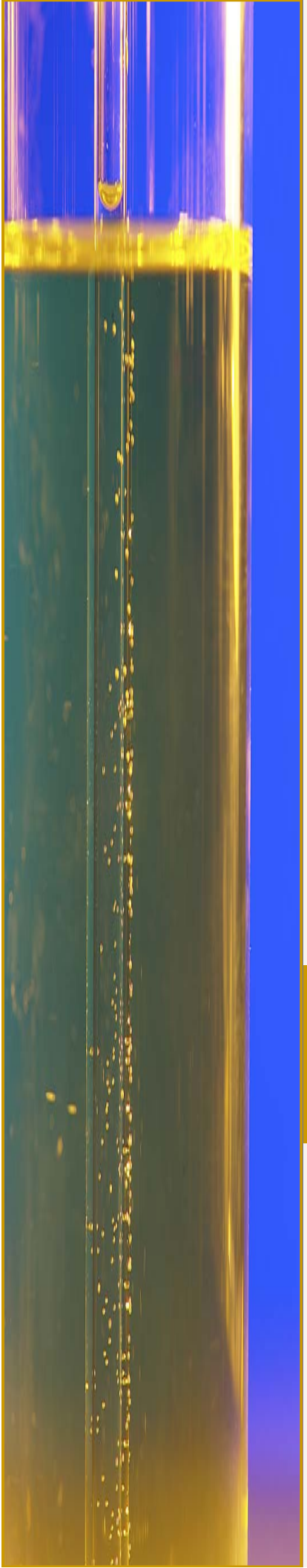

NEMC
National Environmental Monitoring Conference

2006 PROCEEDINGS

22nd Annual National Environmental Monitoring Conference

The Health, Depth, and Breadth of the Environmental Monitoring Industry

Arlington, Virginia August 28 - 31, 2006

Sponsored by:

inela Institute for National Environmental Laboratory Accreditation

United States Environmental Protection Agency

ILI Independent Laboratories Institute

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NEMC 2006

PROCEEDINGS

MONDAY, AUGUST 28, 2006

SPECIAL SESSION ON DETECTION AND QUANTITATION LIMITS

Clean Water Act Programs: Analytical Method Activities

Richard Reding, Chief
Engineering & Analytical Support Branch
August 2006

EPA Office of Water

Analytical Methods Activities

- Development of Analytical Methods
- Rulemakings
- Federal Advisory Committee on Detection and Quantitation

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Development of Analytical Methods

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Development and Validation of EPA 1668

- Method 1668A: Hi Res GC/MS for PCB congeners published in 1999
- Method not promulgated yet at part 136
- Used in EPA's fish tissue study and by others for ambient monitoring
- Additional validation study in wastewater completed

EPA Office of Water

Development and Validation of EPA 1614

- **Method 1614:** GC/Hi Res MS for PBDEs - brominated flame retardants – published August 2003
- Method not promulgated yet at part 136
- **Developed at Axys Analytical**
  - 8 PBDEs of primary concern – measured by isotope dilution
  - 36 other PBDE congeners – measured by internal standard
- Multiple single-laboratory validation of Method 1614 completed in 2005

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EPA/ASTM Method for NP and APEs

- Nonylphenol (NP) and alkylphenol ethoxylates (APEs) are surfactants
- Collaborating with ASTM to develop & validate method
- Status
  - Draft ASTM method written by Schenectady International, Inc.
  - Holding time study by EPA Region 5 showed sample holding time can be 28 days when samples are preserved with acid
  - Interlab validation study started June 2006
    - All laboratories are volunteers
    - Region 5 lab is EPA lead

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Microbiological Method Development and Validation

- Method 1600: Enterococci in wastewater and Combined Sewer Overflows (CSOs)
- Method 1603: *E. coli* in wastewater and CSOs
- Both methods:
  - Validated in wastewater at 12 laboratories
  - Wastewater report completed May 2005
  - Validation in CSOs ongoing (weather dependent)

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Microbiological Method Development and Validation (cont.)

- Method 1103.1: *E. coli* in wastewater and CSOs
  - Validated in wastewater at 10 laboratories
  - Wastewater report completed June 2005
  - Validation in CSOs ongoing (weather dependent)
- Method 1106.1: Enterococci in wastewater and CSOs
  - Validated in wastewater at 10 laboratories
  - Validation study report completed in May 2005
  - Validation in CSOs ongoing (weather dependent)

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Microbiological Method Development and Validation (cont.)

- Method 1680 and 1681: Fecal coliforms in biosolids
  - Study completed December 2002
  - Evaluated in 5 biosolids matrices at 12 participant laboratories
  - Validation study report completed in January 2005
- Method 1682: *Salmonella* in biosolids
  - Study completed May 2003
  - Evaluated in 4 biosolids matrices at 12 participant laboratories
  - Validation study report completed in January 2005

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Microbiological Method Development and Validation (cont.)

- Method 1693: *Cryptosporidium* and *Giardia* in wastewater and CSOs
  - Single-laboratory study completed December 2005
  - Interlaboratory validation in CSOs and wastewaters
- Method 1606 and 1607: Enterococci in fresh water, wastewater, and marine waters
  - Both methods use quantitative polymerase chain reaction (PCR)
  - Interlaboratory validation underway

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Microbiological Method Holding Time Studies

- Methods 1600, 1603, 1103.1, 1106.1 (enteroc., e. coli,)
  - Ambient waters (recreational, beaches, fresh, and marine)
    - 13 laboratories total
    - Analyses complete
    - Report expected soon
- Methods 1680, 1681, and 1682 (fecal & salmonella)
  - Biosolids
    - 29 participant laboratories
    - Expected completion date September 2006
    - Report expected in 2006

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Other Ongoing or Potential Projects

- Revised "Pumpkin Book" expected Fall '06
  - Suggests how to demonstrate then fix matrix problems
- Depending on program priorities and resources
  - Hi Res GC/MS for pesticides
  - Hormones, steroids, prescription and OTC drugs – PPCPs
  - Helminth ova (parasite) in biosolids
  - Enteric (human) viruses in biosolids

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ANALYTICAL METHODS CONTACTS

- Our methods website
  - **www.epa.gov/waterscience/methods**
- Chemistry Methods
  - Lemuel Walker: Walker.Lemuel@EPA.gov
    - ATPs, oil & grease, pumpkin book, metals, cyanide
  - Brian Englert: Englert.Brian@EPA.gov
    - PPCPs, PBDEs, NPs, APEs
- Microbiology Methods and ATPs
  - Robin Oshiro: Oshiro.Robin@EPA.gov

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Methods Rules

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August 2005 Microbiology Proposed Rule

- Proposed EPA Methods 1600, 1603, 1103.1, 1106.1, 1680, 1681, and 1682 at 40 CFR part 136
  - Includes enterococci, e. coli, fecal coliforms, salmonella
  - August 16, 2005 (70 FR 48255)
  - Comment period closed
  - Final rule expected in fall of 2006

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April 2004 CWA/SDWA Methods Proposed Rule

- EPA proposed revisions and updates to wastewater and drinking water methods and monitoring regulations on April 6, 2004 (69 FR 18166).
  - Drinking water methods
  - Wastewater methods
  - Other updates to wastewater regulations
- Final rule signed in 2006; publish Sept '06?
  - Pretty much approves everything proposed in 2004

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2004 Proposal - Wastewater (cont.)

- EPA proposed part 136 methods for:
  - Methods using ICP-MS (e.g., EPA Method 200.8), stabilized temperature GFAA (EPA Method 200.9), and ion chromatography (e.g., EPA Method 300.0)
  - Updated versions of EPA methods for inorganic compounds and withdrawal of the equivalent MCAWW methods
  - **Withdrawal of CFC-113 oil and grease methods**

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2004 Proposal – Wastewater (cont.)

- Updates to clarify requirements for grab and composite sampling (at 40 CFR parts 122, 136, and 403)
- **New sample handling, collection and preservation requirements, e.g. cyanide interferences**
- **Increased options for method flexibility, including new requirements that clarify procedures for validation of minor modifications to approved methods and the use of capillary columns with GC methods – 40 CFR 136.6**

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RULEMAKING CONTACTS

- Our methods website
  - **www.epa.gov/waterscience/methods**
- Rule Managers
  - Meghan Hessenauer: Hessenauer.Meghan@EPA.gov
  - Marion Kelly:Kelly.Marion@EPA.gov
  - Pat Fair (drinking water): Fair.Pat@EPA.gov
  - Robin Oshiro: Oshiro.Robin@EPA.gov

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EPA's MDL and ML: Status of a Federal Advisory Detection and Quantitation Committee

www.epa.gov/waterscience/methods/det

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Why are we looking at detection & quantitation?

- Longstanding concerns about how an MDL or ML is calculated and used in lab & regulatory programs
- EPA proposed changes to the MDL and ML in 2003
- 136 comments - some supportive, most not. Theme:
  - We could do better
  - Let's try a **collaborative process**
- We decided to:
  - Withdraw proposed changes
  - Commission a **"situation assessment"** by a neutral facilitator

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Common Issues From the Situation Assessment

- Variability and reliability of results within and between laboratories and over time
- Need to address background contamination, matrix and recovery effects, false positive and negative rates
- What results should be reported – MDL? ML?
- Need for common set of terms and definitions
- Inconsistent uses of detection and quantitation limits by Federal, State and local regulators; inconsistencies among EPA programs - CWA, RCRA, SDWA

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Detection/Quantitation Committee Formation

- May 2005 established a FACA committee to recommend ways to improve the calculation and use of MDLs and MLs
  - **21 members**
  - **Scope is CWA programs**
  - **Committee considering several alternatives to the "Appendix B" MDL**
- Name - Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs (the FACDQ or Committee)
- FACDQ website www.epa.gov/waterscience/methods/det

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Purpose of this Advisory Committee

Provide group advice and consensus recommendations on approaches for development of detection and quantitation procedures, and uses of these procedures in EPA's *Clean Water Act Programs*.

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FACDQ Desired Product

- Reach agreement on
  - Definition of terms
  - One or more specific approaches for detection and quantitation for CWA
  - Interpretation and uses of the numbers
- Revised detection and quantitation approaches
  - acceptable to most or all
  - easy to carry out
  - practical and
  - cost-effective
- Produce accurate, consistent and uniform results
- Used to inform a rulemaking

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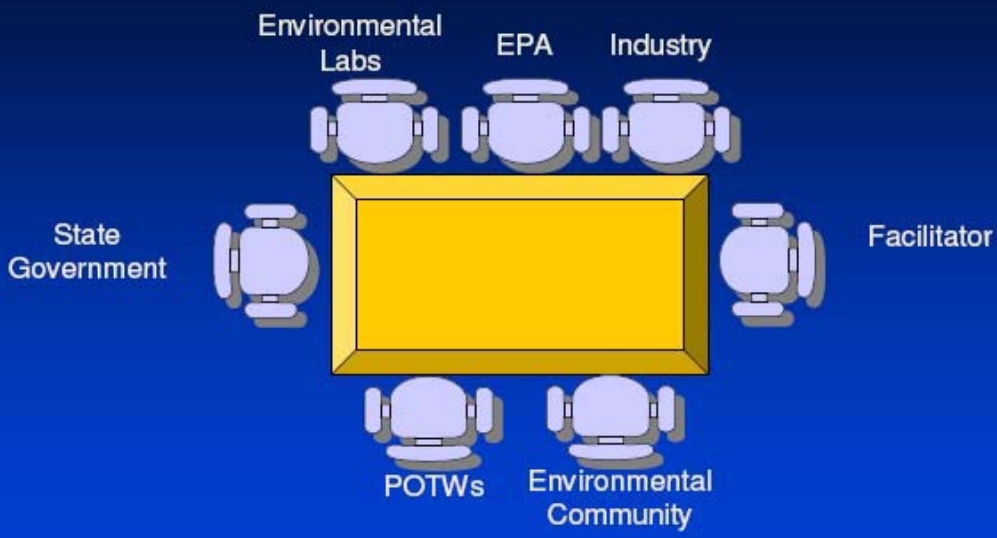
FACDQ Committee Composition



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FACDQ Membership

- Environmental Community – 4 members
  - NWF, Environmental Advocates of NY, TN Public Employees for Env. Responsibility, University Professor
- Environmental Laboratory Community – 4 members
  - Large, Medium, Small Laboratories; Instrument Manufacturer
- Regulated Community – 4 members
  - Ford Motor Co., Pulp and Paper Industry, API, Exelon
- Water Utility Community – 4 members
  - NACWA, Hampton Roads VA, Louisville KY, ACWA (CA)
- State Government – 4 members
  - CO, MI, WI, FL
- EPA – 1 member
  - Office of Water, Office of Science & Technology (CWA)

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FACDQ Committee Process

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FACDQ Committee Meetings and Workgroups

- FACDQ Meetings – Open to Public
  - June 21-22, 2005
  - September 29-30 2005
  - December 8-9, 2005
  - March 29-30 2006
  - July 13-14, 2006
  - Pending - December 6-8, 2006
- Established Two Workgroups
  - Policy Workgroup
  - Technical Workgroup
- Working documents and meeting notes on website

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FACDQ Committee Policy Workgroup (cont'd)

- Actions of Policy Workgroup
  - Developed descriptions of uses
    - Extensive outreach, polling within each caucus
  - Developed preliminary data quality objectives (DQOs) and measurement quality objectives (MQOs) for:
    - Detection and quantitation procedures
    - Pilot studies for establishing detection and quantitation limits

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Calculation Procedures Under Consideration

- Detection limit procedures
  - American Council of Independent Laboratories (ACIL)
  - Consensus Group
  - Hubaux-Vos
  - ASTM D6091 Interlaboratory Detection Estimate (IDE)
  - EPA "Appendix B" Method Detection Limit (MDL)
- Quantitation limit procedures
  - ASTM D6512 Interlaboratory Quantitation Estimate (IQE)
  - EPA Lowest Concentration Minimum Reporting Level
  - EPA Minimum Level of Quantitation (ML)
  - ACIL
  - Consensus Group

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Pilot Status

- Piloting three candidate procedures developed by labs (ACIL), ASTM (IDE/IQE), EPA (not the MDL/ML)
  - 5 analytical methods to be evaluated with each candidate procedure
    - Metals by EPA Method 200.7 (ICP-OES)
    - Inorganic ions by EPA Method 300.0 (ion chromatography)
    - Total cyanide by spectrophotometry (EPA Method 335.x)
    - Organochlorine pesticides by GC/ECD (EPA Method 608)
    - Semi-volatile organics by GC/MS (EPA Method 625
  - Schedule
    - Pilot design approved - July 2006
    - Labs analyze samples – September – October 2006
    - Draft report - late 2006
    - Report to FACDQ – February 2007

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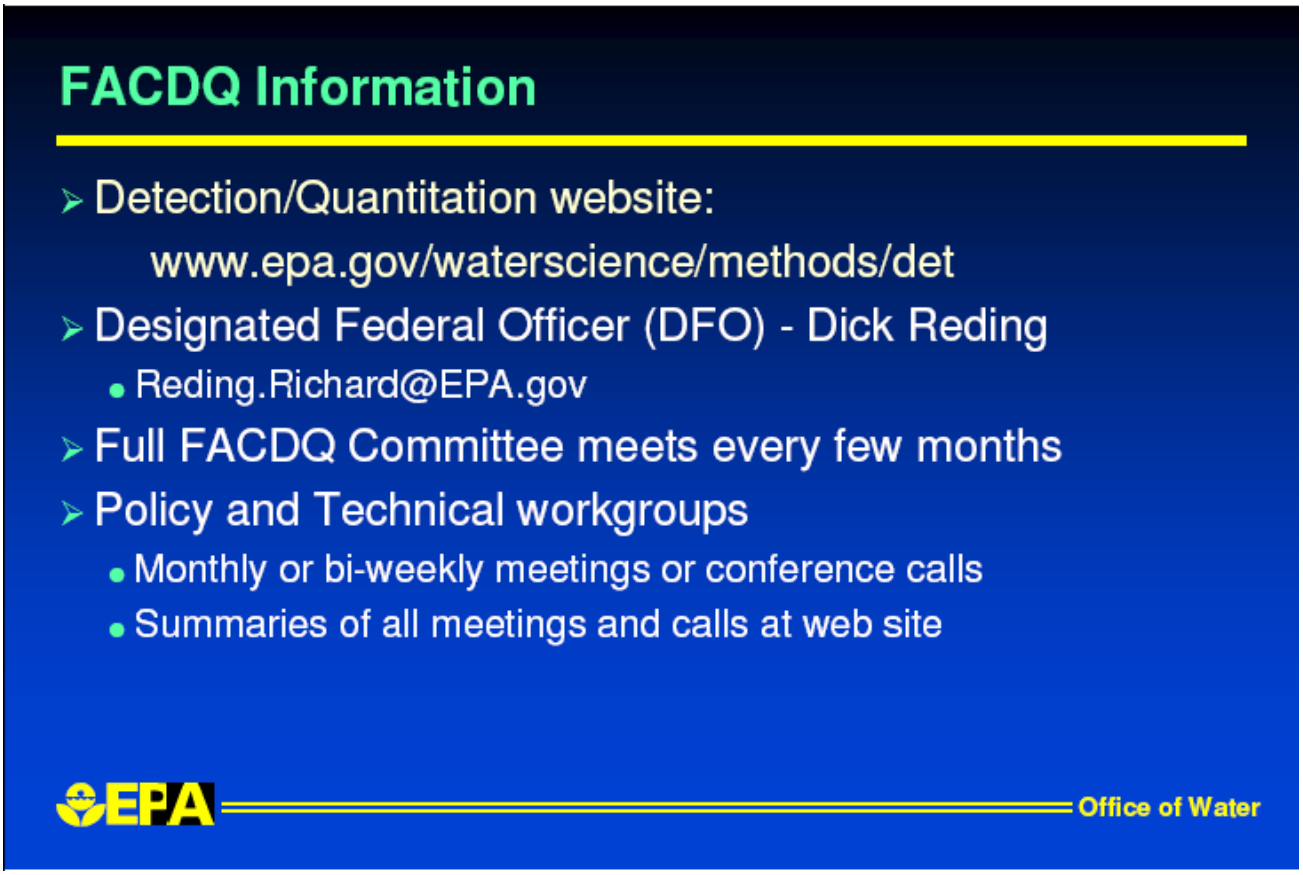
FACDQ Information
Detection/Quantitation website:
www.epa.gov/waterscience/methods/det
Designated Federal Officer (DFO) - Dick Reding
Reding.Richard@EPA.gov
Full FACDQ Committee meets every few months
Policy and Technical workgroups
Monthly or bi-weekly meetings or conference calls
Summaries of all meetings and calls at web site
EPA
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ESTIMATING DETECTION QUANTITATION LIMITS

Burrows, Richard; Severn Trent Laboratories

A Procedure for estimating detection and quantitation limits has been drafted by ACIL (American Council of Independent Laboratories). This paper will describe the details of the procedure and the reasons for each of the steps

- Censored vs. Uncensored methods
- Precision and Bias
- False positives and False negatives
- Data reporting recommendations

The ACIL Detection and Quantitation Limit Procedure

Richard Burrows

NEMC 2006

New Detection and Quantitation Procedures

- Why
- What
- When

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Why a New Detection Limit Procedure?

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Why

- Existing ML and ML procedures have limitations
  - MDLs below the level of blank contamination are routine for some analyte / method combinations
  - MDLs that are below the limit of qualitative identification are routinely generated for other analyte method combinations

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Why

- There is no requirement for or measure of precision at the ML
- There is no measurement of or requirement for accuracy at the ML

,1-dichloroethene from Episode 6000 524.2 d

Spike	Mean Rec.
0.035	0
0.05	0
0.075	0
0.1	0
0.15	0.01 (two ND)
0.2	0.11
0.35	0.25
0.5	0.41
0.75	0.66

← EPA MDL 0.054

Episode 6000 data, Chromium by 200.8

Spike Level	STD	N	Mean	Recovery %	
0.007	0.03261	8	**0.900**	12860	
0.01	0.02191	8	**0.901**	9013	
0.015	0.02406	8	**0.903**	6021	
0.02	0.04697	8	**0.840**	4201	
0.03	0.25555	8	**0.734**	2448	
0.04	0.23866	8	**0.943**	2357	
0.07	0.03795	8	**0.950**	1357	← EPA MDL 0.073
0.1	0.07147	8	**1.01**	1007	
0.15	0.16215	8	**1.04**	695	
0.2	0.24956	8	**1.16**	582	← EPA ML 0.2
0.3	0.05539	8	**1.26**	418	
0.4	0.02806	8	**1.08**	270	
0.7	0.02448	8	**1.40**	200	
1	0.19004	8	**1.79**	179	
1.5	0.03847	8	**2.24**	149	

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What

- The ACIL detection / Quantitation Limit Procedure

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Detection limit drivers

- Two things can drive the detection limit

1. Variability of the blank

Typical examples in environmental analysis include ICP, gravimetric methods

Characterized by blanks with numerical results

"Uncensored methods"

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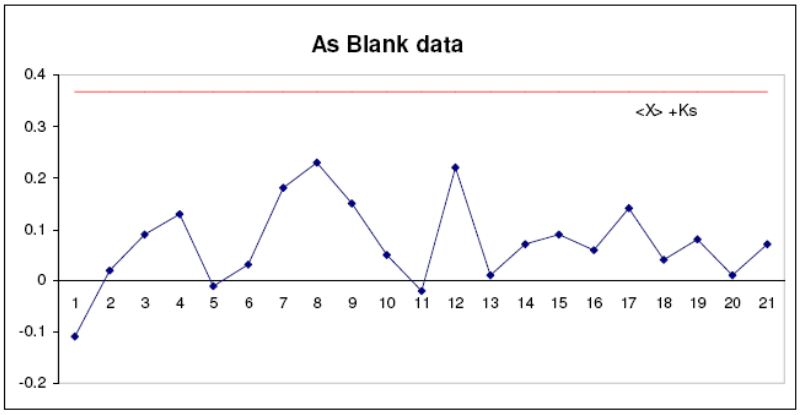
- Arsenic method blanks, method 200.7



-0.11
0.02
0.09
0.13
-0.01
0.03
0.18
0.23
0.15
0.05
-0.02
0.22
0.01
0.07
0.09
0.06
0.14
0.04
0.08
0.01
0.07

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Use of Blanks

- If we have results for method blanks we should use them
  - Represents routine operating conditions (included with every batch)
  - No extra analytical work required
  - Avoids any issues with dependence of variability on concentration

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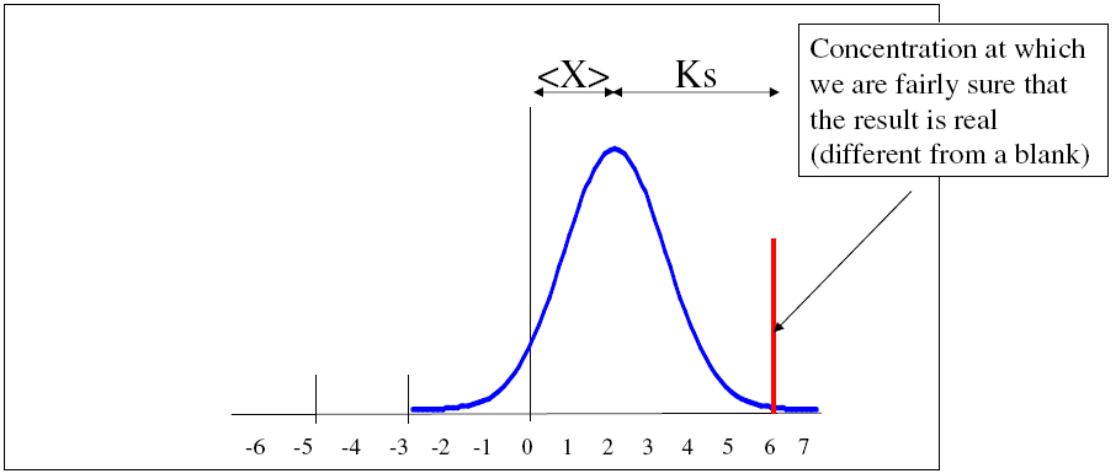
L_C



$L_C = <X> + Ks$

K is the tolerance interval that contains 99% of the population with 99% confidence

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Definitions Review

- The critical value (L_C) is the lowest result that can be distinguished from a blank. The MDL is a type of critical value.

- The detection limit (L_D) is the lowest true concentration that can be reliably detected.

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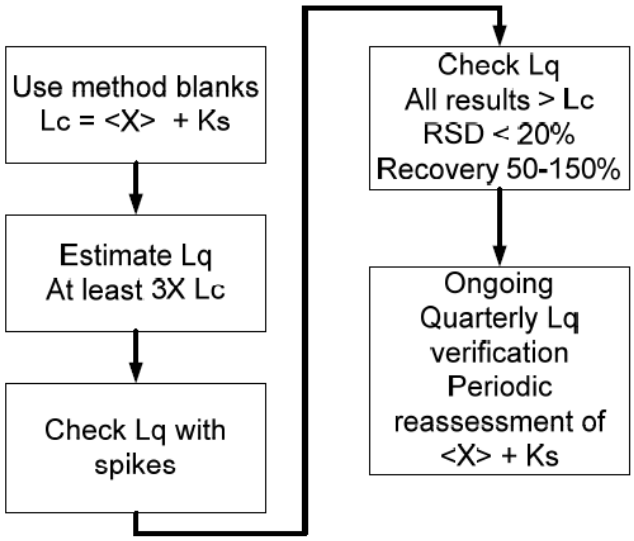
Detection limits for uncensored methods



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Detection limit drivers

2. Ability to Qualitatively identify analytes

Typical environmental examples are GC and GC/MS

- Is the peak above the threshold?
- Is the peak integrated?
- Are the qualifier ions present and integrated?
- Are the ion ratios correct?

Characterized by blanks that are usually ND

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- Benzyl Alcohol
  - Quant ion 108
  - Qualifier ions 79, 77, must co-elute
  - Relative peak intensity
  - Integration parameters
  - Threshold

Method blank results	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND

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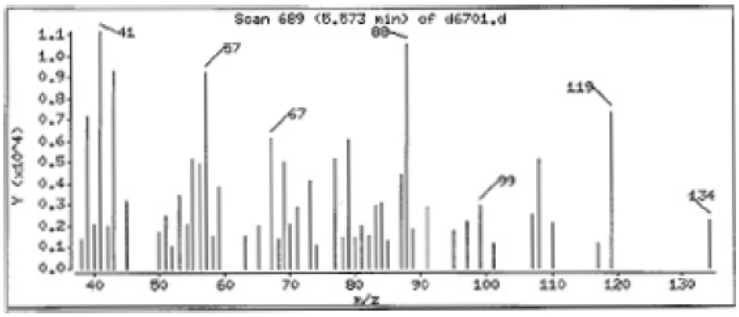
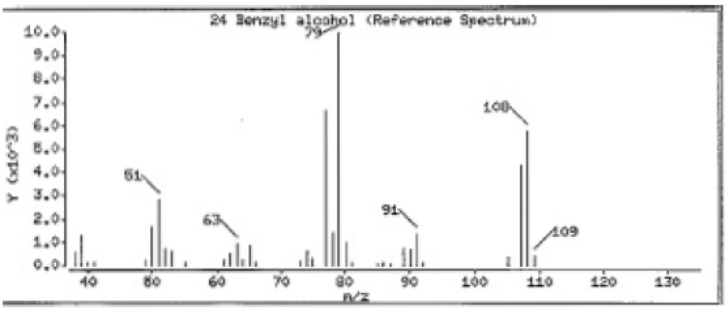
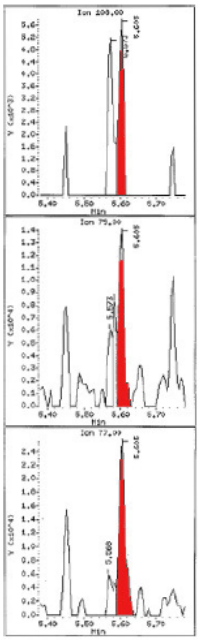
Benzyl Alcohol







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Censored methods

- For censored method we do not have any numerical blank results
  - So, must start with spikes

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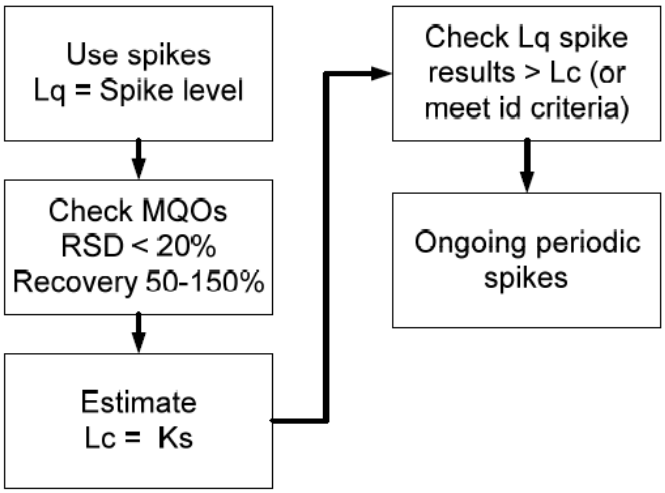
Detection limits for censored methods



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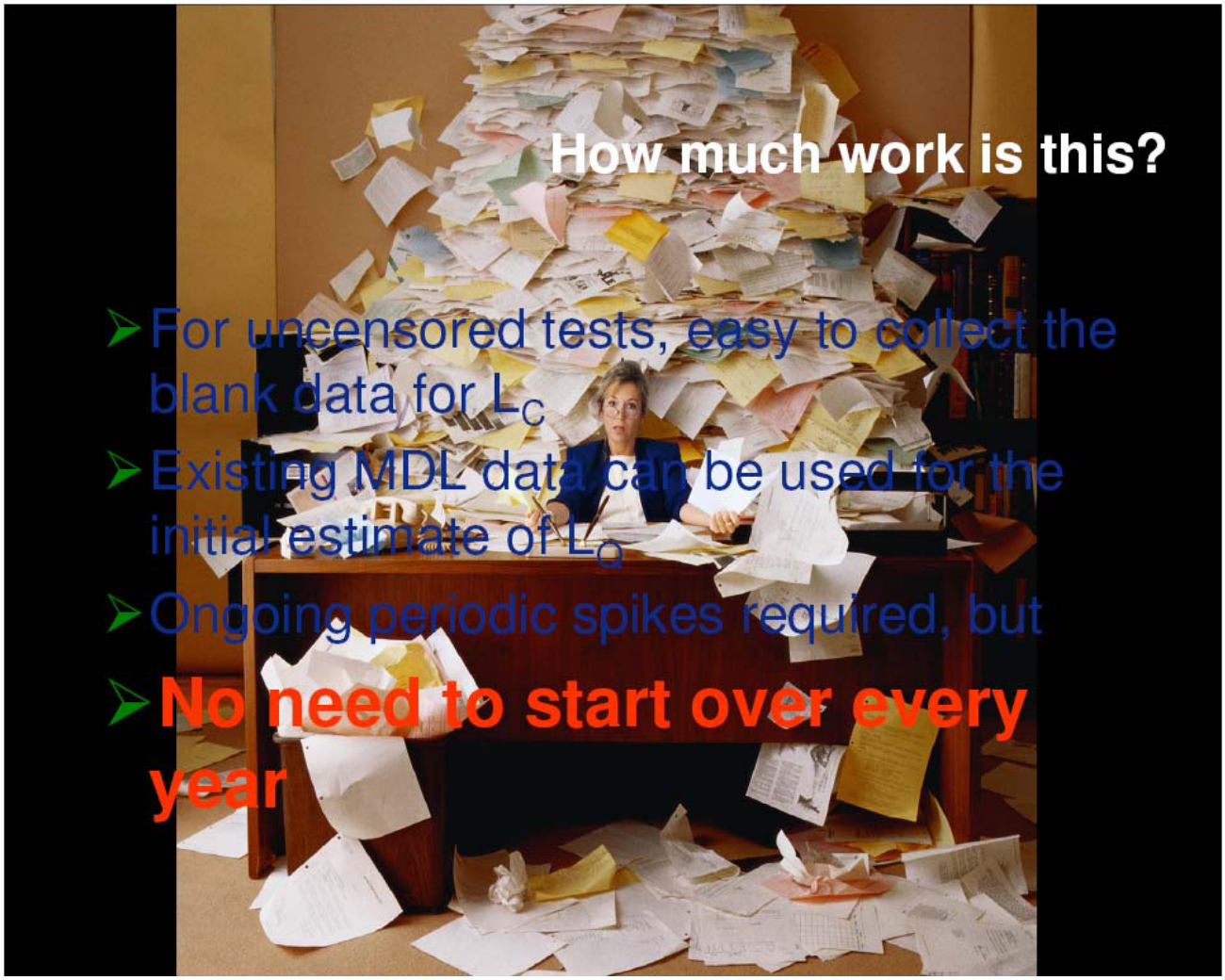
Ongoing confirmation

- Once per year recalculate Lc based on recent blanks and update if necessary
- Run Lq verifications once per quarter



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Questions?

A Simple Procedure for Determination of Method Quantitation Limits

Chung-Rei Mao
U.S. Army Corps of Engineers; HTRW Center of Expertise, Omaha, Nebraska

ABSTRACT
Method Quantitation Limit (MQL) is the lowest amount of analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy (bias) under stated analytical conditions.

MQL is commonly determined or estimated based on professional judgments, multiples of the Method Detection Limit (MDL), or empirical methods of replicate analyses of fortified samples at low concentrations. Information on precision and accuracy are usually not available for an estimated MQL so that the estimated MQL would be of limited or no practical value. Empirical methods may produce MQL of known precision and bias; however, consistent and cost effective procedures are not established yet.

This paper presents a simple procedure for determination of MQL based on laboratory's MDL and the Laboratory Control Sample (LCS) data, which are readily available in most environmental laboratories. An MQL determined based on the LCS and MDL data has well defined precision and bias and does not need additional analysis. Environmental data at or above the determined MQL will have reliable precision and bias for decision-making.

INTRODUCTION
Method Quantitation Limit (MQL) is an important analytical parameter that does not have a consistent and universal definition, determination procedure, and usage in the environmental testing industries. There are many different names for MQL, such as Limit of Quantitation (LOQ), Minimum Level (ML), Practical Quantitation Limit (PQL), Estimated Quantitation Limit (EQL), Contract-Required Quantitation Limit (CRQL), etc., each with somewhat different definitions, determination procedures, and applications (USEPA October 2004).

The MQL is defined here as "*the lowest amount of analytes in a sample that can be quantitatively determined with stated, acceptable precision and accuracy (bias) under stated analytical conditions*". This definition is based on the International Conference on Harmonization (ICH) Harmonised Tripartite Guideline (ICH 1994). According to this definition, the data precision and bias of MQLs must be known and reported.

MQL is generally determined or estimated based on the following categories of common procedures: (1) professional judgment, (2) multiples of detection limit, (3) lowest calibration standard, and (4) empirical procedures. The "professional judgment" procedure is based on historical quantitation limits, USEPA Performance Evaluation Study data, or arbitrary data uncertainty (e.g., RSD < 10%). The "multiples of detection limit" procedure determines MQLs usually based on an arbitrary multiple of 3 – 10 times the detection limits. The "lowest calibration standard" procedure establishes the MQL at the lowest calibration standard. For most

analytical methods, however, calibration standards do not take into account of sample preparation uncertainty, and the acceptance of the lowest calibration standard depends significantly on the calibration techniques (e.g., number, distribution, weighing factor of the calibration standards). The "empirical procedures" is probably the best method for determining reliable MQLs and is based on replicate analyses of a series of spiked samples of various concentrations around the MQL. However, standard procedures and consistent criteria for empirical procedures have not been established, and reliable empirical procedures are generally very expensive.

USEPA recently proposed an empirical procedure for determining the "Lowest Concentration Minimum Reporting Level (LCMRL)" for the Unregulated Contaminant Monitoring Regulation (UCMR). This USEPA-proposed procedure determines the LCMRL or quantitation limit based on percent recoveries and prediction intervals of a series of replicate samples (USEPA November 2004). The LCMRL procedure is complicated and expensive for implementation, and it may not be reliable due to issues on the use of parametric statistics, prediction intervals, etc. This paper presents a simple empirical procedure for determination of MQLs based on laboratory's in-house QC data of Method Detection Limit (MDL) study and LCS control limits (CL_{LCS}).

Concepts and Procedures

The proposed procedure for MQL determination is based on the data precision of an analytical system. Data precision at various concentrations is estimated based on the routine laboratory QC data of MDL study and LCS control limits. Data bias is not considered because of larger relative error in quantifying censored data at lower concentrations than the lowest calibration standard. Figure 1 shows data uncertainty versus analyte concentrations of a typical analytical system.

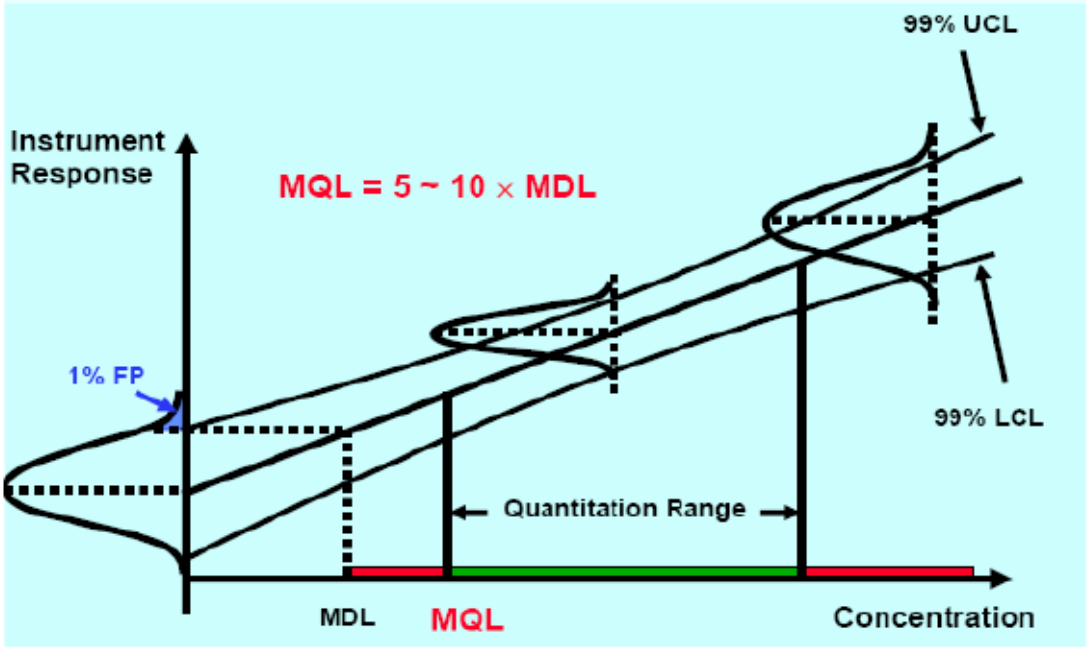


Figure 1: Uncertainty versus Concentration

Data uncertainty is approximately constant within the quantitation range and increases at concentrations outside the quantitation range. The lower limit of the quantitation range is the MQL, which may be 5 – 10 times greater than the MDL. The data precision and bias at the MQL is reported based on the relative standard deviation (RSD) and mean percent recovery (%R) of the LCS, respectively.

Based on physical characteristics of constant measurement uncertainty at low concentrations and proportionally increasing uncertainty at higher concentrations, Rocke and Lorenzato proposed a two-component model for measurement uncertainty (Rocke and Lorenzato 1995)

$$c = \varepsilon + \mu e^{\eta} \qquad (1)$$

where c is measured concentration, μ is true concentration, and ε and η are normally distributed uncertainty with mean 0 and standard deviations σ_ε and σ_η, respectively. The uncertainty of a measurement at concentration c, σ_c, would be:

$$\sigma_c = \sqrt{\sigma_\varepsilon^2 + \mu^2 e^{\sigma_\eta^2}\left(e^{\sigma_\eta^2} - 1\right)} \qquad (2)$$

Equation 2 illustrates the key feature of the two-component model, i.e., the nearly constant component, σ_ε^2, at low concentrations and the proportional component, $\mu^2 e^{\sigma_\eta^2}\left(e^{\sigma_\eta^2} - 1\right)$, at high concentrations. Figure 2 shows the constant component (dashed line), proportional component (dotted line), and the total standard deviation (solid line) versus concentration.

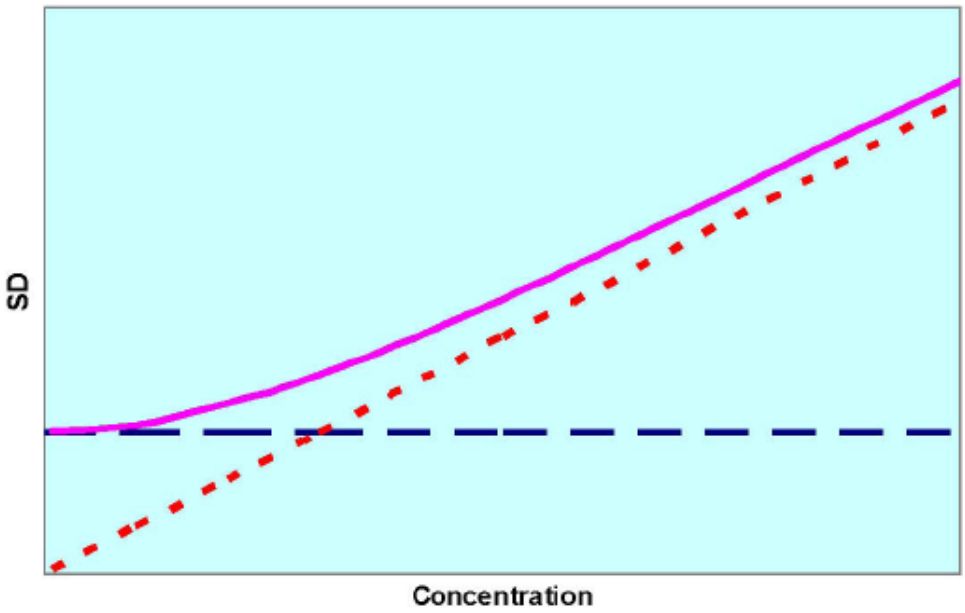


Figure 2: Uncertainty versus Concentration Based on Rocke-Lorenzato Two-component Model

For a linear calibration curve, Rocke-Lorenzato model approximates a constant SD at low concentrations and a constant RSD at high concentrations (Figure 3).

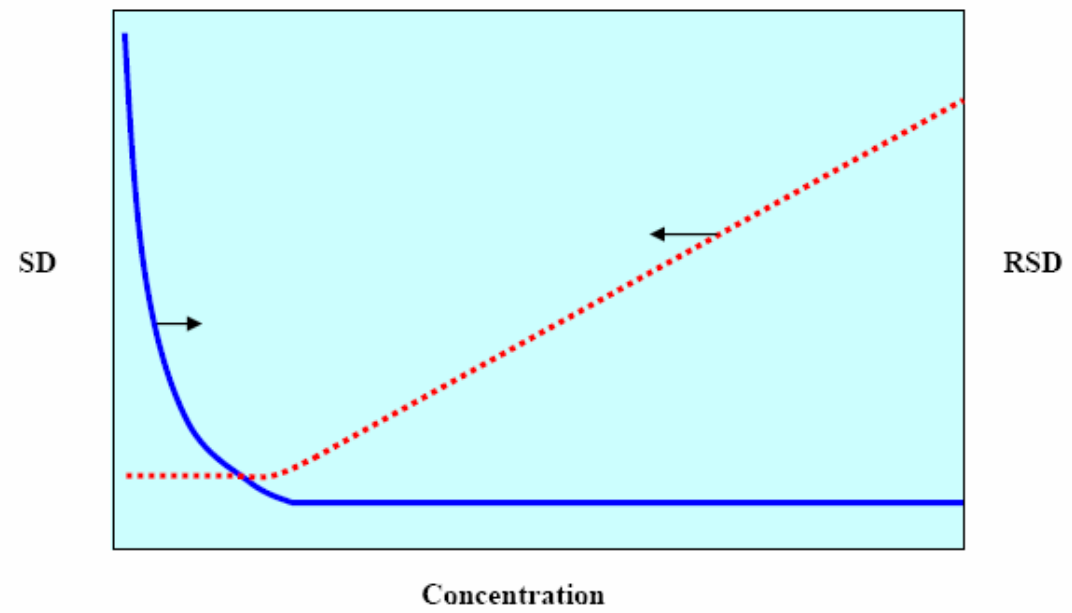


Figure 3: SD and RSD versus Concentration

Figure 3 shows that the RSD decreases quickly as the concentration increases and reaches a constant value, which is equal to the RSD at higher concentrations. The RSD at lower concentrations may be estimated based on the MDL study (or method blank data) and the RSD at higher concentrations may be estimated based on the LCS control limits. The minimum concentration where the RSD based on the MDL study equals to the RSD based on the LCS control limits determines the MQL. Analytical data should have constant RSD at and above the MQL within a quantitation range.

The relative uncertainty, $U_{95\%}$, at low concentration c is defined as:

$$U_{95\%} = \pm \frac{t_{(n-1,.975)} \times \sigma_c}{c} \times 100\% \qquad (3)$$

where $t_{(n-1,.975)}$ is the two-tailed Student's t value for an estimated SD, σ_c, with $n-1$ degrees of freedom at a 95% confidence level, and σ_c is the estimated SD of replicate analyses at a low concentration c and may be expressed with the Rocke-Lorenzato two-component model.

$$U_{95\%} = \pm \frac{t_{(n-1,.975)} \times \sqrt{\sigma_\varepsilon^2 + \mu^2 e^{\sigma_\eta^2}\left(e^{\sigma_\eta^2} - 1\right)}}{c} \times 100\% \qquad (4)$$

The proportional component of the Rocke-Lorenzato model may be expanded and approximated with the first order of Taylor series if σ_η is small and approximately equal to σ_ε at low concentration c.

$$U_{95\%} \approx \pm \frac{t_{(n-1,.975)} \times \left(\sqrt{2} \times \sigma_\varepsilon\right)}{c} \times 100\% \quad (5)$$

Let $c = N \times MDL$ and $MDL = t_{(n-1,.99)} \times \sigma_\varepsilon$,

$$U_{95\%} = \pm \frac{t_{(n-1,.975)} \times \left(\sqrt{2} \times \sigma_\varepsilon\right)}{t_{(n-1,.99)} \times \sigma_\varepsilon} \times \frac{100\%}{N} \quad (6)$$

where $t_{(n-1,.99)}$ is the one-tailed Student's t value for an estimated SD, σ_ε, with $n-1$ degrees of freedom at a 99% confidence level, and σ_ε is the estimated SD of replicate analyses of an MDL study. For concentrations near an MDL study,

$$U_{95\%} \approx \pm \frac{100\%}{N} \quad (7)$$

Equation (7) shows that the relative uncertainty, $U_{95\%}$, at low concentration c may be approximated as ± 100% divided by N, a multiple of the MDL. For example, $U_{95\%} \approx \pm$ 100%, 50%, 33%, 20%, and 10% at $N = 1$, 2, 3, 5, and 10, respectively. The relative uncertainty cannot continuously decrease at higher N or concentrations, i.e., $U_{95\%} \neq 1\%$ at $N = 100$, but would be superseded by the warning limits of the LCS (WL_{LCS}).

Figure 4 shows that the relative uncertainty drops as the concentration increases and the MQL is set at the concentration where the $U_{95\%} = WL_{LCS}$.

$$\frac{100\%}{N} = \frac{t_{(n-1,.975)} \times \sigma_{LCS}}{C_{LCS}} \quad (8)$$

$$\approx 2 \times RSD_{LCS}\% \quad (9)$$

where $t_{(n-1,.975)}$ is the two-tailed Student's t value for an estimated SD, σ_{LCS}, with $n-1$ degrees of freedom at a 95% confidence level, and σ_{LCS} and RSD_{LCS} are the estimated SD and RSD of replicate LCS analyses at mean recovered concentration, C_{LCS}, respectively.

$$N = \frac{100}{WL_{LCS}} = \frac{100}{2 \times RSD_{LCS}} \quad (10)$$

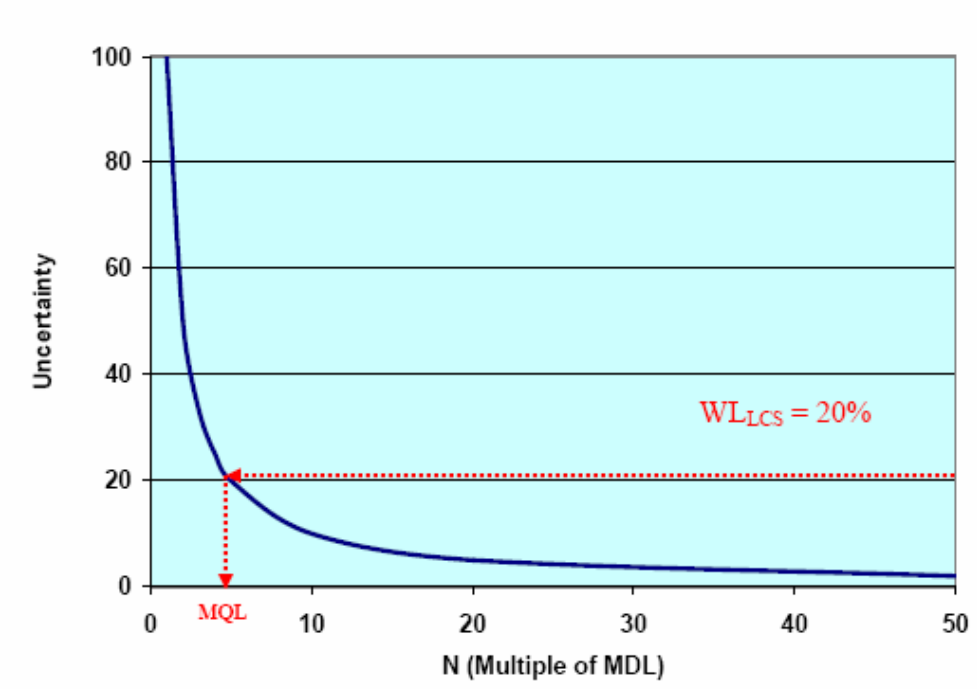


Figure 4: Relative Uncertainty, $U_{95\%}$, versus N

An MQL is therefore a multiple of the MDL, i.e., $MQL = N \times MDL$, where the multiple, N, is determined based on laboratory's in-house performance data of MDL study and LCS control limits. The data precision and bias at concentrations at and above the MQL are the same as the RSD and mean %R of the LCS. An example determination of MQL using the proposed MQL procedure is shown below:

For a laboratory with MDL = 1 ppb and LCS control limits = 60 – 120%, what would be the MQL?

Because $RSD_{LCS} = 10\%$, $MQL = N \times MDL = \dfrac{100}{2 \times RSD_{LCS}} \times MDL = 5$ ppb, with a precision RSD = 10% and bias %R = 90%.

In 1997 and 1998, USEPA conducted a study (Episode 6000) of variability versus concentration for a number of analytical methods. Five laboratories were employed for the analyses; each analyte and method combination was tested by one of these laboratories (USEPA July 1998). The proposed MQL procedure is evaluated using two arbitrarily selected Episode 6000 data sets of 1,1,1,2-tetrachloroethane (1112-PCA) and 1,1,1-trichloroethane (111-TCA) by Method 524.2. Figures 5 and 6 show that the SD and RSD data in the shaded areas of Tables 1 and 2 fit well to the Rocke-Lorenzato two-component model of nearly constant SD at low concentrations and proportionally increasing SD at high concentrations.

Table 1: USEPA Episode 6000 Study of Variability versus Concentration of 1112-PCA

Analyte	Method	Spike Level	Mean Conc.	Mean (% Recovery)	SD Conc.	RSD (based on Mean)
1112-PCA	524.2	0.035				
1112-PCA	524.2	0.05				
1112-PCA	524.2	0.075				
1112-PCA	524.2	0.1				
1112-PCA	524.2	0.15	0.032	21.178	0.023	72.898
1112-PCA	524.2	0.2	0.090	44.886	0.020	22.297
1112-PCA	524.2	0.35	0.253	72.367	0.019	7.417
1112-PCA	524.2	0.5	0.416	83.143	0.013	3.211
1112-PCA	524.2	0.75	0.660	88.000	0.012	1.797
1112-PCA	524.2	1	0.830	82.986	0.035	4.185
1112-PCA	524.2	2	1.760	88.000	0.062	3.533
1112-PCA	524.2	5	4.239	84.771	0.132	3.104
1112-PCA	524.2	10	8.800	88.000	0.234	2.661
1112-PCA	524.2	20	16.729	83.643	0.486	2.902
1112-PCA	524.2	50	43.957	87.914	0.846	1.925
1112-PCA	524.2	100	94.543	94.543	2.625	2.776
1112-PCA	524.2	200	235.429	117.714	9.253	3.930

Table 2: USEPA Episode 6000 Study of Variability versus Concentration of 111-TCA

Analyte	Method	Spike Level	Mean Conc.	Mean (% Recovery)	SD Conc.	RSD (based on Mean)
111-TCA	524.2	0.035				
111-TCA	524.2	0.05				
111-TCA	524.2	0.075				
111-TCA	524.2	0.1	0.146	146.000		
111-TCA	524.2	0.15	0.036	24.133	0.013	36.624
111-TCA	524.2	0.2	0.105	52.250	0.011	10.410
111-TCA	524.2	0.35	0.262	74.980	0.021	7.864
111-TCA	524.2	0.5	0.428	85.629	0.021	4.822
111-TCA	524.2	0.75	0.658	87.714	0.021	3.137
111-TCA	524.2	1	0.829	82.886	0.066	7.992
111-TCA	524.2	2	1.861	93.071	0.075	4.049
111-TCA	524.2	5	4.426	88.514	0.252	5.688
111-TCA	524.2	10	9.265	92.650	0.300	3.236
111-TCA	524.2	20	17.614	88.071	0.847	4.811
111-TCA	524.2	50	46.686	93.371	1.468	3.144
111-TCA	524.2	100	98.729	98.729	4.436	4.494
111-TCA	524.2	200	220.857	110.429	11.276	5.105

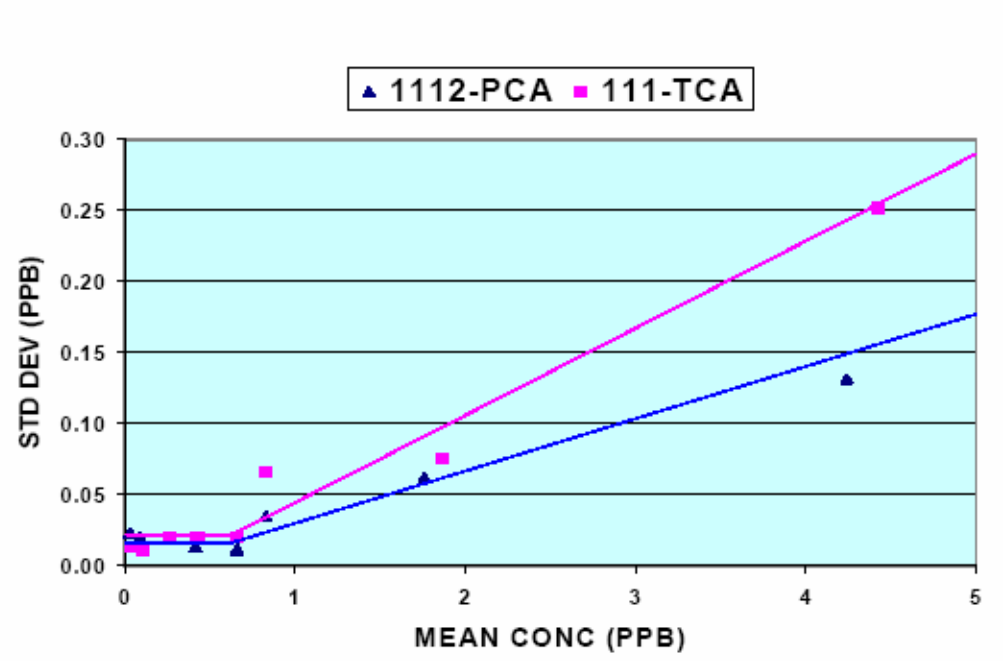
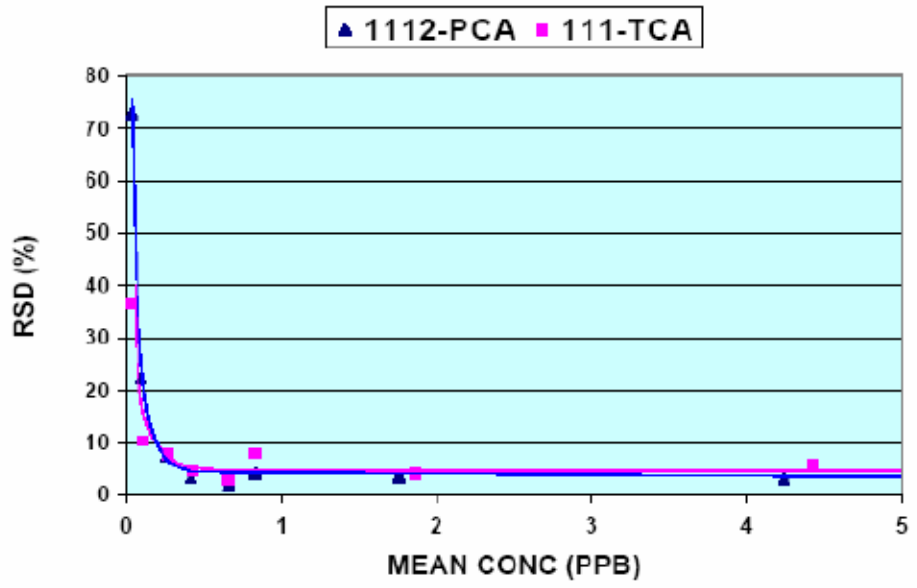


Figure 5: SD versus Concentration

Figure 6: RSD versus Concentration



Visual examination of Figure 6 shows that the MQL for 1112-PCA and 111-TCA should be around 0.5 ppb, where the data variability, RSD, starts to stabilize and stay constant at higher concentrations.

Table 3 shows a comparison of various MQLs determined based on the Episode 6000 data using common MQL procedures and the proposed MQL procedure.

Table 3: Comparison of Various MQLs using USEPA Episode 6000 Data and Various Determination Procedures

	1112-PCA	111-TCA
MDL	0.05 ppb	0.06 ppb
CL_{LCS}	± 9%	± 15%
3 × MDL	0.15 ppb	0.18 ppb
5 × MDL	0.25 ppb	0.30 ppb
10 × MDL	0.50 ppb	0.60 ppb
EPA ML	0.2 ppb	0.2 ppb
ISO LOQ	0.18 ppb	0.10 ppb
Proposed MQL (RSD / %R)	0.83 ppb (3% / 91%)	0.60 ppb (5% / 93%)

The MDLs were reported by USEPA based on the procedure in 40 CFR 136 Appendix B. The LCS control limits, CL_{LCS}, were estimated based on the SDEpisode 6000 data. The MQLs based on the proposed procedures are slightly greater than other MQLs and are the only ones reported with data on precision and bias.

QA/QC Issues

Table 3 shows that the MQL of –TCA, which has higher MDL and CL_{LCS} , is greater than the MQL of 1112-PCA, which has lower MDL and CL_{LCS}. This seemingly controversial situation is depicted in Figure 7, which shows higher of ± 40% gives lower MQL, compared with WL_{LCS} of ± 20%.

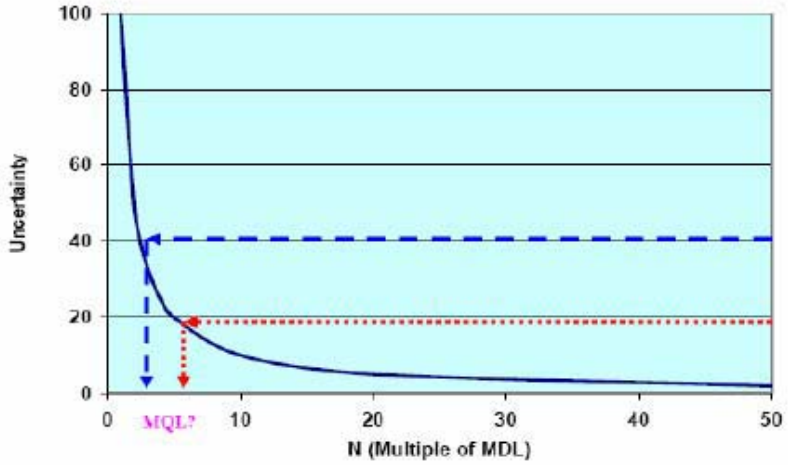


Figure 7: MQL versus RSD_{LCS}

Normally this situation will not happen because an analyte (or a laboratory) with less uncertainty will usually have lower MDLs, which will give lower MQLs. However, if two analytes have the same MDLs but different LCS warning limits, the analyte with tighter warning limits (e.g., ± 20%) will have a higher MQL than the other analyte with looser warning limits (e.g., ± 40%). The data uncertainty of the analyte with a higher MQL will be less than that of the analyte with a lower MQL. Nevertheless, the analyte with a higher MQL and lower data uncertainty may be reported at a lower MQL with higher data uncertainty, but the analyte with a lower MQL and higher data uncertainty may not be reported at a higher MQL with lower data uncertainty. This controversy shows that MQL must be reported with associated precision and bias at a specified confidence level. An MQL with unknown precision and bias has limited or no practical value.

The proposed MQL procedure is based on two approximations: (1) the uncertainty within the quantitation range is constant and (2) the standard deviation $\sigma_c \approx \sqrt{2} \times \sigma_\varepsilon$ at concentrations less than the MQL. The uncertainty over the quantitation range is not constant (dashed lines) but falls within the two arms of a hyperbola (solid lines) in Figure 8 (Mandel and Linnig 1957). The exact shape of the hyperbola arms depends on the number and distribution of calibration standards, calibration methods, etc. Approximation 1, constant uncertainty, will lead to a high biased MQL with low biased uncertainty over a small concentration range around the MQL, if the LCS concentration is at the middle of a quantitation range.

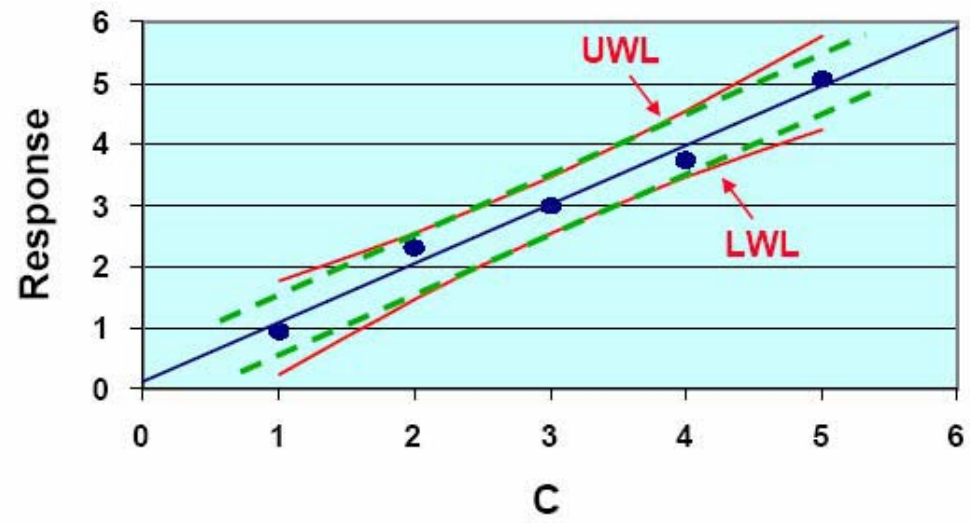


Figure 8: Assumption 1 of the Proposed MQL Procedure

The dashed line in Figure 9 is an approximation to the data uncertainty based on the Rocke-Loranzato two-component model. Approximation 2, $\sigma_c \approx \sqrt{2} \times \sigma_\varepsilon$ at low concentrations, overestimates the data uncertainty at low concentrations and will lead to a high biased MQL with high biased uncertainty at concentrations less than the MQL. The net effect of assumptions 1 and 2 will give a high biased MQL and slightly biased uncertainty.

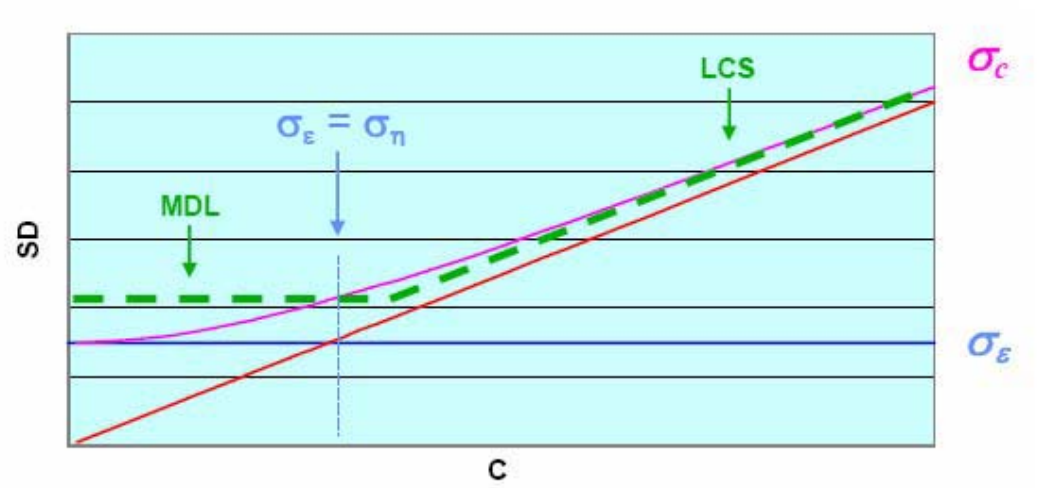


Figure 9: Assumption 2 of the Proposed MQL Procedure

Compared with $N = 3.18$ for the EPA ML, the N of the proposed MQL procedure is 6 and 10 for 1112-PCA and 111-TCA, respectively. Figure 10 shows that the N for 1112-PCA and 111-TCA could be set at slightly lower values and the N for ML appears too low. The data uncertainties of 1112-PCA and 111-TCA at the ML ($N = 3.18$) seems to be too high for reliable quantitation at low concentrations.

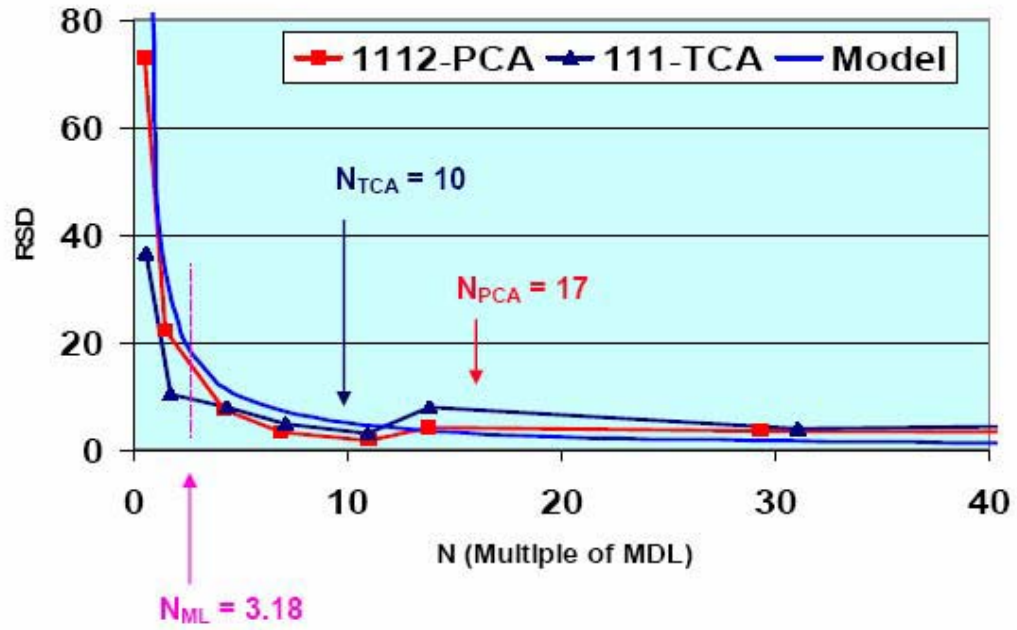


Figure 10: RSD versus N

Because of the two approximations and the inherent uncertainties associated with an MDL study, it is important to verify the empirically determined MQL with an MQL verification sample (e.g., a clean matrix spiked at the MQL) on a routine basis (e.g., one per batch). The MQL verification sample shall go through all sample preparation processes and meet the same acceptance criteria of the LCS. In addition, due to the higher relative uncertainty at lower concentrations, it is recommended that MQL never be set below three times the MDL.

CONCLUSIONS

This paper presents a simple, practical, reliable, conservative, and cost effective procedure for determination of analytical MQL. This proposed procedure determines MQL based on routine, in-house performance data of MDL study and LCS control limits. The empirically determined MQL reflects a laboratory's in-house performance and has reliable precision and bias data that are often not available for MQLs determined with other common methods. To ensure reliable and comparable MQLs among laboratories, consistent procedures must be established for performing MDL study and determining LCS control limits. The empirically determined MQL shall be verified on a routine basis and reported with precision and bias data based on the control limits of LCS.

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U.S. ARMY HTRW CENTER OF EXPERTISE

A Simple Procedure for Determination of Method Quantitation Limits

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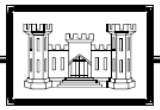
HTRW Center of Expertise
U.S. Army Corps of Engineers

28 August 2006



U.S. ARMY HTRW CENTER OF EXPERTISE

Overview of Topics

- Introduction
- Concepts and Procedures
- Examples
- QA/QC Issues
- Conclusions

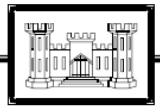
U.S. ARMY HTRW CENTER OF EXPERTISE

Definition

Method Quantitation Limit (MQL) is

the lowest amount of an analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy under stated analytical conditions.

– International Conference on Harmonization (ICH) Harmonised Tripartite Guideline



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Common Procedures

- Professional judgment
- Multiples of detection limit
- Lowest calibration standard
- Empirical procedures
- Lowest Concentration Minimum Reporting Level (LCMRL)

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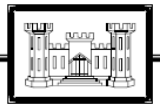
Professional Judgment

- Based on historical PQLs
- Based on EPA PE study data
- Based on arbitrary RSD
- Questionable data quality



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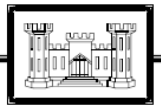
Multiples of Detection Limits

- LOQ = 10 x SD = 3.3 x LOD
- MQL = 5 ~ 10 x MDL, but never < 3 x MDL
- Arbitrarily defined or determined
- Questionable precision and bias



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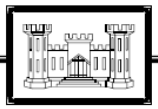
Lowest Calibration Standard

- MQL = Lowest calibration standard
- Method preparation not taken into account
- MQL depends on calibration techniques
- Questionable precision and bias



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Empirical Determination

- Repetitive measurements at concentrations close to MQL
- MQL is determined based on the minimum concentration giving acceptable precision and bias
- Lacking standard procedures
- Expensive

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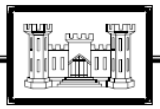
LCMRL (Lowest Concentration Minimum Reporting Level)

- EPA procedure for single-laboratory LCMRL and MRL (PQL) of UCMR
- Lowest concentration that future recovery will fall within specified recovery range and confidence
- Based on linear regression and prediction intervals for next observation
- Complicated and expensive



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Concepts of Proposed Procedure

- Determine MQL based on precision versus concentration
- Determine precision based on routine QC data of MDL/MB, and LCS
- Verify MQL on a routine basis

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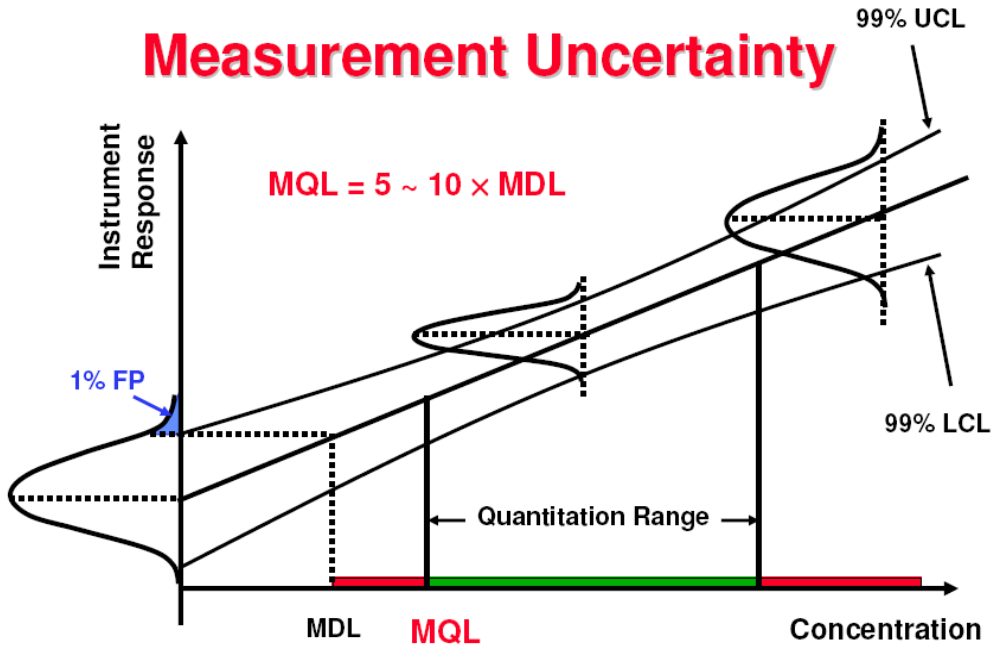
Measurement Uncertainty



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Two-Component Model for Measurement Uncertainty

Rocke-Lorenzato Model

$$c = \varepsilon + \mu e^{\eta}$$

C measured concentration

μ true concentration

ε, η normally distributed uncertainty with mean 0 and standard deviation $\sigma_\varepsilon, \sigma_\eta$

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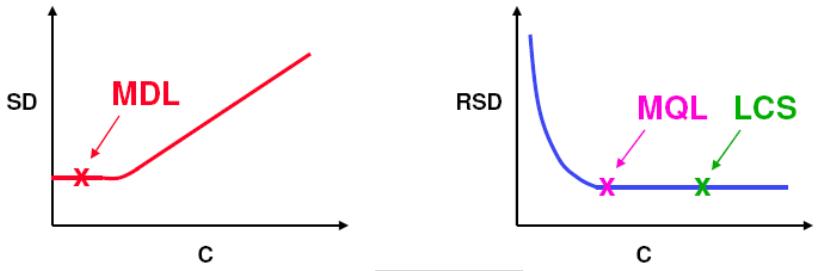
Two-Component Model for Measurement Uncertainty

Rocke-Lorenzato Model

$$\sigma_C = \sqrt{\sigma_\varepsilon^2 + \mu^2 e^{\sigma_\eta^2}(e^{\sigma_\eta^2} - 1)}$$



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Estimated Uncertainty at C < MQL

$U_{95\%}$ Relative uncertainty at 95% confidence

$$U_{95\%} = \pm\frac{t_{(n-1,.975)} \times \sigma_C}{C} \times 100\%$$

$$= \pm\frac{t_{(n-1,.975)} \times \sqrt{\sigma_\varepsilon^2 + \mu^2 e^{\sigma_\eta^2}(e^{\sigma_\eta^2} - 1)}}{C} \times 100\%$$

$$\approx \pm\frac{t_{(n-1,.975)} \times \sqrt{2} \times \sigma_\varepsilon}{N \times MDL} \times 100\%$$

$$= \pm\frac{t_{(n-1,.975)} \times \sqrt{2} \times \sigma_\varepsilon}{t_{(n-1,.99)} \times \sigma_\varepsilon} \times \frac{100\%}{N} \approx \pm\frac{100\%}{N}$$

for C near MDL and $C = N \times MDL$.

