 5%.

Bringing Elemental Speciation to Commercial Laboratories: Advances in Arsenic and Chromium Analysis

Marshall Pattee
Ionomic

ABSTRACT

The growth of elemental speciation has developed new methods, new instrumentation and provided laboratories with new sample production over the past few years. Ionomic will present new opportunities for commercial laboratories in elemental speciation. Incorporating laboratory and end user data quality objectives and assessing new developments in arsenic speciation & chromium speciation by EPA 6800.

Evaluation of Extraction Methods for Determining Mercury Speciation in Tuna Fish Samples

Laura Reyes
Duquesne University

ABSTRACT

Mercury is a very important environmental contaminant. Each mercury species differs greatly in properties, however all are toxic to humans and animals. Organic forms, e.g. methyl mercury, show the higher toxicity and the greatest accumulation in living organisms, in particular in aquatic ecosystems. Methyl mercury is of particular concern since this compound can cause severe neurological damage to people and wildlife. One of the most important source of human exposure to mercury is dietary intake of methyl mercury in fish and fish products. As public awareness regarding the toxicity and the environmental impact of mercury contamination increases, the demand for a simple, fast and reliable analytical method for determination of mercury species also increases.

The aim of this study was to evaluate different analytical procedures commonly used to extract mercury species from fish and biological samples, by analyzing a Tuna Fish Reference Material (ERM-CE464) certified for the content of total mercury and methyl mercury. The extraction methods tested were based on: alkaline extraction with KOH/MeOH and TMAH/MeOH, acid leaching with HCl and CH3COOH, enzymatic hydrolysis with protease and extraction with L-cysteine hydrochloride. The determination of mercury species was also compared using HPLC-ICP-MS and ESI-LC-MS and other techniques. Speciated isotope dilution mass spectrometry (SIDMS, EPA Method 6800) was used to quantify mercury species and for the evaluation of species transformations during sample-pretreatment steps. The total mercury extraction recovery was also evaluated by ICP-MS.

Hexavalent Chromium by Method 6800, One Year of Commercial Experience

Mark Bruce
Severn Trent Laboratories

ABSTRACT

Accurate site characterization of hexavalent chromium contamination is needed to assess risk and direct cleanup responses. Colorimetric analysis with EPA Method 7196A is the most common. An alkaline digestion (Method 3060A) is used to prepare solid samples for analysis. Ion chromatographic analysis (Method 7199) diminishes the colorimetric interferences experienced by Method 7196A, but can still produce low biased results on reducing or highly absorptive matrices. Speciated isotope dilution analysis (Method 6800) monitors hexavalent chromium losses and transformations and then mathematically compensates to produce more accurate results in difficult matrices.

Method 6800 became available as an analytical option from commercial environmental laboratories in 2006. The development path from interesting technology to highly valued environmental testing service requires contributions and cooperation from many different companies and government agencies.

The process starts with an analytical technology such as speciated isotope dilution mass spectrometry that has the potential to provide useful data to facilitate informed environmental decisions. Next the technical process must be transformed into an EPA-acceptable method. The laboratory must find affordable vendors for both supplies and instrumentation. Implementation within the laboratory requires careful coordination among sample receiving, preparation, analysis, quality assurance, project management and sales. Regulatory acceptance must be gained from state and local government agencies. Existing certification programs must be expanded to include the new method. The laboratory must communicate the benefits of the new service to those responsible for site cleanup (site owners, PRPs, engineering firms). The laboratory should also work with data validators and auditors when the new method is significantly different from previous methods to establish evaluation criteria. After successful validation the data is then used to make environmental assessment decisions. Finally, the data purchaser determines if the value of the data is greater than its cost. If so, then additional samples will be submitted for analysis as needed.

The new service is fully commercialized once a continuing cycle of sample submissions, accurate data reports and environmental decisions is established and each participating company receives acceptable value for its contribution.

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THE LEADER IN ENVIRONMENTAL TESTING

Hexavalent Chromium by Method 6800, One Year of Commercial Experience

Mark Bruce Ph.D.
Albert Vicinie III
William Reinheimer

National Environmental Monitoring Conference
Cambridge, Massachusetts

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August 20, 2007

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Path to Commercialization

- EPA method
  - ~ Preferred starting point
- Regulatory acceptance of method
- Certification of the laboratory
- Vendors
  - ~ Supplies & Instrumentation
- Laboratory space configuration
- Analytical process implementation
- Support processes implementation

2

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Path to Commercialization

- Communicate the benefits of the service
- Facilitate data validation and auditing
- Environmental assessment decisions
- Determine value of the data
- Additional samples analyzed as needed
- Sustaining cycle

3

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Method 6800 Review

- Speciated Isotope Dilution - Mass Spectrometry
- Definitive method for EPA use
- Monitors and corrects for species transformation
- Designed for difficult matrices
- Initial example for Chromium speciation
- Included in SW-846 Update IV

4

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Regulatory acceptance of method

- **Method Deficiencies:**
  - ~ … regulatory-approved methods … (EPA Methods 3060a, 7196a and 7199) underestimate its in-situ [Cr (VI)] concentration in certain types of soil.
- **Additional Analytical Methods:**
  - ~ EPA Method 6800 … is approved and included in SW846 … Should the OQA offer certification for EPA Method 6800?

NJDEP CHROMIUM WORKGROUP 2004

5 http://www.state.nj.us/dep/dsr/chromium/subgroup-anal.htm

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Regulatory acceptance of method

- **Site Remediation: Stu Nagurney (NJDEP-OQA) ... He also reported that site remediation samples whose recovery data for the hexavalent chromium methods is <75% will need to be tested utilizing EPA Method 6800.** Final ELAC Meeting Minutes June 2005
- **USEPA Method 6800 is acceptable for analyzing Cr(VI) in all instances …**
  Public Comment Draft Chapter 4 Analytical Chemistry Subgroup

http://www.state.nj.us/dep/oqa/docs/ELAC_Minutes050609.pdf
6 http://www.state.nj.us/dep/dsr/chromium/chapter%204.pdf

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Certification of the laboratory

- NJ DEP and PA DEP review of analytical SOP and supporting documents
- Response to comments and SOP revision
- State auditor visit laboratory
- Applied Isotope Technologies certification
  - http://www.sidms.com/epa_method_certification.html
- Analysis of performance evaluation sample(s)
- NIST reference material inter-lab study

7

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Vendors - Supplies & Instrumentation

- Isotopically labeled Cr(VI) and Cr(III)
  - Applied Isotope Technologies
- ICP/MS - Thermo X series
- Ion Chromatograph - Metrohm-Peak
- General supplies & labware
  - Liquid reagents
  - Solid reagents
  - Sample handling supplies
  - Sample handling equipment

8

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Laboratory space configuration

- Optimize for
  - ~ heath & safety protection
  - ~ data quality
  - ~ contamination control
  - ~ productivity

9

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Analytical process implementation

- Monitor interconversion from sampling through final analysis
- Field spiking with isotopically labeled Cr(VI) and Cr(III)
  - ~ Water (Not requested yet)
    - Lower concentration (ug/L)
      - Affordable
  - ~ Soil
    - Large quantity of isotopes
      - Sample concentration mg/kg and higher
      - Prohibitively expensive at present
    - How to determine spike concentration?
    - Field mixing difficulty

10

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Analytical process implementation

- Representative sub-sample (0.1 – 1 g)
  - ~ To grind or not to grind?
    - Yes
      - Smaller particles improve sub-sampling
      - Mixing during grinding improves sub-sampling
      - Increases recovery of Cr(VI) bound inside hard particles for a more "protective measurement"
    - No
      - If air dried, no longer field moist sample, shift chemical equilibrium
      - Smaller particle size might increase treatment chemistry reaction rate above the actual site
      - Releases Cr(VI) from stabile particles and increases perceived risk.

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Analytical process implementation

- Method 6800 general procedure
- Select sample prep method
  - ~ 3060A adapted for SIDMS
- Separation
  - ~ Ion chromatography for Cr(III) & Cr(VI)
- Detection
  - ~ ICP/MS for ions 50, 52 & 53
- Data Processing
  - ~ Peak integration, calculations

12

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Analytical process implementation

Applied Isotope Technologies, Inc.

Chromium Speciated Analytic Calculation Software (*)

Answer the following questions by filling the appropriate information in the bordered cells:

(A)	Did you double spike a solid sample?	Yes		Place the mouse cursor on the blue cell to see the Entry Instructions
(B)	How much sample did you double spike?	0.2500	g	User Entry Is Required
(C)	How much $^{53}Cr(III)$ did you spike?	0.1000	g	User Entry Is Required
(D)	How much $^{50}Cr(VI)$ did you spike?	0.2500	g	User Entry Is Required
(E)	What is the concentration of $^{53}Cr(III)$ spike?	10	µg/g	User Entry Is Required
(F)	What is the concentration of $^{50}Cr(VI)$ spike?	10	µg/g	User Entry Is Required

(G) What are the isotope ratios you obtained after analyzing the sample extractor the sample with an appropriate instrument? Enter in table below.

Analysis Replicates	Cr(III) $^{52}Cr/^{53}Cr$	Cr(III) $^{52}Cr/^{53}Cr$	Cr(VI) $^{52}Cr/^{50}Cr$	Cr(VI) $^{52}Cr/^{50}Cr$
1	1.65301247	0.11220275	0.05414001	1.05888695
2	1.65920006	0.11176309	0.05832431	1.05001617
3	1.67117339	0.11083105	0.05452973	1.07469373
4	1.68347635	0.11226253	0.05436856	1.09442324

Place the mouse cursor on any of the four cells on the "Analysis Replicates, 1 line" to see User Entry Instructions.

Deconvoluted Concentration and Interconversion Results

Analysis Replicates	Deconvoluted Concentration Cr(III) (lbs/yd)	Deconvoluted Concentration Cr(VI) (lbs/yd)	Interconversion (%) Cr(III) to Cr(VI)	Interconversion (%) Cr(VI) to Cr(III)
1	0.000	11.3274	0.776%	0.000%
2	0.000	11.4424	1.772%	0.000%
3	0.000	11.6002	0.868%	0.000%
4	0.000	11.3810	0.210%	0.000%
Average	0.000	11.688	1.02%	0.00%
Stdev	7.02985-21	0.1982881 01	0.47%	0.00%
95% CL	1.11735-20	0.3 1208 7371	0.76%	0.00%

Place the mouse cursor on any of the four cells on the "Analysis Replicates, 1 line" to see User Entry Instructions.

13

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Analytical process implementation

- How to handle very high Cr(VI) concentrations (>500 mg/kg)?
  - ~ Cost of isotope spike
  - ~ Minimum representative sample size
  - ~ Minimum ratio, isotope spike / natural Cr
  - ~ Handle balance between accuracy and cost on a case by case basis

14

TestAmerica

Analytical process implementation

- How to handle complete conversion of Cr(VI) to Cr(III)?
  - ~ Can not perform the calculations
  - ~ Can not demonstrate MS recovery in 75-125% window
  - ~ Does demonstrate no Cr(VI) when sample at equilibrium

15

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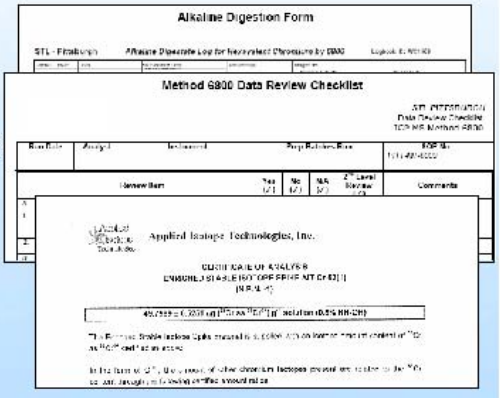
Support processes implementation

- Quality Assurance
  - ~ SOP, RL, MDL, LCS %R, LIMS
- Project management training
  - ~ New questions for client
  - ~ New info to transmit to lab operations
- Sample Receiving
- Information Technology
- Report Generation
  - ~ Expanded deliverables



16

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Communicate benefits of the service

- More accurate Cr(VI) data in very difficult solid matrices
- Increased ability to meet NJ DEP Cr(VI) recovery criteria

ID	7196A		6800	
	mg/kg	MS %R	mg/kg	MS %R
WT	< 0.49	31	6.5	100
V6	< 2.1	0.03	6.4	99
5X	< 0.45	8	19.9	81
57	< 0.45	7	7.9	89
58	< 0.45	29	6.7	92
6A	< 0.45	13.5	9.6	89

17

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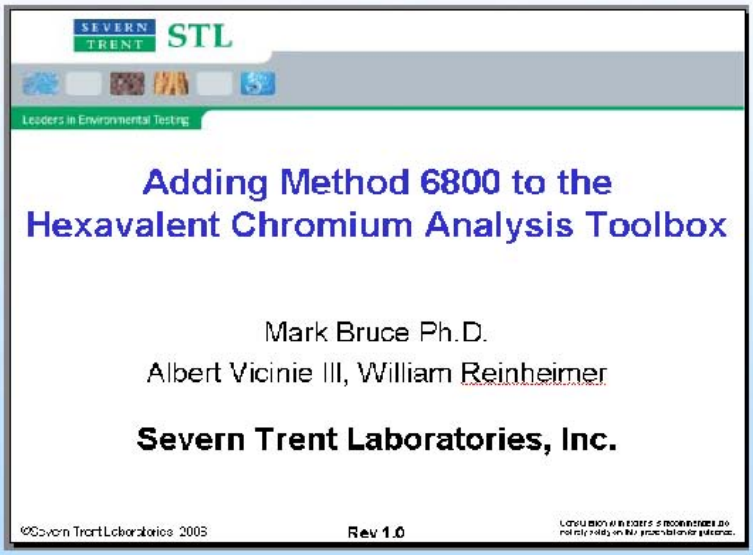
Communicate benefits of the service

- Training
  - ~ Client services and project management
  - ~ Sales force
- Marketing Literature
  - ~ One page summary
  - ~ "White" paper
- Conference exhibits
- Conference presentations
- Technical "brown bag" sessions

18

TestAmerica

Communicate benefits of the service



19

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Reducing or absorbing matrices will decrease Cr (VI) recovery

$$Cr\ (VI) + 3e^- \longrightarrow Cr\ (III)$$

Explain the source of the benefit

20

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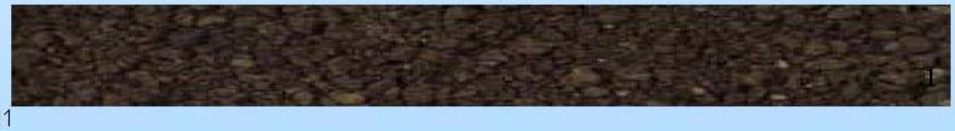
Illustrate the Method 6800 process with a reducing sample

^{52}Cr (III)
^{52}Cr (III)

^{52}Cr (VI)
^{52}Cr (VI)



21

TestAmerica

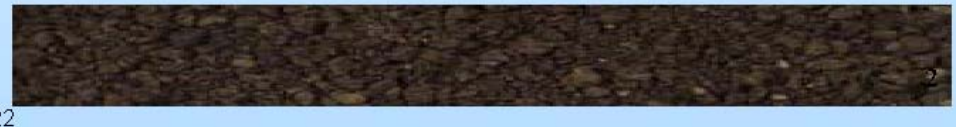
Illustrate the Method 6800 process with a reducing sample

spike labeled Cr(VI)

^{53}Cr (VI)
^{53}Cr (VI)

^{52}Cr (III)
^{52}Cr (III)

^{52}Cr (VI)
^{52}Cr (VI)



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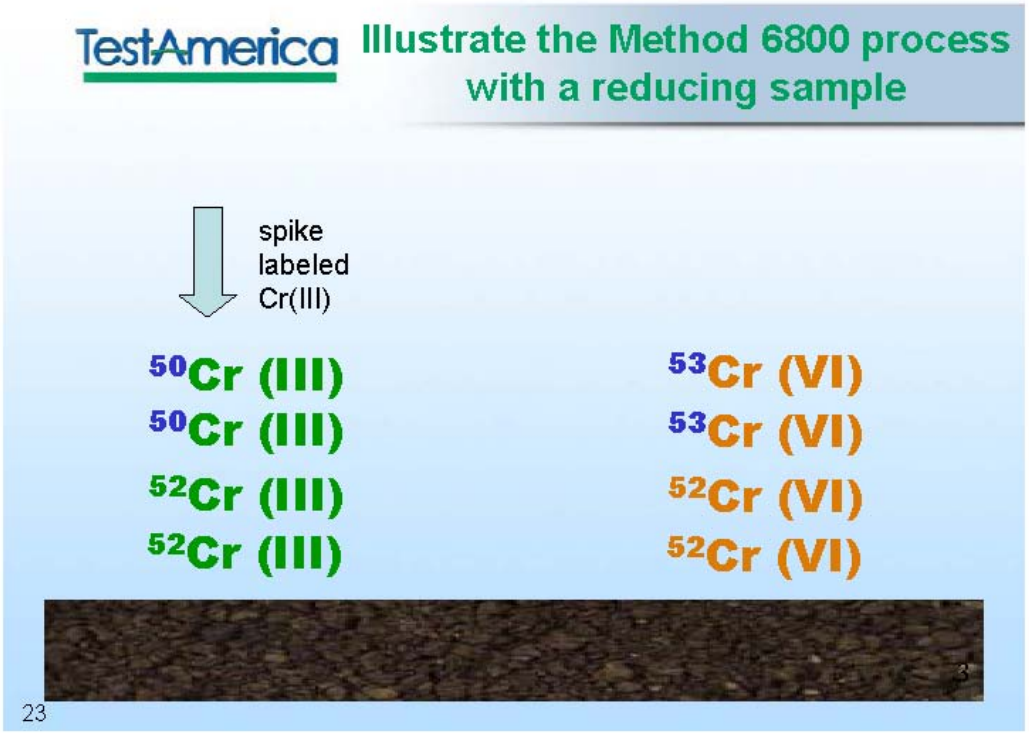
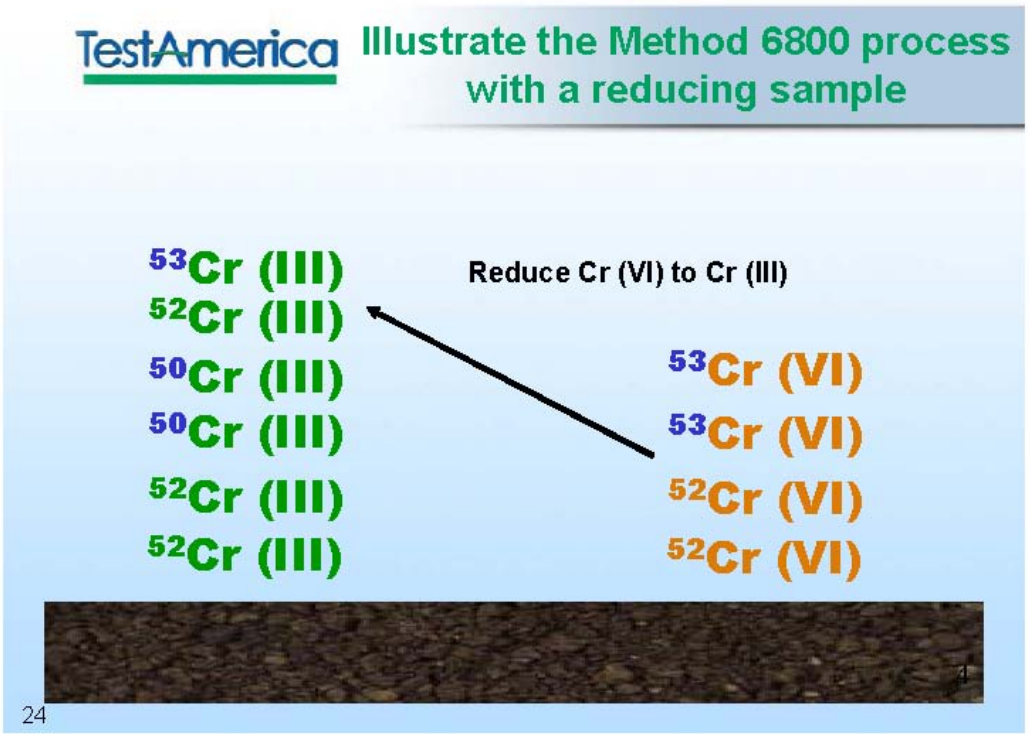

TestAmerica
Illustrate the Method 6800 process with a reducing sample
spike labeled Cr(III)
50Cr (III)
50Cr (III)
52Cr (III)
52Cr (III)
53Cr (VI)
53Cr (VI)
52Cr (VI)
52Cr (VI)
23


TestAmerica
Illustrate the Method 6800 process with a reducing sample
53Cr (III)
52Cr (III)
50Cr (III)
50Cr (III)
52Cr (III)
52Cr (III)
Reduce Cr (VI) to Cr (III)
53Cr (VI)
53Cr (VI)
52Cr (VI)
52Cr (VI)
24

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Calculate original Cr (VI) conc.

from ^{53}Cr (VI) / ^{52}Cr (VI) ratio & the spiked conc. of ^{53}Cr (VI)

^{53}Cr (III) ← Indicates reduction occurred

^{52}Cr (III)

^{50}Cr (III)

^{50}Cr (III)

^{52}Cr (III)

^{52}Cr (III)

Key quantitation ratio

$$\frac{^{53}Cr\ (VI)}{^{52}Cr\ (VI)}$$

25

TestAmerica

Facilitate data validation and auditing

- Method 6800 Cr(VI)
  - ~ Premium test service for premium clients and data users
  - ~ Data validation is common
  - ~ New type of EPA method (SIDMS)
    - Calculations and data usability
    - More limited experience than 3060A with 7196A or 7199
  - ~ General equations in 6800 and literature
  - ~ Proprietary solutions in commercial software

26

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General Equations

$$R^{III}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{III}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{III}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{III}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

27

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Environmental assessment decisions

- NJ DEP recovery criterion 75-125%
- NJ DEP maximum Cr (VI) 20 mg/kg
- Acceptable risk?

ID	7196A		6800	
	mg/kg	MS %R	mg/kg	MS %R
WT	< 0.49	31	6.5	100
V6	< 2.1	0.03	6.4	99
5X	< 0.45	8	19.9	81
57	< 0.45	7	7.9	89
58	< 0.45	29	6.7	92
6A	< 0.45	13.5	9.6	89

28

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Determine value of the data

- TestAmerica clients have not shared these details
- There have been repeat customers

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Sustaining cycle, value for all companies

- Identify data need
- Sample collection
- Sample analysis
- Data report
- Data validation

- Environmental decisions
- Cleanup / on-going monitoring / closure

30

TestAmerica Comparison to expectations

- High skill process ☑
- High labor process ☑
- Expensive Cr standards ☑
- Expensive instrumentation ☑
- Difficult samples ☑
- Small number of samples ☑
- Long time to certification ☑
- High level of client / validator interaction ☑

31

TestAmerica Acknowledgements

Skip Kingston Ph.D.
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Patricia McIsaac
Susan Mazur
Nasreen DeRubeis

TestAmerica

32

Human Exposure to Different Mercury Species and Its Fate

G.M. Mizanur Rahman
Duquesne University

ABSTRACT

Mercury has been well known as an environmental pollutant for several decades. Generally, human exposure of mercury occurs in three ways: as methylmercury from contaminated fish consumption, ethylmercury from vaccination, or by breathing mercury vapors emitted from various sources such as metallic mercury, dental amalgams, and ambient air. Hair mercury levels have been found to be a good indicator of dietary, environmental and occupational exposures to the element. In order to assess the extent of mercury exposure and risk to health, it is essential to determine the levels of both inorganic mercury ethylmercury and methylmercury species.

Hair samples from several volunteers (autistic patients and non-autistic subjects) have been analyzed using direct mercury analyzer-80 (DMA-80) (without extraction) and HPLC-ICP-MS after extraction using EPA Method 3200. EPA Method 6800 has been applied as a diagnostic tool and determinative technique. EPA Method 6800 is uniquely capable of being used as a correction tool to evaluate species transformation and corrections of both species simultaneously, and the protocol can also be used as an evaluation tool, trapping errors from specific steps on procedures. Any interconversions that occur after spiking are traceable and can be quantitatively corrected by monitoring isotopes in each species.

Speciation – An Industrial Perspective: Remaining Challenges in Sample Preparation, Automation and Expansion of Applications

Matt Pamuku
Applied Isotope Technologies

ABSTRACT

The versatile method for elemental and speciated analyses, Method 6800 is supported by nearly ten years of scientific scrutiny and scholarly publications since it was drafted by the US Environmental Protection Agency (EPA) in 1998. The unique dual-species and three-species, ratio-based, simultaneous chemical and computational measurement approach utilized by Method 6800 eliminates instrument calibration, saves time, money and reduces inaccuracies from instrument signal drift. In the past, the obstacles that limited greater acceptance of this powerful method have been unavailability of standards, reagents and a convenient, straightforward way to prepare and analyze samples in matrices that range from soil, sediment, water, petroleum, industrial products, and biological specimens. Although some of the challenges were addressed by the impending Update-IV of Method 6800, a number of formidable obstacles remain.