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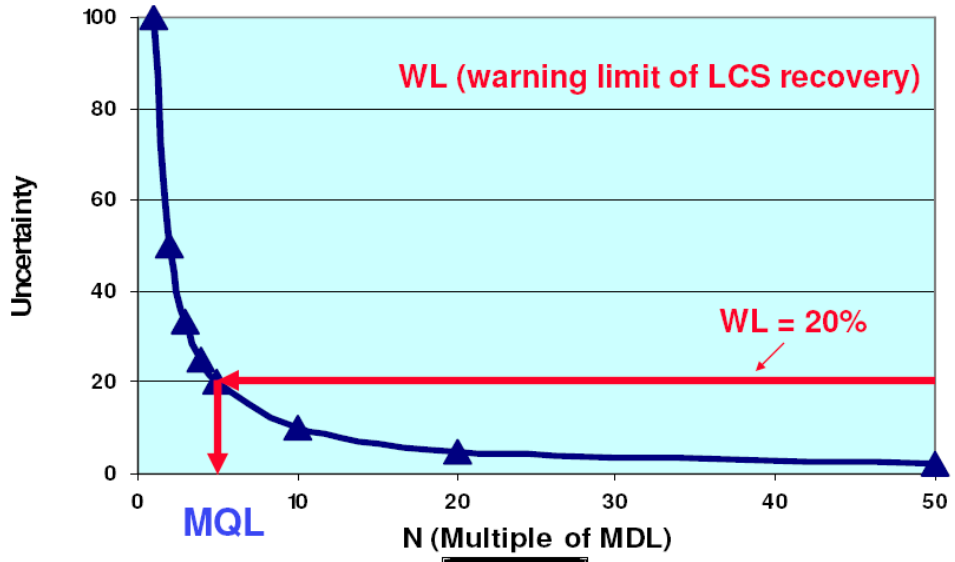
$U_{95\%}$ vs. Concentration



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MQL Determination

MQL is established at the minimum concentration where $U_{95\%,\,MDL} = WL_{LCS}$

$$\frac{100\%}{N} = WL_{LCS} = \frac{t_{(n-1,\,.975)} \times \sigma_{LCS}}{\overline{C}_{LCS}} \approx 2 \times RSD_{LCS}\%$$

$$N = \frac{100}{WL_{LCS}} \approx \frac{100}{2 \times RSD_{LCS}}$$

MQL = N x MDL

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Example

$$MDL = 1 \text{ ppb}, CL_{LCS} = 60 - 120\%, \; MQL = ?$$

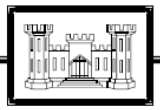
$$WL_{LCS} = \pm 20\%$$

$$MQL = N \times MDL$$

$$= \frac{100}{WL_{LCS}} \times MDL$$

$$= \frac{100}{20} \times 1 = 5 \; ppb$$

with RSD = 10% and %R = 90%



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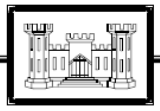
Two-Component Model for Measurement Uncertainty

Analyte	Method	Spike Level	Mean Conc.	Mean (% Recovery)	SD Conc.	RSD (based on Mean)
1112-PCA	524.2	0.035				
1112-PCA	524.2	0.05				
1112-PCA	524.2	0.075				
1112-PCA	524.2	0.1				
1112-PCA	524.2	0.15	0.032	21.178	0.023	72.898
1112-PCA	524.2	0.2	0.090	44.886	0.020	22.297
1112-PCA	524.2	0.35	0.253	72.367	0.019	7.417
1112-PCA	524.2	0.5	0.416	83.143	0.013	3.211
1112-PCA	524.2	0.75	0.660	88.000	0.012	1.797
1112-PCA	524.2	1	0.830	82.986	0.035	4.185
1112-PCA	524.2	2	1.760	88.000	0.062	3.533
1112-PCA	524.2	5	4.239	84.771	0.132	3.104
1112-PCA	524.2	10	8.800	88.000	0.234	2.661
1112-PCA	524.2	20	16.729	83.643	0.486	2.902
1112-PCA	524.2	50	43.957	87.914	0.846	1.925
1112-PCA	524.2	100	94.543	94.543	2.625	2.776
1112-PCA	524.2	200	235.429	117.714	9.253	3.930



MDL = 0.05

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Two-Component Model for Measurement Uncertainty

Analyte	Method	Spike Level	Mean Conc.	Mean (% Recovery)	SD Conc.	RSD (based on Mean)
111-TCA	524.2	0.035				
111-TCA	524.2	0.05				
111-TCA	524.2	0.075				
111-TCA	524.2	0.1	0.146	146.000		
111-TCA	524.2	0.15	0.036	24.133	0.013	36.624
111-TCA	524.2	0.2	0.105	52.250	0.011	10.410
111-TCA	524.2	0.35	0.262	74.980	0.021	7.864
111-TCA	524.2	0.5	0.428	85.629	0.021	4.822
111-TCA	524.2	0.75	0.658	87.714	0.021	3.137
111-TCA	524.2	1	0.829	82.886	0.066	7.992
111-TCA	524.2	2	1.861	93.071	0.075	4.049
111-TCA	524.2	5	4.426	88.514	0.252	5.688
111-TCA	524.2	10	9.265	92.650	0.300	3.236
111-TCA	524.2	20	17.614	88.071	0.847	4.811
111-TCA	524.2	50	46.686	93.371	1.468	3.144
111-TCA	524.2	100	98.729	98.729	4.436	4.494
111-TCA	524.2	200	220.857	110.429	11.276	5.105

MDL = 0.06

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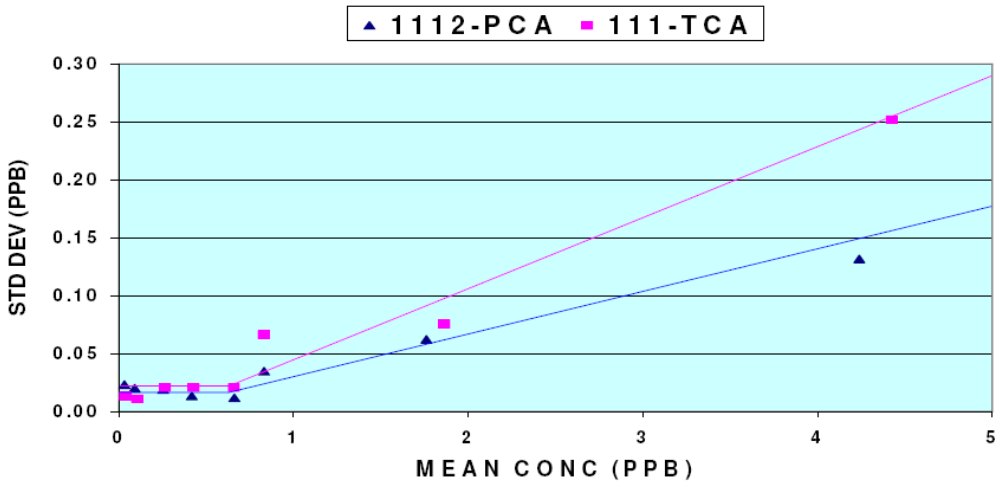
Two-Component Model for Measurement Uncertainty



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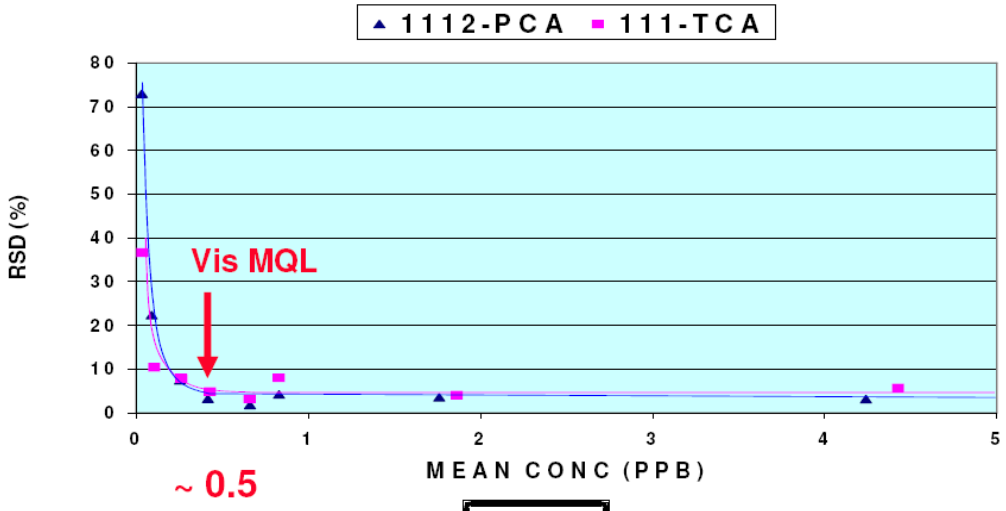
Two-Component Model for Measurement Uncertainty



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Example: 1112-PCA

MDL = t x σ = 3.143 x 0.017 = 0.05 ppb
MQL = 3 x MDL = 0.15 ppb
MQL = 5 x MDL = 0.25 ppb
MQL = 10 x MDL = 0.50 ppb
Which one is a reliable MQL? Unknown

RSD_{LCS} = 3.0% ⇒ 2 x RSD_{LCS} = 6.0%
MQL = (100/6) x MDL = 0.83 ppb
with RSD = 3% and %R = 91%

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Example: 111-TCA

MDL = t x σ = 3.143 x 0.018 = 0.06 ppb
MQL = 3 x MDL = 0.18 ppb
MQL = 5 x MDL = 0.30 ppb
MQL = 10 x MDL = 0.60 ppb
Which one is a reliable MQL? Unknown

RSD_{LCS} = 5% ⇒ 2 x RSD_{LCS} = 10%
MQL = (100/10) x MDL = 0.60 ppb
with RSD = 5% and %R = 93%

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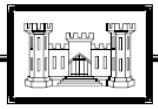
Comparison of MQLs

	PCA	TCA
MDL	0.05	0.06
CL_{LCS}	± 9%	± 15%
3 x MDL	0.15	0.18
5 x MDL	0.25	0.30
10 x MDL	0.50	0.60
EPA ML	0.2	0.2
ISO LOQ	0.18	0.10
Calc MQL (RSD/%R)	0.83 (3%/91%)	0.60 (5%/93%)



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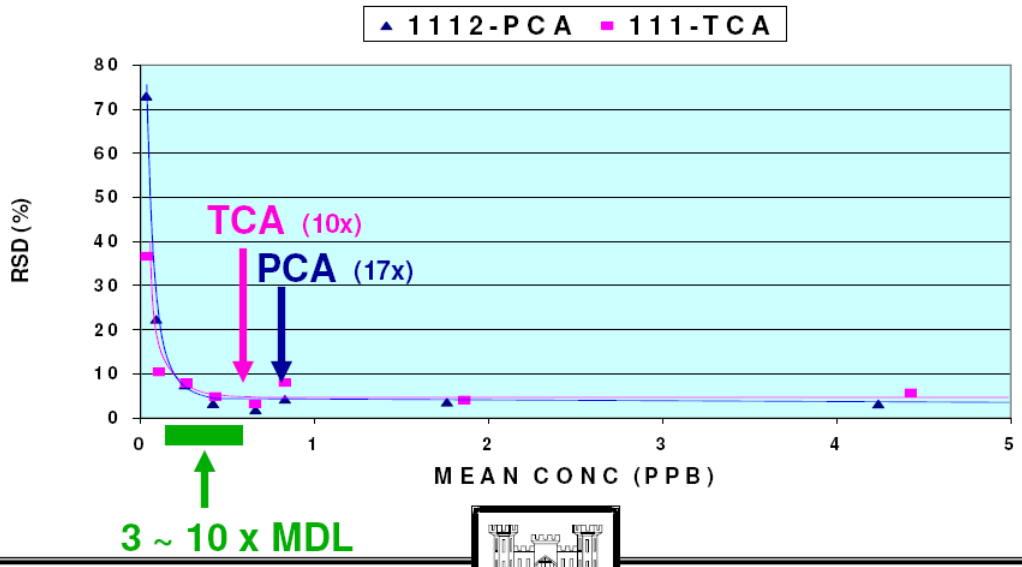
Two-Component Model for Measurement Uncertainty



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MQL Calculator

ANALYTE	4-Nitrophenol	4-Nitrophenol
MATRIX	water	water
METHODS	3520C/8270C	3510C/8270C
MDL (ppb)	10	10
LCS LCL (%)	70	40
LCS UCL (%)	130	160
MRL (ppb)	50	25
PRECISION (RSD)	10	20
BIAS (%R)	100	100

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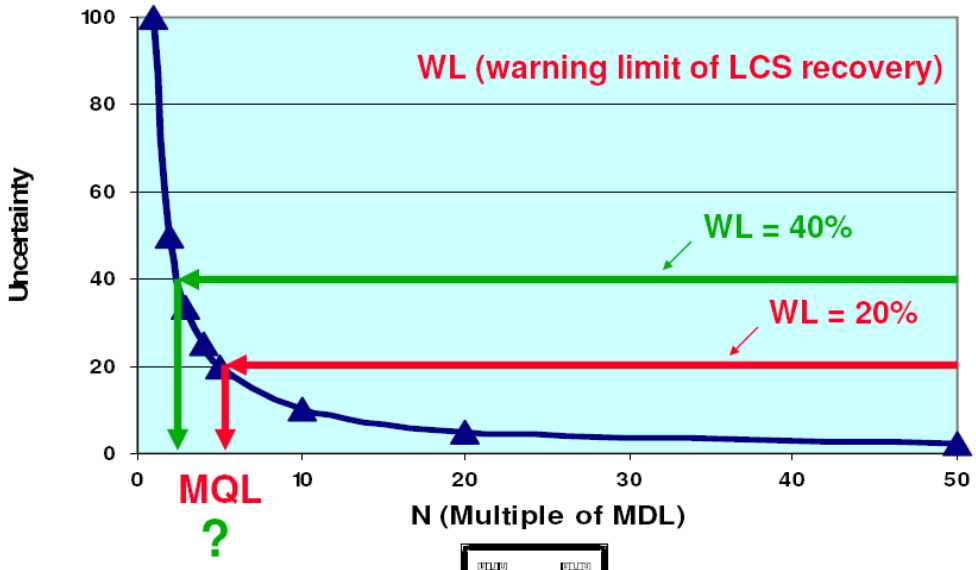
MQL vs. RSD_{LCS}



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MQL Protocol

- MQL shall be reported and used with reliable precision and bias. MQL without precision and bias has no or limited use.
- Precision and bias of analytes with C ≥ MQL in a blank matrix would be similar to the LCS'.
- MQL ≥ 3 × MDL

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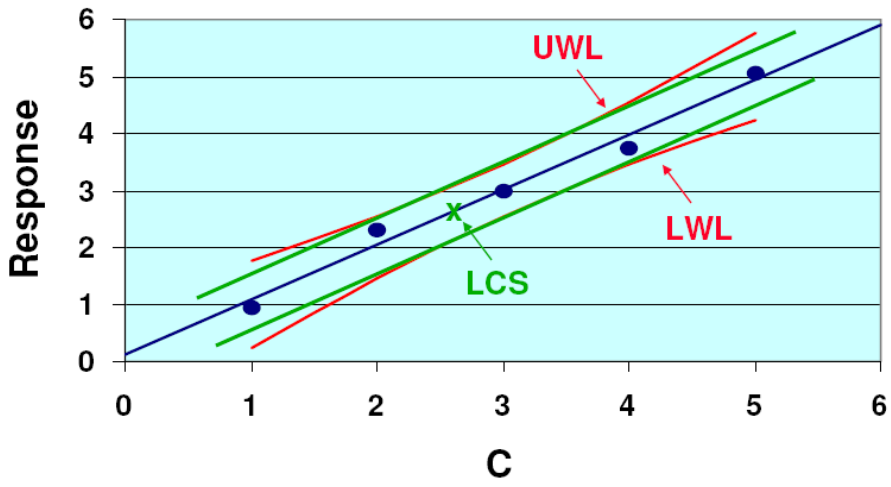
Accuracy of MQL Procedure

Mandel-Linnig Hyperbola



Assumption 1: Constant RSD at C ≥ MQL ⇒⇒⇒⇒⇒⇒⇒⇒ **High biased MQL with low biased uncertainty**

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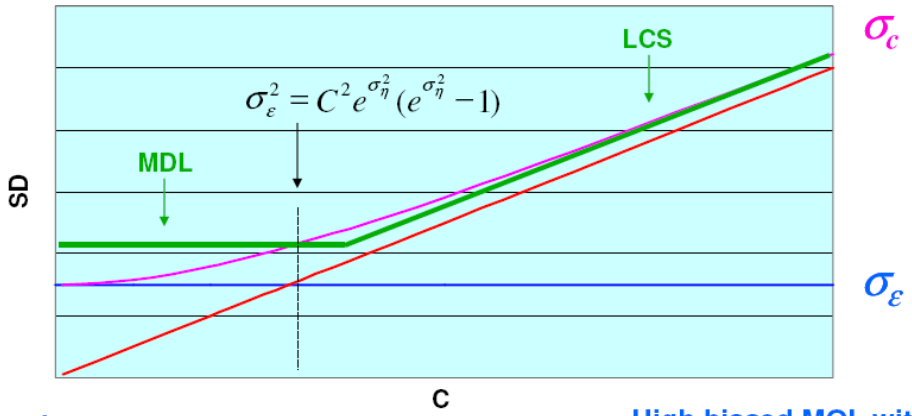
Accuracy of MQL Procedure

Rocke and Lorenzato Model

$$\sigma_C = \sqrt{\sigma_\varepsilon^2 + C^2 e^{\sigma_\eta^2}(e^{\sigma_\eta^2} - 1)} \approx \sqrt{2} \times \sigma_\varepsilon \quad for\ small\ C.$$



Assumption 2: Constant SD at C < MQL. ⇒⇒⇒ ⇒⇒ **High biased MQL with high biased uncertainty**

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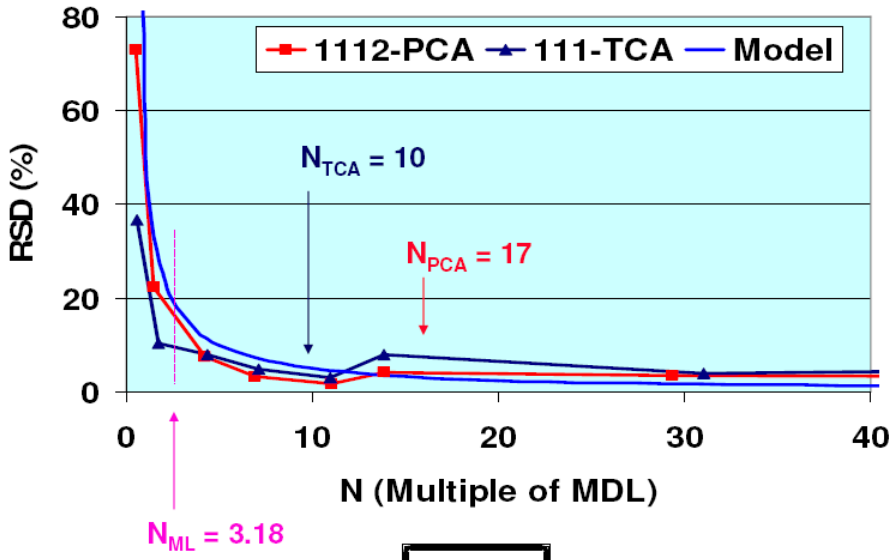
Accuracy of MQL Procedure



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QC Issues

- MQL shall be verified on a routine basis
- MDL shall be properly determined
- LCS control charts shall be properly maintained
- $U_{95\%,\ MDL}$ may be replaced with $U_{95\%,\ MB}$

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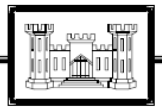
MQL vs. LCMRL

Method 521

Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry

Version 1.0, September, 2004
Document #: EPA/600/R-05/054

National Exposure Research Laboratory
Office of Research and Development, USEPA



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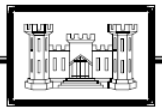
MQL vs. LCMRL

Table 1. Detection Limits and Lowest Concentration Minimum Reporting Levels [a, b]

Analyte	DL (ng/L)	LCMRL (ng/L)
NDMA	0.28	1.6
NMEA	0.28	1.5
NDEA	0.26	2.1
NPYR	0.35	1.4
NDPA	0.32	1.2
NPIP	0.66	1.4

a. DLs determination from LFBs fortified at 1.0 ng/L (n = 8).
b. LCMRLs determined from LFBs fortified at 1.0, 2.0, 3.0, and 4.0 ng/L (n = 5 or 6 at each concentration).



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MQL vs. LCMRL

Table 6. Precision and Accuracy Data Obtained from Fortified Reagent Water at Four Concentrations

Analyte	Fortified Conc 2.0 ng/L (n = 7)		Fortified Conc 4.0 ng/L (n = 6)		Fortified Conc 10.0 ng/L (n = 4)		Fortified Conc 20.0 ng/L (n = 6)	
	Accuracy (%R)	Precision (RSD)	Accuracy (%R)	Precision (RSD)	Accuracy (%R)	Precision (RSD)	Accuracy (%R)	Precision (RSD)
NDMA	94.7	12	92.7	11	88.7	3.8	89.5	7.8
NMEA	81.8	9.6	83.1	6.3	86.5	4.5	90.9	6.9
NDEA	84.6	9.0	92.0	14	87.5	9.1	95.6	11
NPYR	92.6	12	102	4.0	101	5.0	101	6.1
NDPA	81.7	8.0	87.6	7.3	97.0	10	87.1	7.7
NPIP	98.3	20	86.3	6.1	91.8	3.7	93.6	4.0

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MQL vs. LCMRL

ANALYTE (Conc)	NDMA (2 ppt)	NDMA (4 ppt)	NDMA (10 ppt)	NDMA (20 ppt)	NDMA (pooled)
MATRIX	water	water	water	water	water
METHODS	3535/521	3535/521	3535/521	3535/521	3535/521
MDL (ppt)	0.28	0.28	0.28	0.28	0.28
LCS LCL (%)	131	126	100	113	113
LCS UCL (%)	59	60	77	66	71
MRL (ppt)	1.2	1.3	3.7	1.8	2.0
PRECISION (RSD)	12	11	4	8	7
BIAS (%R)	95	93	89	90	92

Method 521: LCRML = 1.6 ppt with %R = 50 - 150% @ 99% confidence.

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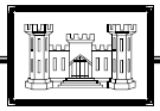
Summary

- Simple, practical, and conservative procedure for determination of MQL.
- MQL is determined based on in-house QC data.
- MDL and LCS studies shall be properly performed and documented.
- MQL shall be verified on a routine basis.
- MQL shall be reported with precision and bias.



U.S. ARMY HTRW CENTER OF EXPERTISE

US Army Corps of Engineers

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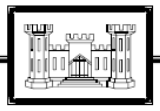

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Method Detection Limit (MDL)

- 40 CFR 136 Appendix B.
- Keep proper ratios between mean MDL spikes and measured MDLs (i.e., 1 - 5 for reagent water and 1 - 10 for other matrices.)
- Verify MDL if very low bias (i.e., recovery) occurs.
- Pool historical MDL data for determination of uncertainty.

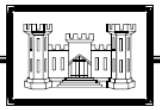
U.S. ARMY HTRW CENTER OF EXPERTISE

Questionable MDL Study

Preparation Method: 3510C Prep. Date: 3/2/01 Analytical Method: 8270C Anal. Date: 3/2/01

Analyte	Spike ug/L	Run 1 ug/L	Run 2 ug/L	Run 3 ug/L	Run 4 ug/L	Run 5 ug/L	Run 6 ug/L	Run 7 ug/L	Run 8 ug/L	Mean ug/L	Std. Dev.	MDL ug/L	%REC %	Mean/MDL Ratio
Phenol	5	2.71	2.92	3.94	4.04	3.66	3.66	3.46	3.46	3.48	0.462	1.39	69.6	2.5
4-Chloroaniline	5	0.79	0.82	0.91	0.68	N.D.	1.44	N.D.	0.63	0.88	0.293	0.98	17.6	0.9
3-Nitroaniline	5	2.48	2.84	2.79	2.73	N.D.	N.D.	2.51	2.86	2.70	0.167	0.56	54.0	4.8
4-Nitroaniline	5	6.41	6.45	6.54	6.46	N.D.	N.D.	6.49	6.52	6.48	0.048	0.16	129.6	40.2
4-Nitrophenol	5	6.9	6.78	6.85	6.17	6.69	6.12	7.24	6.64	6.67	0.373	1.12	133.5	6.0
Pentachlorophenol	5	9.09	9.24	8.9	8.4	9.17	8.78	9.85	9.56	9.12	0.451	1.35	182.5	6.7
Pyrene	5	3.8	4.18	4.86	5.05	3.77	3.8	4.15	4.28	4.24	0.487	1.46	84.7	2.9

MDL= Standard Deviation * t factor (3.00 for 8- and 3.14 for 7- replicates)



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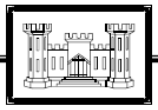
Lab Control Sample (LCS)

- Follow ISO/ASTM guidance to establish LCS control limits.
  - Number of points
  - Treatment of outliers
  - Confidence, prediction, or tolerance intervals
- Verify reported LCS control limits with laboratory's in-house control charts.



MULTI-EVENT DETECTION LIMIT STUDY

Carter, Mark J.; Environmental Research Associates
Huff, Craig; Environmental Research Associates
Laferty, John; Environmental Research Associates
Lowry, Jeff; Environmental Research Associates

Regulatory action levels are being set at lower concentration levels, which are challenging the ability of promulgated methods and laboratories to produce reliable data at these levels. USEPA has proposed to revise the method detection limit procedure in 40CFR136, Appendix B and has established a Technical Work Group to consider alternative procedures. A large multi-national manufacturing company with concerns about the reliability of their monitoring data at the low levels of concern engaged Environmental Resource Associates to manage a detection limit study. ERA prepared whole volume samples with analytes at concentration levels designed to challenge the ability of both methods and laboratories to detect and accurately quantify the results. Separate samples were prepared with volatile organics, trihalomethanes, semivolatiles/pesticides, carbamate pesticides, herbicides, metals, inorganic disinfection by-products, and nitrate analytes. A total of seven samples including a blank and three raw and treated water samples were prepared in preserved and unpreserved form. From three to five complete sets of samples were shipped to two U.S. and three international laboratories for analysis on defined days over a three week period. Laboratories with a demonstrated ability to report reliable results at the low levels of concern to the study were selected to participate. The laboratories used a variety of USEPA and technology based methodologies. The reliability of results at the laboratories' reporting and detection limits will be reported relative to international reporting and action levels as well as the detection limits reported in USEPA methods.

Report on a Multi-Event, Multi-Analyte, Multi-Method Detection Limit Study

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INTRODUCTION

Regulatory action levels are being set at lower concentrations which is challenging the ability of promulgated methods and laboratories to produce reliable data at these levels. Recently, there has been a lot of recognition that the procedures used historically to determine detection limits may not represent what is routinely achievable. USEPA has proposed to revise the method detection limit procedure in 40CFR136, Appendix B and has established a Federal Advisory Committee to evaluate alternative procedures.

A large multi-national manufacturing company with concerns about the reliability of their monitoring data at low concentration levels engaged Environmental Resource Associates (ERA) to manage a study. While there were several objectives of the study, the primary one was to determine the reliability of the data that were routinely reported to them during on-going monitoring programs at the company's required reporting limits (RLs). The company was concerned about determining the potential for both false positive and negative results. While false positive results can be verified by additional monitoring, false negatives are by definition undetectable and therefore potentially seriously misleading and damaging.

ERA designed and prepared whole volume samples with analytes at concentration levels designed to challenge the ability of both methods and laboratories to detect and accurately quantify the results, both above and just below the client company's required reporting limits. Five identical sets (required to be analyzed on different days over a three week period) of seven samples were prepared including one blank and six untreated or treated drinking water-like matrix samples with aliquots containing a representative suite of volatile organic, trihalomethane, semivolatile/pesticide, Carbamate pesticide, herbicide, metal, inorganic disinfection by-product, and nitrate analytes. The analyte concentrations were randomly prepared at levels from just below to about twenty times the required reporting limits. The laboratories were told the number of samples, analytical fractions, and schedule and that they would need to employ methods to reliably achieve their client's reporting limits. The laboratories were paid by their client to run these samples as though they were from a routine monitoring program.

Laboratories with a demonstrated ability to report reliable results at the low levels of concern were selected to participate. The client has had experience with and used these laboratories for its routine monitoring programs. From three to five complete sets of samples were shipped to two U.S. and three international laboratories in Europe and Asia for analysis on defined days over a three week period. The laboratories used a variety of USEPA and/or technology-based methodologies. The identity of the samples was randomized for each of the required analysis days of the study.

The reliability of results at the laboratories' reporting and detection limits will be reported relative to the client's international reporting and action levels as well as relative to the detection limits reported in USEPA methods.

STUDY DESIGN

Study Samples and Protocol

In order to address all issues of concern in the study, seven different samples were manufactured and supplied to the laboratories: Blank (sample 1); Untreated Waters, both preserved and unpreserved at two different concentration levels (samples 2-5); and two Treated Waters at different concentration levels, both preserved (samples 6 & 7). The Untreated Water samples were designed to simulate drinking waters from a municipal source and contained residual chlorine at about 1 ppm before preservation. The Treated Water samples were from a municipal water supply that was processed through a commercial water treatment system. Each of the seven samples were then split, spiked and preserved as necessary to produce eight analytical fractions: VOAs, THMs, Semivolatiles/Pesticides, Carbamates, Herbicides, Metals, Inorganic Disinfection Byproducts (DBPs), and Nitrate. Based on the analyte list and analytical methodologies in use by the study laboratories, the preparation of two identical aliquots with different preservatives was necessary for the Semivolatiles/Pesticides fraction as needed by each laboratory depending on the analytical procedure they employed. Several laboratories analyzed this fraction by several different GC, GC/MS and LC/MS methods.

A 'set' consisting of one sample each of the seven sample types for each analytical fraction was analyzed on each of five study days - days 1, 3, 7, 14 and 21 – by the two U.S. laboratories; four study days – days 3, 7, 14 and 21 by the two European laboratories; and three study days – days 7, 14 and 21 by the Asian laboratory. To allow for possible sample breakage or need for reanalysis of a sample, an extra set of samples, equivalent to the entire set of samples required on one analysis day, was included in each lab's shipment. All samples were brought to 4°C prior to packaging, placed in bubble pouches to minimize breakage and surrounded by gel ice refrigerant packs to maintain the sample temperature during shipment. Each sample was identified only by a randomly assigned number so that the laboratories could not relate the sample results from day to day.

Analytes and Concentrations

The analytes included in the study were selected from the complete list of target analytes of concern to the client company in both their U.S. and international monitoring programs. The analytes in each fraction and the concentration level of each analyte in each sample are shown in Table 1. Intentionally, the analyte concentrations in each sample was designed to be just below to no more than twenty times the client company's required reporting limits (RLs).

Three of the five participant laboratories employed USEPA 500 Series methods. All but two study analytes – Dimethoate and Malathion – are included in one or more EPA methods referenced by these three laboratories. The two European laboratories employed various separation and LC/MS as well as GC/MS methods for the Pesticide/Semivolatile, Carbamate and Herbicide analyte fractions. Other than very brief references to separation techniques and

analytical technologies, no detailed methods were provided by the European laboratories. These as well as the Asian laboratory did not analyze every analyte included in some of these fractions.

With a few exceptions, the detection limits reported in the published EPA 500 Series methods are slightly or significantly below the client's required Reporting Limits. The client's RLs were established based on monitoring and compliance requirements in the U.S. and internationally. In this regard, the exceptions of concern to this study were primarily focused on some of the analytes in the Herbicide and Pesticide/Semivolatile (e.g., see Hexachlorocyclopentadiene) fractions. However, all laboratories bid and accepted the work from the client understanding that they were required to meet the client's required reporting limits. Some laboratories charged extra to modify the methods to meet these required RLs.

Sample Preparation and Shipping

Because of the unique concentration required for each analyte in each sample, separate spiking concentrates were prepared for each study sample. The target analyte spiking concentrates were prepared in advance and analytically verified prior to use against at least one second source standard or NIST SRMs where available and reliable. Several batch manufacturing processes were used, depending on the technical requirements of each analyte group to ensure consistency and homogeneity of all like samples. In order to meet the scheduling needs of the study and realities of international shipping, all shipments had to be made on a Monday. Over 1,650 samples were prepared, preserved, labeled with a unique number, cooled to 4° C and packaged over the preceding three day period. Manufacturing was sequenced according to expected sample stability. All bottles were labeled with the client name, analytical fraction, temperature storage requirements and the sample I.D. number. In addition, a color-coded dot with the required analysis day printed on it was placed on each sample bottle and sample coolers.

Chain-of-Custody (COC) documents were generated for each laboratory for each day that each laboratory was required to analyze samples. The sample order within each fraction listed on each COC was also randomized. Therefore, while each laboratory knew that while they would be analyzing the same samples each day of the study they did not know which sample was which as the sample order was randomized for each day of the study.

ACHIEVABILITY OF DETECTION LIMITS

Volatile Organics and Trihalomethanes

The required Reporting Limits (RLs) for Volatile Organics and Trihalomethanes were consistently achievable. However, each laboratory reported results for one or more analytes in one or more samples that were either randomly or consistently biased low or high. In a few cases, there was a consistent bias in calibration, which impacted the laboratory's data by typically 15-20% but up to 50%. With a few exceptions, the laboratories correctly reported "less than" values for analytes spiked at concentrations below the required RLs. In general, the laboratories correctly detected these compounds when spiked at concentrations just above the required RLs.

Semivolatiles and Pesticides

The current analytical practices of the five laboratories do not support the conclusion that the results for most Pesticide and Semivolatile analytes at the required RLs are consistently reliable or supportable. One or more laboratories reported false positive results or Detection Limits that were above the required RLs for eight of the fifteen Pesticide and Semivolatile analytes. One or more laboratories also reported false negative results for most of the fifteen compounds in one or more samples spiked with the Pesticide and Semivolatile analytes in the samples where the true concentrations were up to twenty times the required RLs. Both of these issues demonstrate that the true DLs of these laboratories using their current practices for many of the Pesticide and Semivolatile compounds are higher than they reported as well as the client's required Reporting Limits. All laboratories to a lesser or greater extent, reported results for some Pesticide and Semivolatile compounds that were consistently biased, either high or low and/or were highly variable at all concentration levels. While potentially achievable under just the right conditions, it is reasonable to conclude that the detection limits reported in the EPA 500 Series methods for these analytes is not reliably achievable.

Carbamates

The results from the three best performing laboratories showed very good and consistent recoveries of the Carbamate Pesticides but still included a few false negatives at concentrations just above the required RLs. The DLs reported by one laboratory for Carbamates were five times the required RLs resulting in many false negatives in the samples spiked at low concentrations. The fifth laboratory reported false positives for three Carbamates in one blank sample and results in general that were highly variable with many false negatives calling into question the validity of all their RLs.

Herbicides

The results from the two best performing laboratories showed good recoveries of the Herbicides with virtually no false negatives at concentrations above the required RLs. The other laboratories reported DLs that were too high compared to the required RLs or had results so variable that it is not possible to come to any conclusion from their data about the general achievability of the required RLs. While two of the laboratories reliably achieved the required RLs, three laboratories clearly did not, indicating that possibly this method is not rugged in other than the most careful and capable laboratory.

Metals

One laboratory consistently reported very accurate results for all metals and reported no false positives or negatives. The other four laboratories reported false positives in some blanks and DLs for one to three metals that were above the required RLs. This caused a number of these laboratories to report false negatives at concentrations above the required RLs. While the technology exists for laboratories to meet the required RLs for metals, the current practices of most of these laboratories are such that these limits are not being consistently being met.

Inorganic Disinfection By-Products

Only three laboratories performed analyses for the three Inorganic Disinfection By-Product (DBP) analytes. Other than one false positive in one blank sample, the three laboratories reported consistently accurate results for the three Inorganic DBP analytes in all samples. It is appropriate to conclude that the RLs for Inorganic DBP analytes are routinely achievable.

Nitrate

Only one laboratory reported results for Nitrate that were consistently accurate at all concentration levels. Two other laboratories reported DLs above the required RLs, which made the evaluation of the reliability of results at this level impossible to determine. While not always reporting false negatives, the other two laboratories' results were consistently biased low. While the technology and laboratory procedures exist for laboratories to meet the required RLs for Nitrate, the practices of all but one laboratory in this study is such that these limits are not being met routinely.

DATA QUALITY ISSUES

In addition to the issues discussed above, most laboratories had one or more data quality issues that are important to address. In routine monitoring situations, most of these problems would not be detectable. What made the detection of the errors possible is the fact that the analyte true values were known and that the laboratories analyzed the same samples from three to five times during the study, albeit in a single blind manner. These errors came from improper calibration, mixed up sample identifications, significant random errors during sample preparation and/or analysis. A few examples are:

Inadequate Reporting Limits

Even after being directed and agreeing to use methods that could achieve the required RLs, every laboratory reported DLs for one to thirteen analytes that were from two to twenty times the client's required reporting limits. This made it difficult or impossible to assess the technical achievability of the required RLs for some analytes.

Misidentification of Samples

One laboratory misreported the identity and therefore results of all analytes in four samples analyzed on one day of the study for the Pesticides fraction. Another laboratory misreported the identity and therefore results for all analytes in four Herbicides samples analyzed on one day of the study. A third laboratory switched all results for two Herbicide samples analyzed on one day of the study. Once ERA received the results and performed simple pattern recognition, the switching of results became apparent. Without inappropriate prompting, the laboratories were able to sort out and correct these data reporting problems. There were a number of other instances of apparent sample misidentification or data mix-up that the laboratories could not resolve without inappropriate prompting. In the vast majority of routine monitoring situations, the switching of sample identifications and misreporting of results would not be detectable. This was one of the most surprising and least anticipated problems that occurred during the study.

Systematic Calibration Errors

One laboratory initially reported results for all Volatile Organic and Trihalomethane compounds that were too high by an order of magnitude. After being appropriately prompted by ERA, the laboratory determined that they made an error that was caused by their purchase and use of a calibration standard that was an order of magnitude lower in concentration than they thought. The problem, if not detected and questioned, would have resulted in all of the data analyzed using these standards being in error by a factor of ten. While the immediate problem was resolved, this situation raised a number of questions about the routine quality control practices of this highly regarded international laboratory.

Un-communicated Study Instructions

While the project manager of one laboratory was informed that separate samples would be provided for analysis of Volatile Organic and Trihalomethane compounds, the laboratory initially reported all results for the Trihalomethane fraction out of the Volatile Organics fraction as "Not Detected." Upon appropriate prompting, the laboratory recognized the reporting error and reported the corrected and ultimately accurate results for these analytes. This situation illustrates the importance of communication and follow-up to ensure the proper reporting of data from non-routine analysis requests.

ASSESSMENT OF OVERALL DATA QUALITY

As one assessment of data quality, all individual results that were reported as a false negative or outside of 50-150% of the true value were identified. Using these criteria, the best overall performing laboratory had almost eight percent of their reported results identified as potentially problematic. For each laboratory, the mean recovery for each analyte for all samples was calculated. Based on ERA's historical Performance Acceptance Limits, the best laboratory had nine of forty-six mean analyte recoveries identified as significantly biased. The other laboratories had from fifteen to twenty-one analytes with a consistent notable bias. Addressing only mean recoveries can be misleading without considering the variability of the data. The analytes in each sample that had mean RSDs above 40% were identified. The best laboratory had only four analytes with RSDs above 40% for all samples they analyzed. The poorest laboratory in this regard had thirteen of forty-two analytes with mean RSDs above 40%.

NOTABLE METHOD ISSUE

One laboratory analyzed five of the Pesticide analytes by both GC/MS (525) and GC (505) techniques. The mean recoveries for these analytes using GC/MS ranged from 38-162% and using GC from 86-111%. The RSDs using GC/MS ranged from 23-47% and using GC from 9-20%. While it's hard to deny the efficiency of the GC/MS technique in producing simultaneous results for a wide suite of analytes, clearly the GC technique produced the most consistently accurate recoveries and best precision.

BEST PERFORMANCE HARD TO DEFINE

In order to determine if there were any consistent measures of a laboratory's ability to analyze samples at the low levels required by the client, the data were ranked by fraction according to mean recovery and RSD. Considering the composite recovery/RSD ranking, one laboratory performed the best on the Volatile Organic, Trihalomethane and Inorganic Disinfection-By Products analytical fractions. While this same laboratory reported the best results for Dimethoate using a solid-phase extraction-LC/MS method, an analyte the analysis of which confounded all other laboratories, their composite performance for the rest of the Pesticides/SVOAs was second to worst among all laboratories. Their results for the Carbamate and Herbicide fractions were among the most biased and highly variable among all laboratories' data. It is not clear if the issue is from calibration and /or sample preparation problems.

Another laboratory reported the best results by far among all laboratories for the Herbicide fraction, the worst by far for the Pesticides and Semivolatile fractions and in the middle for the other organic analyte fractions. In addition, this laboratory's Metals and Nitrate data were either the most variable or least accurate in the study. The laboratory's use of atomic absorption techniques for Arsenic, Cadmium and Lead demonstrated the inappropriateness of this approved method to analyze samples at the low Reporting Limits required in this study.

Overall, the best performing laboratory reported the best results for only the Carbamate analyte fraction. The only exception to their otherwise good to excellent performance was for the metals analyte fraction, which had low and high biased results, respectively, for iron and lead.

CONCLUSION

While the results of this study might suggest that the participant laboratories have a few or many analytical problems, the fact is that the samples were designed to provide a stern test of both the laboratories and the methods they used. The concentration of the lowest level study standards was often more than an order of magnitude lower than the corresponding NELAC PT standards for many of the analytes. While it can be concluded that the published detection limits for the Volatile Organic, Trihalomethane, Metal and Inorganic analyte fractions are generally routinely achievable, the study supports the contrary conclusion for many if not most of the Pesticide, Semivolatile, Carbamate and Herbicide analyte fractions. The current effort by EPA to improve and standardize the protocol to quantitatively determine detection limits will help ensure the reliability and realism of low level analytical results.

Table 1: Detection/Reporting Limit Study Sample Concentrations, µg/L

Analytes	Req'd Reporting Limit	Method Detection Limit			NELAC PTRL	Blank Sample 1	Untreated Water (1) Samples 2&3	Untreated Water (1) Samples 4&5	Treated Water (2) Sample 6	Treated Water (2) Sample 7
Volatile Organics		**502.2**	**524.2**							
Benzene	0.50	0.01	0.04		1.5	0.00	2.24	0.89	0.61	0.43
Ethylbenzen	0.50	0.01	0.06		1.2	0.00	1.21	3.62	0.59	0.91
Tetrachloroethylene	0.50	0.04	0.14		1.2	0.00	0.89	1.83	0.48	0.74
Toluene	0.50	0.01	0.11		1.2	0.00	3.30	1.11	0.92	0.48
Trichloroethylene	0.50	0.01	0.19		1.2	0.00	1.81	0.91	0.47	0.85
Total Xylenes (m & o)	0.50	0.04	0.29		1.2	0.00	1.39	2.90	1.11	0.56
Trihalomethanes		**502.2**	**524.2**	**551.1**						
Bromoform	0.50	0.09	0.2	0.035	5	0.00	4.11	2.59	0.68	0.38
Dibromochloromethane	0.50	0.17	0.07	0.026	5	0.00	3.68	1.90	0.45	0.92
Bromodichloromethane	0.50	0.10	0.08	0.068	5	0.00	2.60	1.48	0.56	0.88
Chloroform	0.50	0.02	0.03	0.080	5	0.00	3.14	2.33	0.81	0.48
Pesticides/SVOCs		**505**	**525.2**	**SPE/LC/MS**						
Alachlor	0.10	0.225	0.16	0.10	1.1	0.00	1.10	0.75	0.18	0.29
Aldrin	0.10	0.007	0.16	-	0.15	0.00	0.33	0.89	0.11	0.078
Atrazine	0.10	2.4	0.081	0.10	1.6	0.00	0.80	1.11	0.19	0.37
Benzo(a)pyrene	0.10	-	0.12	-	0.10	0.00	1.00	0.75	0.13	0.26
Chlorpyrifos	0.10	-	0.066	-	-	0.00	0.61	0.97	0.14	0.090
Dieldrin	0.10	0.012	0.15	-	0.32	0.00	1.19	0.96	0.10	0.077
Di(2-Ethylhexyl)adipate	0.60	-	0.20	-	1.6	0.00	1.92	1.61	0.33	0.51
Dimethoate	0.10	-	-	0.10	-	0.00	0.97	0.63	0.15	0.33
Heptachlor	0.10	0.003	0.11	-	0.22	0.00	0.46	0.72	0.16	0.29
Hexachlorocyclopentadiene	0.020	0.13	0.12	-	0.24	0.00	0.97	1.28	0.039	0.056
Lindane	0.10	0.003	0.15	-	0.11	0.00	1.87	1.40	0.57	0.16
Malathion	-	-	-	-	0.20	0.00	0.98	1.50	0.49	0.21
Methoxychlor	0.10	0.96	0.13	-	5.5	0.00	1.22	0.80	0.16	0.29
Metolachlor	0.10	-	0.09	0.10	5.3	0.00	0.91	0.49	0.13	0.35
Trifluralin	0.10	-	0.24	-	0.33	0.00	0.76	1.31	0.41	0.18

Table 1: Detection/Reporting Limit Study Sample Concentrations, µg/L (cont.)

Analytes	Req'd Reporting Limit	Method Detection Limit			NELAC PTRL	Blank Sample 1	Untreated Water (1) Samples 2&3	Untreated Water (1) Samples 4&5	Treated Water (2) Sample 6	Treated Water (2) Sample 7
Carbamates		**531.1**	**531.2**	**SPE/LC/MS**						
Aldicarb	0.10	0.22	0.042	0.10	11	0.00	0.90	0.51	0.093	0.21
Aldicarb Sulfone	0.10	1.0	0.057	0.10	16	0.00	1.24	0.56	0.13	0.27
Aldicarb Sulfoxide	0.10	0.59	0.059	0.10	11	0.00	0.93	0.61	0.33	0.18
Carbofuran	0.10	0.52	0.058	0.10	8.3	0.00	1.32	0.80	0.26	0.11
Herbicides		**515.3**	**515.4**	**SPE/LC/MS**						
2,4-D	0.10	0.19	0.21	0.10	2.5	0.0	1.10	0.86	0.15	0.32
2,4-DB	0.10	0.66	0.25	0.10	6.0	0.0	0.98	1.20	0.29	0.24
Dichlorprop	0.10	0.51	0.43	0.10	4.7	0.0	2.79	1.90	0.44	0.38
Pentachlorophenol	0.10	0.085	0.084	0.50 (3)	0.50	0.0	0.68	0.47	0.11	0.18
2,4,5-T	0.10	0.20	0.033	0.10	3.9	0.0	1.11	0.78	0.16	0.096
2,4,5-TP (Silvex)	0.10	0.14	0.033	0.10	2.5	0.0	0.90	0.65	0.087	0.14
Metals		**200.7**	**200.8**	**3113/3114**						
Arsenic	2	53	0.9	-	20	0.0	15	9.0	1.8	3.3
Cadmium	0.5	3.4	0.1	0.1	1.6	0.0	4.9	2.2	0.6	1.9
Chromium	10	6.1	0.07	-	8.5	0.0	37	61	14	7.8
Copper	10	5.4	0.03	-	45	0.0	85	48	21	13
Iron	10	6.2	-	-	70	0.0	150	96	12	48
Lead	0.5	42	0.08	1.0	3.5	0.0	13	7.0	0.4	1.0
Zinc	20	1.8	0.2	-	360	0.0	130	190	16	31
Disinfection By-Products		**300.0**	**300.1**	**317**						
Bromide	-	10	14	-	52	0.0	140	75	8.3	17
Bromate	5.0	-	1.3	0.71	3.5	0.0	31	7.0	9.6	4.6
Chlorate	20	-	2.6	-	47	0.0	110	49	18	29
Nitrate		**300**	**300.1**	**353.2**						
Nitrate as Nitrate	50	4.0	8.0	-	2700	0.0	1300	549	42	71

(1) Untreated waters were prepared as both preserved and unpreserved samples.
(2) Treated waters were prepared only as preserved samples.
(3) Stir Bar Sorptive Extraction-GC/MS

Report on a Multi-Analyte, Multi-Method Detection Limit Study

Mark J. Carter, John Laferty, Craig Huff
and Jeff Lowry
Environmental Resource Associates
August 28, 2006

Study Sponsor

- Fortune 500 company with multi-national monitoring requirements.
  - Regulatory limits low & going lower.
  - Established required lab reporting limits (RLs).
  - A challenge for labs and methods to produce reliable data at these low levels.

Multiple Study Objectives

- Determine data reliability.
  - At concentration levels from just below to ≤20-30X required RLs.
  - False positives - can be verified by additional monitoring.
  - False negatives - by definition are undetectable and a greater concern.
- Study also designed to look at preservation issues at these levels.

Laboratory Participants

- Five laboratories selected with proven capability to analyze samples at low levels.
  - Two U.S. , two European & one Asian.
- Intent to challenge methods and assess routine data quality in samples with analytes at low concentration levels.

Seven Study Samples

- One blank.
- Two raw waters.
  - Each split with preserved and unpreserved fractions prepared.
- Two treated waters.
  - Each with only preserved fractions prepared.

Each Sample Had Nine Separate Fractions

- Volatile Organics (6 analytes)
- Trihalomethanes (4)
- Pesticides/Semivolatiles (15) – one fraction each for GC and GC/MS & LC/MS
- Carbamates (4)
- Herbicides (6)
- Metals (7)
- Inorganic Disinfection By-Products (3)
- Nitrate (1)

Sample Designs

- Whole volume samples.
- Analytes selected from client's list.
- Analyte concentrations randomly but logically set.
- Generally higher levels in raw waters.
- Levels in treated waters just above & below RLs.
- Compromises made in sample bottles, volumes and preservatives.

VOA & THM Analytes, µg/L

Analytes	Req'd Reporting Limit	Method Detection Limit			Blank	Raw Water		Treated Water	
					Sample 1	Samples 2&3	Samples 4&5	Sample 6	Sample 7
VOAs		502.2	524.2						
Benzene	0.50	0.01	0.04		0.00	2.24	0.89	0.61	0.43
Ethylbenzene	0.50	0.01	0.06		0.00	1.21	3.62	0.59	0.91
Tetrachloroethylene	0.50	0.04	0.14		0.00	0.89	1.83	0.48	0.74
Toluene	0.50	0.01	0.11		0.00	3.30	1.11	0.92	0.48
Trichloroethylene	0.50	0.01	0.19		0.00	1.81	0.91	0.47	0.85
Total Xylenes (m & o)	0.50	0.04	0.29		0.00	1.39	2.90	1.11	0.56
THMs		502.2	524.2	551.1					
Bromoform	0.50	0.09	0.2	0.035	0.00	4.11	2.59	0.68	0.38
Dibromochloromethane	0.50	0.17	0.07	0.026	0.00	3.68	1.90	0.45	0.92
Bromodichloromethane	0.50	0.10	0.08	0.068	0.00	2.60	1.48	0.56	0.88
Chloroform	0.50	0.02	0.03	0.080	0.00	3.14	2.33	0.81	0.48

Pesticide/SVOC Analytes, µg/L

Analytes	Req'd Reporting Limit	Method Detection Limit			Blank	Raw Water		Treated Water	
					Sample 1	Samples 2&3	Samples 4&5	Sample 6	Sample 7
Pesticides/SVOCs		505	525.2	SPE/LC/MS					
Alachlor	0.10	0.225	0.16	0.10	0.00	1.10	0.75	0.18	0.29
Aldrin	0.10	0.007	0.16		0.00	0.33	0.89	0.11	0.078
Atrazine	0.10	2.4	0.081	0.10	0.00	0.80	1.11	0.19	0.37
Benzo(a)pyrene	0.10	-	0.12		0.00	1.00	0.75	0.13	0.26
Chlorpyrifos	0.10	-	0.066		0.00	0.61	0.97	0.14	0.090
Dieldrin	0.10	0.012	0.15		0.00	1.19	0.96	0.10	0.077
Di(2-Ethylhexyl)adipate	0.60	-	0.20		0.00	1.92	1.61	0.33	0.51
Dimethoate	0.10	-	-	0.10	0.00	0.97	0.63	0.15	0.33
Heptachlor	0.10	0.003	0.11		0.00	0.46	0.72	0.16	0.29
Hexachlorocyclopentadiene	0.020	0.13	0.12		0.00	0.97	1.28	0.039	0.056
Lindane	0.10	0.003	0.15		0.00	1.87	1.40	0.57	0.16
Malathion	-	-	-		0.00	0.98	1.50	0.49	0.21
Methoxychlor	0.10	0.96	0.13		0.00	1.22	0.80	0.16	0.29
Metolachlor	0.10	-	0.09	0.10	0.00	0.91	0.49	0.13	0.35
Trifluralin	0.10	-	0.24		0.00	0.76	1.31	0.41	0.18

Carbamate & Herbicide Analytes, µg/L

Analytes	Req'd Reporting Limit	Method Detection Limit			Blank	Raw Water		Treated Water	
					Sample 1	Samples 2&3	Samples 4&5	Sample 6	Sample 7
Carbamates		531.1	531.2	LC/MS					
Aldicarb	0.10	0.22	0.042	0.10	0.00	0.90	0.51	0.093	0.21
Aldicarb Sulfone	0.10	1.0	0.057	0.10	0.00	1.24	0.56	0.13	0.27
Aldicarb Sulfoxide	0.10	0.59	0.059	0.10	0.00	0.93	0.61	0.33	0.18
Carbofuran	0.10	0.52	0.058	0.10	0.00	1.32	0.80	0.26	0.11
Herbicides		515.3	515.4	LC/MS					
2,4-D	0.10	0.19	0.21	0.10	0.0	1.10	0.86	0.15	0.32
2,4-DB	0.10	0.66	0.25	0.10	0.0	0.98	1.20	0.29	0.24
Dichlorprop	0.10	0.51	0.43	0.10	0.0	2.79	1.90	0.44	0.38
Pentachlorophenol	0.10	0.085	0.084	0.50	0.0	0.68	0.47	0.11	0.18
2,4,5-T	0.10	0.20	0.033	0.10	0.0	1.11	0.78	0.16	0.096
2,4,5-TP (Silvex)	0.10	0.14	0.033	0.10	0.0	0.90	0.65	0.087	0.14

Metal, DBP & Nitrate Analytes, µg/L

Analytes	Req'd Reporting Limit	Method Detection Limit			Blank	Raw Water		Treated Water	
					Sample 1	Samples 2&3	Samples 4&5	Sample 6	Sample 7
Metals		**200.7**	**200.8**	**3113/3114**					
Arsenic	**2**	**53**	**0.9**	**-**	0.0	15	9.0	1.8	3.3
Cadmium	**0.5**	**3.4**	**0.1**	**0.1**	0.0	4.9	2.2	0.6	1.9
Chromium	**10**	**6.1**	**0.07**	**-**	0.0	37	61	14	7.8
Copper	**10**	**5.4**	**0.03**	**-**	0.0	85	48	21	13
Iron	**10**	**6.2**	**-**	**-**	0.0	150	96	12	48
Lead	**0.5**	**42**	**0.08**	**1.0**	0.0	13	7.0	0.4	1.0
Zinc	**20**	**1.8**	**0.2**	**-**	0.0	130	190	16	31
DBPs		**300.0**	**300.1**	**317**					
Bromide	**-**	**10**	**14**	**-**	0.0	140	75	8.3	17
Bromate	**5.0**	**-**	**1.3**	**0.71**	0.0	31	7.0	9.6	4.6
Chlorate	**20**	**-**	**2.6**	**-**	0.0	110	49	18	29
Nitrate		**300**	**300.1**	**353.2**					
Nitrate as Nitrate	**50**	**4.0**	**8.0**	**-**	0.0	1300	549	42	71

Laboratory Communication

- Labs paid to run as routine samples.
  - Client did not dictate methods.
  - Requirement to achieve client's RLs.
- Labs told:
  - Number and type of samples.
  - Analytical fractions and target analytes - latter reluctantly.
  - Approx. concentration range.
  - Schedule.

Sample Preparation

- Separate spiking stocks prepared for each fraction in each sample.
  - Verified against 2nd source standards.
- Final sample preparation occurred from Saturday am - Monday pm, staged in order of stability.
  - Different prep. techniques used to ensure consistency & homogeneity of all samples.
  - Over 1,650 whole-volume sample fractions prepared.

Study Protocols

- Random sample numbers assigned & order scrambled for each day's run.
- An extra bottle of each fraction was supplied for problems.
- Samples/shipping containers coded for I.D. of each day's samples.
- Samples chilled, packed with blue ice, palletized and air shipped for 1-3 day delivery, depending on location.
- Labs to report data after each day's run.

Analysis Schedule

- Six identical sets to US labs.
  - Analyzed on days 1, 3, 7, 14 & 21.
- Five sets to European labs.
  - Analyzed on days 3, 7, 14 & 21.
- Four sets to Asian lab.
  - Analyzed on days 7, 14 & 21.
  - Later schedule due to customs issues.

Method Summary

- US & Asian labs - EPA 500 methods.
  - One lab used both GC & GC/MS methods for pesticides.
- European labs referenced technology-based methods – few details.
  - Multiple methods per analyte group.
  - Reliance on LC/MS as well as GC/MS.
- No comforting definition of how labs (or EPA?) determined DLs or RLs.

Analytical Methods

- VOAs & THMs.
  - 524.2 (Purge/Trap-GC/MS).
  - Headspace-GC/MS & -GC/ECD (THMs).
- Pesticides/Semivolatiles.
  - 525.2 (Liquid/Solid Extraction-GC/MS).
  - Pesticides by 505 (Microextraction-GC).
  - SPE-GC/MS & -LC/MS, SBSE-GC/MS.
- Carbamates
  - 531.1 (Direct Inject.-HPLC).
  - SPE-LC/MS.

Analytical Methods

- Herbicides
  - 515.4 (Liq.-Liq. Microextract.-GC/EC).
  - 515.3 (Liq.-Liq. Extraction-GC/EC).
  - Direct inject & SPE-LC/MS; SBSE-GC/MS.
- Metals
  - 200.8 (ICP/MS), Optical ICP, Hydride & Furnace AA.
- Inorganic DBPs
  - 300.1 (IC); 317 (post-column IC).
- Nitrate
  - 300 (IC); 353.2 (Colorimetric).

Evaluation of Problematic Data

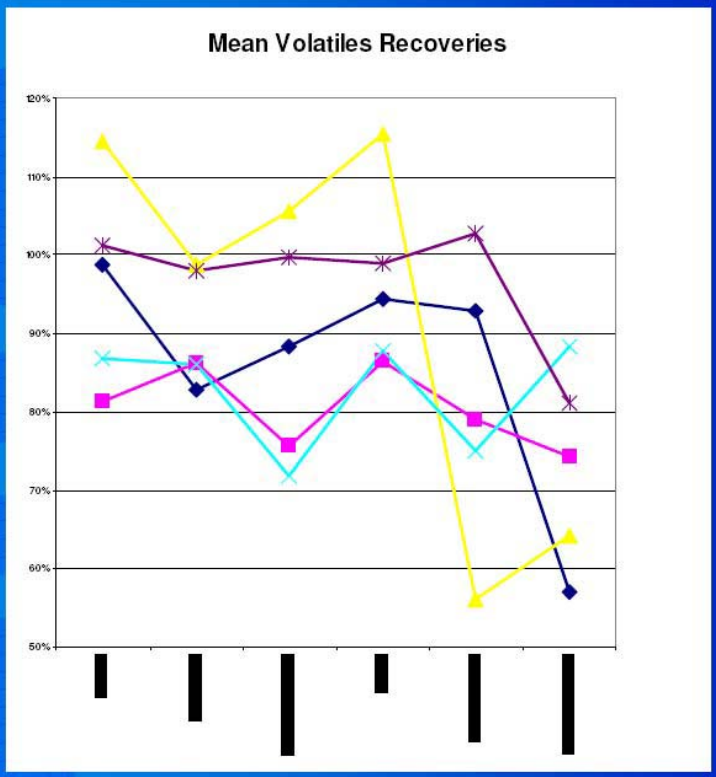
- DLs or RLs too high.
  - Issue for 1-13 analytes/lab.
- False negatives (55%) or positives (45%).
- Result outside of 50-150% of true value.
  - No magic to this range.
- Problematic data by lab ranged from 10-21%.
  - Performance varied widely by fraction.

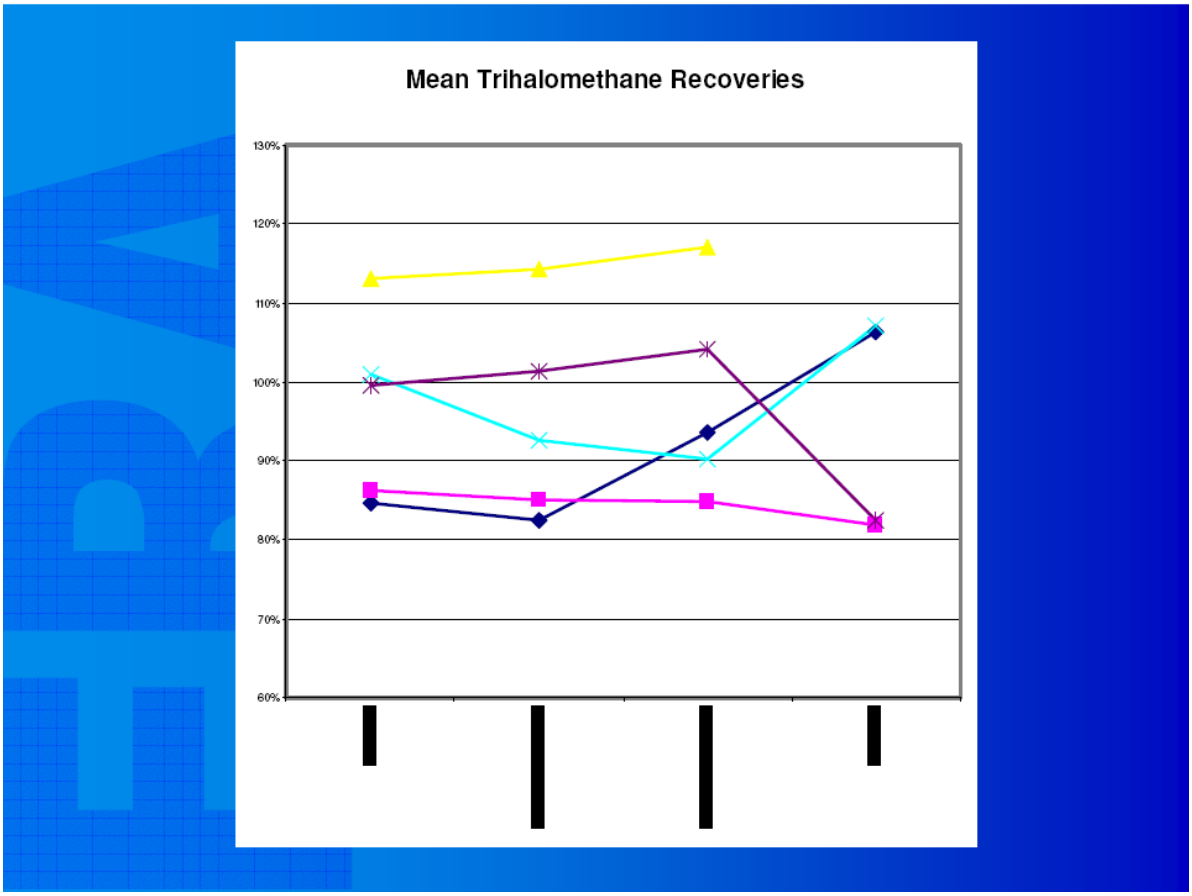
% Problematic Study Data by Analytical Fraction

VOAs	4.4%
THMs	3.3%
Pests/SVOCs	18.4%
Carbamates	25.2%
Herbicides	24.6%
Metals	13.5%
DBPs	0.5%
Nitrate	27.6%

VOAs & THMs

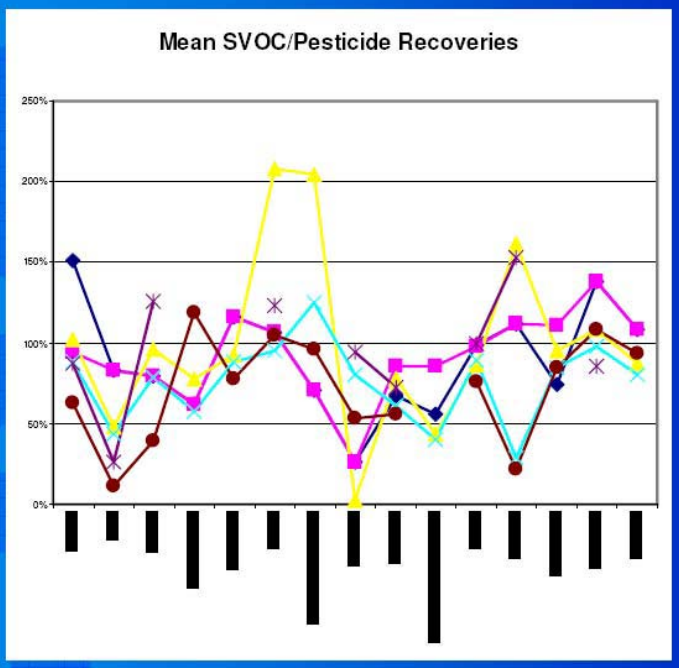
- Results generally reliable at required RLs.
- In a few cases, consistent bias by 15-20%, but up to almost 50%.
- One lab initially reported all VOAs & THMs too high by 10X.





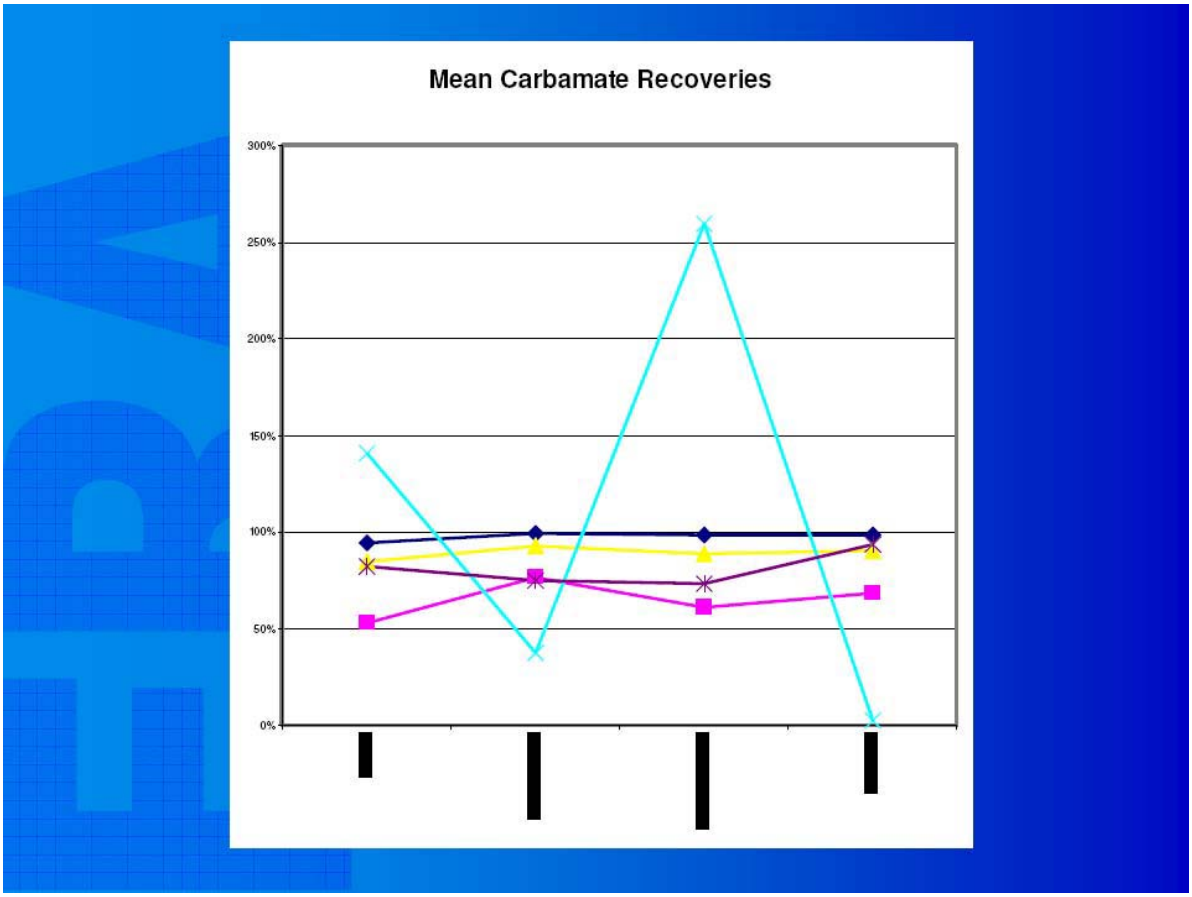
Pesticides & SVOCs

- One or more labs reported false negs. for most analytes in one or more samples at concs. up to 20X RLs.
- Results highly variable - which does not support conclusion that RLs are generally achievable.
- For pesticides, GC data more accurate and precise than GC/MS.
  - Mean recoveries for GC (86-111%) & GC/MS (38-162%).
  - Mean RSDs for GC (9-20%) & GC/MS (23-47%).



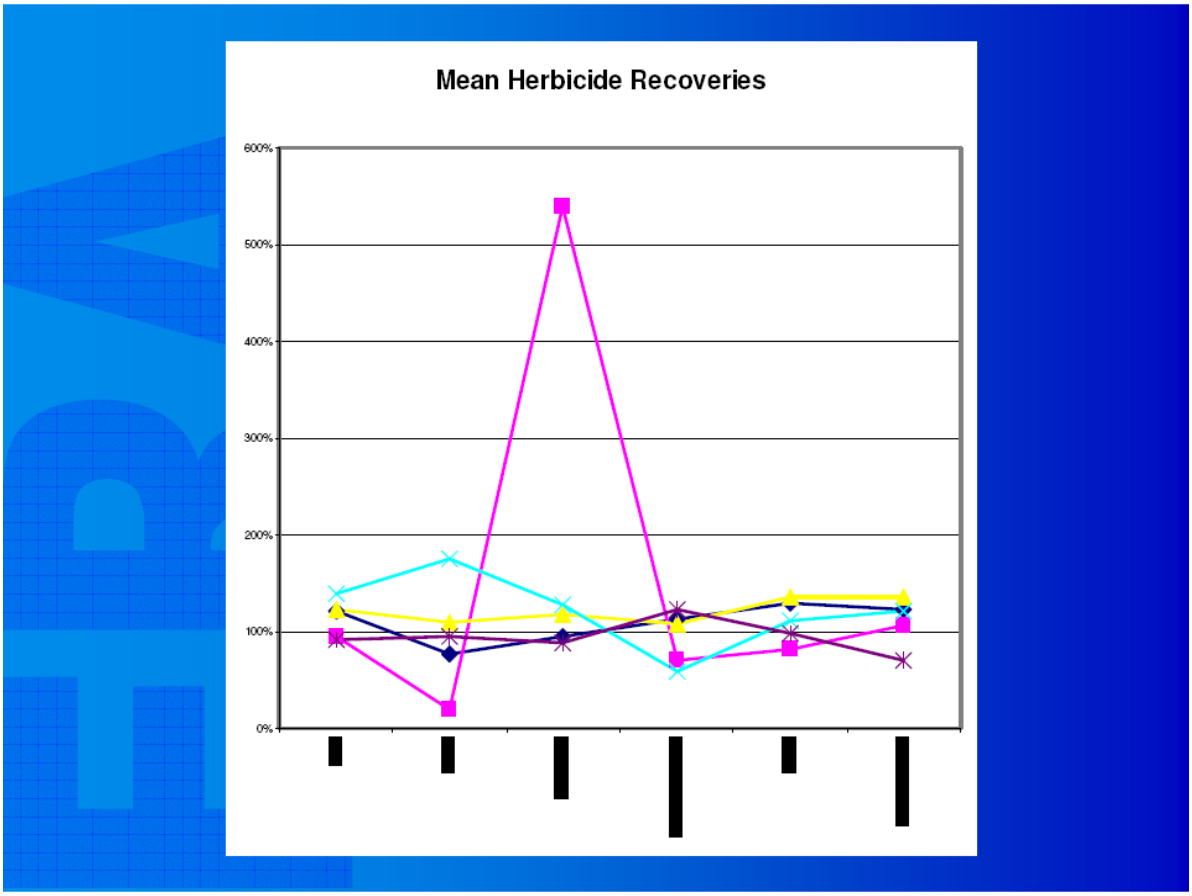
Carbamates

- Three best labs had good & consistent recoveries.
  - Still a few false negatives.
- Other two labs' results.
  - DLs too high, both false negs. & pos.
  - Results highly variable.
- Different labs using LC & LC/MS methods had good data.
- RLs achievable, but not consistently.



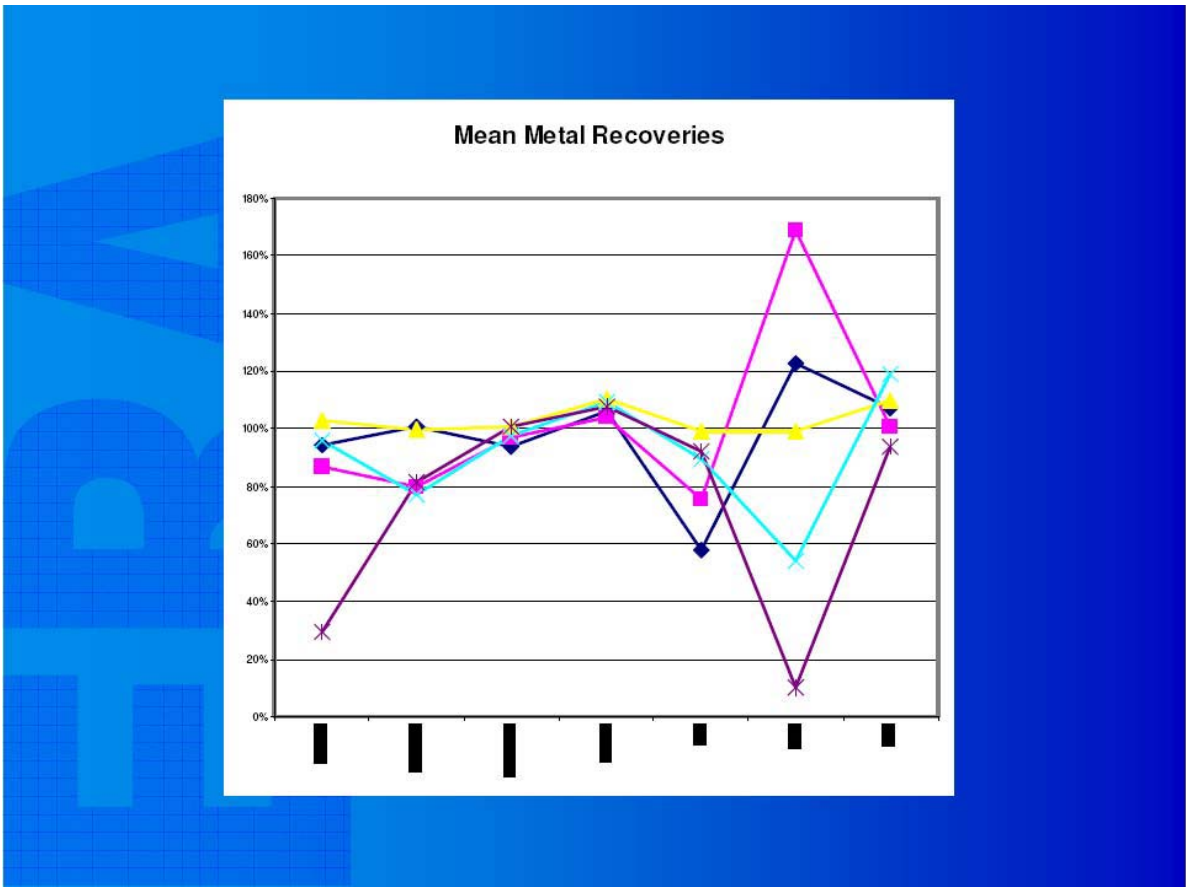
Herbicides

- Two labs.
  - Good recoveries & no false negatives.
- Other three labs.
  - Some DLs too high, false negs. & pos. & results quite variable.
- Methods not rugged.
- RLs achievable, but certainly not consistently.



Metals

- One lab's results quite accurate & precise.
  - Mean recovery (99-111%) and mean RSDs (1-5%).
- Other labs – false pos. in one or more blanks.
- DLs reported above required RLs.
- ICP/MS clearly best, but contamination an issue.
- Data from AA methods problematic.
- RLs achievable; but not consistently achieved.



Thanks

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FALSE-FALSE POSITIVES

Dechant, Gary; Analytical Quality Associates, Inc.

Among the greatest challenges that exist in the environmental industry today are those associated with defining, measuring near, and regulating near the detection limit of an analytical technique. Of specific concern are detects that cannot be reliably confirmed and the associated reaction to these detects. The term "false-false positive" is used for this occurrence and is defined as a result that is a true positive value above the detection limit but that cannot be confirmed with any degree of confidence and, therefore, is routinely classified as a false positive.

Two of the more misused and misunderstood statements concerning detection of an analyte are (1) We are 95% confident that the measured analyte is a detect, and (2) We are 95% confident that we have a detectable concentration in the sample. While these two statements appear similar, they are very different, and that difference defines the realm of the false-false positive.

To understand the difference between these two statements, one must look at the definition of a detection. For the purpose of comparison, a detect is considered to be a result at or above the concentration at which one is 95% confident the value is not zero. To determine this concentration, methods such as those described in *40 CFR 136, Protection of Environment: Guidelines Establishing Test Procedures for the Analysis of Pollutants*, are used. The "detection limit" is defined as the concentration at which there is only a 5% probability of a positive result being derived from a zero concentration true value. Results above this value are considered to be detects at the 95% confidence level.

While this definition supports the first statement, it should be noted that this is a pass/fail test for the comparison of a result against a reference value, the MDL, and it implies only that this specific result derives from a non-zero concentration.

The second statement, "We are 95% confident that we have a detectable concentration in the sample," is a predictive statement implying that given a large number of samples, the laboratory will measure a value greater than the detection limit 95% of the time. To fully understand how this works, one must look at the response distribution of a zero-concentration measurement used to determine the detection limit. Under ideal conditions, this distribution is normal and has an average of zero, and the value at two standard deviations of the response variability above zero is the detection limit. At zero concentration, only 2.5% of a large number of measurements will be greater than the detection limit. As the true value in the sample increases, the actual probability of the result being greater than the detection limit increases, and the probability of the result being less than the detection limit decreases. As the distribution moves up the true concentration axis, one finds that when the true value of the sample is exactly equal to the detection limit, the probability of the measured result being greater than the detection limit is 50% and the probability of the result being less than the detection limit is 50%. At this concentration, regardless of how many samples are analyzed, there is still only a 50% chance of measuring a value greater than the detection limit. If a sample is split with the regulator, there is a 50% chance that one laboratory will show a detect and the other laboratory will show a non-detect. Upon re-sampling, there will be a 50% chance that the detect will confirm and a 50% chance that

the detect will not confirm. Regardless of how many times a sample is taken, for a large population, the distribution of detects and non-detects will be 50% of each centered on the detection limit. Values at these concentrations cannot reliably be used for decision-making.

As this does not meet the criterion of the second statement, one must continue to move the distribution up the true value axis until the point where 95% of all results in a large population, will be greater than the detection limit it reached. That is the point at which the true value is equal to two standard deviations above the detection limit. This point is the minimum concentration value at which it can be predicted that 95% of the laboratory results will be greater than the MDL.

While the laboratories may be required to report down to the detection limit, the data user in the environmental community cannot make sound decisions based on single measurements whose results are between the MDL and two times the MDL. One must also be cognizant of the fact that for true values at or slightly above the MDL concentration, even under extensive research and re-sampling, it is highly probable that whether the true value is above or below the detection limit will be unable to be determined.

In order to better facilitate the appropriate use of data in this category, it is proposed that a new data validation flag be used to identify data that may be able to support decision making, but by itself should not be used in decision making.

Understanding False Positives and False-False Positives

Gary Dechant
Analytical Quality Associates, Inc.

ABSTRACT

In the environmental laboratory, analytical results can sometimes be misleading. One particular case of this is where the analytical result falls near the method detection limit. True values will often be categorized as false positives when they are actually true values, or false-false positives. In order to determine where the potential for false-false positives lies, one must first understand the difference between a "detect" and a "detectable concentration." In order to do so, it is important to know the definition of method detection limit and to review the response distribution at zero concentration used to determine the method detection limit. Because the false-false positive range is equal to the analytical uncertainty of the measurement, it can be quantified using an equation given in *Quantifying Uncertainty in Analytical Measurement* (EURACHEM/CITAC 2000), and the probability that the sample result will fall within that range can be determined. Although less than one percent of laboratory results fall into the false-false positive range, the impact of this occurrence can be significant. It is important to understand the false-false positive and its impact on the environmental community, and once understood, to develop a system that will effectively deal with it.

INTRODUCTION

Among the greatest challenges that exist in the environmental industry today are those associated with defining, measuring near, and regulating near the detection limit of an analytical technique. Of specific concern are detects that cannot reliably be confirmed and the associated reaction to these detects. The term "false-false positive" is used for this occurrence and is defined as a result that is a true positive value above the detection limit but that cannot be confirmed with any degree of confidence and, therefore, is routinely classified as a false positive.

Of particular concern are the common responses to measured values that fall within this classification. These responses include re-analysis, re-sampling, and other additional investigations that are generally costly and time consuming. Even after expending more resources investigating these results, one cannot definitively determine whether or not the sample or sample location has a detectable concentration of analyte. In fact, multiple sampling and replicate analyses of these samples can yield results that support opposite conclusions.

It is important to fully understand where the false-false positive originates from and the impacts it has on the environmental community. From there, a commonly accepted industry standard practice can be adopted to lessen the impact of the false-false positive.

UNDERSTANDING THE FALSE-FALSE POSITIVE

Detect Versus Detectable Concentration

Two of the more misused and misunderstood statements concerning detection of an analyte are (1) We are 98% confident that the measured analyte is greater than zero; that is, the result is a detect, and (2) We are 98% confident that we have a detectable concentration in the sample. While these two statements appear similar, they are very different, and that difference defines the realm of the false-false positive.

To understand the difference between these two statements, one must look at the definition of detection. The currently accepted definition of a detect is considered to be a result at or above the concentration at which one is 98% confident the value is not zero. To determine this concentration, methods such as those described in 40 CFR 136, Protection of Environment: Guidelines Establishing Test Procedures for the Analysis of Pollutants, are used. This defines the detection limit as three standard deviations above zero of the variation, or uncertainty, of the signal or response. The "detection limit" is the concentration at which there is only a one percent probability of a positive result being derived from a zero concentration true value. Results above this value are considered to be detects at the 98% confidence level. While this definition supports the first statement, it should be noted that this is a pass/fail test for the comparison of a result against a reference value, the method detection limit (MDL), and it implies only that this specific result derives from a non-zero concentration.

The second statement, "we are 98% confident that we have a detectable concentration in the sample," is a predictive statement implying that given a large number of samples, the laboratory will measure a value greater than the detection limit 98% of the time. To fully understand how this works, one must look at the response distribution of a zero-concentration measurement used to determine the detection limit.

Response Distributions

Under ideal conditions, the response distribution of a zero-concentration measurement is normal and has an average of zero (Figure 1), and the value at three standard deviations of the response uncertainty above zero is defined to be the detection limit. At zero concentration, only one percent of a large number of measurements will have values greater than the detection limit. As the true concentration in the sample increases, the actual probability of the result being greater than the detection limit increases, and the probability of the result being less than the detection limit decreases. As the distribution moves up the true concentration axis, one finds that when the true concentration of the sample is exactly equal to the detection limit, the probability of the measured result being greater than the detection limit is 50% and the probability of the result being less than the detection limit is 50%.

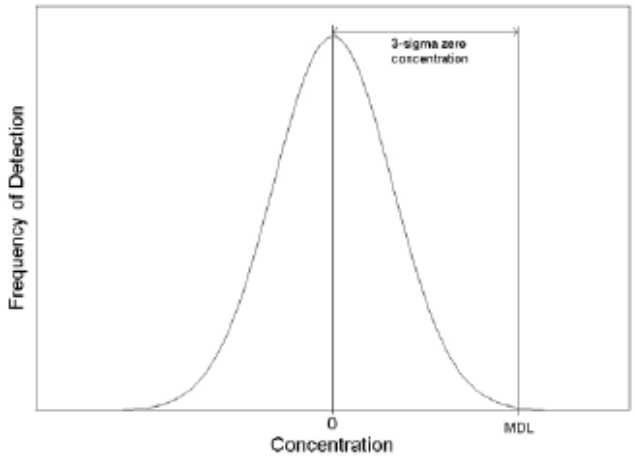

Figure 1: MDL Normal Distribution

At concentrations near the MDL, regardless of how many samples are analyzed, there is still only a 50% chance of measuring a value greater than the detection limit. If a sample is split between two laboratories, there is a 50% chance that one laboratory will show a detect and the other laboratory will show a non-detect. Upon re-sampling, there will be a 50% chance that any detect will confirm and a 50% chance that a detect will not confirm. Regardless of how many times a sample is taken, for a large population, the distribution of detects and non-detects will normally be distributed around the MDL, with 50% of the results detects and 50% of the results non-detects (Figure 2). Therefore, values at these concentrations cannot reliably be used for decision-making. Additionally, re-analysis, re-sampling, and other investigations resulting from any unreliable results will most likely be inconclusive and not at all cost effective.

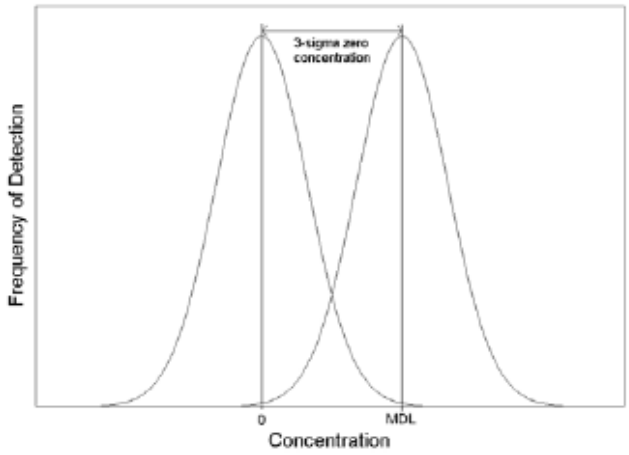

Figure 2: Distribution around the MDL

As this distribution does not meet the criterion of the second statement, one must continue to move up the true concentration axis until the point at which 98% of all results in a large population will be greater than the detection limit is reached. That is, the point at which the true concentration is equal to three standard deviations above the detection limit (Figure 3) is reached. That point is the minimum concentration value at which it can be predicted that 98% of the laboratory results will be greater than the MDL.

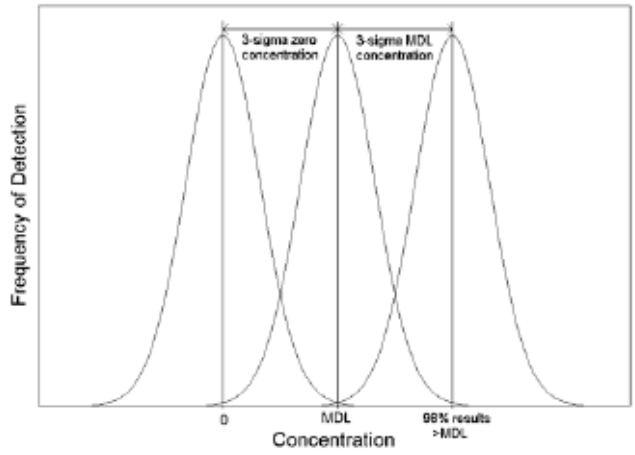

Figure 3: Distribution at Three Standard Deviations above the Detection Limit

Other Factors

Random problems associated with laboratory blanks and general laboratory contamination also exacerbate the issue of false-false positives. Just as with a sample that has a true concentration at the MDL, a blank with a true concentration at the MDL will show up as a low level detection in only 50% of a set of measurements; however, 50% of the samples that have blank or laboratory contamination at this level will have detections identified. In this case, positive sample results with related non-detect blank results will be inaccurately reported as positives.

The Uncertainty

One practice that has been used to minimize the problems with "false positives" is to shift the detect or non-detect decision point to above the MDL and into a range where the measurement is more reliable. While this would appear to be a good idea on the surface, it actually makes the situation worse.

The false-false positive range is actually the three-sigma uncertainty of the value. In keeping with the definition of MDL, the three-sigma uncertainty at the MDL is almost equal to the MDL. Therefore, the false-false positive range above the MDL is approximately equal to the MDL. Because the false-false positive range is equal to the three sigma analytical uncertainty of the measurement, the false-false positive range will increase as the true concentration is increased.

To estimate the uncertainty, a method based on Section E.4 of *Quantifying Uncertainty in Analytical Measurement* (EURACHEM/CITAC 2000) is used. This approach asserts that although general analytical chemical measurements have, over a large range, a dominant uncertainty that can be approximated using a proportionality constant, it is more appropriate to use a fixed uncertainty at low concentrations near the detection limit. This model was chosen because it is a simple, straightforward approach and the values required are readily available. This principle can be expressed using the general equation:

$$Uc = \sqrt{S_0^2 + (S_1 \times C)^2}$$

Where:

Uc = Total uncertainty at the 68% confidence level (one sigma)
S_0 = Fixed uncertainty
S_1 = Proportionality constant
C = Measured concentration

From this equation, S_0 is the uncertainty associated with a zero concentration sample. According to the definition of MDL given in 40 CFR 136, the MDL is three times the uncertainty of a sample with zero concentration. Assuming a relatively normal distribution around zero, S_0 can be estimated as MDL/3.

The proportionality constant (S_1) is the relative uncertainty of the measurement as a function of concentration. A laboratory control sample (LCS) is generally defined as a known matrix spiked with analytes representative of the target analytes at known concentrations that is taken through the same analytical process as the samples. The variability of the LCS is an estimate of the uncertainty of the LCS at that concentration, and the relative variability at one sigma can be used to estimate S_1 if the concentration of the LCS is very large compared to the MDL; that is, the contribution of the variability from the constant S_0 is small relative to that from S_1*C. For comparative purposes, the ideal matrix of an aqueous LCS is used.

Both the MDL and the relative variability of the LCS are values readily available in a laboratory database.

Using this model, the false-false positive range, as defined by the three sigma uncertainty, at the MDL is:

$$FFR = 3 \times \sqrt{\left(\frac{MDL}{3}\right)^2 + (RU_{LCS} \times MDL)^2}$$

Where:

FFR = False-false positive range
MDL/3 = Fixed uncertainty
RU_{LCS} = Relative variability of the LCS at one sigma
MDL = Concentration of the MDL

For a metals analysis by inductively coupled plasma-atomic emission spectroscopy, RU_{LCS} may be somewhere around 3%, or about 0.03. Therefore,

$$FFR = 3 \times \sqrt{\left(\frac{MDL}{3}\right)^2 + (0.03 \times MDL)^2}$$

$$FFR \cong MDL$$

If the detect/non-detect decision point is raised to 10 times the MDL, then:

$$FFR = 3 \times \sqrt{\left(\frac{MDL}{3}\right)^2 + (0.03 \times 10 \times MDL)^2}$$

$$FFR \cong 1.34 \times MDL$$

Given that the decision point is now at a more reliable concentration, the increase in that false-false positive range may be considered acceptable. However, when this same model is applied to compounds where the RU_{LCS} may be as high as 20%, the model now becomes the following:

$$FFR = 3 \times \sqrt{\left(\frac{MDL}{3}\right)^2 + (0.2 \times MDL)^2}$$

$$FFR \cong 1.17 \times MDL$$

And at 10 times the MDL,

$$FFR = 3 \times \sqrt{\left(\frac{MDL}{3}\right)^2 + (0.2 \times 10 \times MDL)^2}$$

$$FFR \cong 6.08 \times MDL$$

The Probability

The concentration range of the false-false positive range is small; therefore, the probability that a sample result will fall within that range is expected to be very small for analyses such as metals, where the variability is also small. However, this may not be the case for analyses that exhibit a large variability. A quick review of ground water data for one fairly common site over two years resulted in the following: Out of a total of ~40,000 analytical results, approximately 500 were reported as detects, and of the detects, approximately 250, or about 0.6% of the results, were detects between the MDL and two times the MDL.

THE IMPACT OF FALSE-FALSE POSITIVES

Although less than one percent of the results fall into the false-false positive range, the impact of this occurrence can be significant.

For results associated with a split sampling event, there could be as much as a 50% chance that any decisions made using the two results from the split would be exactly opposite. That is, a decision that the analyte is present would be made based on one result, and a decision that the analyte is absent would be based on the other result. This could potentially cause many problems for decisions made regarding regulatory compliance, including the added expense of re-analysis and/or re-sampling.

When compared against historical data, a false-false positive result could be found to be inconsistent, requiring the laboratory to perform re-analysis. The laboratory would then incur a loss of revenue for a quick response re-analysis. In addition, there is a high probability that the re-analysis will produce a non-detect purely by random chance, and although the end result would be the desired result (a non-detect), it may not be the most accurate result.

If the re-analysis produced another detect, re-sampling may be required to verify the result. In this case, in addition to the funds expended for the routine analysis and re-analysis of the sample, there is an additional cost to acquire another sample and have that sample analyzed. And once again, there is a high probability that the re-sampling and re-analysis will result in a non-detect based purely on chance.

CONCLUSIONS

When a detect/non-detect decision point is defined, any result above that value is a detect. However, a detect does not necessarily identify a detectable concentration. Detects between any detect/non-detect decision point and three standard deviations of the uncertainty in the measurement above that point are real detects but may not be reliably reproduced. While the laboratories may be required to report down to the MDL, the data user in the environmental community cannot make sound decisions based on single measurements whose results are between the MDL and three standard deviations above the MDL (that is, two times the MDL). One must also be cognizant of the fact that for true values at or slightly above the MDL concentration, even under extensive research and re-sampling, it is highly probable that whether the true value is above or below the detection limit will be unable to be determined. Decisions must be made on detectable concentrations, and a detect that cannot be reliably reproduced can only be used as part of a data set and not as a stand-alone data point.

The amount of data that is included within the false-false positive range is small; however, the potential ramifications and cost to the environmental community of mishandling this data is significant enough that the data within this range needs to be specifically identified. In order to better facilitate the appropriate use of data in this category, a new data validation flag should be used to identify this data. This flag should specifically identify data that is not reproducible and that should not be used by itself for decision-making. In addition, it should specifically state that

further investigations are not recommended. A commonly accepted industry standard practice of not responding to these types of detects should be established so that any data challenged by non-technical groups such as concerned citizen groups, the general public, or any other external entity can be justified based on this accepted practice.

REFERENCES

1. 40 CFR 136. *Protection of Environment: Guidelines Establishing Test Procedures for the Analysis of Pollutants*.

2. EURACHEM/CITAC, 2000. *Quantifying Uncertainty in Analytical Measurement* (EUROCHEM/CITAC Guide CG 4, second edition). EUROCHEM/CITAC Working Group.

TUESDAY, AUGUST 29, 2006

PLENARY SESSION

Special Panel: The Health, Depth, and Breadth of the Environmental Monitoring Industry

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The Health, Depth and Breath of Environmental Monitoring in the United States

- A Commercial Laboratory Perspective -

Robert K. Wyeth
General Manager
Severn Trent Laboratories, Inc.

Health

…whether the U.S. environmental testing industry is delivering the quality of data needed?

Health as Data Quality

- Simple “yes” or “no” answer can’t be given!
- Sometimes and from some commercial labs
- All (most) labs strive to provide data that meets the needs of its intended use
- Some labs (fortunately only a few) can’t be trusted to provide quality data.

How do we measure Quality?

- Accreditation
- Audits
- Establish DQO’s
  - Precision
  - Accuracy
  - Representativeness
  - Completeness
  - Sensitivity
- Blind Duplicates/Spikes
- Data Validation

…but what are we measuring?

- Accreditation doesn't assure performance but it's a good start!
  - Reportedly there are more than 10,000 labs in the US
  - Approximately 50% are estimated to be "commercial"
  - Some but not all are accredited
  - Those that aren't don't want to be!
  - NELAC and State accreditations are widely variable and inconsistent in application (and in competence)
- The choice of a laboratory based solely on accreditation is like measuring competence based upon a person holding a degree.

…but what are we measuring?

- Audits
  - Conducted independent of accreditation or certification audits can be valuable.
  - Skill and experience of auditor/assessor dependent
  - Should have validator participation (if required)
  - Need to be interactive with opportunity for significant laboratory input
  - Audits can too frequently show what you may want to see

…but what are we measuring?

- Establishing Data Quality Objectives (DQO)
  - Great in theory but all too infrequently used
  - Client or clients agent establish PARCS without consultation with the laboratory actually doing the work
  - Need to select laboratory and then establish PARCS
  - PARCS must be reasonable and attainable
  - Must be open to changes in Project Scope and even costs.

…but what are we measuring?

- Blind duplicates and spiked blinds are one of the best measures of lab's performance.
  - Prepare spikes in appropriate "matrix"
  - Only use analytes of true interest to the project
  - Cover all methods of interest
  - Gives "true" precision and accuracy estimates to compare with lab QA/QC finding
  - Realize that perfection is not a valid expectation
  - Adds costs and management expertise

…but what are we measuring?

- Data Validation should be an unnecessary expense
- Don't just adopt "Functional Guidelines"
- Insure validation is done by qualified professionals
- Open a dialogue with the laboratory

So what is the Health of the commercial environmental testing industry?.....

Acceptable for the majority of the data but not necessarily from the majority of laboratories. There are numerous actions that both purchasers and providers of these services could/should be made to do to significantly improve our Health!

Depth

....how well the available technologies can detect all contaminants of concern at the required levels with adequate quality.

We are definitely swimming in the shallow end of the pool!

A little History….

We tend to think of ourselves as a rather mature industry but in fact (at least in this regard) we are far from it.

- This industry began with Water Pollution control.
- The tests or methods we used (and still use today) were screening tests at best.
  - BOD
  - COD
  - TOC
  - Solids
  - Phenols

A little History….

- As methods developed we continued in the private and public sectors of the testing business to develop screening tests; more sophisticated but screening nonetheless.
- While analyte specificity was added to some methods they, still tended to be used to screen for potential contaminants of concern.
  - TOX
  - RCRA Metals
  - HSL / TAL
  - 8260
  - 8270

Depth as technology to detect all contaminants.

- In combining all approved methodologies, estimate that we can analyze for <5 % of all the potential contaminants of possible concern to Human Health and the Environment.
- Primarily social and regulatory drivers.
- Very little emphasis is apparently given to increasing the depth of our science.

Depth as technology to detect all contaminants.

- Alkyl benzene-sulfonates and degradation products in soil
- Brominated flame retardants (tetrabromobisphenol A)
- Endocrine disruptors
- Estrogens
- Halonitromethanes
- Octyl- and nonylphenols and ethoxylates
- PFOA, PFOS
- Pharmaceutical compounds

Depth as technology to detect all contaminants.

- Personal care products
- Polychlorinated naphthalenes
- Organotins and other organo-metallics
- Steroids
- Antibiotics
- Hormones
- Disinfection Byproducts
- Degradation products

…at required levels with adequate quality.

- Sensitivity is a concern for all method constituents
- Have for years been estimating sensitivities inappropriately
- Too frequently sensitivity reflects what client requests as opposed to what a method can accurately provide
- Generally QA/QC results and ability to obtain DQOs are determined at inappropriate levels to provide meaningful insight at lower reporting levels

So what is the Depth of the commercial environmental testing industry?.....

To meet regulatory requirements, the Depth of the commercial testing industry is adequate.

To provide data which will assist in protection of human health and the environment, the Depth of our industry is shallow and there are few drivers to change this situation.

Breath

… how well the industry is able to measure all contaminants of concern in all matrices of concern.

Measurement by matrices

- Probably the industries greatest weakness
- Industry has grown primarily as a result of concerns in aqueous matrices
- Vast majority of approved methods support aqueous sample analyses
- Air, soil, solid and hazardous wastes, biota, tissues are problematic for many contaminants of concern.

So what is the Breath of the commercial environmental testing industry?.....

- Frankly, pretty narrow!
- Current literature does support activity in this area.
- Too frequently attempts are made to adapt existing approved aqueous methods to fit a new need.
- Need to apply Sound Science!

From the Commercial Laboratory Perspective, how can we enhance the Health, Depth and Breath of Environmental Monitoring in the US?

First, a few bits of reality…

- We are a commodity!
- The industry remains in an over-capacity situation.
- Quality is assumed.
- Labs are caught in a cost spiral.
- Accreditations are insufficient differentiator.
- Cost is King
- Laboratory services are too infrequently included in the planning process.
- Method and technology development is virtually impossible in a commercial lab
- We are in a political environment which provides no regulatory drivers for change.
- Commonly thought of and/or treated as if fraudulent.
- Qualified chemists at a premium and very difficult to attract/retain.

…but hope is not lost!

Protection of Human Health and the Environment as well as Environmental decision making requires our data!

We have to get better at delivering it.

How Commercial Labs Compete

According to economists, business compete (will survive) based on three premises:

- Product Superiority
  - Labs virtually barred from competing at this level
  - Special products in our business revolve around innovation to processes not products
  - Enhancing data product & delivery our only option
- Customer Intimacy
- Operational Excellence

Proposed Actions for the Commercial Laboratory Community

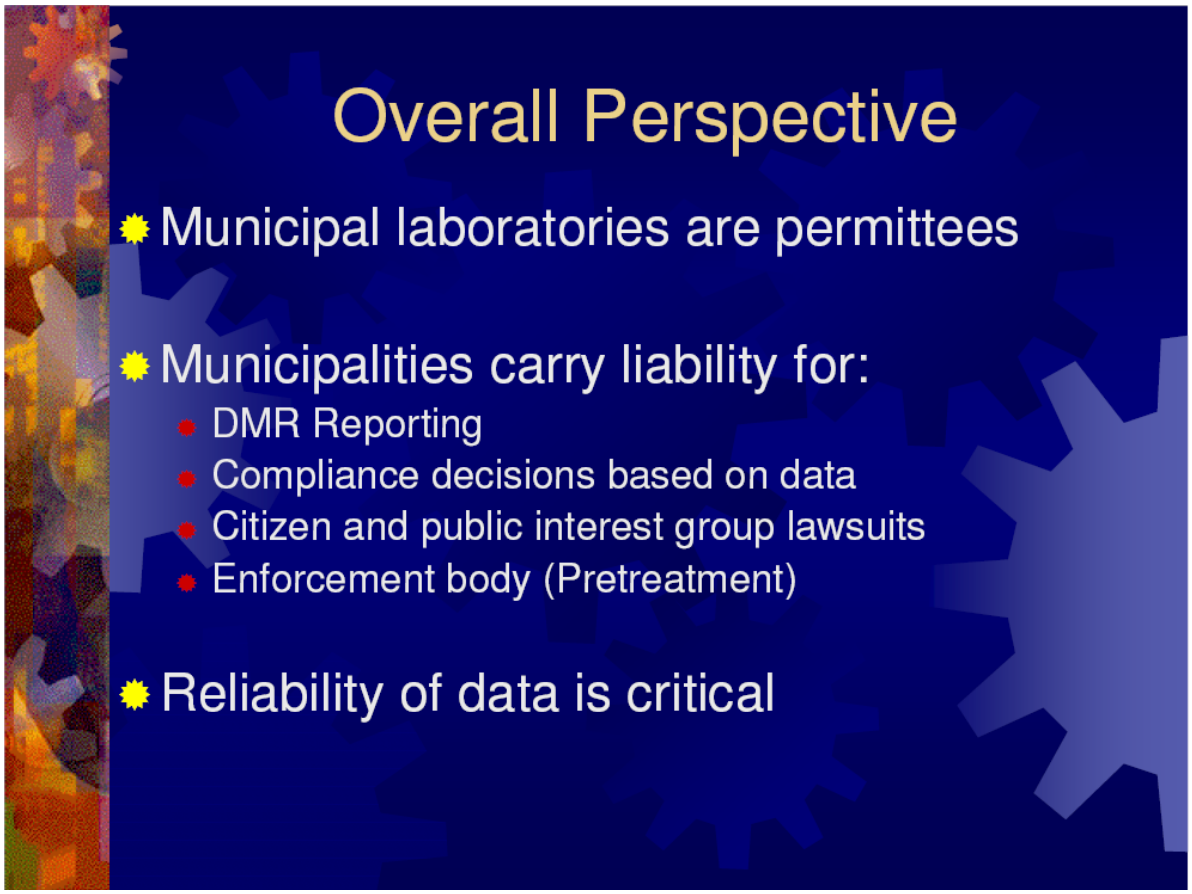
- Require Laboratory Accreditation
- Develop, implement a mandatory requirement for Quality Systems in all labs
- Promote PBMS/Performance Approach
- Employ Sound Science over convenient policy
- Develop a partnership with EPA
  - Stress critical nature of what we do
  - Share common goals of serving the public

THE ENVIRONMENTAL MONITORING INDUSTRY: MUNICIPAL PERSPECTIVE

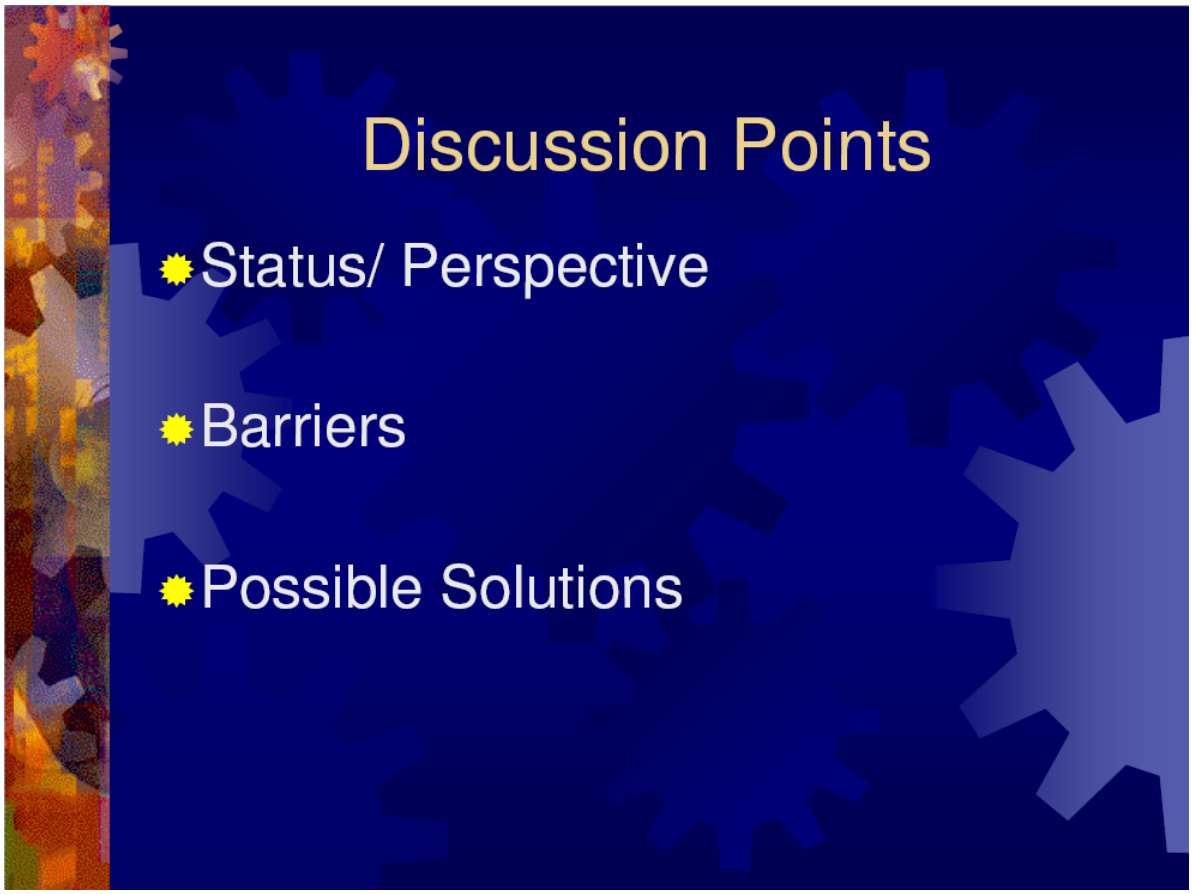
Jim Pletl, Chief, Technical Services
Stacie Metzler, Quality Assurance Manager
Paula Hogg, Chief, Laboratory
HRSD
Virginia Beach, VA

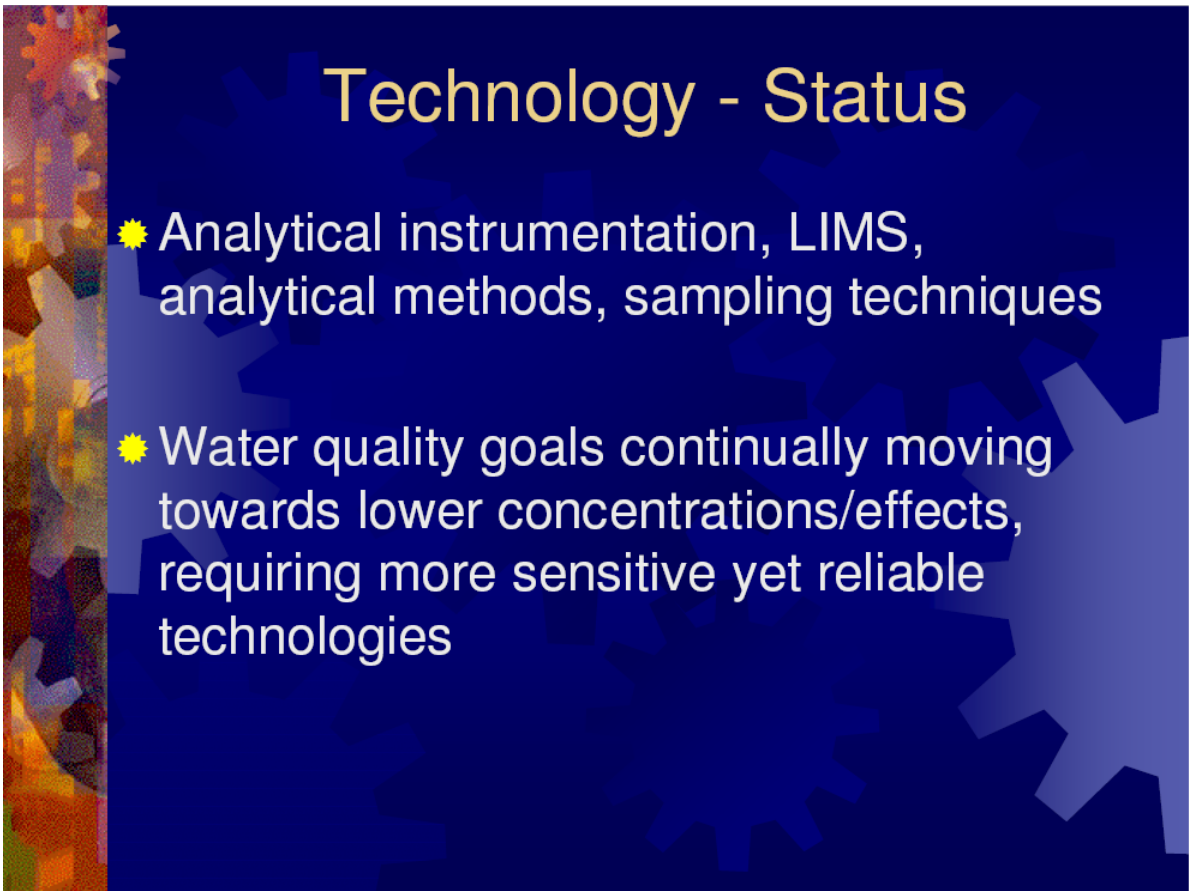
Overall Perspective

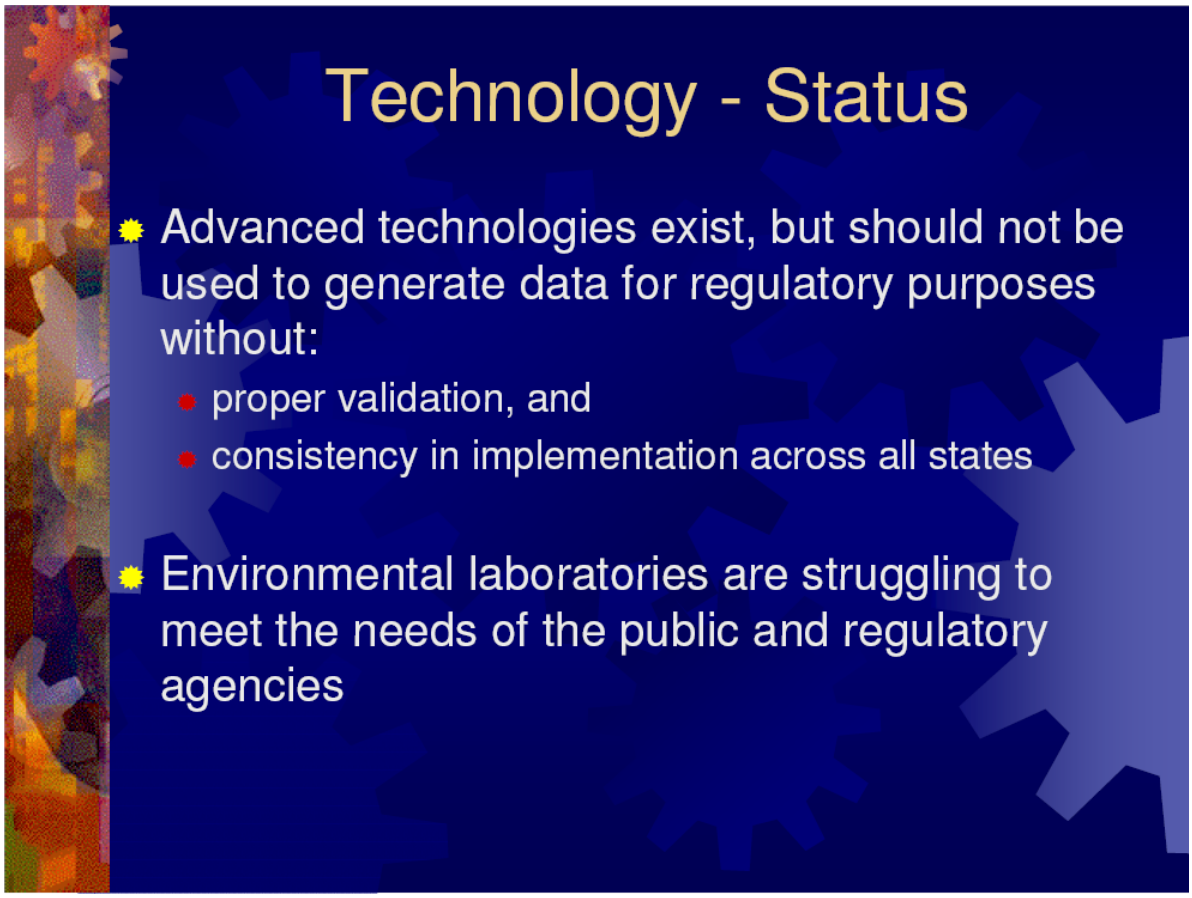
- Measurement systems and their objectives form the foundation for the environmental monitoring industry
- The federal government must ensure these systems are properly developed, tested and implemented nationally
  - Consistency
  - Legal equity
  - Environmental protection
- Only 40 CFR methods can be used to generate compliance data for regulatory uses

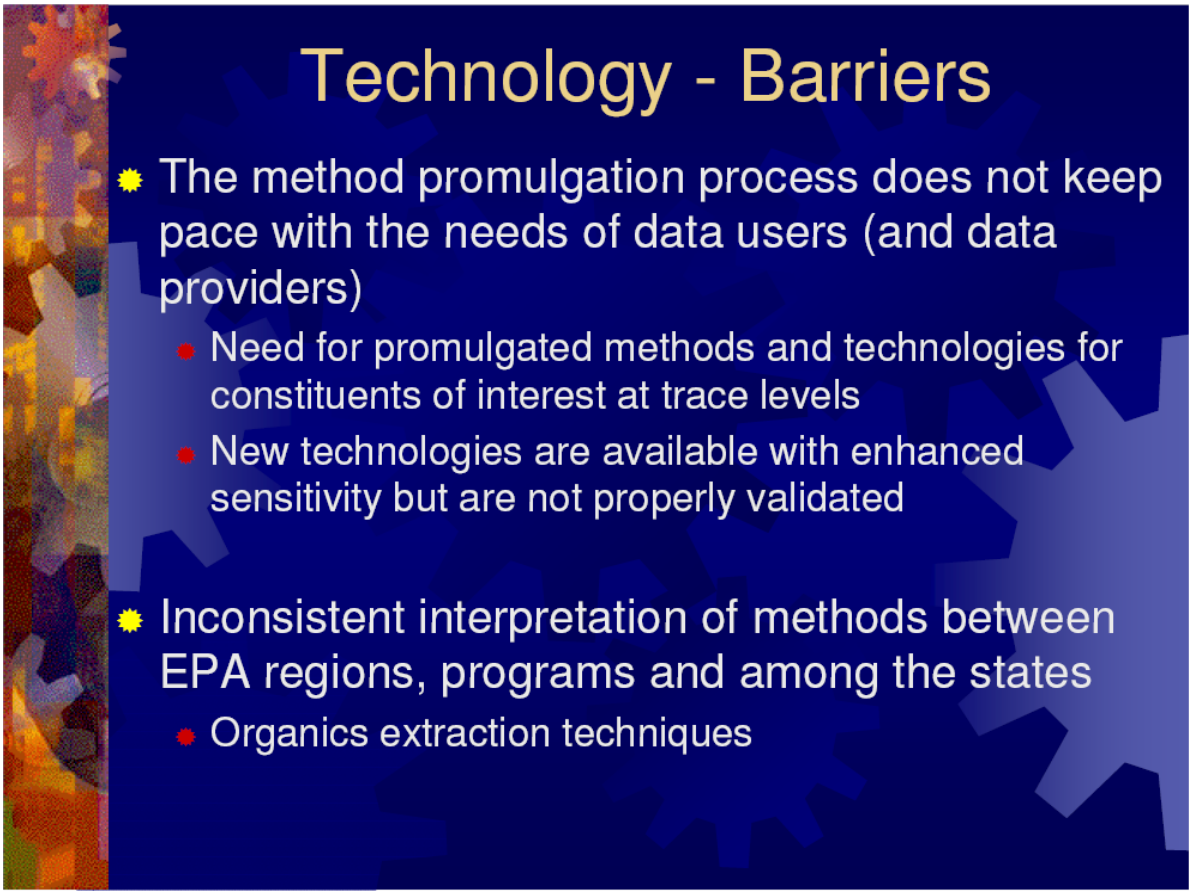

Overall Perspective
Municipal laboratories are permittees
Municipalities carry liability for:
DMR Reporting
Compliance decisions based on data
Citizen and public interest group lawsuits
Enforcement body (Pretreatment)
Reliability of data is critical


Topics
Technology
Emerging Contaminants
Detection/Quantitation
Laboratory Accreditation


Discussion Points
Status/ Perspective
Barriers
Possible Solutions


Technology - Status
Analytical instrumentation, LIMS, analytical methods, sampling techniques
Water quality goals continually moving towards lower concentrations/effects, requiring more sensitive yet reliable technologies


Technology - Status
Advanced technologies exist, but should not be used to generate data for regulatory purposes without:
proper validation, and
consistency in implementation across all states
Environmental laboratories are struggling to meet the needs of the public and regulatory agencies

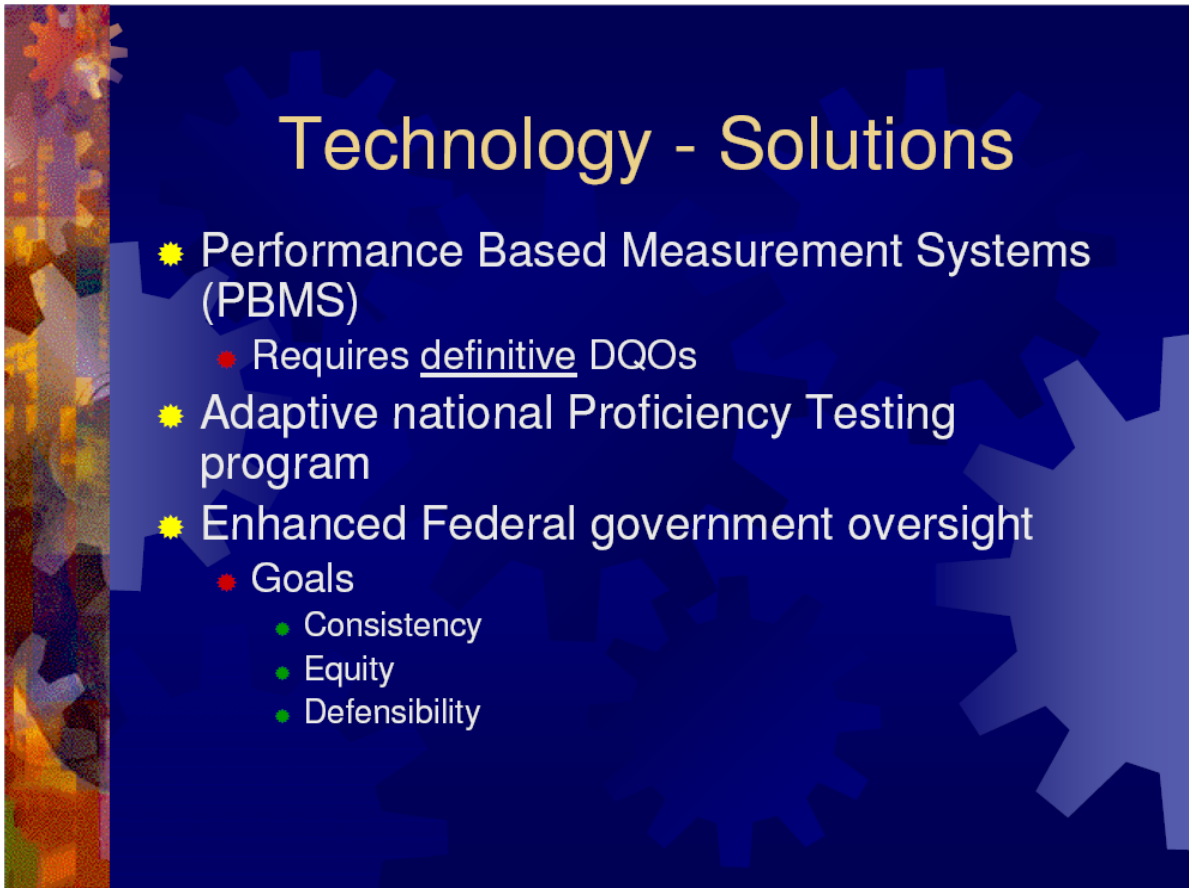

Technology - Barriers
The method promulgation process does not keep pace with the needs of data users (and data providers)
Need for promulgated methods and technologies for constituents of interest at trace levels
New technologies are available with enhanced sensitivity but are not properly validated
Inconsistent interpretation of methods between EPA regions, programs and among the states
Organics extraction techniques

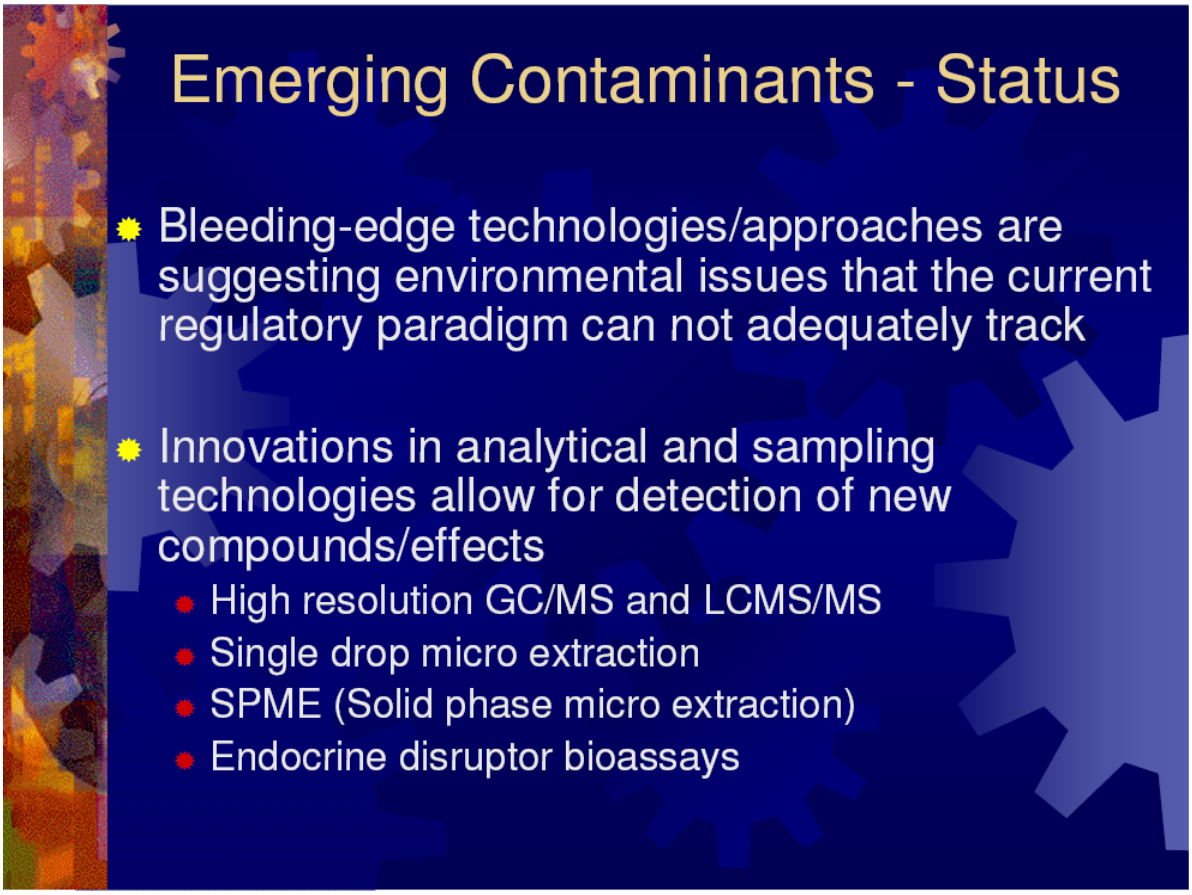
Technology - Barriers

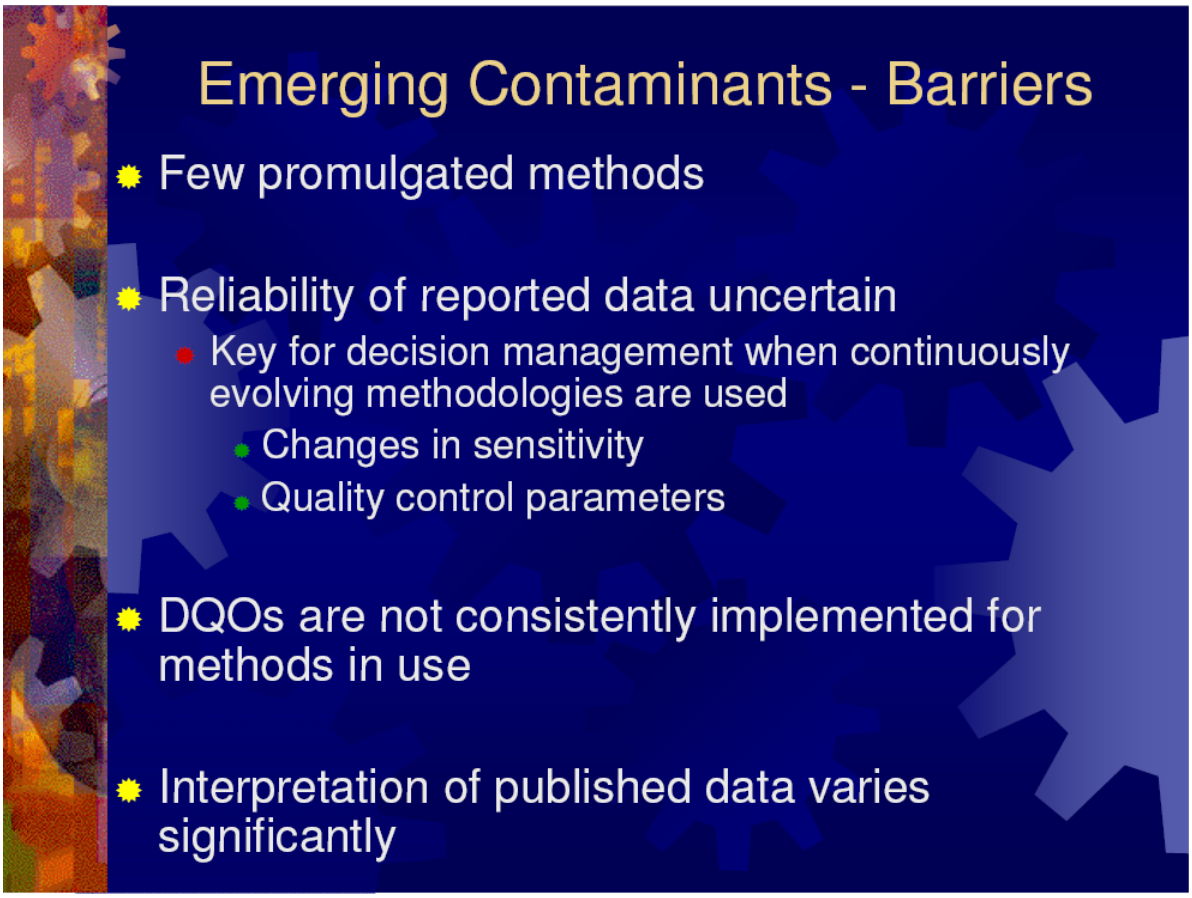
- Where is the line between "improvement" and "modification"?
  - Improvements to approved methods are not accepted though determinative steps remain the same
- Alternative Testing Procedure (ATP)
  - Designed to address new technology
  - Does not guarantee method promulgation
  - Can lead to interstate inconsistencies

Technology - Solutions

- Promulgated system for timely method development, validation and approval
  - Stakeholder involvement
    - Identify issues
    - Include feedback mechanism
- Partnership between EPA and technology industry
  - Facilitate and support technological advancements


Technology - Solutions
Performance Based Measurement Systems (PBMS)
Requires definitive DQOs
Adaptive national Proficiency Testing program
Enhanced Federal government oversight
Goals
Consistency
Equity
Defensibility


Emerging Contaminants - Status
Bleeding-edge technologies/approaches are suggesting environmental issues that the current regulatory paradigm can not adequately track
Innovations in analytical and sampling technologies allow for detection of new compounds/effects
High resolution GC/MS and LCMS/MS
Single drop micro extraction
SPME (Solid phase micro extraction)
Endocrine disruptor bioassays


Emerging Contaminants - Barriers
Few promulgated methods
Reliability of reported data uncertain
Key for decision management when continuously evolving methodologies are used
Changes in sensitivity
Quality control parameters
DQOs are not consistently implemented for methods in use
Interpretation of published data varies significantly


Emerging Contaminants - Solutions
EPA must be more active in addressing public concerns from a scientifically sound perspective
DQOs must be established before samples collected, measurements and interpretation
Partnership between EPA and technology developers needed

Detection/Quantitation - Status

- 40 CFR Part 136 Appendix B – technical and policy issues
  - Lack of MQO's
  - Lack of verification
  - Reporting relative to D/Q limits
  - Matrix effects
- EPA formed FACDQ in 2005 to provide recommendations on how to address issues by 2008

Detection/Quantitation - Barriers

- Varied interpretation of current procedure
  - Instructions
  - Terminology
  - Results in inconsistent detection/quantitation limit determinations
- Inconsistent reporting policies
  - Regulatory decisions

Detection/Quantitation - Barriers

- Insufficient Data Quality Objectives
  - No standards for laboratory performance
  - Current procedure only has one MQO: 1% false positive rate for detection
  - MQOs for precision and bias are not included
- Impact of changing procedures
  - Procedural - laboratory operations
  - Reporting – laboratories, permittees, States

Detection/Quantitation - Solutions

- Consensus on objectives for using D/Q limits
  - Stakeholders
- Procedure must meet consensus objectives:
  - MQOs
  - Continuing verification
  - Concise and clear
  - Applicable in multiple matrices

Detection/Quantitation - Solutions

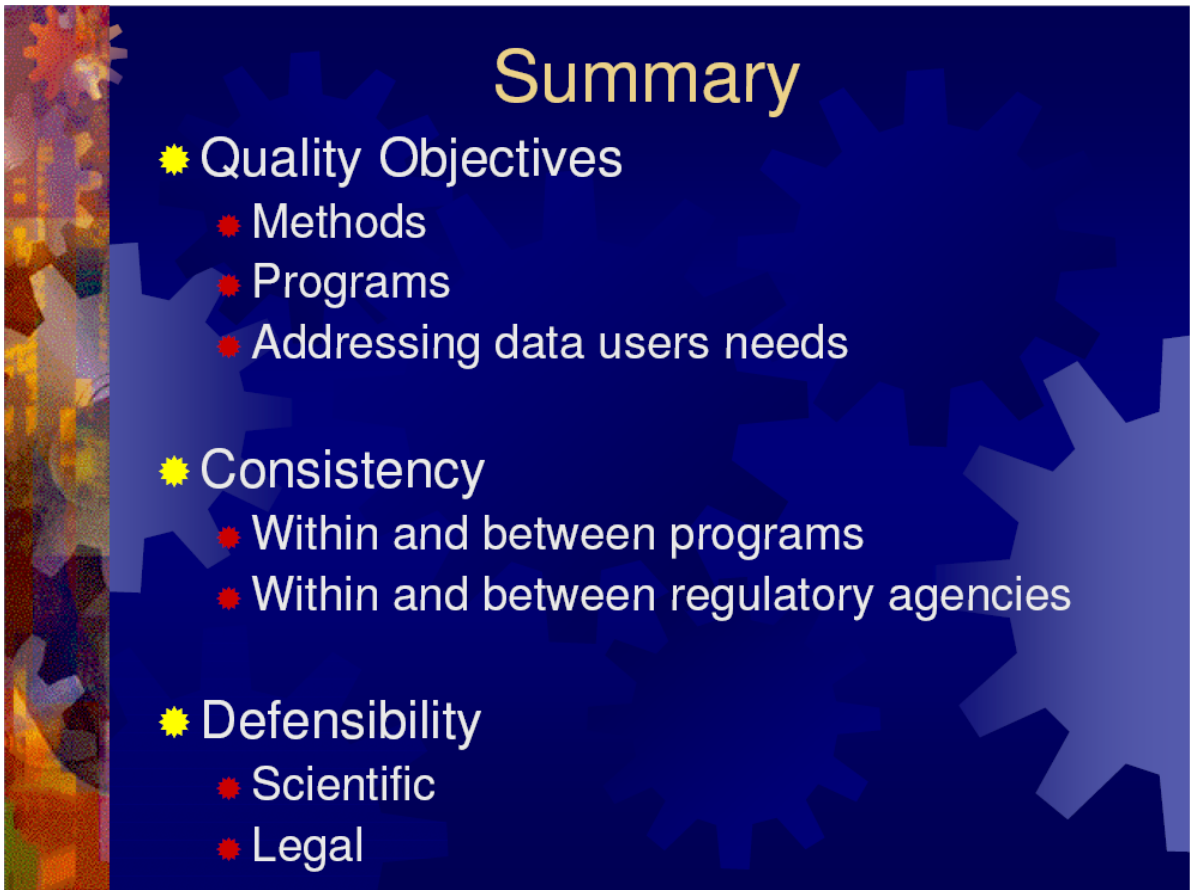
- Promulgate for all EPA programs
- Guidance for consistent implementation
- Training and communication on new procedures and guidance from EPA

Lab Accreditation - Status

- National accreditation program non-existent
- Accreditation/certification programs exist:
  - States (SDWA)
  - NELAC
  - Various program-specific inspections
- Inconsistency between programs
  - Multiple standards


Lab Accreditation - Barriers
Lack of consensus across all stakeholders on many issues
Waning federal support or oversight for national accreditation
No infrastructure for support
Program data quality objectives largely not available
National PT program unavailable


Lab Accreditation - Solutions
Federally funded and managed program
Assemble stakeholder groups to achieve consensus
Standards
Programs
Develop objectives for programs
National PT program
Avoid prescriptive standards


Summary
Quality Objectives
Methods
Programs
Addressing data users needs
Consistency
Within and between programs
Within and between regulatory agencies
Defensibility
Scientific
Legal

Health, Depth, & Breadth of the Environmental Monitoring Industry

Dr. Duane Boline
Director, Div. of Health and Environmental Laboratories
Kansas Dept. of Health and Environment

Health

Is the U.S. environmental testing industry delivering the quality of data needed?

Data Quality Objectives

- Data quality requirements are determined by the intended use of the data.
- Data quality objectives are normally established based upon the most restrictive potential use of the data vs. the intended use.

Technical Quality

- Accuracy
- Precision
- Representativness
- Comparability

Defensibility

- Does the analyst have the education and/or experience required to perform the test?
- Is the test method used approved by the accreditating authority for determination of the analyte?
- Was calibration performed within the required time period.

Defensibility (con't)

- Were all QC criteria required by the method achieved?
- Were sample preparation and analysis procedures completed within the required holding time?
- Are all actions related to analysis of the sample properly documented and traceable?

Ask the Customer

- "Delays in completion of environmental projects are often due to the need to assure the data (actually the information based upon the data) is correct."
- "In some cases the quality of testing could be less rigorous and still provide the information needed." (e.g. MDLs, method used, etc.)

Ask the Customer

"The issues involved in sampling provide more variability than the testing methods."

"Anticipate the project manager may not be familiar with testing methods and know there is a faster, cheaper method that will provide the information needed."

Health?

Is the U.S. environmental testing industry delivering the quality of data needed?

How is quality defined and by whom?

Health

- Quality has become a legal measurement vs. a technical measurement.
- The emphasis is focused on high quality analytical data obtained for samples of questionable validity.

Priorities

Politics
Money
Science

Depth

- Are the achievable detection limits adequate?
- How are required limits of detection determined?

Customer Comment

- "A chemist can find almost anything almost anywhere."
- "The detection levels may provide information on concentrations far below that of any significant impact"
- "But do we really know?"

Detection Limits

- Advances in technology have made lower detection limits achievable.
- The toxicity of a substance to a specific organism is unlikely to have changed significantly.
- Do we go lower because it is necessary to obtain information or because we can?

Depth

How well do the current technologies detect all of the contaminants of concern?

- If a substance is not detected it does not become a contaminant of concern.
- As technology advances new concerns will be discovered.

Philosophical Consideration

"I became a chemist before chemicals became toxic!"

Breadth

How comprehensive is testing relative to the needs?

Protection and sustainability of our environment.

Protection of human health.

Philosophical Question

Do the needs drive advances in technology?

or

Do advances in technology expose needs of which we are unaware?

Ask the Client

"We need tests that will provide faster more accurate results for bacteria and viruses in our public water supplies. The results are variable and normally available after the fact."

Data Usability

- A link between environmental data and public health data is needed.
- Epidemiological data (e.g. cancer clusters) compared to environmental data could be informative.

Biomonitoring

- Toxicity and required MDLs for test methods are primarily empirical.
- Bio-monitoring is in its infancy!
- Environmental Health Tracking and Environmental Health Programs are needed.

Succession Planning

"We have trained our successors to think the same way we think."

"Our industry has developed tunnel vision."

"There is a need for a return to the scientific values of curiosity, creativity, and ingenuity to ensure identification and solutions for the new questions of the future."

Update on Activities Affecting the Industry

National Environmental Monitoring Conference

August 29, 2006

Jerry L. Parr

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AGENDA

Part I: EPA Efforts

- Regulations
- Detection and Quantitation
- Method updates
- Other activities

Part II: Related Activities

- New and emerging analytes
- Laboratory accreditation
- DOD Quality System Manual

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Regulations with New/Revised EPA Methods and Monitoring

- 2004 Water Methods Rule (Proposed)
- Stage 2 DBP Rule
- UCMR 2 Rule (Proposed)
- LT2ESTWR Rule
- Biological Methods Rule (Proposed)
- Methods Innovation Rule

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Water Methods Rule

- Proposed April 6, 2004
- 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

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19 New Chemical Test Methods

- ASTM D6508, Dissolved Inorganic Anions by Capillary Ion Electrophoresis,
- QuikChem Method 10-204-00-1-X, Cyanide using MICRO DIST and flow injection analysis,
- Kelada-01, Automated Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate,
- Method CP-86.07, Chlorinated Phenolics by In situ Acetylation and GC/MS,
- EPA 245.7, Mercury by Cold Vapor Atomic Fluorescence Spectrometry,
- SM 4500-Cl, Chlorine by Low Level Amperometry,
- ASTM D6888-03 Available Cyanide by Ligand Exchange-FIA,
- ASTM D 6919-03, Cations and Ammonium in by IC,
- SM 4500-Cl-D. Chloride by Potentiometry,

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New Chemical Test Methods (Cont.)

- ASTM D512-89 Chloride by Ion Selective Electrode,
- SM 4500-CN-F, Cyanide by Ion Selective Electrode,
- ASTM D2036-98 A, Cyanide by Ion Selective Electrode,
- SM 4500-S2-G, Sulfide by Ion Selective Electrode,
- ASTM D4658-92, Sulfide by Ion Selective Electrode,
- SM 4500-NO3-D, Nitrate by Ion Selective Electrode,
- ASTM D99-003, Free Chlorine by Color Comparison Test Strip,
- Method OIA-1677, DW Available Cyanide by Ligand Exchange—FIA,
- Radium-226 and 228 by Gamma Spectrometry, and
- EPA 327.0, Chlorine Dioxide by Colorimetry

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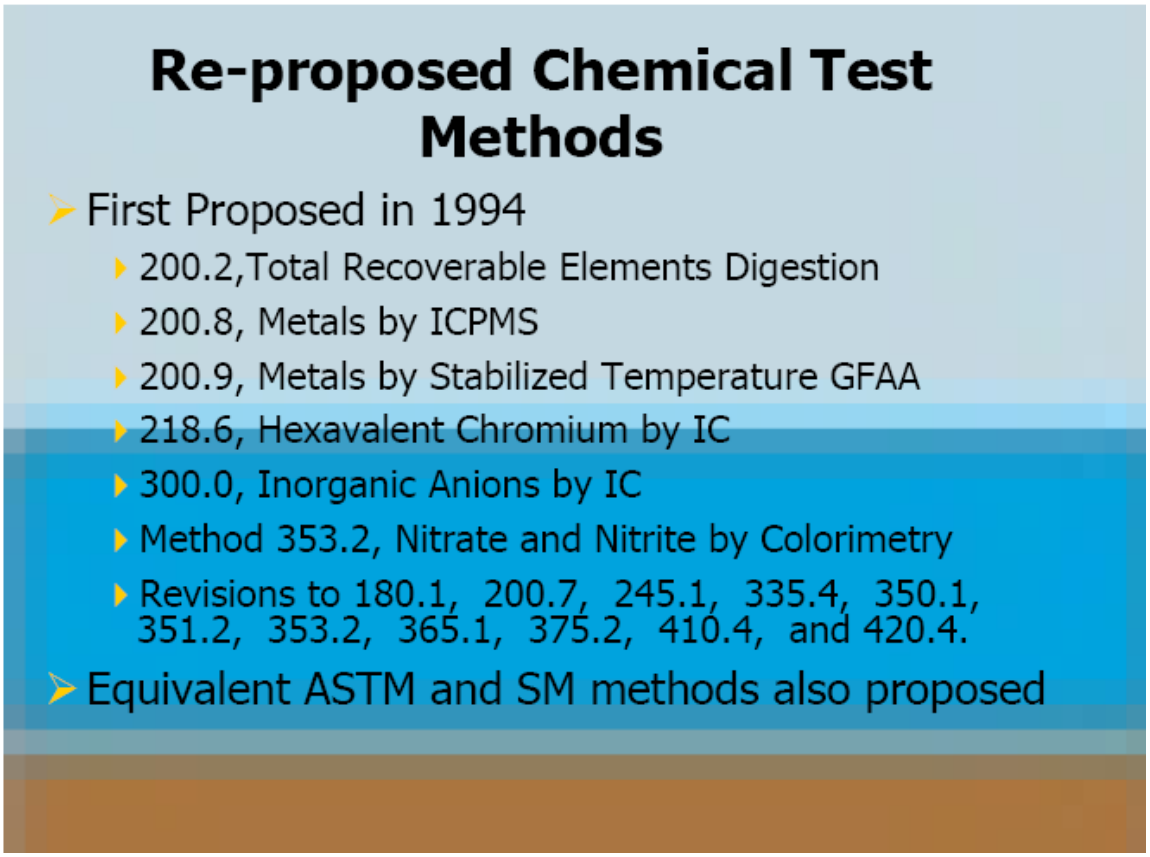
New WET Test Procedure
Microtox 1010
NEM


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
Method 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 proposed

Updated Versions of Current Methods

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

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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

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Revised Method Requirements

- Clarify that analysts need only meet method performance requirements for target analytes
- Allow method modifications without prior EPA approval by passing QC checks
- **QC failure does not allow reporting of results**
- Clarify that results be reported to the level specified in the method or required in the permit, whichever is lower.

NEM

136.7 Reporting

- (a) Demonstration of compliance with a permit must be based upon testing which meets QC requirements in this part, including QC requirements in the method used for the testing.
- (b) **Failure to meet the QC requirements** in this part, including QC requirements in the approved method, **does not relieve a discharger or permittee of timely reporting of test results**.
- (c) Results from tests must be reported to the level specified in the analytical method or permit, whichever is lower.
- (d) Where a conflict is created between reporting requirements in this section and the reporting requirements in an analytical method listed in this part, reporting requirements in this section supersede reporting requirements in the analytical method.

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Withdrawal of Methods

- Delete Methods 612 and 625 for dichlorobenzenes
- Withdraw approval for all oil and grease methods that use Freon-113
- Withdraw Syngenta Method AG-625 for monitoring atrazine

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Side Note Regarding Freon

- Essential Laboratory Use Rule (2/11/02 Federal Register)
  - Three-year exemption for the use of Freon in environmental test methods, until 12/31/05
  - Rule does not apply to laboratories!
- EPA planning to remove 413.1 from Part 136; 413.2 and 418.1 were never promulgated
- EPA Clarification Memo, 12/30/05

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Sampling and Preservation

- Change 4 C to 0-6 C
- Change HT for Cr^{+6} to 28 days
- Various changes for mercury
- No acid preservation for metals in the field
- HT starts at end of composite period
- Other minor changes
- Probable typographical errors

NEM

Side Note on Holding Times

- **EPA Publishes Data on Holding Times!**
  - Hexavalent chromium: 140 days,
  - Polynuclear aromatic hydrocarbons: 100 days,
  - PCBs: 260 days,
  - Pesticides: 217 days,
  - Metals: 364 days.
- **www.epa.gov/nerlesd1/cmb/research/bs_033cmb06.pdf**

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Current Status of this Proposal

- Comment period closed in June, 2004
- Hundreds of comments received
- Microtox method appeared to have the most negative comments
- Method flexibility second, for and against
- EPA indicates final rule this fall (but 1994 proposal was supposed to be done in 1995)

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Disinfection By-Products Rule

- Finalized January 4, 2006
- Monitoring of drinking water for 11 chemicals
  - 4 Trihalomethanes
  - 5 Haloacetic acids
  - Chlorite
  - Bromate

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DBP Methods

- Approved 15 Standard Methods
- Approve three ASTM methods
- Approve EPA Methods:
  - 327.0 Revision 1.1
  - 552.3
  - 317.0 Revision 2
  - 326.0
  - 321.8
  - 415.3 Revision 1.1
- Update the citation for Method 300.1
- Standardize the HAA5 sample holding times and the bromate sample preservation procedure and holding time.