Accurate, legally-defensible measurement of inter-transforming species is essential for a true, accurate assessment of toxicity. The importance of accurate metal-species measurement is underscored by an increasing number of biomedical and environmental health papers which identify environmental exposure as one of critical factors that may trigger the early onset and accelerate progression of life-threatening diseases like cancer and autism. Although some early work holds great promise, there is still much work ahead. This talk will address key areas that need improvement before SIDMS turn into a mainstream tool across many disciplines and industries that are impacted by environmental factors.

Update on "Action and Reaction: An ANSI Conference on Developing a Sustainable Approach to Emerging Chemical Issues."

Michael Taubitz
General Motors Corp Representing ANSI CMF

ABSTRACT

ANSI, the American National Standards Institute, is hosting a national conference on August 9-10, 2007 to address the impact of chemical controls and regulations such as REACH, RoHS, WEEE, GHS, etc… and to explore how ANSI can help to balance the social and economic impact of these regulations.

This conference is the result of a several year journey by the ANSI Company Member Forum to develop a collaborative US process for proactively addressing future chemical and environmental issues. It is a follow-up to the NIST - Industry Workshop held in September of 2006. The conference is intended to be the starting point for an ANSI Panel on Chemicals and the Environment. ANSI panels are custom tailored to address a given set of issues. Panels are a proven process for stakeholders to work collaboratively and solve US issues. It is envisioned that companies, industry groups, government, labor, academia, professional groups and other stakeholders will find that an ANSI panel is the solution for an on-going process to develop sustainable approaches for future chemical and environmental issues.

This presentation will report on the outcomes of the ANSI conference.

ANSI
American National Standards Institute

ACTION AND REACTION

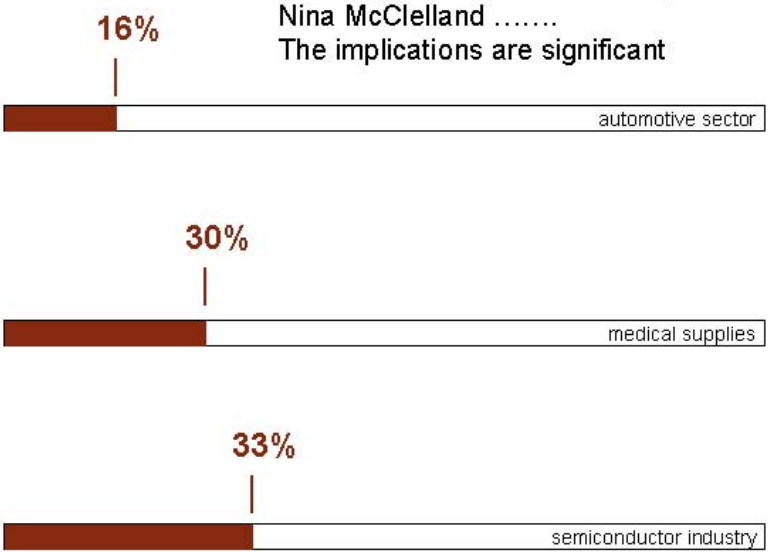
Developing a sustainable approach to emerging chemical issues

Overview of ANSI Conference

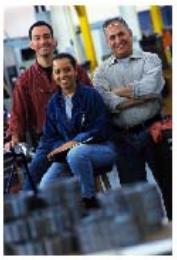
August 9-10, 2007

Mike Taubitz, General Motors Corporation

Setting the Tone: Remarks by Dr. Nina McClelland …….
The implications are significant



U.S. Industry: Annual output of $6 trillion



more than **14.3 million employees**

more than **200,000 locations**

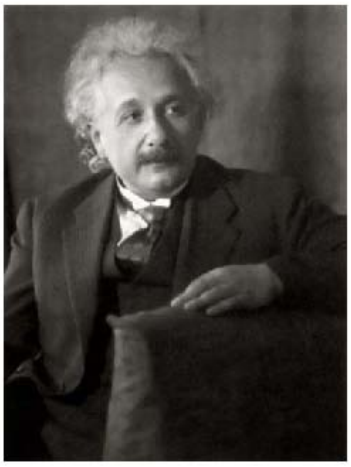
ANSI American National Standards Institute

				R
	W			o
R	E	A	C	H
	E			S
	E	L	V	

Alphabet soup

+ GHS **WHN**

ANSI American National Standards Institute



The significant problems we face cannot be solved at the same level of thinking we were at when we created them.

— Albert Einstein

We need a mindset change. We must work together to inject science into policy.

120 Registered Participants

- ❑ **Companies**
- ❑ **Government**
- ❑ **Academia**
- ❑ **Industry associations**
- ❑ **Professional organizations**
- ❑ **Standards Developers**

Representatives
- Policy
- Standards
- Scientists
- HSE
- Journalists

Action & Reaction Overview

- Registration & hospitality room
- **Opening remarks** – Dr. McClelland
- **Welcome** – Joe Bhatia, ANSI President & CEO
- **Keynote** – Dr. John Marburger, Director Office of Science & Technology, Exec Office of the President
- **Four Panel discussions** 

Panel Discussions / conclusion of Day 1

- **Perspectives on REACH**
  - SOCMA, GM & ITA (Int'l Trade Administration)
- **Current Activities / Issues in Industry**
  - Pratt & Whitney, USCIB (US Council for Int'l Business)
    Design Chain Associates
- **Current Activities / Issues in Government**
  - NIST, OSHA, Department of Defense, EPA
- **International Perspectives**
  - Japanese Chemical Association, UNITAR (United Nations Institute for Training & Research), Suwon University (Korea)

Networking reception and banquet

Action & Reaction Overview: Day 2

- **Working Breakfast**: Establishing a Manufacturer's Network on Chemical Regulation
  - NAM & GM
- **Breakout groups**: 3 Tracks with 2 sessions:
  1. Track One: Product Life Cycle
  2. Track Two: Supply Chain
  3. Track Three: Influencing Policy
- Luncheon – **comments by US Chamber**
- **Report outs** by Track co-moderators
- **Wrap-up** and adjournment

Working Groups……

Track One: Product Life Cycle

- **Discussion**
  - **Design and Development – Current Issues**
    - What needs to be done with products already in the marketplace or that are now ready to enter the market?
  - **Design and Development – Planning for the Future**
    - What needs to be done now to design and plan for the future in terms of product design, manufacturing processes, and delivery systems?
- **Diverse group of 30+**
  - Standards developers, corporations, academia, testing and evaluation, certification organizations, third-party quality assurance organizations, chemical industry reps, regulators, government, product stewardship and environmental, science policy advocacy firms, trade associations, press

A quick summary of the Track 1 issues

- Toxics in products
  - definition of "toxic"
- Communicating information on "chemistry" of products and parts
  - cascading through the supply chain
  - to internal employees
- Quality of information from suppliers
- Uniform format to collect data
- Traceability of recycled products
- Transparency vs. proprietary information
- Communicate safe use of chemicals in products
- Biomonitoring
  - awareness/scan information
  - early warning system
- Balancing industry concerns with health and environmental concerns
- Educating public on what manufacturers do (i.e., toxicology, testing) in chemical management to protect consumers
- Integrating data into *all* aspects of business
  - R&D
  - Materials selection

Track 1: What's underway now

- **Developing Industry Coalitions**
  - Aerospace - work groups (liaise with Europe)
  - Apparel and Footwear
  - Wal-Mart initiative — "value" networks
  - Associations within pharmaceutical, hi-tech industry, bio, furniture industries

- Programs, initiatives, and applicable standards and compliance activities that can help to address the issues

  Organizations/Initiatives
  - OECD
  - UNEP
  - GEMI
  - World Business Council for Sustainable Development
  - SCHC and British counterpart – SHCS
  - American Chemical Council (biomonitoring program)

  Standards
  - ISO 14040 (Product life cycle – energy use)
  - IPC1752-2 (format for collecting data)
  - Other?

What do we still need?

- **Gaps**:
  - communicating information about chemicals
  - defining toxics
  - quality of information on parts
  - recycled content
  - format for collecting data (IPC1752-2)
  - biomonitoring
  - material assessment framework
- **Opportunities for coordination, harmonization and partnering:**
  - International Organization for Standardization (ISO)
  - ASTM International (F40 Committee)
  - OECD
  - GEMI
  - UNEP
  - World Business Council for Sustainable Development
  - SCHC and British counterpart – SHCS
  - American Chemical Council (biomonitoring program)
  - Non-NGO groups

Action Plans: 1 & 2

1. **Establish a Safe Use Communication Process**
   - Focus on manufactured, finished goods
   - Who needs to be involved: major manufacturing sectors (i.e., automotive, aerospace, electronics, apparel and footwear, and others)

   Lead Organization: NAM manufacturers' network association; ANSI

   Lead Person: Dr. Patricia Beattie
2. **Consider the formation of a forum/clearinghouse to *proactively* address future legislation, use of chemicals in products**
   - create a process that acts *before* regulations - focus on scientific health and environmental literature

   Organizations to be engaged:
   - American Chemistry Council
   - American Chemicals Society

Action Plan - 3

- **Develop a Materials Selection Process Encompassing Health and Environmental Impacts of Finished Products**
  - Understand more about the Department of Defense Scan-Watch-Act process
  - Expand automotive sector materials assessment strategy activities (Suppliers Partnership for the Environment)

  - Engage cross-industry involvement
    - Input from session attendees, NAM network
  - Identify NGOs
  - International outreach

Resources/Points of contact

- ANSI
- NAM manufacturers' network association

Track 2 Overview

- **Discussion**
  - Duty of Care vs. Duty of Proof
    - *Who has the burden of proof? Are suppliers responsible for verifying compliance with regulations, or is the final manufacturer responsible?*
  - Crossing Borders
    - *Different countries and regions are defining different environmental regulations and expectations around common issues – the EU's RoHS directive, for instance, has mutated as it has been adopted around the world and the same should be expected for REACH. What is the implication to the supply chain and to product delivery?*

- **19 and 26 participants in respective sessions**
  - *Chemical, semiconductor, aerospace, automotive, IT sectors (8 participants), federal regulator (1), NGOs (4), academia (1), consultants (3), legal (1), media (1)*

A quick summary of the Track 2 issues

- Burden of proof –
  - Regulator or Customer?
- Legal issues
- Current models
- Collaborative frameworks
- Regulation mutation
- Supply chain risk
- Compliance mechanisms
- Other concerns

Track 2

- **What's underway**
  - Collaborative frameworks
    - EU mandate for collaboration incomplete/unrealistic
      - Bidirectional questionnaire?
    - RoHS: absence of collaboration was bad
    - Upstream not best informed, downstream more industrial hygiene than toxicology
    - Pre-registration (upstream) solves most of the (proprietary) problems, except SVHC
  - Basic supplier management & control may return
    - beyond "trust but verify"
- **What's needed**
  - Push to provide information from Regulators
  - Educate community on how standards gaps are identified and process to instigate standards to fill them
  - Bidirectional information exchange up and down the supply chain ("coffee klatsch")
  - Method to prove compliance

Track 2 Action Suggestions for Action

- Survey SDOs to identify relevant standards
- Band together and formulate pointed questions for EU
- Create compendium of countries, organizations, acronyms, standards (a la Wikipedia)
- Identify appropriate management system standard to apply or consider specific variant in this context
- Topics to start with
  - What's the requirement – regulatory or customer driven?
  - Legal/contractual obligations?
  - Current models for comparable issues (responsibility)?
  - Collaborative frameworks?

Track 3 Overview

- **Discussion**
  - Laying the Groundwork for Compliance Verification
    - *What needs to be done to define, measure, and agree on a set of minimum baseline criteria that can be applied across jurisdictions?*
  - Injecting Science into Policy
    - *How do we balance social consciousness with economic impact? How do we advocate for risk-based vs. list-based regulations?*
- **30 participants**
  - ITA, ACS, DuPont, AIA, IBM, Information Technology Industry Council, JJI-Technologies, UNITAR, GM, SOCMA, 3M, ASTM, Soap and Detergent Association, Korean Agency Technology and Standards, NEMA, Lexmark, and more...

Laying the Groundwork for Compliance Verification

- Tackle Emerging Chemical Regulations Cross Industry
  - Address existing needs
  - Determine how to influence foreign governments
- Instead of getting ahead of the curve, lets try to shape the curve.
- Not just a REACh & RoHS issue. All emerging regulations should be considered.
- US Government needs increased involvement
- STANDARDS! STANDARDS! STANDARDS!
  - Example ASTM F40
- Industries need to collaborate their efforts
- Finding where to focus the efforts

We need PROCESSES!

Injecting Science into Policy Summary

- **Awareness Critical!**
  - Surveillance/Radar Screen
  - Early Action within US government agencies (Example- Nano)
- **Be Proactive – Get Involved**
- **Explaining Benefits with the Right Messenger**
  - Trade Offs
- **Eliminate Silos – Collaboration**
  - Company Level to Global Level

Injecting Science into Policy Outcomes

- **Coordination Cutting Cross Silos**
  - Communication is key!
- **Everyone wants action, but actual action is not happening.**

- We need PROCESSES!

Suggestions for an Action Plan

- **Develop a process for industry to offer its scientific and technical expertise to federal and state regulatory agencies, as well as international forums** (such as OECD), especially in the area of emerging issues
  - Timeline – August 30th for first draft
    - SOCMA, ASTM & GM
  - Next steps to be identified once proposal is complete

Cross cutting issues

- Issues have common impact across business sectors
- role of government
- Thirst for communication and information
- Better education (especially executive) required
- Better planning required
- Bust the silos
- New processes are need
- Collaboration & coopeteition

Is there much different between the two???

Recent Problems with RoHS

To better understand what happens when science is absent from regulation…….

Recent Problems with RoHS

To better understand what happens when science is absent from regulation…….

- **RoHS has been in effect in the EU since July 1st 2006.**

To date, no official testing methods have been approved to demonstrate RoHS product compliance.

- **If a product's RoHS compliance is questioned by EU authorities, the case will inevitably be resolved in the EU courts.**
- **RoHS can not be enforced in the current scenario!**
  - —**In the absence of suitable test methods-**

Industry must have the ability to prove compliance through scientifically appropriate methods

- Test methods for compliance must proceed and appropriately guide the regulations
- What are the measurement needs under RoHS
  - — Total Cd, Hg, Pb, Cr(VI), PBB and PBDE concentrations.
- One need - Suitable methods and defined compliance
- Cooperation with international community including EPA, NIST, ANSI, ASTM and other testing and compliance methods organizations

Action & Reaction Summary

- **Conference follow-up**
  - One page executive summary and Powerpoint overview
- **Near – term action will happen**
  - REACH compliance verification and personnel certification
  - Collaborative network
- **Longer term initiatives**
  - Science in the forefront
  - **More strategic and timely use of voluntary standards**
  - **Up to all to "slice through the silos"**
  - Becoming proactive
  - Injecting science and technology into policy deliberations

Must become proactive or WHN will surely hammer us

Ultra Trace Mercury Speciation Analysis by HPLC-ICP-MS

Russ Gerads and Dr. Hakan Gürleyük
Applied Speciation and Consulting LLC

ABSTRACT

Optimization of analytical conditions associated with HPLC-ICP-MS for mercury speciation analysis has resulted in methodology which rivals detection limits associated with EPA Method 1630. The capacity of HPLC-ICP-MS to quantify Hg(II), MMHg, EtHg and other soluble mercury species in a single analytical run provides a competitive advantage over CV-GC-AFS. With HPLC-ICP-MS the recovery of each species can be monitored which significantly increases the level of quality control and quality assurance associated with the results. The applicability of the analytical method to real world samples and advantages over EPA Method 1630 will be discussed.

VAPOR INTRUSION

Ensuring Long-Term Data Usability by Reducing Uncertainty in Monitoring for Vapor Intrusion of Toxics

Henry Schuver
US Environmental Protection Agency/OSW

ABSTRACT

The intrusion of subsurface toxic vapors into the indoor air of overlying buildings remains a rapidly developing field of investigation. Monitoring results supporting 'screen-out' or 'sample-out' decisions needs to retain its validity through time. To help ensure the long-term usability of vapor intrusion monitoring results it may be helpful to review the purpose of monitoring for vapor intrusion and the history of the federal regulatory thinking on the various approaches. The existing state of uncertainty that can be associated with monitoring approaches using various sampling media, locations, methods, and durations will be discussed. Comparisons will be made to lessons learned from long-term experiences with monitoring for other soil-gas contaminants (e.g., radon) and for groundwater drinking-water ingestion exposures.

Ensuring Long-Term Data Usability by Reducing Uncertainty in Monitoring for Vapor Intrusion of Toxics

National Environmental Monitoring Conference
Cambridge, MA
August. 20, 2007

Presented by:
Henry Schuver*, US EPA – OSW
A personal perspective, does not represent Agency positions
See: http://iavi.rti.org

Purpose of Monitoring for Vapor Intrusion

- Risk Management Decisions:
  - "Sample-out" or "Screen-out" - walk away
  - Continue to monitor (w/ interim controls?)
  - Control exposures &/or sources
  - i.e., so you can use the data
    - In decisions that will improve health

Ensuring **Long-Term** Data **Usability** by **Reducing** Uncertainty

- Given Uncertainty = lack of knowledge
- This Includes Elements of Increasing Knowledge of:
  - Temporal variability
  - Spatial variability
    - If you want to interpolate or extrapolate beyond the measurement point

Temporal variability

- Two sources:
  - Environmental changes
  - Methods (sampling & assessing VI)

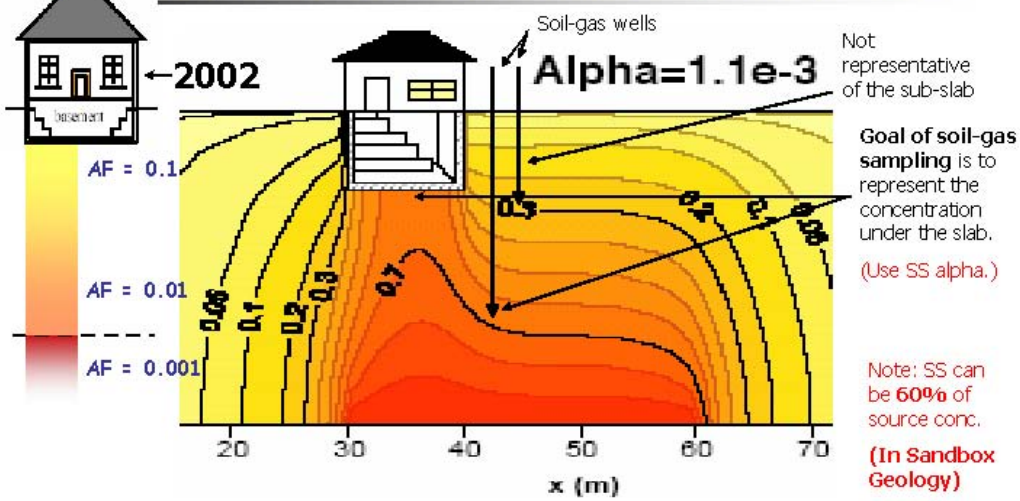
Changes in the Environment

- Sub-surface/Natural
  - Plume migration (natural and pumping influen),
  - Concentrations + or – w/ time
  - New chemicals (from degradation)
  - Water table level, soil moisture, ground disturbance (grade, utilities, leaking pipes)
  - Weather
- Man-Built
  - Bldg or not, surface cover/asphalt
  - New bldgs, types, occupants, operations, HVAC,…
  - Bldg modifications

Some of what we have learned since 2002 – effect of building

3-D Modeling [& Exterior samples]

by L. Abreu & P. Johnson, **EST, 2005**



In NY state 5 out of 11 sample pairs shows conc. > under slab than nearby soil-gas implants – Bill Wertz of NYS 2/7/06 e-mail w/ Westside soil gas vs subslab.xls [up to 30 x higher under slab]

Changes in Sampling Methods

- "rapidly evolving field" (USEPA, 1999)
- "difficult and ever evolving" (ITRC, 2007)

- **Sampling**
  - Groundwater – methods "well" developed
    - (but not focused on VI path?)
  - Soil-Gas – methods in development
    - Soil-gas workshop (AEHS, March 2007)
      - Variability due to sampling methods (only)
        - Sample & purge volumes & rates
        - Adds to complexity of assessing natural systems
    - Research continues in this area, e.g., expanded Vandenberg study
  - Indoor Air – methods established (but ideal for risk?)

Changes in Assessment Methods

- Assessing VI (Interpretation / Decisions)
  - Predictions of indoor air quality
    - Attenuation (sub-surface & sub-slab), Model predictions
  - Changing assessment/screening tech. (per state)
  - Multiple Lines of Evidence (when conflicting)
  - Changing health science (children, etc.)
  - Changing regulatory-toxicology standards (RfC, CSF)
  - Changing social expectations/awareness

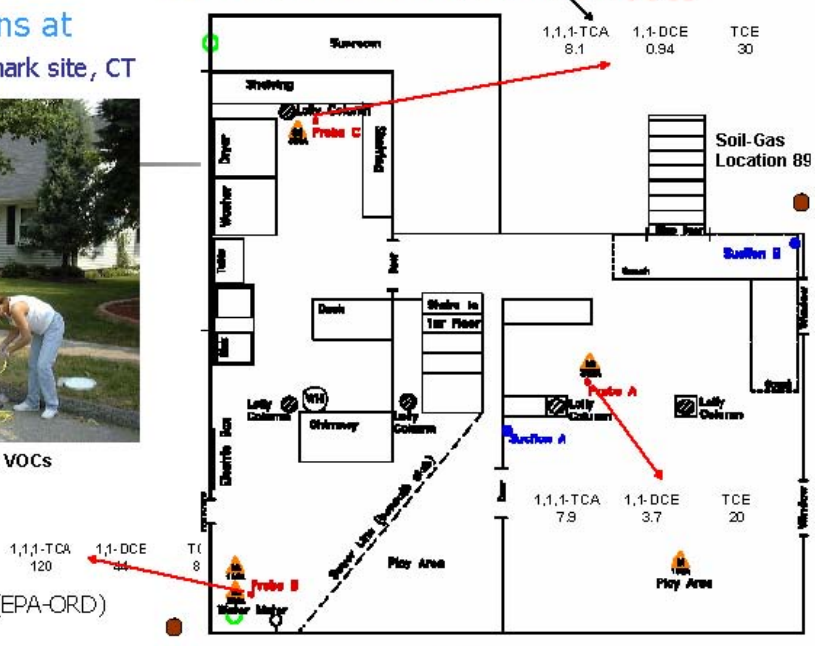
Examples of Spatial & Temporal variability

- X, Y - Dom's Raymark
- X, Y, Z - Wertz' Endicott
- Time – Folkes' Redfields, +

Sub-Slab Concentrations at House B Raymark site, CT

MW215 showed no VOCs

Not a sample of the intruding vapors? > 44 x



Slide by D. Digiulio (EPA-ORD)

w/ mod. HJS

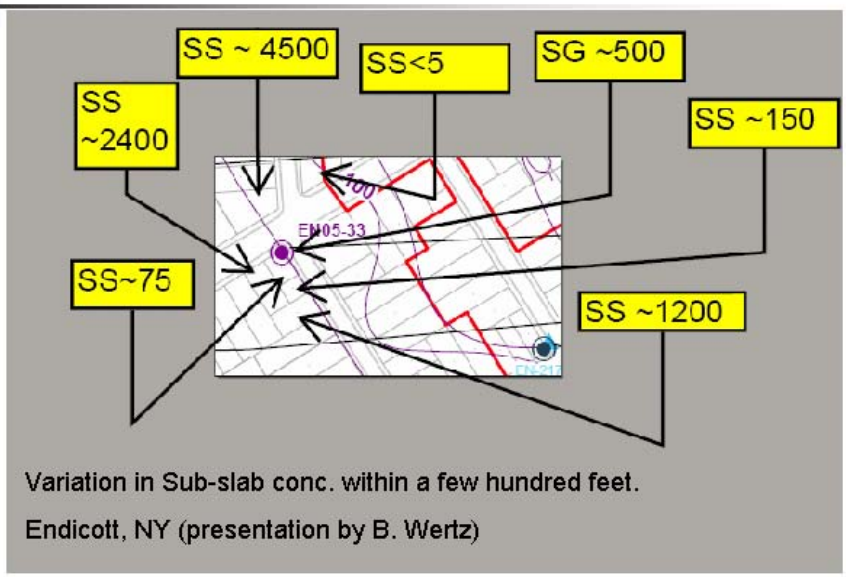
IAQ of 11DCE = 0.11 ug/m3

Using sub-slab *mean* – $Alpha_{ss}$ = 0.11/16 = 0.0065

Using sub-slab point – $Alpha_{ss}$ = 0.11/0.94 = 0.118

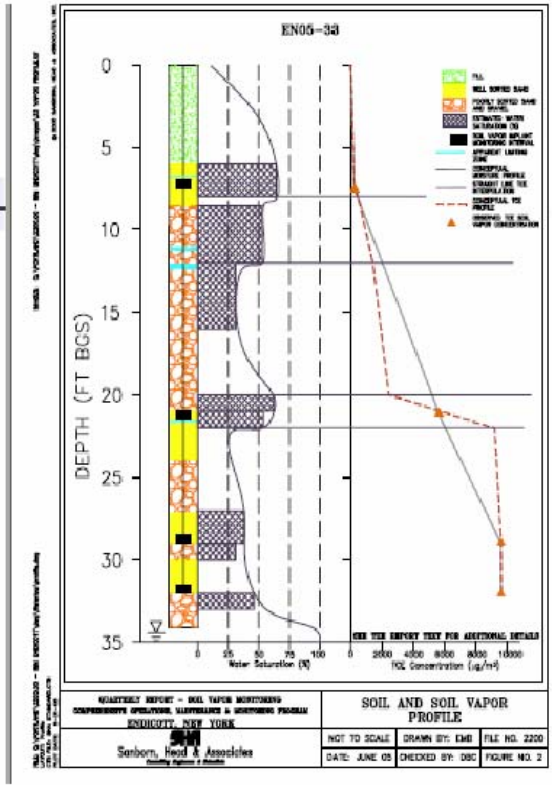
How much external data is needed to predict (i.e., model) this reality (SS conc.) ?

[And this is only SubSlab (add bldg variability to IA)]



Variation in Sub-slab conc. within a few hundred feet.

Endicott, NY (presentation by B. Wertz)



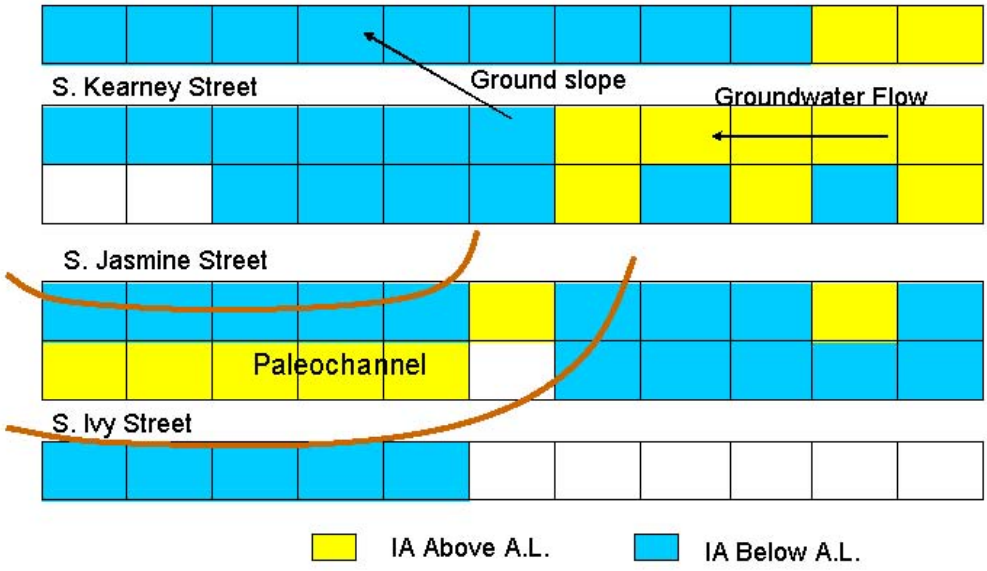
Z

Decreasing soil-gas concentrations above lenses of finer-grained material w/ higher moisture contents

Endicott, NY;

Slide from B. Wertz

Redfield Site (1,1-DCE)



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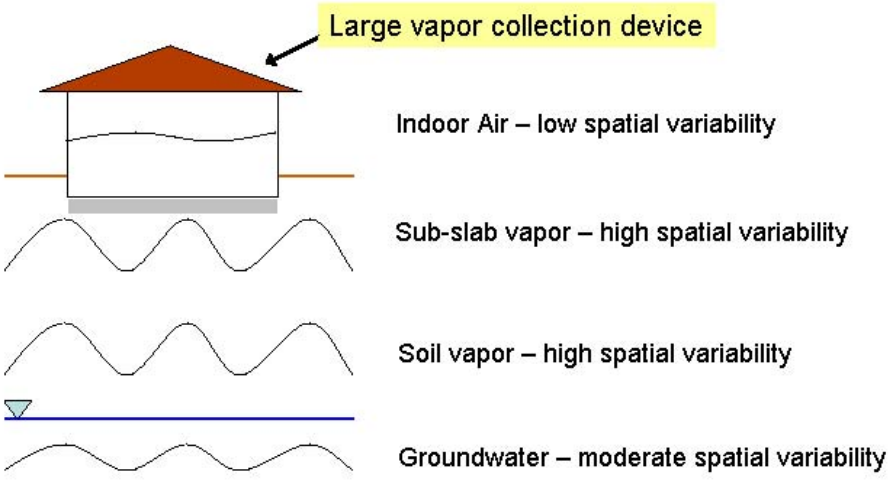
Spatial Variability



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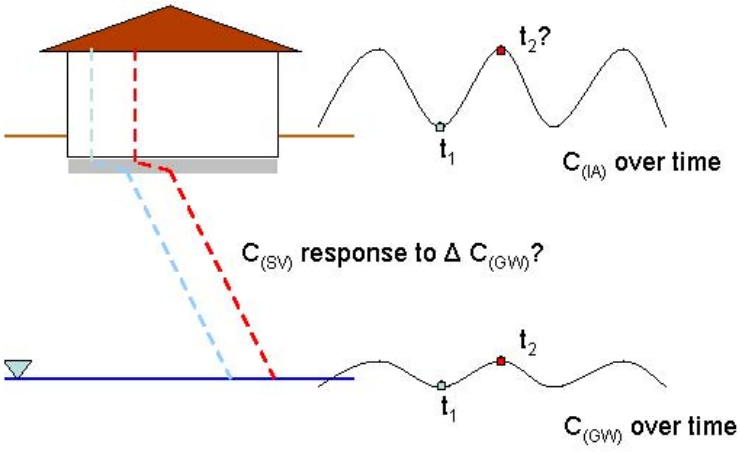
Response to Change in [GW]?



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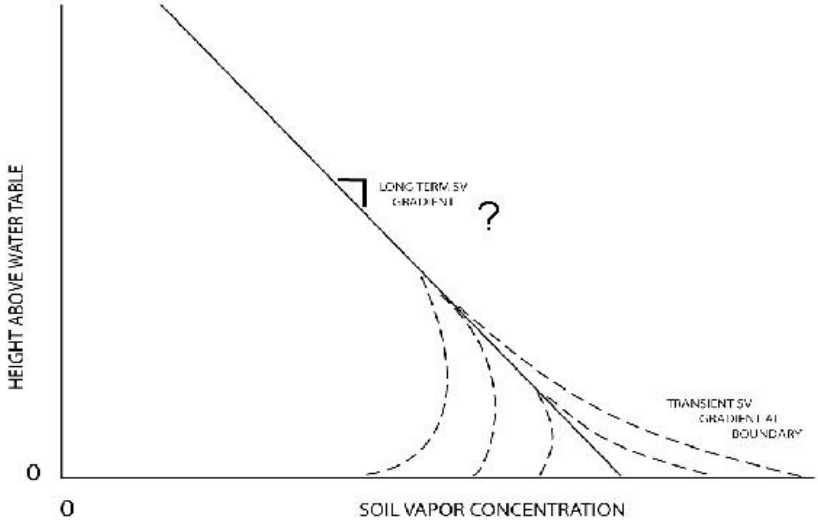
Vapor Flux Response to Boundary Condition Change?



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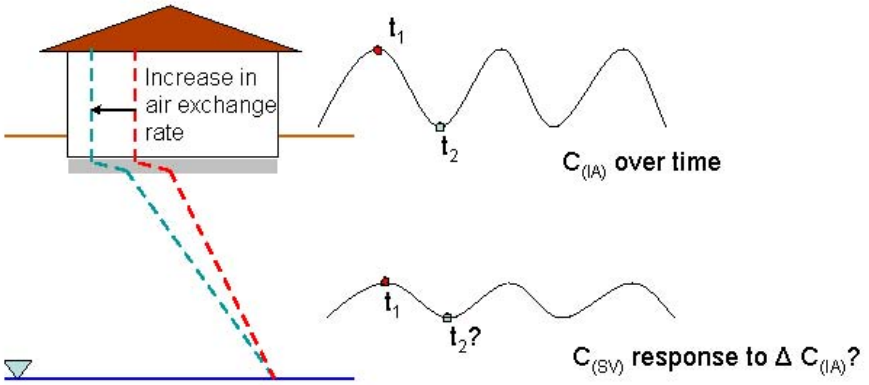
Response to Change in [IA]?



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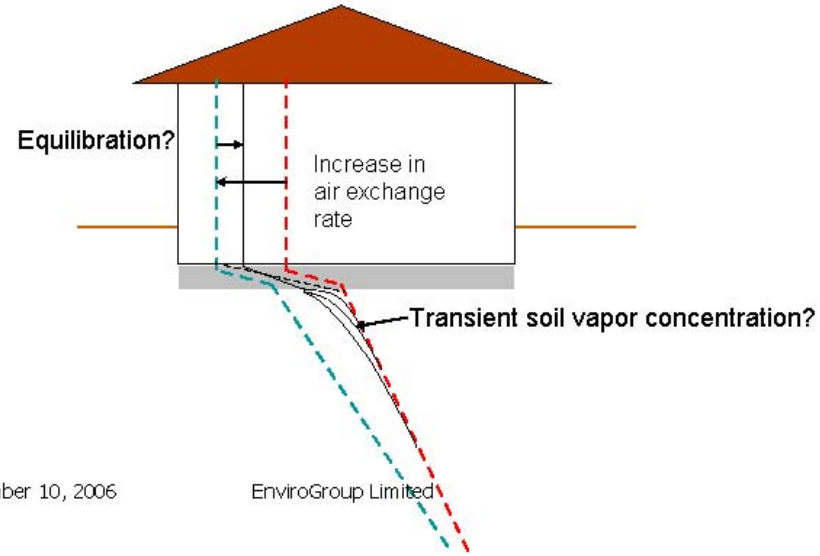
Response to Change in [IA]?



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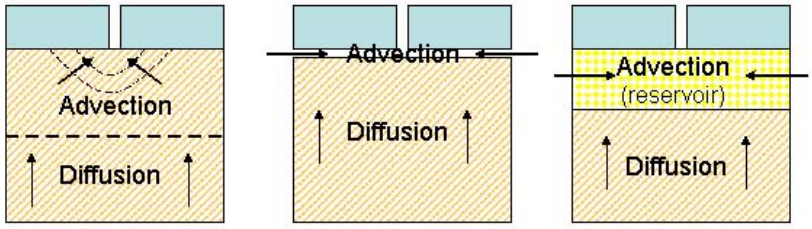
Transient Sub-Slab Response?

Indoor Air Concentration changes due to HVAC



Sub-Slab Vapor Concentration Response?

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Transient Data Concerns

- Use of single point in time data for
  - Screening levels
  - Attenuation factors
  - Calibration of models
  - Prediction of long term risk
- Less impact on
  - Correlations based on average behavior

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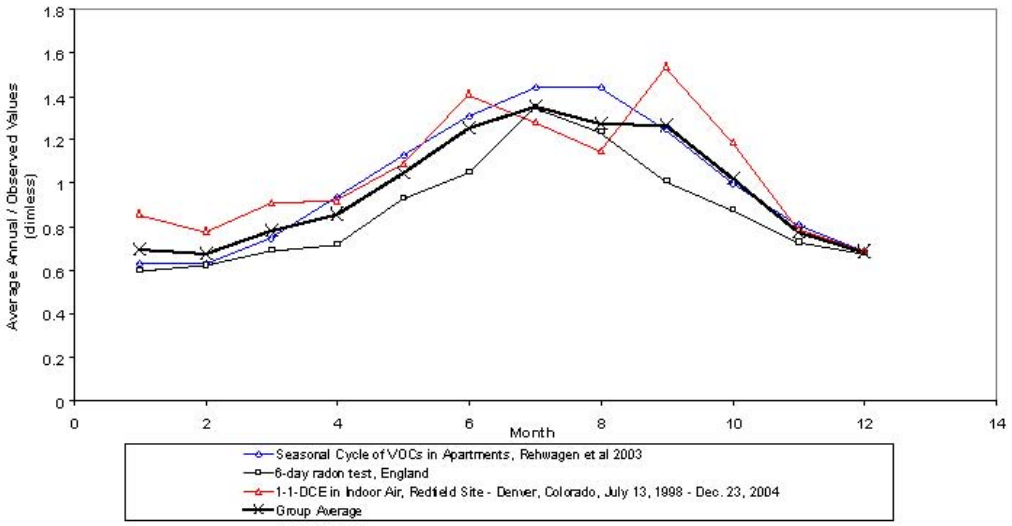
Figure 8
Monthly Seasonal Factors (Annual average / Observed Values)



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Conclusions

- Indoor air data can be useful for making risk management decisions
  - If background sources are addressed
  - Results are typically well above or below action level
- Indoor air data should be used with caution for correlation purposes
  - Natural variability
  - Transient conditions may significantly affect results

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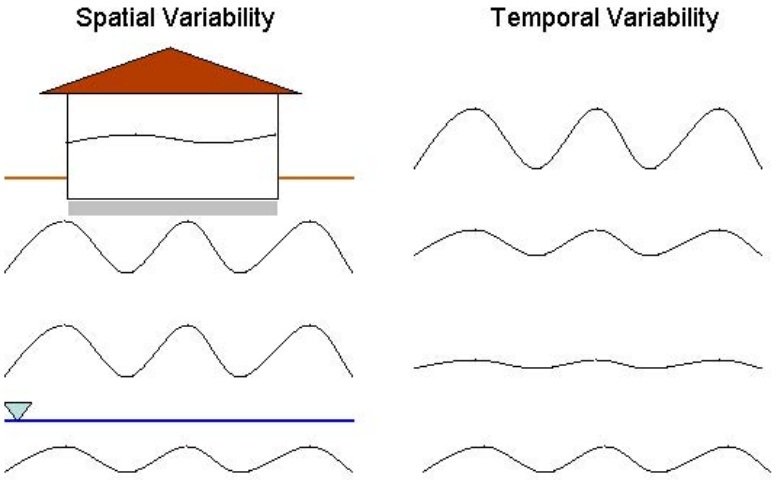
Conceptual Model



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Recommendations

- Consider potential for transient conditions to impact any correlation
- Base empirical attenuation factors (e.g., screening levels) on long term data
- Focus research on time dependent nature of vapor intrusion processes

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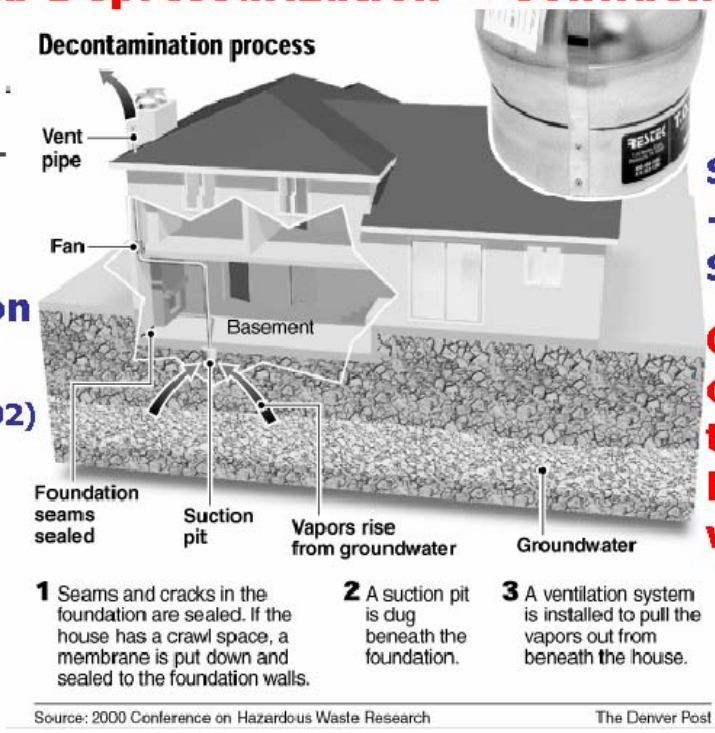
So how do we retain validity through time?

- This is only about Decisions for
  - "Sample-out" or "Screen-out" – walk aways
    - Since decisions for
      - Controls of exposures and/or sources are designed to work through time

Sub-Slab Depressurization = Confidence

99.5% Reduction Possible

(Folkes, 2002)



$1,500 - $2,500

Cuts off the Path-way

10

Some lessons learned

- From long-term experiences
  - With other soil-gas contaminants
- **Radon**
  - > 30 yrs experience

Radon in Homes [European] BMJ Darby, et al., 2004

- "Radon measurements made in the same home but in ***different years*** showed considerable random variability"
- How often do we (VI) have indoor measurements over several years?
  - For "screen-out decisions?

Spatial and temporal indoor radon variations (Alavanja, et al., 2000)

- "Substantial ***year-to-year*** variability in radon concentrations has been routinely observed in homes [Steck, 1992],
- making it clear that a radon measurement made at a single point in time,
- ***even if measurement continued for an entire year***,
- can result in increased exposure misclassification."

Radon in Homes [European] BMJ Darby, et al., 2004

- Radon measurements for each individual covered a mean period of 23 yrs !
  - How often do we (VI of toxics) have indoor measurements over 23 years?

Radon in Homes [European] BMJ Darby, et al., 2004

- Only with improved (long-term) sampling:
- "residential radon produces substantial hazards, particularly among smokers, even at concentrations below the action levels"
- "radon in homes currently accounts for about 9% of the deaths from lung cancer and hence 2% of all cancer deaths in Europe."

Residential Radon [NA] and Risk of Lung Cancer (Krewski, et al., 2005)

- More direct evidence of an association
  - Compatible w/ extrapolation from miners (workers)
  - Consistent w/ animal and in-vitro studies
- OR = 1.12 at 100 Bq/m3 (i.e., 12% increase)
  - (4 pCi/L = 148 Bq/m3)
  - Sub-sets w/ more accurate data show higher risks
  - ***Long-term*** [alpha]-track detectors
    - Min. 1 yr sample duration (few 6 mos., if winter)

IA Sampling Durations & Events

Lessons from 30 yrs of Radon work

- Radon – longer term sampling – resulted in
  - reduced misclassification & observed higher RRisks
  - Min. of 1-yr samples used to show residential radon risks (in North America)
    - 20,000 lung cancers in US/yr
    - (est. from workers (Beir VI), now seen in residential Epi.)
  - How confident should we be about our bldg-specific VI sample-out decisions when they are based on only a few hrs. of sampling?

Existing VI Guidance

Duration & # of IA samples (Eklund et al, AWMA, 2006)

Units are HOURS

Table 6. Sampling and Analysis Guidance

State	Soil Gas		Indoor Air					
	No. Samples	Leak Check	No. Rounds	Sampling Duration (hr)	No. Samples (1st Floor)	No. Samples (Basement)	No. Ambient Samples (per event)	QC Samples (per event)
Alaska	NA	NA	NA	NA	NA	NA	NA	NA
California	≥2	Yes	2	24[a]	1	1	NA	1 trip blank
Colorado	NA	NA	≥2	24	1	Not required	NA	5% dups. and blanks
Connecticut	NA	NA	3	8	1	1	1	1 dup., field blank, trip blank
Indiana	1 (2 locations)	Yes	NA	24	1[b]	1[b]	1	5% dup., 1 field blank
Louisiana	NA	NA	1	NA	1	NA	1 – 2	5% dups. and blanks
Maine	NA	NA	2	24	NA	NA	NA	NA
Massachusetts	≥ 1–2	NA	3	2 – 24	1	1	1	1 dup., field blank
Michigan	NA	NA	NA	NA	NA	NA	NA	NA
Minnesota	1 – 2	To be added	≥2	24	1 – 2	1 – 2	1 or 5%	To be added
New Hampshire	Site specific	Yes	Site specific	24[a]	1	1	1	NA
New Jersey	2	Yes	2	24	1	1	1 or 5%	NA
New York	NA	Yes	2–	8 or 24	NA	NA	NA	Not specified
Ohio	NA	NA	NA	NA	NA	NA	NA	NA
Oklahoma	NA	NA	NA	NA	NA	NA	NA	NA
Oregon	NA	NA	NA	NA	NA	NA	NA	NA
Pennsylvania	NA	NA	2	NA	NA	NA	NA	1 dup., trip blank

[a] Eight hours for commercial buildings

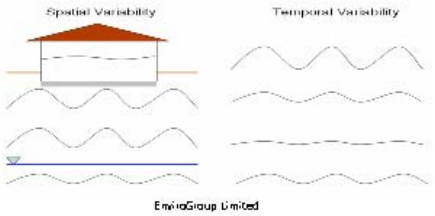
[b] Minimum of two samples per building

Only hours long but, the most experienced states recommend the most events (3)

Recommendations for enduring Sample-out decisions

Sampling (using the best available methods)

Indoor Air	few locations/bldg	&	many events, or long durations
Shallow Soil-gas	many locations	&	mod. # of events
Deep Soil-gas	many locations	&	few events
Groundwater	mod. # locations	&	mod. # of events



Extraction-Related Quality Assurance and Control Issues Associated with Active Soil-Gas Sampling

Dominic C. DiGiulio
US Environmental Protection Agency/ORD

ABSTRACT

A number of extraction-related quality assurance and control issues should be considered prior to or during soil-gas sampling. These issues include selection or evaluation of: (1) flow rate, (2) vacuum, (3) purge volume, (4) total extraction volume, (5) equilibration time, (6) leakage, and (7) gas permeability. A two-dimensional, axisymmetric gas flow model is used to evaluate the relationship between applied flow and vacuum for a given borehole geometry, isotropic conditions, and gas permeability ranging from 10-13 to 10-6 cm2. Simulations indicate that soil-gas sampling may be impractical in soils having gas permeability below 10-13 to 10-12 cm2. Vapor partitioning in soil–water, –gas, and –solids is presented to show that vapor concentration is not a direct function of vacuum under conditions normally encountered during soil-gas sampling. Thus, specification of an arbitrary maximum vacuum during sampling is unjustified unless elevated vacuum results in combined fluid and gas extraction. A mass-balance equation and soil-gas data from two sites is utilized to demonstrate how sequential sampling can be used to evaluate attainment of vapor equilibration and the impact of pre-sample purge volume on sample results. Removal of only one internal volume, excluding the gas-filled porosity of the sandpack, was necessary for stabilization of vapor concentration at a dedicated vapor probe that had been sealed for at least three months indicating likely attainment of equilibration prior to extraction. However, removal of greater than ten internal volumes, including the gas-filled porosity of sandpacks, was necessary for stabilization of vapor concentrations at dedicated vapor probes installed several days prior to extraction indicating likely non-attainment of equilibration. This may indicate the need for extensive purging when sampling soon after probe installation.

The potential impact of excessive purging on sample concentration was evaluated at three sub-slab vapor probes and one dedicated vapor probe. Air flow modeling conducted on the sub-slab probes indicated little potential for impact at extraction of up to 12 liters. This finding was confirmed using sequential sampling. Sequential sampling at the dedicated vapor probe indicated little impact on vapor concentration after removal of 103 liters of gas. Thus, extraction of a fairly large volume of gas may be necessary to significantly perturb vapor concentration during soil-gas sampling. A heuristic model is used demonstrate that leakage is simply a function of the permeability contrast between the formation and borehole and geometric factors. As the ratio of formation to borehole permeability decreases, the potential for leakage increases. Leakage can only be minimized by properly sealing a borehole. Applied flow and vacuum are irrelevant. If a tracer concentration is held constant in a chamber above a probe and there is no source of the tracer in the sub-surface, leakage can be quantified simply as the ratio of tracer concentration in a sampling vessel to tracer concentration in a chamber and adjusted for injection time if desired. Injection of helium with a denser balance gas to avoid a buoyancy effect or a fluorocarbon in a chamber appears to be the cleanest and most robust method of leak testing. Large-scale gas permeability testing is impractical

for vapor intrusion investigations. Single-interval, steady-steady-state gas permeability testing can be conducted but requires estimation of pressure at a screened interval which in turn requires measurement of friction factors as a function of flow rate. Friction factors can be obtained by injecting air through a length of pipe or tubing with the attached screen and fittings that will be used in the field. An example of this procedure is provided for sub-slab gas sampling and compared with a full-scale test.

Overview of US EPA's ORD Technical Outreach and Support Activities on Vapor Intrusion Impacts

Douglas Grosse
US Environmental Protection Agency/ORD

ABSTRACT

Increasing attention has been given to understanding the impacts of subsurface vapor contaminant migration into overlying buildings. Many of these impacted structures are residences, where occupants face undesirable health risks. The science of determining, characterizing and managing these risks is constantly evolving. Much remains to be done in assisting regulators, consultants and other decision-makers to make informed decisions in mitigating the problem and reducing these risks. ORD has been very proactive in providing technical assistance and support to EPA program offices (OSWER), regional offices and states and other interested parties in dealing with vapor intrusion issues.

This overview will describe some of the more significant technical support activities offered, to date. In addition to describing significant ORD site-specific technical support activities, key findings and recommendations will be summarized from major technology transfer activities including electronic products, seminars and workshops. Some of this information will be extrapolated from the following:

- CDROM U.S.EPA Seminars on Indoor Air Vapor Intrusion EPA/625/C-03/004;
- Specialty Workshop AEHS 14th Annual West Coast Conference on Soils, Sediments and Water, San Diego - March 15-18, 2004;
- Modeling Vapor Attenuation Workshop The Annual International Conference on Soils, Sediments and Water, University of Massachusetts at Amherst - October 18-19, 2004;
- Specialty Workshop on Integrating Observed & Modeled Vapor Attenuation, AEHS 15th Annual West Coast Conference on Soils, Sediments and Water, San Diego, CA, March 14th, 2005;
- Specialty Workshop on: Development, Review and Use of US EPA's Updated J&E Model Spreadsheet, The 16th Annual West Coast Conference on Soils, Sediments and Water – March 21-22, 2007 – San Diego, CA;
- Specialty Workshop on: Soil-gas Sample Collection and Analysis, The 17th Annual West Coast Conference on Soils, Sediments and Water – March 16, 2006 – San Diego, CA; and
- Vapor Intrusion Seminars - San Francisco - December 3&4, 2002, Dallas - January 14&15, 2003, and Atlanta - 25&26, 2003.