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Other DBP Issues

- Minor clarifications/revisions
- Changes in PT acceptance limits
- Changes in MRLs

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Unregulated Contaminant Monitoring Rule: Phase 2

- Proposed August 22, 2005
- Monitoring of drinking water for 26 chemicals using 9 methods
- Monitoring to occur 2007-2011

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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
- Perchlorate

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

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Proposed Methods

- 314.0 enhanced (IC/Conductivity)
- 314.1 (IC/Conductivity)
- 331.0 (LC/MS or LC/MS/MS)
- 332.0 (IC/MS or IC/MS/MS)
- 527 (SPE/GC/MS)
- 521 (SPE/GC/CI/MS/MS)
- 535 (SPE/HPLC/MS/MS)
- 525.2 (SPE/GC/MS)

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Other Aspects of UCMR 2

- Lowest Concentration Minimum Reporting Limit (LCMRL) proposed
- Participating laboratories must be approved by EPA
- Expected to be final Fall, 2006

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Long-Term 2 Enhanced Surface Water Treatment Rule

- Finalized January 6, 2006
- Monitoring of source water used for drinking water for *Cryptosporidium, E. coli,* and turbidity
- Labs must be approved by EPA for *Cryptosporidium* monitoring
- Promulgated Methods 1622 and 1623 for *Cryptosporidium*
- Established holding time of 30 hours for *E. Coli*

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Biological Methods Rule

- Proposed August 16, 2005
- 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" on preservation and holding time
- Proposed Methods 1600, 1603, 1103.1, 1106.1, 1680, 1681, and 1682

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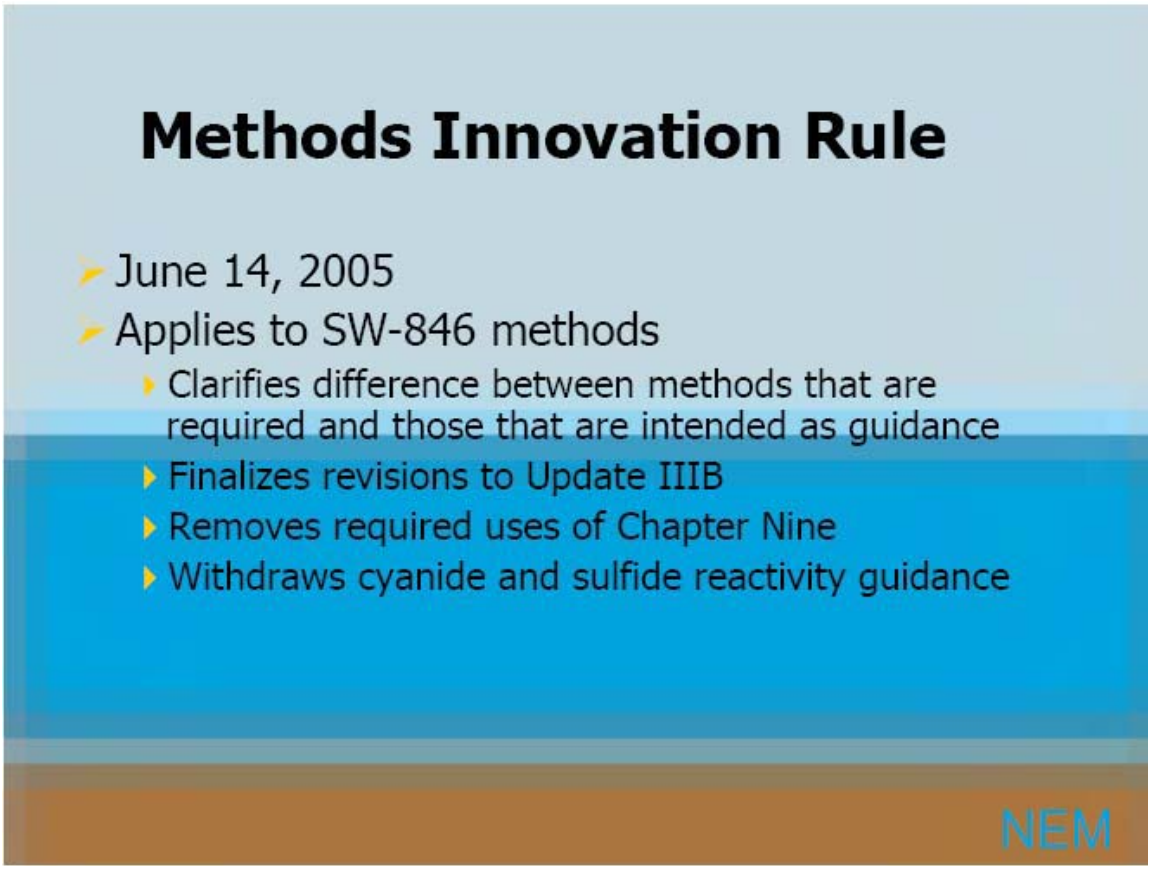
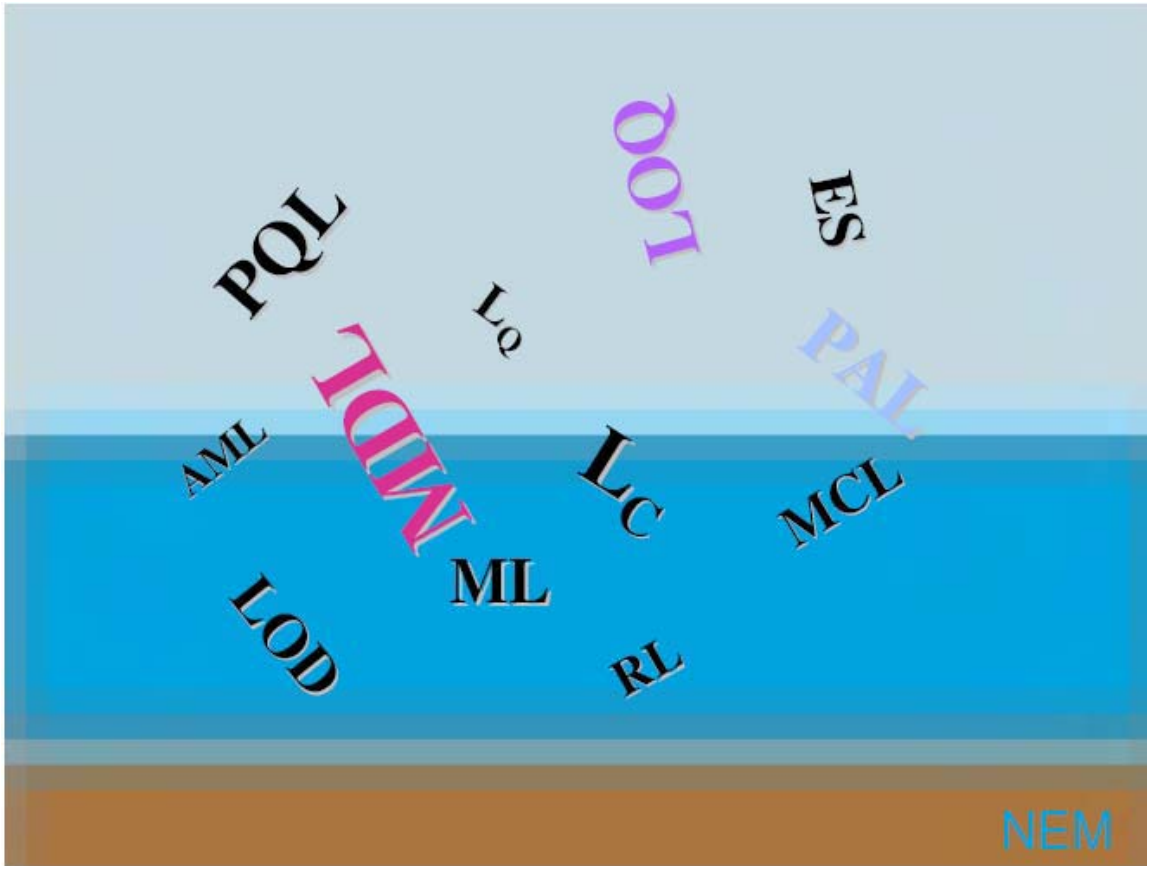

Methods Innovation Rule
June 14, 2005
Applies to SW-846 methods
Clarifies difference between methods that are required and those that are intended as guidance
Finalizes revisions to Update IIIB
Removes required uses of Chapter Nine
Withdraws cyanide and sulfide reactivity guidance
NEM


PQL
LOQ
ES
LQ
MDL
PAL
AML
LC
MCL
ML
LOD
RL
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Lloyd Currie's Fundamental Work

Analytical Chemistry, 1968

- **Critical Level** (L_C)
  - Result indicates detection
- **Detection Limit** (L_D)
  - Procedure may be relied upon to lead to detection
- **Determination Level** (L_Q)
  - Procedure sufficiently precise to yield quantitative result
- Procedure: Standard deviation (*s*) from blank measurements (i.e., precision-only)

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Method Detection Limit (MDL)

- Published in 1981
- Promulgated in 40 CFR Part 136 in 1984
- Fairly easy to do

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Assumptions in the MDL

- Sample standard deviation (7 replicates) represents the population standard deviation
- Blank results are centered around zero
- Qualitative identification is possible
- Sample recoveries are centered around 100%

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What Happened Since 1984?

- 1984 to 2000
  - Many articles, comments and lawsuits about problems with the MDL
  - MDL is widely used (US)
  - Most US labs run MDL studies
- 2000
  - Settlement Agreement
- March 2003
  - EPA proposes MDL revision
- June 2003
  - Consensus Principles provided during comment period
- November 2004
  - EPA withdraws MDL proposal
- December 2004 to Present
  - Federal Advisory Committee (FAC) working on consensus procedure

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Findings

- Some methods give positive blank results.
- 7 replicates analyzed at one time are not representative of the population.
- Some methods cannot detect analytes at calculated detection limits.
- For some methods, low recoveries were observed at low concentrations.

The assumptions use to establish the MDL procedure are not valid!

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A New Approach

- Developed by work group representing broad cross-section of commercial, governmental and scientific organizations (e.g., ASTM, ACIL, Alliance of Automobile Manufacturers, and AWWA).
- Based on definitions of L_Q, L_D and L_C

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Consensus Principles

- Procedures must take into account the variability and bias of method blanks
- The definition of quantitation must include both precision and bias
- False positives and false negatives must be addressed
- Precision, bias and qualitative identification must be addressed
- Must include procedures for ongoing demonstration of sensitivity

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Status of This Approach

- FAC to evaluate 3 options
  - EPA MDL/ML not one of the 3
- Pilot study in 2006
- More detailed "how-to" currently available
- Follow the efforts of the FAC:
  - www.epa.gov/ost/methods/det/index.html

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Lowest Concentration Method Reporting Level (LCMRL)

- Lowest true concentration for which future recovery is predicted with high confidence (99%) to be between 50 and 150% recovery
- Determined during method development
- Implementing laboratory has to verify that level can be achieved
- Rigorous, complex approach for developer; fairly simple for implementing lab
- Proposed as part of UCMR 2
- See *Environ. Sci. Technol.*, **40** (1), 281, 2006

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Forum on Environmental Measurements

- Very high level EPA group
- Address issues on:
  - Competency of EPA laboratories
  - Method validation guidelines
  - Errors in EPA methods
  - Use of the performance approach
- www.epa.gov/osa/fem/fem.htm

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Other Recent Developments

Approval of Discrete Analyzer Methods

- Manufacturer must provide
  - a certificate indicating that the same chemistry was involved
  - a table comparing the performance for a list of criteria

Candidate Contaminant List 2 for Drinking Water

- 9 Microbiologicals and 43 Chemicals
- *70 FR 907*

Manual for Certification of Drinking Water Labs

- www.epa.gov/safewater/labcert/labindex.html

Water Quality Criteria

- Diazinon: 0.17-0.82 ug/L
- Nonylphenol: 7-28 ug/L

Collision Cell Technology Disallowed for Method 200.8

- Drinking water only

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Recent Method Developments

Water Methods

- **529** - Explosives by SPE and GC/MS
- Several new wastewater methods in validation phase

SW-846 Methods

- **3200**: Differentiate mercury species into extractable organic mercury, extractable inorganic mercury, semi-mobile mercury and non-mobile mercury
- **8270D**: Updated version of method for semivolatile organics
- **8260C**: Updated version of method for volatile organics
- **6850** and **6860:** Perchlorate methods under review

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New and Emerging Analytes

- Perchlorate
- PBDEs
- PPPs
- Other PBT
- Bacteria
- Others

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Perchlorate

- 1-4 ppb DLs needed (or is it 24.7 ug/L?)
- Method 314 = 4 ppb
- Contamination Sources:
  - Rocket fuels
  - Pyrotechniques
  - Explosives
  - Dyes
  - Herbicides
  - Bleaching agents
  - Natural sources?
- Included in UCMR 2
- A major focus of this conference

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Method Options

- IC/Conductivity (Method 314)
  - 4 ppb PQL
  - Interferences with high TDS
- IC/MS
- IC-MS-MS
- LC-MS
- LC-MS-MS

Anal. Chem., **76** (2), 469, 2004.

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More Information

- DOD Information
  - Active DOD Website:
    - www.denix.osd.mil/denix/Public/Library/MERIT/Perchlorate/index.html
  - DOD Workshop
    - www.navylabs.navy.mil/DoDChemistmeeting.htm
  - DOD SOPs
    - www.navylabs.navy.mil/Perchlorate.htm#Methods
  - DOD Handbook
    - www.navylabs.navy.mil/Archive/DODPerchlorateHandbook.pdf
- Santa Fe Conference, September 2005
  - www.environmentalforensics.org/workshops.htm
- NEMC 2006

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Polybrominated Diphenyl Ethers

- Flame retardants
- HR-GCMS methods needed
- Increasing bioaccumulation; see:
  - www.epa.gov/waterscience/fish/forum/2004/agenda.htm
- On CDC's list of "nominated chemicals"
  - www.cdc.gov/exposurereport/candidatechemicals
- EPA beginning to regulate
- Included in UCMR 2

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Personal and Pharmaceutical Products

- Widespread occurrence
- USGS very active
  - http://toxics.usgs.gov/highlights/impact.html
- 1 ng/L sensitivity needed
- LC/MS for most analytes

See also: *Anal. Chem.*, 75 (22), 6265, 2003

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A Few Analytes

- hydrocodone
- trimethoprim
- acetaminophen
- caffeine
- erythromycin
- sulfamethoxazole
- fluoxetine
- pentoxifylline
- meprobamate
- dilantin
- TCEP
- carbamazepine
- DEET
- atrazine
- diazepam
- oxybenzone
- progesterone
- iopromide
- naproxen
- ibuprofen
- diclofenac
- triclosan
- gemfibrozil
- ethynylestradiol
- androstenedione
- estradiol
- testosterone
- progesterone

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Persistent, Bioaccumulative and Toxic Substances

- AKA: Persistent Organic Pollutants (POPs)
- International Efforts
- A few anaytes:
  - Hexabromobiphenyl (HBB)
  - Pentabromodiphenyl ether (PBDE)
  - Chlordecone
  - Lindane
  - Perfluorooctane sulfonate (PFOS)
  - Dechlorane Plus ($C_{18}H_{12}Cl_{12}$)

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Other Analytes

- Acetaminophen products
  - 1,4-benzoquinone
  - *N*-acetyl-*p*-benzoquinone imine (NAPQI)
  - chloro-4-acetamidophenol
  - dichloro-4-acetamidophenol
- Glycolic acid
- 28 New disinfection by-products
  - www.epa.gov/athens/publications/DBP.html

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Bacteria

- Listed in the UCMR
  - Aeromonas Hydrophila
  - Algae and toxins
  - Echoviruses
  - Coxsackieviruses
  - Helicobacter pylori
  - Microsporidia
  - Caliciviruses
  - Adenoviruses
- General public concern
- Homeland security issue as well
- Chemical methods being developed

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Possible Methods

- Mouse and invertebrate bioassays
- Protein phosphatase inhibition assays
- Immunoassays
- LC/UV
- LC/MS

See: *Anal. Chem.*, **76** (5), 1342, 2004.

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National Program for Accreditation of Environmental Laboratories
NELAC
Accreditation of >1000 laboratories
13 recognized AAs
Approval of a PTOB
INELA
Significant progress on a new accreditation standard
Other activities to provide assistance
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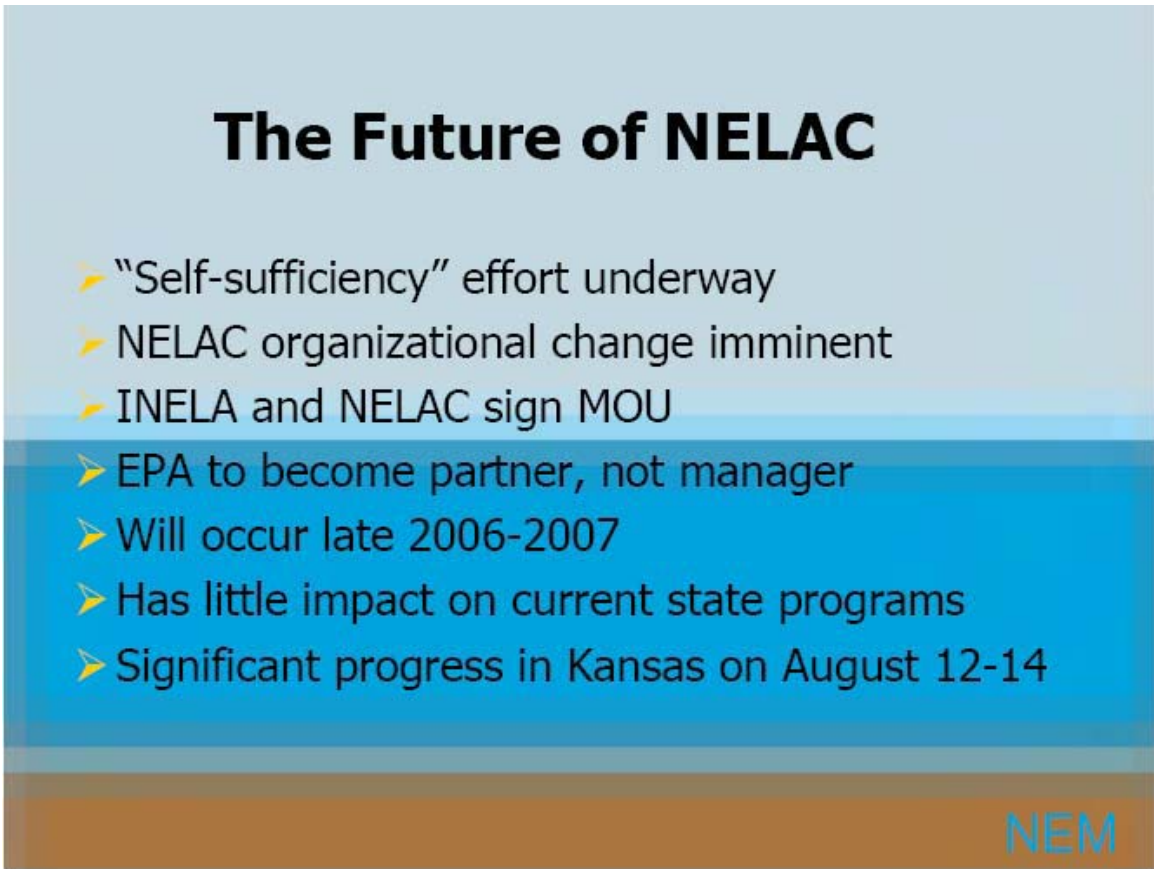
The Future of NELAC
"Self-sufficiency" effort underway
NELAC organizational change imminent
INELA and NELAC sign MOU
EPA to become partner, not manager
Will occur late 2006-2007
Has little impact on current state programs
Significant progress in Kansas on August 12-14
NEM


The Future of the National Program
Secure funding available until 2010.
Large and growing stakeholder group shares common vision of a true national accreditation system.
New INELA standard will make implementation for new states and new laboratories easier.
EPA will continue to have a significant role.
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FORUM ON
LABORATORY ACCREDITATION
Westin Tabor Center
Denver, Colorado
January 28 – February 2, 3007
www.inela.org
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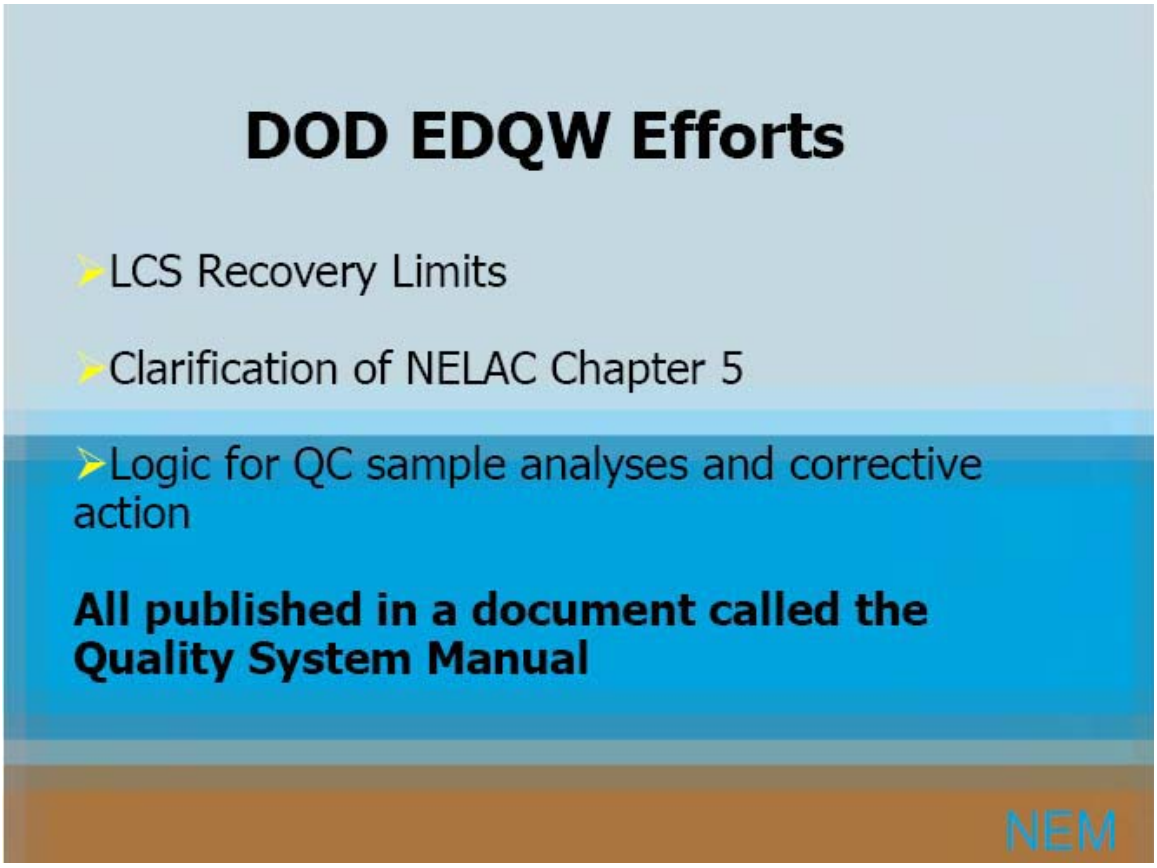
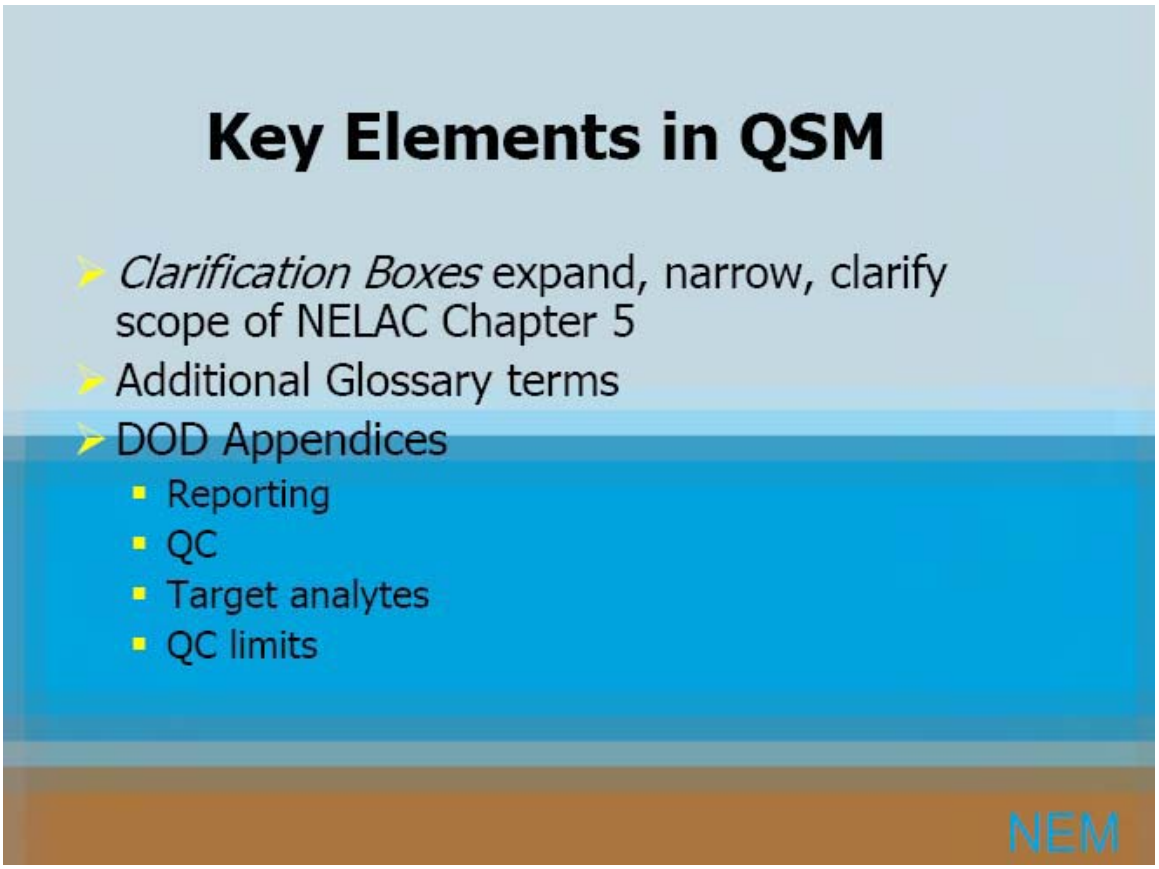
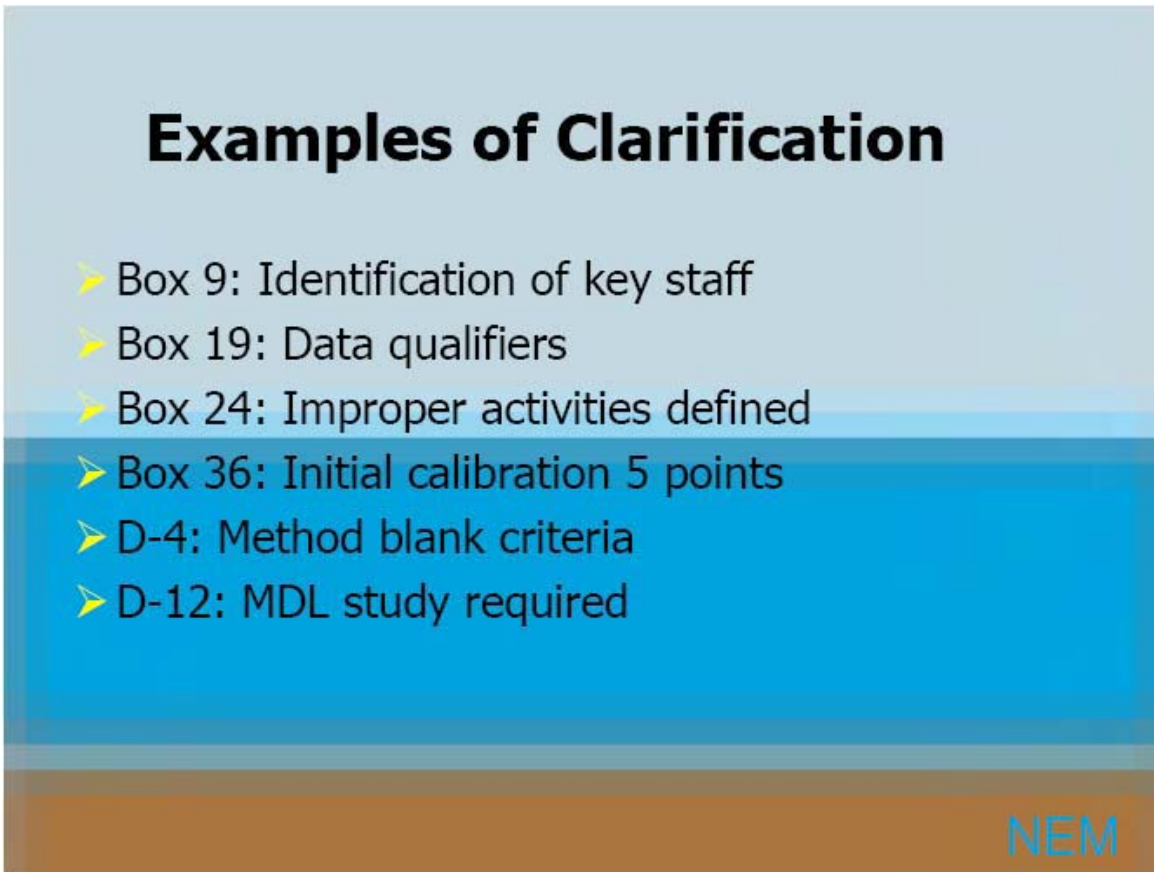
DOD Efforts
to Improve Data Quality
NEM


DOD EDQW Efforts
LCS Recovery Limits
Clarification of NELAC Chapter 5
Logic for QC sample analyses and corrective action
All published in a document called the Quality System Manual
NEM


Key Elements in QSM
Clarification Boxes expand, narrow, clarify scope of NELAC Chapter 5
Additional Glossary terms
DOD Appendices
Reporting
QC
Target analytes
QC limits
NEM


Examples of Clarification
Box 9: Identification of key staff
Box 19: Data qualifiers
Box 24: Improper activities defined
Box 36: Initial calibration 5 points
D-4: Method blank criteria
D-12: MDL study required
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LCS Recovery Limits

- Interlab study of:
  - 10 widely-used methods; soil and water
  - > 200 analytes
  - > 400 samples and > 100,000 data points
- Mean recovery for all analytes were reasonable
  - Mean LCS recoveries ranged from 42% - 114%
  - Median **LCS recovery limit** is **89%**
- Standard deviations were relatively large, making the LCS recovery limits wide
  - **SD** values ranged from **3- 51**
  - Some compounds have minimum recovery limits of 15% or less

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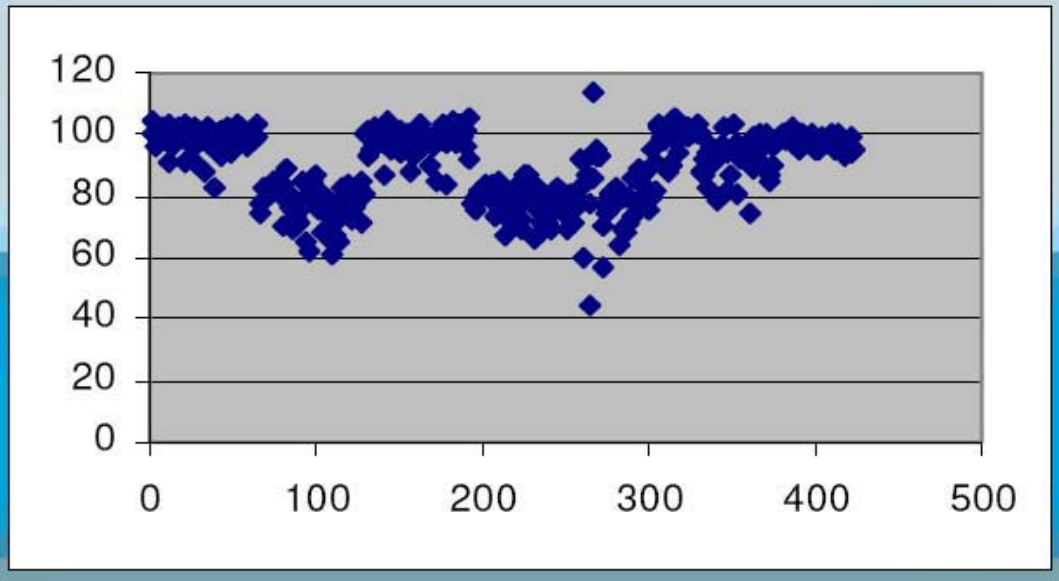
Mean Recovery of All Analytes



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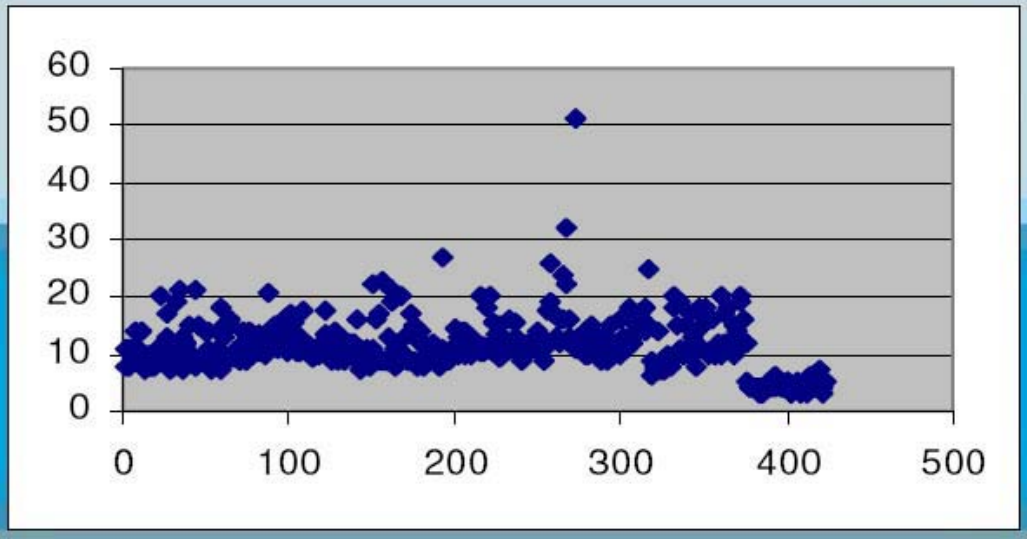
SD of all Analytes



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Benchmark Comparisons

- Limits generally more stringent than PT limits and 1979 EPA limits
- Limits comparable to those in DOD documents
- 95% of mean recoveries and SD are "good" for trace measurements:
  - Recovery > 70%
  - SD < 20%

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Summary

- QSM represents model for providing improved data quality, especially when using SW-846 methods
- LCS limits represent the best performance in a good laboratory
- LCS limits provide foundation for MQO goals under the performance approach

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Issues

- How good do limits need to be (esp. metals)?
- Is 0% recovery an acceptable result?
- Should limits be based on all methods in use, or on those methods that yield better data?
- Is a NELAC accreditation a requirement for performing work for DOD?

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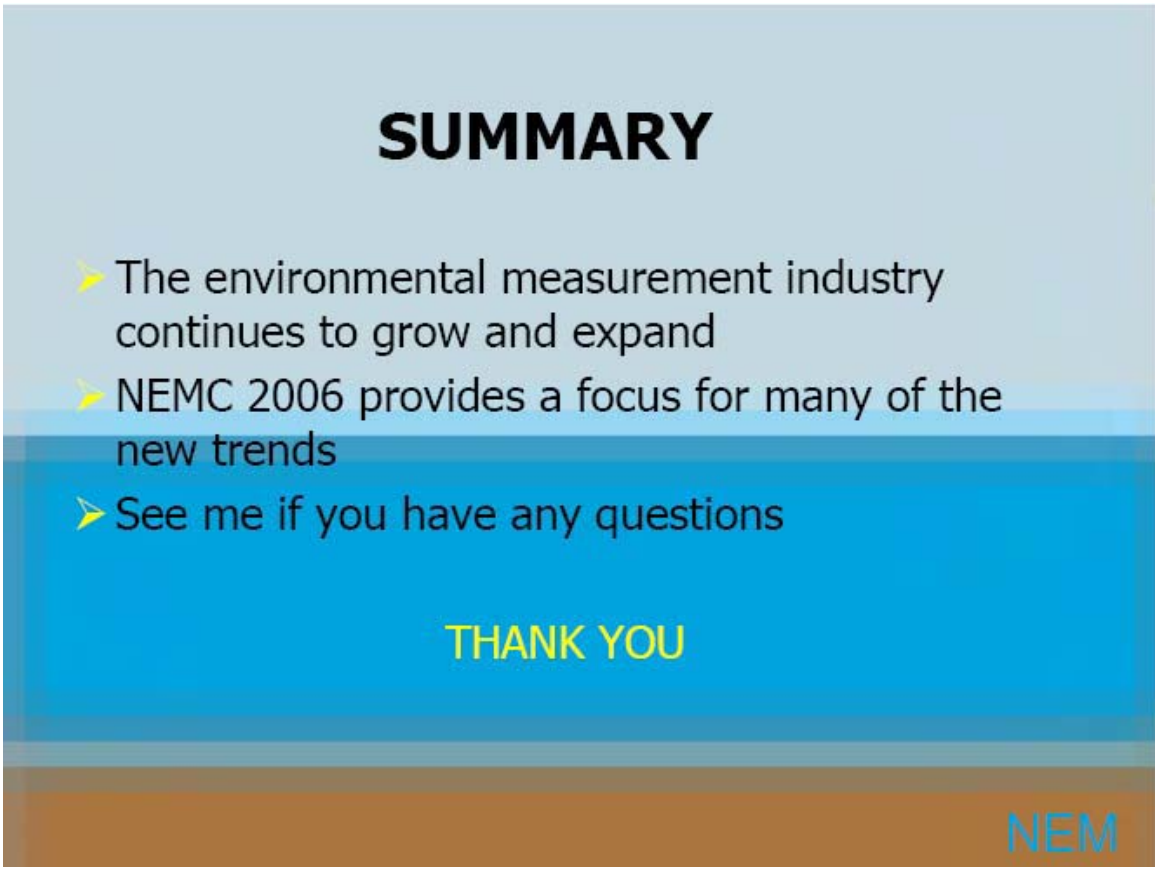
SUMMARY
The environmental measurement industry continues to grow and expand
NEMC 2006 provides a focus for many of the new trends
See me if you have any questions
THANK YOU
NEM

TUESDAY, AUGUST 29, 2006

CONCURRENT SESSIONS

Organic Methods

SPE DETECTION OF CONTAMINANTS IN PUBLIC WATER

Hall, Thomas; Horizon Technology, Inc.

With the growing threat of hazardous chemical agents possibly being introduced into public water supplies and in-coming process water, there is a greater need for monitoring and detection of trace quantities of chemical contaminants. Recent advancements in Solid Phase Extraction (SPE) adsorbent chemistries and new technologies for drying and concentrating samples for GC and GC/MS analysis, allow many water samples to be analyzed quickly and accurately to determine if there are any chemical agents present.

Solid phase extraction (SPE) is based on the principals of classical chromatography. XAD resins were used as early as 1972 to isolate drugs from biological fluids. Since that time, numerous adsorbents for size exclusion, normal and reverse phase, and ion exchange SPE have been developed. Originally configured as a cartridge, SPE disks were introduced in the late 1980s and have been incorporated into many extraction methods. Recently, new adsorbents have been introduced that show improved performance for a wide range of analytes including acid, base and neutral compounds. These adsorbents feature divinyl benzene polymers that have been modified to improve interactions with aqueous sample matrices and provide a mixed mode for solute retention.

In addition to improved chemistries, SPE equipment has also advanced. Automated systems are now available for the extraction, water removal, and concentration steps that are normally required prior to GC-MS analysis. Hydrophobic membranes are now available to remove trace water from the organic extract. In contract to the traditional drying method employing Na2SO4, these membranes permit the drying process to be automated. Concentrators have been commercially available for years; however, because the drying step had to be performed manually they could not be integrated with automated evaporators/concentrators. Today the entire process can be automated from start to finish.

This presentation will demonstrate the effectiveness of automated SPE techniques for extracting a wide range of chemical classes and functionalities to meet these emerging needs. Using EPA Method 3535A as a starting point, extraction methods and techniques will be discussed and recovery data will be reviewed for acid, base, and neutral compounds of interest.

Fast Automated SPE for the Detection and Analysis of a wide spectrum of Chemical Contaminants in Public Water Supplies and Process Waters

Tom Hall
Horizon Technology
www.horizontechinc.com

HORIZON TECHNOLOGY

Agenda

- Overview of Solid Phase Extraction SPE (Using Disks)
- Benefits of SPE vs. Liquid-Liquid Extraction (LLE)
- Discuss EPA Methods for SPE
- Benefits of Automation of SPE
- Optimizing the Extraction
- Drying and Concentration
- Recovery Data
- Summary

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What is SPE?

Solid Phase Extraction is an extraction process whereby an aqueous sample is filtered through a bed of sorbent particles, the analytes of interest are removed from the aqueous sample, and concentrated onto the sorbent. Once concentrated, the analytes are removed from the sorbent by a series of eluting solvent rinses.

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Comparison of LLE vs. SPE Disk Methods

LLE	SPE Disk
Uses 200 - 500 ml solvent	Uses 20 - 30 ml solvent
Shaking / Continuous process	Filtration process
Forms emulsions / surfactants	No emulsions formed
Little Selectivity	Wide Selectivity (adsorbent)
Requires solvent removal	Optional
Takes 2 hours / sample	Takes 20 min /sample

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What are the Advantages of SPE?

- SPE Uses Less Solvent than a Typical LLE Procedure
- SPE is Faster; only 20-30 min for a 1-liter sample
- SPE costs considerably less than LLE
- SPE Provides comparable / better recoveries than LLE
- EPA Methods are constantly being developed for SPE

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Current EPA Methods for SPE

- Drinking Water (500 Series)
- Waste Water (600 Series)
- Oil and Grease (1664A)
- SW-846 (3535A--8000 Series Prep)
- Metals (Evolving)

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The Procedure for Using SPE Disks

- Pre-wash the disk with the final eluting solvent.
- Pre-wet the disk with solvent compatible
- Filter the water sample through disk.
- Elute / Extract the disk with solvent.
- Dry, concentrate, and analyze the extract.

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Why Automate SPE ?

- Increases productivity by improving sample throughput
- Improves accuracy and precision by eliminating variations due to human operators
- Reduces laboratory costs by reducing operator time, glassware, and solvent usage
- Reduces worker exposure to solvents
- Consistent control over critical air dry steps

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SPE-DEX® 4790 Extractor

- Fully Automated, Modular Design
- Run up to 8 Extractors
- Run independently
- Run individual methods
- Use 47, 50, and 90-mm SPE disks
- Designed for all SPE Chemistries
- Preprogrammed EPA methods
- Bench top operation
- High Sample Throughput

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Automated Extractor System
% Recovery of 525 analytes in Lab Fortified Blanks
target conc = 2.0 ug/L

Target Compounds	1	2	3	4	5	Average Std	Dev
Hexachlorocyclopenta	94	98	95	95	96	96	1.4
Propachlor	91	94	96	93	99	95	2.7
Hexachlorobenzene	92	97	94	97	93	95	2.1
Simazine	70	86	83	81	80	80	5.4
Atrazine	90	89	91	87	92	90	1.7
Metribuzin	69	97	86	69	86	81	10.9
Alachlor	95	93	100	100	98	97	2.8
Aldrin	85	88	93	80	94	88	5.2
Metolachlor	84	90	88	100	91	91	5.3
Butachlor	93	84	89	84	93	89	4.0
Bis (2-ethylhexyl) adipate	95	93	94	88	97	93	3.0
Bix (2-ethylhexyl) phthalate	99	100	100	99	98	99	0.7
Benzo(a) pyrene	99	98	98	98	97	98	0.6

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Measuring Throughput

- Measurements include:
  - Number of Samples extracted
  - Samples / FTE
  - Overtime/ Labor Cost Reduction
  - Turn Around Time Reduction

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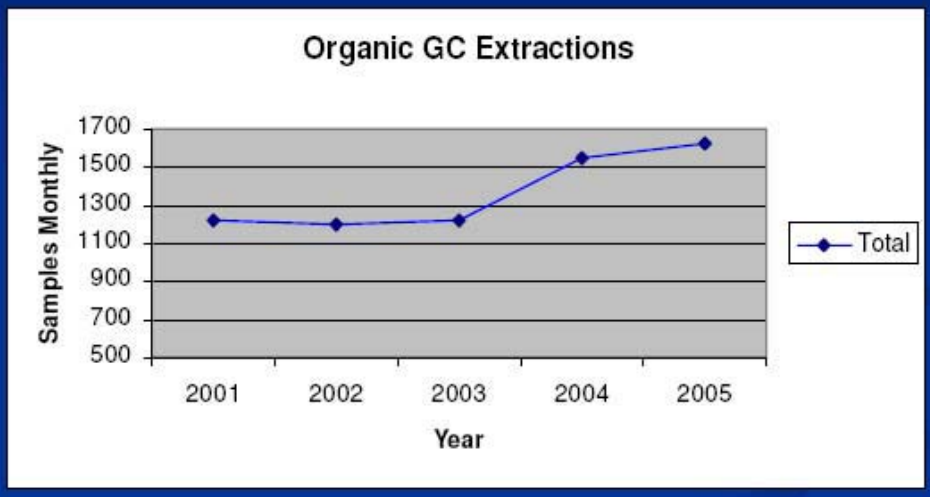
Sample Workload



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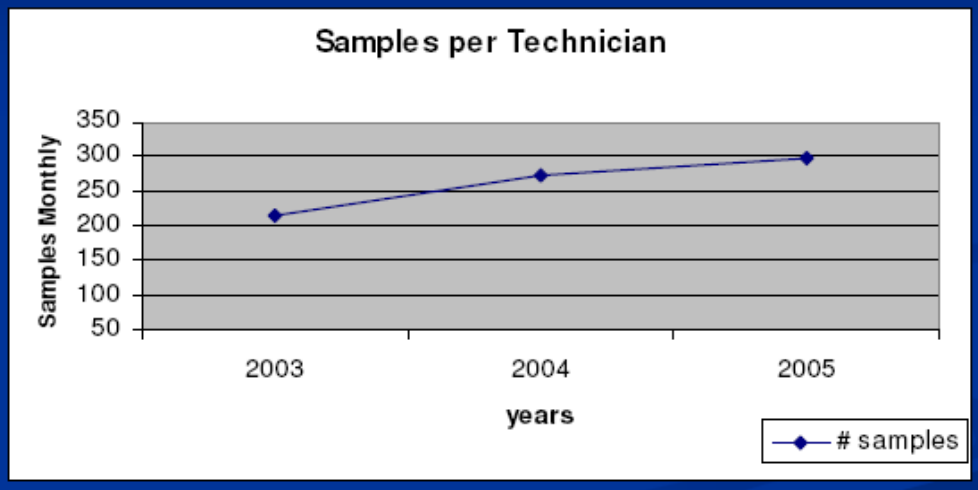
Increased Productivity



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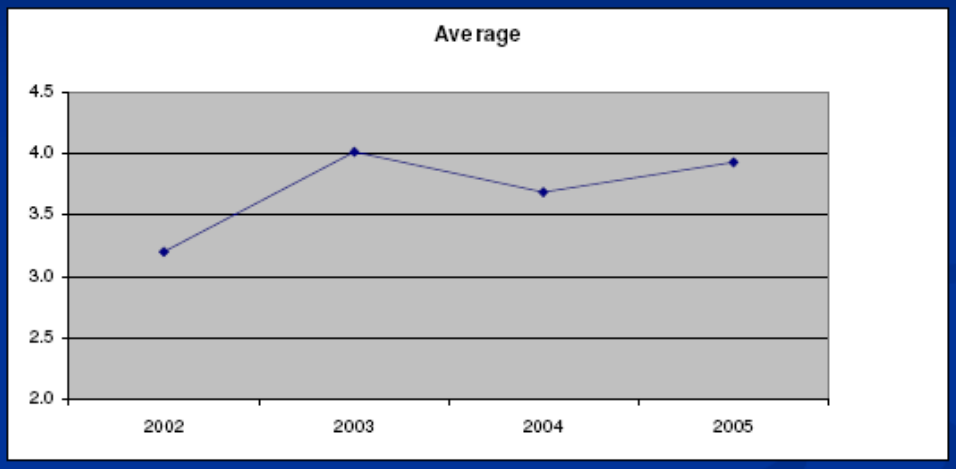
Reduced Labor Cost



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Traditional Concentration Steps

- Drying done with Sodium Sulfate
- Water bath
- Glassware
  - KD flask, Concentrator, Snyder Column
- Nitrogen Concentration
  - N-evap

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How to Solve the Drying Problem?

- Horizon developed the DryDisk ™ Separation Membrane.
- The DryDisk™ is a PTFE membrane, of the proper pore size and thickness, whereby the solvent can pass through, while retaining the residual water.
- The DryDisk™ has been optimally designed to use vacuum to increase the drying process.
  - Typical flow rates are 100 ml / min
- Retained residual water can be re-extracted; improved recoveries.
- DryDisk™ is available in 2 sizes:
  - 65 mm diameter disk
  - 20cc syringe barrel

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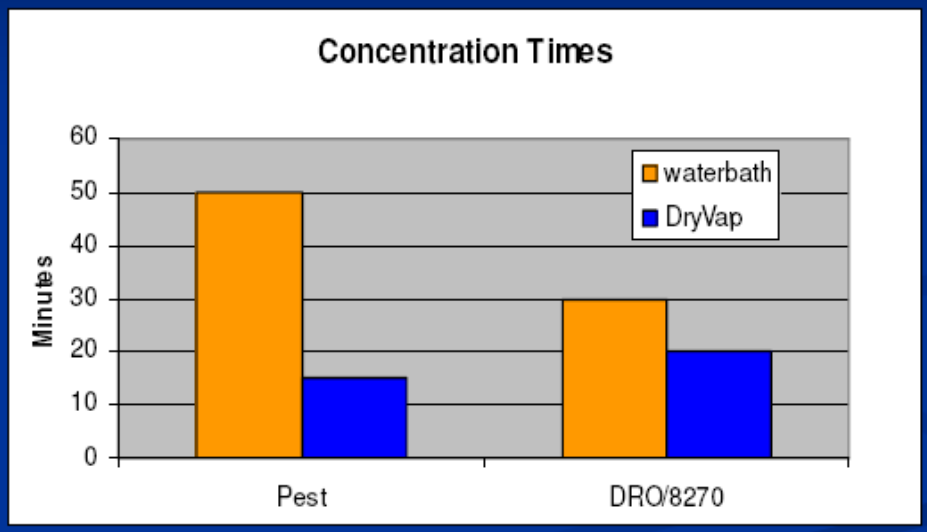
DryVap™ Concentration system

- Automatic In-Line Solvent Drying
- Selectable Solvent Dry Times
- Internal Heating Elements
- Automatic Heater Shutoff
- Utilizes Vac, Gas, and Heat
- Innovative Gas Sparging System
- Individually Sealed Vessels
- Reliable End Point Detection
- Bench Top Operation
- Combines KD and Nitrogen blow down into a single system

HORIZON TECHNOLOGY

Water Bath vs. Dry Vap



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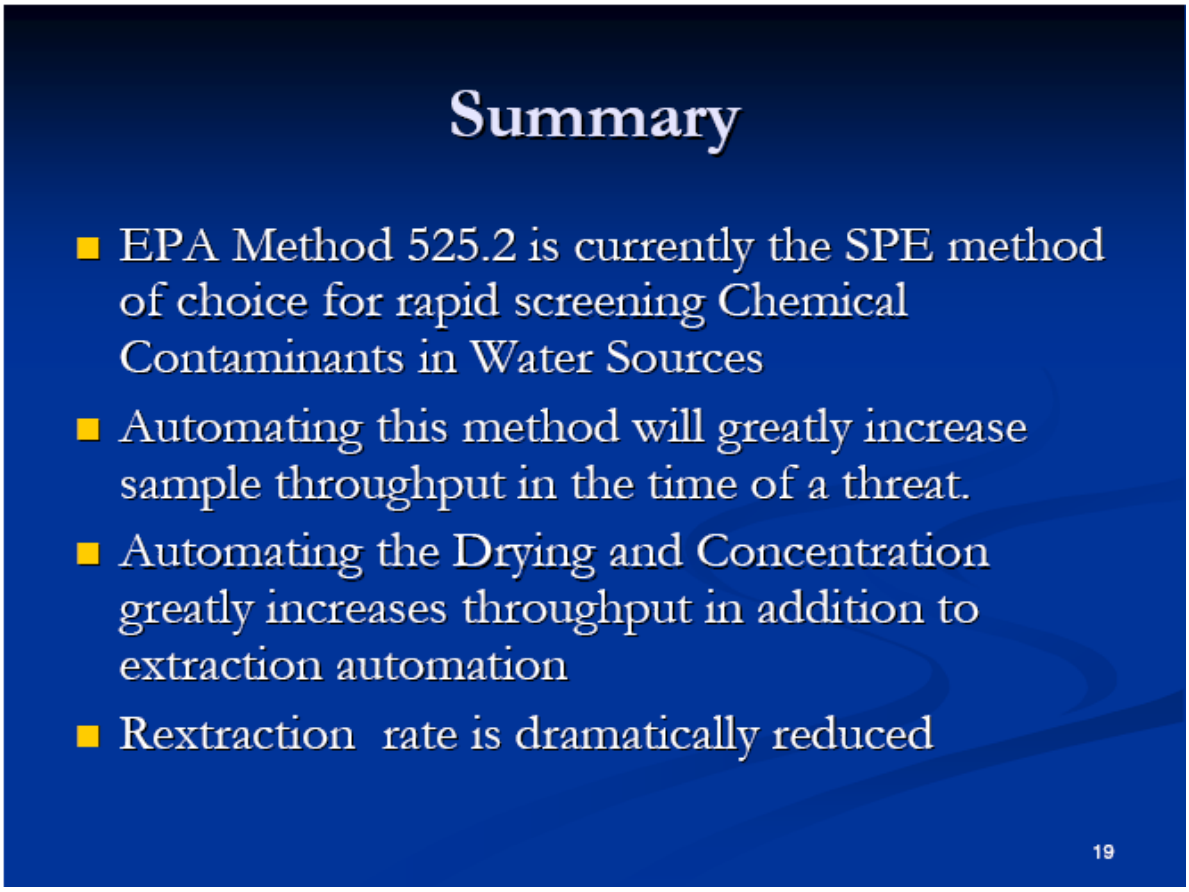
Summary
EPA Method 525.2 is currently the SPE method of choice for rapid screening Chemical Contaminants in Water Sources
Automating this method will greatly increase sample throughput in the time of a threat.
Automating the Drying and Concentration greatly increases throughput in addition to extraction automation
Rextraction rate is dramatically reduced
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ENDOCRINE DISRUPTING COMPOUNDS IN RIVER WATER

Borton, Christopher; Applied Biosystems
Ellis, Robert; MDS Sciex
Ghobarah, Hesham; Applied Biosystems
Jones, Elliott; Applied Biosystems
Olson, Loren; Applied Biosystems
Schreiber, Andre; MDS Sciex

Endocrine disrupting compounds (EDCs) are a wide range contaminates ranging from pesticides, herbicides, pharmaceuticals, personal care products (PPCP), and steroids that are thought to disrupt the endocrine function of mammals and fishes. Recently the biological effects of EDCs have been at the forefront of concern. In order to properly assess the effects of these compounds on our environment it is necessary to accurately monitor the presence in their environment. Presented is a method for analyzing up to 100 EDC compounds using LC/MS/MS. This method presents a straight forward approach for the analysis of these compounds with excellent sensitivity and ruggedness.

The method uses an API 4000™ LC/MS/MS system equipped with a Shimadzu Prominence autosampler and binary LC pump. Ionization is achieved by using electrospray ionization (ESI) and Atmospheric Chemical Ionization (APCI) in the DuoSpray source. All compounds are monitored using two multiple reaction monitoring (MRM) transitions per compound. The most sensitive MRM is used for quantitation while the second MRM is used for qualitative confirmation using ion ratio determinations. Ionization in negative and positive polarity is necessary to detect compounds of various chemical properties. Chromatography is performed on a C18 reverse phase column. A water/actetonitrile gradient with 0.01% formic acid is used for separation. Sample preparation is performed using solid phase extraction.

Up to 100 endocrine disrupting compounds have been analyzed using this methodology. Detection and quantitation of all compounds is achieved down to low part per trillion levels.

Applied Biosystems

LC/MS/MS Analysis of 75 Endocrine Disrupting Compounds, Pharmaceuticals, and Personal Care Products in River Water

Christopher Borton, Loren Olson, Hesham Ghobarah, Elliott B Jones, and Andre Schreiber
LCMS Applications Group
Applied Biosystems/MDS Sciex

Outline

- Introduction
  - What are endocrine distruptors (EDC)
  - Method development strategies and hardware
- 75 EDCs using QqQ scans on a 4000 Q TRAP® System
  - Single injection with polarity switching
  - Simultaneous quantitation and confirmation
- 25 EDCs using hybrid scans on a 4000 Q TRAP® System
  - Multiple injection with dedicated ionization modes (DuoSpray™ Source)
  - High throughput quantitation and spectral confirmation
  - Hybrid scan mode approach

Introduction – Why Study Endocrine Disruptors?

- Endocrine disruptors affect health of humans and aquatic ecosystems
- Pesticides, industrial waste, pharmaceuticals, and personal care products
  - Many act as hormone mimics
- Endogenous hormones - potent effects on development
  - Thus, ECDs can also have adverse effects, even at seemingly low levels
- Criteria for testing not set or are outdated
- Transgenerational effects / bioaccumulation
- Population growth
- New tools and techniques are needed
  - Identify threats to the environment
  - Take action before adverse health effects are seen in organisms

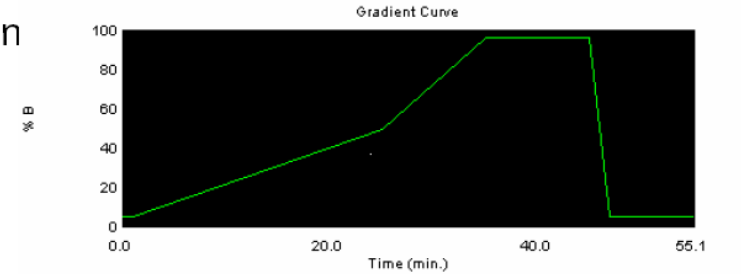
LC/MS/MS Approach to Endocrine Disruptors and PPCP

Strategies for LC/MS/MS Method Development

- Demonstrate feasibility of using different strategies LC/MS/MS for EDCs.
  - Screen, quantitate and confirm in environmental water samples.
  - ESI vs. APCI or DuoSpray™ Source
  - Polarity switching
  - Single vs. multiple injections
  - Performance and practicality
- Evaluate sample preparation
  - SPE
  - Direct detection - no derivatization
- Hardware and software automation
  - Increase efficiency data thoughput
  - Less manual review of data
- Data Reduction
  - Analyst® 1.4.1 and accessory software
  - Draw conclusions quickly and with confidence

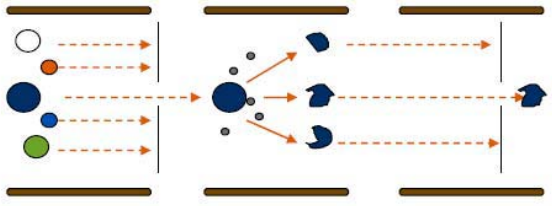
HPLC Method

- Shimadzu LC system
- Column: Phenomenex Ultracarb C_{18} 250 x 4.6mm
- Mobile Phase A: water + 0.01% formic acid
- Mobile phase B: acetonitrile + 0.01% formic acid
- Column oven temperature 28 °C
- Flow of 600µL/min
- Injection of 50µL



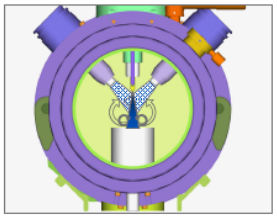
Mass Spec Method

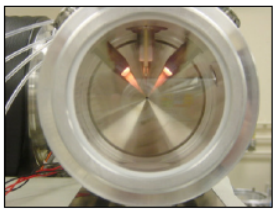
- 4000 Q TRAP® LC/MS/MS system
- Turbo V™ source (ESI)
- Heater temperature of 600 °C
- Polarity switching
- 2 MRM transitions per compound



Turbo V™ Ion Source

- Flowrates: 10µL/min - 2 mL/min
- Orthogonal spray
- Excellent desolvation capacity
- Entrainment of Taylor cone
- Exhaust baffles to minimize tailing
- Fast changeover from ESI to APCI

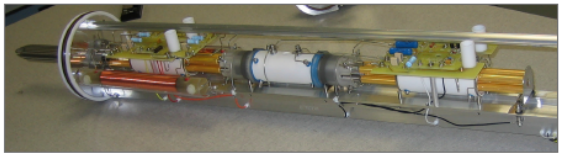




LC/MS/MS Approach to Endocrine Disruptors and PPCP

LINAC® Collision Cell Axial Field Gradient (Linear Accelerator)

Collision Cell Entrance Collision Cell Exit



- Because of a field gradient, ions pass through the collision cell much faster than standard collision cells
- Q2 LINAC® collision cell eliminates cross-talk and allows faster MS/MS scanning without sensitivity losses
- Q2 rods are tilted and separate DC potentials are applied to each pair of rods to create an axial electric field

LC/MS/MS Approach to Endocrine Disruptors and PPCP

Applied Biosystems

Compound	Type	Compound	Type
Acetaminophen	Analgesic	Estradiol 17a	Estrogen
Ketoprofen	Analgesic	Estradiol 17b	Estrogen
Codeine	Analgesic	Ethynylestradiol	Estrogen
Hydrocodone	Analgesic	Progesterone	Estrogen
Acetylsalicylic Acid	Analgesic	Equilin	Estrogen replacement
Ibuprofen	Analgesic	Diethylstilbestrol	Estrogen replacement
Androstenedione	Androgen	Simazine	Herbicide
Testosterone	Androgen	Isoproturon	Herbicide
Warfarin	Anti coagulant	Chlorotoluron	Herbicide
Diclofenac	Anti-arthritic	Atrazine	Herbicide
Meprobamate	Anti-axiety	Chloridazon	Herbicide
Sulfadiazine	Antibiotic	Propazine	Herbicide
Sulfamethoxazole	Antibiotic	Diuron	Herbicide
Sulfathiazole	Antibiotic	Hexazinone	Herbicide
Sulfamerazine	Antibiotic	Bromacil	Herbicide
Sulfamethizole	Antibiotic	Metazachlor	Herbicide
Sulfamethazine	Antibiotic	Metolachlor	Herbicide
Sulfachloropyridazine	Antibiotic	2,4-D	Herbicide
Trimethoprim	Antibiotic	DEET	Insect Repellant
Sulfadimethoxine	Antibiotic	Bezafibrate	Lipid Regulator
Ciprofolxacin	Antibiotic	Clofibric Acid	Metabolite of Lipid Regulator
Penicillin G	Antibiotic	Diazepam	Muscle-relaxant
Amoxicillin	Antibiotic	Norethisterone	Ovulation Inhibitor
Lincomycin	Antibiotic	Theophylline	Stimulant
Oxytetracycline	Antibiotic	Theobromine	Stimulant
Chlortetracycline	Antibiotic	Caffeine	Stimulant
Viginiamycin	Antibiotic	Oxybenzone	Sunscreen
Erythromycin	Antibiotic	Sildenafil	Virility regulator
Roxithromycin	Antibiotic	Vardenafil	Virility regulator
Tylosone Tartrate	Antibiotic	Cotinine	
Carbadox	Antibiotic	Ketorolac	
Triclosan (Irgasan)	Antibiotic	Meclofenamic Acid	
Chloamphenicol	Antibiotic	Nifedipine	
Fluoxetine	Anti-depresant	Indomethacin	
Carbamazepine	Anti-seizure	Diatrizoate	
Pentoxifylline	Blood Viscosity Reducing Agent	2,4-Dichlorobenzoic Acid	
Estrone	Estrogen		

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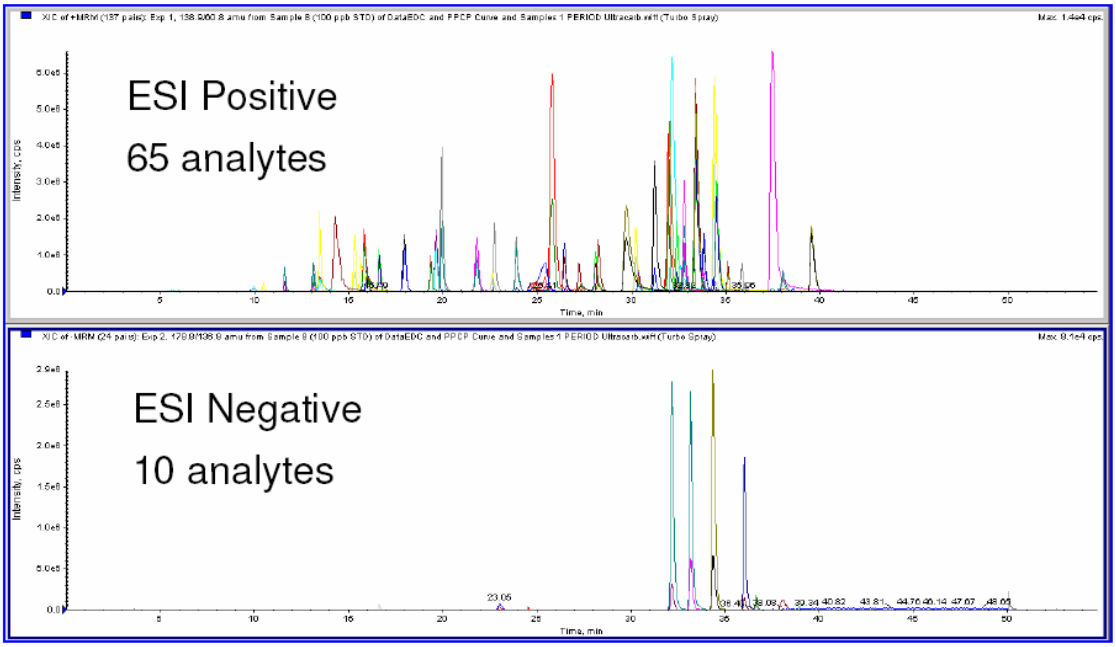
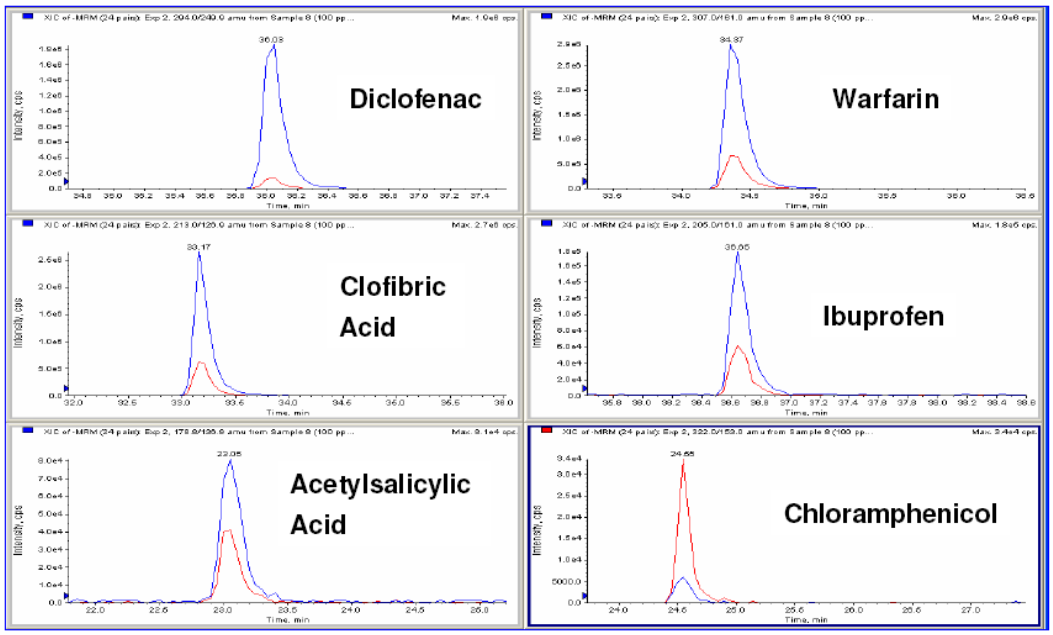
LC/MS/MS Approach to Endocrine Disruptors and PPCP

Applied Biosystems

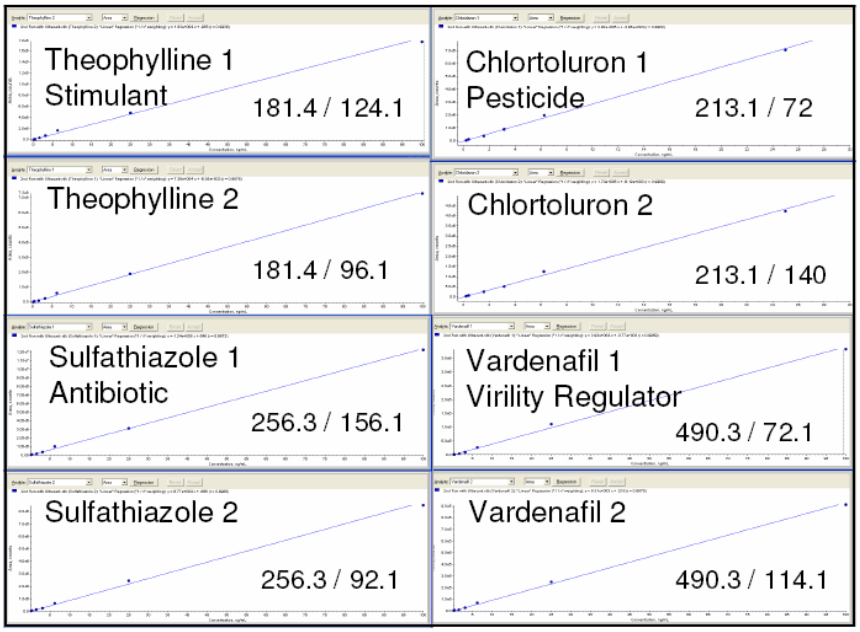
100 ppb Standard – ESI with Polarity Switching



2 MRMs Per Analyte Were Used for Confirmation



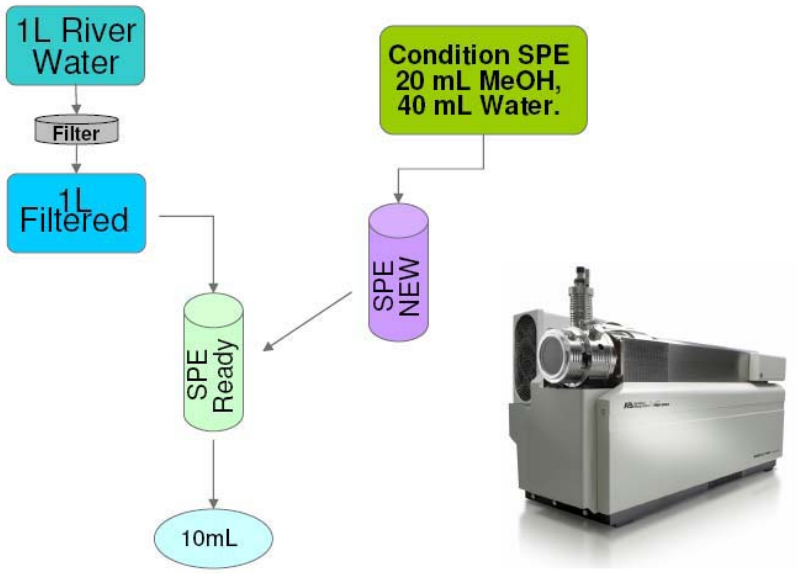
Linear Over 3-4 Orders of Magnitude ($R^2 > 0.995$)



LC/MS/MS Approach to Endocrine Disruptors and PPCP

Applied Biosystems

Solid Phase Extraction Results in a 100X Concentration of Analytes



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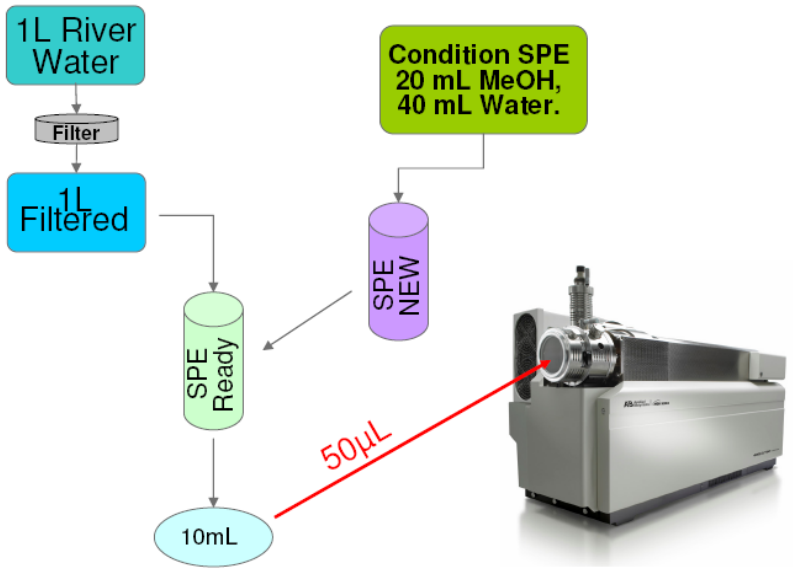
25 YEARS ADVANCING SCIENCE