Overview of USEPA's ORD Technical Outreach and Support Activities on Vapor Intrusion Impacts

Authors: *Doug Grosse, USEPA, ORD*
Robert Truesdale, RTI International

Presented at: The National Environmental Monitoring Conference (NEMC)
August 20-24, 2007
Cambridge, Massachusetts

Office of Research and Development
National Risk Management Research Laboratory

October 5, 2007

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- Ron Mosley, USEPA, ORD
- Jim Weaver, USEPA, ORD
- Dominic Digiulio, USEPA, ORD
- Cindy Paul, USEPA, ORD
- William Wertz, New York State, DEC
- Brian Schumacher, USEPA, ORD
- John Boyer, NJ, DEP
- Blayne Hartman, H&P Mobile Geochemistry
- Gina Plantz, Newfields Consultants

1

ORD Technical Support

- Site Characterization and Data Acquisition
- Regional Technical Assistance
- OSWER Guidance Document Development
- Technology Transfer

2

Indoor Air Vapor Intrusion Technology Transfer Activities

- Vapor Intrusion Seminars: San Francisco - December 3&4, 2002, Dallas - January 14&15, 2003, and Atlanta - 25&26, 2003.
- CDROM U.S.EPA Seminars on Indoor Air Vapor Intrusion EPA/625/C-03/004.
- Specialty Workshop on Vapor Intrusion Attenuation, AEHS 14th Annual West Coast Conference on Soils, Sediments and Water, San Diego - March 15-18, 2004.
- Modeling Vapor Attenuation Workshop The Annual International Conference on Soils, Sediments and Water, University of Massachusetts at Amherst - October 18-19, 2004.
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- Specialty Workshop on: Development, Review and Use of US EPA's Updated J&E Model Spreadsheet, The 16th Annual West Coast Conference on Soils, Sediments and Water, March 21-22, 2006, San Diego, CA.
- Specialty Workshop and Field Demonstration of Soil Gas Sampling Methodology, 2006 Midwestern States Risk Assessment Symposium, Indianapolis, IN, August 21-24, 2006.
- Specialty Workshop on: Soil-gas Sample Collection and Analysis, The 17th Annual West Coast Conference on Soils, Sediments and Water, March 16, 2007, San Diego, CA.

3

Main Topics Presented at the Technology Transfer Workshops:

- The EPA OSWER guidance document development and rollout (3 Seminar Series);
- Vapor intrusion attenuation factors;
- Observed and modeled vapor attenuation;
- Updates on and evolution of the USEPA's interpretation of the J&E Model and spreadsheets; and
- Soil gas sampling, collection, analysis and interpretation

4

Typical VOC Contaminants Found at IAVI Sites

- 1,1-Dichloroethane
- 1,1-Dichloroethylene
- 1,2-Dichloroethane
- Cis-1,2-Dichloroethylene
- Tetrachloroethylene
- trans-1.2-Dichloroethylene
- Trichloroethylene
- Trichloroethylene
- Vinyl chloride (chloroethene)

5

How can we use groundwater or soil gas data to evaluate the vapor intrusion pathway?

- **Is existing groundwater and/or soil gas data adequate?**
- **How is indoor air concentration related to subsurface concentration?**

Attenuation factor:

$$\alpha = \frac{\text{indoor air concentration}}{\text{subsurface vapor concentration}}$$

Subsurface screening level:

$$\text{target groundwater concentration} = \frac{\text{target indoor air concentration}}{\alpha \times H_c}$$

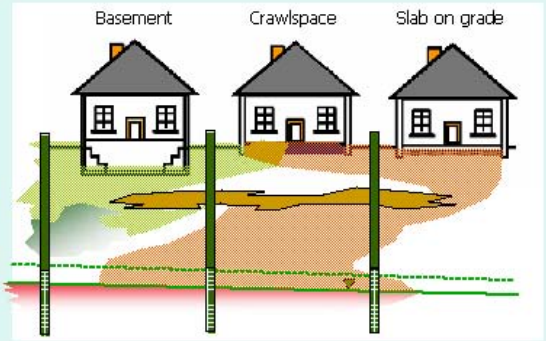
6

Groundwater Sampling Issues

- Most reliable samples, but farthest from receptors.
- Alpha factor assumes Henry's law partitioning into soil-gas.
- Only upper-most water table concentration is important.

Sampling Considerations

- Location of screen
- Screened interval
- Water table fluctuations
- Recharge



7

Soil Gas Sampling Issues

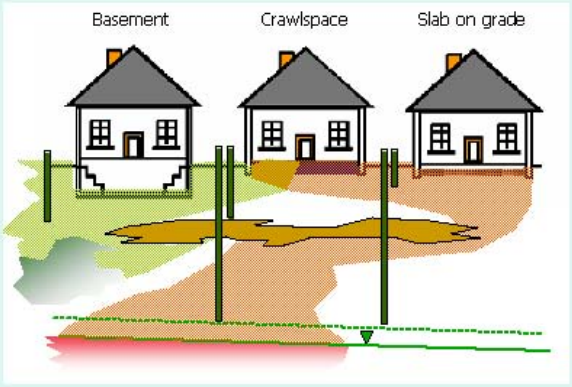
- Least reliable samples (using traditional methods)
- Temporal and spatial variability

Sources of Variability

- Barometric pressure fluctuations
- Surface cover, preferential pathways
- Soil moisture content & permeability
- Building depressurization
- Biodegradation

Sources of Sampling Error

- Sampling equipment
- Protocols



8

Specialty Workshop on Vapor Intrusion Attenuation, AEHS 14th Annual San Diego - March 15-18, 2004.

(1) what can be learned from measurements of vapor attenuation processes in the subsurface.

(2) how this knowledge can be applied to improve the default vapor attenuation factors in the draft EPA, OSWER Vapor Intrusion Guidance.

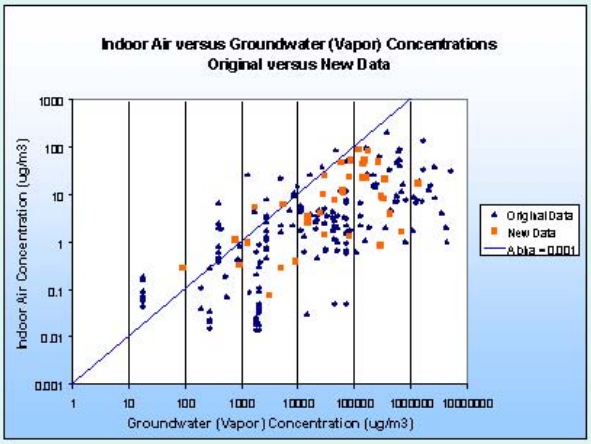
(3) to gather empirically measured attenuation factors for comparison with these generic attenuation factors and to study the relationships between site and building conditions and vapor intrusion attenuation

9

Significant Workshop Findings (Helen Dawson, USEPA)

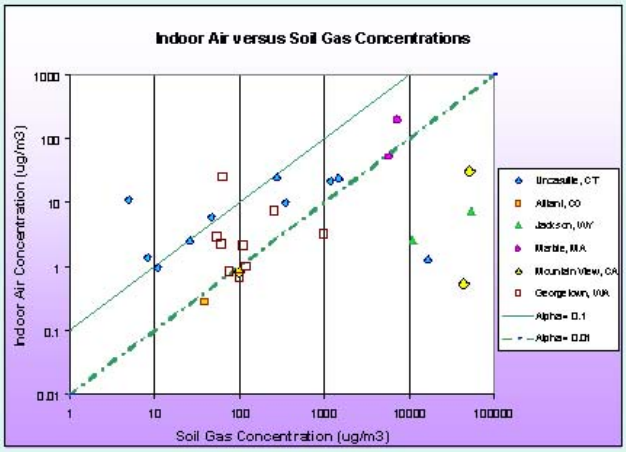
10

Groundwater Attenuation Factors – 2004 versus 2002 Data



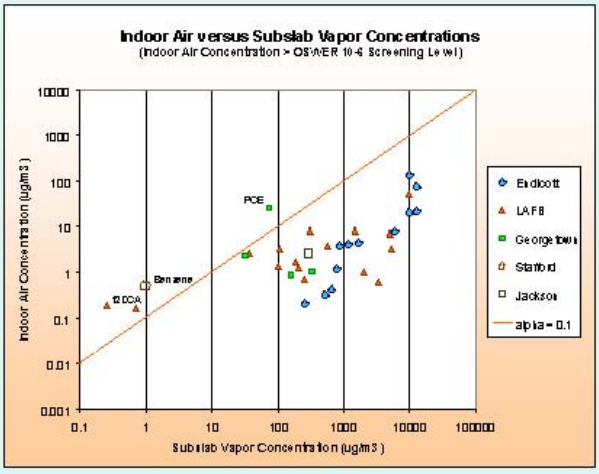
11

Soil Gas to Indoor Air Attenuation Factors – 2004



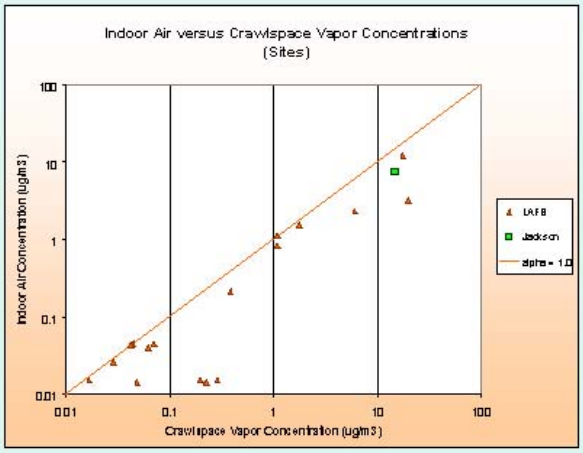
12

Sub-Slab to Indoor Air Attenuation Factors – 2004



13

Crawlspace to Indoor Air Attenuation Factors – 2004



14

Conclusions

- Radon can be useful as a tracer in VI investigations.
- Consistent alphas should be expected across chemicals for VOC intrusion into a building.
- Ratios of the contaminants or concern to checmicals less likely to have background indoor air sources (i.e., 1,1-DCE or TCE) may be useful for evaluating background influences.
- Sub-slab sampling very useful for evaluating background influences.
- Soil gas probes should be installed and sampled with the same care as groundwater monitoring wells.
- Seasonal variation in indoor air can be as high as a factor or 3 – to achieve annual average concentrations, the best time to sample is spring or fall.

15

Modeling Vapor Attenuation Workshop The Annual International Conference on Soils, Sediments and Water, University of Massachusetts at Amherst - October 18-19, 2004.

- Comparison of Measured Data to the EPA *Guidance* Figure 3 Attenuation Factors
- Improvements to Semi-Site Specific Attenuation Factors
- The Role of Modeling in the *Guidance*
- Approaches and Methods for Measuring Vapor Intrusion

16

Conclusions and Recommendations

- The current generic and semi-site-specific attenuation factors provide protective estimates of vapor intrusion at most sites.
- The semi-site-specific attenuation factors are also very protective, but need to be expanded to commercial settings (in addition to residential settings).
- The semi-site-specific attenuation factors are also very protective, but need to be expanded to commercial settings (in addition to residential settings).
- An expanded role for modeling in vapor intrusion decision making may be appropriate for the revised *Guidance*.

17

Specialty Workshop on Integrating Observed & Modeled Vapor Attenuation, AEHS 15th Annual West Coast Conference, San Diego, CA, March 14th, 2005.

- Using observational data sets
- Making measurements in soil gas and indoor air
- Applying scenario-specific modeling techniques to integrate these two data sources in improving the validity and usefulness of the *Guidance*.

18

Conclusions

EPA *Guidance* improvements suggested at the 2005 San Diego workshop include:

- Simplifying and clarifying the guidance structure and framework
- Strengthening the site-specific screening step (Question 5) to allow more site-specific determinations of attenuation factors for soil gas and groundwater measurements taken close to a building
- Revising EPA's spreadsheet version of the J&E model to support the expanded site-specific screening, including changes to constrain inputs to prevent unreasonable results
- Formulating and implementing criteria and procedures for filtering and analyzing empirical data to improve the generic attenuation factors in the *Guidance*; and
- Assembling the latest data collection strategies for VI site investigations to include in the updated guidance, including tools for discriminating indoor air background sources from vapor intrusion.

19

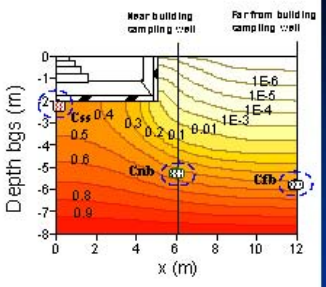
Specialty Workshop on: Development, Review and Use of US EPA's Updated J&E Model Spreadsheet, The 16th Annual West Coast Conference, March 21-22, 2006, San Diego, CA.

- Peer Review of the Spreadsheet Implementation of the J&E Model
- Model Simulations
- EPA's Vapor Intrusion Database
- Soil Gas Sampling Results

20

Definitions

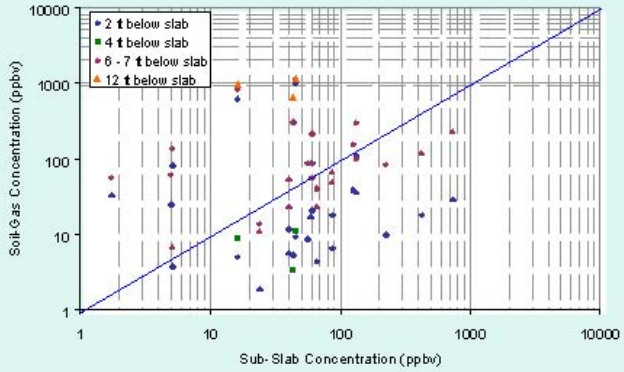
- Css is the highest subslab vapor concentration
- Cnb is the near building soil gas sample that best estimates Css (Cnb is collected 1 m from building)
- Cfb is the soil gas, collected far from building influence, that best estimates Css



GeoSyntec

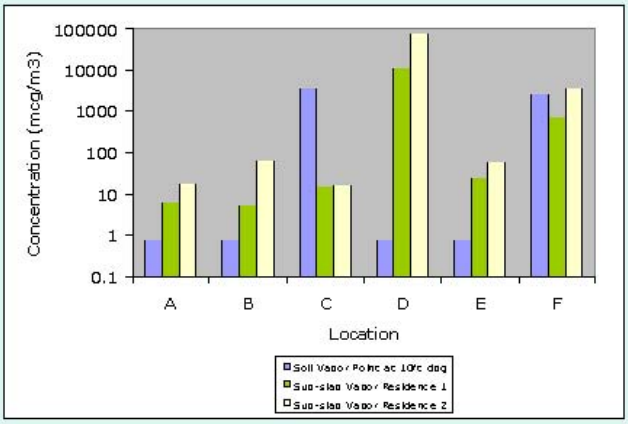
3D Model results illustrating exterior soil gas sampling depths to best represent soil concentrations beneath a building (courtesy of Dr. Lilian Abreu, Geosyntec Consultants)

21



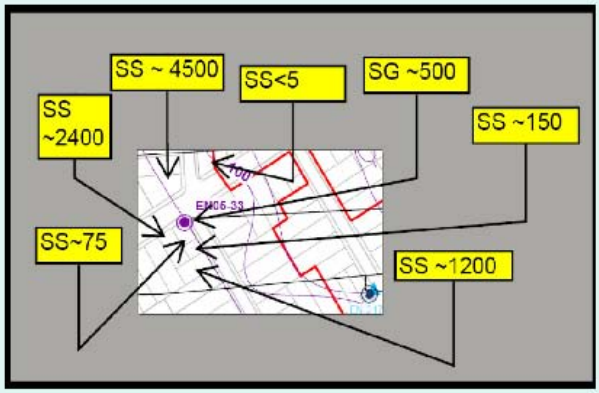
Soil-gas samples 1 meter (2 – 4 ft) below a slab systematically under-predict sub-slab concentration. No clear pattern was present for soil-gas samples 2 meters (6 – 7) feet below a slab indicating that conservative estimation of sub-slab concentration would have required soil-gas measurement in excess of 2 meters. (taken from a presentation by Dr. Dominic DiGiulio, U.S. EPA ORD, at the 2006 San Diego vapor intrusion workshop)

22



Shallow soil gas samples can underpredict or overpredict subslab concentrations under nearby buildings. (taken from a presentation by Krista Anders, NYSDEH, at the 2006 San Diego vapor intrusion workshop)

23



Variation in Sub-slab conc. within a few hundred feet at Endicott, NY (taken from a presentation by Dr. Bill Wertz, NYSDEC, at the 2006 San Diego vapor intrusion workshop)

24

Specialty Workshop and Field Demonstration of Soil Gas Sampling Methodology, 2006 Midwestern States Risk Assessment Symposium, Indianapolis, IN, August 21-24, 2006

- Demonstrate state-of-the-art soil gas sampling methods, sharing knowledge among leading practitioners (the volunteers) and approximately 100 'students'
- Improve understanding of soil gas sampling and how site-specific and methodological factors impact results
- Directly compare methods at the same site at the same time
- Identify and document strengths and weaknesses of methods to improve regulatory guidance

25

Passive Soil Gas Sampling

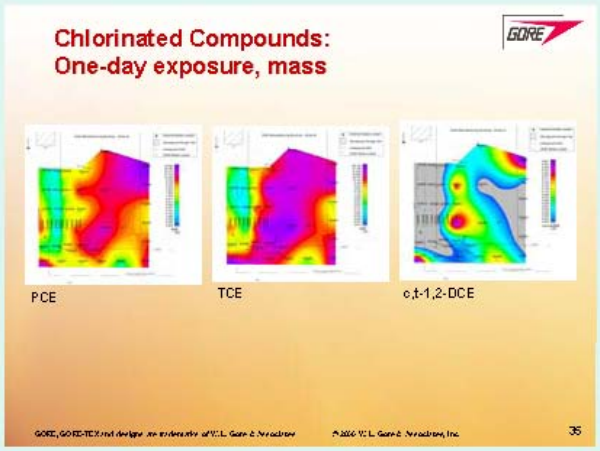
- Shallow passive probes provided and excellent initial line of evidence for delineating the subsurface VOC impact at the Ertel site
- Analysis of compounds desorbed from the probes provided a rich dataset of CHCs, PHCs, and PAHs released during past site activities that was used to focus subsequent sampling events
- Sample mass estimates showed strong correlation with the active data, but the algorithms to convert mass to concentration tended to underpredict the concentrations measured using the active probe. Additional work is needed on adapting the conversion algorithm to site specific conditions.

26

Active Soil Gas Sampling

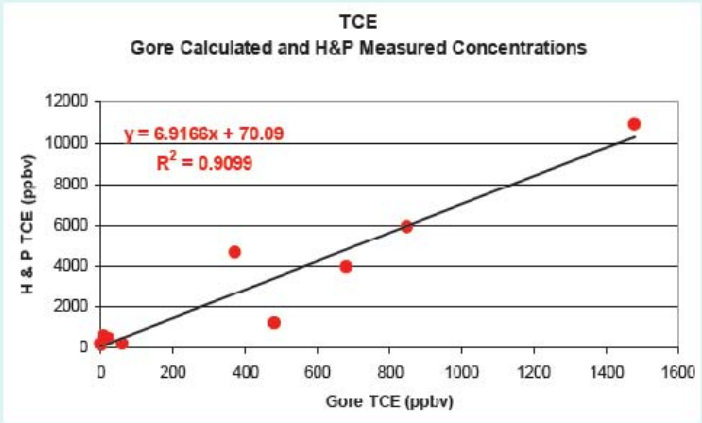
- Good correlation between laboratory TO-17 and TAGA whole air methods.
- Very good comparability between a portable, handheld field screening PID (Foxboro TVA 1000) to data measured with an the onsite TAGA for values exceeding 4 ppmv.
- Good correlation between mobile laboratory 8021 and TAGA TCE measurements.

27



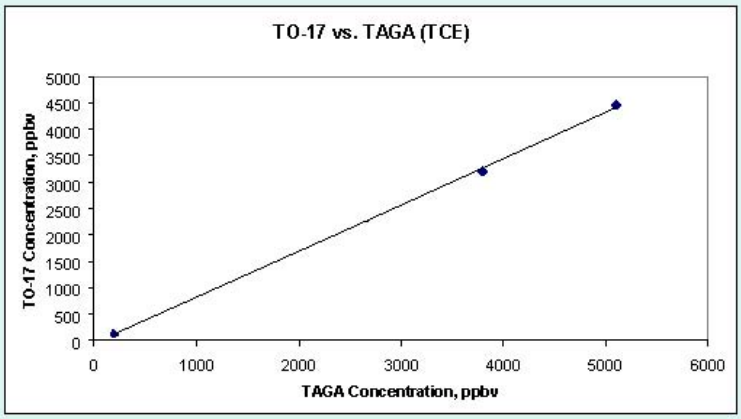
Maps of contaminant distributions from shallow passive soil gas probes – Ertel Site.

28



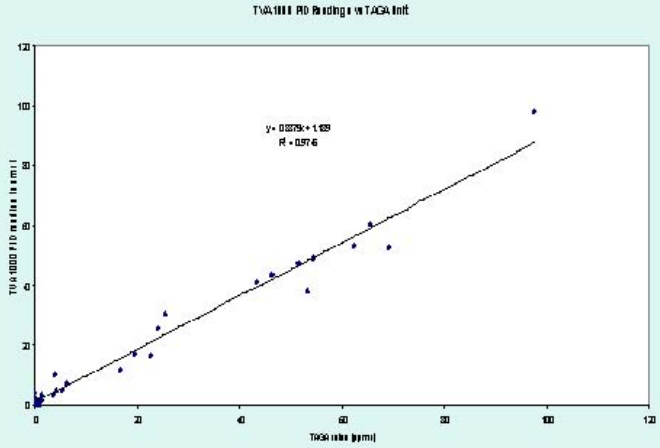
Comparison of TCE soil gas concentrations by active (H&P) and passive (Gore) methods/

29



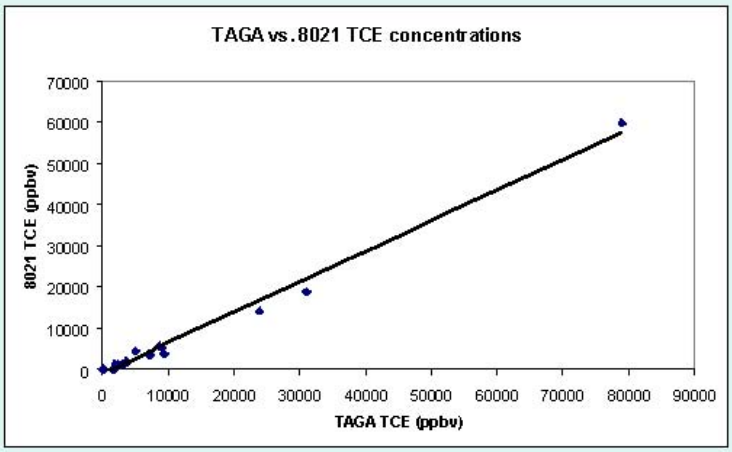
MSRAS analytical comparison – TO-17 versus TAGA results

30



Good correlation between field screening PID and TAGA (R2 = 0.97)

31



Comparison of onsite 8021 and TAGA TCE measurements.

32

Specialty Workshop on: Soil-gas Sample Collection and Analysis, The 17th Annual West Coast Conference, March 16, 2007, San Diego, CA.

- Probe Installation and Sample Collection: probe installation method, tubing type, Tedlar bags, adsorptive media (active and passive), and tracer/leak detection methods.
- Air Extraction Issues: equilibration time, purge and sample volume, sample flow rate, air permeability testing.
- Analytical Methods: available analytical methods (selection and use), field analytical methods.

33

Coming Events in Vapor Intrusion

- ITRC Web-Training: Web-training is available for those who would prefer to receive an overview of the ITRC Guidance, without having to read through both documents in detail September 18.
- Visit http://clu-in.org/studio/seminar.cfm#upcoming to register.
- AWMA Conference - Vapor Intrusion: Learning from the Challenges, Providence, Sept. 26 – 28, 2007. This promises to be another strong line-up, following on from two conferences in Philly (January) and LA (September) last year. http://www.awma.org/events/view_event.html?typeid=1&id=11
- Specialty Workshop on: The 18th Annual West Coast Conference, San Diego, CA TBD.

34

All presentations provided in these featured VI workshops can be found at:

http://iavi.rti.org/WorkshopsAndConferences.cfm

35

Passive Vapor Sampling and Vapor Intrusion Investigations

Jay Hodny
W.L. Gore & Associates, Inc.

ABSTRACT

Air, soil gas, and sub-slab soil gas sampling provide a direct measurement of chemicals in vapor. Inhalation represents the most direct exposure route to those chemicals. Therefore, vapor sampling is a direct method to investigate the intrusion of vapors into buildings. Guidance documents, produced rapidly by numerous state and national organizations, address the complexities of sampling, analysis, and interpretation of data, collected to assess the vapor intrusion pathway.

Passive sampling is a method to collect volatile and semi-volatile organic compounds in vapor, accurately and at significantly reduced costs. Passive samplers have an extensive record of proven science and success. Though design dependent, passive samplers are generally simple to deploy and operate, and deliver a wide range of compound information and can be used in challenging site conditions. To address the health risk, the detection levels in a vapor intrusion investigation are considerably more stringent than levels used in general site characterization. Thus, the detection of compounds at risk-based screening levels can be achieved when effective passive samplers are combined with appropriate analytical techniques.

The role of passive samplers in vapor intrusion investigations is growing. Recent publications, workshops and conference presentations on the topic of vapor intrusion are recognizing and discussing the benefits of passive samplers. Passive sampling provides a line of evidence that refines conceptual site models, characterizes and delineates the compound presence and type in vapor, and focuses more invasive and expensive sampling techniques. The simplicity of the technique minimizes field costs and potential handling errors, a major source of data uncertainty.

This presentation includes discussions on how passive sampling has been integrated into vapor intrusion investigations using a versatile, membrane-based, adsorbent sampler. The method used to convert the measured mass data to vapor concentration values is discussed. The presentation also includes results and learnings from comparative studies.

Passive Vapor Sampling and Vapor Intrusion Investigations

George Shaw
Jay W. Hodny, Ph.D.
W. L. Gore & Associates, Inc.

National Environmental Monitoring Conference
Cambridge, MA
August 20-24, 2007

Outline

- Introduction
- GORE™ Module
- Deriving concentrations
- Examples
  - Soil gas
  - Indoor air
  - Vertical profiling
- Conclusion

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Vapor Sampling Techniques

Active Sampling

- Forced extraction
- Canisters, syringes, probes
- Complex set-up
- Potential for error

Courtesy of Severn Trent Laboratories

Courtesy of ZEBRA Environmental Corporation

Passive Sampling

- No forced extraction
- Simple set-up
- Minimal error

Adsorbent inside glass vial open on end

Source: www.skcinc.com

Adsorbent inside hygiene badge

Adsorbent inside vapor permeable, waterproof membrane

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Benefits of Passive Sampling

- Rapid, inexpensive, unobtrusive installation & retrieval
  - Minimal operator & field sampling error
- Time-integrated sampling
  - ppt sensitivity
  - Sensitivity to broad range of compounds: VOCs, SVOCs, PAHs
  - Minimizes sampling variability
- Virtually any soil and moisture condition
- No forced extraction
- No mechanical parts or connections
- No energy required

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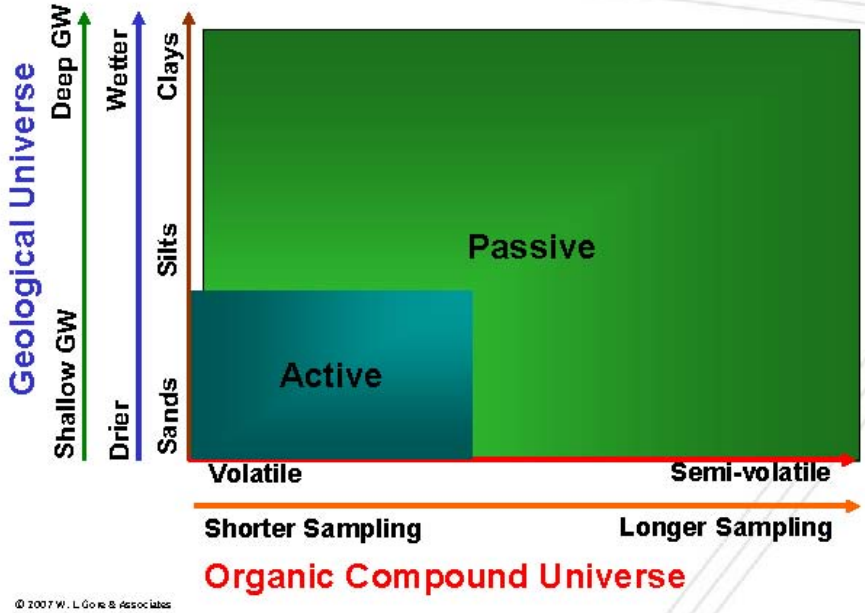
Why Passive Soil Gas Sampling?



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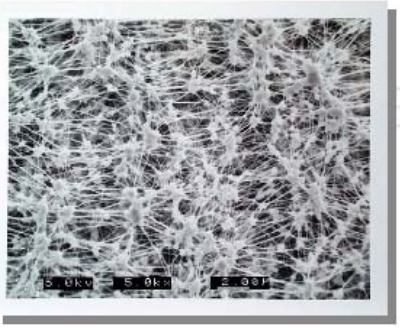
The GORE™ Module

- GORE-TEX® Membrane
  - Chemically inert
  - Waterproof
  - Vapor permeable
- Engineered sorbents
  - Hydrophobic
  - VOCs, SVOCs, PAHs
- Sample analysis
  - EPA 8260/8270 or TO-15
  - Duplicate samples

- Direct compound detection
- Sample integrity protected



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The versatile GORE™ Module can be installed in:

- Soil

Slam bar

Hammer drill

Module insertion

© 2007 W. L Gore & Associates

The versatile GORE™ Module can be installed in:

- Soil
- Subslab
- Any depth

Angle beneath slab

Courtesy of Ecology & Environment

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The versatile GORE™ Module can be installed in:

- Soil
- Subslab
- Air

Crawlspace air

Indoor air

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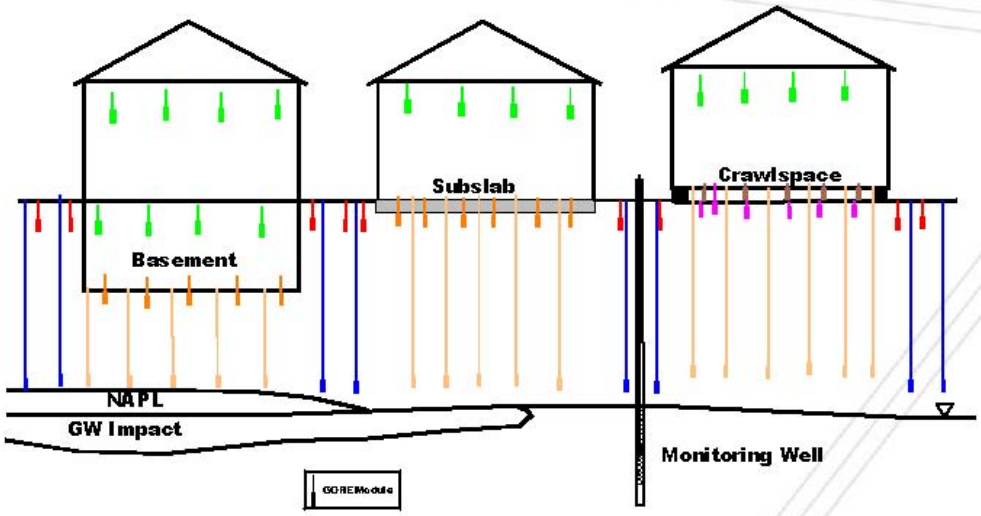
Vapor Intrusion Investigation



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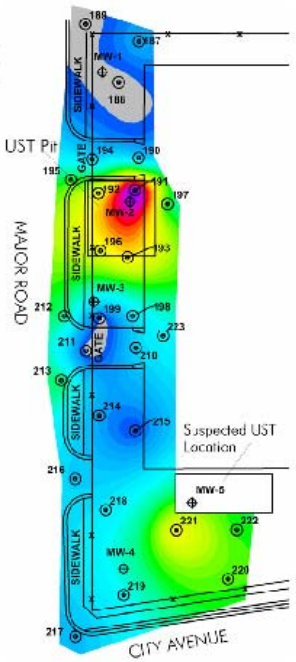
Historical Application

- Vapor data - mass (µg)
- Relative distribution of subsurface impact
- Strong correlation
- Economical means of obtaining richer, high-resolution, datasets (CSM)
  - Site screening
  - Future use scenarios
  - Site monitoring
- Focuses subsequent sampling & remedial activities



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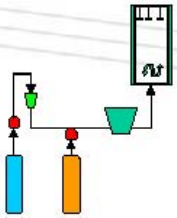
Concentration Calculations

- Quantify (measure) uptake rate
  - Experimental conditions
- Exposure period
- Quantify (measure) mass desorbed
- Soil gas
  - Eff. Diff.= *f*[total porosity, water-filled porosity]*
    - Johnson-Ettinger VI model terms
    - Millington-Quirk



Conc = *f*[volume= *f*(uptake rate, time), mass, soil*]

- Approach – IH methods-solid, sorbent-based diffusion samplers
- ASTM 6306 (1998); 6246 (1998); 4597 (1987)
- MDHS 70 (1990); 80 (1995); 27 (1983)

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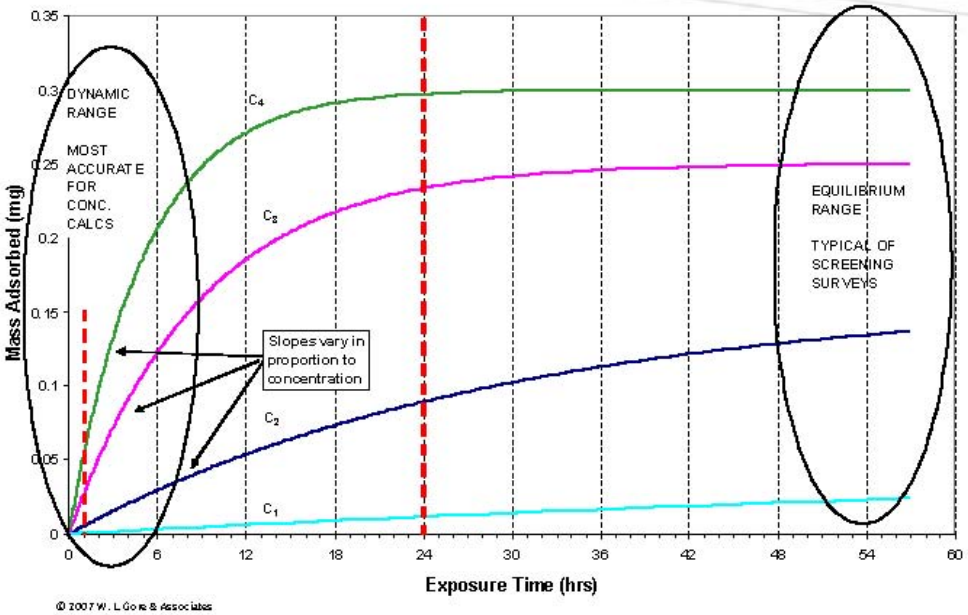
Example Adsorption Curves



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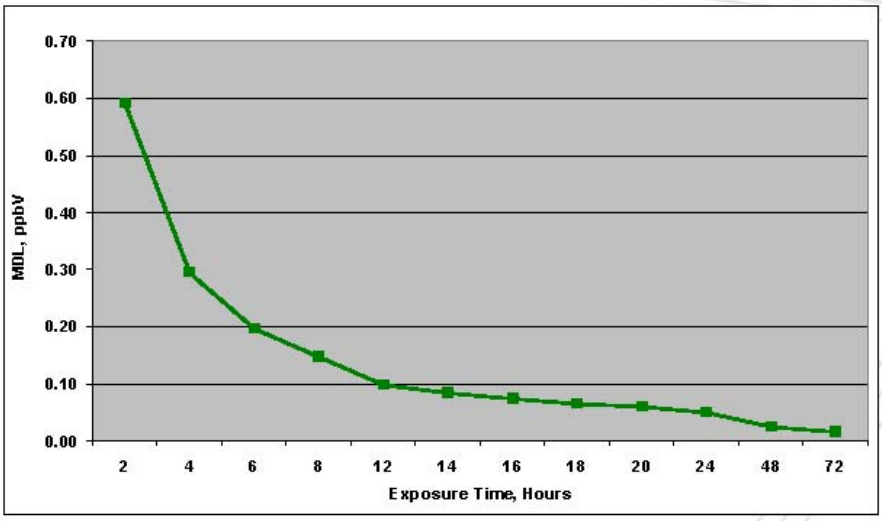
Method Detection Limits: Air



Tetrachloroethene

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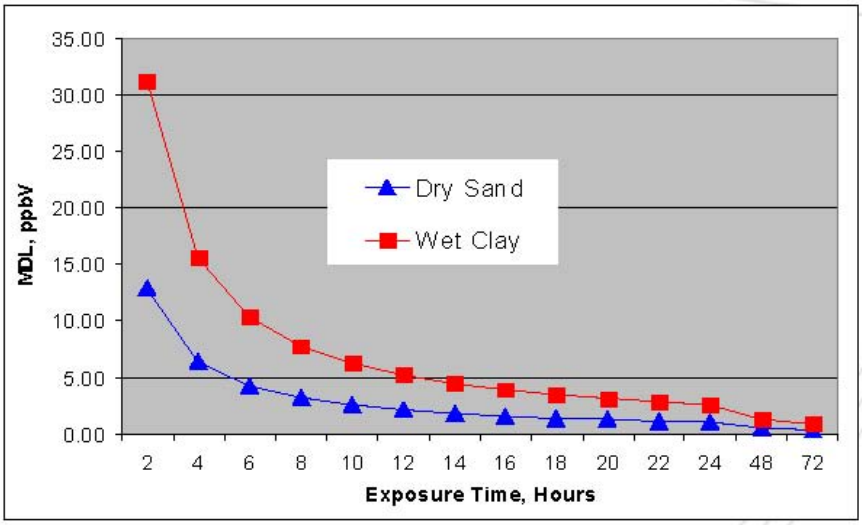
Method Detection Limits: Soil Gas



Tetrachloroethene

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Vapor Intrusion Examples

- Initial site screening
  - "Early tier/preliminary" site screening steps
- Side-by-side data comparison
- Air sampling

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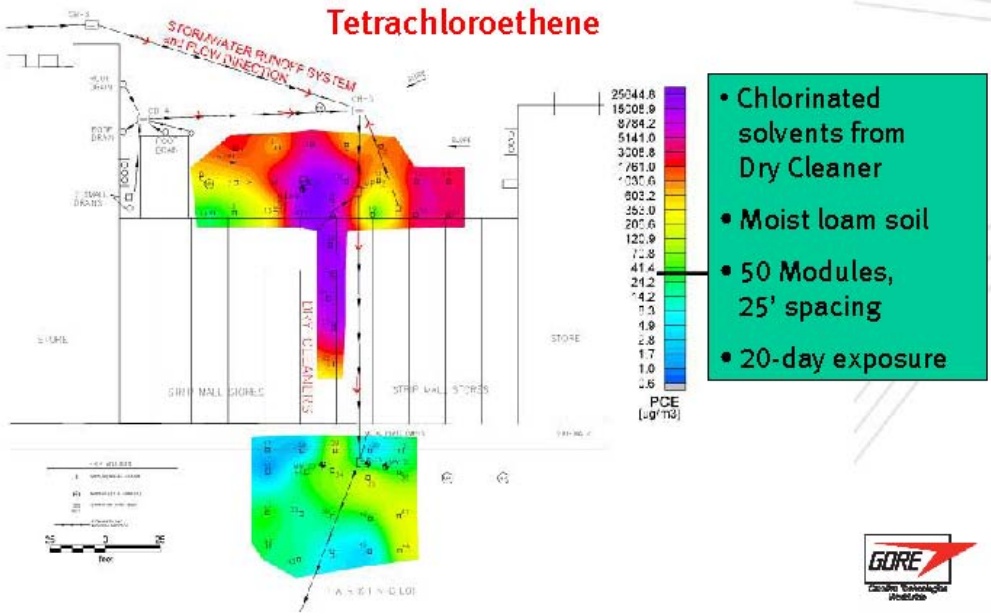
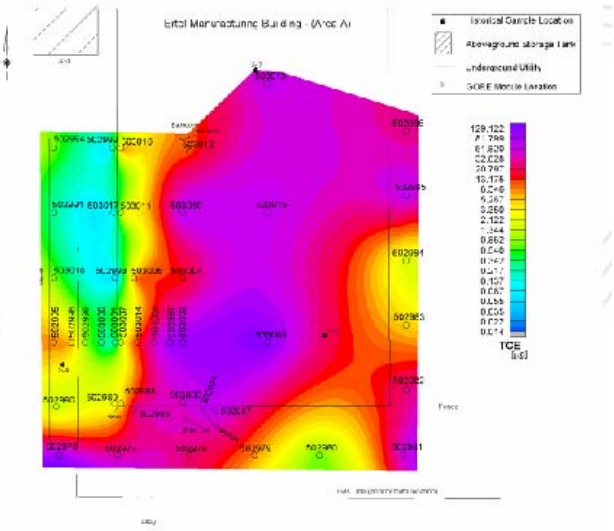
VI Investigation at Strip Mall



Site Screening

- US EPA - IDEM
- Indianapolis site
- Objectives:
  - "First Look"
    - July
    - VOCs, SVOCs, PAHs
  - Guide next sampling
    - July, August
    - "Sampling Boot Camp"



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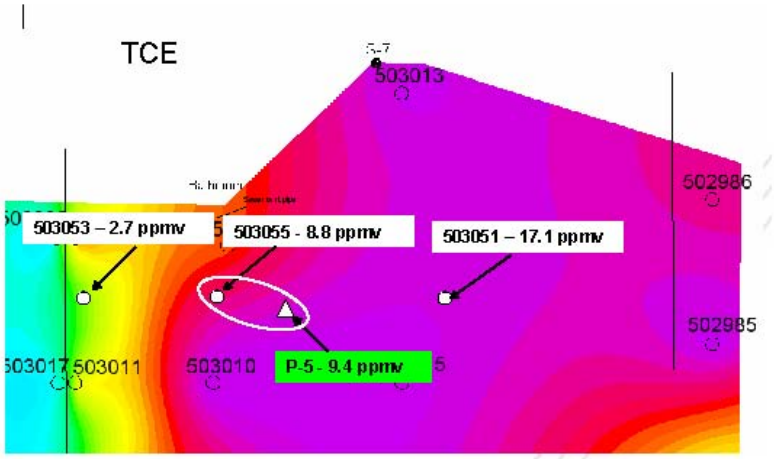
Calculated and Measured Concentrations

- 3 ft sample depth
- One hour exposure
- Correlates spatially
- Matches P5



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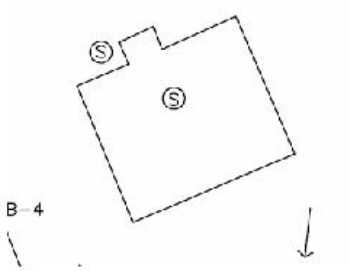
Indoor & Outdoor Air Sampling

- Former Dry Cleaner/Credit Union
  - Two sample locations: One outside, one inside
  - Summa canister and 2 GORE™ Modules
  - 24-hour sampling period



ppbV	PCE	TCE	c12DCE
Summa in	0.047	nd	nd
Gore	0.046	nd	nd
Gore	0.046	nd	nd
Summa out	0.048	nd	nd
Gore	0.040	0.01	0.017
Gore	0.021	nd	nd

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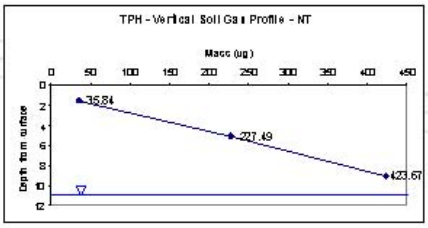
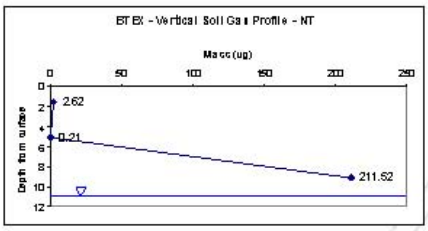
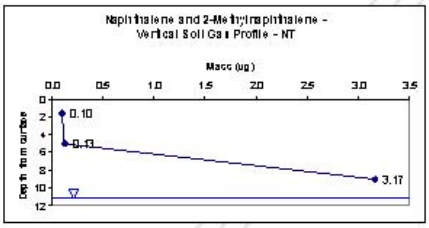
Vertical Profiling

- Gas Station
- Clustered boreholes
  - 1.5 inch diameter
  - 1.5 (uncased), 5, 9 ft depths
  - PVC pipe
    - Open end, bottom foot slotted
  - GW – 11ft
  - Two hour exposure







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Conclusions

Passive Sampling is...

- Simple
  - No mechanical parts,
  - Easy to install,
  - Reduced field costs
- Effective
  - Low detection limits
  - Finds areas of VI concern
  - Focusing further investigations
- Versatile
  - Soil Gas
  - Sub-slab
  - Vertical Profiling
  - Indoor Air
- Well-suited for providing concentration data

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THANK YOU.
gshaw@wlgore.com
jhodny@wlgore.com
GORE

Use of Radon to Establish a Building-Specific, Sub-slab, Attenuation Factor for Comparison with Similar Quantities Measured for Other Vapor Intrusion Contaminants

Ronald Mosley
US Environmental Protection Agency/ORD

ABSTRACT

Vapor intrusion (VI) refers to the situation in which harmful chemicals (such as halogenated or chlorinated volatile organic compounds [VOC] or petroleum products) in the groundwater or soil volatilize in the vadose zone and migrate into the indoor environment. These chemicals typically arise from landfills, superfund sites, RCRA sites, CERCLA sites, Brownfields, or leaking underground storage tanks. Hundreds of thousands of these sites across the nation are surrounded by residential and commercial communities that may be at risk from VI problems. Before applying reduction methods to reduce indoor exposure to these toxic chemicals, one needs to identify the houses in which vapor intrusion problems exist. Because of indoor and ambient sources, a simple indoor measurement of the chemical of concern (COC) does not necessarily indicate whether the chemical came from the soil. Current methods of characterizing these sites are expensive and do not result in clear interpretations of the apparent sources of measured indoor concentrations of these toxic chemicals. Consequently, better methods for identifying the sources of these indoor contaminants are needed.

This paper will describe the use of naturally occurring radon in the soil to establish the entry rate of soil gas and consequently numerous other soil gas contaminants into the indoor environment. These radon measurements are less costly to perform than traditional VOC analyses and result in less ambiguous interpretations of an effective sub-slab attenuation factor that should apply to all sub-slab COC. This presentation will also discuss some further complications in relating sub-slab concentrations to indoor concentrations of soil gas contaminants.

Use of Radon to Establish a Building-specific Sub-slab Attenuation Factor for comparison with Similar Quantities measured for Other Vapor Intrusion Contaminants

Ronald Mosley
EPA/ORD/IEMB

Presented at the National Environmental Monitoring Conference
In Cambridge, Massachusetts
August 19 – 25, 2007

PROJECT OBJECTIVES

- To demonstrate that radon measurements represent a viable low-cost surrogate for measuring the entry rate of soil gas VOCs even in moderate and low radon potential areas.
- To use SF_6 as a tracer to better understand the entry of soil gas into the indoor environment.

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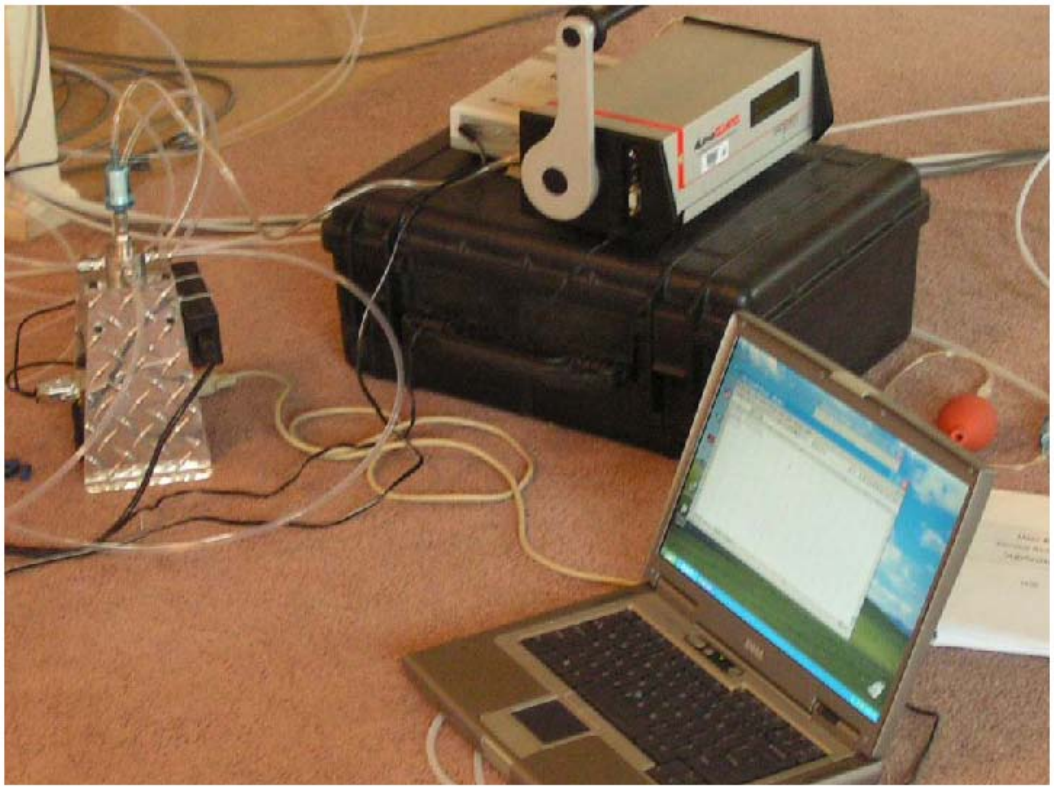
AIR TOXICS LTD.