LC/MS/MS Approach to Endocrine Disruptors and PPCP

Applied Biosystems

Solid Phase Extraction Results in a 100X Concentration of Analytes



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25 YEARS ADVANCING SCIENCE

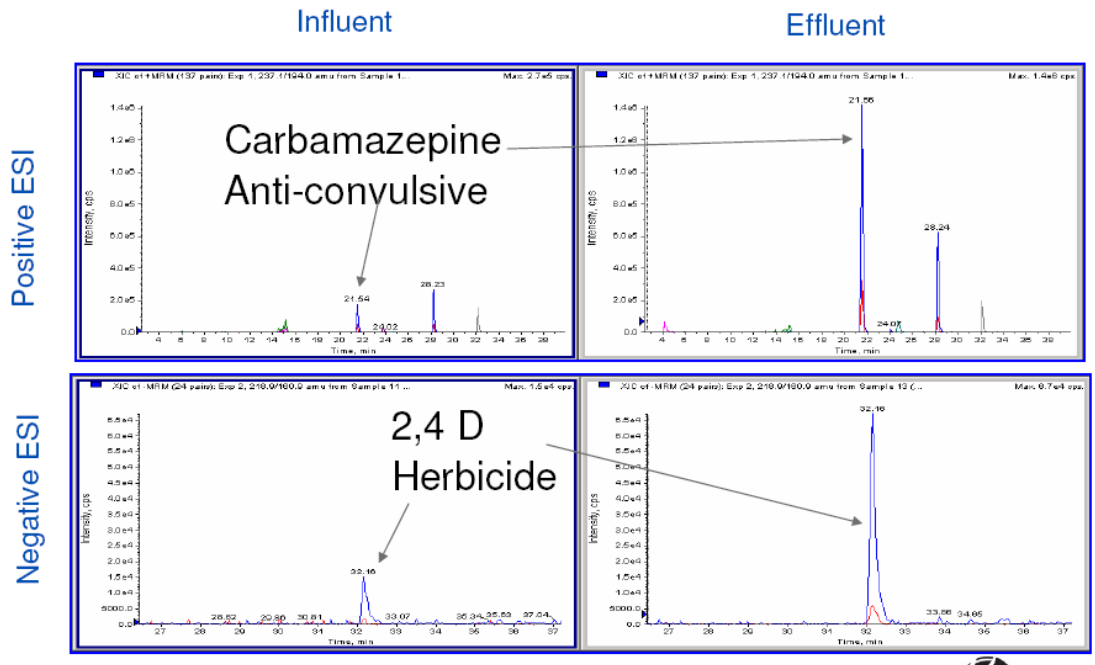
Collection of River Water Samples

River 1 – Influent and effluent samples of a river in a rural area

River 2 – Influent and effluent samples of a river running through an urban area

LC/MS/MS Approach to Endocrine Disruptors and PPCP

Chromatograms - River 1 – A Rural Area

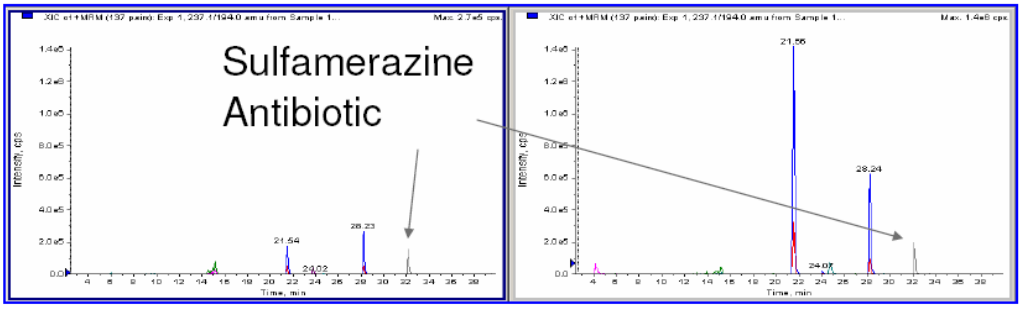


Chromatograms - River 1 – A Rural Area

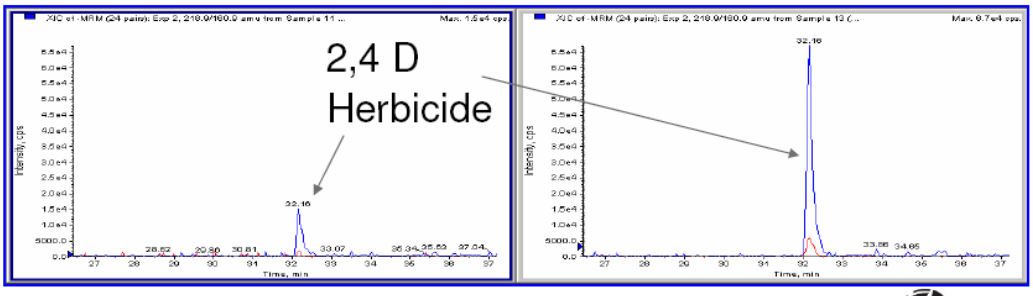
Influent

Effluent

Positive ESI



Negative ESI



LC/MS/MS Approach to Endocrine Disruptors and PPCP

Results Table - River 1 – A Rural Area

	Influent [C]	Effluent [C]	
Analyte	ng/L (ppt)	ng/L (ppt)	
Erythromycin	3.08	53.5	↑
Carbamazepine	65.5	151.5	↑
2,4-D	ND	9.35	↑
DEET	1.49	1.67	→
Sulfamethoxazole	13.15	13.3	→
Caffeine	40.95	23.5	→
Ciprofloxacin	3.805	ND	↓
Cotinine	2.05	ND	↓

ND = not detected

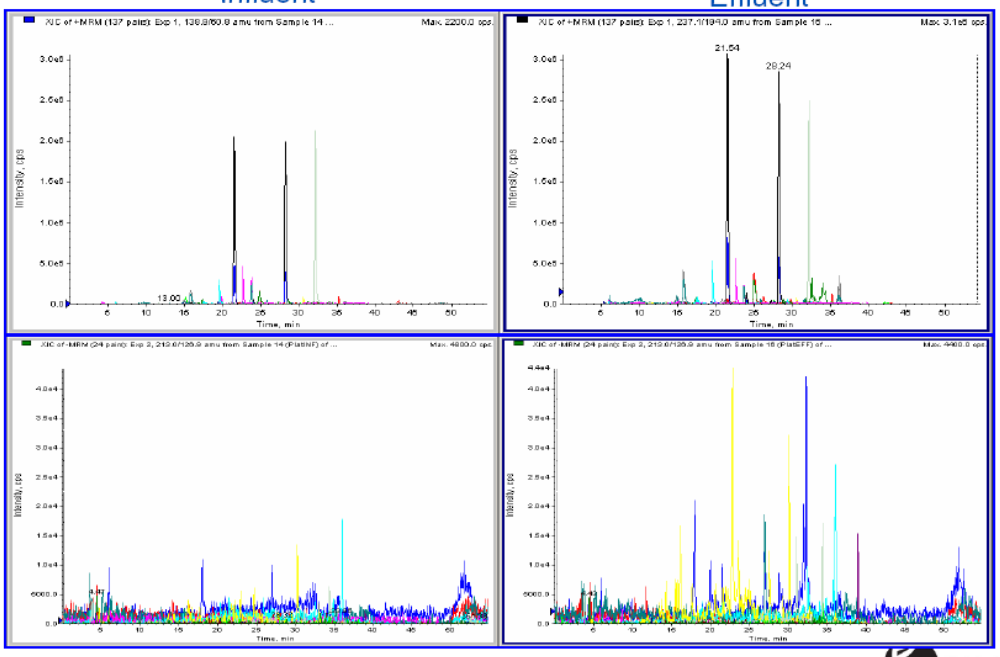
Increases by >2X
Within 2X
Decreases by >2X

Chromatograms - River 2 – An Urban Area

Influent | Effluent

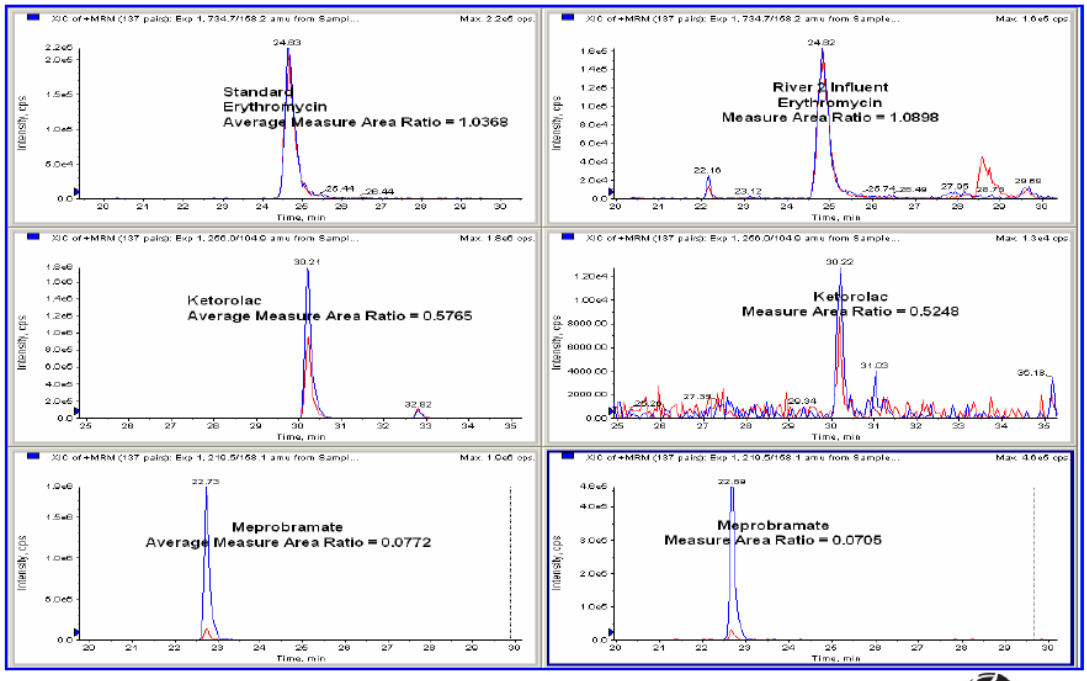
Positive ESI

Negative ESI



LC/MS/MS Approach to Endocrine Disruptors and PPCP

Detection and Confirmation Using MRM Area Ratios of Contaminants in River 2



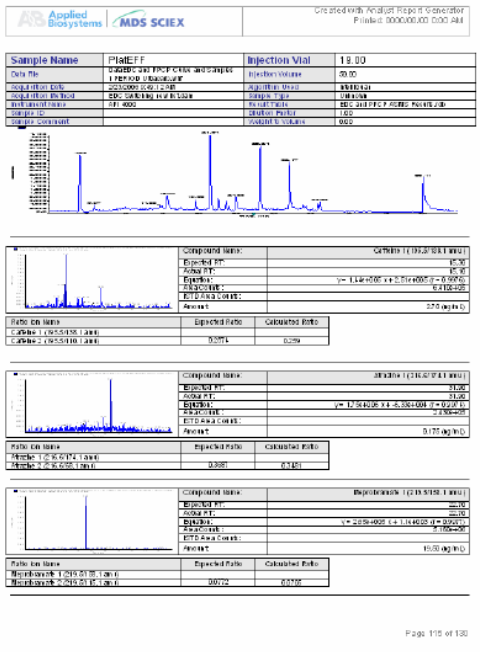
Results Table - River 2 – An Urban Area

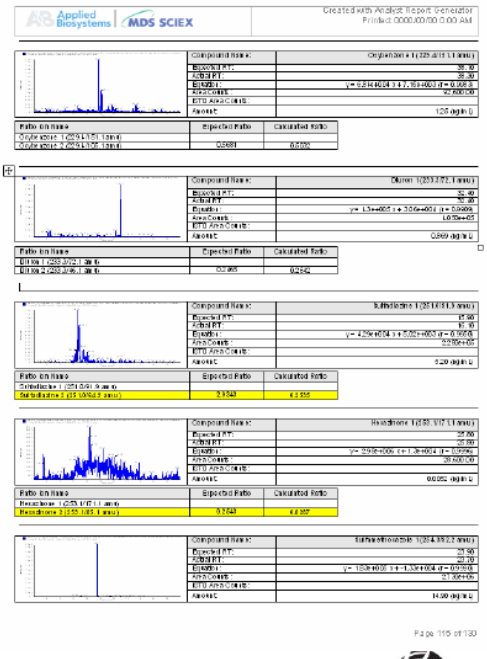
Analyte	Influent [C] ng/L (ppt)	Effluent [C] ng/L (ppt)	
Oxybenzone	ND	6.25	↑
Bromacil	ND	7.4	↑
Diazepam	ND	0.3875	↑
Warfarin	ND	0.93	↑
Triclosan (Irgasan)	5.9	31.4	↑
Codine	17.05	77.5	↑
Diuron	1.375	4.345	↑
Trimethoprim	58.5	122.5	↑
Lincomycin	1.525	3.015	→
Carbamazepine	870	1305	→
DEET	24	29.9	→
Ketorolac	2.49	3.06	→
Meprobramate	85.5	97.5	→
Atrazine	1.075	0.875	→
Sulfamethoxazole	95.5	74.5	→
Pentoxifylline	6.6	3.385	→
Caffeine	57	13.5	↓
Cotinine	14.4	ND	↓
Simazine	1.01	ND	↓
Norethisterone	1.15	ND	↓
Erythromycin	134.5	ND	↓
Tylosone Tartrate	4.275	ND	↓
2,4-D	3.24	ND	↓

Increases by >2X
Within 2X
Decreases by >2X

ND = not detected

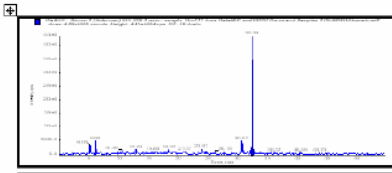
Example Reports from Ion Ratio Report Generator Software





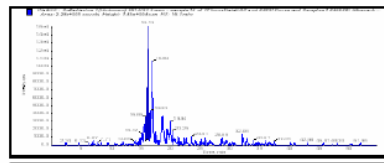
Example Reports from Ion Ratio Report Generator Software

Example Reports



Compound Name:	Diuron 1 (233.3/72.1 amu)
Expected RT:	32.40
Actual RT:	32.40
Equation:	y = 4.3e+005 x + 3.06e+004 (r = 0.9909)
Area Counts:	4.050e+05
ISTD Area Counts:	
Amount:	0.869 (ng/mL)

Ratio Ion Name	Expected Ratio	Calculated Ratio
Diuron 1 (233.3/72.1 amu)		
Diuron 2 (233.3/46.1 amu)	0.2465	0.2642



Compound Name:	Sulfadiazine 1 (251.0/91.9 amu)
Expected RT:	15.90
Actual RT:	16.10
Equation:	y = 4.29e+004 x + 5.02e+003 (r = 0.9950)
Area Counts:	2.280e+05
ISTD Area Counts:	
Amount:	5.20 (ng/mL)

Ratio Ion Name	Expected Ratio	Calculated Ratio
Sulfadiazine 1 (251.0/91.9 amu)		
Sulfadiazine 2 (251.0/64.9 amu)	**2.0343**	**0.2535**

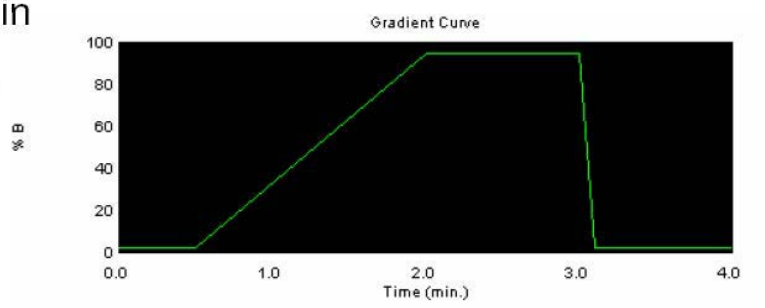
4000 Q TRAP® Method for Optimized Quantitative Performance and Qualitative ID in Treated Tap Water

- Not sample limited
  - Multiple injections possible
  - Higher throughput chromatography
- Sensitivity, robustness, linearity, precision are a priority
  - DuoSpray™ Source
  - Dedicated polarity
- Smaller, more focused analyte list (25 total)
- Spectral confirmation and the ability to do qualitative ID on unknowns
  - MRM IDA (Information Dependant Acquisition)

LC/MS/MS Approach to Endocrine Disruptors and PPCP

HPLC Method

- Shimadzu LC system
- Column: Phenomenex Polar RP 50 x 2.0mm
- Mobile Phase A: water + 0.1% formic acid
- Mobile phase B: acetonitrile + 0.1% formic acid
- Flow of 800µL/min
- Injection of 10µL



Mass Spec Method

- 4000 Q TRAP® LC/MS/MS system
- DuoSpray™ source (automated ESI and APCI switching)
- Heater temperature of 600 °C
- Dedicated ionization – Positive or Negative only
- 1 MRM transition per compound
- Total run time of 4min

LC/MS/MS Approach to Endocrine Disruptors and PPCP

LLOQ from a Higher Throughput Multiple Injection Approach.

Compound	fg on column	ppt
carbofuran	14.9	1.5
triazophos	17.9	1.8
linuron	493.1	49.3
Acetominophen	200.0	20.0
Erythromycin	7.5	0.8
Sulfamethoxazole	101.4	10.1
Tetracycline	1.9	0.2
Caffeine	314.0	31.4
Oxybenzone	213.7	21.4
DEET	6.0	0.6
Diazepam	153.8	15.4
Atrazine	38.5	3.8
Estradiol	469.5	46.9

Compound	fg on column	ppt
Progesterone	340.1	34.0
Ethynyl estradiol	1000.0	100.0
Chloramphenicol	13.3	1.3
2,4-D	87.7	8.8
Silvex	348.4	34.8
ibuprofen	362.3	36.2
Aldicarb - 116 frag	47.6	4.8
Methomyl	21.7	2.2
Aldicarb - NH4	18.9	1.9
Hydrocodone	10.0	1.0
Buspirone	2.2	0.2
Androstenedione	135.1	13.5
Testosterone	100.0	10.0

LLOQ are based on a signal to noise of 10 and an injection volume of 10 µL.

%RSD were 1 to 3%

LLOQ from a Higher Throughput Multiple Injection Approach.

Compound	fg on column	ppt
carbofuran	14.9	1.5
triazophos	17.9	1.8
linuron	493.1	49.3
Acetominophen	200.0	20.0
Erythromycin	7.5	0.8
Sulfamethoxazole	101.4	10.1
Tetracycline	1.9	0.2
Caffeine	314.0	31.4
Oxybenzone	213.7	21.4
DEET	6.0	0.6
Diazepam	153.8	15.4
Atrazine	38.5	3.8
Estradiol	469.5	46.9

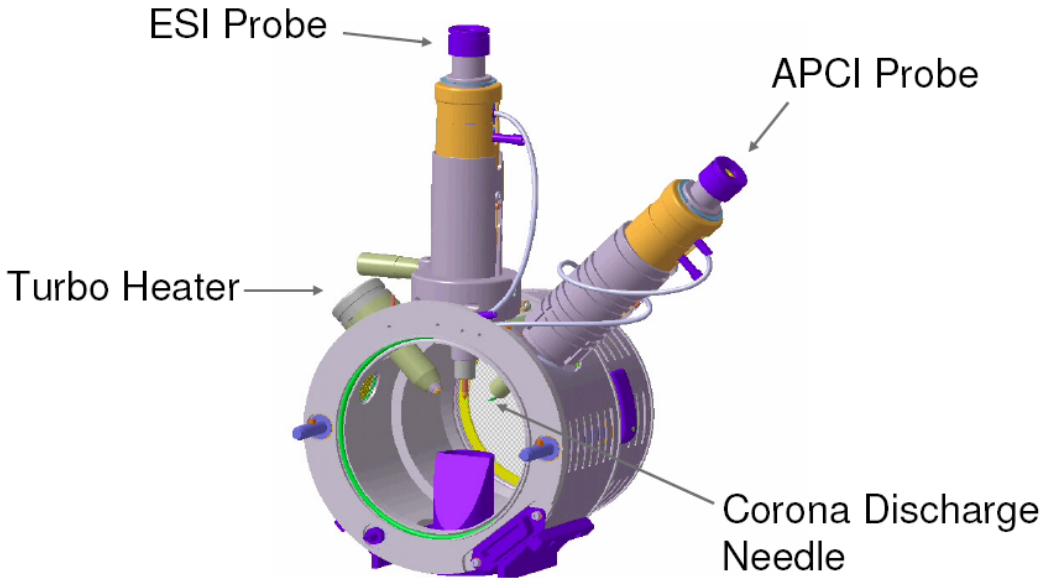
Compound	fg on column	ppt
Progesterone	340.1	34.0
Ethynyl estradiol	1000.0	100.0
Chloramphenicol	13.3	1.3
2,4-D	87.7	8.8
Silvex	348.4	34.8
ibuprofen	362.3	36.2
Aldicarb - 116 frag	47.6	4.8
Methomyl	21.7	2.2
Aldicarb - NH4	18.9	1.9
Hydrocodone	10.0	1.0
Buspirone	2.2	0.2
Androstenedione	135.1	13.5
Testosterone	100.0	10.0

Positive ESI
Negative ESI
Postive APCI

29

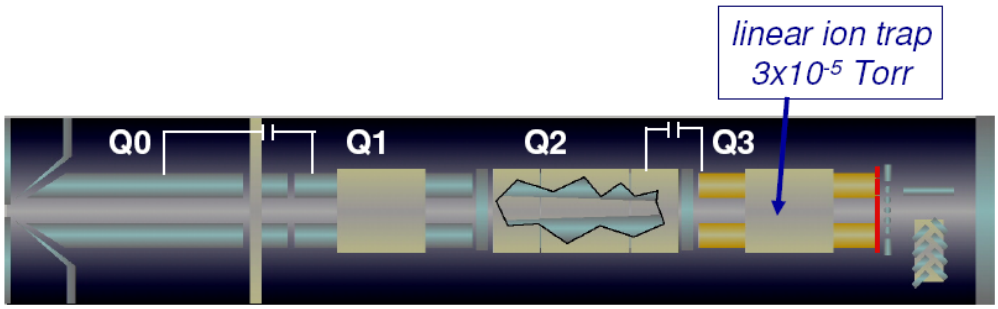
LC/MS/MS Approach to Endocrine Disruptors and PPCP

DuoSpray™ Source - for Diverse Sets of Analytes



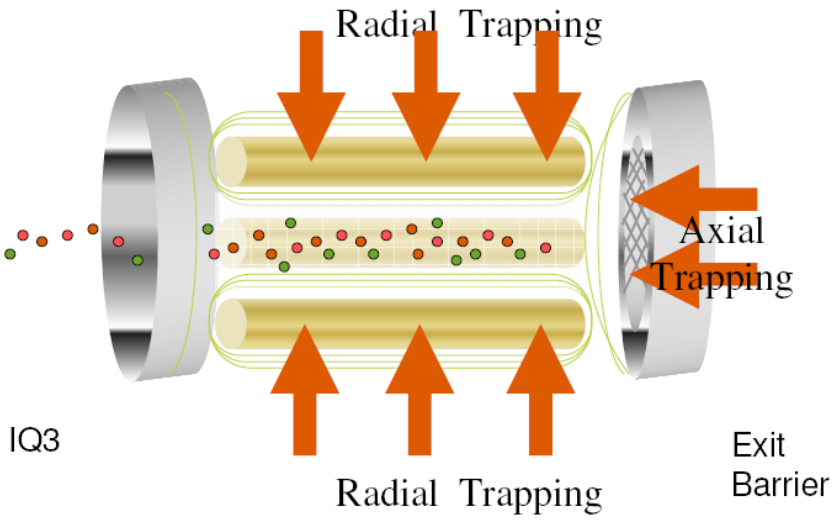
30

A Schematic of the 4000 Q TRAP® system's Ion Path

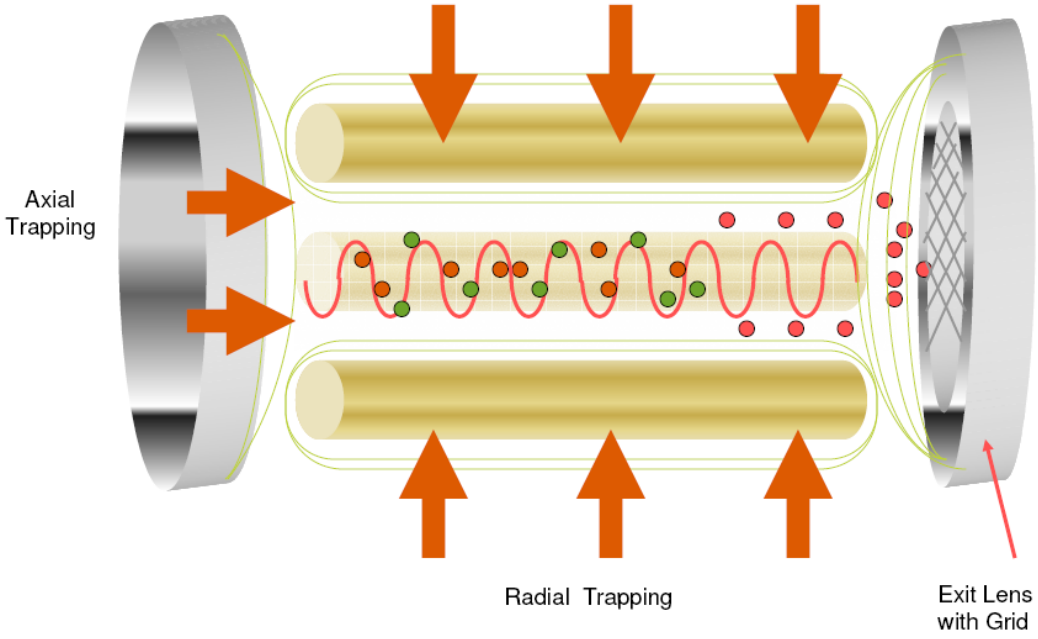


- Hybrid QqQ / Linear Ion Trap (LIT)
- QqQ - selectivity and sensitivity
- Fast and sensitive full scan performance
- Greater ion capacity and higher resolution
- MS3 and other scan modes

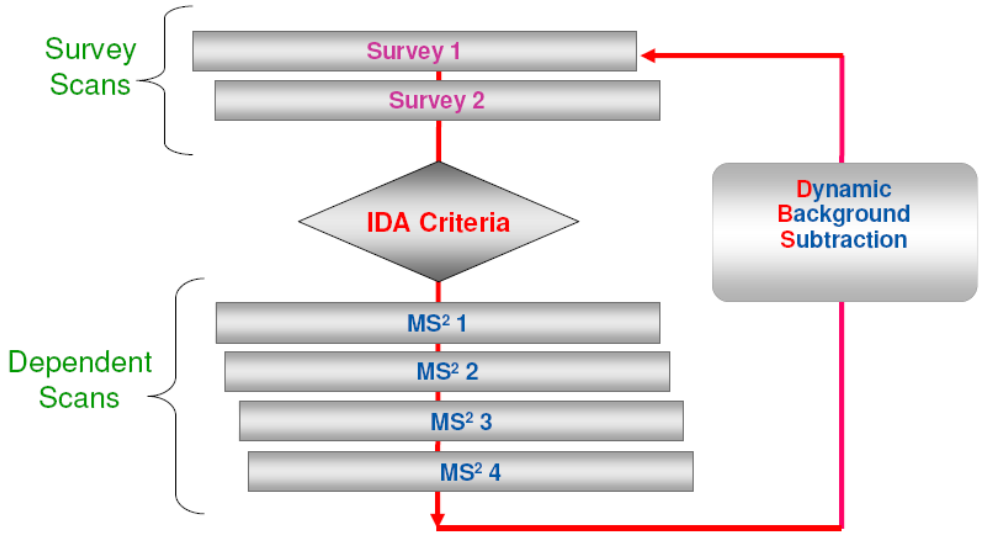
LIT Trapping Ions



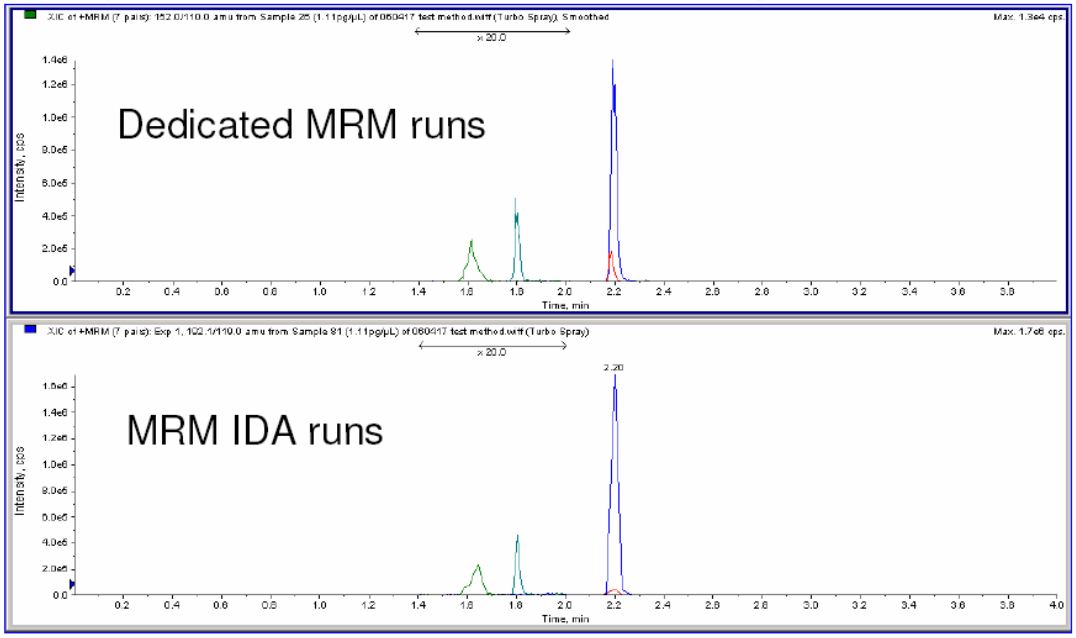
LIT Scanning



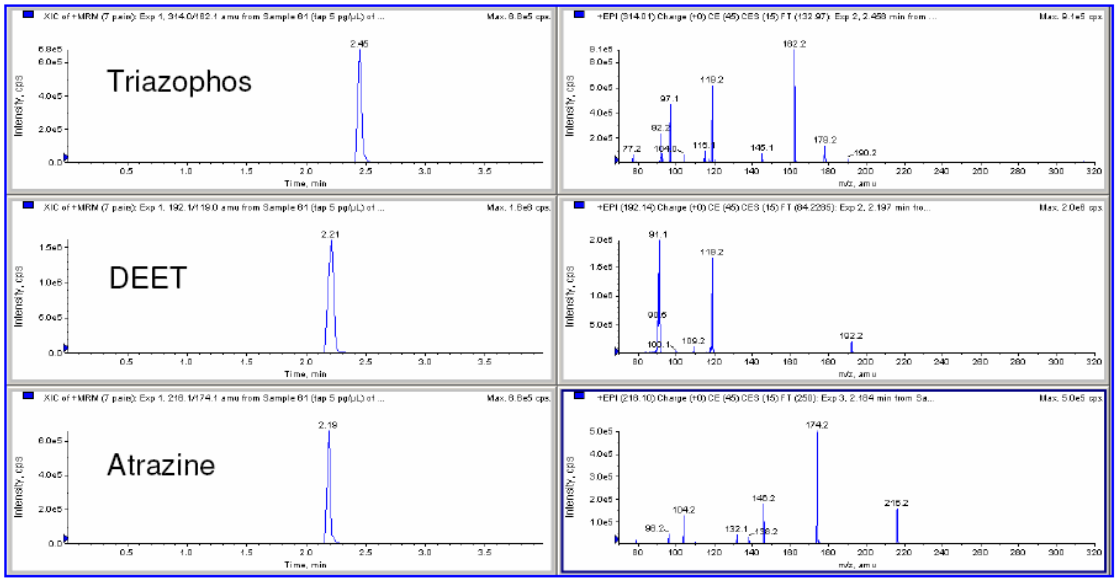
The Structure of an IDA Experiment



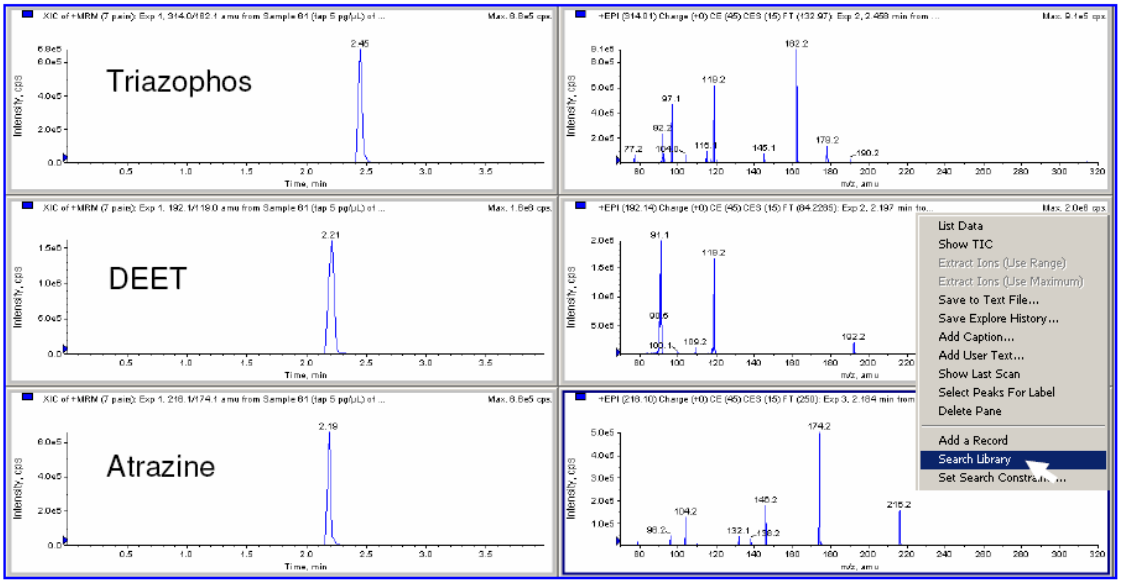
Comparison - MRM vs. MRM IDA Experiments



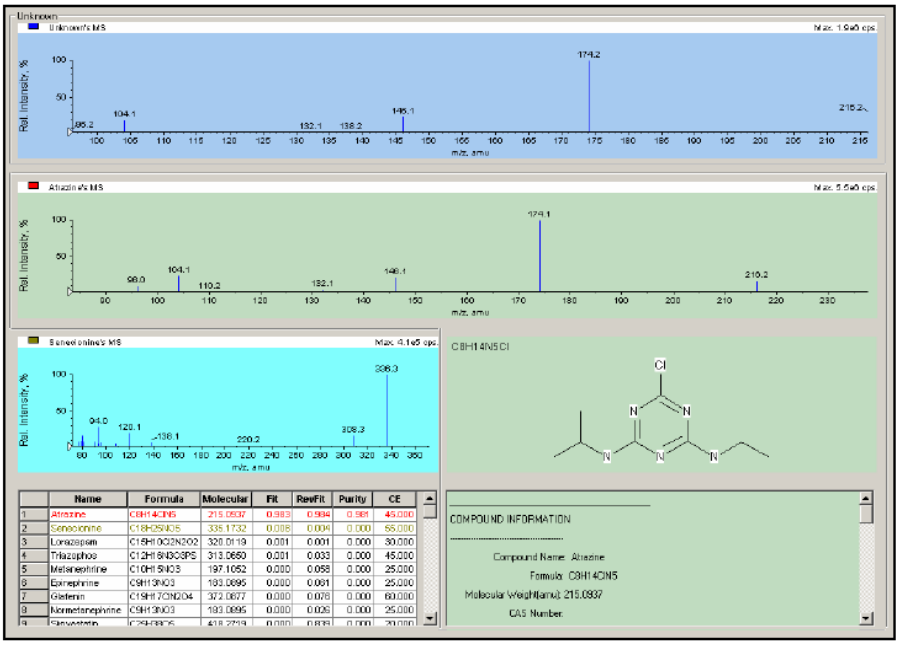
Automatically Generated EPI (MS/MS) Spectra for ID / Structural Elucidation



Automatically Generated EPI (MS/MS) Spectra for ID / Structural Elucidation



Library Search Confirms the Presence of Atrazine



Conclusion

- EDCs are growing in importance in environmental monitoring
- Quantitative analysis of 75 EDCs by triple quadrupole
  - Single injection with polarity switching
  - Simultaneous quantitation and confirmation
- Analysis of EDCs using a Q TRAP® System
  - Multiple injection with dedicated ionization modes
  - High throughput quantitation and spectral confirmation

LC/MS/MS Approach to Endocrine Disruptors and PPCP

Legal Acknowledgements

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Thank you for your time. Questions?

The authors would like to thank…

Renee Huang for logistical support and Tania Sasaki and Matt Champion editorial support, as well as the entire Foster City demo team and applied markets division of ABI.

HALOACETIC ACIDS BY ION CHROMATOGRAPHY

Antonsen, Stephen; Dionex Corporation
Aribi, Houssain El; MDS Sciex
Sakuma, Takeo; MDS Sciex

Disinfection of drinking water by chlorination can lead to generation of carcinogenic species, such as haloacetic acids (HAA).

Chlorination has been linked epidemiologically to bladder, kidney and rectal cancers. Brominated acids are linked to nephrotoxic, neurotoxic and hepatotoxic effects, and Chlorinated acids have been shown to induce tumours.

Analysis of HAA in chlorinated drinking water is described in EPA method method 552.1. Monitored species are monochloroacetic acid, monobromoacetic acid, dichloroactic acid, dibromoacetic acid, trichloroacetic acid, tribromoacetic acid, chlorodibromoacetic acid, dichlorobromoacetic acid and chlorobromoacetic acid. Method 552.1 required acidification to pH5 with Sulfuric acid followed by a 2 hour hot-methanol derivatization and analysis by GC-ECD. Detection limits are in the fractional ppb range.

Ion chromatography (IC) linked to triple quadrupole mass spectrometry (MS/MS) offers significant advantages to the testing laboratory: no derivatization, lower detection limits (low ppt) and greater specificity.

In this work, an ion chromatography method was developed and interfaced to a triple quadrupole mass spectrometer. The requirements and considerations in linking IC to MS/MS will be demonstrated and the use of the method will be illustrated using natural and spiked chlorinated drinking water matrices.

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Analysis of Haloacetic Acids and Bromate by IC-ESI-MS/MS

Houssain El Aribi, Ph. D.

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LC- or IC- MS/MS Topics in Environmental Analysis

- Pesticides (target analysis, screening, very polar pesticides)
- Perchlorate
- Disinfection by-products: haloacetic acids, bromate, trihamethanes, etc…
- Estrogens and endocrine disruptors
- Fluorinated compounds
- Brominated flame retardants
- Polycyclic aromatic hydrocarbons
- Explosives
- Algal toxins and shellfish toxins
- Biogenic amines
- Antibiotics
- Screening for emerging compounds, etc….

They are found in contaminated water, food, beverages, soils, etc.. .
They could pose a serious threat to human health.

2

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Challenges

- Screening for hundreds of emerging compounds using analytical instruments
  - Sample preparation (*as simple as possible*)
  - Separation (*HPLC, IC, etc…*)
  - Detection *(as sensitive as possible i.e., MS/MS)*
  - Confirmation (*using ISTD and isotope ratios*)
- Analyzing very polar compounds *(IC-MS/MS)*
- Ease-of-use *(software)*

3

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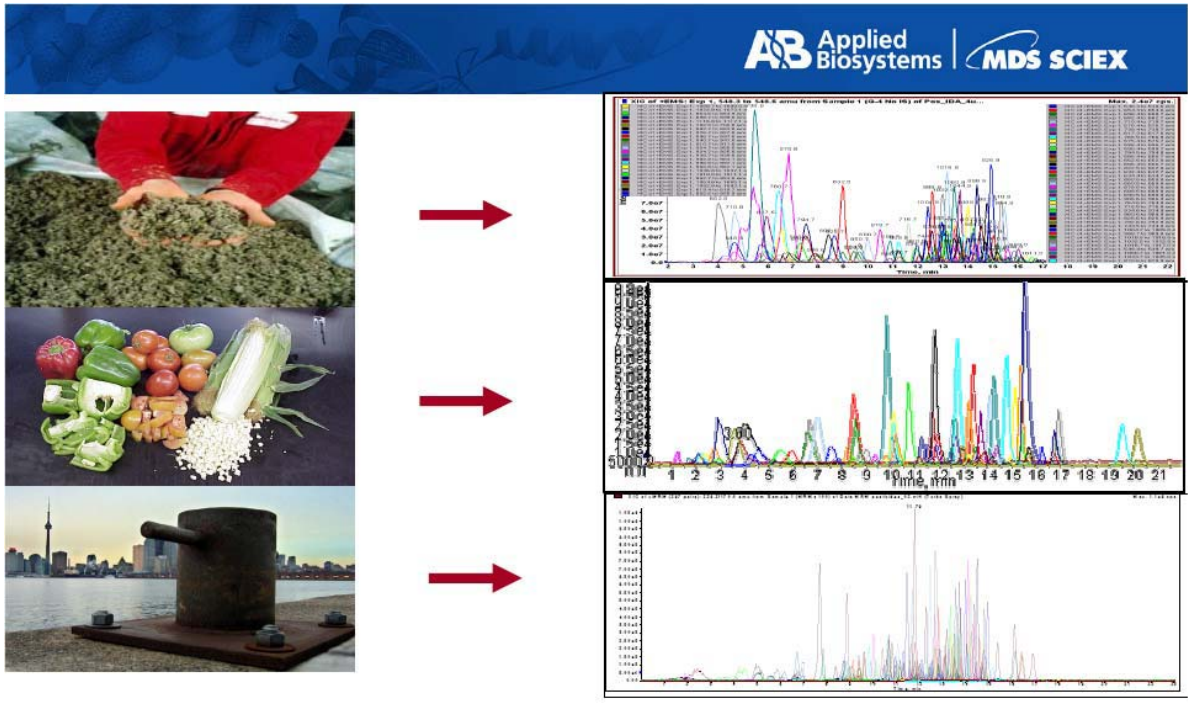
LC- or IC-MS/MS Involves…

- **Chromatography – separation of analytes**
  - Pumps
  - Autosampler
  - Column
- **Ionization – ion production**
  - Electrospray (ESI, TurboIonSpray® source)
  - Atmospheric Pressure Chemical Ionization (APCI)
  - Atmospheric Pressure Photo Ionization (APPI)
- **MS filtering – ion transmission**
  - Q_1 Selected Ion Monitoring (SIM)
  - Q_1-Q_3 parent to product ion transitions (MRM); highly specific
  - Other possibilities as well…
- **Detection – ion detection (signal to peak)**
- **Data analysis**
  - Qualitative (what is it?)
  - Quantitative (how much is present?)

4



How to go from this .....to this

(Sample xxxxx).....(quantitation with high reliability)

5

Small Molecule Quantitation

The API 3200™, 4000™, 5000™ LC/MS/MS Systems and the 4000 Q TRAP® and 3200 Q TRAP® LC/MS/MS Systems all use the *Turbo V™ source technology*.

6

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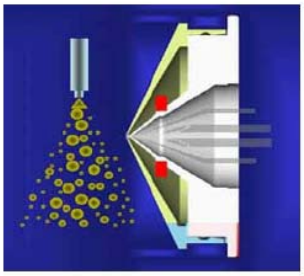
Turbo V™ Source



- Rugged, Reliable, Easily Interchangeable
- Orthogonal Sprayer: Enhance sensitivity and minimize contamination
- Covers a wide range of applications and compounds
- Accommodates diverse range of flow rates up to ***3 mL/min***
- Quick change between ***ESI*** and ***APCI*** probes

7

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Turbo V™ Source and Methods Transfer

API 3200™ and
3200 Q TRAP® Systems

All these platforms can operate with the same software…
Re-optimize your compound dependent parameters using Analyst® software's automated optimization routine, roll up your LC equipment, and run your samples.

API 4000™ and
4000 Q TRAP® Systems

API 5000™ system

…and this can be done in any order or combination…

8

Haloacetic Acids (HAAs) and Bromate in Water

Chloronated HAAs: MCAA, DCAA and TCAA are usually formed during the disinfection of water with chlorine or chloramine[1-4].

Brominated HAAs: MBAA, DBAA,TBAA are formed during disinfection when the source water also contains bromide ions[1-4].

The presence of bromide ions and MCAA may also lead to mixed CBAA[5,6].

Human consumption of chlorinated drinking water has been epidemiologically linked to bladder, kidney, and rectal cancers[7,8].

DCAA and TCAA are animal carcinogens[9,10].

Bromate (BrO_3^-) is also a disinfection by-product formed during ozonation of drinking water supplies containing bromide ions[11] and has been judged as a potential carcinogen.

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Analysis of haloacetic acids and bromate using API 3200™

Analytical Methods for HAAs and Bromate in Water

- The analytical methods required for compliance monitoring of the HAAs are the US EPA methods **552 series**, which involve GC-ECD analysis [12-15]. These methods require acidification to pH 0.5 with sulfuric acid, a liquid/liquid extraction, and a two-hour hot methanol derivatization.
- HPLC and CE have been also used for the determination of HAAs, however, the detection limits were unsatisfactory, and recoveries of some analytes were poor[16-18].
- The US EPA methods for the analysis of bromate are the **300 series** using either ion chromatography (IC) with conductivity[19-22] or IC with ion coupled plasma (ICP)/MS[23] .

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23. H. P. Wagner, B. V. Pepich, D. P. Hautman, D. J. Munch, US EPA 317, US Environmental Protection Agency, Cincinnati, OH, **2000**.

EPA Regulations

- MCAA, DCAA, TCAA, MBAA, and DBAA are cited in the US EPA HAA5 regulation. These five HAAs do not exceed a MCL of ***60 µg/L*** in drinking water.
- EPA has also established a rule to regulate bromate at an average of ***10 µg/L*** in drinking water.

Because of the high toxic and carcinogenic risks of some of the HAAs, reliable and fast analytical methods without derivatization are needed to monitor their presence in water.

Direct determination of HAAs and bromate by suppressed ion chromatography (IC) with hydroxide eluents coupled with electrospray (ESI) and tandem mass spectrometry (MS/MS) is an alternative and desirable solution.

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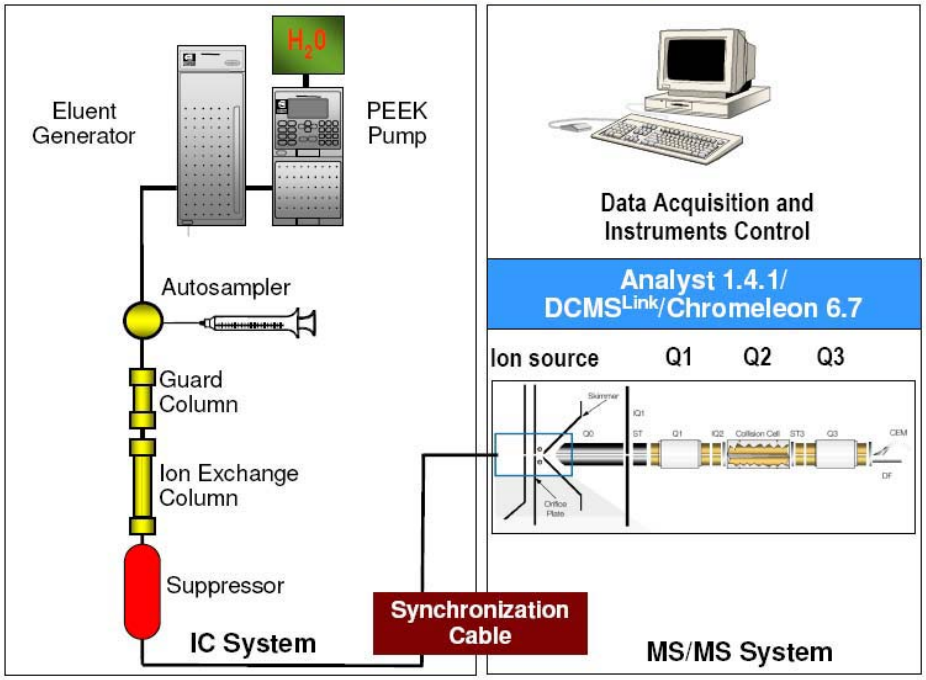
Analysis of haloacetic acids and bromate using API 3200™

IC-MS/MS Schematic



Analyst 1.4.1 is featured with AAO, which allows integration of other hardware to be controlled by Analyst. This integration can be achieved by a companion software DCMS link that can be launched from within Analyst.

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Analysis of haloacetic acids and bromate using API 3200™

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IC Experimental Procedure

- Dionex GS 50 pump (1), EG50 eluent generator (2), AS50 auto-sampler (3), CD25A conductivity detector (4), LC30 chromatography oven with rear-loading Rheodyne injection valve (100-µL loop) (5),
- IC Columns: IonPac® AS20; 250 x 2-mm i.d.; guard column: IonPac® AG20; 50 x 2-mm i.d.
- Suppressors: ASRS® MS, 2-mm
- Dionex AXP-MS auxiliary pump (6), Eluent: 90% acetonitrile + 10% water at 0.3 mL/min.
- Analytical flow rate: 0.3 mL/min;
- IC oven temperature: 40 °C
- Injection volume: 100 µL.

ICS-2500™
Reagent-Free™ System

Gradient: 4 – 45 mM KOH

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Applied Biosystems | MDS SCIEX

MS Experimental Procedure

- ***Electrospray (negative mode)***
- IonSpray™ Voltage: –4500 V
- Declastering Potential: –20 V
- Entrance Potential: –10 V
- Collision Energies: –15 to –30 eV
- Collision Exit Potentials: –11 to –15 V
- Curtain Gas™: 20 psi
- Gas Supply 1: 40 psi
- Gas Supply 2: 60 psi
- Source Temperature: 550 °C

API 3200™
LC-MS/MS System

Quantitation (MRM)

Q1/Q3:	unit resolution
Dwell Time:	200 ms

^{13}C-bromoacetic acid as is used as an internal standard and is monitored at MRM 138/79.

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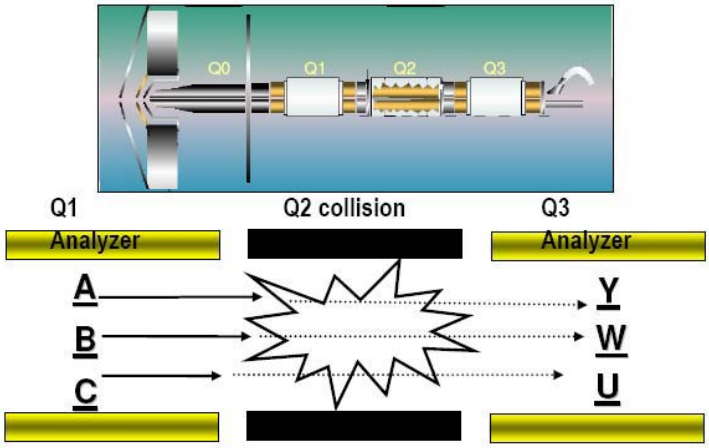
Multiple Reaction Monitoring



Quantitative Analysis

In the case of MBAA analysis:

A-Y (139-79): $CH_2{}^{79}BrCO_2^-$ (m/z 137) – $^{79}Br^-$ (m/z 79) _ **Quantitation**
B-W (137-93): $CH_2{}^{79}BrCO_2^-$ (m/z 137) – $CH_2{}^{79}Br^-$ (m/z 93) _ **Confirmation**
C-U (138-79): $^{13}CH_2{}^{79}BrCO_2^-$ (m/z 138.0) – $^{79}Br^-$ (m/z 79.0) _ **ISTD**

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Analysis of haloacetic acids and bromate using API 3200™

Applied Biosystems | MDS SCIEX

SIM and MRM Transitions

Analyte	SIM of $[M–H]^-$ (*m/z*)	MS/MS Neutral loss	MRM Transition (*m/z*)
Chloroacetic acid, $CH_2ClCOOH$, (MCAA)	93 ($CH_2{}^{35}ClCOO^-$)	CH_2CO_2 CO_2	93/35[a] ($^{35}Cl^-$)[a] 93/49[b] ($CH_2{}^{35}Cl^-$)[b]
Bromoacetic acid, $CH_2BrCOOH$, (MBAA)	137 ($CH_2{}^{79}BrCOO^-$)	CH_2CO_2 CO_2	137/79[a] ($^{79}Br^-$)[a] 139/93[b] ($CH_2{}^{79}Br^-$)[b]
Dichloroacetic acid, $CHCl_2COOH$, (DCAA)	127 ($CH^{35}Cl_2COO^-$)	CO_2 $CHClCO_2$	127/83[a] ($CH^{35}Cl_2^-$)[a] 127/35[b] ($^{35}Cl^-$)[b]
Bromochloroacetic acid, CHBrClCOOH, (BCAA) (not an HAA5 acid)	171 ($CHBrClCOO^-$)	$CHClCO_2$ CO_2	171/79[a] ($^{79}Br^-$)[a] 171/127[b] ($CH^{35}Cl^{79}Br^-$)[b]
Dibromoacetic acid, $CHBr_2COOH$, (DBAA)	215 ($CH^{79}Br_2COO^-$)	CO_2 CH_2CO_2	215/171[a] ($CH^{79}Br_2^-$)[a] 215/79[b] ($^{79}Br^-$)[b]
Trichloroacetic acid, CCl_3COOH, (TCAA)	161 ($C^{35}Cl_3COO^-$)	CO_2 CCl_2CO_2	161/117[a] ($C^{35}Cl_3^-$)[a] 161/35[b] ($^{35}Cl^-$)[b]
Bromate, BrO_3^-	129 ($^{81}BrO_3^-$)	O	129/113 ($^{81}BrO_2^-$)

[a] MRM transitions used for quantitation
[b] MRM transitions used for confirmation

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MRM Transitions, DP and CE

Analyte Name	MRM Transitions	DP (V)	CE (eV)
Chloroacetic Acid (MCAA)	1- 93/35	–15	–15
	2- 93/49	–15	–20
Bromate	1- 138/79	–10	–15
Bromoacetic Acid (MBAA)	1- 137/79	–10	–15
	2- 139/81	–10	–15
Dichloroacetic Acid (DCAA)	1- 127/83	–10	–15
	2- 127/35	–10	–25
Bromochloroacetic Acid (BCAA)	1- 171/79	–15	–15
	2- 171/127	–15	–15
Dibromoroacetic Acid (DBAA)	1- 215/171	–20	–30
	2- 215/79	–20	–30
Trichloroacetic Acid (TCAA)	1- 161/117	–15	–15
	2- 161/35	–15	–20

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Analysis of haloacetic acids and bromate using API 3200™

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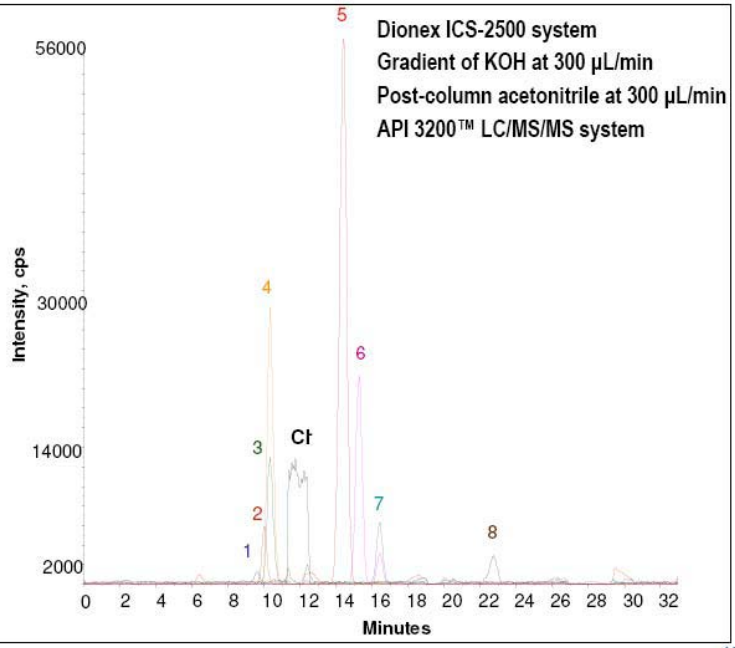
IC-MS/MS Separation of HAAs and Bromate

Column: IonPac AS 20 (2 mm)

Analytes:	µg/L
1- MCAA	1
2- Bromate	1
3- MBAA	1
4- ^{13}C-MBAA	2
5- DCAA	1
6- BCAA	1
7- DBAA	1
8- TCAA	1

Matrix:	mg/L
Chloride	50
Sulfate	100
Nitrate	100



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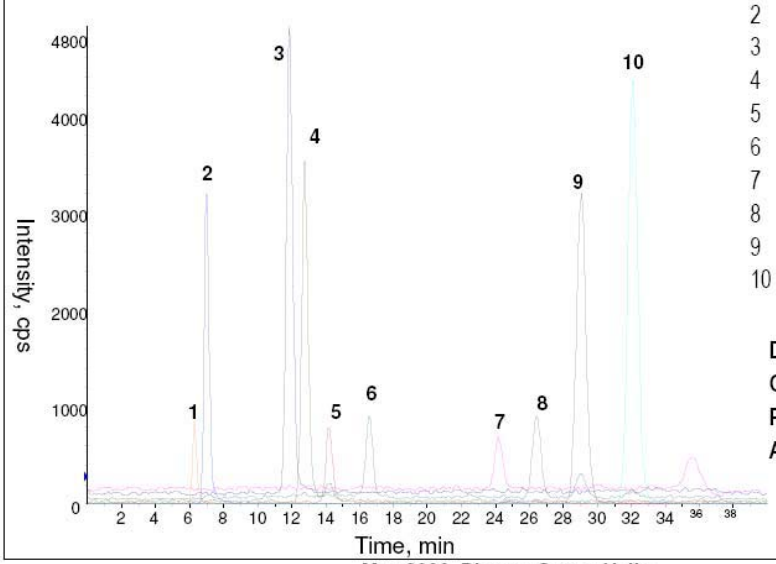
Feb 2005, MDS SCIEX, Toronto

Analysis of haloacetic acids and bromate using API 2000™

Applied Biosystems | MDS SCIEX

IC-MS/MS Separation of HAAs and Bromate

Column: IonPac AS 24 (1 mm)



1 - Chloroacetic acid
2 - Bromoacetic acid
3 - Dichloroacetic acid
4 - Bromochloroacetic acid
5 - Dibromoacetic acid
6 - Bromate
7 - Trichloroacetic acid
8 - Bromodichloroacetic acid
9 - Chlorodibromoacetic acid
10 - Tribromoacetic acid

Dionex ICS-3000 system
Gradient of KOH at 150 µL/min
Post-column acetonitrile at 250 µL/min
API 2000™ LC/MS/MS system

May 2006, Dionex, Sunny Valle

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Analysis of haloacetic acids and bromate using API 3200™

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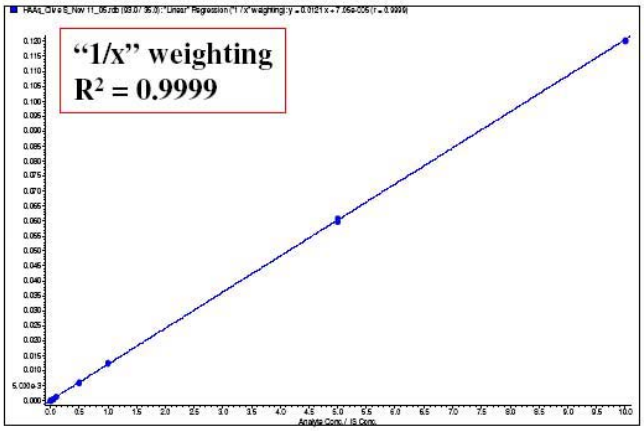
Statistics and calibration curve for MRM m/z 93/35

Metric: Concentration Analyte: 93.0 / 35.0 Sample Type: Standard

Expected Concentration	Sample Name	Number Of Values Used	Mean	Standard Deviation	%CV	Accuracy
0.005000, 0.005000	HAAs_ISTD_0.005u	2 of 2	0.005042	0.000138	2.733158	100.838262
0.010000, 0.010000	HAAs_ISTD_0.01ug	2 of 2	0.010635	0.000184	1.725803	106.350986
0.050000, 0.050000	HAAs_ISTD_0.05ug	2 of 2	0.043220	0.000890	2.059187	86.439376
0.100000, 0.100000	HAAs_ISTD_0.1ug_	2 of 2	0.104130	0.000506	0.486006	104.130271
0.500000, 0.500000	HAAs_ISTD_0.5ug_	2 of 2	0.494374	0.013461	2.722791	98.874779
1.000000, 1.000000	HAAs_ISTD_1ug_L	2 of 2	1.035662	0.021865	2.111225	103.566197
5.000000, 5.000000	HAAs_ISTD_5ug_L	2 of 2	5.008076	0.070479	1.407307	100.161513
10.000000, 10.0000	HAAs_ISTD_10ug_	2 of 2	9.963862	0.016615	0.166748	99.638615



MCAA

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Limits of Quantification (LOQ)

Analyte Name	MRM	LOQ (µg/L)	Linear range (µg/L)	R^2
MCAA	93/35	0.1	0.01 – 10	0.9999
Bromate	138/79	0.01	0.005 – 10	0.9991
MBAA	137/79	0.01	0.005 – 10	1.0000
DCAA	127/83	0.01	0.005 – 10	0.9998
BCAA	171/79	0.01	0.005 – 10	0.9999
DBAA	215/171	0.1	0.01 – 10	0.9998
TCAA	161/117	0.3	0.05 – 10	0.9993

The LOQs of the different HAAs and bromate were calculated from the chromatograms, at a signal-to-noise-ratio of > 10:1.

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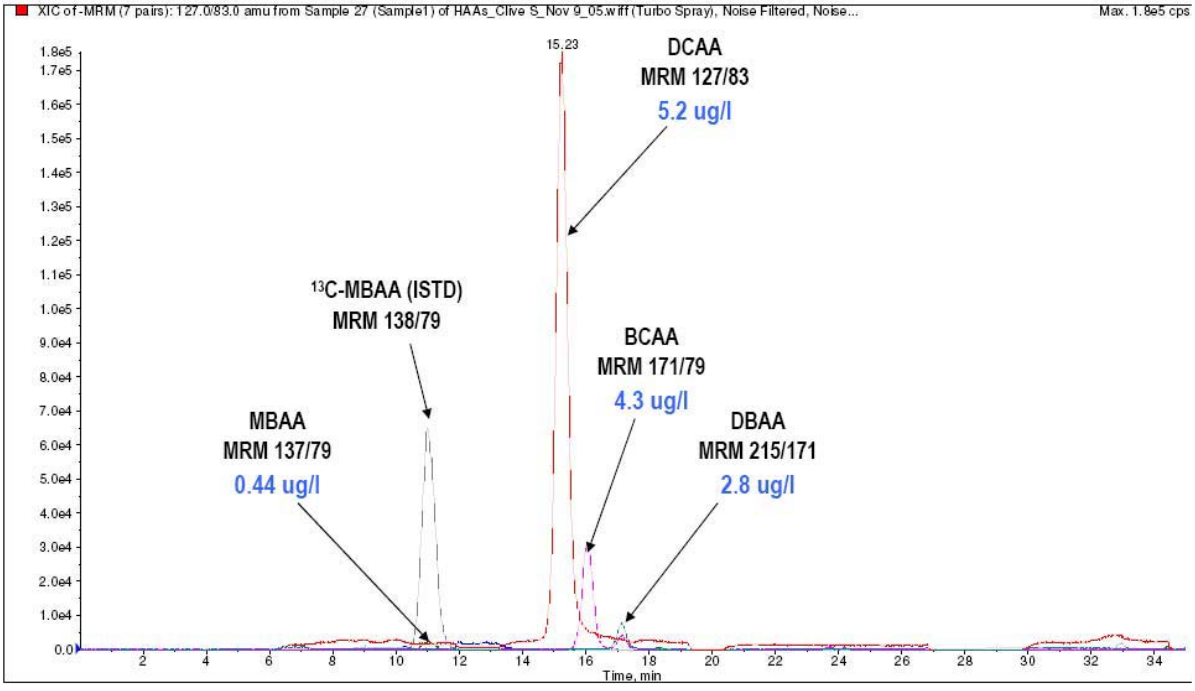
Analysis of haloacetic acids and bromate using API 3200™

Treated Water Sample #1



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Analysis of haloacetic acids and bromate using API 3200™

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Results for *Treated* and *Untreated* Water Samples

Samples	(MCAA), 93/35 µg/L	(MBAA), 137/79 µg/L	(DCAA), 127/83 µg/L	(BCAA), 171/79 µg/L	(DBAA), 215/171 µg/L	(TCAA), 161/117 µg/L
Sample 1	1.210 1.230	0.446 0.444	5.210 5.250	4.340 4.350	2.810 2.770	2.02 2.05
Sample 2	1.600 1.670	0.170 0.182	4.630 4.710	1.700 1.680	0.167 0.176	8.65 8.71
Sample 3	2.680 2.580	0.180 0.174	26.800 26.600	2.940 2.890	0.184 0.194	25.0 24.3
Sample 4	1.710 1.760	0.107 0.107	6.100 6.240	1.600 1.650	0.430 0.389	1.57 1.64
Sample 5	2.280 2.280	0.327 0.346	20.100 19.600	6.920 6.870	1.450 1.430	13.5 13.8
Sample 6	2.450 2.440	0.174 0.165	24.200 24.500	2.930 2.960	0.180 0.190	20.1 20.3
Sample 7	0.471 0.444	0.112 0.102	0.082 0.085	<0.005 <0.005	0.049 0.050	<0.005 <0.005
Sample 8	0.432 0.420	0.005 0.006	0.080 0.075	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005
Sample 9	0.471 0.486	<0.005 <0.005	0.058 0.054	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005
Sample 10	0.459 0.464	0.015 0.017	0.150 0.154	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005
Sample 11	0.591 0.580	0.008 0.009	0.156 0.157	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005

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Analysis of haloacetic acids and bromate using API 3200™

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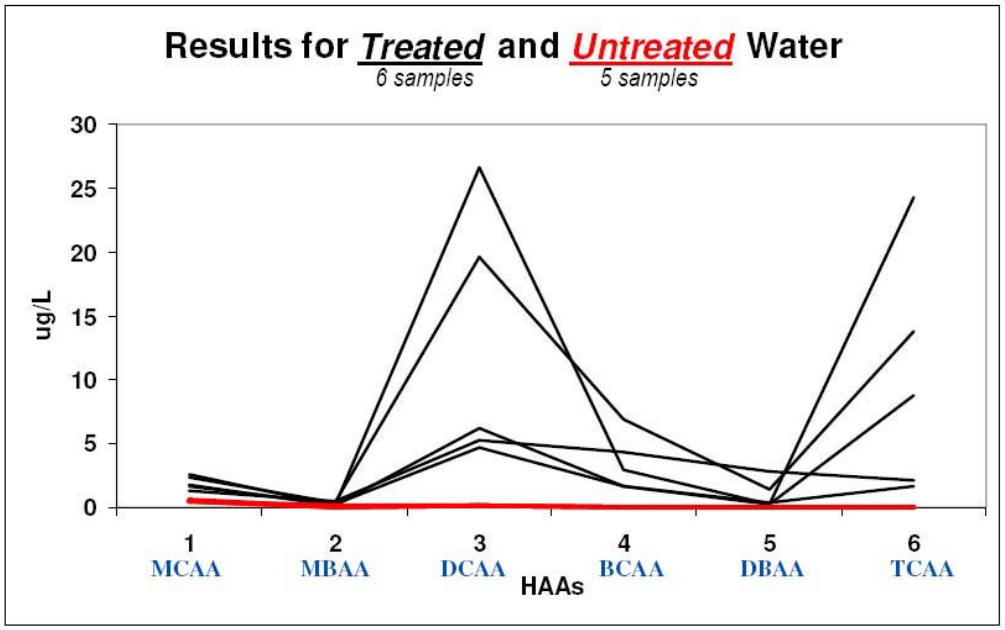

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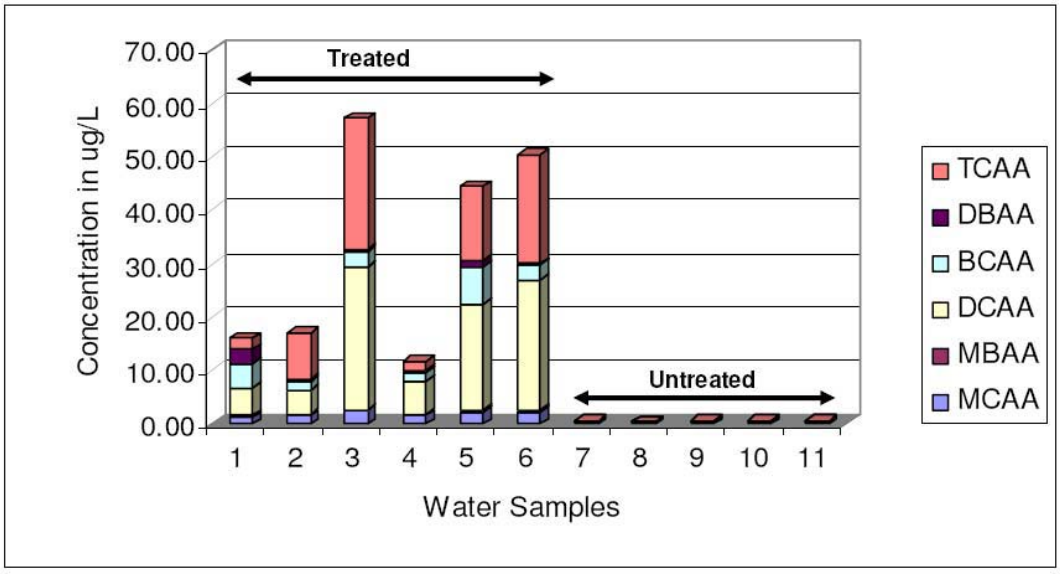
Results for Treated and Untreated Water Samples



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Conclusion

- The IC-ESI-MS/MS method was found to be a robust, specific and sensitive system for the determination of HHAs and Bromate.
- A very significant advantage over GC methods is that no sample pre-treatment or derivatisation is required.
- Dionex and Applied Biosystems/MDS Sciex are providing a sensitive validated package for the analysis of polar compounds.

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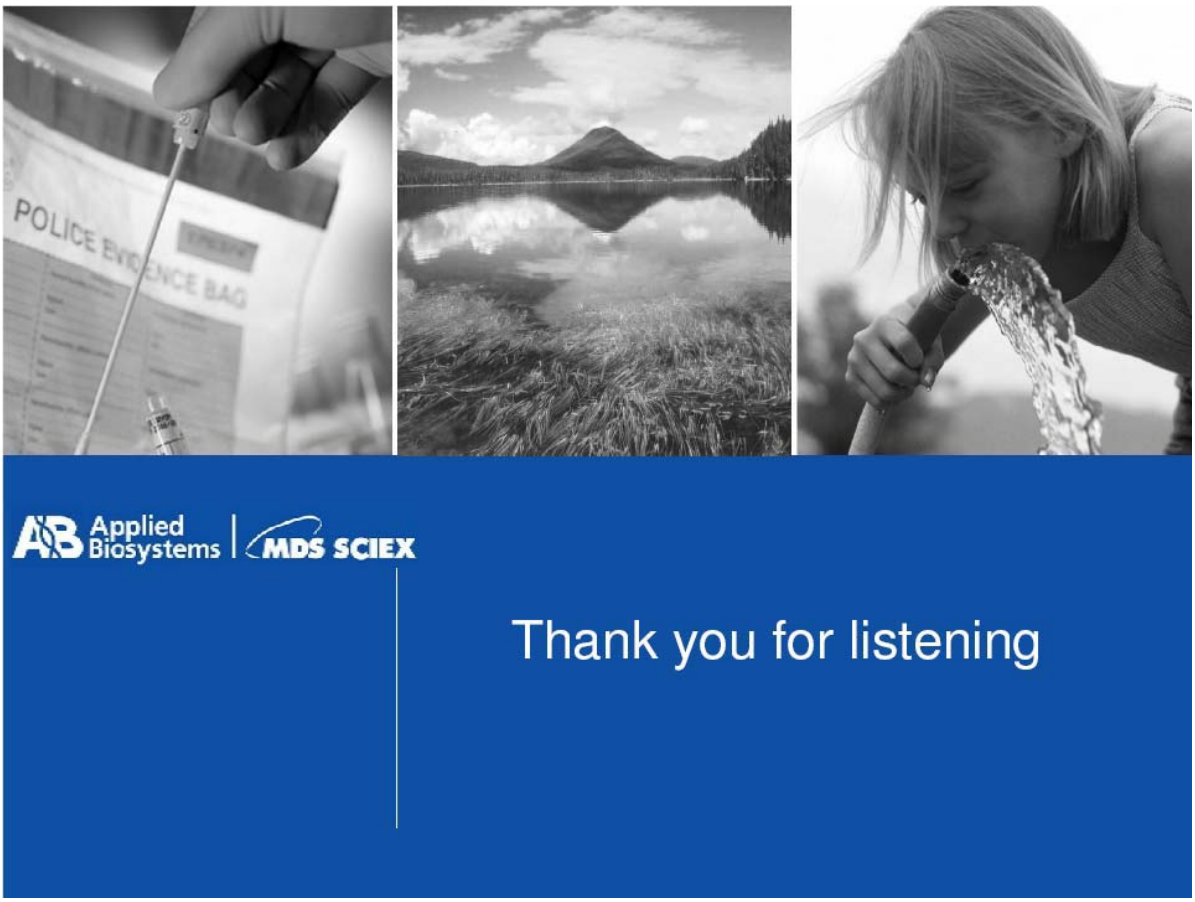
POLICE EVIDENCE BAG
Applied Biosystems
MDS SCIEX
Thank you for listening

ADVANCES IN PREPARATION AND ANALYSIS OF ORGANIC COMPOUNDS: IMMOBILIZED LIQUID EXTRACTION OF DRINKING OR WASTE WATER AS A NEW SAMPLE PREPARATION TECHNIQUE FOR GC/LC ANALYSIS

Gullett, Robert; Wohleb, Ian; Wohleb, Robert, and Wohleb, Thomas – Wohleb Scientific, Inc.