04.25.2006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04.27.2006
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WARNING
AVISO


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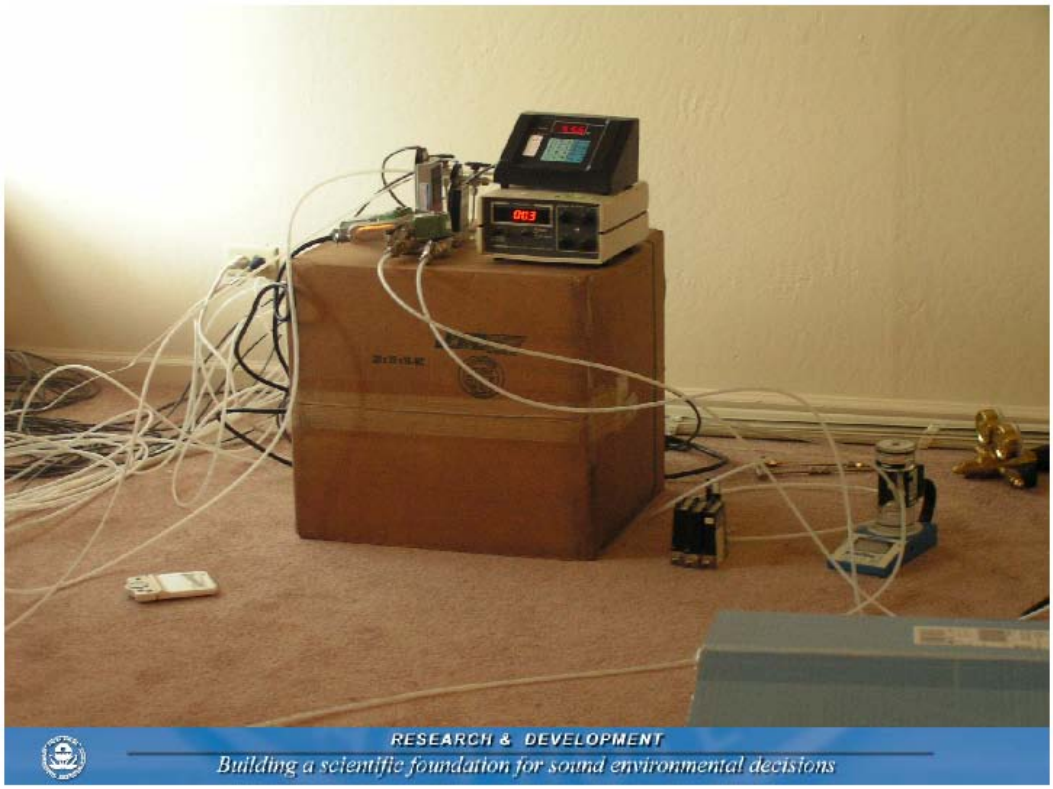
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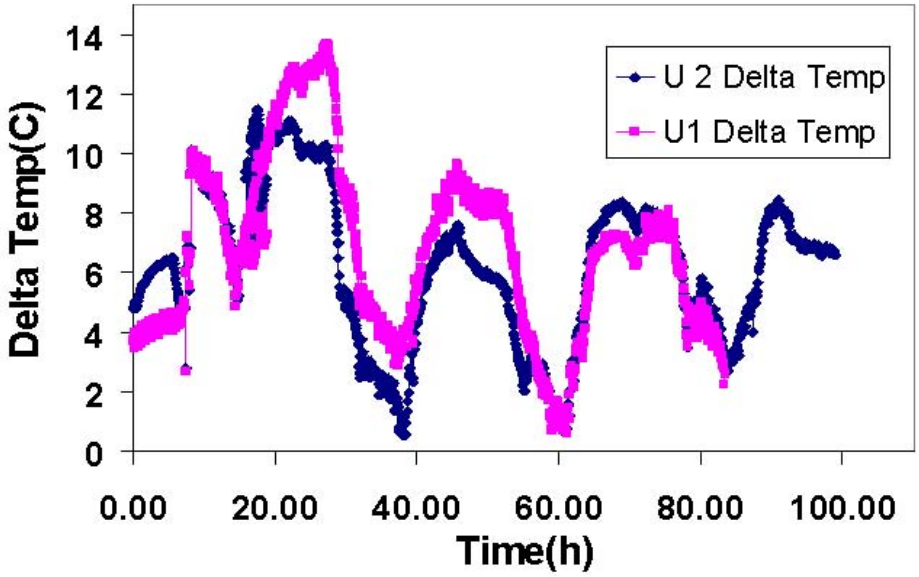

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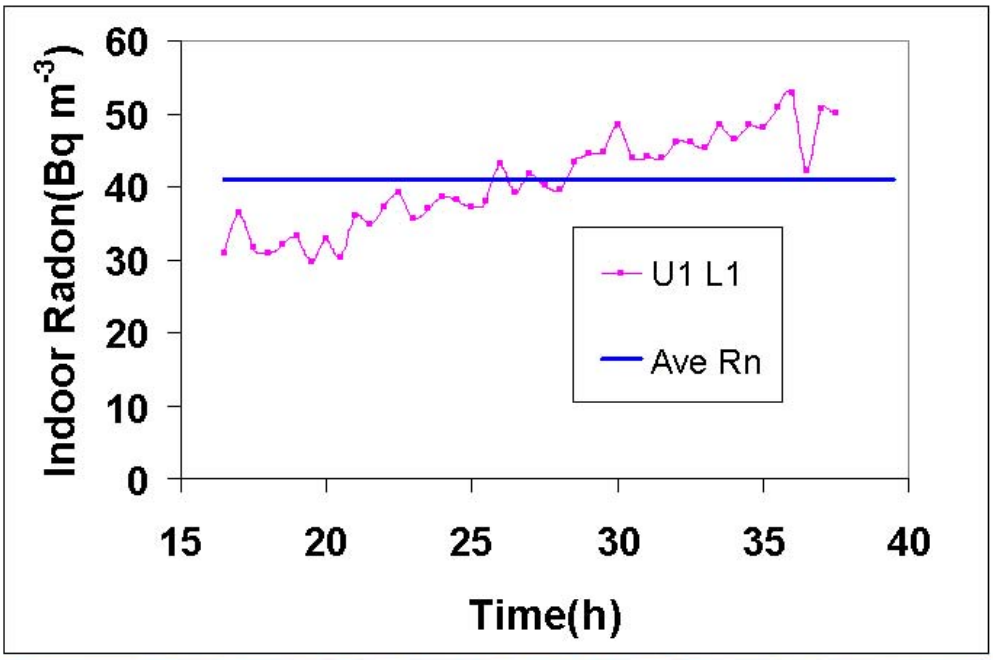

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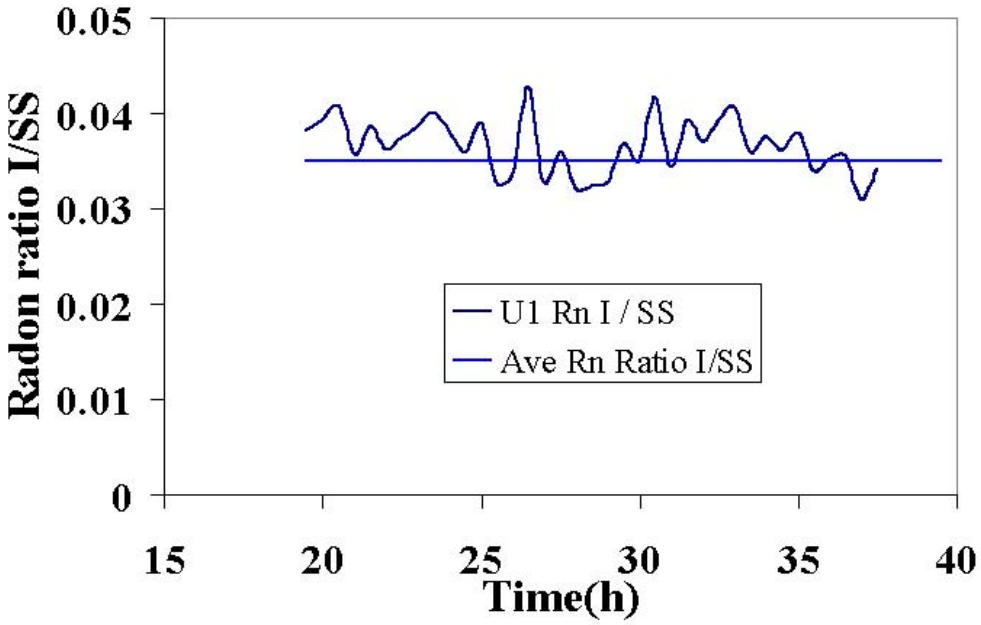

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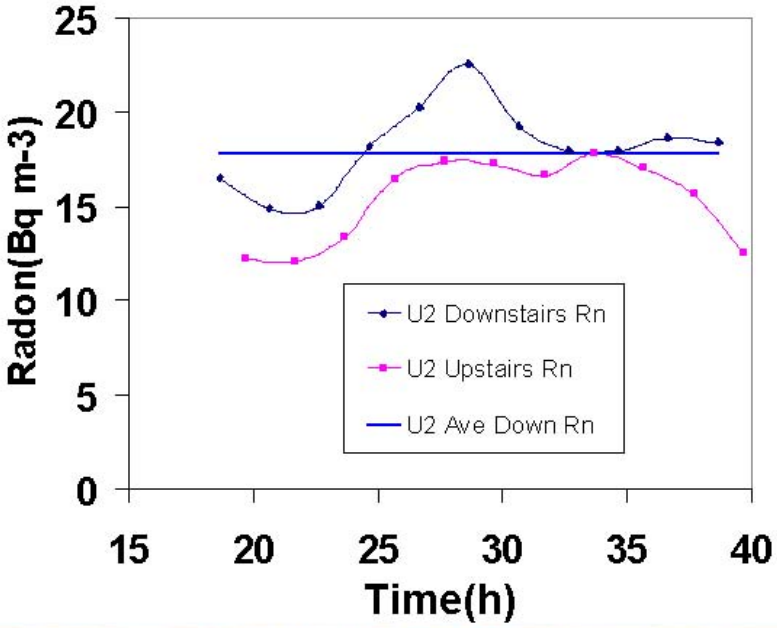

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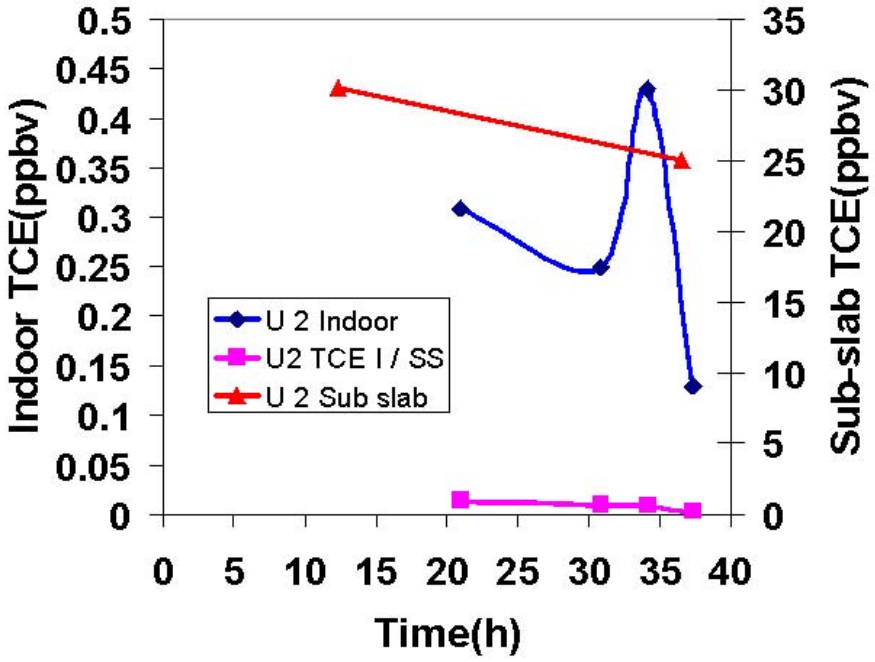

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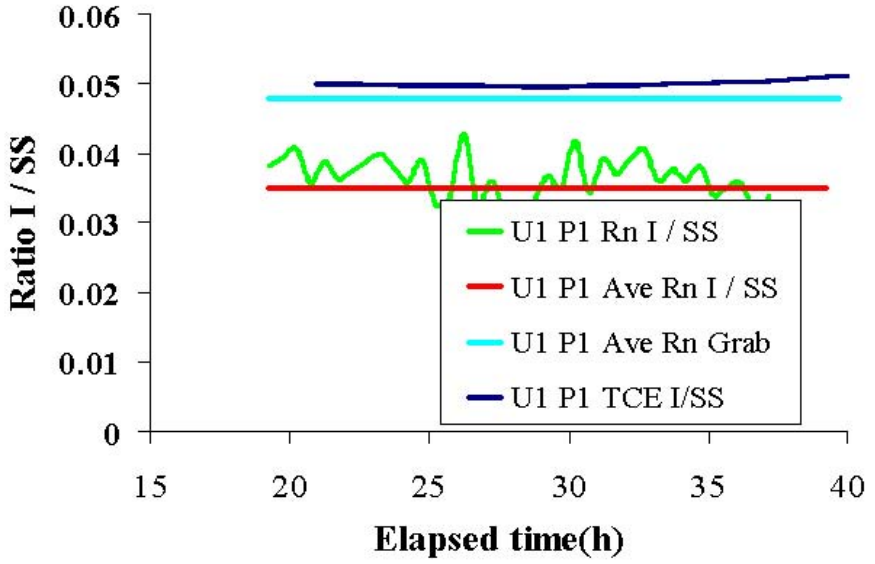

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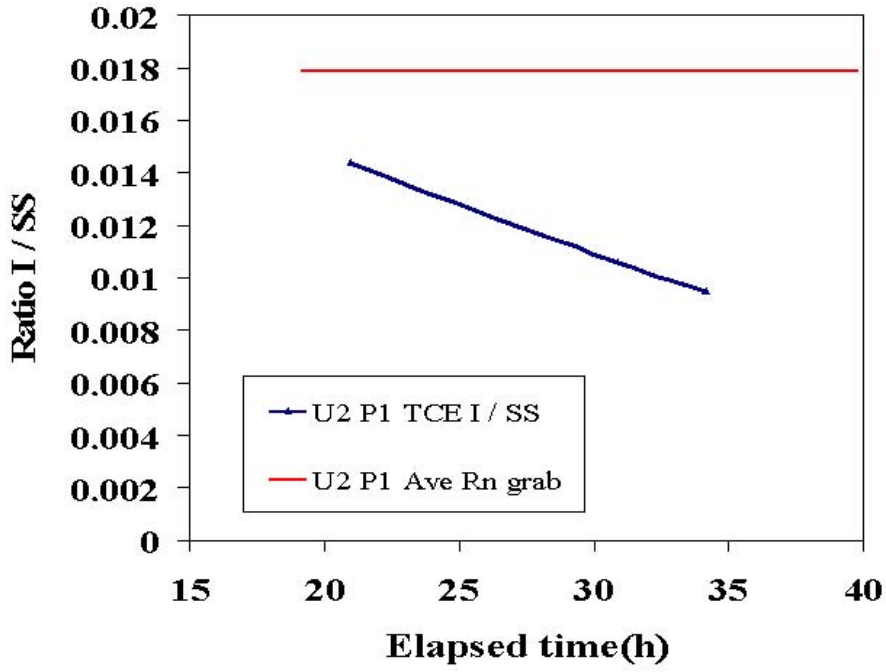
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Ratio I / SS
U2 P1 TCE I / SS
U2 P1 Ave Rn grab
15
20
25
30
35
40
Elapsed time(h)


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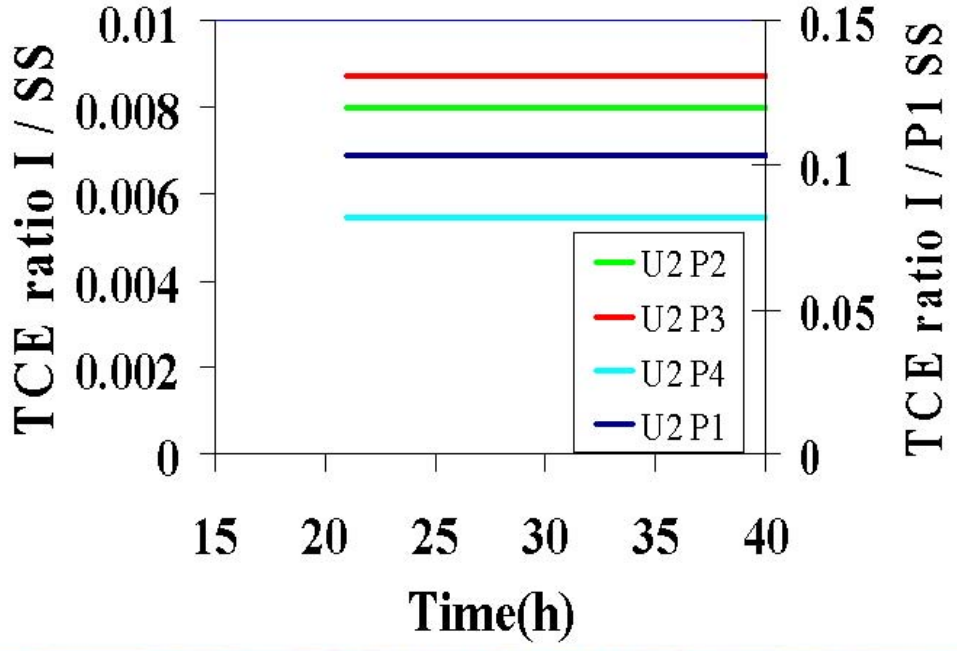
0.01
0.008
0.006
0.004
0.002
0
TCE ratio I / SS
0.15
0.1
0.05
0
TCE ratio I / P1 SS
U2 P2
U2 P3
U2 P4
U2 P1
15
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30
35
40
Time(h)


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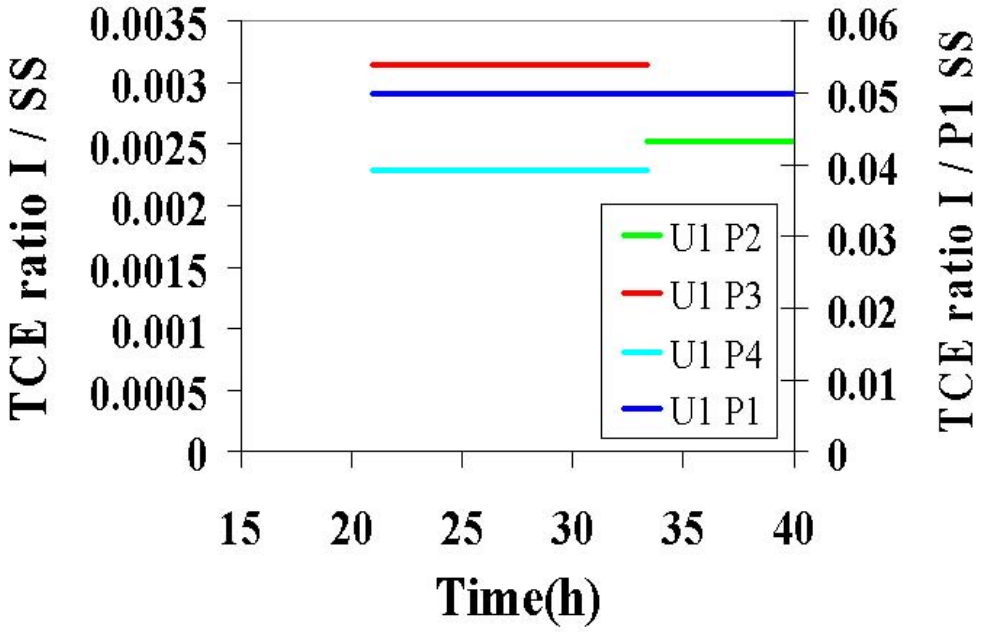

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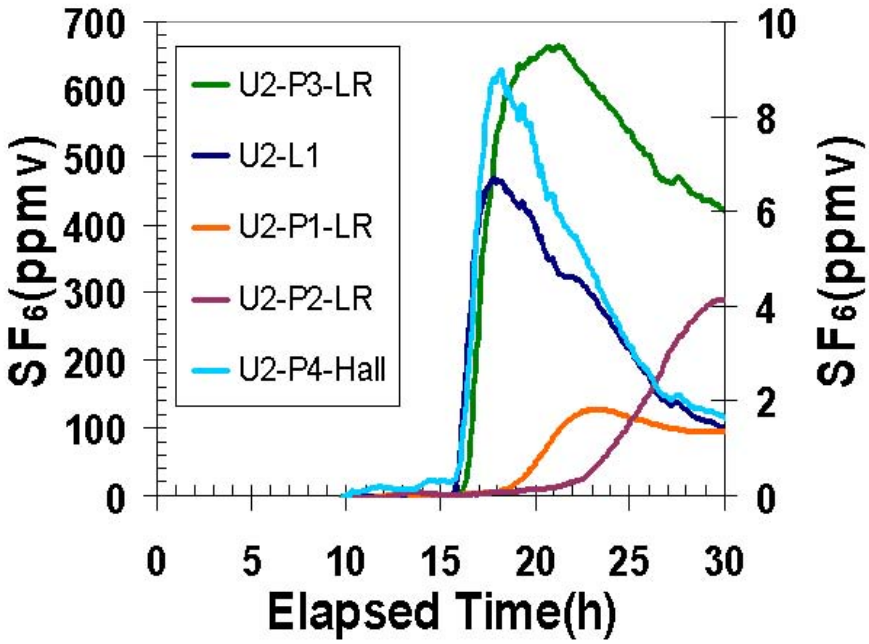

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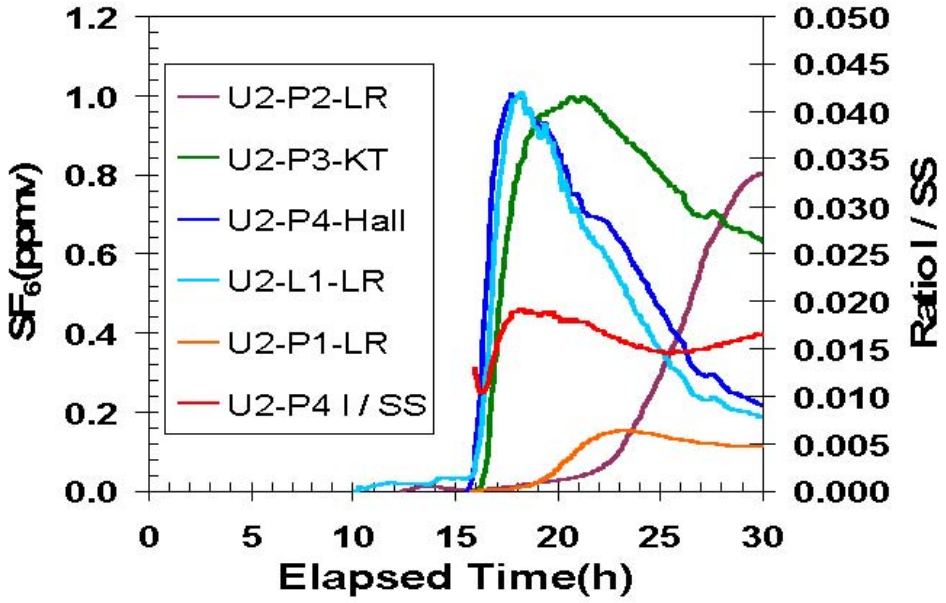
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SF6(ppmv)
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
Ratio I / SS
U2-P2-LR
U2-P3-KT
U2-P4-Hall
U2-L1-LR
U2-P1-LR
U2-P4 I / SS
0
5
10
15
20
25
30
Elapsed Time(h)


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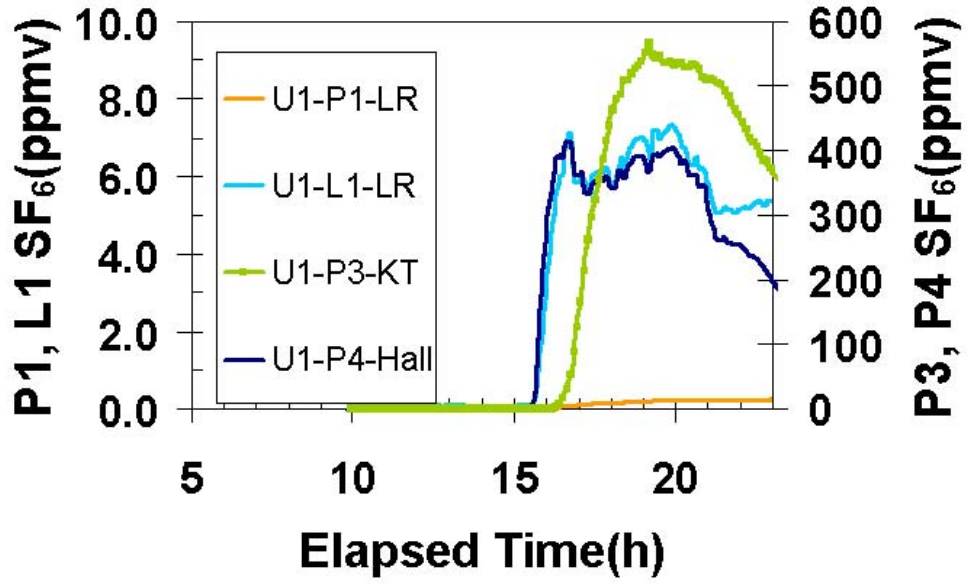
10.0
8.0
6.0
4.0
2.0
0.0
P1, L1 SF6(ppmv)
600
500
400
300
200
100
0
P3, P4 SF6(ppmv)
U1-P1-LR
U1-L1-LR
U1-P3-KT
U1-P4-Hall
5
10
15
20
Elapsed Time(h)


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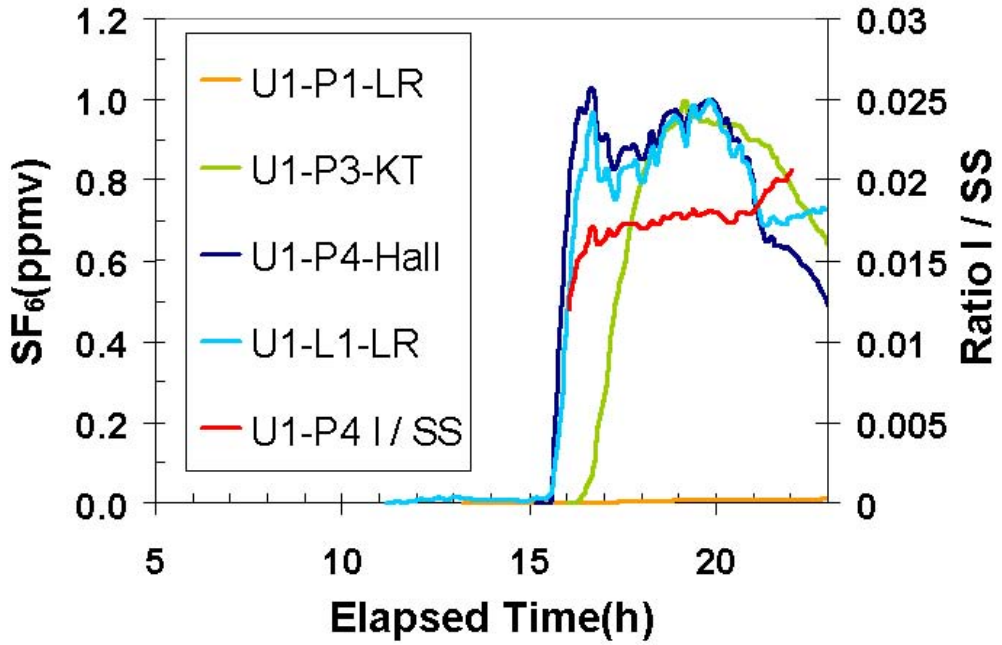

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Conclusions

- Low levels of radon can be measured with sufficient accuracy to be used in analysis of vapor intrusion problems.
- Radon is a promising, low-cost surrogate for soil gas contaminants, however, as with VOCs themselves, the complete distribution under the slab must be known in order to properly interpret its impact on indoor measurements.
- Communication underneath these slabs was more restricted than anticipated.
- When the sub-slab communication is poor, it may be necessary to identify the locations of the entry routes to fully understand the relationship between indoor and sub-slab concentrations.
- Because of the low permeability soil, the building was more difficult to analyze than expected.
- SF_6 moved very slowly and not very uniformly under the slab.
- It was demonstrated in this case that I/SS can differ by orders of magnitude depending on where a single sub-slab probe is placed.

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Vertical Profiling of Soil Gas Concentrations at UST Sites: Comparison of Passive Diffusion Sampling and Active Soil Gas Sampling

Cindy Paul
US Environmental Protection Agency/ORD

ABSTRACT

Understanding the transport of volatile contaminants in soil gas, particularly those associated with underground storage tanks (USTs), requires a detailed knowledge about the depth-dependent distribution of chemical species in the subsurface. Traditional monitoring wells generally provide an average concentration across the screened interval which may not be representative of the concentration at a specific discrete depth where the sampling port is located. A simple and affordable passive diffusion sampler (PDS) was developed that can be used to estimate depth-discrete concentrations of contaminants in soil gas and ground water. The PDS consists of a 40-ml VOA vial fitted with a modified cap where the Teflon-lined septa is replaced by a permeable membrane to allow contaminants to diffuse into the water-filled VOA vial. The PDS is inserted into a holder or "messenger" for deployment down monitoring wells.

A field study was conducted to provide three dimensional site characterization of a gasoline plume at an underground storage tank site to evaluate the effectiveness of the PDS for determining BTEX concentrations in soil gas. PDS concentrations were compared with those obtained with traditional soil gas sampling techniques. A monitoring system was installed at the Hal's Chevron site in Green River, Utah, consisting of an array of 2-in diameter PVC monitoring wells installed at discrete depths with 2-in screens. The monitoring wells were installed adjacent to existing vapor probes for comparison purposes. The messengers containing the PDS were lowered into each monitoring well so that the cap of the PDS was exposed within the well screened interval. The PDS was left in the monitoring wells for approximately one month. Previous laboratory studies showed that one month was sufficient time for BTEX compounds to diffuse across the membrane and reach equilibration.

Results of this study show that the PDS provides a simple and affordable alternative to traditional sampling techniques at UST sites. Additionally, results of discrete depth contaminant concentrations may be used to provide information on whether natural attenuation processes are controlling risk associated with the site.

Vertical Profiling of Soil Gas Concentrations at UST Sites: Comparison of Passive Diffusion Sampling and Active Soil Gas Sampling

Cynthia J. Paul, Dominic DiGiulio, John Wilson, Ken Jewell
U.S. EPA, ORD, NRMRL, GWERD
Ada, Oklahoma 74820
(paul.cindy@epa.gov)

Robin Davis and John Menatti
Utah Department of Environmental Quality

National Environmental Monitoring Conference
Cambridge, MA
August 20-23, 2007

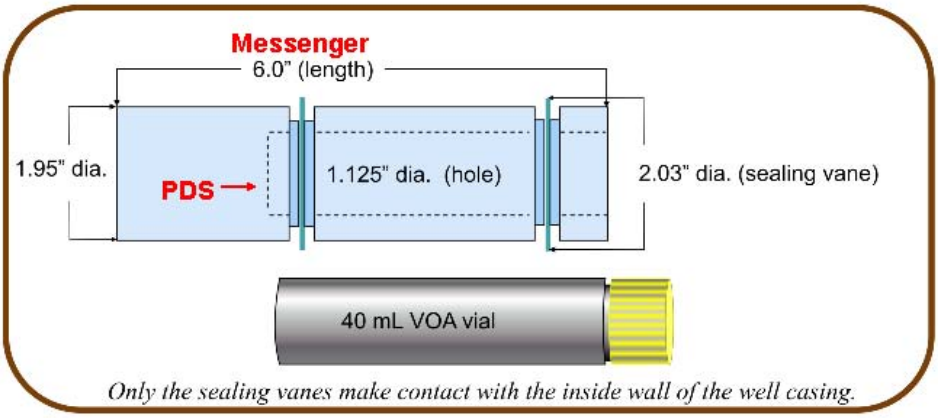
Considerations

- If oxygen is available at the capillary fringe, biodegradation may remove the fuel vapors before they have a chance to diffuse upward into buildings
- Our approach using modified passive diffusion samplers (PDS) replaces the estimates of a mathematical model with monitoring, to see if there are vapors in the soil gas immediately above the capillary fringe that can diffuse into buildings
- Field study was conducted to compare PDS data with active soil gas sampling from monitoring wells and vapor probes

New Passive Diffusion Sampler (PDS)

- 40 ml VOA vial where the Teflon-lined septa is replaced by a permeable membrane
- Trisodium phosphate (TSP) added and filled with deionized water
- PDS inserted in "messenger" and emplaced within monitoring well screened interval for at least one month

PDS and Messenger for 2-inch well



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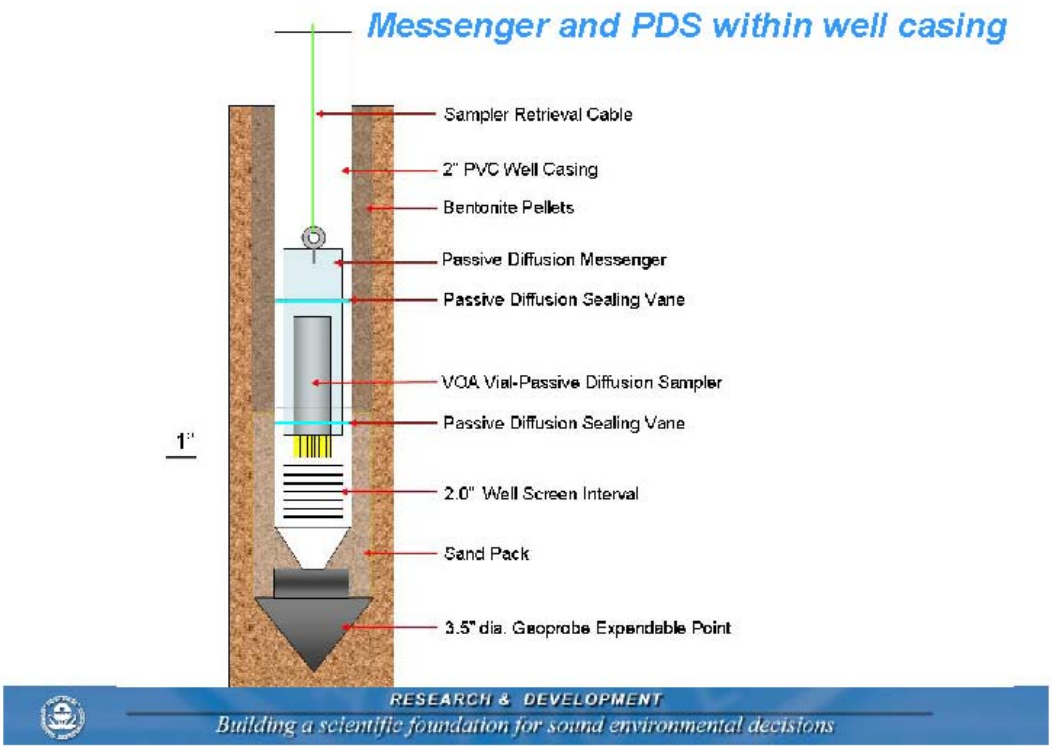

Advantages of PDS

- Allows more discrete samples from smaller volume of subsurface material
- Can detect sharp vertical gradients of BTEX compounds in soil gas and ground water
- Averages concentrations over several days - less susceptible to temporal variation
- No purge water produced

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- Does not extract fluids - minimal affect on concentration gradients during sampling - less question of "where the sample really came from."
- The PDS is indifferent to the position of the water table – provides a sample from either ground water or soil gas.
- Low cost to analyze PDS samples compared to other methods.

Limitations of PDS

- Requires installation of several discrete wells to sample along a vertical concentration gradient.
- Sampler may not come to equilibrium with short term exposures - they must be emplaced during one site visit and recovered on a second visit.
- Samples can't be duplicated.

Field Site: Hal's Chevron, Green River Utah

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Several thousand gallons of gasoline leaked from USTs and migrated down through the vadose zone soils (silty clays, clayey silts, and silts) to the groundwater table at about 18 feet bgs.

The gasoline plume migrated under the adjacent Oasis Motel and Fairway Club restaurant.

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Conventional Practice

- Traditional monitoring wells generally provide an average concentration across the screened interval which may not be representative of the concentration at a specific discrete depth where the sampling port is located

- Uses screening models (i.e. Johnson Ettinger) to estimate the affect of biodegradation on removal of hydrocarbon vapors.

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Gasoline plume migrated laterally on the groundwater table to about 300 feet down gradient of the Hal's Chevron LUST site.

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Stainless-Steel Soil Vapor Sampling Screen Polyethylene Tubing to Ground Surface

UDEQ direct buried vapor probes

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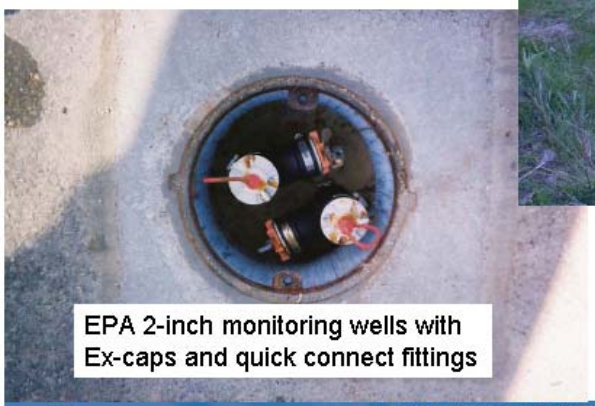
EPA Installed 12 2-inch PVC monitoring wells with 2-inch screened interval using Geoprobe direct push technique



EPA 2-inch monitoring wells with Ex-caps and quick connect fittings

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EPA Monitoring Wells		UDEQ Vapor Probes	
ID	Depth (ft)	ID	Depth (ft)
EPA 2	3	VW 7	3
EPA 2	7	VW7	7
EPA 1	11	VW7	11
EPA 1	15	VW7	15
EPA 4	2.5		(none)
EPA 4	4	VW11	4
EPA 3	8	VW11	8
EPA 3	12	VW11	12
EPA 5	3	VW10	3
EPA 5	7	VW10	7
EPA6	11	VW10	11
EPA 6	15	VW10	15

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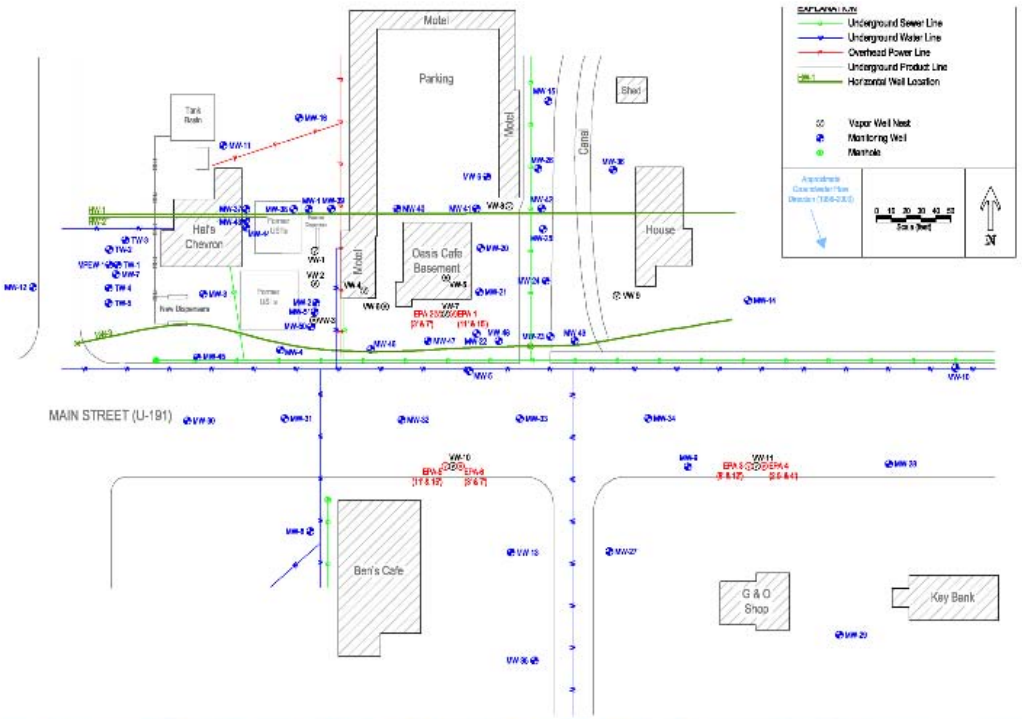

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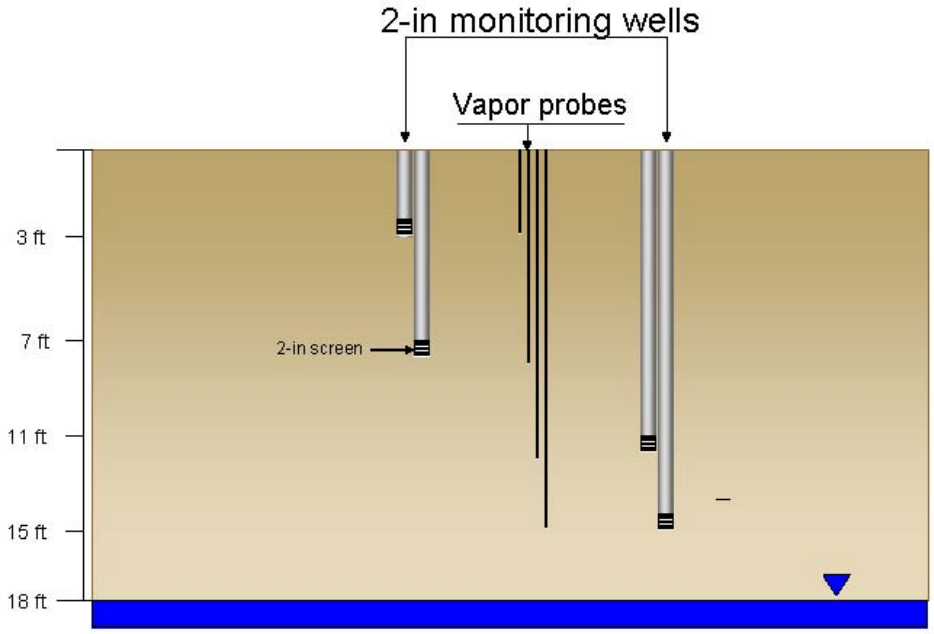

Soil Gas Sample from UDEQ Multi-Depth Vapor Wells

Using a plastic syringe, purged 3 tubing volumes from each sampling tube. Vapor samples were collected in 1-liter Summas. Did not use flow controllers, but had vacuum gauges on each canister

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Active soil gas sampling EPA monitoring wells with 1-liter Summa canisters

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Inserting PDS and messenger into 2-inch monitoring well

Air was evacuated with a peristaltic pump as messenger was lowered into monitoring well

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PDS after retrieval showing sulfide production on vial – evidence of BTEX biodegradation

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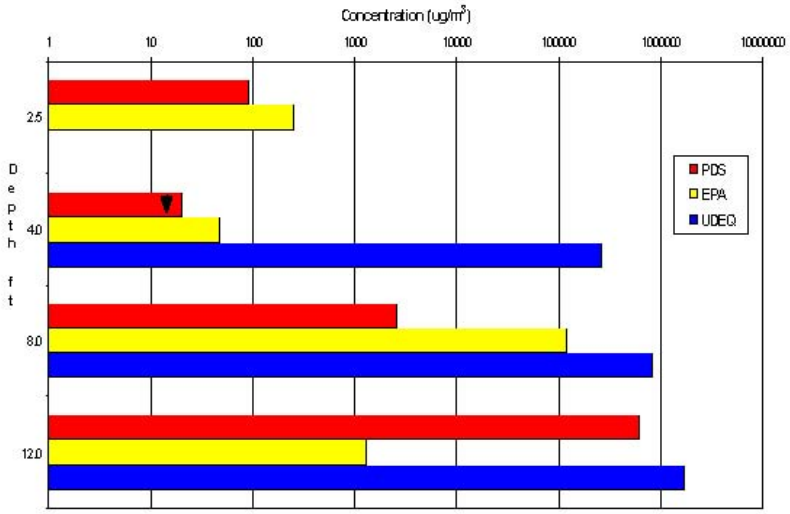
Benzene WW11



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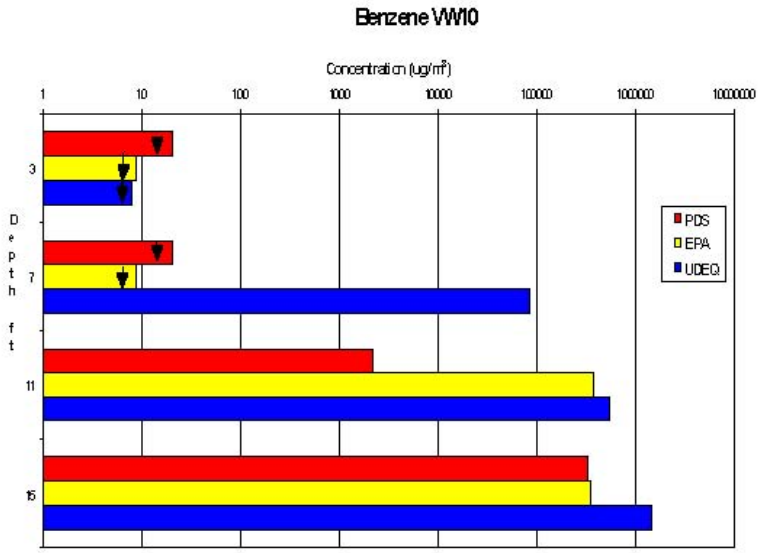

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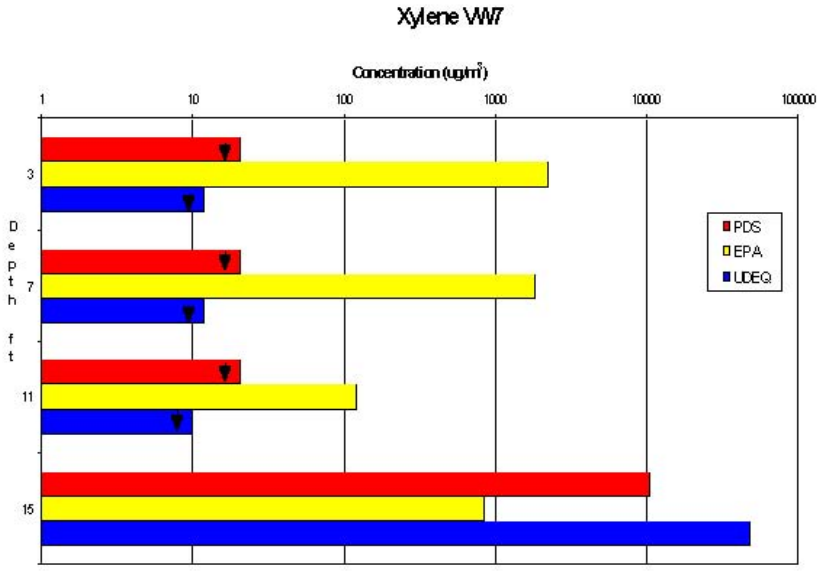

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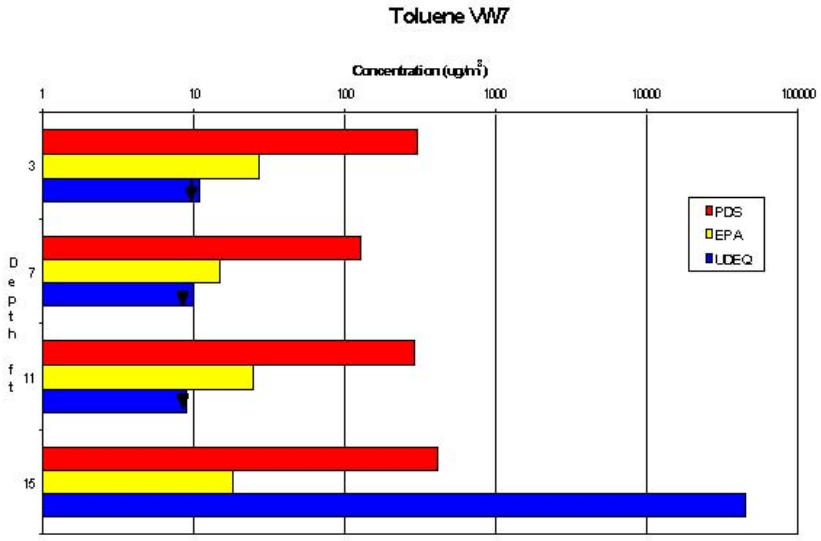

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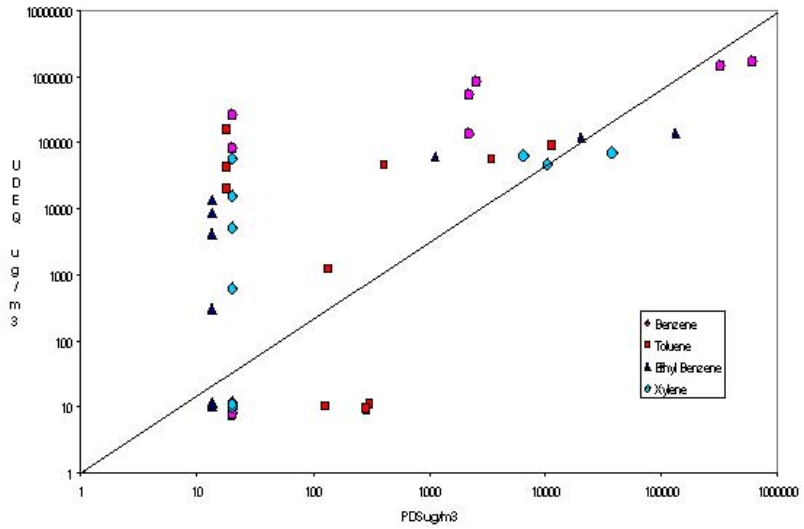
Correlation between PDS and UDEQ Data