Classical methods for the extraction of water samples employed in EPA and Standard Methods for the analysis of drinking water or waste water are based on either liquid/liquid extraction or liquid/solid extraction employing solid phase extraction disks (SPE) disks. Liquid/liquid extraction is the less desirable of the two because it involves considerable time, labor, and expense. SPE disks reduce solvent consumption but still require sample concentration and are impractical to use when large quantities of particulates are present.

In this study we investigated the use of Immobilized Liquid Extraction (ILE) for aqueous environmental samples. ILE is a simplified procedure for extracting organic compounds from aqueous matrices (drinking water, groundwater, wastewater and etc.). ILE is a form of liquid/liquid extraction in which the "organic" phase is immobilized on the surface of an ILE device.

We chose ILE caps for this study. A portion of each ILE Cap was coated with a thin layer of a non-extractable homogeneous sorptive polymer. We evaluated the most commonly used hydrophobic elastomer polydimethylsiloxane (PDMS) and compared it to the more selective fluoro, phenyl and cyano siloxanes. The coating acts as the extraction medium, into which a targeted compound, or analyte(s), partition(s) from the sample.

For each extraction we placed an ILE cap on a bottle or vial that contained an aqueous sample. The vessel was agitated by a mechanical wrist-shaker such that the cap came in repeated contact with the aqueous sample. Upon completion of the extraction, the analyte-laden cap was removed and placed on a vial containing a small amount of suitable solvent (100-300 µL). The analytes were "back-extracted" into the solvent. The resultant extract was then ready for analysis by gas or liquid chromatography.

In this study we evaluated extraction efficiency and detection limits for pesticides, TPH, PCBs and semivolatiles. We present data on the effect of complex matrix interferants and evaluate increased throughput, decreased costs, greater precision, and reduced solvent usage and subsequent disposal.

Immobilized Liquid Extraction of Drinking or Waste Water as a New Sample Preparation Technique for GC/LC Analysis

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ABSTRACT

Traditionally, techniques used for the extraction of organic compounds from drinking and waste water samples employed in EPA and Standard Methods are based either on liquid/liquid extraction or liquid/solid extraction employing solid phase extraction (SPE) disks or cartridges. Liquid/liquid extraction is the less desirable of the two because it involves considerable time, labor, and expense. SPE reduces solvent consumption, but still requires sample concentration, and is impractical when large quantities of particulates are present in a sample.

This study investigates Immobilized Liquid Extraction (ILE) as an alternative technique for preparing aqueous environmental samples for analysis by gas or liquid chromatography. ILE is a form of liquid/liquid extraction in which the "organic" phase is immobilized on the surface of an ILE device. Though the ILE method may be applied to a number of procedures involving the extraction of organic compounds from aqueous matrices (drinking water, blood serum, wastewater, etc.), the scope of this study is strictly environmental, specifically relating to EPA methods 508, 525, 8270 and 8082. The effectiveness of the ILE method was evaluated in the extraction and subsequent analysis of polychlorinated biphenyls (PCBs) and other semivolatiles from spiked water samples. Method detection limits, reduced sample sizes and solvent usage, complex matrix effects, and enhanceable selectivity are discussed.

INTRODUCTION

To best evaluate the viability of ILE as a potentially effective EPA method for preparing aqueous environmental samples, we performed a series of experiments to determine method detection limits, extraction efficiency and data precision.

ILE shares many of its fundamental principles with liquid/liquid extraction (LLE), solid phase micro extraction (SPME), and stir bar sorbtive extraction (SBSE). The extraction is performed by an equilibrium process that depends on the analyte's partition ratio between the aqueous phase and the immobilized organic phase ($K_{PDMS/w}$), and on the phase ratio (β). As the ratio of the volume of organic phase relative to the volume of the sample (i.e., the phase ratio) increases, extraction efficiency increases. The partition ratio is analyte-specific, and defined as the concentration of an analyte in the PDMS relative the concentration of the same analyte in an equilibrated sample (note: the partition ratio of PDMS/Water is approximately equal to the partition ratio for octanol/water). From only this information one can estimate the expected efficiency of the extraction of any compound.

As stated earlier, the "organic," or extracting, phase is immobilized on the surface of an ILE device. This surface may be the inside of an autosampler vial, the inside surface of a bottle or vial cap, the inside surface of a disposable pipette or tip, or a number of other possibilities.

ILE Caps were chosen for this study. The septum of each ILE Cap is coated with a thin layer of a non-extractable homogeneous sorptive polymer. In this case, the most commonly used hydrophobic elastomer, polydimethylsiloxane (PDMS), was used, although selectivity may be altered or enhanced by using fluoro, phenyl or cyano siloxanes.

The polymer coating acts as the extraction medium, into which a targeted compound, or analyte(s), partition(s) from the sample matrix. Optionally a co-solvent may be used to enhance extraction speed and selectivity. The analyte(s) are then back-extracted from the polymer into a small amount of suitable solvent, and the resultant extract is ready for analysis by gas or liquid chromatography (in this experiment, all extracts were analyzed by a GCMS).

MATERIALS & METHODS

Instrumentation

Extracts were generated using the Wohleb Scientific, Inc. 24mm Immobilized Liquid Extraction (ILE) Cap. Each ILE cap septum is coated with a 508 micron thick layer of polydimethylsiloxane, resulting in a 122 uL "organic" phase. The appropriate volume of organic phase is determined by sample size, and caps with different volumes of polymer may be available to ensure the best results for samples of a variety of sizes.

Analysis of the extracts was performed by a Hewlett Packard 5971 GC-MS with a splitless injection port in scan mode and a 30 m x 0.25 mm i.d. x 0.25 µm VB-5 column. All samples were injected manually, which may be a source of additional uncertainty in recovered data.

Method

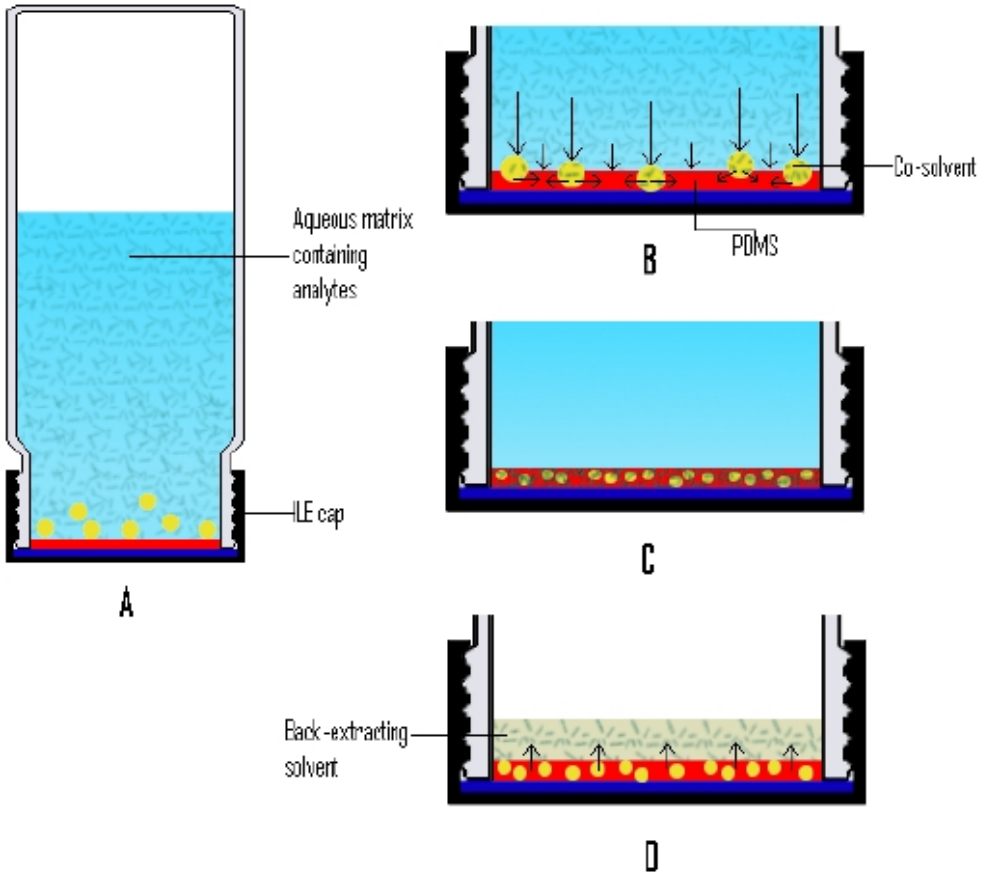
For each extraction, an ILE cap was placed on a 250 mL bottle containing a 100 mL water sample that was spiked with known quantities of one or more analytes. All internal standards and analytes of interest were present in each sample at concentrations of 0.5 µg/L (other than pentachlorophenol, which was at a concentration of 2.0 µg/L). A 100 µL aliquot of methylene chloride was added to each sample to add selectivity to and enhance the partitioning of analytes from the sample into the polymer (this co-solvent extraction step is described and evaluated in greater detail in the discussion section). The sample-containing vessel was then agitated by a mechanical wrist-shaker for 1 hour in a manner such that the cap came in repeated contact with the sample. This agitation disrupts the sample-polymer interface, thereby accelerating partitioning from the sample into the PDMS.

Upon completion of the extraction, the analyte-laden cap was removed and placed on a 10 mL conical bottom vial containing 100 µL of acetone. The vessel was then agitated for 30 minutes to accelerate partitioning from the methylene chloride swelled PDMS into any solvent that exceeds the swelling capacity of the polymer. The resultant extract was then analyzed by gas chromatography coupled with mass spectrometry.

The complete extraction procedure is detailed in Figure 1 below. **(A)** The initial sample containing analytes and co-solvent is inverted to allow contact between the sample and polymer. **(B)** When adding a co-solvent to the ILE process, the rate of extraction is enhanced by increasing

both total solvent surface area and volume. Analytes are first rapidly sorped into the co-solvent followed by concurrent sorption of the co-solvent and analytes into the polymer phase. The resultant partition ratio will be analogous to that of an aqueous phase and a mixed solvent system. **(C)** The polymer layer, swollen with a water immiscible co-solvent contains partitioned analyte(s). **(D)** The back-extraction process consists of the partitioning of the analyte(s) into a suitable solvent from the co-solvent swollen polymer.

Figure 1: ILE Cap Procedure



Calibration

Calibration spike solutions were composed by diluting appropriate aliquots of Accustandard M-525.2-SV-ASL in a 50:50 mixture of acetone and methylene chloride such that the concentrations of analytes of interest would correlate to a 100mL sample that is extracted with one-hundred percent efficiency. Calibration spikes were then analyzed by GCMS, and the MS response of the quantitation ion of each analyte in the spike was then related to the MS response of the quantitation ion of the internal standard with the nearest retention time, and an average response factor (RF) was assigned to each compound of interest (Equation 1). This response factor was later used to calculate the observed concentration, and subsequently, the extraction efficiency of a processed sample.

Equation 1: Response Factor

$$RF = \frac{(A_x) \cdot (Q_{is})}{(A_{is}) \cdot (Q_x)}$$

Where:
A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion internal standard
Q_x = quantity of analyte in calibration spike (µg)
Q_{is} = quantity of internal standard in calibration spike (µg)

Data Collection

The observed concentration of an identified compound in an extracted sample was calculated by relating the MS response of the quantitation ion of said compound to the MS response of the quantitation ion produced by a compound used as an internal standard (Equation 2).

Equation 2: Observed Concentration Calculation

$$C_x = \frac{(A_x) \cdot (Q_{is})}{(A_{is}) \cdot RF \cdot V}$$

Where:
C_x = concentration of analyte in water sample (µg/L)
A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion internal standard
Q_{is} = total quantity of internal standard added to water sample (µg)
V = original water sample volume (L)
RF = mean response factor of analyte from the initial calibration

Additionally, standard deviations and method detection limits (MDL) were determined for all compounds of interest.

RESULTS

Table 1 (below) displays a cross section of analytes of varying volatility, mass, and polarity. This data indicates that ILE has the capability to reproducibly extract a variety of semi-volatile analytes in the sub-nanogram/Liter range from 100 mL drinking and waste water samples.

Table 1: Calculating Method Detection Limits

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Acenaphthalene	0.5	0.37	8.3	73.9	0.17
Benzo(b)fluoranthene	0.5	0.48	6.8	95.6	0.14
Benzo(g,h,i)perylene	0.5	0.50	28.2	99.9	0.57
2-Chlorobiphenyl	0.5	0.49	6.3	97.1	0.13
2,3- Dichlorobiphenyl	0.5	0.57	1.2	113.1	0.02
Dibenz(a,h)anthracene	0.5	0.48	4.7	96.4	0.09
2,2,4,4,5,6-Hexachlorobiphenyl	0.5	0.53	8.8	106.4	0.18
Indeno(1,2,3-cd)pyrene	0.5	0.52	1.7	104.9	0.03
Pyrene	0.5	0.47	8.5	93.3	0.17
2,4,5- Trichlorobiphenyl	0.5	0.55	10.9	110.7	0.22

DISCUSSION

Smaller Sample Sizes, Reduced Solvent Usage, Matrix Effects

Current EPA-approved methods for analyzing semivolatiles in water require the use of an entire 1 L sample in order to provide data that is within the parameters that are required by the EPA (MDLs, precision, etc.). The ILE method requires only 100 mL of a 1 L sample to provide precise results and sufficient detection limits. This is possible because the ratio of extract volume to sample volume is identical to that associated with current EPA-approved methods. In current methods, a 1 mL extract is formed from a 1 L sample, whereas in ILE, a 100 µL extract is composed from a 100 mL sample (both result in a concentration factor of 1,000).

There are a number of advantages involved with this reduction in required sample size. First, in the case of operator error or equipment malfunction, the entire sample is not lost. Additionally, an analyst has the capability to archive an analyzed sample or to analyze the sample under similar conditions to permit verification of data. Last, a sample may be analyzed using a range of co-solvent / polymer combinations to enhance or alter selectivity.

The ILE procedure provides many other distinct advantages over currently accepted and practiced methods for environmental sampling. Both SPE, and especially LLE, involve complex, labor-intensive, multi-step procedures in which each step can introduce errors or loss of analytes.

The ILE procedure is composed of two non laborious steps. Additionally, solvent usage is decreased by factors greater than 100 and 1000 relative to SPE and LLE, respectively.

Many significant problems associated with the SPE method are avoided by ILE caps. ILE caps are immune to clogging by dirty samples, particulates, and viscous samples, and analyte breakthrough is avoided because ILE is an equilibrium reaction. Similarly, problems involved with LLE, such as the formation of emulsions, are avoided.

Co-Solvent Extraction & Sample Cleanup

In this series of experiments, a small amount of methylene chloride was added to each sample as a co-solvent to enhance partitioning from the sample into the polymer extraction medium. Compounds that may have a relatively low affinity for the PDMS may partition into the methylene chloride, which is effectively absorbed into the polymer, causing a sponge-like swelling effect. This co-solvent may be any organic solvent that is both absorbed by the polymer and is immiscible in water.

Different co-solvent/polymer combinations will yield different results, as many analytes may have a greater or lesser relative affinity for different solvents and/or polymers. For example, the appropriate combination of solvent and polymer may enhance selectivity for isolating (non)-halogenated analytes, PCBs from other interferants, or polar from non-polar analytes.

The addition of a co-solvent to a sample may also be omitted. Data collected from extractions both with and without co-solvent assistance suggests that some analytes may have a significantly greater affinity for methylene chloride than for either acetone or the PDMS. Because PDMS is capable of absorbing a much greater quantity of methylene chloride than acetone, analytes that retain a high concentration in the methylene chloride through the back-extraction process may yield a lesser MS response than expected. An analyst may also strategically determine his or her back-extracting solvent to enhance or alter specificity as he or she desires.

Additional specificity may be obtained by adding a rinsing or solvent cleanup step prior to the back-extraction of analytes from the polymer coating. This step is composed of rinsing the cap with a water miscible aqueous phase to essentially remove, or clean up, unwanted analytes (this step is common in SPE).

CONCLUSIONS

ILE is a promising new method for extracting organic compounds from aqueous matrices, and has terrific potential for environmental applications. The method consists of a simplified procedure that requires minimal operator effort, reduces solvent usage and allows for the analysis of smaller samples without compromising limits of detection and data precision. The possibilities to alter selectivity through strategic combinations of solvents and polymers will allow an experienced analyst to zero in on a compound, or type of compounds, with incredible ease. Further studies investigating the potential of the method in environmental and other applications are in progress.

REFERENCES

1. U.S. Environmental Protection Agency, 1995. *Method 525.2 – Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography / Mass Spectrometry*. Office of Research and Development.

Immobilized Liquid Extraction™ of Drinking or Waste Water as a New Sample Preparation Technique for GC/LC Analysis

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Introduction

- ***Traditional EPA and Standard Methods to extract organic compounds from water samples are based either on liquid/liquid extraction (LLE) or liquid/solid extraction employing solid phase extraction (SPE) disks or cartridges***
- ***Each technique plagued by shortcomings***
  - ***LLE is laborious, time-consuming, uses solvent excessively, may suffer from emulsions and requires solvent evaporation***
  - ***SPE requires sorbent conditioning, sample concentration, and is impractical when a sample contains particulates***
- ***This study investigates Immobilized Liquid Extraction™ (ILE) as a novel technique for extracting organic compounds from aqueous environmental samples***

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Scope of This Study

- *Discuss and study fundamental principles of Immobilized Liquid Extraction*
  - *ILE method, theory and devices*
- *Demonstrate viability of ILE as a method for preparing aqueous environmental samples*
  - *Analyse diesel, pesticides and semivolatiles from a variety of aqueous matrices*
  - *Enhance selectivity*
  - *Method detection limits*
  - *Reduced sample size and solvent usage*
  - *Complex matrix effects*

Wohleb Scientific

What is ILE?

- *ILE utilizes 'surface sorption extraction'*
  - *Popular 'surface sorptive extraction' systems include Solid Phase Micro Extraction (SPME), Stir Bar Sorbtive Extraction (SBSE) and Open Tube Sorptive Extraction*
- *Extracting phase immobilized on surface of ILE device*
  - *Surface may be the septum of a bottle or vial cap, the inner surface of a vial or disposable pipette (tip), or a number of other possibilities*
  - *True liquid liquid extraction*
  - *Non-extactable elastomers above T_g*

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How Does ILE Work?

- ***Liquid/liquid extraction in which the "organic" phase is immobilized on the surface of an ILE device***
  - ***Similar fundamentals to SPME, SBSE and LLE***
  - ***Equilibrium technique***
- ***Based on preferential sorption of analytes into immobilized sorbent***
- ***Analytes partition from sample matrix into immobilized polymer***
  - ***Optionally, a sample may be diluted with a small amount of solvent, salted out, or acidified to enhance extraction speed or selectivity***
- ***Analytes next desorped from immobilized polymer into a small amount of suitable GC or HPLC solvent***

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General ILE Method

- ***Two Step Method***
  - Extraction
    - Sorbent of ILE device directly exposed to aqueous sample
    - Targeted compounds partition from sample into immobilized phase until equilibrium is reached
      - Note: agitation will accelerate this process
  - Back-Extraction
    - Analytes desorped from immobilized phase into small amount of suitable solvent
    - Resultant extract ready for GC or HPLC analysis

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ILE Devices

- *ILE Cap*
- *ILE Direct Vial Extraction*
- *High Throughput ILE Devices*
- *Back Extraction Adapter*

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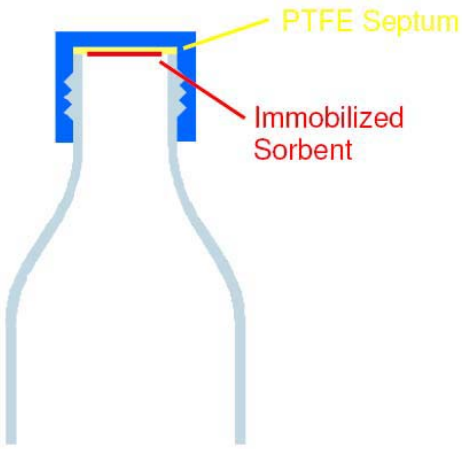
ILE Cap



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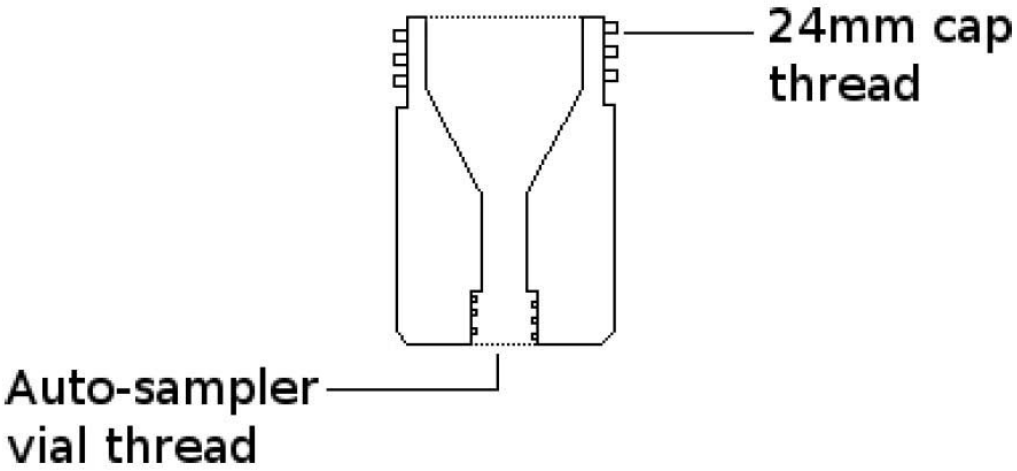
Back-Extraction Adapter

- ***Allows a technician to perform back-extraction directly into autosampler vial from 24mm ILE cap.***



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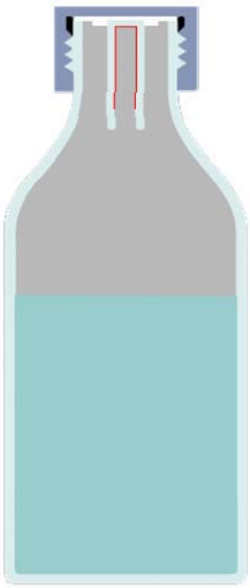
Direct Vial Extraction (DVE)



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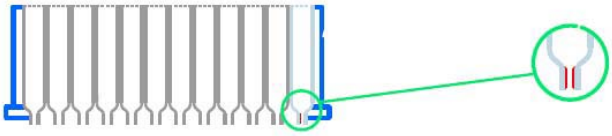
High Throughput ILE Devices

Standard well

Flow-through well



Pipette tip

Patents pending

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ILE Theory

- ***From only analyte specific partition ratios and the relative ratios of each of the phases (sample, polymer, residual solvent) one can easily calculate his or her expected total extraction efficiency:***

$$\%\ \text{Recovery} = \underbrace{\left(100 \cdot \frac{\frac{K_{Polymer/Sample}}{\beta_1}}{1 + \frac{K_{Polymer/Sample}}{\beta_1}}\right)}_{\text{Extraction Efficiency}} \cdot \underbrace{\left(100 \cdot \frac{\frac{K_{Solvent/Polymer}}{\beta_2}}{1 + \frac{K_{Solvent/Polymer}}{\beta_2}}\right)}_{\text{Back-Extraction Efficiency}}$$

$$\beta_1 = \frac{V_{Sample}}{V_{Polymer}} \qquad \beta_2 = \frac{V_{Polymer}}{V_{Solvent}}$$

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Enhancing Selectivity

- *Choice of extracting phase (non-polar to polar)*
- *Use and/or choice of co-solvent*
- *Adjusting pH of sample*
- *Salting a sample*

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Enhancing Selectivity

- *Series of experiments*
  - *20mL water samples spiked with a pesticide mix (525) such that each targeted analyte was at a concentration of 25 µg/L*
  - *Samples extracted using ILE caps*
  - *Effects of phase selection, co-solvent use, pH adjusting and sample salting investigated*

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Phase Selection

- ***ILE phases tested:***
  - ***PDMS***
  - ***Phenyl Siloxane***
  - ***50/50 PDMS/Fluorosilicone blend***
  - ***Carbon Black***
  - ***PDMS +10% acrylate ester***
  - ***Nitrile***
  - ***PEG***
  - ***PDMS/porous polymer blends***

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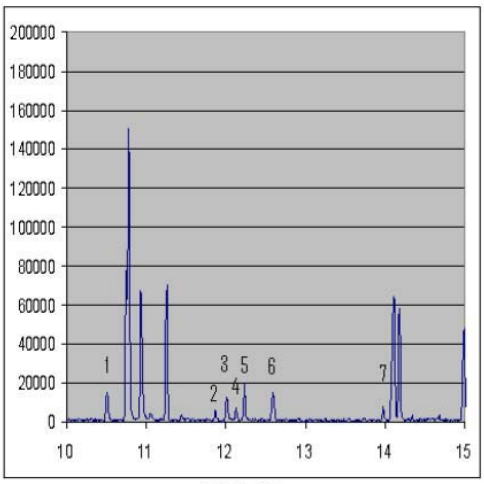
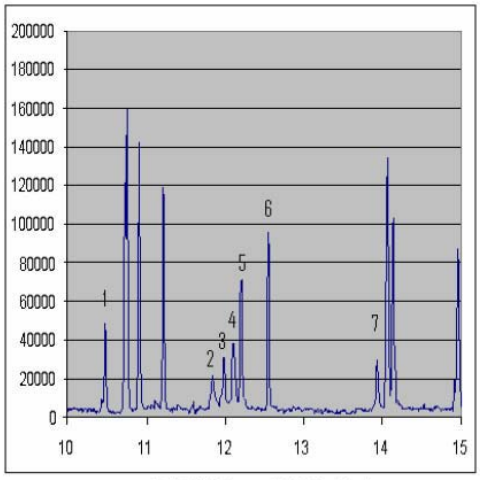
Phase – PDMS vs. PDMS + 10% Ester

1 – Propachlor
2 – Atraton
3 – Prometon
4 – Atrazine
5 – Propazine
6 – Pronamide
7 – Simetryn



– PDMS



- PDMS + 10% Ester

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Phase Selection Trends

- *Trends*
  - *MS response was dramatically increased with the PDMS + 10% ester for polar compounds that do not partition well into PDMS*
    - *Specifically, polar compounds that do not generally partition well into PDMS are attracted to the acrylate ester*
- *The availability of multiple phases that range in polarity allows an analyst to extract compounds that may otherwise be difficult, or impossible, using exclusively a PDMS phase*

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Selecting and Using a Co-Solvent

- *ILE polymers absorb solvents*
  - *ILE polymers swell when exposed to solvents*
    - *The polymer effectively acts like a sponge, soaking up the solvent*
    - *Each polymer has solvent-specific swelling capacities*
- *An appropriate co-solvent must be both sufficiently absorbed by the polymer being used, and water immiscible*
  - *The quantity of co-solvent used should be no greater than the swelling capacity of the polymer*

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Advantages of Co-Solvent Usage

- *Rate of extraction is enhanced by increasing both total solvent surface area and volume*
  - *Analytes first rapidly sorped into co-solvent, followed by concurrent sorption of co-solvent and analytes into polymer phase*
- *Different co-solvent/polymer combinations will yield different results*
  - *Ex: isolating (non)-halogenated analytes, PCBs from other interferants, or polar from non-polar analytes.*

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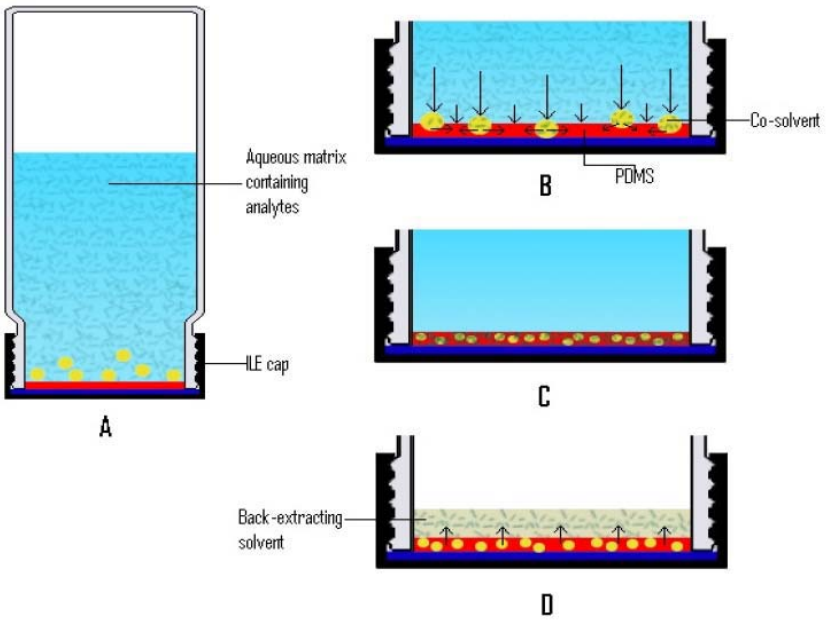
Co-Solvent Assisted Extraction



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An Example

- *The following slides depict the enhancement that resulted from introducing hexane as a co-solvent with a phenyl ILE cap*
  - *MS response was significantly increased across the board when the co-solvent was used*
    - *Eleven additional compounds were detected at quantifiable levels*

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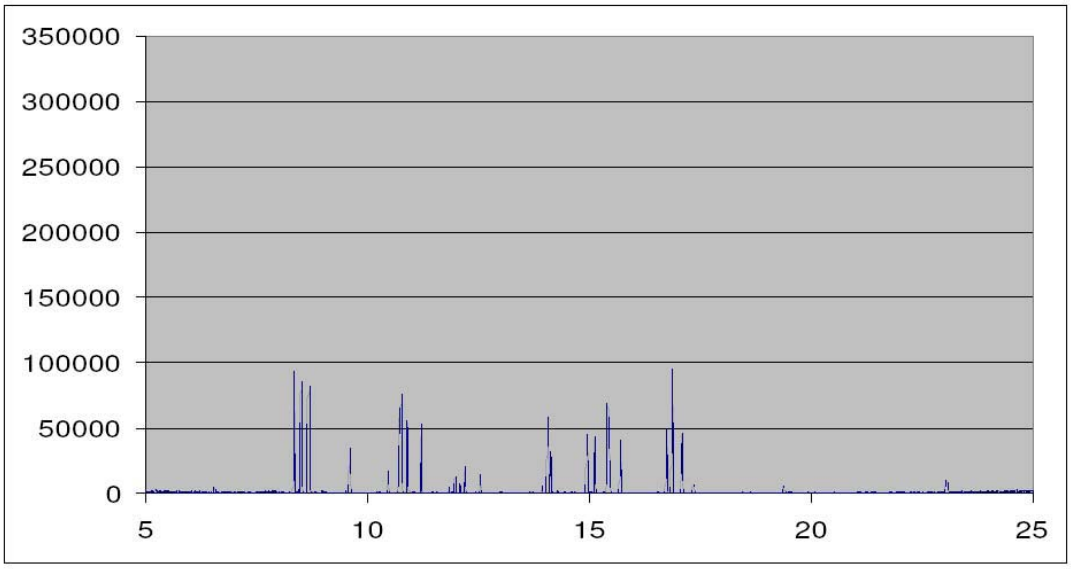
Phenyl / No Co-Solvent



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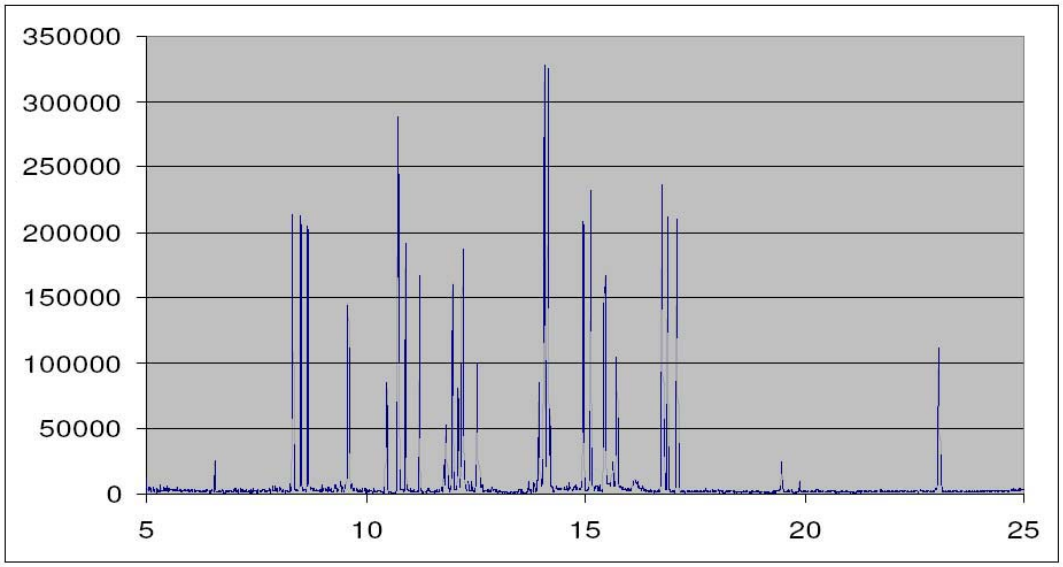
Phenyl / Hexane



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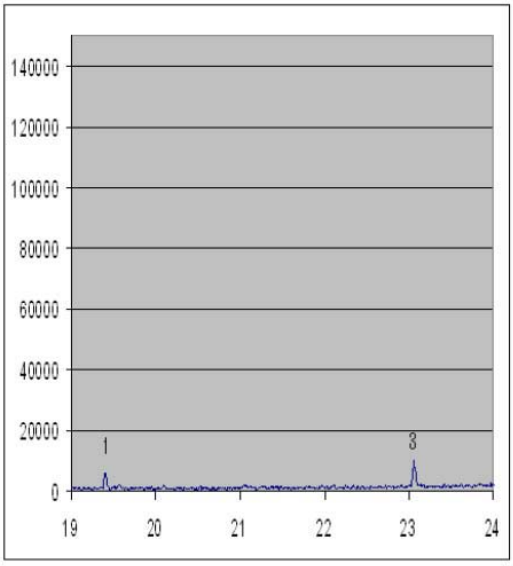
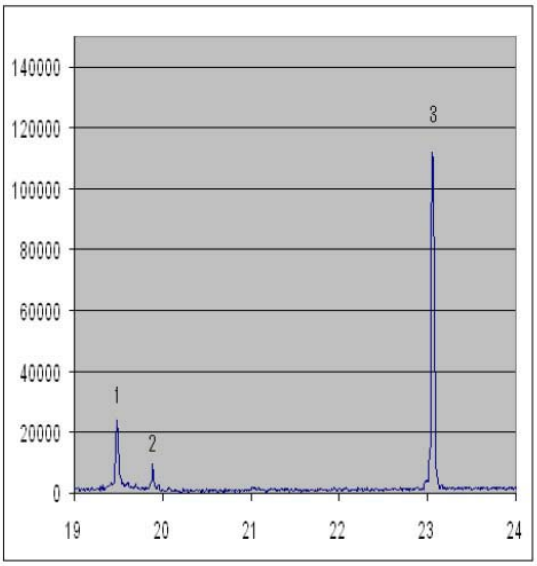
1 – Norflurazon
2 – Hexazinone
3 – Fenarimol



No Co-Solvent



Hexane

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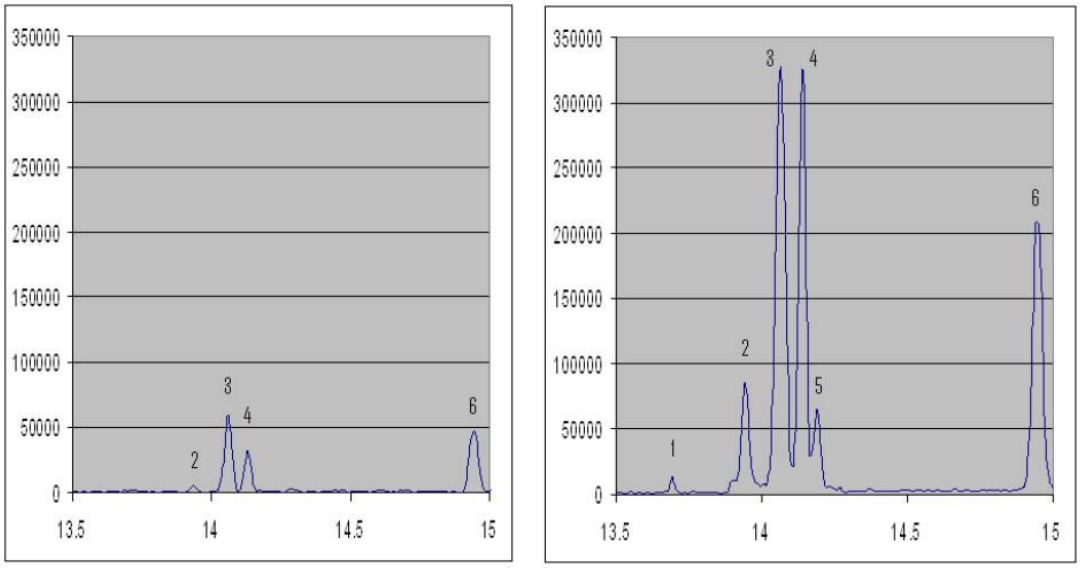
1 – Metribuzin
2 – Simetryn
3 – Alachlor
4 – Prometryn
5 – Bromacil
6 – Metolachlor



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Co-Solvent Summary

- ***The possibilities to alter selectivity through strategic combinations of solvents and polymers allows an experienced analyst to zero in on a compound, or type of compounds, with incredible ease***
  - ***Each targeted analyte in the pesticide mix was reproducibly extracted with at least one polymer/co-solvent combination***

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Sample Salting

- *The following chromatograms display the effect of sample salting on the ILE process*
  - *Two 20mL samples were spiked with pesticides and extracted using a PDMS ILE cap and methylene chloride as a co-solvent*
    - *One sample had 2 grams of table salt added*

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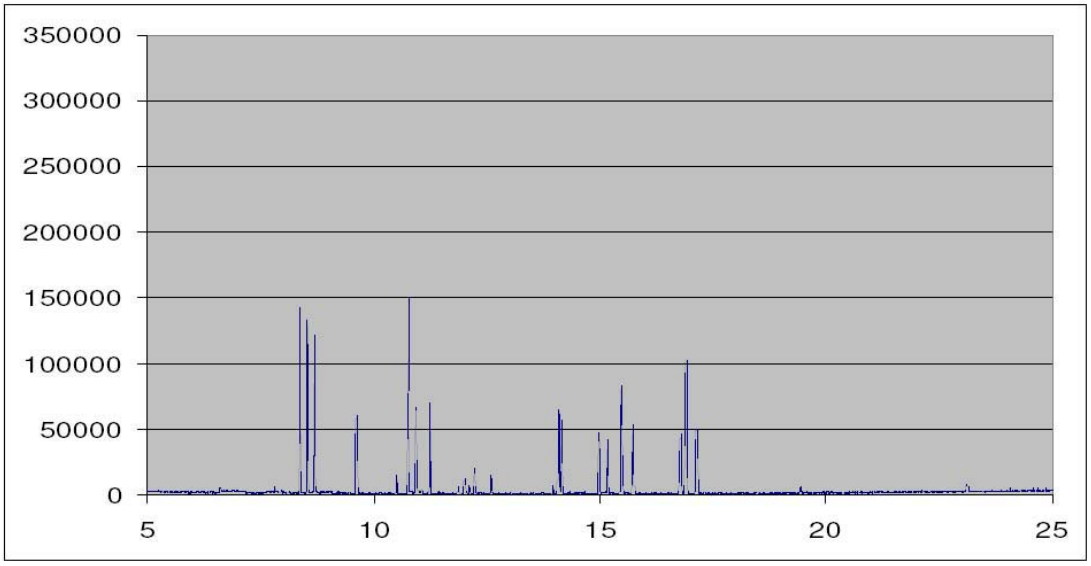
PDMS / Methylene Chloride



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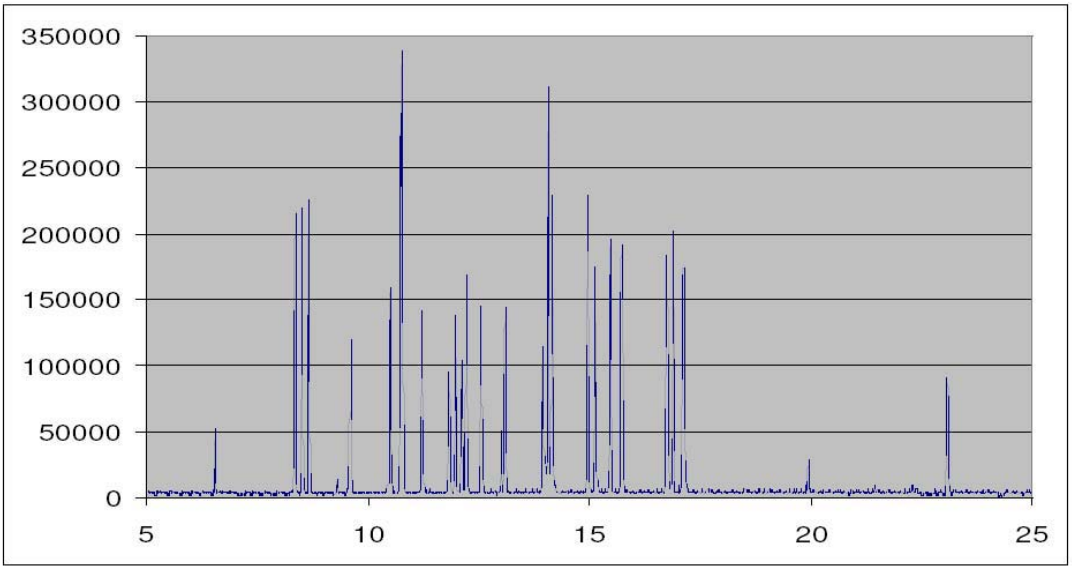
PDMS / Methylene Chloride + Salt



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Sample Salting

- ***Trends***
  - ***All compounds in the pesticide mix were detected in salted sample***
  - ***MS response was increased for most compounds of interest with sample salting***
    - ***The unsalted sample yielded significantly higher extraction efficiency with only four compounds***
      - ***Trifluralin (+145%), Butachlor (+25%), Cycloate (+18%), Butylate (+8%)***
      - ***Of 37 compounds in the pesticide mix, these are 4 out of the 5 compounds with highest Octanol:Water partition ratios***

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Adjusting pH (Semi-volatiles)

- ***Positive effects of sample acidification were realized in the extraction and analysis of a semi-volatile standard mixture in water***
  - ***All PCB's extracted more efficiently from acidified samples (increases ranged from 1-31%)***
  - ***The following table displays significant increases and decreases due to sample acidification (pH ~ 1.5)***

COMPOUND	+/-	Log $K_{O/W}$		COMPOUND	+/-	Log $K_{O/W}$
Acenaphthalene	-90%	3.94		Chrysene	43%	5.81
Pentachlorophenol	209%	5.12		Benzo(b)fluoranthene	39%	5.78
Anthracene	-42%	4.45		Benzo(k)fluoranthene	60%	6.11
Benz(a)anthracene	30%	5.76		Dibenz(a,h)anthracene	79%	6.75

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Selectivity & Efficiency - Diphenamid

	PHASE				
	PDMS	Phenyl	50:50 PDMS:Fluoro	Carbon Black	PDMS + 10% Ester
No Co-Solvent	38%	50%	18%	29%	28%
No Co-Solvent	49%				
No Co-Solvent	39%				
No Co-Solvent	51%				
Methylene Chloride	59%	75%	27%	37%	
Methylene Chloride	81%				
Hexane	55%	89%	40%		
Hexane		107%			
Hexane	58%				
MTBE	19%	28%	7%		

- No Salting / No pH Adjustment
- Salted Sample / No pH Adjustment
- No Salting / pH Adjusted to ~2
- Salted Sample / pH Adjusted to ~2

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Semi-Volatiles from Drinking Water

- *Series of experiments*
  - *100mL water samples spiked with a semivolatile mix where each analyte was at a concentration of 0.5 µg/L*
  - *Samples were extracted using methylene chloride as a co-solvent*

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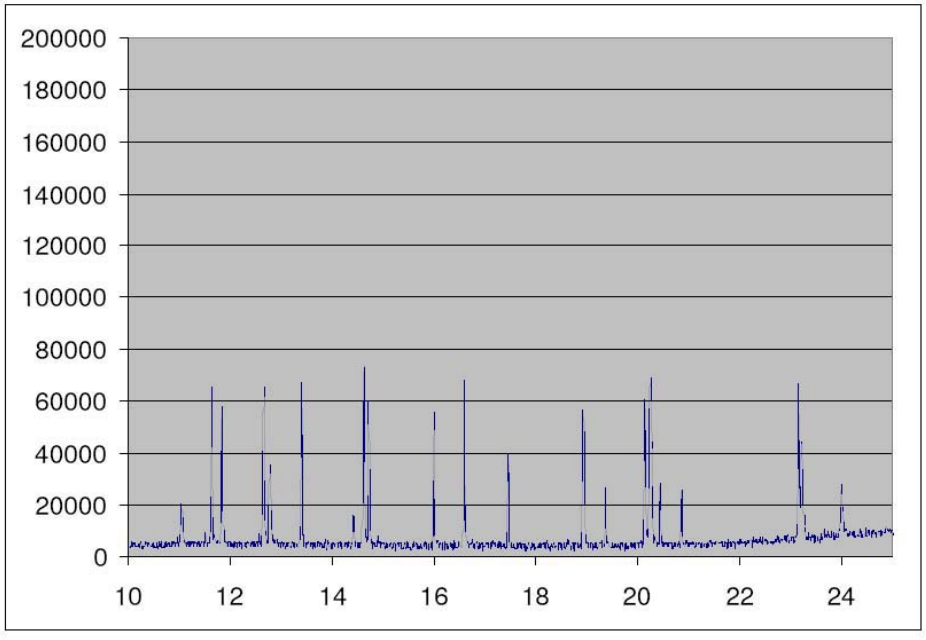
Semi-Volatiles from Water



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Method Detection Limits

- *ILE Caps tested for conformity to EPA protocols*
  - *Method Detection Limits were determined using the procedure outlined in Chapter 1 of SW-846*
    - *Sub-PPB Limits of Quantification were accomplished for 21 of 32 compounds tested*

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Method Detection Limits

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Acenaphthalene	0.5	0.37	8.3	73.9	0.17
Benzo(b)fluoranthene	0.5	0.48	6.8	95.6	0.14
Benzo(g,h,i)perylene	0.5	0.50	28.2	99.9	0.57
2-Chlorobiphenyl	0.5	0.49	6.3	97.1	0.13
2,3- Dichlorobiphenyl	0.5	0.57	1.2	113.1	0.02
Dibenz(a,h)anthracene	0.5	0.48	4.7	96.4	0.09
2,2,4,4,5,6-Hexachlorobiphenyl	0.5	0.53	8.8	106.4	0.18
Indeno(1,2,3-cd)pyrene	0.5	0.52	1.7	104.9	0.03
Pyrene	0.5	0.47	8.5	93.3	0.17
2,4,5- Trichlorobiphenyl	0.5	0.55	10.9	110.7	0.22

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Diesel From Ground Water

- *ILE Caps were tested for their ability to extract diesel from water*
  - *20mL of water was spiked with diesel at a concentration of 170 ppm and extracted with a PDMS ILE cap (no co-solvent)*

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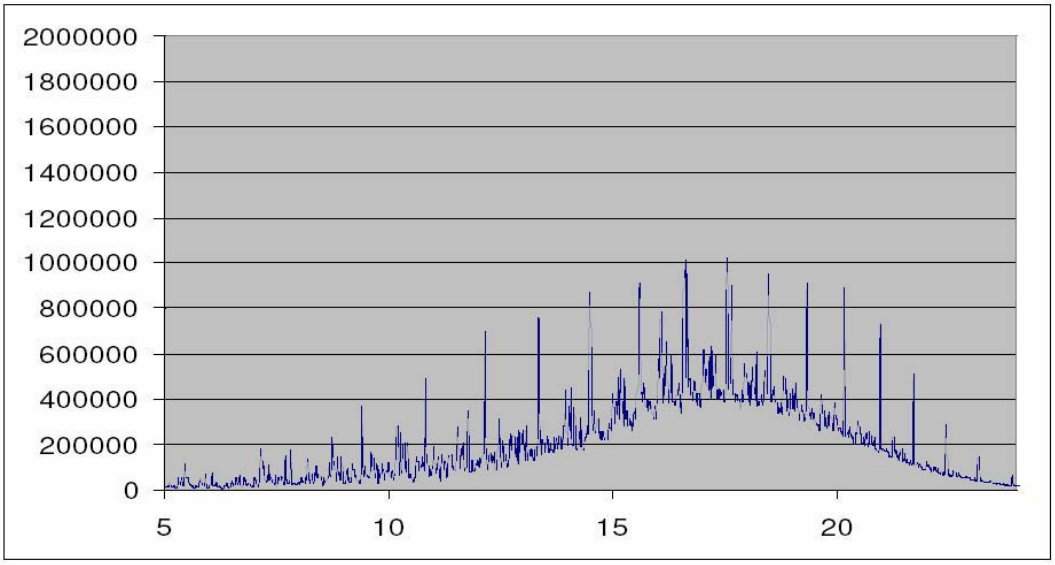
Diesel From Ground Water (170 ppm)



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Further Discussion

- *Smaller samples*
- *Reduced solvent usage*
- *Matrix effects*
- *Field extractions*

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Analyze Smaller Samples

- *Current EPA-approved methods for extracting diesel, pesticides, PCBs and semivolatiles from water require the use of an entire 1L sample*
- *ILE requires that only 100mL of a 1L sample be used to provide data within the parameters required by the EPA (MDL's, precision, etc.)*
- *Concentration effects*
  - *EPA methods: 1L sample to 1mL extract*
  - *ILE: 100 mL sample to 100µL extract*
  - *Same 1000:1 concentration factor*
    - *A large volume injector would increase sensitivity and/or reduce sample size further*

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Analyze Smaller Samples

- *Advantages*
  - *Operator error or equipment malfunction no longer results in loss of entire sample*
  - *Samples may be extracted and archived for later analysis*
  - *Duplicate analyses permit data verification*
  - *A sample may be analyzed under a variety of conditions (different phase, co-solvent, pH & etc.*

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Reduced Solvent Usage

- *ILE Cap extractions use less than 300 microliters of solvent*
  - *Solvent usage decreased by factors greater than 100 and 1000 relative to SPE and LLE, respectively*
  - *Save money on purchase and disposal of solvents*
  - *Environmentally favorable method*

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Matrix Effects

- *ILE caps are immune to clogging by dirty samples, particulates, and viscous samples*
- *Analyte breakthrough is avoided because ILE is an equilibrium reaction*
- *Problems associated with LLE, such as the formation of emulsions, are avoided.*

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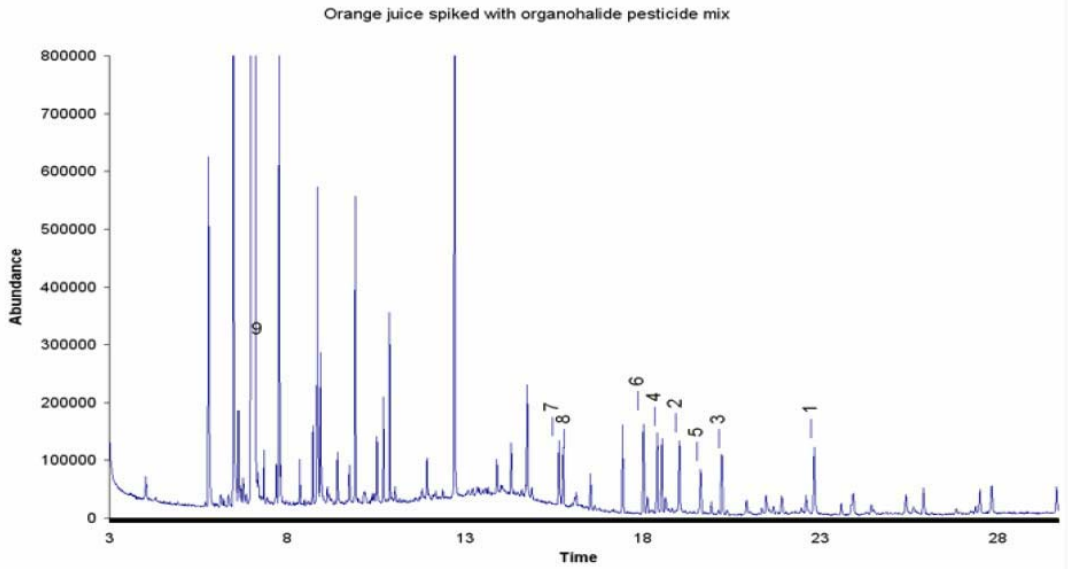
Matrix Effects



1. Methoxychlor, 2. Dieldrin, 3. Trans-Nonachlor, 4. Trans-Chlordane, 5. Endrin, 6. Chlordane, 7. Alachlor, 8. Heptachlor, 9. Limonene.

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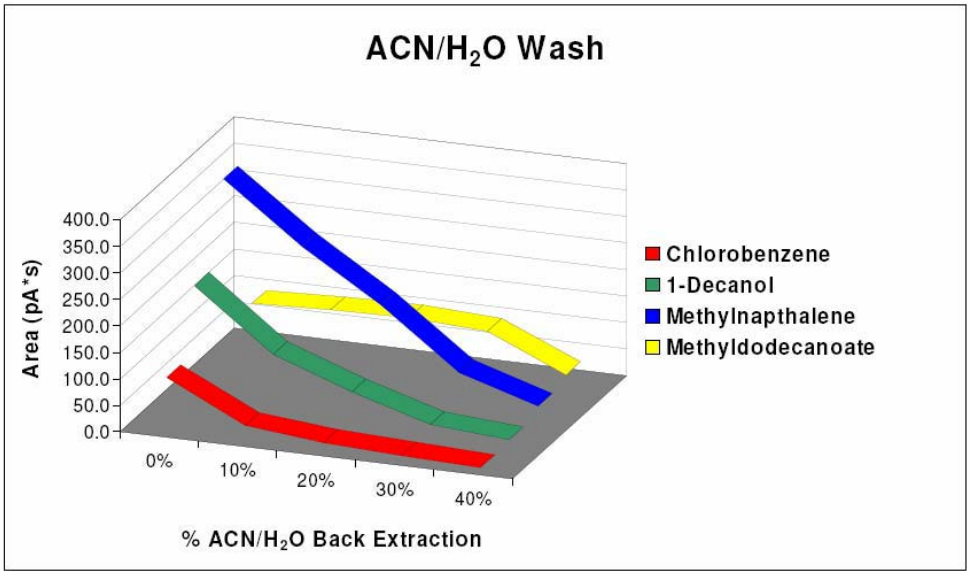
Sorbent Washing



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Field Extractions?

- A sample may be collected and immediately placed in an ILE bottle or vial, or in a container that is sealed by an ILE cap
  - Extraction performed during transportation of sample to laboratory
    - This gives the sample ample time to reach complete equilibrium
      - Back-extraction and injection consequently become only steps in a laboratory analysis

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Conclusions

- *ILE is a promising new method for extracting organic compounds from aqueous matrices*
  - *Terrific potential for environmental applications*
  - *Simplified procedure requires minimal operator effort, reduces solvent usage, and allows the analysis of smaller sample size without compromising limits of detection or precision*
  - *An experienced analyst may strategically adjust his experimental conditions through choice of phase, use of co-solvent, etc., to zero in on a specific compound, or group of compounds*

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Thank You!

Accelerated Solvent Extraction (ASE) as a Innovative Sample Preparation Technique for Conventional and Emerging Pollutants in Environmental Samples

Sheldon Henderson, Eric Francis, Richard Carlson and Bruce Richter
Dionex Corporation

ABSTRACT

Accelerated solvent extraction (ASE) is an innovative approach to liquid-solid extraction. It is accepted under Method 3545A for the extraction of conventional environmental toxins such as PCBs, dioxins, PAHs, diesel range organics and chlorinated pesticides. This technique uses elevated temperature and pressures to achieve analyte extractions from solid or semi-solid matrices in about 15 minutes and with small volumes of solvents. For example, a 10-g sample can be extracted in about 12 minutes and with about 15 mL of solvent.

There has been increasing concern from scientists and public health officials about emerging pollutants such as brominated flame retardants, perchlorate, hexavalent chromium and perfluorooctanoic acids. These compounds are derived from various sources in the manufacturing of consumer electronics and consumer products. These contaminants may also come from chemical or industrial manufacturing sources. These compounds have been shown to enter the ecosystems via disposal into landfills and have been found in groundwater, soils and sediments, plant and animal tissues and eventually into the human system.

Traditional methods such as Soxhlet or shakers have been used to extract samples containing these toxins. These methods require long periods of time (16 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 and emerging contaminates. Comparisons of analyte recovery and sample handling efforts to traditional methods of extraction will be presented.

Accelerated Solvent Extraction (ASE®) as an Innovative Sample Preparation Technique for Conventional and Emerging Pollutants in Environmental Samples

Sheldon Henderson, Eric Francis, Richard Carlson, Brett Murphy and Bruce Richter

Dionex Corporation, Salt Lake City, Utah

Summary Slide

- Accelerated Solvent Extraction (ASE®) as an Innovative Sample Preparation Technique for Conventional and Emerging Pollutants in Environmental Samples

Sample Preparation Issues

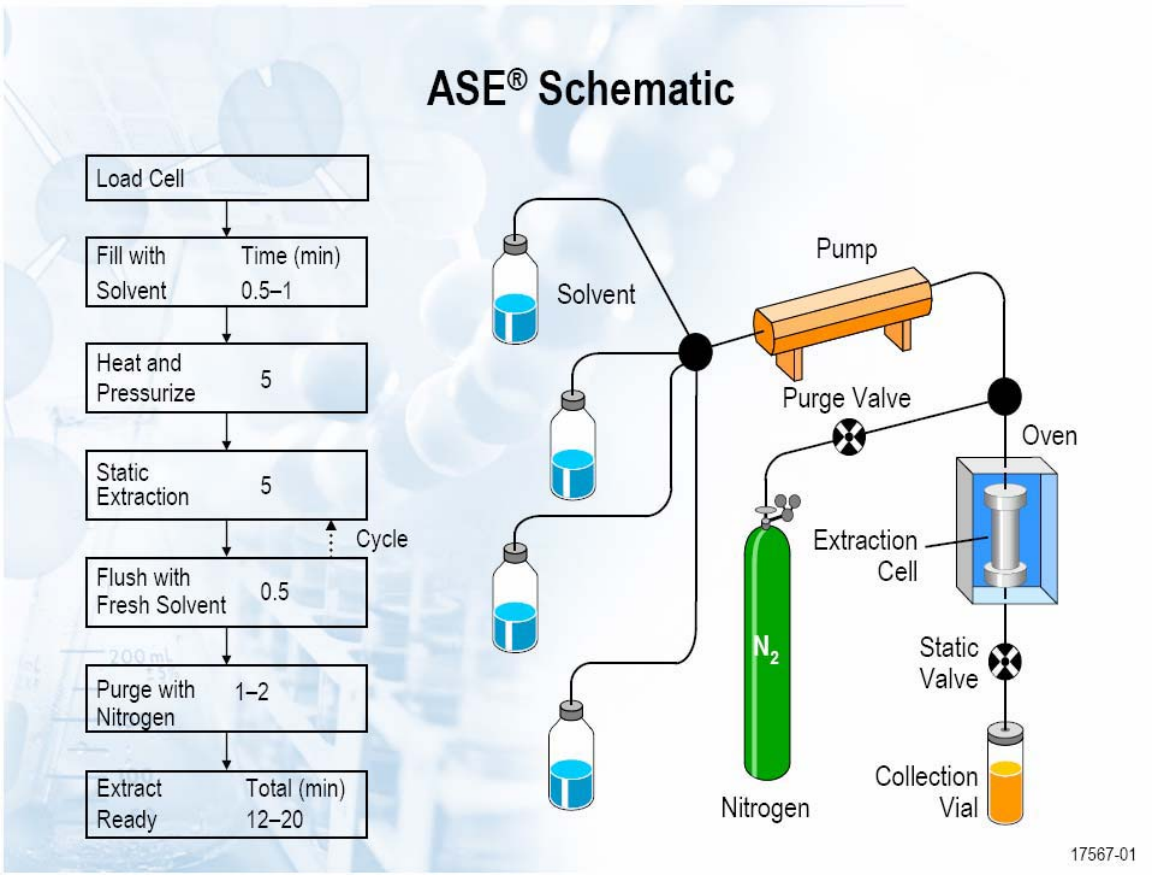
- Sample handling is the single biggest source of errors
- Single biggest bottleneck in an analytical process
- All laboratories are being asked to do more with less resources
- Time is money
- Costs of solvent purchase and disposal are increasing
- Dionex has developed ASE® compatible techniques to address these issues

22863

What Is ASE®?

- An automated extraction technique that uses liquid solvents and solvent mixtures
- Extracts solid or semisolid samples
- Uses elevated temperatures (40–200 °C) and pressures (500–3000 psi)
- Use of elevated temperatures and pressures accelerates the extraction process

20034


ASE® Schematic
Load Cell
Fill with Solvent
Time (min) 0.5–1
Heat and Pressurize
5
Static Extraction
5
Cycle
Flush with Fresh Solvent
0.5
Purge with Nitrogen
1–2
Extract Ready
Total (min) 12–20
Solvent
Pump
Purge Valve
Oven
Extraction Cell
Static Valve
Collection Vial
Nitrogen
N_2
17567-01

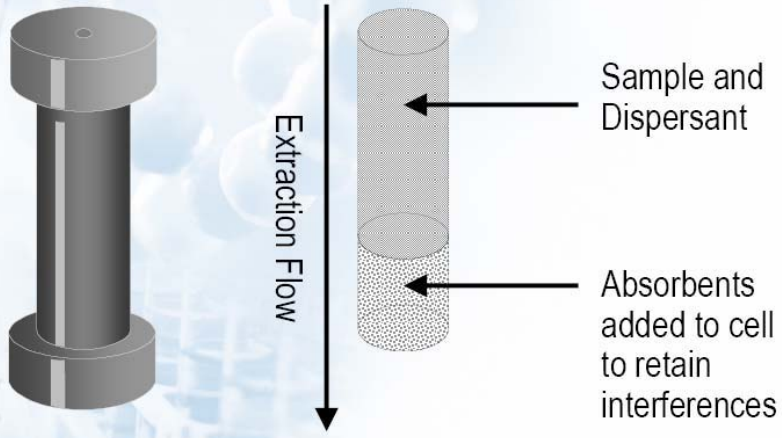

Dionex Tools and Techniques for Sample Prep
ASE® 100, 200, and 300
20037

Dionex Tools and Techniques for Sample Prep

SE 500 and SE 400

22868

Dionex Tools and Techniques for Sample Prep

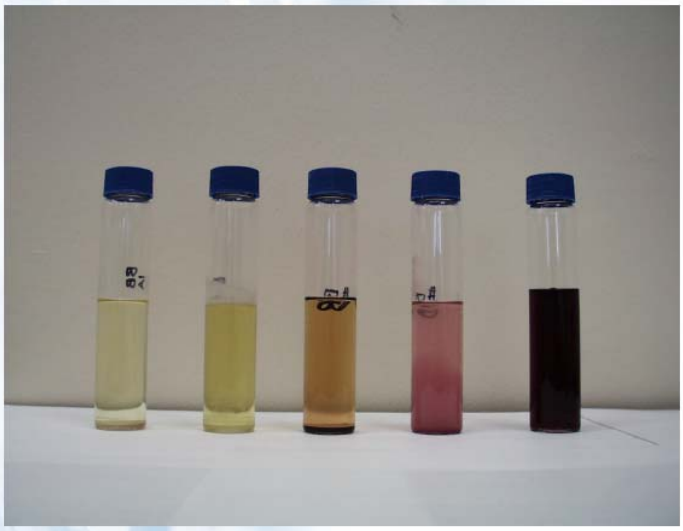


Schematic of In-Cell Cleanup with ASE®

20045

Dionex Tools and Techniques for Sample Prep

Selective Extraction of Blueberries



Hexane, DCM, ethyl acetate, acetonitrile, ethanol

Environmental Matrices Investigated

- Soils
- Sludges
- Sediments
- Plant and animal tissues
- Air Samples
  - Quartz filters
  - Tenax resins
  - Charcoal adsorbents
  - PUF and XAD resins
- Essentially all solid or semi-solid matrices analyzed for environmental contaminants

ASE Environmental Applications (Conventional Pollutants)

- US EPA Method 3545A
  - Pesticides and Herbicides
  - Semi-volatiles and PAHs
  - PCBs
  - PCDDs and PCDFs
  - TPH (DRO)
- Explosives
- Organotin and organoarsenic compounds
- Ionic materials

ASE Applications (Emerging Pollutants)

- Perchlorate
  - Explosives and Rocket Propellants
- PBDE
  - Flame Retardants
- Chrome (VI)
  - Curing agent
- Perfluorooctanoic acid
  - Oil or water repellant

TUESDAY, AUGUST 29, 2006

CONCURRENT SESSIONS

Chemical Speciation -- As

ANALYZING ARSENIC SPECIES IN SEAFOOD

Chamberlain, Isa; EPA Region 10 Laboratory

Arsenic, a known carcinogen and toxin at low concentrations, is a naturally occurring and man-introduced element found in all environmental matrices (soil, water, and air), as well as living matter. Therefore, arsenic exposure assessment requires evaluation of the relative contribution of both media (water, food, etc.) and routes of exposure (ingestion, inhalation, dermal). Seafood is known to contain high levels of arsenic. EPA Region 10 seafood consumption rates are above average national values due to a large population of Native American and Alaska Native. In addition, the Asian and Pacific Islander population in the Puget Sound Area favors shell fish species and bottom fish which ingests sediment and does not solely filter marine water. Thus, Superfund and RCRA Clean-Up goals in the Puget Sound are derived from food modeling risk assessments. However, understanding the risk from eating seafood is a complicated issue, as different chemical forms of arsenic vary significantly in their toxicity.

This is a procedure for extracting different forms or species of arsenic from seafood using tetramethyl ammonium hydroxide (TMAOH). The extract is then analyzed using ion chromatography (IC) to separate the species prior to detection by inductively coupled plasma – mass spectrometry (ICP-MS). The types of seafood for which this method has been developed are seaweed, finfish, and shellfish. The species separated and analyzed by this method are: arseneous acid (As3+), arsenic acid (As5+), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), arsenocholine (AsC), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TMA) and arsenosugars [As(328), As(392), As(408), etc.]. This procedure allows for the calculation of mass balance and the effectiveness of the arsenical extractions enabling the data users to more accurately estimate exposures.

A Procedure for Extracting and Analyzing Arsenic Species in Seafood

By
Stephanie Le, Isabel Chamberlain, and Katie Adams

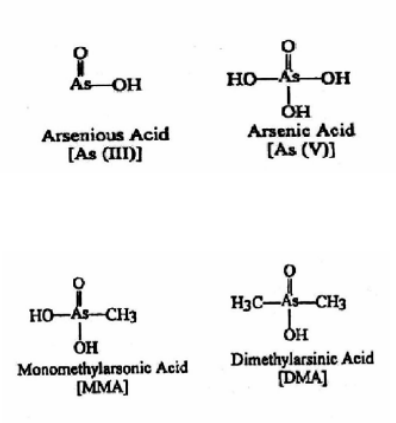
1

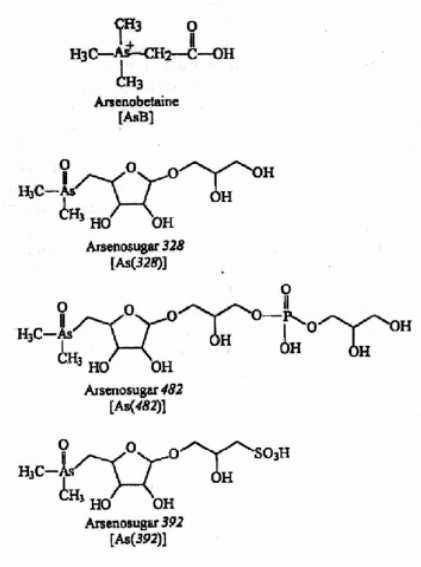
Why our interest in Arsenic Speciation analysis?

- **Two major sources of arsenic exposure are drinking water and dietary ingestion.**
- **Seafood typically contains high levels of arsenic**
- **In Region 10 (Alaska, Idaho, Oregon, and Washington), seafood consumption rates are often well above national values.**

2

Examples of Arsenic Species:





4

Arsenic Species Toxicity

Most Toxic ▸ **Inorganic Arsenic** (As III and As V)

▸ **MMA and DMA**

Least Toxic ▸ **AsB and Arsenosugars**

5

Risk Assessment…

How much of the toxic species are present

- In different seafood types?
- In different seafood sources?



6

The Birth of a Method...

RARE (Regional Applied Research Effort)

Region 10's $$

EPA Research Laboratory

Product for Region 10
(As Speciation Method)

7

Collaboration with Cincinnati

Method developed by Dr. Jack Creed's research group

- Extraction Method
- Chromatography (Columns, Eluents)
- ICP-MS detector

8

Collaboration with Cincinnati

- Transferred technique to Region 10 Laboratory
- Inter-Laboratory comparison

9

Collaboration with Cincinnati

R10 made contributions for routine analysis

- Determined the chromatography detection and quantitation limits
- Refined calibration scheme
- Developed QC checks and criteria
- Tested/incorporated Duplicates, Spikes, and Controls with criteria
- Wrote/submitted method in SW-846 format

10

Instrumentation

Instruments used at Region 10 Laboratory are:

- Perkin Elmer Series 200 LC Pump, Autosampler, Vacuum Degasser
- Perkin Elmer ICPMS ELAN 6100 DRC Plus

11

Analytical Approach – Extraction

- Sample preparation (Freeze Dry, Homogenize)
- Extraction of arsenicals with 0.83% Tetramethylammonium hydroxide (TMAOH) at 60 ˚C
  - High extraction efficiency
  - Works well for shellfish, finfish, and seaweed
  - Minimal degradation of arsenosugars
  - But, does not preserve As III / As V
- Neutralization of extract with acetic acid at 80 ˚C
  - Removes some excess protein
  - Preparation for chromatography

12

Analytical Approach – Anion Chromatography

- Hamilton PRPX-100 column
- Ammonium Carbonate eluent
- Inorganic As (As III + As V), MMA, DMA, some sugars
- Cations in void volume

13

Analytical Approach – Cation Chromatography

- Chrompack Ionosphere® column
- Pyridinium eluent
- AsB, Arsenocholine (AsC), Trimethylarsonium (TMA), Trimethylarsine Oxide (TMAO), some sugars
- Anions in void volume

14

Analytical Approach – Detection

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

- Monitor mass 75 (arsenic)
- Post-column Reference Peak to compensate for sensitivity drift from cone occlusion

15

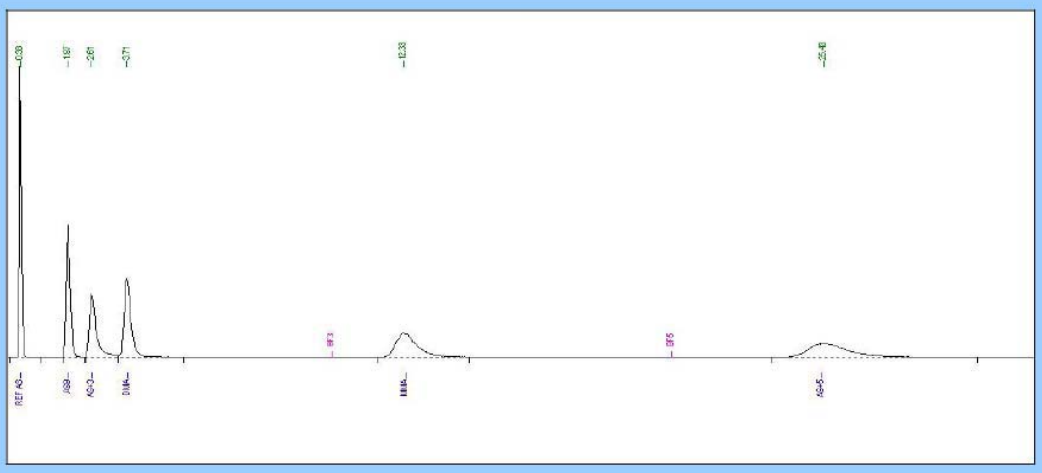
Analytical Approach – Efficiency

Potential for losses during extraction, chromatography steps, therefore:

- Total arsenic determination on FISH
- Total arsenic determination on EXTRACT
- Sum of arsenic species after chromatography

16

Example: Anion Chromatogram



Run time: 32 minutes

17

Example: Report to Data User

1	2	3	4	5	6	7	8	9	10	11	12	13
Sample Number	Sample Type	Total Arsenic in tissue (ug/g)	Total Arsenic in extract (ug/g)	Extraction Efficiency (%)	As Speciation					Sum of All Species (ng/g)	Chromatographic Recovery (%)	Overall Speciation Recovery (%)
					Anion Chromatography							
					DMA (ng/g)	MMA (ng/g)	Inorganic As (ng/g) As3 + As5	AsB + Cation species (ng/g)	unknown species (ng/g)			
05204050	Geoduck	15.6	9.90	63	890	204 U	1020	3150	3300	8360	84	54
05204050DU	Geoduck	15.6	10.1	65	791	204 U	1020	2920	3050	7781	77	50
05204050S1	Geoduck	NA	NA	NA	91%	103%	101%	87%	NA	NA	NA	NA
05204050S2	Geoduck	NA	NA	NA	98%	108%	104%	99%	NA	NA	NA	NA
04320042	English Sole	25.9	21.6	83	408 U	408 U	408 U	19800	408 U	19800	92	76
04320042DU	English Sole	25.9	22.1	85	408 U	408 U	408 U	19800	408 U	19800	90	76
04364102	Clam	11.4	8.32	73	754	102 U	1130	2480	2210	6574	79	58
04364102DU	Clam	11.4	8.41	74	803	102 U	1160	2580	2300	6843	81	60
MEF080205AC0	Dorm	18.0	19.4	108	300	408 U	408 U	15400	408 U	15700	81	87
MEF080205AL1	Spike blk	10.0	10.5	105	97%	99%	101%	99%	NA	NA	95	99
MEF080205ABL	Blank	NA	NA	NA	204 U	204 U	204 U	204 U	204 U	NA	NA	NA

18

Method 1632A – a Hydride Generation technique

- Only detects hydride-forming species (inorganic As, MMA, DMA)
- Not possible to perform mass balance to determine efficiency

19

Challenges! Limited Standards

"Why should we create standards? There are no methods that use them" -Standards Providers

"But we need standards to validate methods!" -Speciation Scientists

20

Challenges! IC-ICPMS Not An Approved Method

VS

21

Currently.....

- Draft method in SW-846 format.
- Method & workplan submitted to EPA Office of Solid Waste in April 06.
- Workgroup review completed in May 06. Comments will be considered/incorporated.
- Proceed with workplan.

22

ARSENIC SPECIES DETERMINATION

Pohl, C.A.; Dionex Corporation
Slingsby, R.W.; Dionex Corporation

Arsenic is ubiquitous in the environment in various forms, including inorganic and organic compounds and trivalent and pentavalent states. In general, methylated and other organo-arsenicals are less toxic than inorganic arsenic, and trivalent arsenic is considerably more toxic than pentavalent arsenic. So arsenic can be classified as highly toxic when in the inorganic form, and as innocuous to human when present as certain organo-arsenicals. The USEPA has classified inorganic arsenic as a known human carcinogen, but arsenobetaine, a water soluble pentavalent organoarsenical, is very stable, metabolically inert, and relatively nontoxic and thus poses little toxicological risk to the organism or its consumers. Therefore the speciation of arsenic in various samples is important to assess the risk to human health.

In this study, ion chromatography has been coupled with electrospray mass spectrometry (IC-ESI-MS) to quantitatively determine five arsenic species. We will present a method for the determination of Arsenite(AsIII), Arsenate(AsV), Monomethylarsonic acid(MMA), Dimethylarsonic acid(DMA) and Arsenobetaine(AsB) using IC-ESI-MS. Relative to ICP-MS, the competitive method, ESI-MS has the advantage of providing mass-to-charge information for each arsenic species. Arsenite and arsenate are retained by anion exchange at high pH and arsenobetaine, monomethylarsinic acid and dimethylarsonic acid are retained at acidic pH. The combined analyses of these analytes can be accomplished using a dual IC system comprising anion exchange and cation exchange columns, or using a mixed phase column.

Since these five species have pKa values ranging from 2-9 and arsenobetaine is amphoteric, this analyte set represents a significant analytical challenge in obtaining good chromatographic retention for all species, especially in complex food matrices. We report progress on a new mixed phase analytical column as well as several hardware configurations that allow the determination of these five arsenic species in a single analysis using an ESI-MS compatible eluent system. Presently, there are no ESI-MS compatible chromatography methods that provide good retention of all five arsenic species.

Separation and Detection of Arsenic Species using Dual Selectivity IC-MS

Rosanne W. Slingsby[1], Rida Al-Horr[1], Christopher A. Pohl[1], and Joung Hae Lee[2]
[1]Dionex Corporation; [2] Korea Research Institute of Standards and Science

ABSTRACT

In this study, two ion exchange selectivities are combined using a dual ion chromatograph that is coupled with electrospray mass spectrometry (IC2-ESI-MS) to determine anionic, cationic and zwitterionic arsenic species. This scheme provides adequate chromatographic retention of all arsenic species while also providing detection using electrospray ionization mass spectrometry for structural information. We present a method for the determination of Arsenite(AsIII), Arsenate(AsV), Monomethylarsonic acid(MMA), Dimethylarsonic acid(DMA) and Arsenobetaine(AsB) using IC2-ESI-MS. Since these five species have pK_a values ranging from 2-9 and arsenobetaine is amphoteric, this analyte set represents a significant analytical challenge in obtaining good chromatographic retention for all species. Relative to ICP-MS, the competitive detection method, ESI-MS has the advantage of providing mass-to-charge information for each arsenic species. Compared to other chromatography methods, this method provides good retention of all five species in one analytical method. The combined analyses of these analytes can be accomplished using a dual IC system comprising anion exchange and anion/cation exchange separations that are delivered sequentially to the mass spectrometer in one data file.

INTRODUCTION

Arsenic is ubiquitous in the environment in inorganic and organic compounds and trivalent and pentavalent states. In general, methylated and other organo-arsenicals are less toxic than inorganic arsenic, and pentavalent arsenic is considerably less toxic than the trivalent state. The USEPA has classified inorganic arsenic as a known human carcinogen, but arsenobetaine, a water soluble pentavalent organoarsenical, is very stable, metabolically inert, and relatively nontoxic and thus poses little toxicological risk to the organism or its consumers [1,2]. The speciation of arsenic in various samples is important to assess the risk to human health.

The use of reversed phase columns with ion-pairing eluents and separate anion exchange and cation exchange systems for the separation of As(III), As(V), MMA, DMA, AsB and other arsenic species have been reported [3,4,5]. Most of the mobile phases are incompatible with electrospray ionization-MS. Use of a combination of anion exchange and cation exchange columns is necessary to retain this mix of arsenic species since this group includes anions, cations and the amphoteric arsenobetaine. Separation schemes that do not include both functionality columns show at least one arsenic compound in or near the void volume, thus not separated from matrix components. In general, the earliest eluting arsenic species, usually arsenite or arsenobetaine depending on the retention mechanism, is barely retained from the void and therefore is susceptible to ionization suppression from sample matrix components when ESI is used.

In the present paper we present an analytical scheme that combines gradient anion exchange with mixed mode anion/cation exchange isocratic elution so that all five arsenic species are well retained and separated in one analytical run. The mobile phases are compatible with ESI-MS detection.

Experimental

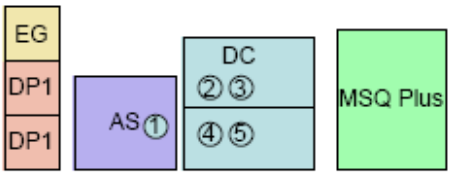
Instrumentation - The ion chromatograph used in this work was the Dionex ICS 3000 (Dionex Corp., Sunnyvale CA USA) that included a Dual pump module with two analytical pumps (DP1, DP1), and eluent generator (EG0), a conductivity detector (CD), autosampler that included a diverter valve (AS) and a chromatography compartment (DC) that included two high pressure valves and two 6-port injection valves. The mass spectrometer was the MSQ™ PLUS single quadrupole mass spectrometer (Dionex and ThermoFinnigan, Santa Clara, CA USA). It has a pneumatically- and thermally-assisted electrospray ion source. Chromeleon® 6.8 software (Dionex) was used for all instrument control, data collection and data reduction.

Chromatography Supplies and Chemicals - The IonPac® AS18 (250 x 2-mm I.D.) and IonPac CS5A (250 x 2-mm I.D., Dionex) analytical columns were used. The IonPac AC15 (50 x 2-mm I.D.) column was used in place of a guard column with the CS5A column in order to increase the anion exchange capacity in the mixed mode CS5A column. An eluent generator was used to produce potassium hydroxide eluent in-line for the AS18 column. A continuously regenerated anion trap device, CR-ATC (Dionex), was used to remove trace level anions from the source water. Formic acid eluent for the cation system was prepared by dilution from formic acid (96%, Sigma Aldrich). Eluent suppression for the anion work was accomplished with a continuously regenerated electrolytic suppressor, the ASRS® MS. The cation system did not use a suppressor. The water for regeneration of the suppressor and operation of the eluent generator and anion trap device was supplied by a pressurized reservoir.

Arsenic (III) and Arsenic (V) stock solutions were obtained from SPEX CertiPrep (Metuchen, NJ, USA). Disodium methylarsonate (MMA) was obtained from Chem Services (West Chester, PA, USA) and the cacodylic acid (DMA) was obtained from Sigma Aldrich (Milwaukee, WI, USA). The arsenobetaine was purchased from the European Commission (Reference Material No. 626). Deionized water (18 Megohm-cm, Milli-Q, Millipore, Cambridge, MA) was supplied to the eluent generator, CR-ATC and suppressor, and was used to prepare all standards and samples.

Hardware Setup - Figure 1 shows the flow diagram of the dual IC2-MS system with shared autosampler, chromatography module and mass spectrometer. The instrument and chromatography conditions are summarized in Table 1. All system control and calculations were accomplished using Chromeleon® 6.8 software (Dionex). Briefly, two injections are made sequentially into two column sets, 15 minutes apart, and the detection data from the conductivity and ESI-MS detectors is collected in one data file.

Figure 1: Configuration of IC2-MS System for the Determination of Arsenic Species



Valves: 1, Diverter; 2 and 3 as below; 4 and 5 injection valves

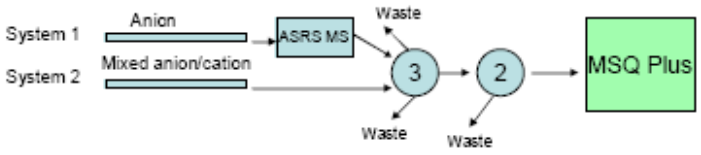


Table 1: IC2-MS Conditions for Determination of Arsenic Species

Anion system
Column: IonPac® AS18, 250 x 2-mm I.D.
Suppressor: ASRS MS
Eluent: KOH gradient (Eluent generator)
Flow rate: 0.3 mL/min
Injection volume: 100 µL

Mixed Mode system
Column: AC15/CS5A, 50 X 2-mm/250 x 2-mm I.D.
Eluent: 80 mM Formic Acid
Flow rate: 0.37 mL/min
Injection volume: 25 µL

Detection
1. Conductivity (anion only); 2. Mass Spectrometry
MS Conditions: Mode: -ESI and +ESI; Probe voltage, 3 kV

Peaks:	Polarity	SIM *m/z*	Cone voltage
1. arsenite, 100 µg/L	-	107	50
2. arsenate, 100 µg/L	-	141	30
3. arsenobetaine, 10 µg/L	+	179	70
4. dimethylarsinic acid, 1 µg/L	+	139	80
5. monomethylarsonic acid, 10 µg/L	+	141	60

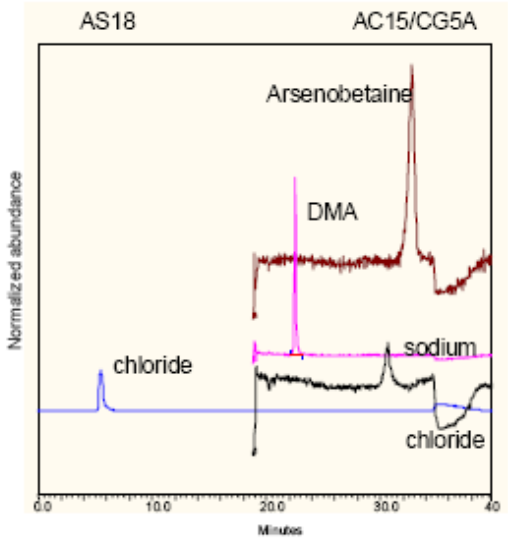
Results and Discussion

Anion exchange and mixed mode anion-cation exchange separations were combined in one analytical method to provide for substantial retention of a model group of five arsenic species that includes anions, cations and a betaine. The overall method illustrates the ability to separate a suite of analytes with diverse acid/base properties from matrix ions with flexibility by design of the eluting conditions.

Anion Exchange - The IonPac AS18 column is a latex-based, hydroxide selective anion exchange column with 75 uEq/column in the 250 x 2-mm format. The anion exchange phase is selective for hydroxide because the quaternary ammonium anion exchange sites bear an alkanol group that increases the hydration of the phase. Hydroxide selectivity is important because it allows use of hydroxide eluting ion that can be neutralized by a cation exchange suppressor (to water) so that the mobile phase entering the ESI-MS contains only water rather than a non-volatile chemical. The selectivity of the AS18 also allows elution of the trivalent arsenate ion while still retaining arsenite. The monomethylarsonate has intermediate selectivity on this column but is well separated from common sample matrix anions including chloride and sulfate. Chloride is well separated from arsenite as well, which is also important since chloride can cause significant signal suppression of co-eluting analytes.

Mixed Anion/Cation Exchange - Arsenobetaine (AsB) is a zwitterion so the best opportunity for retention is as a cation at acidic pH. Dimethylarsinic acid (DMA) has a pKa of about 6.2, which allows it to cross the cation exchange membrane of the suppressor during the neutralization process. This means that the DMA cannot be determined using the AS18 system. These two analytes separately require cation exchange and anion exchange with no suppression for analysis. The IonPac CS5A column is a mixed mode anion/cation exchange column with 10 µEq/column of anion exchange capacity and 5 µEq/column of cation exchange capacity. This means that both anions and cations are retained on the CS5A phase and that an eluent such as formic acid supplies formate as the anionic eluting ion and hydronium ion as the cationic eluting ion. Chloride elutes very close to arsenobetaine using a CS5A column. Sodium chloride is an important matrix consideration because many of the potential samples for the method, e.g. seaweed, fish, are derived from the ocean. The separation of chloride from arsenobetaine is not adequate and signal suppression is observed on the SIM +179 channel during the elution of chloride. The additional anion exchange capacity in the form of an AC15 column added enough retention of the chloride to allow adequate separation of chloride and arsenobetaine as shown in Fig 2.

Figure 2: Improved detection of arsenobetaine using additional anion exchange capacity



Anion system
Column: IonPac® AS18, 250 x 2-mm I.D.
Suppressor: ASRS MS
Eluent: KOH gradient (Eluent generator)
Flow rate: 0.3 mL/min
Injection volume: 100 µL

Mixed Anion/Cation system
Column: AC15/CS5A, 50 X 2-mm/250 x 2-mm I.D.
Eluent: 80 mM Formic Acid
Flow rate: 0.37 mL/min
Injection volume: 25 µL

Detection
1. Conductivity (anion only); 2. Mass Spectrometry
MS Conditions: Mode: -ESI and +ESI;

Peaks:	Polarity	SIM m/z	Cone voltage
Chloride	-	35	50
DMA	+	139	80
Sodium	+	23	50
AsB	+	179	70

Detection - In the gas phase of ESI-MS, most of the arsenicals can be detected as anions, as cations, as M^-, M+H, M+H.xH2O etc. or as fragments. Detection conditions for each analyte were compared and optimized to provide the lowest detection limits within the capability of the single quadrupole mass spectrometer. Table 2 summarizes both the chromatographic retention requirements and the optimized detection conditions for the arsenicals. Figure 3 shows the separation and detection of the arsenic standards using the conditions provided in Table 1. Arsenite is retained by anion exchange on the AS18 column (in the void volume of the AC15/CS5A system) and can be detected as the $H_2AsO_3^-$ ion or as the AsO_2^- ion with better sensitivity. Arsenate is retained by anion exchange on both ion exchange systems and is detected with the best sensitivity as the $H_2AsO_4^-$ ion. It can also be detected as an acid-water adduct in positive mode at m/z 179. Arsenobetaine is protonated in 80 mM formic acid eluent and is therefore retained by cation exchange. It is detected as a cation since the As bears a permanent positive charge. The monomethylarsonate is retained as an anion on the AS18 column but is detected with good sensitivity as the protonated species using positive polarity ESI. Likewise the DMA is retained as an anion and detected as a cation but since its pKa precludes the use of a suppressor it is determined using the AC15/CS5A system. Table 3 provides the linearity over the range of 5-100 µg/L and reproducibility values in water obtained using this method. The minimum detection limits were calculated using external standard quantification since internal standard are under development. The MDL calculation used seven replicates and the standard Student T test calculation. Quantification using internal standards is preferred and often necessary using ESI-MS detection and is the topic of another paper.

Table 2: Analytical needs for the separation and detection of 5 arsenic species

Analyte	Separation	ESI-MS Detection	Species Detected
Arsenite	Anion exchange (with suppressor)	SIM 107, neg	AsO_2^-
Arsenate	Anion exchange (with suppressor)	SIM 141, neg	$H_2AsO_4^-$
Arsenobetaine	Cation exchange (no suppressor)	SIM 179, pos	$(CH_3)_3As{+}CH_2COOH$
Monomethylarsonic acid (MMA^V)	Anion exchange (with suppressor)	SIM 141, pos	$CH_3AsO(OH)_2 .H^+$
Dimethylarsinic acid (DMA^V)	Anion exchange (no suppressor)	SIM 139, pos	$(CH_3)_2AsO(OH).H^+$
Sodium	Cation exchange	SIM 23, pos	Na^+
Chloride	Anion exchange	SIM 35, neg	Cl^-

Figure 3: Separation and Detection of 5 Arsenic Species using IC2-MS

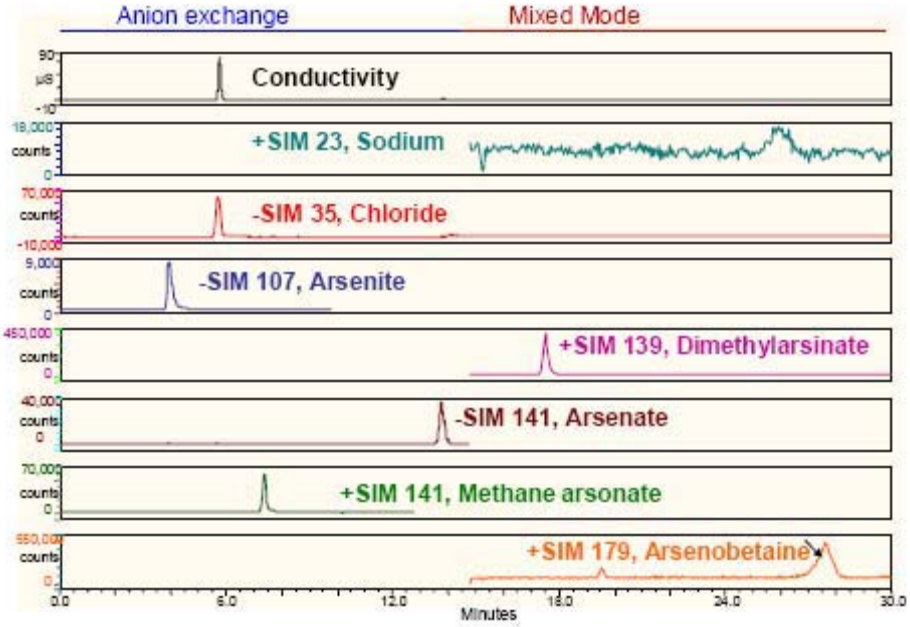


Table 3: Reproducibility and linearity of detection for arsenic species using IC2-ESI-MS

Analyte (in water)	Linearity 5-100 µg/L 100 µL inj. vol.	% RSD N=7 100 µg/L	MDL (ESTD) µg/L N=7, 100 µL
Arsenite SIM -107	0.9999	4.6	10
Arsenate SIM -141	0.9992	5.3	8
Arsenobetaine SIM +179	0.9990	7.7	15
MMA SIM +141	0.9992	5.1	4
DMA SIM +139	0.9999	1.6	1

SUMMARY

This paper provides an ion exchange-based chromatography scheme that offers good retention and separation of arsenicals having anionic, cationic and zwitterionic properties. The scheme is compatible with electrospray ionization- MS detection.

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5. IonPac AS7 Product Information Bulletin, Dionex Corp. (2003).

Determination of Five Arsenic Species Using Dual Ion Chromatography Coupled with Electrospray Ionization Mass Spectrometry

R. W. Slingsby[1], R. Al-Horr[1], J. H. Lee[2], and C. A. Pohl[1]
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NEMC
August 29, 2006

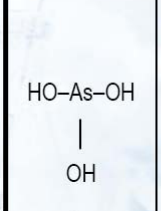
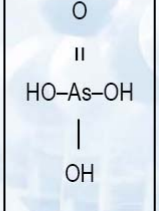
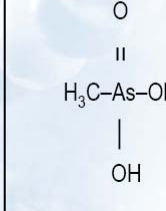
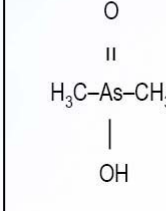
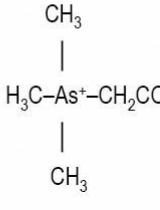
Outline

- Why Is There Continued Interest in New Methods for Arsenic Speciation?
- What Is the Analytical Challenge?
- How Does "Dual" IC2-ESI-MS Address These Needs?
- Description of the Chemistries and Results to Date
- What About Use of Internal Standards?
- What About Sample Preparation?
- Real World Samples

Arsenic in the Environment

- Naturally-contained in bedrock and enters the drinking water supply
- Single most important environmental contaminant (Anal. Chem., Jan. 2004)
- Some arsenic species are not toxic
- WHO and USEPA MCL = 10 ppb
- Seawater contains about 3 ppb
- Speciation and identification of arsenic species are needed along with low detection limits

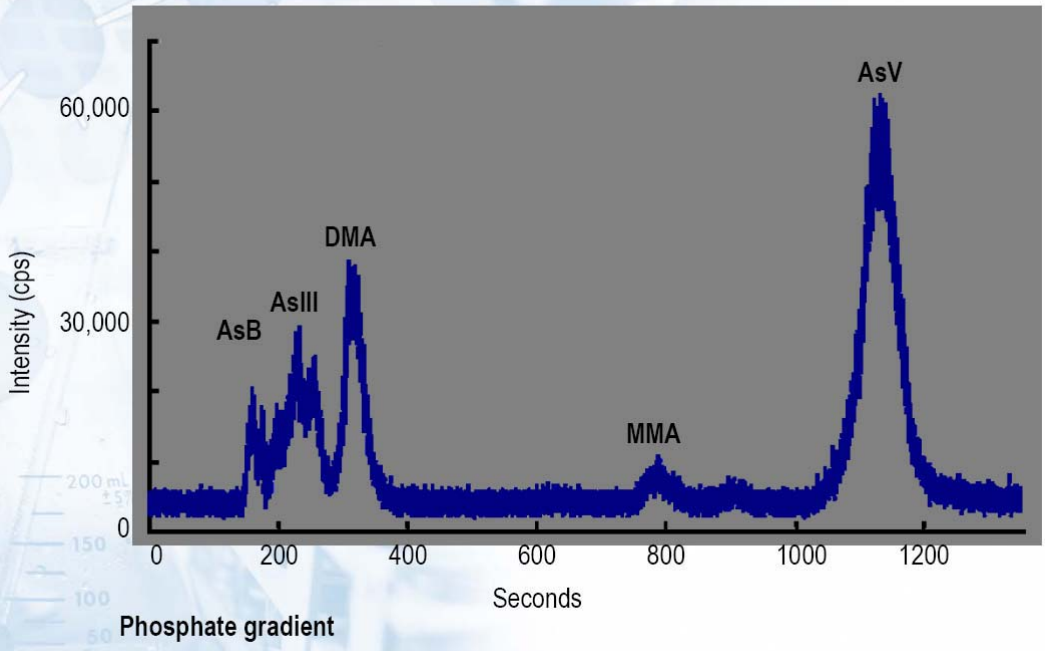
Major Arsenic Species in the Environment

Arsenite (As^{III})	Arsenate (As^{V})	Monomethylarsonic Acid (MMA^{V})	Dimethylarsinic Acid (DMA^{V})	Arsenobetaine (AsB)
–ESI	–ESI	+ESI	+ESI	+ESI
				
pKa = 9.29	pKa_1 = 2.26 pKa_2 = 6.76	pKa_1 = 3.6~4.1	pKa = 6.2	pKa = 2.2

Current Methods

- HPLC/ICPMS using multiple columns offers ng/kg detection limits as As (75 amu)
- HPLC/HG-AFS provides very low detection limits for arsenic species that can form gaseous hydrides with borohydride: arsenite, arsenate, MMA, and DMA
- ESI-MS has been applied to the identification of arsenosugars
- No quantification standards in literature using ESI-MS

Chromatogram of Arsenic Species as As in Hizikia Seaweed Using IonPac® AS7-ICP/MS



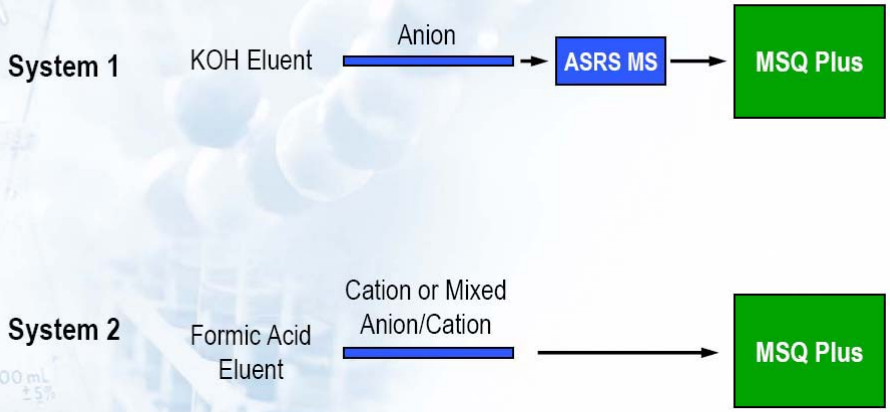
The Analytical Challenge

- Arsenic species include anions, cations, and amphoteric compounds
  - Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine
  - Arsenosugars
- pK_a values cover the range of 2–9
- DMA crosses the ion exchange membrane in an IC suppressor
  - MMA and DMA are best separated as anions but best detected by +ESI
- Sodium, chloride and other common matrix ions interfere with detection of co-eluting analytes
- One analytical run desirable
- Structural information with detection limits below 10 ppb desirable
- Internal standard quantification is desirable

Possible Separation Chemistries for Arsenic Speciation

- Anion exchange
- Cation exchange
- Ion exchange and another retention mechanism
- Mixed anion/cation exchange

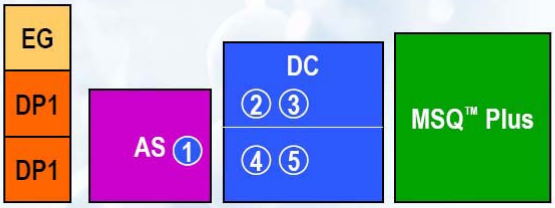
IC-MS Configurations for Arsenic Speciation



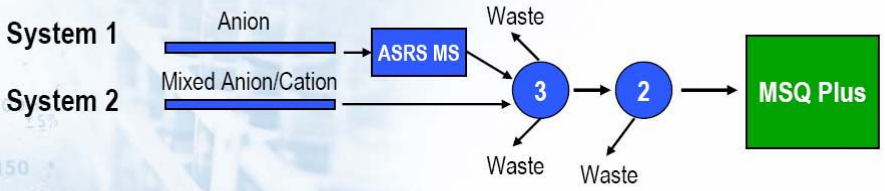
Analytical Needs for the Separation and Detection of Five Arsenic Species

Analyte	Separation	ESI-MS Detection	Species Detected
Arsenite	Anion Exchange (with Suppressor)	SIM 107, Neg	AsO_2^-
Arsenate	Anion Exchange (with Suppressor)	SIM 141, Neg	$H_2AsO_4^-$
Arsenobetaine	Cation Exchange (No Suppressor)	SIM 179, Pos	$(CH_3)_3As{+}CH_2COOH$
Monomethylarsonic Acid (MMA^V)	Anion Exchange (with Suppressor)	SIM 141, Pos	$CH_3AsO(OH)_2.H^+$
Dimethylarsinic Acid (DMA^V)	Anion Exchange (No Suppressor)	SIM 139, Pos	$(CH_3)_2AsO(OH).H^+$
Sodium	Cation Exchange	SIM 23, Pos	Na^+
Chloride	Anion Exchange	SIM 35, Neg	Cl^-

Configuration of IC2-MS System for the Determination of Arsenic Species



Valves: 1, Diverter; 2 and 3 as below; 4 and 5 Injection Valves



IonPac AS18 Selectivity

- Latex-based anion exchange
- Hydroxide gradient
- Low hydrophobicity
- Alkanol quaternary ammonium functionality
- 75 µEq/column anion exchange capacity

Mixed Anion/Cation Exchange Selectivity

- IonPac CS5A
  - Latex-based
  - Mixed mode anion/cation exchange
  - 10 µEq/5 µEq per column capacities
  - Formic acid eluent
- IonPac AC15
  - Latex-based anion exchange
  - Low hydrophobicity
  - Alkanol quaternary ammonium functionality similar to the CS5A selectivity
  - 2.2 µEq/column capacity
  - Adds anion exchange retention without adding cation exchange capacity

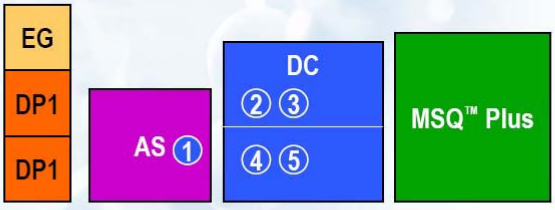
Detection of Ions Using ESI-MS

- ESI-MS provides detection at *m/z* ratio
  - Structural information
  - Higher background than ESI-MS/MS especially in complex matrices
- ESI-MS requires volatile eluent systems
  - Formic acid provides formate as an anionic eluting ion and hydronium ion as a cationic eluting ion
- Ion chromatography suppressors provide desalting as long as the analytes remain charged
  - Can use alkali hydroxide eluent systems
  - Background entering ES interface has very low ionic strength

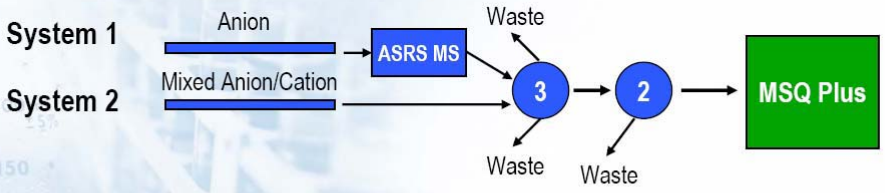
IC2-MS Hardware/Software Configuration for Arsenic Speciation

- ICS-3000 Ion Chromatograph
  - Autosampler can inject into two injection valves in one method
    - » Software control for sequential injection
    - » Diverter valve selects one of two injection valves
  - Data from two injections can be collected into one data file
  - Using two separation chemistries provides maximum selectivity control to handle matrix and many analytes

Configuration of IC2-MS System for the Determination of Arsenic Species



Valves: 1, Diverter; 2 and 3 as below; 4 and 5 Injection Valves



IC2-MS Conditions for Determination of Arsenic Species

Anion System

Column: IonPac® AS18, 250 x 2 mm I.D.
Suppressor: ASRS® MS
Eluent: KOH gradient (eluent generator)
Flow Rate: 0.3 mL/min
Inj. Volume: 100 µL

Mixed Mode System

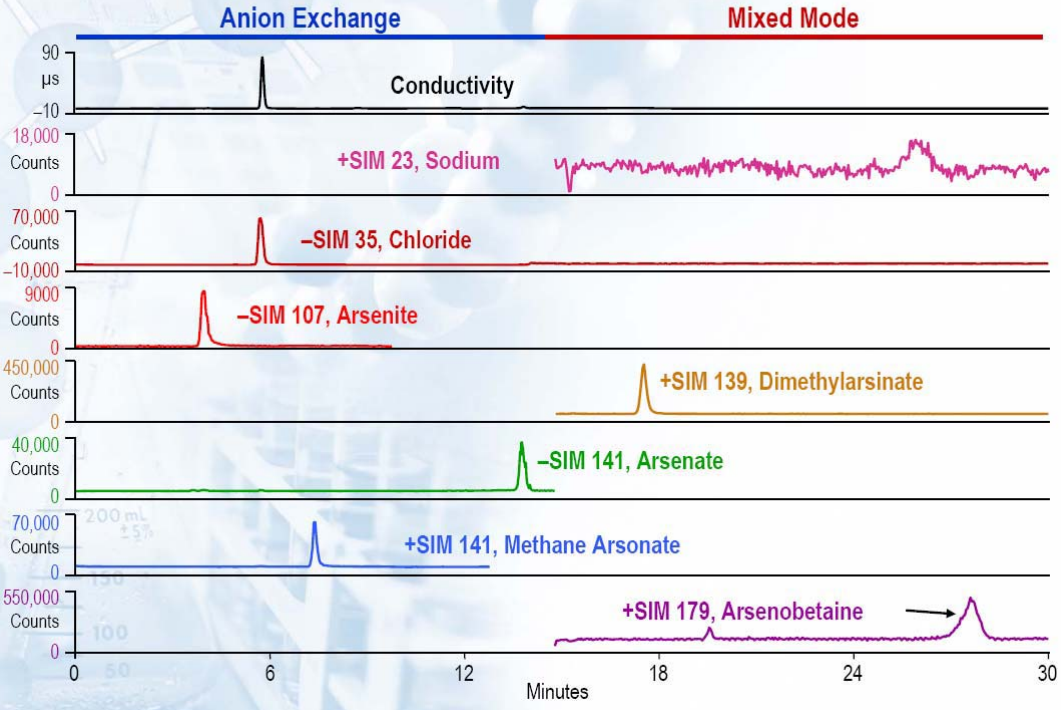
Column: AC15/CS5A, 50 X 2 mm/250 x 2 mm I.D.
Eluent: 80 mM Formic acid
Flow Rate: 0.37 mL/min
Inj. Volume: 25 µL

Detection

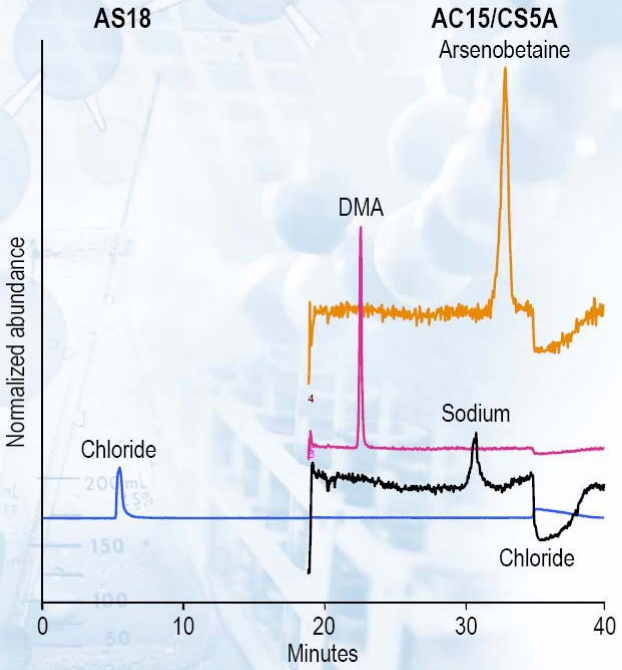
1. Conductivity (anion only); 2. Mass Spectrometry
MS Conditions, Mode: –ESI and +ESI; probe voltage, 3 kV

Peaks:	Polarity	SIM *m/z*	Cone Voltage
1. Arsenite, 100 µg/L	–	107	50
2. Arsenate, 100 µg/L	–	141	30
3. Monomethylarsonic acid, 10 µg/L	+	141	60
4. Dimethylarsinic acid, 1 µg/L	+	139	80
5. Arsenobetaine, 10 µg/L	+	179	70

Separation and Detection of Five Arsenic Species Using IC2-MS



Improved Detection of Arsenobetaine Using Additional Anion Exchange Capacity



Anion System

Column:	IonPac® AS18, 250 x 2 mm I.D.
Suppressor:	ASRS® MS
Eluent:	KOH gradient (eluent generator)
Flow Rate:	0.3 mL/min
Inj. Volume:	100 µL

Mixed Anion/Cation System

Column:	AC15/CS5A, 50 X 2 mm/ 250 x 2 mm I.D.
Eluent:	80 mM Formic acid
Flow Rate:	0.37 mL/min
Inj. Volume:	25 µL

Detection

1. Conductivity (anion only); 2. Mass Spectrometry
MS Conditions, Mode: –ESI and +ESI

Peaks:	Polarity	SIM *m/z*	Cone voltage
Chloride	–	35	50
DMA	+	139	80
Sodium	+	23	50
AsB	+	179	70

Reproducibility and Linearity of Detection for Arsenic Species Using IC2-ESI-MS

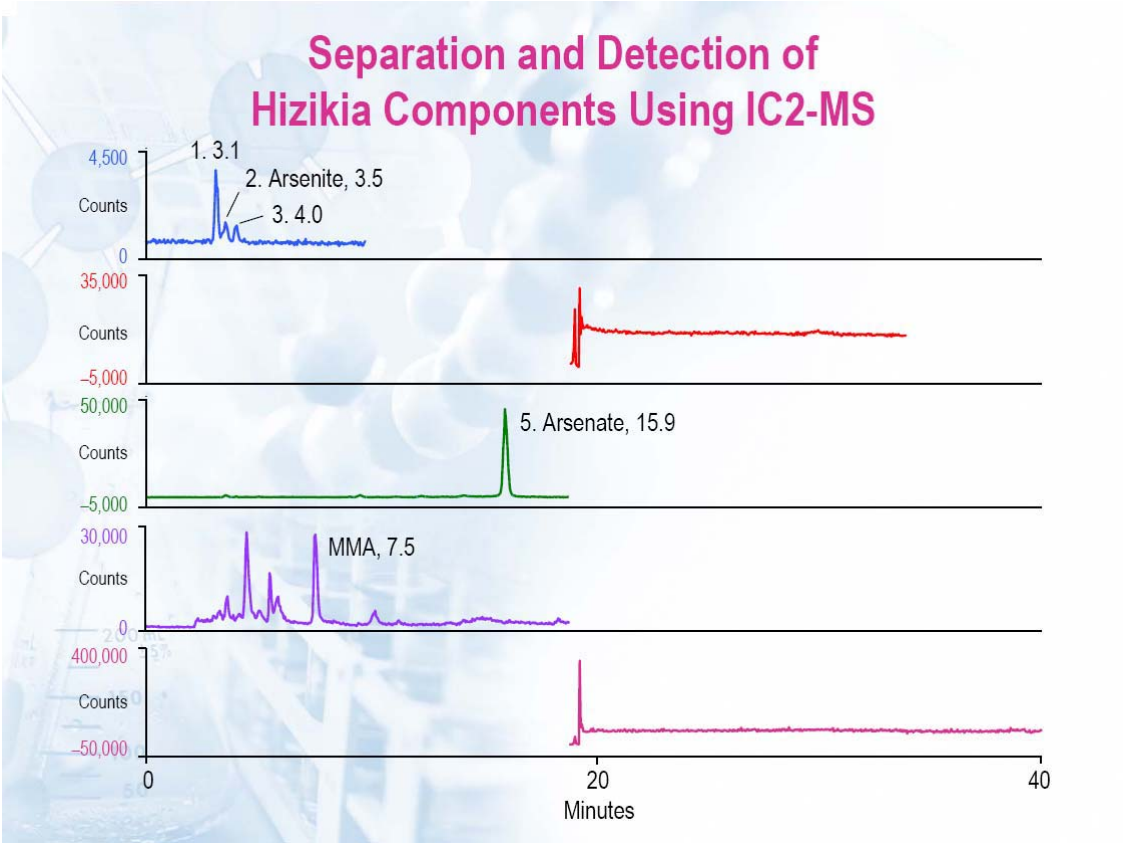
Analyte (in Water)	Linearity 5–100 µg/L 100 µL Inj. Volume	% RSD N = 7 100 µg/L	MDL (ESTD) µg/L N = 7, 100 µL
Arsenite SIM –107	0.9999	4.6	10
Arsenate SIM –141	0.9992	5.3	8
Arsenobetaine SIM +179	0.9990	7.7	15
MMA SIM +141	0.9992	5.1	4
DMA SIM +139	0.9999	1.6	1

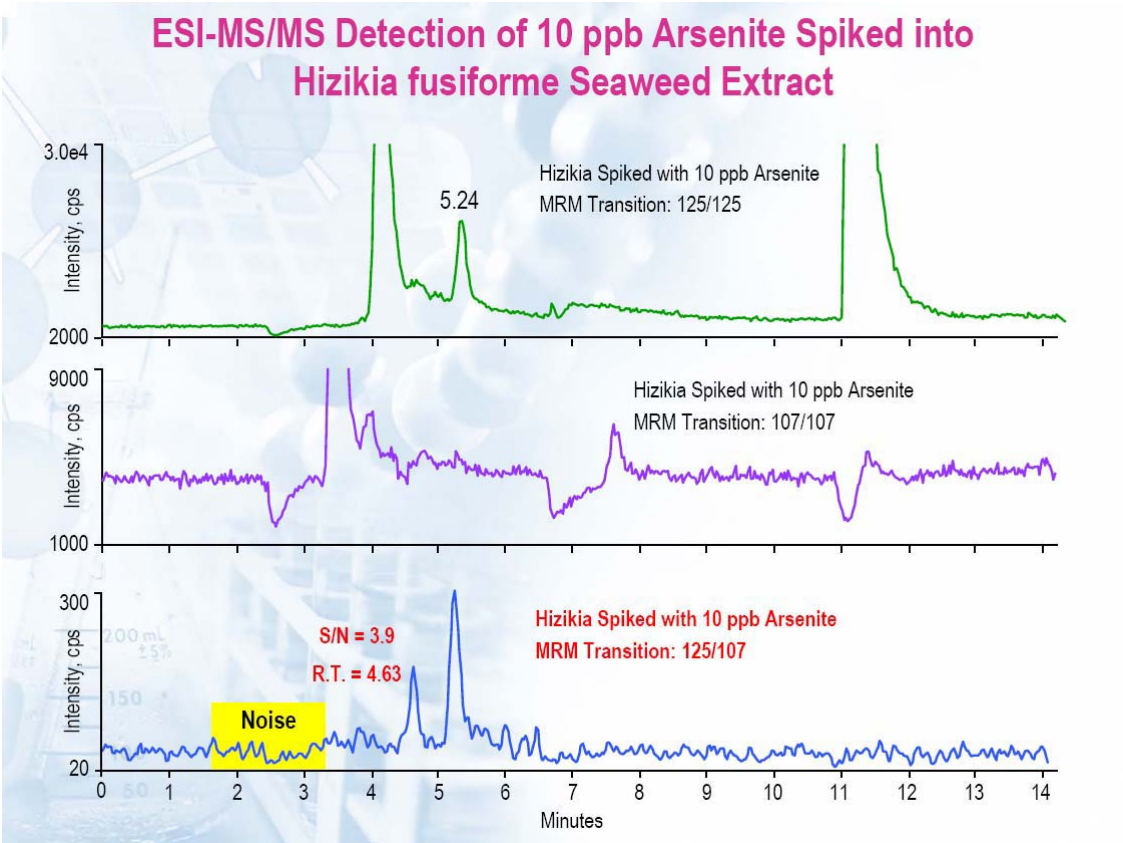
Options for Internal Standards

- Stable-labeled arsenic compounds
  - $As^{18}O_3^-$
- Similar species
  - Fluorophosphate

Extraction Method Used for Hizikia fusiforme Seaweed

1. 0.5 g of the dried sample was placed in a polyethylene beaker
2. 20 mL of 75/25 methanol:water was added
3. The whole was homogenized for 24 hours using a shaker unit
4. The mixture was maintained at 20 °C for four hours in an ultrasonic unit
5. The sample was centrifuged for 25 min at 8000 rpm, and decanted into 100 mL volumetric flask
6. The residue was washed with DI water and filtered through a 20 µm filter paper
7. The filtered sample (6.) was mixed with the decanted sample (5.) in the 100 mL volumetric flask, the volumetric flask filled with water to the mark


Separation and Detection of
Hizikia Components Using IC2-MS
4,500
Counts
0
1. 3.1
2. Arsenite, 3.5
3. 4.0
35,000
Counts
–5,000
50,000
Counts
–5,000
5. Arsenate, 15.9
30,000
Counts
0
MMA, 7.5
400,000
Counts
–50,000
0
20
40
Minutes


ESI-MS/MS Detection of 10 ppb Arsenite Spiked into
Hizikia fusiforme Seaweed Extract
3.0e4
Intensity, cps
2000
5.24
Hizikia Spiked with 10 ppb Arsenite
MRM Transition: 125/125
9000
Intensity, cps
1000
Hizikia Spiked with 10 ppb Arsenite
MRM Transition: 107/107
300
Intensity, cps
20
S/N = 3.9
R.T. = 4.63
Noise
Hizikia Spiked with 10 ppb Arsenite
MRM Transition: 125/107
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Minutes

Summary

- New, broad-range separation scheme to optimize retention and separation of arsenic species
- Use of ESI-MS detection for structural information
- MS/MS necessary for determination of arsenite in complex matrices
- Next steps include
  - Qualification of ISTDs
  - Full application of IC2-ESI-MS/MS detection
  - Faster sample preparation method using ASE® extractor
  - Additional arsenical analytes

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IDENTIFICATION, CHARACTERIZATION, AND QUANTITATION OF SPECIES OF ARSENIC AND SELENIUM BY HYBRID TRIPLE QUADRUPOLE - QTRAP™ MASS SPECTOMETERS

Robert Ellis, John Gibbons, Takeo Sakuma and Chris Borton.

Applied Biosystems/MDS Sciex

Speciation

- What form is the element in
  - Amino acids, proteins, methylated species, valence states
- Different species vary in function, nutritional value, toxicity
- Total elemental determination tells us little about fate and function
- Different types of experiment
  - Discovering the different forms
  - Quantifying the different forms

How do we discover and quantify species?

- ICP-MS – the most sensitive elemental analyzer, especially with the newer DRC™ technology, *but completely blind to speciation*
- LC coupled to ICP-MS allows species to be separated in time, BUT identification requires standard addition or retention-time matching.
- What if we don't have the standard, have no idea what species may exist, have co-eluting compounds or just need to be absolutely sure that the species sought is the one seen?

Speciation

Another complimentary approach…

- LC-MS/MS is an alternative technique that gives *A LOT* more information on structure
  - Its less sensitive than ICP-MS but samples can easily be pre-concentrated. It is probably worth the hassle given the information that can be gained.
- There is a case for both techniques, but in this presentation we will concentrate on the benefits of LC-MS/MS…

Speciation

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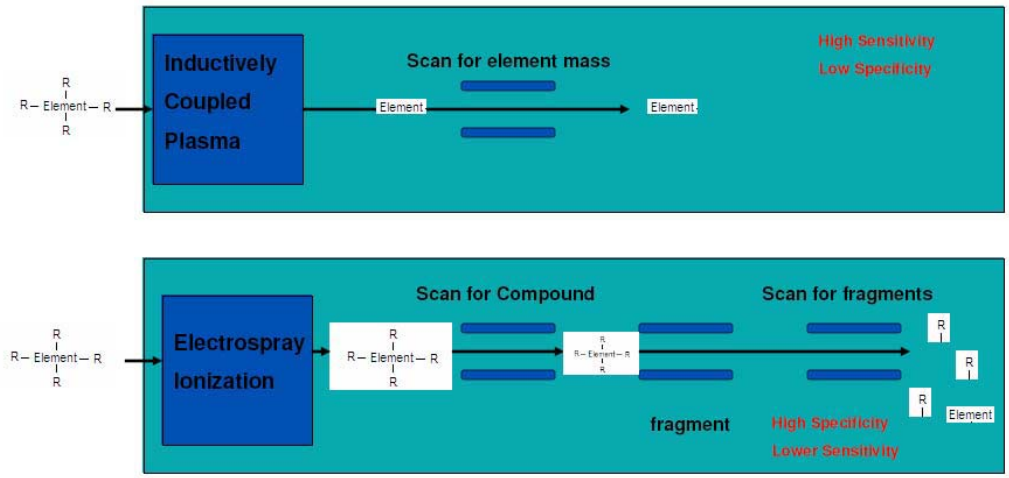
Different MS Methods



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Speciation

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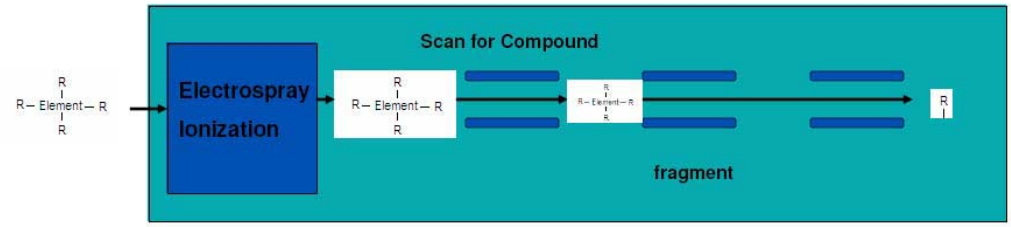
Quantitation of Known Species

- Multiple Reaction Monitoring



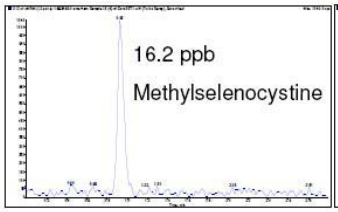
Scan for diagnostic fragment – very high specificity

- as little as 5ms per transition
- Up to 300 transitions

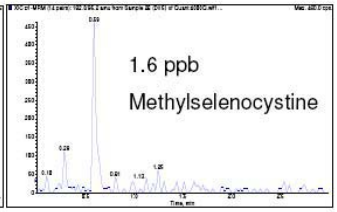
6

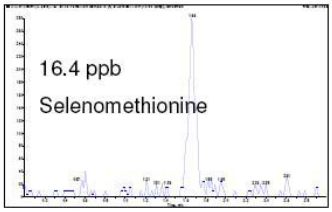
Examples of Quantitation

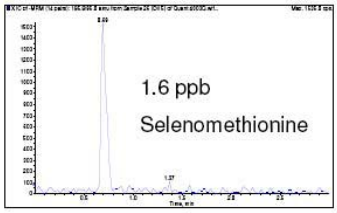
3200 QTrap®



4000 QTrap®







Compound	LOQ (ng/ml)	Calibration range	R^2
Selenomethionine	1	1 - 1600	0.99
Methylselenocysteine	1	1 - 1600	0.99

Compound	LOQ (ng/ml)	Calibration range	R^2
Selenomethionine	0.1	0.1 - 1600	0.99
Methylselenocysteine	0.1	0.1 - 1600	0.99

Note - concentrations are expressed as ppb Se (not ppb molecule)

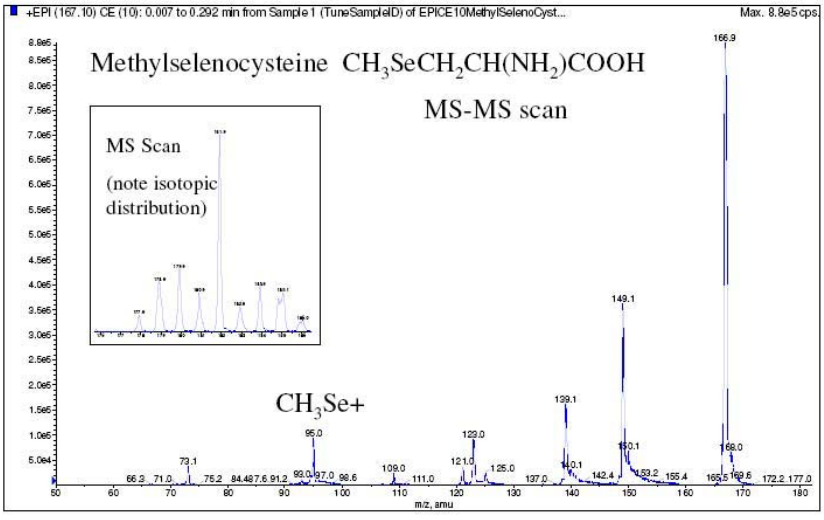
Quantitation

- Highly specific transitions
  - Signal is obtained for only species of interest – other species do not show up in that MRM channel
  - Multiple transitions are used to quantify many species
- In this case we are working with KNOWN species, as would be the case with ICP-MS analysis

Qualitative

- What if we don't know the species of interest?
- We can generate an MS/MS spectrum to examine the molecule.
  - Fragmentation pattern shows diagnostic fragments that can be used to elucidate structure.
  - We can do this with a standard.
  - We can also do this on unexpected species.

MS/MS data



Speciation

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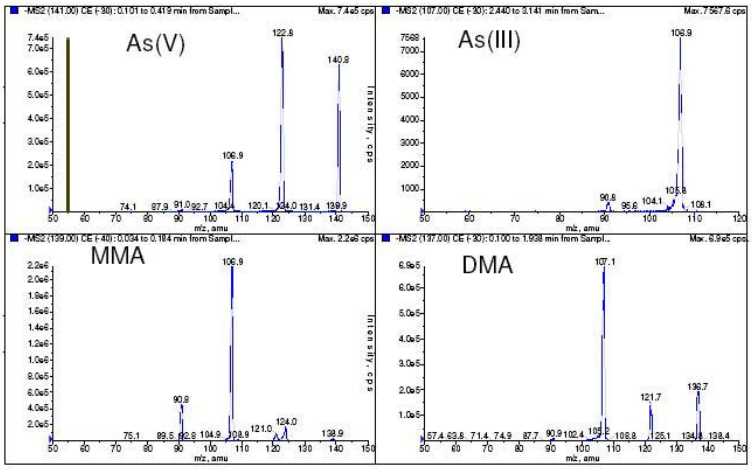
MS/MS data

Negative Mode



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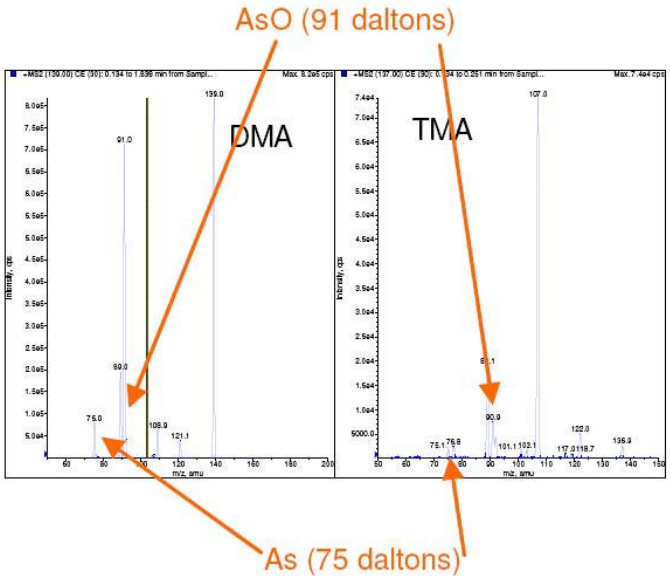
MS/MS data

Positive Mode



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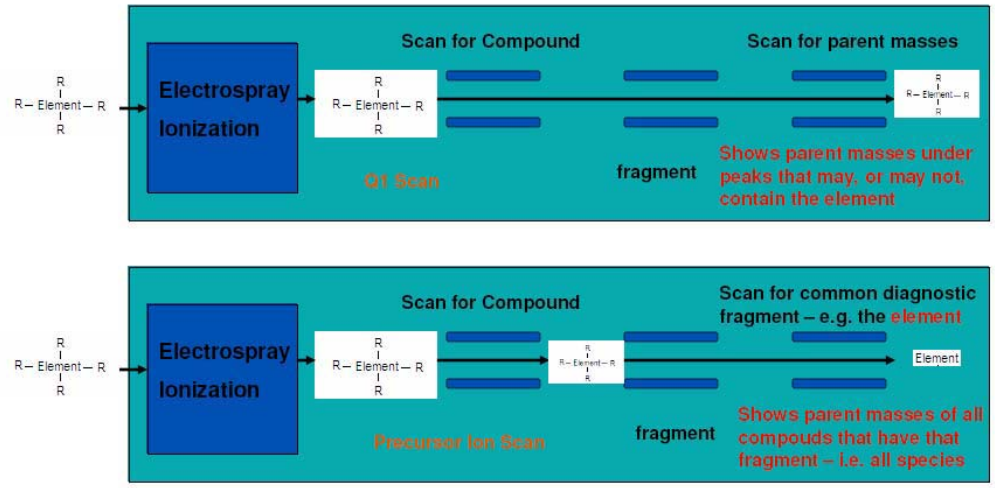
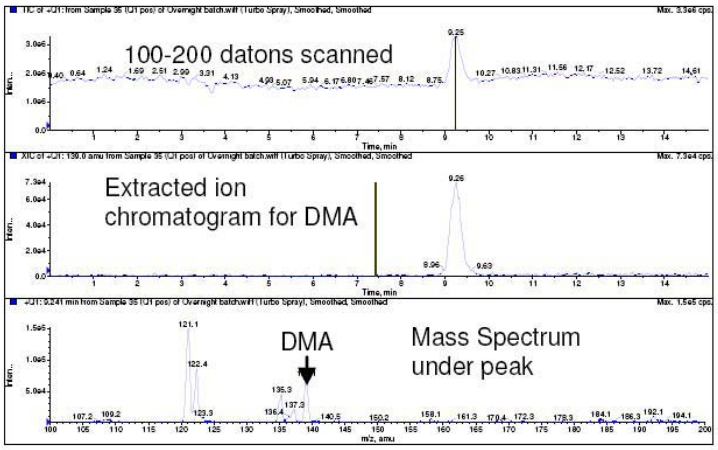
So how do we look for unknown species in a mixture?



Single MS Scans – not very specific



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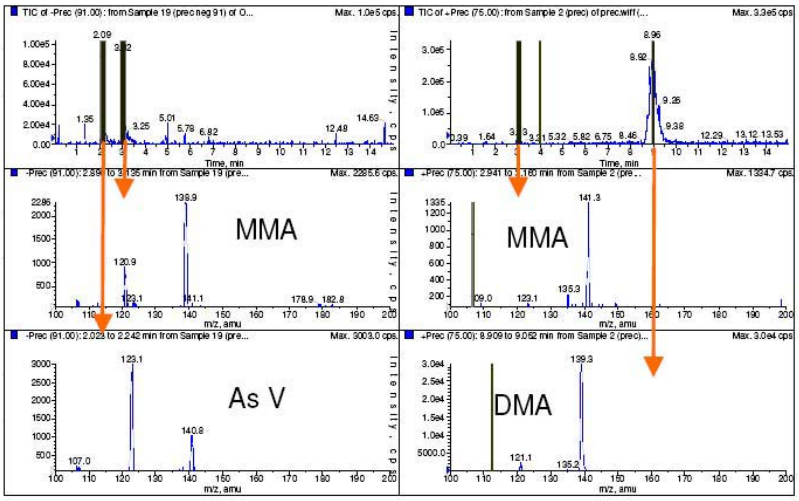
Precursor Ion Scan – quite specific



Speciation

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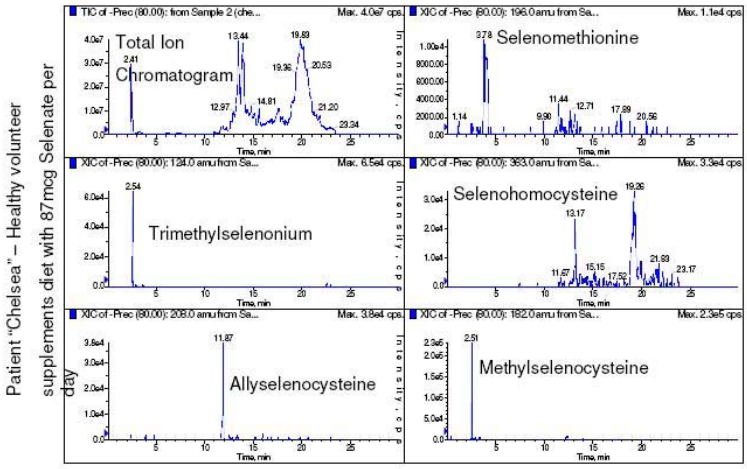
Precursor Ion Scan



Speciation

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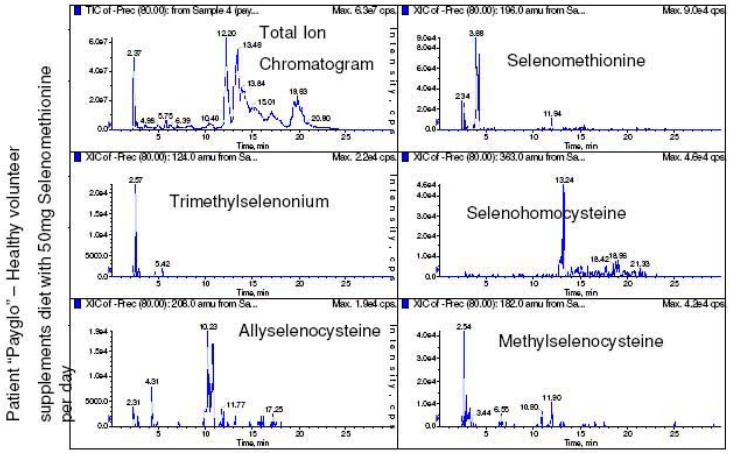
Precursor Ion Scan



Speciation

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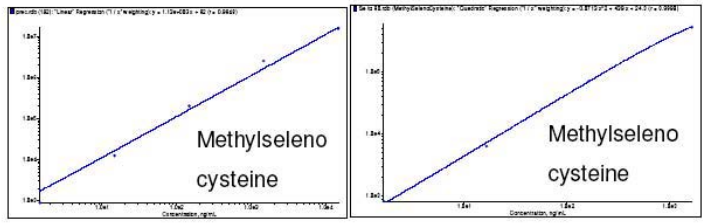
How sensitive is a precursor ion scan

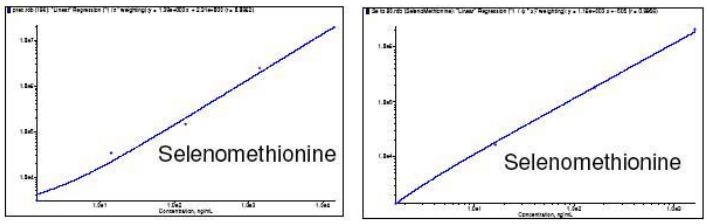
3200 Q TRAP ®

4000 Q TRAP ®



LOQ = 8 ppb

LOQ = 1 ppb



Note - concentrations are expressed as ppb Se (not ppb molecule)

Re-cap

- MRM uses known fragmentation pattern to produce highly specific transitions for quantitation of known compound
  - does not rely on retention time or standard addition
- Precursor ion scans are useful to look only for compounds that contain a common fragment (*e.g. the element*)
  - Parent mass is identified so that compound can be identified
- MS/MS spectra are used to
  - Examine species
  - Confirm species

Can we combine scans?

- We have discussed various scan types available on a single instrument.
- In many environmental cases we need to know for certain that a specific species is present and that the quantified species actually is that species.
- Some strategies involve multiple MRM per analyte and analyte ratio. We can also use a full scan MS-MS spectra for each compound.
- Also note that you can still do standard addition and retention time matching, as in ICP-MS, but here we have much greater opportunities.

Speciation

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Information Dependent Acquisition

- Step 1 – Survey scan – MRM, Precursor, etc.
- Step 2 – Automatic review of scan – has a peak of "X" size/shape/mass shown up?
- Step 3 –
  - yes, do an MS/MS scan on it, then return to step 1
  - No, go to step 1
- Whole cycle takes around a second, so fits LC timescale

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Speciation

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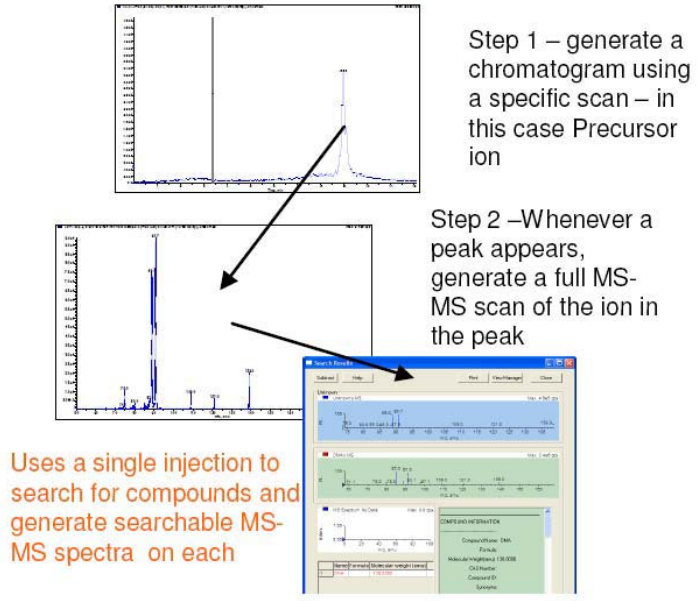
Information Dependent Acquisition



Step 1 – generate a chromatogram using a specific scan – in this case Precursor ion

Step 2 –Whenever a peak appears, generate a full MS-MS scan of the ion in the peak

Uses a single injection to search for compounds and generate searchable MS-MS spectra on each

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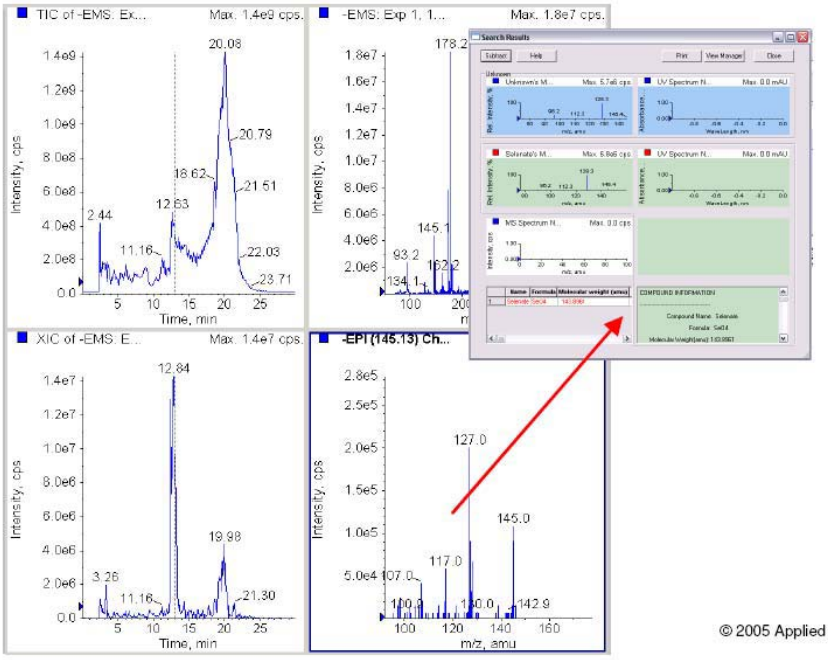
Information Dependent Acquisition



Speciation

Conclusion

- ICP-MS has excellent sensitivity, but poor selectivity for speciation
- MS/MS has excellent selectivity, but lower sensitivity than ICP-MS
- Both instruments form part of a strong speciation strategy

ROUTINE ARSENIC SPECIATION ANALYSIS BY IC-ICP-MS? ARE WE THERE YET?

Gerads, Russell and Gürleyük, Hakan; Applied Speciation and Consulting, LLC

Currently, speciation data are usually accepted only by some regulators since there seems to be no set laws or regulations on this matter. The lack of species-specific regulations may be attributed to the belief that there are no analytical methods that can reliably measure the analytes of interest at the regulatory levels. On the other hand, Method 1632a which uses hydride generation – cryo trapping – gas chromatography –atomic absorption spectrometry has been around for a long time but it is not as widely utilized since there are only a few commercial laboratories that provide this service. This operationally-defined method is known to cause false positives due to the presence of thio-arsenic species that may be present in anoxic conditions. In addition, high concentrations of iron in the sample may cause loss of arsenic during the hydride generation reaction since the borohydride reagent is preserved in alkaline conditions. If the analyst does not have a good understanding of this type of analysis and unless appropriate QA/QC protocols are followed, negatively biased results are commonly reported. Coupling Liquid Chromatography or Ion Chromatography to Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS) has been applied for the determination arsenic speciation in a variety of matrices in the last 20 years. Unfortunately, there are no EPA methods that utilize this technique and there are only two commercial laboratories that provide this analytical service. This analytical method has significant advantages over the old hydride generation method but it is not recognized by EPA and some regulatory entities. The application of IC-ICP-MS is limited to only a handful progressive companies who understand the benefits and limitations of both methods.

This presentation will include a detailed comparison of analytical techniques for arsenic speciation analysis and will provide performance data for IC-ICP-MS in a variety of matrices including, wastewaters, ground waters, soils, and tissues.

Routine Arsenic Speciation Analysis by IC-ICP-MS?

Are We There Yet?

Hakan Gürleyük

(hakan@appliedspeciation.com)

Russell Gerads

APPLIED SPECIATION AND CONSULTING, LLC

info@appliedspeciation.com
www.appliedspeciation.com

Speciation: The Hottest Topic!

- **SPECIATION ANALYSIS**: Separation and quantification of different oxidation states or chemical forms of a particular element.
- Interest increased exponentially in the last decade.
- Different forms can have totally different properties.
- Essential for predicting and modeling fate, risk, and effects
- A MUST HAVE for designing custom - tailored treatment strategies.
- Critical for toxicology, bioavailability, and bioaccumulation.
- FINALLY, species specific regulation.

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2

Why Doesn't Everyone Do it?

- Rarely required under current legislation in US
- Very few (promulgated) methods are available for speciation
- Although speciation can save time and money with respect to remediation and risk assessment, it is more expensive than routine analyses
- Speciation requires experienced personnel who understand proper sampling and analytical protocols
- Still not enough interest = Low ROI

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Most Common Methods for As Speciation Analysis

- Selective Hydride Generation (HG-CT-GC-AAS)
- Chromatography Coupled to ICP-MS
  - Ion exchange
  - Ion Pair
- Voltammetry (not discussed)
- Other (not discussed)
  - Fluorometry
  - XANES

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Selective Hydride Generation

- Only protonated species form hydrides
- HG reaction conditions can be adjusted so AsH_3 is generated from As(III) only.
- Two separate analysis is required.

	pK_{a1}	pK_{a2}	pK_{a3}
As(III)	13.4	9.2	12.1
As(V)	2.2	7.0	11.5
MMAA	3.6	8.2	-
DMAA	6.2	-	-

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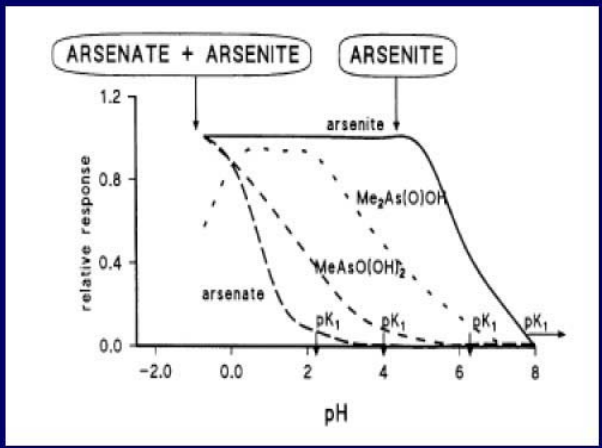
Selective Hydride Generation

- As(III) can be determined at high pH (> 6)
- Adding a reductant to the sample, and reanalyzing As(III)+As(V) can be determined at the same pH.
- At high pH the efficiency of HG is lower.
- AFS or AAS is the most common detector
- Detection limits could be 1-5 ppb for AAS and 0.05 ppb for AFS



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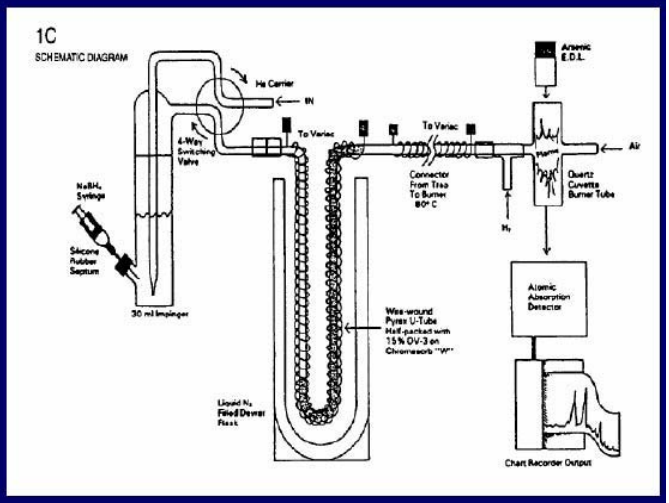
HG-CT-GC-AAS

- The arsines are collected on a GC column placed in a LN_2 dewar.
  - bp: -55 °C (AsH_3), 2 °C ($MeAsH_2$) and 36 °C (Me_2AsH)
- After collection, the Column is removed from the dewar and heated to thermally desorb and separate the arsines.
- The mobilized arsines are atomized by a H_2 flame and detected by AAS.



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Reference: EPA Method 1632a

HG-CT-GC-AAS

- The sample is acidified to pH < 2 for the determination of total inorganic arsenic, DMAs(V), MMAs(V)
- Sample is buffered to pH ~5 for As(III)
- Promulgated EPA method 1632a
- Detection limits are less than 10 ppt for 15 mL sample volume. Usually limited with how clean the reagents are.
- This method can be very useful for difficult matrices as long as some type of method development is performed on the samples before aplication on the whole sample batch.

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Issues with HG-CT-GC-AAS

- Samples high in Fe, Mn, Al may result in losses of arsenate due to co-precipitation.
  - Matrix Spikes may catch this if As(V) is used as a spike.
- Operationally defined so may not account for other As species present
  - Species that do not form hydrides can not be determined (Arsenobetaine, Arsenocholine, Hexafluoroarsonate, Roxarsone, arsenosugars, etc)
- If these other species also form arsine, they would be false positives
  - Thioarsenic species are false positives for As(III)
  - Note that Matrix Spikes can not correct for false positives!
  - Thioarsenic species are almost always present in sulfidic conditions

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Quality Control Criteria for 1632a

TABLE 2. QUALITY CONTROL ACCEPTANCE CRITERIA FOR EPA METHOD 1632[1]

	IPR (Section 9.2)		OPR	Calibration Verification	MS/MSD (Section 9.3)	
Analyte[2]	s	X	(Section 9.7)	(Section 9.5)	%R	RPD
IA	< 25%	60-140%	50-150%	80-120%	50-150%	< 35%
As^{+3}	< 25%	40-160%	30-170%	70-130%	30-170%	< 35%
MMA	< 20%	70-130%	60-140%	80-120%	60-140%	< 25%
DMA	< 30%	50-150%	40-160%	70-130%	40-160%	< 40%

[1] Acceptance criteria based on quality control data generated during As speciation analysis for the Cook Inlet Study (1998). Details can be found in Reference 16.16.

2 IA - Inorganic arsenic (As^{+3} + As^{+5}); MMA - monomethylarsonic acid; DMA - dimethylarsinic acid.

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Quality Control (Variability)

- Quantification by difference = compounded variability
- When the concentration of one species is much higher than the other, variability between analyses prevent accurate and precise results

	UCR					BR		
	Total Se	Selenate (difference)	Selenite	OrganoSe (difference)	Selenite plus organoSe	Total Se	Selenate (difference)	Selenite
	3.8	0.4	2.7	0.7	3.4	3.7	1.2	2.5
	3.7	0.5	2.6	0.6	3.2	3.1	3.1	
	3.5	0.3	2.7	0.6	3.2	3.3	1.1	2.2
	3.9	0.6	2.6	0.7	3.3	3.3	1.4	1.9
	4.1	0.8	2.6	0.7	3.3	3.5	1.1	2.4
	4.0	0.7	2.6	0.7	3.3	3.2	1.7	1.6
	3.9	0.6	2.6	0.8	3.3	3.5	1.4	2.1
average=	3.83	0.54	2.59	0.70	3.29	3.37	1.56	2.11
stdev=	0.20	0.17	0.05	0.08	0.08	0.20	0.70	0.34
(PRECISION) %RSD=	**5.1**	**31.5**	**1.9**	**11.3**	**2.3**	**6.0**	**44.9**	**16.1**

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Quality Control (Spikes)

- The first question to ask your lab is what species are used as spikes
- The most appropriate spike should contain all species of interest for each analysis
  - To confirm absence of false positives and/or negatives from each species
  - Spikes for Tissue extracts should even contain arsenobetaine to make sure no false positives are generated
- Spiking with As(III) for TInAs is not only bad science but cheating!