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Summary

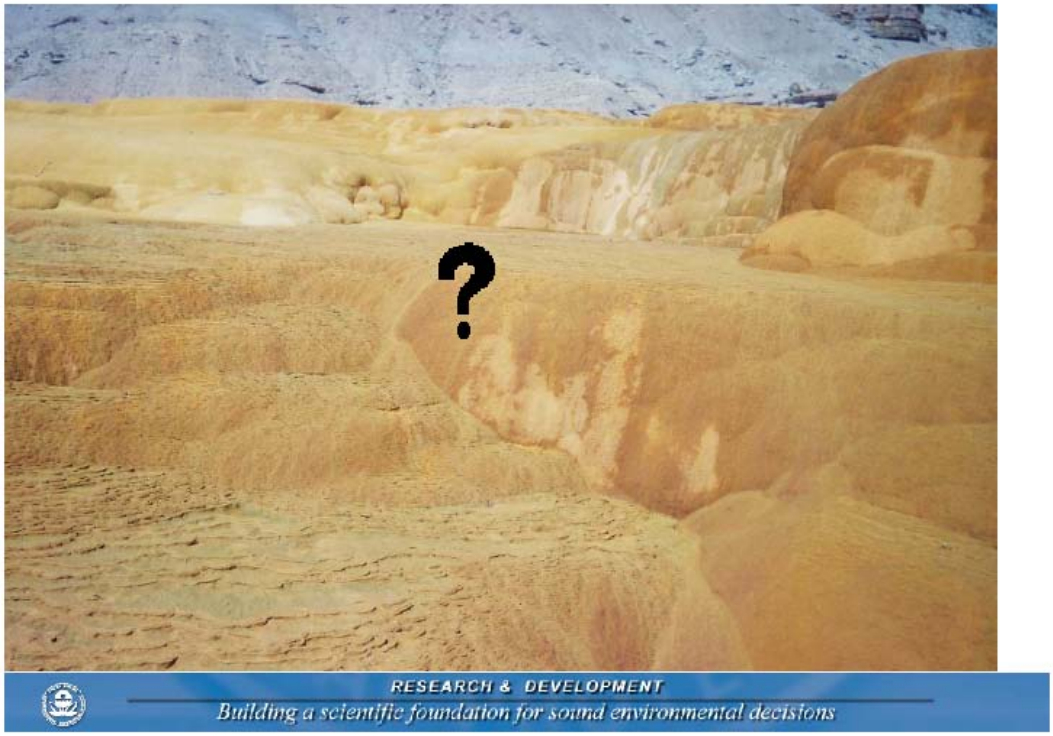
- PDS data showed an obvious low bias when compared to UDEQ data in most cases
- No difference seen among compounds
- PDS performed better than active soil gas sampling in monitoring wells

Future Plans

- Conduct more well leak testing with the messenger within the casing
- Evaluate if enough air is being extracted as messenger is lowered into the well
- Evaluate PDS performance with active soil gas sampling at additional sites

- Monitoring wells CAN BE "Holes in the Ground that Lie"

Although the research described in this presentation has been funded wholly or in part by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement may be inferred.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POSTERS

Analysis of Water for Pesticides at Low Parts Per Trillion (ppt) Levels Using Two Dimensional LC/MS/MS

André Schreiber
Applied Biosystems/MDS Sciex

ABSTRACT

The provision of clean, uncontaminated drinking water is of paramount importance to the water industry. In recent times the requested limits of detection for pesticides have been decreasing as methodologies improve. Typically water companies need to be able to have limits of quantitation for pesticides between 0.02 – 1 µg/L (20 - 1000 ppt) which often means that methods should have limits of detection for certain pesticides at 10 – 50 ppt. These low levels often mean that water samples have to be extracted either using liquid/liquid or solid phase extraction in order to concentrate these contaminants to such a level where they can be detected. Sample pre-treatment can often be time consuming and add an additional cost to the analyses.

This poster presents data acquired on the 3200 QTRAP LC/MS/MS system where pesticides have been detected in the low ppt range with no sample pre-treatment. High injection volumes were used with on-line solid phase extraction to pre-concentrate the pesticides before separation by reverse phase HPLC and detection.

Data displayed in the poster indicated CV from spiked samples, were less than 15% at low ppt levels. Calibration lines over the range 20 – 1000 ppt were observed to be linear. For confirmation full scan enhanced product ion data was also acquired at low ppt levels using an MRM trigger to start the acquisition of an enhanced product ion scan where a collision energy spread was used to enhance the spectral quality. Cycle times for a fifty pesticide screen were less than 1s allowing quantitative and qualitative data to be acquired in one run.

Novel Approach in the Profiling of Volatile Organic Compounds in Water

James Cox
Teledyne/Tekmar

ABSTRACT

EPA Methods 524.and 624 outline the general criteria for Volatile Organic Compounds in water and wastewater analysis. In recent years, laboratories have run into an environmental barrier in their efforts to increase throughput and productivity for the analysis of Volatile Organic Compounds (VOCs). Conventional purge and trap technology had reached a limit where the speed of analysis could not be increased further without severely affecting analytical performance and quality. This paper compares the standard purge and trap technology and the new Tekmar purge and trap showing that reduced run time can be achieved while maintaining EPA compliance with improved data quality.

Rapid Dual GC Column Analysis of Pesticides, PCB's and Herbicides, Using Two Unique Stationary Phases

Jason Thomas
Restek Corporation

ABSTRACT

Analysis of organochlorine pesticides, PCB's and phenoxy-acid herbicides has become a routine assay in the environmental sector. Although many of these agents were phased out decades ago, they can still be found in the environment. Environmental laboratories are expected to rapidly analyze extracts of samples with very complicated sample matrices without sacrificing target compound identification. These tests require a gas chromatographic stationary phase with proper selectivity and high thermal stability.

There is, also, a constant desire for even faster and faster analysis times, to help increase sample throughput and thereby increase laboratory productivity. Fast GC is a good solution to this need, however, the reduced internal diameter and thinner phase coatings associated with the fast GC movement have been a deterrent to the environment sector due to concerns of the columns capability to handle the oftentimes harsh sample matrices encountered in environmental samples.

A proposed solution to this ever-present conundrum is to use a 0.53mm ID guard column at the head of a dual column setup to act as the depository for high molecular weight sample interferences, thus saving the integrity of the columns down stream. This configuration would allow 20m x 0.18mm ID, thin film columns to be used, with their associated high efficiency, to achieve a greatly reduced analysis time without the repercussions usually encountered when using small bore columns with difficult samples.

This poster will focus on the use of two unique stationary phases, in this configuration, to perform a variety of EPA methods for pesticides, including 608, 8081, 8151A, 8082, and 8081A as well as other compounds of interest.

A Split Injection for EPA Method 8270D with a High Column Flow Rate

Jessie Butler
Thermo Fisher Scientific

ABSTRACT

Conventional gas chromatography follows the theory of the Van Demeter curve where the best separation is achieved for helium at a linear velocity of 20 to 50 cm/sec, low column flow rates of 1 mL/min. Several experiments have been run to test the effect of higher carrier gas flows by GC/MS. These elevated flow rates of 3 mL/min require fast scanning speeds of 5 scans/sec or 1,618 amu/sec. The actual capacity for the stationary phase can be increased with these higher flow rates, allowing for the use of thinner films. Run times are shortened and final oven temperatures can be lowered, reducing the run time and column bleed. Another interesting advantage was observed in minimizing irreversible absorption of active compounds such as pentachlorophenol by shortening the time spent in the analytical column and the inlet.

Another parameter studied was the flow of the carrier gas thru the inlet during injection of the sample. A split injection minimizes breakdown by reducing the stress of a flash vaporization in a constant temperature injection, although a more sensitive mass spectrometer is required.

No adverse effects were noted in precision, sensitivity, or separation at elevated column flow rates. The split injection actually enhanced the separation of more volatile compounds like N-nitrosodimethylamine (NDMA) and pyridine. The target list studied in this project were those in EPA Method 8270D.

Single Method Screening for US and EU Variations of PAHs Using GC

Kory Kelly
Phenomenex

ABSTRACT

Polynuclear Aromatic Hydrocarbons (PAHs) are common pollutants with highly carcinogenic properties and heavily regulated both here and in Europe. However, the common PAHs in the United States are not the same common PAHs monitored in Europe. This leads to difficulties when trying to create one gas chromatographic screening method that can be used for either or both sets of PAHs. Isomers from one group tend to co-elute with the isomers of another, which causes sacrifices in resolution and therefore quantitation.

The method proposed in this presentation tackles this dilemma. A single set of conditions and instrument a configuration has been developed that will allow both sets of PAH pollutants to be analyzed simultaneously while surpassing current EPA requirements for resolution and quantitation.

Single Column GC/MS Analysis of the 12 PCBs Designated Most Toxic by the World Health Organization

Kory Kelly
Phenomenex

ABSTRACT

Polychlorinated Biphenyls (PCBs) are a class of Priority environmental pollutants that have been identified for international regulation. Until 1977, PCBs were commonly used as an insulator in transformers and capacitors, as well as for other industrial applications. Their high chemical stability has made them a persistent environmental pollutant subject to long-range transport and bioaccumulation.

The World Health Organization (WHO) has identified 12 of the 209 congers to have toxicity characteristics similar to 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD). These "dioxin-like" PCBs have been assigned Toxic Equivalency Factors (TEF) relative to the 2,3,7,8-TCDD isomer. The identification of these compounds is specified by EPA Method 1668, Revision A. The method requires confirmation using two different GC columns in order to completely resolve all 12 isomers.

The current work greatly simplifies this analysis by providing resolution of all 12 toxic congeners using one column: the Zebron ZB-5ms column (Phenomenex, Torrance, CA). The phase utilizes a Si-Arylene bonded polymer that has been demonstrated to provide enhanced resolution of multi-aromatic compounds.

Sensitivity Characteristics of GC/MS Analysis for PAHs in the Presence of Hydrocarbon Interferents

Larry Penfold
Severn Trent Laboratories

ABSTRACT

Environmental investigations frequently include analysis for low concentrations of polynuclear aromatic hydrocarbons (PAHs) in the presence of significant levels of interfering hydrocarbons. GC/MS analysis (e.g., Method 8270), whether performed in the full scan or selective-ion monitoring mode, is often the technique of choice in order to minimize false positive results from the hydrocarbon background in the samples. However, PAH concentrations of concern can extend down to the method detection limit capabilities of the EPA approved methods. The reliability of PAH detection limits in the presence of significant hydrocarbon concentrations may be called into question, particularly when internal standard recoveries are low (e.g., < 50%).

Data will be presented from a controlled study conducted by Severn Trent Laboratories that demonstrate the detection capabilities of the GC/MS system under these conditions. The results have implications for the validation and ultimately the usability of GC/MS PAH data, which will be illustrated with examples from a large U.S. Department of Defense RCRA closure project.

Using the Pulsed Flame Photometric Detector (PFPD) for Low-Level Analysis of Organophosphorus Pesticides

Laura Chambers
OI Analytical

ABSTRACT

Organophosphorus (OP) pesticides are among some of the most widely applied commercial pesticides in the world. These toxic pesticide residues are detected in food, water, plants, and soils, often at concentrations in the low parts-per-billion (ppb) range. Two of the most common USEPA methods for analyzing OP pesticides specify the use of a flame photometric detector (FPD) operated in the phosphorus mode for selective detection of OP pesticides. The Pulsed FPD (PFPD) has emerged as the phosphorus-selective detector of choice for trace-level OP pesticide analysis because it introduces a time-dependent variable to the analysis which improves selectivity for phosphorus with respect to hydrocarbon or sulfur. The PFPD also has the advantage of lower detection limits, long-term stability, and dual-element detection for simultaneous detection of both phosphorus and sulfur.

This poster will discuss the consideration for configuring the PFPD for low-level analysis of OP pesticide residues, including modifying the gate settings to extend the calibration range, using dual-gate subtraction to eliminate residual sulfur interference, and parallel configurations with MS to confirm peak identification in complex matrices. Real world examples will be shown.

An Innovative Approach to Low Mass, Zero Dead Volume Connection of Fused Silica Columns

Robert Freeman
Restek Corporation

ABSTRACT

A common problem when joining fused silica columns together is obtaining a secure and leak tight seal. There are many different types of connectors available on the market today that allow the user to repair a broken column, or connect a transfer line or guard column to an analytical column.

Metal type connectors are often used and offer a secure connection, but it is often difficult to obtain a good, zero dead volume union. Press-Tight® connectors offer an inert connection, but these can disconnect when subjected to high temperatures, pressures and turbulence in the GC oven. There is a new type of connector that offers both a secure connection at high temperatures and pressures with zero dead volume.

This new connection features a small union that will not disconnect after repeated heating and cooling cycles. This poster will illustrate the effectiveness and advantages of the new connector. We will show that the new connector gives the analyst a reliable seal, zero dead volume in the flow path, and has a lower thermal mass than standard metal type connectors.

Fast Analysis for Several EPA Water Methods Using UltraPerformance LC®

Mark Benvenuti
Waters Corporation

ABSTRACT

Fast analysis of target analytes is important to any laboratory in terms of throughput, cost control, and overall efficiency. Various US Environmental Protection Agency (EPA) water methods describe chromatographic separations which can be as long as thirty minutes or more.

Recently, a new technology known as UltraPerformance LC® based on columns packed with a Bridged Ethyl Hybrid (BEH) 1.7 micron particle size material and using a high pressure fluidics module generating pressures up to 14000 psi has allowed the high efficiency separation of numerous analytes in fifteen minutes or less.

Our poster will demonstrate the application of this technology to several EPA Water Methods including Method 532- Phenylureas, Method 549.2- Diquat and Paraquat, Method 554- Derivatized Carbonyl Compounds, Method 555- Chlorinated Pesticides Method 610- Polynuclear Aromatic Hydrocarbons, and Method 8330- Explosives.

Trace Level Analysis of Explosives in Ground Water and Soil with LC/MS/MS Using Negative Ion Atmospheric Pressure Chemical Ionization

Christopher Borton[1], Loren Olson[1], André Schreiber[2], Hesham Ghobarah[2], Robert Ellis[2]
[1]Applied Biosystems
[2]Applied Biosystems/MDS Sciex

ABSTRACT

The analysis of explosive residues in ground water and soil samples is an ever increasing challenge. Due to the production and expulsion of military weaponry, there is an increasing need for accurate and definitive detection of explosive compounds and their degradation products. Both military installations and local municipalities surrounding these installations are concerned about these hazardous compounds entering water supplies. The standard technique used for the analysis of these compounds has been HPLC with UV detection, following the guidelines set by USEPA Method 8330. Although this method has been successful, so far, there are several drawbacks. The lack of sensitivity of UV detection requires a costly and time consuming concentration step during preparation of samples. More importantly, UV detection is not selective and requires a second analysis using a separate HPLC column. Even after this second analysis, there is still possibility of false positive detection. Especially with the increasing terror threat, environmental, forensic and criminal laboratories need to quickly and unambiguously screen for common explosive compounds at trace levels.

Presented is a sensitive method for the detection of a wide range of nitroaromatic and nitroamine compounds by LC/MS/MS. Instrumentation consisted of a High Performance Liquid Chromatography (HPLC) system equipped with an autosampler and coupled with a triple quadrupole mass spectrometer using negative ion Atmospheric Pressure Chemical Ionization (APCI). The mass spectrometer was tuned and optimized to use two Multiple Reaction Monitoring (MRM) transitions per analyte. The most sensitive MRM transition was used for quantitation while the second one was used for detection confirmation. By using MS/MS detection the concern of false positive detections is virtually eliminated.

After sample preparation all analytes could be detected at levels ranging from 0.05 µg/L to 2.0 µg/L in water samples and 25.0 µg/kg to 1000 µg/kg in soil samples. Additionally, studies were performed to show that ion suppression is not present for these samples when using APCI.

Detection of Ethanesulfonic Acid and Oxanilic Acid Degrates of Chloracetanilides and Other Acetamide Herbicides in Drinking Water by LC/MS/MS

Christopher Borton[1], André Schreiber[2], Loren Olson[1], Hesham Ghobarah[2], Robert Ellis[2], Greg Eppink[1]
[1]Applied Biosystems
[2]Applied Biosystems/MDS Sciex

ABSTRACT

The analysis of environmental contaminants is an ever increasing challenge. Due to their extensive use in industry and households pesticides are one of the most important classes of environmental pollutants next to endocrine disrupting compound, pharmaceuticals and personal care products.

Screening methods and targeted quantitation methods are used to investigate the presence and distribution of pesticides in environmental matrices, such as drinking water, surface water and soil. Traditionally GC, GC/MS, and LC/UV have been used to perform this analysis. Although these methods have been successful, so far, there are several drawbacks. GC-based analysis suffers from problems with thermal degradation and requires costly and time consuming derivatization and concentration steps. LC/UV lacks of sensitivity and selectivity requiring time consuming concentration steps with a high risk of poor recovery and false positive results.

Presently more LC/MS/MS-based methods are developed, such as the presented method for the analysis of ethanesulfonic acid and oxanilic acid degrates of chloracetanilides and other acetamide herbicides in drinking water. Modern developments in LC/MS/MS technology are applied to a simplified procedure of EPA Method 535.

The developed method can be used with traditional Solid Phase Extraction (SPE) or to directly inject water samples into the LC/MS/MS system. Both approaches were investigated and compared regarding detection limits, accuracy, robustness, and possible matrix effects. In addition the ration of two Multiple Reaction Monitoring (MRM) transitions was used for confirmatory analysis to eliminate the detection of false positives.

New Approach in the Profiling of VOCs in Soil Utilizing the Purge and Trap Autosampler

James Cox
Teledyne/Tekmar

ABSTRACT

EPA methods for the determination of VOCs in soil following methods 5030 and 8260 parameters can be a challenge when trying to ensure the fastest possible run time without sacrificing analytical integrity. Two main aspects that are often compromised when optimizing a purge and trap concentrator and autosampler are carryover and lowered sensitivity. Teledyne/Tekmar is offering a new approach to purge and trap optimization that is achieving unprecedented performance. Data presented demonstrate advances in analytical abilities without sacrificing any data integrity.

Revolutionary Advances in P&T Analysis for the Profiling of VOCs

James Cox
Teledyne/Tekmar

ABSTRACT

Purge and trap technology provides the fastest cycle time for purge and trap analysis by greatly reducing the time to complete dry purge and bake modes. The Teledyne/Tekmar purge and trap system achieves these reduced cycle times while maintaining minimal levels of carryover without sacrificing data quality. By utilizing an electronic flow controller to increase gas flow rates, dry purge time can be reduced to one minute and bake time can be reduced to two minutes. Because the same bake volume is used, carryover is minimal, even at these reduced times. With this capability, the Teledyne/Tekmar purge and trap cycle time can be greatly reduced. Attempts to achieve the same shortened cycle times on older purge and trap systems by reducing bake time will result in increased sample-to-sample carryover and poor data quality. This study will examine carryover levels at various system conditions.

Double Your Lab's Productivity By Using Fast GC Columns

Kory Kelly
Phenomenex

ABSTRACT

Cutbacks in budgets and increased competition have forced labs to improve productivity while decreasing cost. In order to achieve this goal, many labs are trying to optimize their current GC methods rather than purchase a new instrument. Fast GC columns are a perfect way to achieve this goal.

GC column efficiency (N) is directly proportional to the internal diameter (ID) of the column. High efficiency columns provide sharper peaks and better resolution. The increase in resolution allows column to be shortened and analysis time to be dramatically reduced.

The separation of 16 Polyaromatic Hydrocarbons commonly analyzed by both US EPA and EU was evaluated on a 0.25mm, 0.18mm, and 0.10mm ID column. The increased efficiency offered by the 0.10mm ID column allowed analysis time to be reduced to less than 8 minutes. Some discussion is made as to the system requirements necessary for Fast GC columns, as well as the limitations of this technique.

Use of Dilution to Avoid False Negative Results Caused by Hydrocarbon Interferences in SVOC Analysis

Mark Bruce
Severn Trent Laboratories

ABSTRACT

Low concentration risk assessment goals such as the EPA Region 9 PRGs, are fueling the drive for analysis at lower and lower analyte concentrations. Hydrocarbon impacted sites must be demonstrated to have key hazardous constituents below certain decision thresholds in order to establish that certain costly remediation steps are not necessary.

Hydrocarbon mixtures are common and significant interferences when determining semi-volatile organic analytes by GC-MS in extracts of environmental soil samples. When the hydrocarbon content of the sample extract is high, the ability to detect and quantify target analytes is degraded. Varying amounts of diesel fuel and motor oil were added to a quantitation limit calibration standard. As the hydrocarbon content increased, a low bias was observed for analytes such as benzyl alcohol, benzidine and 2,4-dichlorophenol. Other the analytes that were not detected when the hydrocarbon content was high. A few of the "disappearing" analytes were nitrobenzene, pyridine, 4-nitrophenol, and pentachlorophenol. In those instances, the non-detect result was a false negative.

Determining the relationship between hydrocarbon content and the frequency of false negatives can guide the analyst toward making the proper extract dilution. This challenging balance point weighs sensitivity and low quantitation limits vs. data accuracy and avoidance of false negatives. For example, diesel fuel concentrations up to 5.9 mg/kg did not affect the quantitation of nitrobenzene at 33 µg/kg. Once the diesel fuel concentration reached 11.7 mg/kg, nitrobenzene was non-detect.

Guidance to produce the minimum dilution necessary to avoid false negatives is being developed. This guidance is tested with real sample extracts spiked with common analytes of concern at the applicable quantitation limits.

EPA Method 314.2 for the Determination of Perchlorate: A 2-D IC Method for Enhanced Selectivity

Richard Jack
Dionex Corporation

ABSTRACT

This method improves upon EPA Method 314.0 and 314.1 for the determination of perchlorate in drinking water, even in the presence of high salt matrices (>1,000 mg/L for Cl-, SO4 and NO3). 2-D IC involves loading a sample onto a 4-mm separation column, and then diverting interfering matrix ions using a heart-cutting technique. The effluent containing perchlorate is then trapped on a concentrator column, and then separated on a 2-mm ion exchange column. This strategy allows the ability to inject large sample volumes, to focus perchlorate partially resolved in the first dimension onto a concentrator column and separate it on a second, higher resolution column. It also combines two different column chemistries to enhance selectivity and reduce the possibility of false positives and eliminates the need for second column confirmation. The new method results in a 4-fold signal enhancement, which yields a lower detection limit (0.04 µg/L). Samples can be directly injected without sample prep, sample rinse or addition of matrix ions. Examples from a wide variety of sample matrices will also be presented.

Unique Column Alternatives for the Determination of Explosives and Propellant Residues via HPLC-UV

Robert Freeman
Restek Corporation

ABSTRACT

The presence of explosive and propellant residues in the environment is a topic of frequent concern. These compounds are persistent in the environment, at ambient conditions, exhibiting little natural degradation. EPA 8330 is a test method for the determination of trace amounts of nitroaromatics, nitramines, and nitrate esters by means of liquid chromatography. The method uses reversed phase HPLC and dual wavelength UV detection (210 & 254nm). The method was recently revised in October 2006 and expanded to include three additional analytes: nitroglycerine (NG), pentaerythritol tetranitrate (PETN), and 3,5-dinitroaniline (3,5-DNA). EPA 8330B now covers seventeen analytes that are commonly found in explosive and propellant residues.

We recently assessed various stationary phases for retention and selectivity of the new analytes in the revised method. Separations on all columns were accomplished with a simple, isocratic water:methanol mobile phase. Since the test method stipulates both primary and confirmation analyses, numerous columns were evaluated for selectivity differences such that an effective primary and confirmation column pair could be identified. This poster will illustrate the effectiveness and advantages of these stationary phases. We will show columns combinations that perform well in a primary-confirmation pair as well as illustrate several unique alternatives.

Chromium Speciation in Water Samples Using HPLC Coupled to the XSeries 2 ICP-MS

Shona McSheehy
Thermo Fisher Scientific

ABSTRACT

The extensive use of chromium in various industrial processes and the erosion of chromium from natural sources have resulted in its widespread occurrence in the environment. Monitoring of chromium in environmental compartments, and food and water sources is central in assessing the potential risk from exposure. The US Environmental Protection Agency (EPA) and the European Union have specified maximum admissible concentrations of 0.1 and 0.05 mg/L for total chromium under their respective drinking water directives.

This presentation describes the use of the HPLC ICP-MS instrument package from Thermo Fisher Scientific for the determination of chromium species in natural waters.

The HPLC reversed phase methodology employed complexation of Cr(III) with EDTA to improve separation. Due to the carbon containing mobile phase, optional collision cell technology (CCT) was used for the prevention of the polyatomic interference 40Ar12C on 52Cr. The use of CCT additionally suppresses interference from additional matrix in the water samples.