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Liquid Chromatography

- Ion-pair (IP) and ion-exchange (IE) chromatography are the most common modes of liquid chromatographic separation of mixtures of metallic and organometallic species.
- Ion exclusion chromatography is a relatively new technique and therefore there are not too many published articles on it.
- There is also some work on separation of As species by Capillary Electrphoresis (or its different versions)

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Liquid Chromatography and ICP-MS

- The most common detector for chromatographic separations is ICP-MS.
- Mature technique and almost all elements can be determined.
- Sub-ppt detection limits for most elements
- More than one element can be monitored
- Polyatomic Interferences:
  - $^{40}Ar^{35}Cl$ on monoisotopic ^{75}As,
- Dynamic Reaction Cell instruments can eliminate interferences

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Ion Exchange Chromatography – ICP-MS

- In IEC, separation is controlled by pH and ionic strength of the eluent, which competes with sample species for ion-exchange sites and elutes the sample from the column.
- Most common separation tecnique for As
- High buffer concentrations used in IE chromatography can result in nebulizer and cone clogging in ICP-MS
  - NH_4^+ salts that decompose into N_2 and H_2 are commonly used.
- Coupling of IC to the ICP-MS is very easy
- Interfering species need to be separated.
- Routinely used in our laboratory for a variety of matrices

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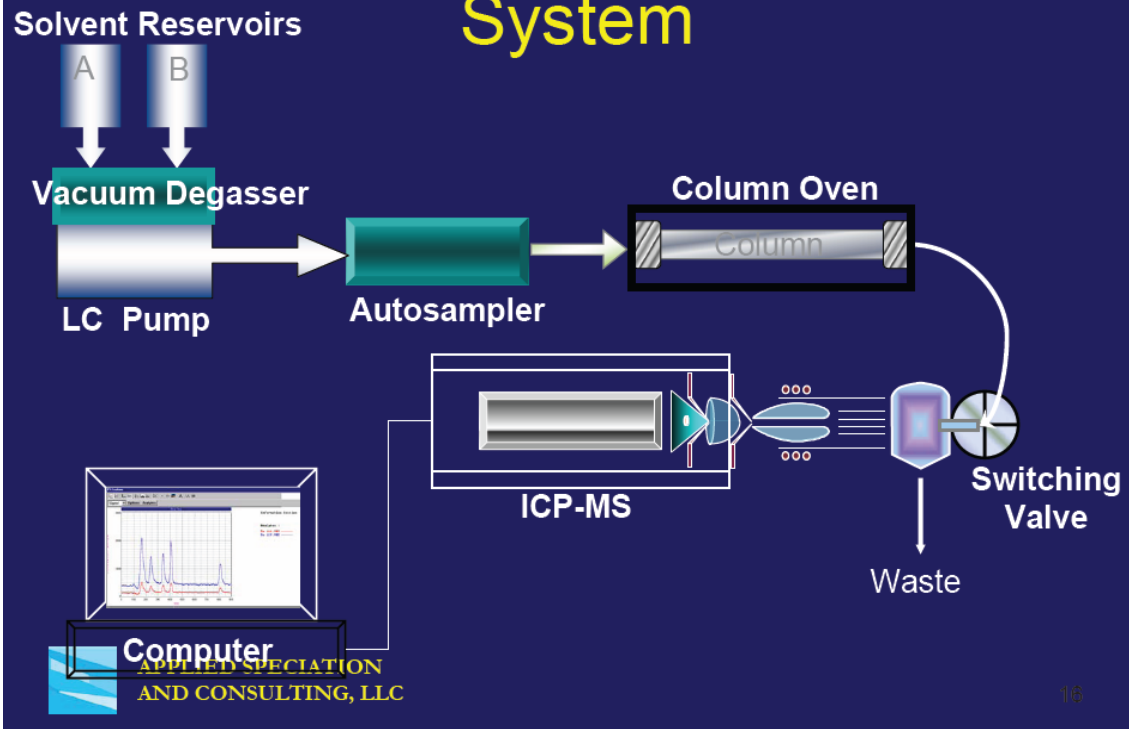
Schematic of an HPLC/ICP-MS System



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LC/IC-ICP-MS

- Chromatography System
  - Dionex AGP-1 Gradient Pump
  - PKI Series 200 Pump, Autosampler, Oven and Vacuum Degasser
- ICP-MS
  - ELAN 6100DRC^{Plus}
- Software
  - ELAN 3.3 with Chromera

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Ion Exchange Chromatography – ICP-MS Interferences?

- Chloride can cause two different types of interference
  - Spectroscopic: Formation of $ArCl^+$ as a peak in the chromatogram
  - Chromatographic: High concentration of chloride can cause column overload or deteriorate separation
- Spectroscopic interference can be removed using a Dynamic Reaction Cell (DRC) instrument.
  - Use of O2 reaction gas forms AsO+ which is monitored at m/z 91
  - Extremely effective and no false positives in blood, urine, seawater, etc.
- Chromatographic interferences can be overcome by diluting the sample or using a different column

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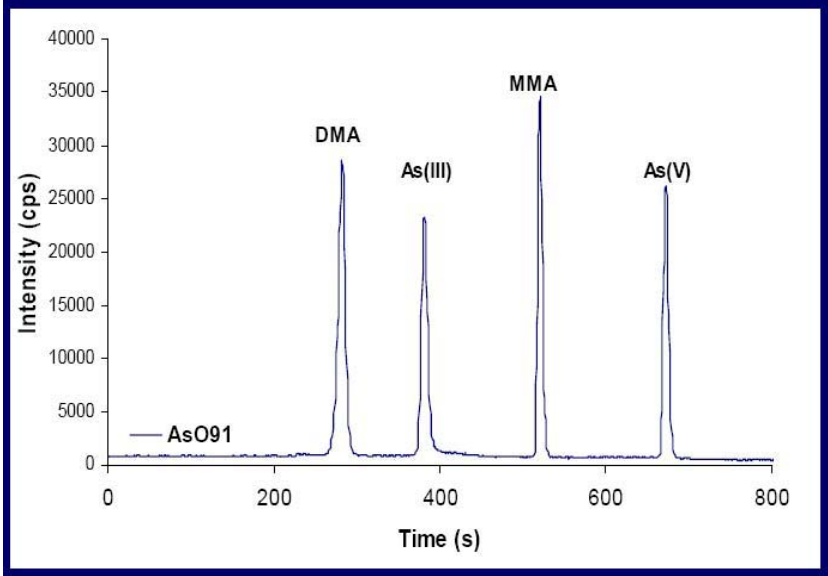

- **Dionex Anion Exchange Column**
- **Hydroxide based mobile phase**
- **Gradient Elution**
- **Detection limits 1-2 ppt for each species (0.1mL sample injected)**

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QA/QC (Variability)

- Single injection produce information on almost all As species present in the sample
- Each species produce a peak of their own
  - Excellent precision
- No excesive sample prep reduces error
- M / MD RPDs for all species are usually less than 2-3%
- eMDLs calculated for each analytical batch by running analyzing the lowest calibration standard in quadruplicate

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QA / QC

- Each As species can be spiked into sample at the same time.
- Highly reducing or oxidizing samples may cause low spike recoveries for As(III) or As(V)
  - When a low spike recovery is obtained for one inorganic As species, the other is usually high
- Compound independent calibration is possible.
  - %RSD between slopes of different As species is usually less than 5%
  - Allows accurate quantification of unknown species without any standards

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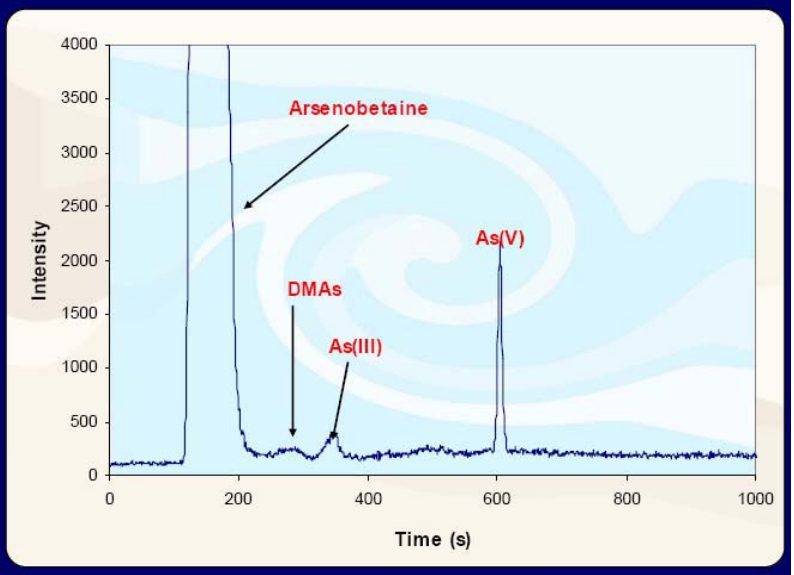
IC-ICP-MS: As in Fish Tissue

- 1 g sample was extracted w/ 5% TMAH
- The extract was cleaned up by a C18 cartridge
- In the fish extract the major As species was arsenobetaine.
- The concentrations of As(III) and DMA were low, while As(V) was found to be around 50 ng/g.



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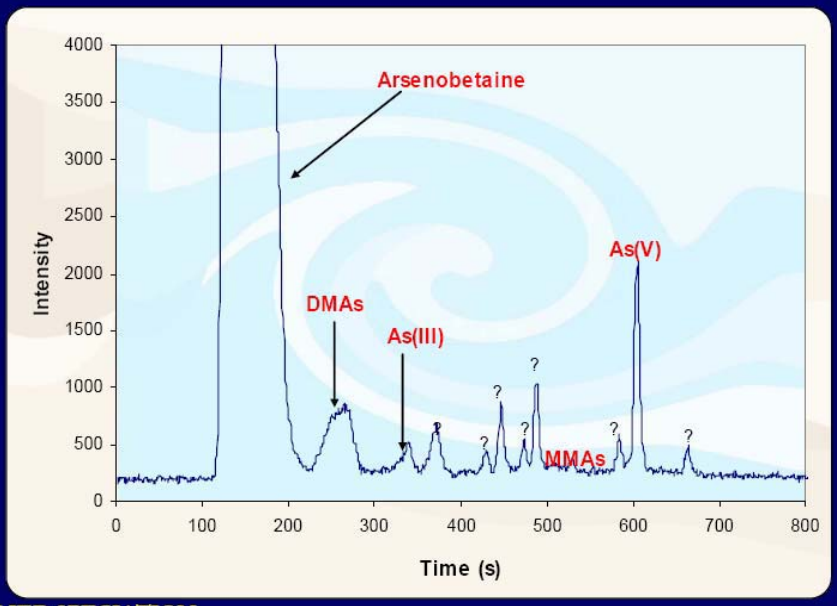
Arsenic Speciation in Fish Meal



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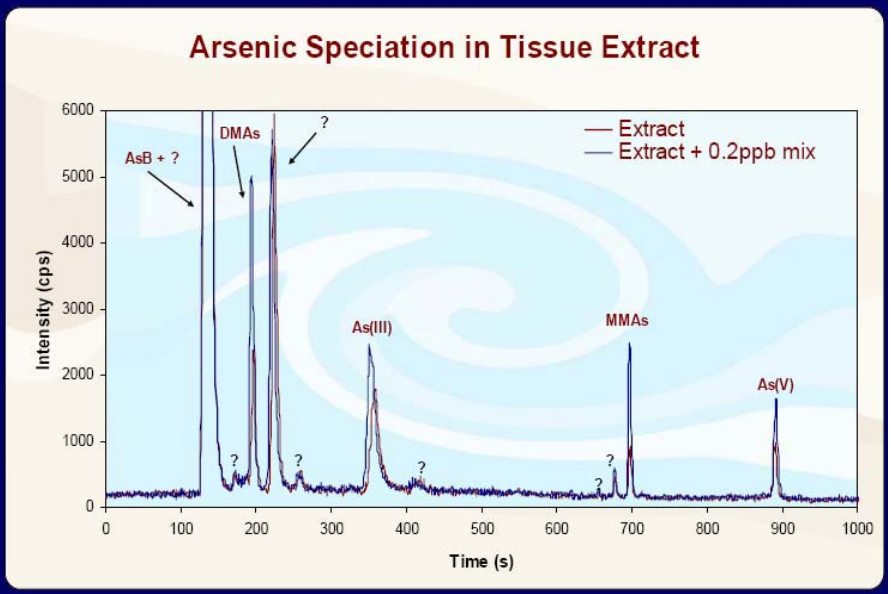
IC-ICP-MS: As in Kelp

- 0.2 g sample was extracted w/ MeOH:H2O
- In the kelp extract the major As species was arsenobetaine
- The concentrations of As(III) and As(V) were significantly high compared to fish (250 – 550) ng/g.



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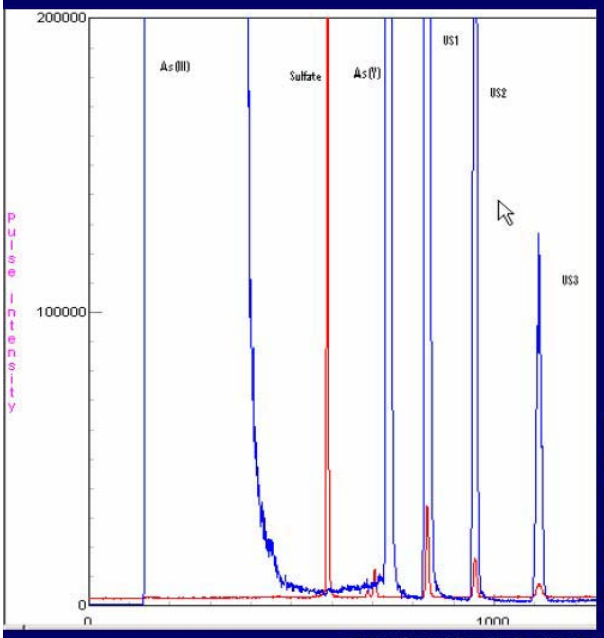
IC-ICP-MS: As Species in a Bacteria Growth Medium

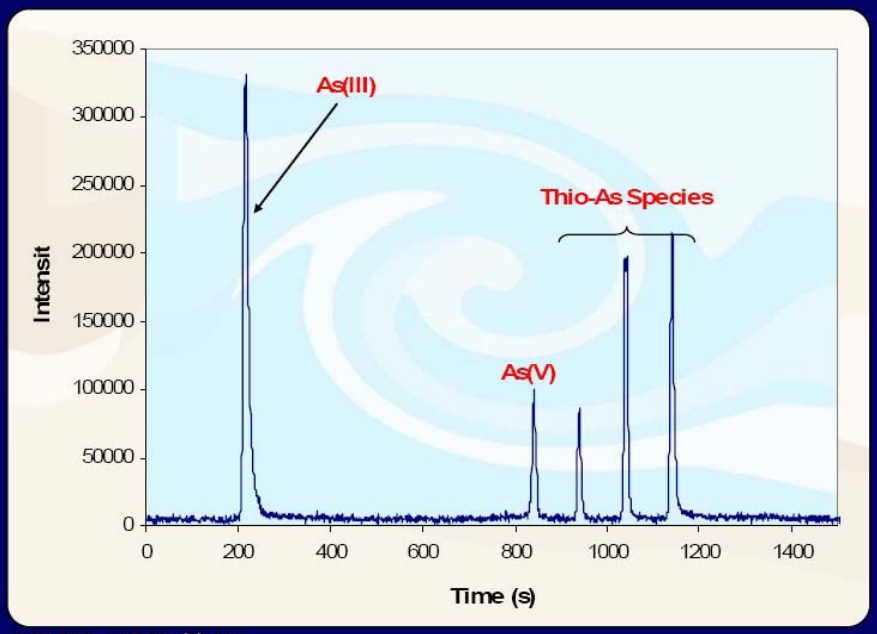


- A bacterial culture was isolated from Mono Lake, CA by scientists from USGS Menlo Park.
- It is a sulfur-reducing bacteria and also resistant to As.
- The growth medium contained high concentrations of sulfide and As(V)
- Monitored SO^+ and As^+ signal
- 3 Unknown peaks were present, all contained both As and S

	(S/As) US1	(S/As) US2	(S/As) US3
t11-1	0.827	2.17	17.4
t11-2	0.991	2.92	99.6
t11-3	1.09	48.7*	51.0
t8-3	1.03	2.23	7.13
Average	0.983	2.44	43.8

APPLIED AND ENVIRONMENTAL MICROBIOLOGY, May 2004, p. 2741–2747

As speciation in Mono Lake



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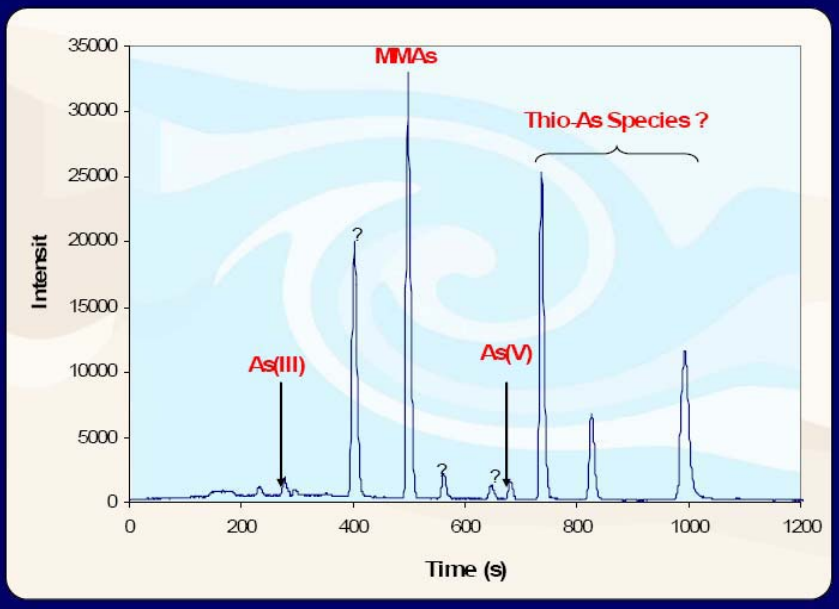
Geochim. Cosmochim. Acta, Vol69, No. 8, pp. 1925-1937

Wastewater Sample (500X dilution)



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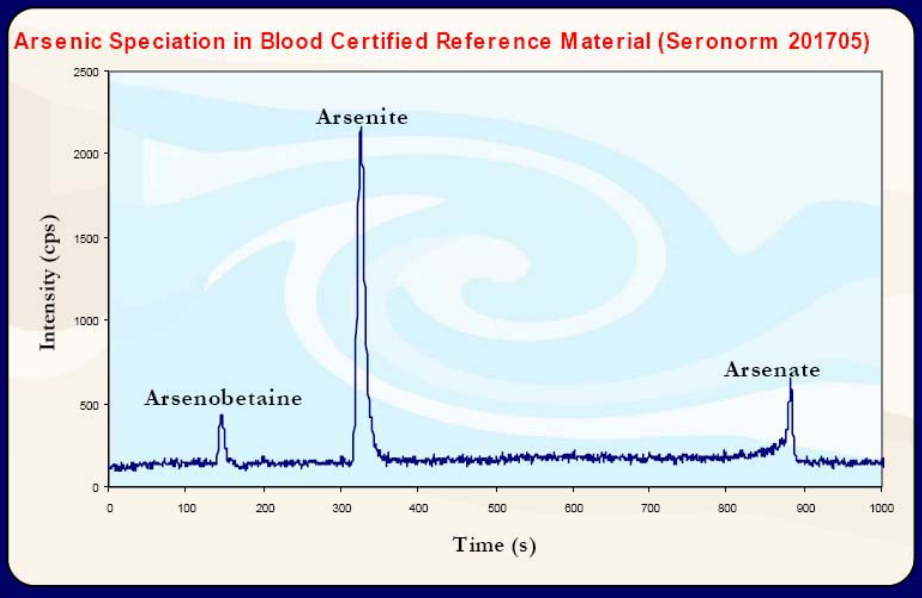
As Speciation in Blood



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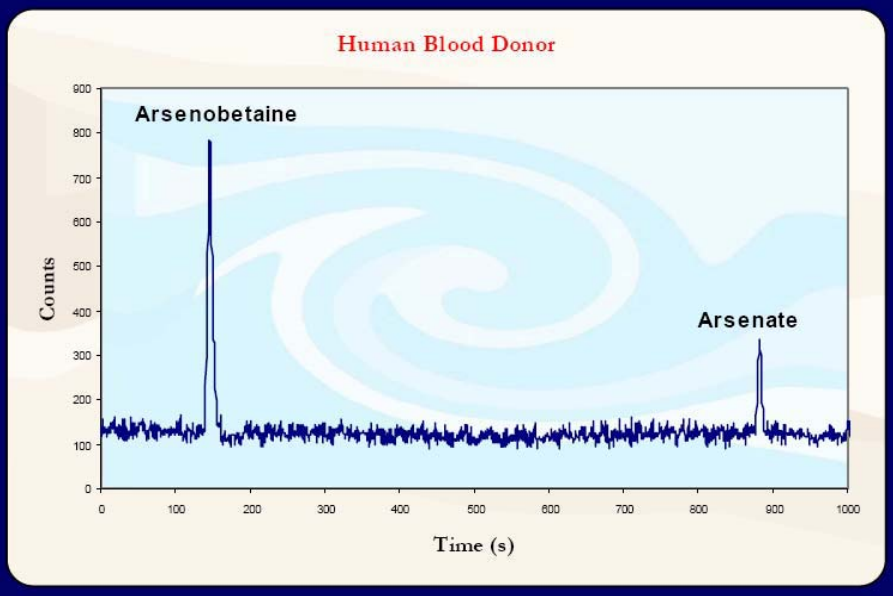
As Speciation in Blood



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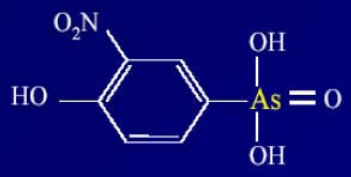
What is Roxarsone?

- The most common additive for poultry and pigs.
- Very little roxarsone is retained in the chicken meat.



3-nitro-4-hydroxyphenylarsonic acid

- FDA limit is 0.5 ppm arsenic in chicken muscle tissue.
- A broiler chicken consumes 3.5 mg of roxarsone per day for six weeks (150 mg total).
- The LD50 value for Roxarsone is 0.11 g/kg.
- A 30-fold increase of the dose kills 50% of the exposed population.*

*G. Momplaisir, et al. (2001)

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Roxarsone Contamination

- Most of the roxarsone appears to be excreted unchanged.
- During a 6 week period, one chicken excretes approximately 150 mg of roxarsone in total.
- USDA estimates that 8.15 billion broiler chickens were produced in the United States in 1999.
- If only half of these chickens were fed feed containing roxarsone, litter that contained more than 600 tons of total arsenic was produced in 1999 alone.
- This is very significant in areas where chicken farming is concentrated.

*G. Momplaisir, et al. (2001)

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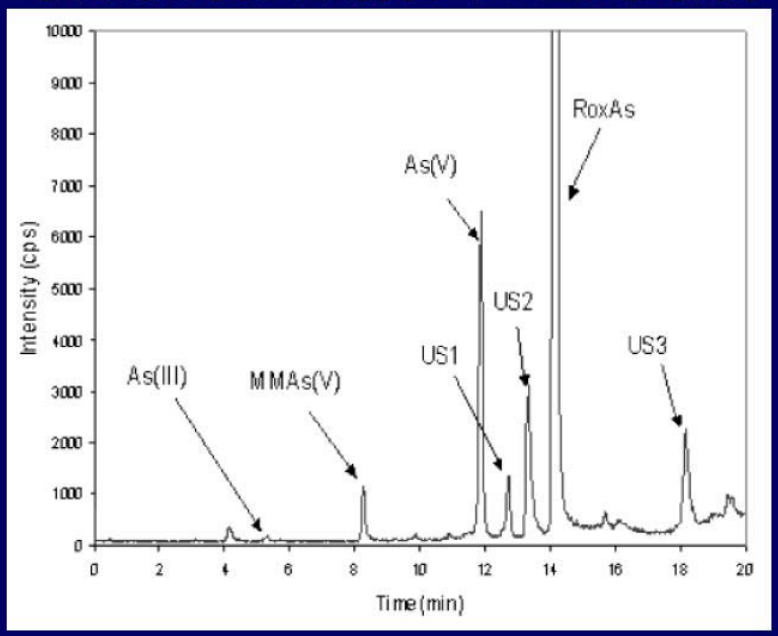
Chicken Litter A Extract



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Gürleyük, et al. Environmental Forensics, 6:83–89, 2005

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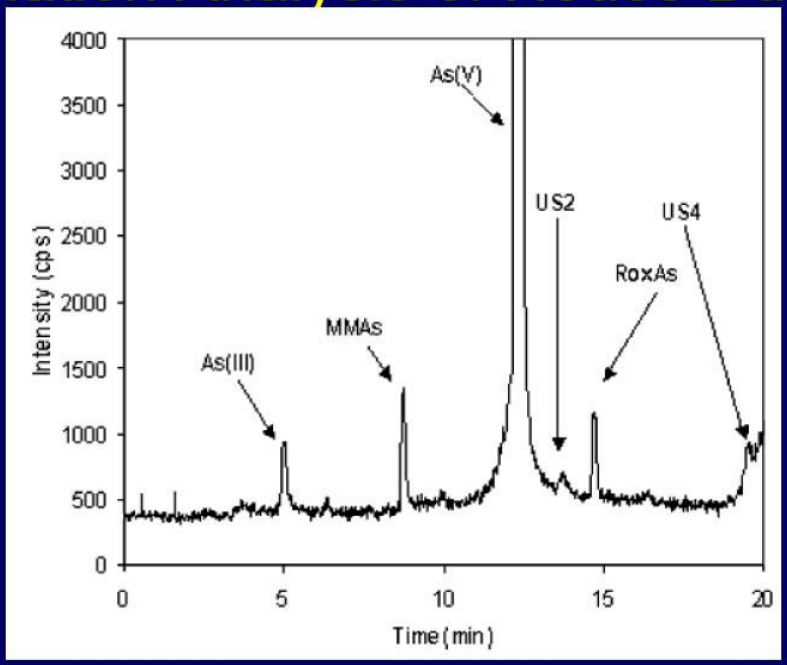
Application of broiler litter to fields results in blowing dusts.

Speciation Analysis of House Dusts



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Gürleyük, et al. Environmental Forensics, 6:83–89, 2005

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Hexafluoroarsenate $(AsF_6)^-$

- Used as pesticides and as electrolytes in lithium batteries
  - Considering the abundance of uses, it is possible this species can be encountered in industrial or natural waters.
  - Very Weak Lewis Base
  - Extremely stable species so possibly does not degrade
- Recent work by Wallschlager et al. showed determination of AsF6 by IC-ICP-MS in wastewaters.
- It is possibe that it has not been observed in industrial or environmental waters
  - Does not respond to Hydride Generation (hidden arsenic?)
  - Possibly haven't been observed since it binds very strongly to IEC columns

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J.Anal.At.Spectrom.,2005,20,993–995

Comparison of As Speciation and Total Arsenic Data

Sample ID	As(III)	As(V)	DMAs	MMAs	Sum of Species	Missing As (%)	Total As
Sample 1	ND (<0.080)	5.41	ND (<0.066)	ND (<0.026)	5.41	93	72.2
Sample 2	ND (<0.080)	0.323	ND (<0.066)	ND (<0.026)	0.32	77	1.38
Sample 3	0.419	ND (<0.080)	ND (<0.066)	ND (<0.026)	0.42	100	187
Sample 4	0.465	ND (<0.080)	0.509	ND (<0.026)	0.97	96	23.1
Sample 5	0.533	49.2	1.29	0.579	51.6	78	237
Sample 6	0.384	22.0	1.28	0.860	24.5	73	90.8
Sample 7	ND (<0.080)	20.9	1.45	1.41	23.8	87	180
Sample 8	ND (<0.080)	2.00	2.19	ND (<0.026)	4.20	97	120
Sample 9	ND (<0.080)	1.13	1.67	ND (<0.026)	2.80	97	86.8

All results are reported in □g/L

- We have had a few cases where the sum of all As species did not match the concentration of total As in the samples
- After a quick screening, we have found that AsF6 was present in the samples

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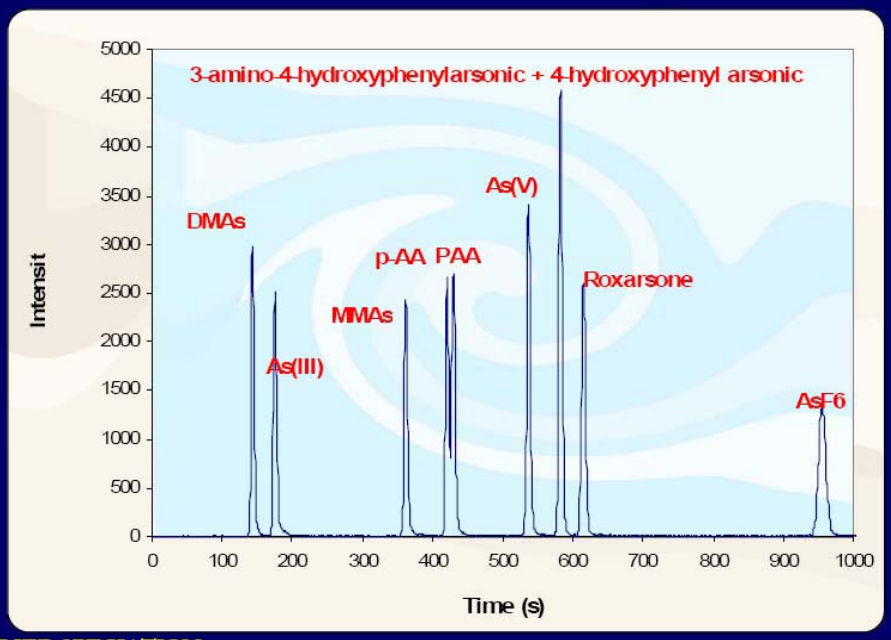
Separation of AsF_6^-



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Preservation of Arsenic Speciation

- Even the most sophisticated analytical methods for speciation are useless if it cannot be assured that the species distribution in the sample remains unchanged between collection and analysis.
- Ideally, speciation should be done in the field immediately after sample collection
- A number of factors, including temperature, pH, light, dissolved oxygen, container material, microbiological activity, or other water constituents, have previously been identified as potentially-detrimental to the stability of As species in waters.
- Every site and sample is different so there is no universal method. The best preservation technique should be selected after reviewing the site characteristics

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Preservation - HCl

- At low pH, the oxidation kinetics of the thermodynamically instable As(III) are slowed down to an extent.
- Acidification prevents the oxidation and/or precipitation of major matrix constituents, especially Fe(II), which would subsequently precipitate as Fe(III)-(oxy)hydroxides.
  - Arsenate binds strongly to such minerals, and would therefore co-precipitate with them.
- Hydrochloric acid itself is redox-neutral, but free chlorine, a very potent oxidizer, is sometimes present or may form during storage which may induce oxidation of arsenic and iron.
- In addition, it has been shown that As(III) can form $AsCl_3$ in the presence of excess chloride (Mester and Sturgeon, 2001). $AsCl_3$ is also a volatile species which can be lost in the sample headspace before analysis.

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Preservation - Complexation

- EDTA forms stable complexes with the Fe(II) and Mn(II) cations, thereby preventing their oxidation and subsequent precipitation as (oxy)hydroxides. (Gallagher et al., 2001).
- This approach functions in waters with different redox potentials.
- The complexation of EDTA with iron is optimum around pH 4.
  - Most water samples, on the other hand, have pH values between 5-8. In order to make sure that all iron is complexed with EDTA, it is also necessary to buffer the samples.
- The only disadvantage: microbiological activity is not eliminated completely.
  - The samples need to be shipped cold followed by storage at cryo temperatures (-80 ºC) in the lab.

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Gallagher, P. A., Schwegel, C. A., Wei, X. & Creed, J. T. (2001): Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection. J. Environ. Monit. 3, 371-376

Preservation – Cryofreezing

- One of the best preservation techniques for arsenic speciation is flash cryo-freezing in the field.
- Storage temperature can affect the stability of As species through a number of different mechanisms. First, reduced temperature slows down all biotic and abiotic reactions, including the diffusion necessary for aqueous phase reactions.
  - As a rule of thumb, for every ten degree temperature difference, reaction rates change by a power of two,
  - Compared to RT conditions, frozen storage on dry ice should reduce those reactions by a factor of 64 and freezing with liquid nitrogen at -196 ºC should reduce the reactions by many orders of magnitude.
- The major advantage of flash cryo-freezing is that no chemicals are added to the sample which does not change the native sample composition and eliminates the the fear of contaminating the sample.
- The major disadvantage of this technique is its practical limitations for routine use.
  - Field sampling personnel may be unable to use it due to a wide variety of reasons, including occupational safety concerns or inaccessibility of liquid N2 in the field.

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Field Spikes

- Applied Speciatio also utilizes field spikes to confirm preservation of species information.
  - A stock solution of As standards is added to specific samples
  - These samples are analyzed to determine if any oxidation or co-precipitation reactions occur during sampling and shipping

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Conclusions

- HG-CT-GC-AAS provides limited amount of information
  - May not produce quality data if applied to every single matrix without prior method development/improvement
  - Projects that require 1632 should consider IC-ICP-MS as a QA/QC check for this method
- IC-ICP-MS has been applied for As speciation in many different matrices sucessfully at Applied Speciation
- ASC does not have a universal method for As speciation
  - Different methods for different matrices
- Experience is very important
  - While setting up an IC-ICP-MS system is very easy, the most important things to consider is:
    - Knowledgeable project managers
    - Experienced analysts who are familiar with both IC/LC and ICP-MS systems
    - Analysts that can interpret and report the data

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Acknowledgements

Perkin Elmer

Anonymous Industrial Clients

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DIRECT INJECTION OF WATER SAMPLES TO ANALYZE PESTICIDES AT CONCENTRATION OF 0.1µG/L USING LC/MS/MS

Besa, Axel – Applied Biosystems; Dahlmann, Jens – Applied Biosystems; El Aribi, Houssain – MDS Sciex; Ellis, Robert – MDS Sciex; Schreiber, André – MDS Sciex

Currently more than 800 pesticides are used worldwide. Many pesticides are difficult or not to analyze by GC/MS but can be identified and quantified by multi-residue methods using Liquid Chromatography combined with tandem Mass Spectrometry (LC/MS/MS). Multiple Reaction Monitoring (MRM) is the preferred scan type for this kind of application. However, a single MRM transition per pesticide is not enough to validate the presence of a pesticide without any doubt. Typically, a second transition (qualifier) or an MS/MS spectrum is used to confirm analytical results. Depending on the number of compounds to be analyzed confirmation should be performed using a qualifier transition using a triple quadrupole MS or by automatically acquired Enhanced Product Ion spectra using a Hybrid Triple Quadrupole Linear Ion Trap MS, such as a QTRAP® system.

Quantitation and confirmation have to be performed reliable at concentrations of legal action level. The maximum residue level of pesticides is set to 0.1µg/L in many countries.

This presentation will focus on recently developed LC/MS/MS methods and software tools to assist method development. Examples of analyzing pesticides of different compounds classes, such as triazines, phenyl ureas, phenoxycarboxylic acids, Glyphosate and metabolites in water samples will be presented. All methods allow quantitation and confirmation at a level of 0.1µg/L without time consuming sample preparation. Reporting of analytical data was done using an automated reporting tool.

A Brief overview of the role of speciation analysis for environmental analysis

Michael Sperling,

European Virtual Institute for Speciation Analysis (EVISA), University of Muenster

NEMC 2006
Arlington, August 28-31, 2006

evisa.

evisa.

Environmental analysis: An important sector of economy

The objectives of pollution monitoring are manifold:

- To identify potential threats to human health and natural ecosystems.
- To inform the public about the quality of the environment and raise public awareness about
- To provide inputs to policy making decisions (land-use planning, traffic, etc.)
- To assess the efficacy of pollution control measures.
- To investigate trends in pollution and identify future problems
- To determine compliance with national and international standards

Environmental analysis is often used in environmental impact assessment (EIA) or risk assessment studies.

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Environmental monitoring: information required

- Data on the emission, transport and exchange of matter between different compartments of the environment.
- Data on the chemistry, geo-chemistry, bio-geo-chemistry of different pollutants and other materials in the environment.
- Data on the mobility, bioaccessibility, bioavailability and toxicity of pollutants towards plants, animals and humans.
- Data on the chemical and physical effects of pollutants with respect to the energy balance, mass and energy flows of the earth.
- Such characteristics depends on **chemical species** not on their **elemental composition** !

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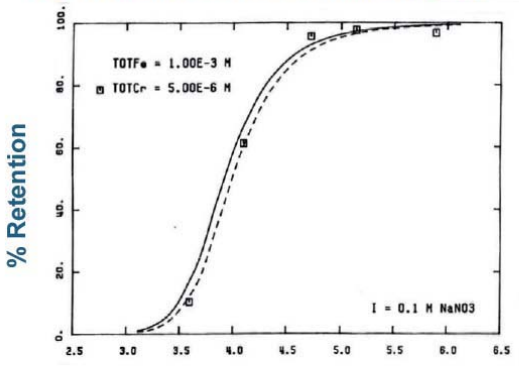
Mobility: A question of sorption properties

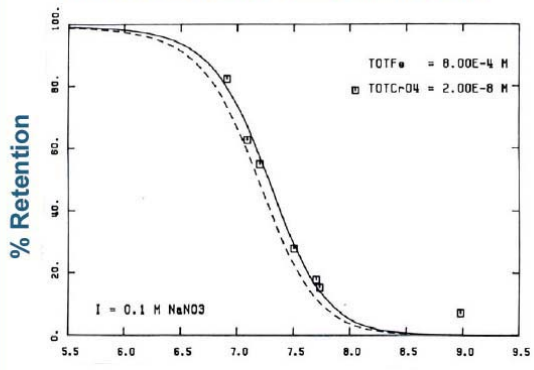
Cr (III)

Rapidly and **strongly** retained on the surface of different solid phases (oxy(hydroxydes) of Fe, Mn, clays,…)



Cr (VI)

Weakly retained on the surface of different solid phases (oxy(hydroxydes) of Fe, Mn, clays)



from: Dzombak et Morel, 1990

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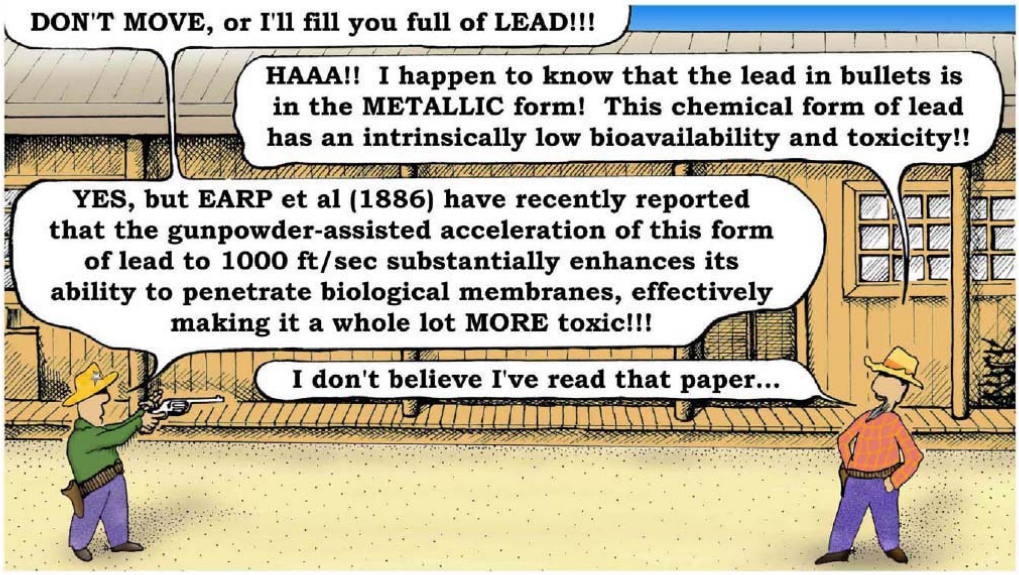
Toxicity of metals – a question of their speciation



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Toxicity and speciation

The toxicity of often called "toxic trace elements" depends on their speciation and concentration not only in a **quantitative** way but also in a **qualitative** way. Some examples:

Chromium:	Cr(III) is considered to be essential while Cr(VI) is carcinogen
Arsenic:	Inorganic As(III) compounds are carcinogen while Arsenobetaine is essential non-toxic
Tin:	Inorganic tin compounds are nutrients for animals but tributyltin (TBT) is an endocrine disruptor

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The information value of a trace element concentration

A so-called *trace element concentration* is a kind of sum parameter over the different element species present in the sample. The question is, what is the information value of a sum parameter, summing-up different species

- ➔ having toxicity levels different by orders of magnitude
- ➔ being cancerogen, toxic, non-toxic or even essential
- ➔ being present in the particular, colloidal, dissolved or gaseous phase
- ➔ being positively, negatively or non-charged
- ➔ being present as a "free" ion, sorbed, complexed or bound

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What is the use for total element concentrations ?

Total element determination can be useful if…..

- ➔ we do have a priori knowledge about the speciation so that total element concentration is sufficient to characterize the sample,
- ➔ speciation is highly dynamic and we need to know an upper limit for a certain species,
- ➔ as a quality check of our speciation analysis (mass balance),
- ➔ we cannot get more specific information,
- ➔ rules and legislation force us to present such data

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Chemical analysis: an information science

- ➔ Data on the presence of elements and their total concentration do have very limited information value and are therefore costly and seldom fit-for-purpose.
- ➔ The real questions to be answered are: In what chemical form do the elements occur and what is their distribution ?
- ➔ Speciation Analysis identifying and/or measuring the quantities of one or more individual chemical species in a sample gives the answer!

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Speciation analysis: Do we have the necessary tools ?

Solid state analysis:

There are some techniques available offering species related information in solid samples, such as

- X-Ray techniques
  - X-ray diffraction (XRD)
  - X-ray absorption fine structure (XAFS)
  - Extended X-ray absorption fine structure (EXAFS)
  - X-Ray absorption near edge structure (XANES)
- Electron spectroscopy
  - ESCA (XPS, Auger)
- Mass spectrometric techniques
  - Secondary ion mass spectrometry (SIMS)
  - Laser ionization mass spectrometry (LIMS)

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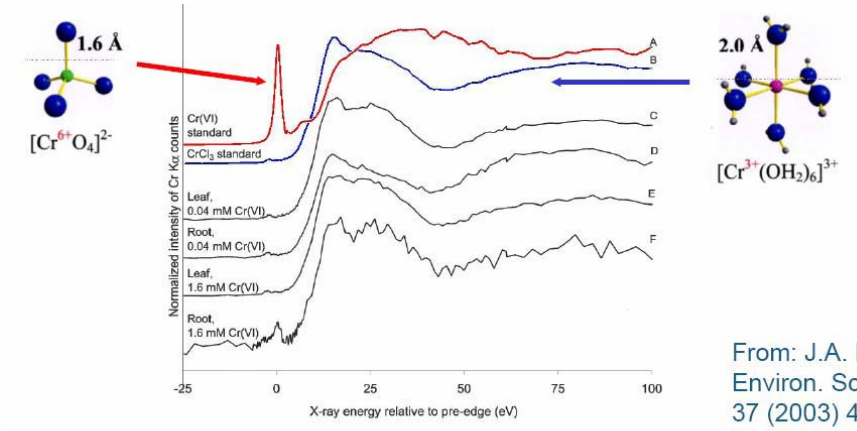
XANES: Direct solid state speciation

The near edge structure of an X-ray absorption spectrum is sensitive to the coordination and oxidation state of the absorbing atom. For example, the XANES region of $Cr^{3+}(aq)$ and $[Cr^{6+}O_4]^{2-}$ (aq) are very different.



From: J.A. Howe, Environ. Sci. Technol., 37 (2003) 4091

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Speciation analysis: Do we have the necessary tools ?

Dissolved species determinations:

Few techniques are available that directly provide species (molecular) information, such as

- Electroanalytical techniques
  - Potentiometry with Ion-specific Electrodes (ISE)
  - Voltammetry
- Magnetic resonance spectroscopy
  - Nuclear magnetic resonance spectrometry (NMR)
  - Electron spin resonance spectrometry (ESR)
- Nuclear spectroscopy
  - Mössbauer spectroscopy

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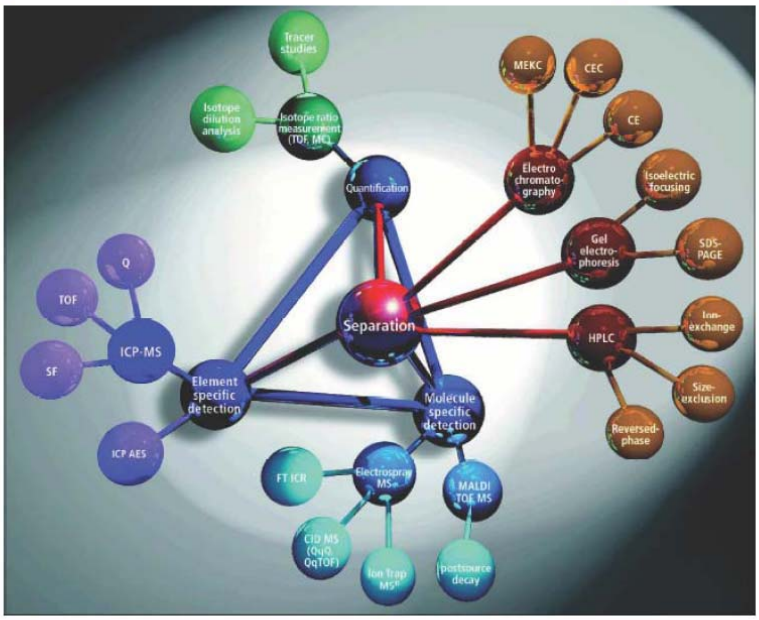
Speciation analysis: Do we have the necessary tools ?

We do have a fully developped tool-box for the

- separation
- detection
- identification
- quantification

of elemental species.



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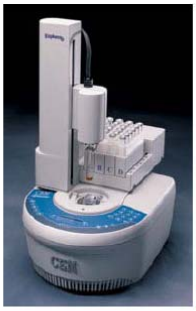
Development towards instrumental sample prep'

Hot-plate wet chemistry

- Following "recipes"
- Tedious manual work
- Poor process control
- Prone to contamination and analyte losses



Microwave-assisted sample preparation

- Closed system
- Temperature/pressure/timing microprocessor controlled
- Automated un-attended operation, highly reproducible
- Much faster !

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Problems in speciation analysis: ERROR SOURCES

- Incomplete extraction from solid samples
- Degradation reactions
- Matrix-dependent recovery of extraction/derivatisation reactions
- Lack of adequate internal standards
- Limited number of Certified Reference Materials
- Matrix effects, calibration drifts
- Poor sensitivity of analytical techniques: Preconcentration steps
- Long and time consuming analytical procedures

.....poor precision and accuracy

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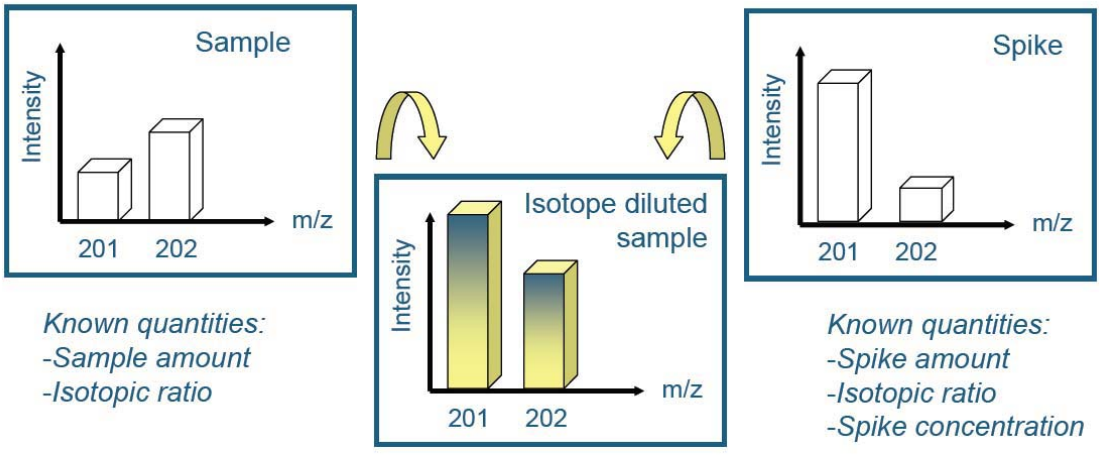
Principle of species-specific isotope dilution analysis



Known quantities:
-Sample amount
-Isotopic ratio

Known quantities:
-Spike amount
-Isotopic ratio
-Spike concentration

Measured quantity: Isotope ratio

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Species-specific isotope dilution – capabilities and limitations

+ Reduction of a determination of a species concentration to a measurement of an isotopic ratio (higher precision and accuracy)
+ Detection and correction of analyte losses taking place after the addition of the spike (e.g. intrinsic extraction yield correction)
+ Detection and correction of species transformation during the analysis (shift of equilibrium between different species)

− All isotopes must be measured free of isobaric interferences (often requires high resolution MS)
− Sample and spike must reach isotopic equilibrium (problematic for solid samples !)
− One isotope required for each species to be determined ! (does not work for mono-isotopic elements like As)

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„Real world" environmental and industrial speciation issues

Drinking water:

- Enhanced characterisation of fresh water with respect to requirements for water treatment (Fe(II)/Fe(III), As(III/As(V))
- Influence of pH, different water sources and disinfection products on remobilisation of deposited minerals from distribution system (e.g. As, Pb)
- Process control and elimination of toxic contaminants from drinking water (As(III)/As(V), Bromate)

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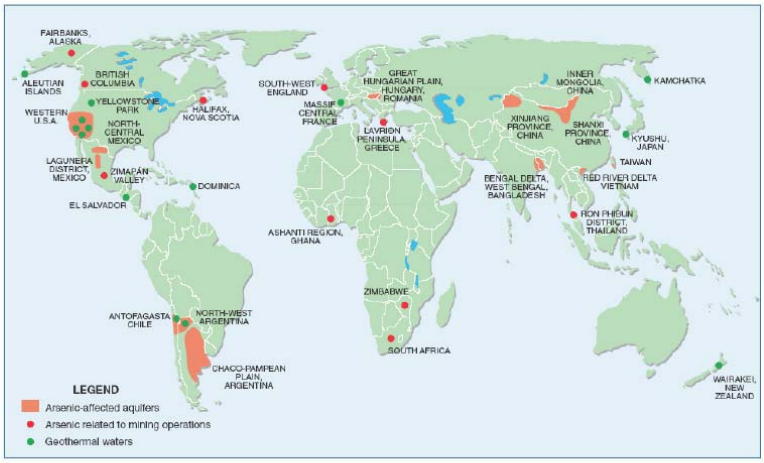
Arsenic in drinking water: World's biggest calamity

The drinking water resources in many areas of the world are contaminated by arsenic:

- Asia: India, West Bengal, China, Taiwan, Thailand, Russia
- Europe: Hungary, Romania, United Kingdom
- America: **USA**, Mexico, Chile, Argentina
- Africa: Ghana
- New Zealand



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Arsenic speciation: A necessary information

Data on arsenic speciation is necessary for:

- ➔ Tracing the source of contamination of drinking water (geological, pesticides, wood preservation, chicken manure)
- ➔ Understanding the bio-geochemistry behind the arsenic cycling
- ➔ Designing remediation strategies
- ➔ Controlling water treatment plants
- ➔ Evaluating of the Health Risk's for the consumers

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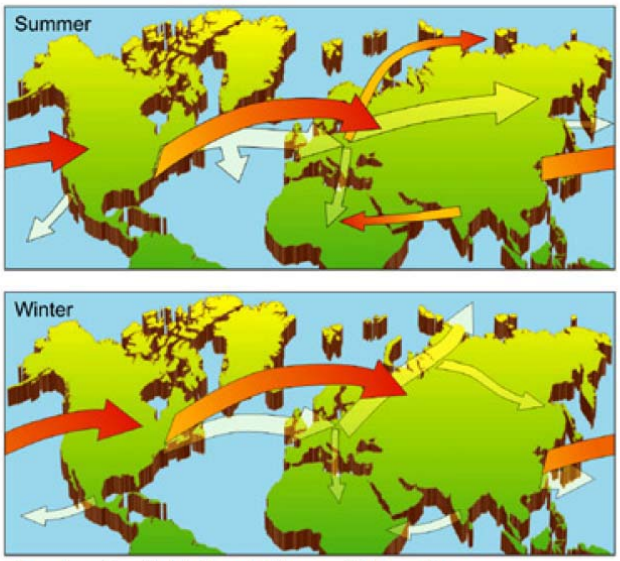
Mercury as a global pollutant

The US sends it to Europe; they send it to Asia. But what happens when China starts sending more our way?

Or....

"Everyone is worrying about everybody else"



Courtesy Daniel J. Jacob, Harvard University

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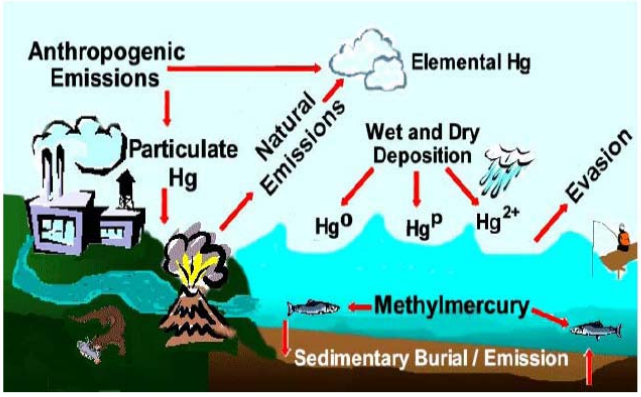
Mercury as a global pollutant

Speciation greatly influences the transport within and between environmental compartments (e.g atmosphere, oceans), e.g. Hg speciation is a determining factor for how far from the source mercury emitted to air is transported:



- ➔ Mercury adsorbed on particles and ionic mercury compounds will fall on land and water mainly in the vicinity of the sources (local to regional distances)
- ➔ Elemental mercury vapour is transported on a hemispherical/global scale making mercury emissions a global concern.

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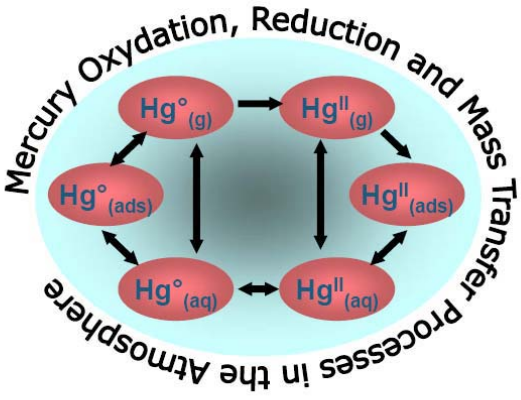
Mercury species and transformation in the atmosphere

The atmospheric chemistry of mercury involves several interactions:

- ➔ Gas phase reactions;
- ➔ Aqueous phase reactions (in cloud and fog droplets and deliquesced aerosol particles);
- ➔ Partitioning of elemental and oxidized mercury species between the gas and solid phases;
- ➔ Partitioning between the gas and aqueous phases; and also
- ➔ Partitioning between the solid and aqueous phases in the case of insoluble particulate matter scavenged by fog or cloud droplets.



Model of interactions between mercury species in the atmosphere. (Frontispiece of the 2001 Special Issue of Atmospheric Environment (vol. 35, no. 17) dedicated to mercury research in Europe.) (Pirrone et al., *2001)*

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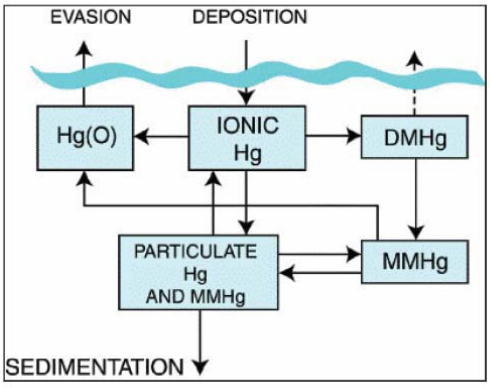
Mercury species and transformation in aquatic environments

Methylmercury can be formed in the environment by microbial metabolism (biotic processes) such as by certain bacteria and by chemical processes that do not involve living organisms (abiotic processes). The formation of methylmercury in aquatic systems is influenced by a wide variety of environmental factors:

- ➔ Microbial activity (sulfur concentration)
- ➔ Mercury availability (temperature, pH, redox potential, inorganic and organic complexing agents)



Dynamic interactions between the various mercury species in ocean waters (based on Mason and Fitzgerald, 1996).
Hg(0) = elemental mercury,
DMHg = dimethylmercury,

MMHg = (mono)methylmercury.

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Toxicity of Mercury – a question of the speciation

Speciation plays an important part in the toxicity and exposure of mercury to living organisms. Among other things, the species influence:

- ➔ The physical availability for exposure - if mercury is tightly bound to in-absorbable material, it cannot be readily taken up (e.g. into the blood stream of the organism);
- ➔ The internal transport inside the organism to the tissue on which it has toxic effects - for example the crossing of the intestinal membrane or the blood-brain barrier;
- ➔ Its toxicity (partly due to the above mentioned);
- ➔ Its accumulation, bio-modification, detoxification in – and excretion from – the tissues;
- ➔ Its bio-magnification on its way up the trophic levels of the food chain (an important feature particularly for methylmercury).

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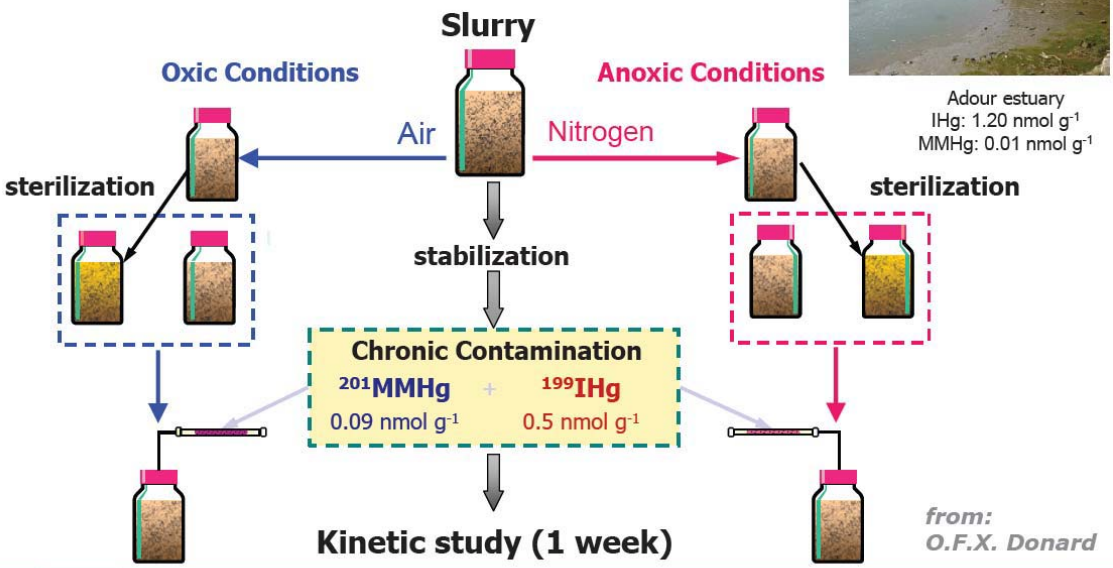
Hg Methylation/Demethylation in estuarine sediments

Adour estuary
IHg: 1.20 nmol g^{-1}
MMHg: 0.01 nmol g^{-1}



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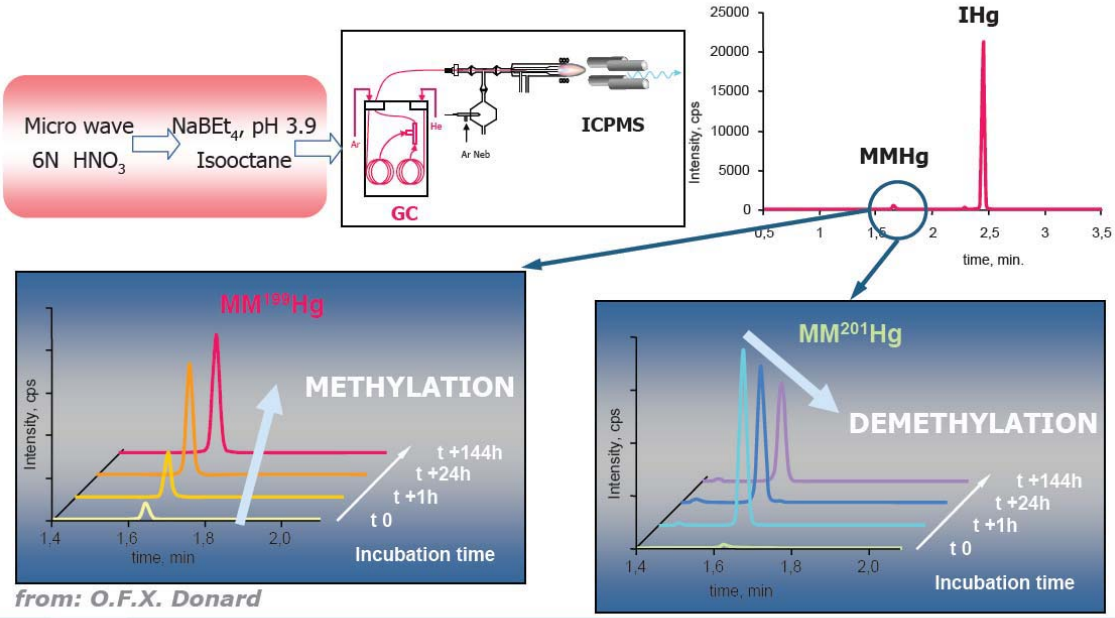
Hg Methylation/Demethylation in estuarine sediments



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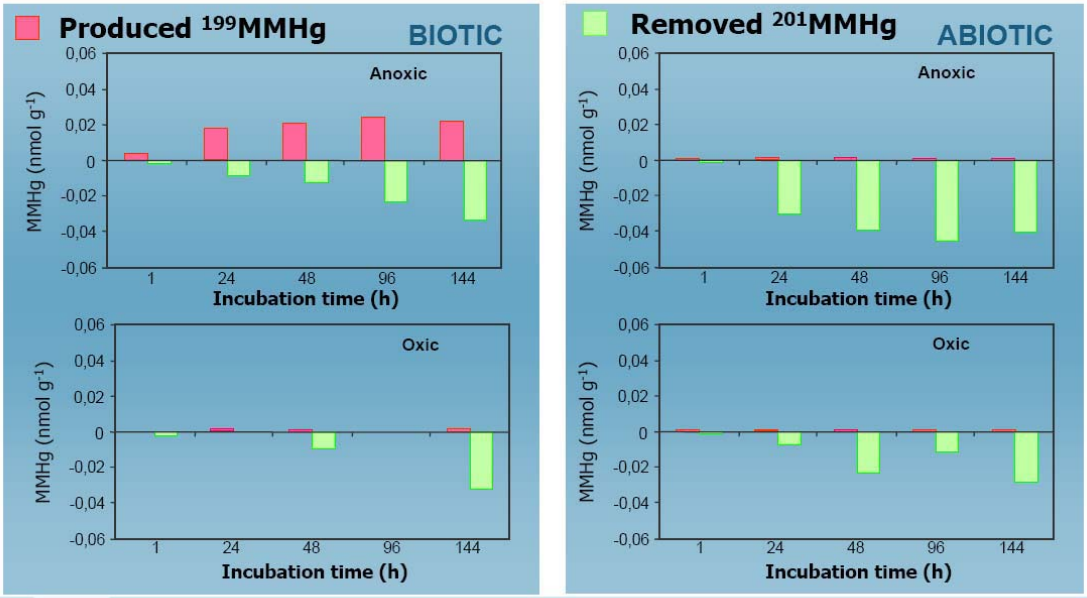
Hg Methylation/Demethylation in estuarine sediments



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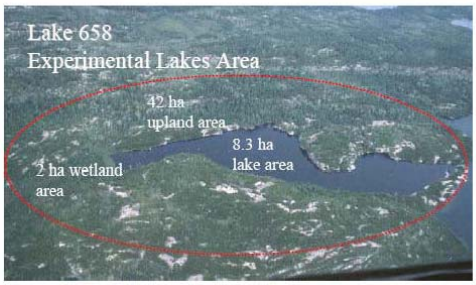
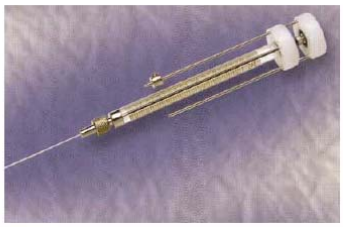
Changing the scale ..... to the ultimate test-tube





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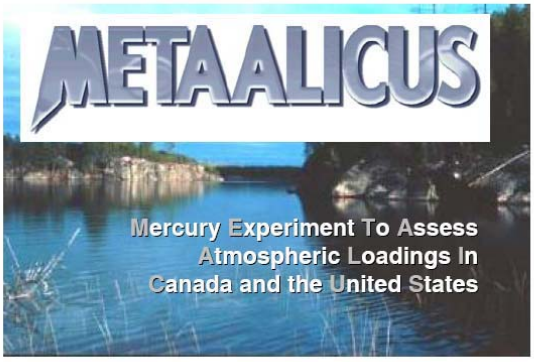
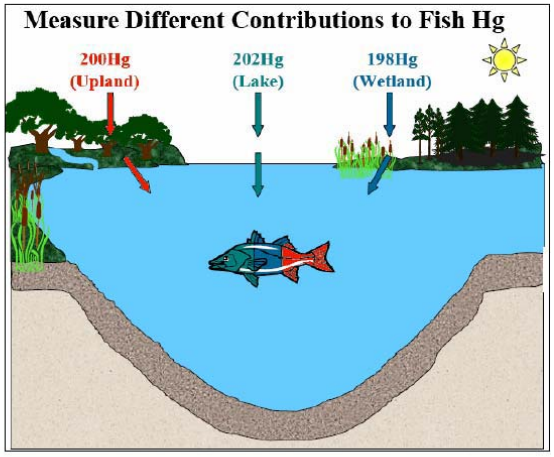
METAALICUS: A loading experiment



Mercury is being added to a lake and its surrounding watershed in form of inorganic mercury with different isotopic composition.



The key question is:

What is the relationship between atmospheric Hg deposition and fish Hg concentrations?

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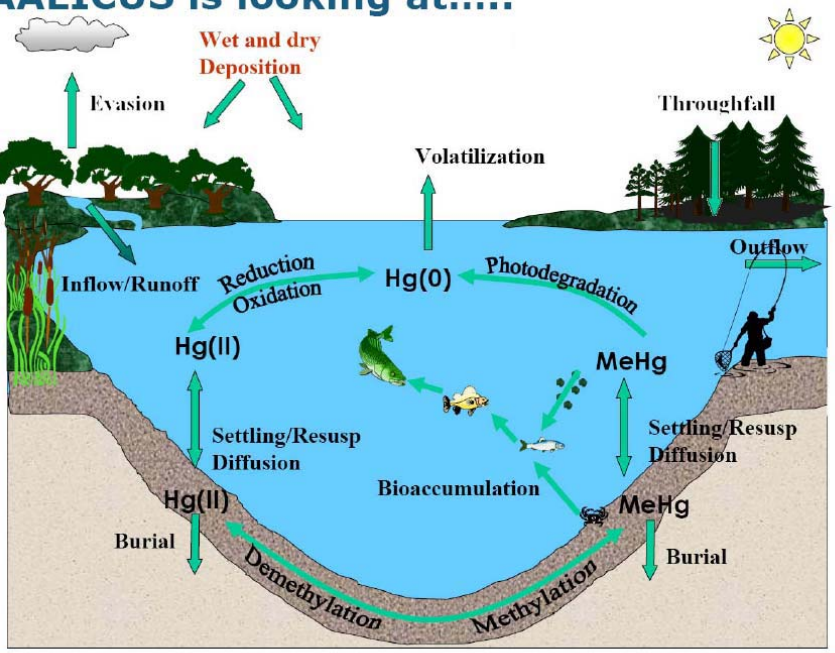
METAALICUS is looking at.....



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„Real world" environmental and industrial speciation issues

Waste management:

- Risk assessment (mobility of pollutants, degradation and transformation, potential toxicity),
- Waste management (Cr in leather tannery waste, Se in waste water, mobility of toxic metals from solid wastes such as fly ashes,
- Optimization of remediation strategies (As, Cd, Cr, Hg and Pb in waste disposal sites, abandoned industrial production places etc.)

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Conclusions, Part 1:

Speciation analysis provides information that is **essential** for following environmental pathways (emission, fate, degradation and cycling of environmental pollutants), especially by:

- identifying sources and sinks (by using isotopic and/or chemical species tracers)
- claryfying transformation processes (such as oxidation, reduction, methylation, demethylation)
- evaluating bioaccessibility and bioavailability of metallic pollutants,
- evaluating exposure routes and toxicity.

NB!: Total element determination does not provide the necessary information to discuss such topics !

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Conclusions, Part 2:

Especially during the last ten years, speciation analysis has reached some degree of maturity that makes it a valuable tool to solve „real world" analytical problems:

- Sample preparation has reached an instrumental level using „sample prep workstations" supporting strict control of operational parameters.
- Instrumental analysis has reached a detection power that often is limited by blank contamination rather than by sensitivity.
- Species specific IDMS can be used for reliable quantification, verification and validation of analytical methods and environmental field studies.
- Some standards and Certified Reference Materials are available as a starting point and CRM manufacturers are working on new ones (e.g. Cr(VI) in soil and waste)

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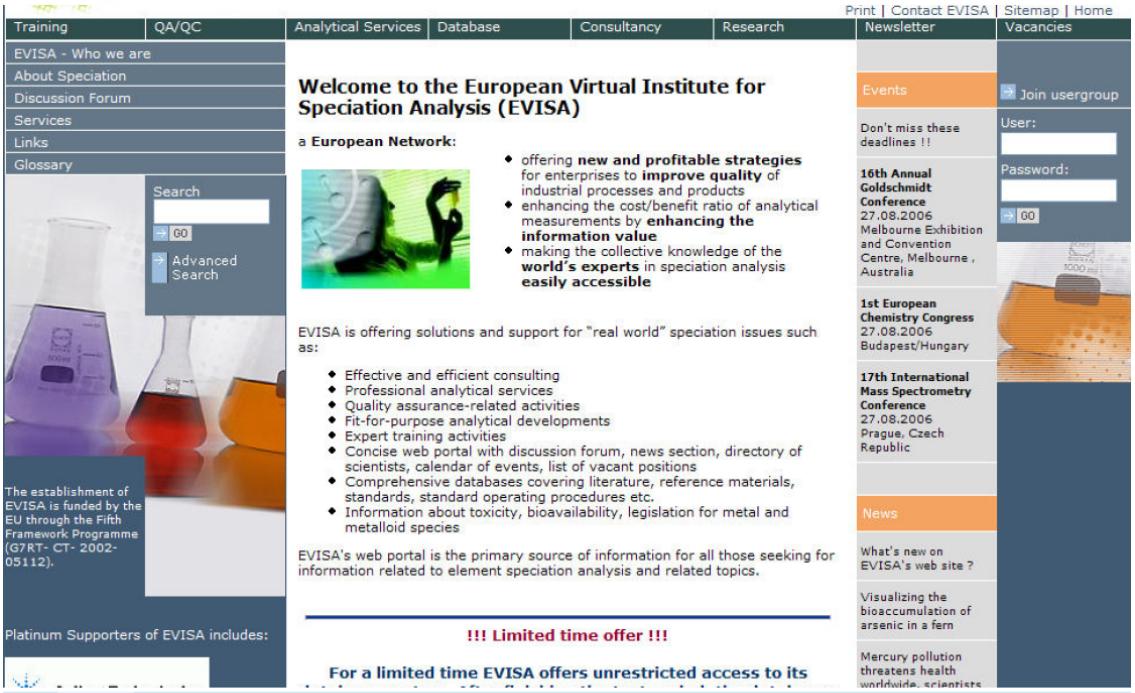
Conclusions, Part 3

- Rule makers have started to consider and implement speciation and more rules are likely to come-up soon (e.g. arsenic species in seafood).
- Instrument manufacturers have entered the field supporting the analysts with commercial products (e.g. GC-ICP-MS, HPLC-ICP-MS, CE-ICP-MS, LC-ESI-MS, GC-MS, GC-AFS, GC-MIP-AES, LC-ESI).
- A Virtual Institute for Speciation Analysis (EVISA) has been founded in order to help Industry and routine laboratories to get easy access to information and knowhow collected within the research community and to empower scientists for interdisciplinary cooperation.

For more information, please visit our web site at: http://www.speciation.net



TUESDAY, AUGUST 29, 2006

CONCURRENT SESSIONS

Managing Uncertainty

TRIAD: WHY ISN'T IT USED MORE?

Nagourney, Stuart J.; New Jersey Department of Environmental Protection Office of Quality Assurance

With improved measurement certainty and documented reductions in project time and cost, Triad should be the de-factor strategy for many if not most remedial projects throughout the United States. The reality is that most State and Federal agencies either do not utilize Triad at all or employ it only sporadically.

With several years of support by State remediation program management and involvement in Federal national implementation efforts, the New Jersey Department of Environmental Protection has been at the forefront in promoting the use of Triad. This paper will discuss a variety of reasons why Triad is not used more and more widely and offer suggestions to make it more broadly applicable.

1

Triad: WHY ISN'T IT USED MORE?

The Triad Approach

Systematic Project Planning

Dynamic Work Strategies

Real-time Measurement Technologies

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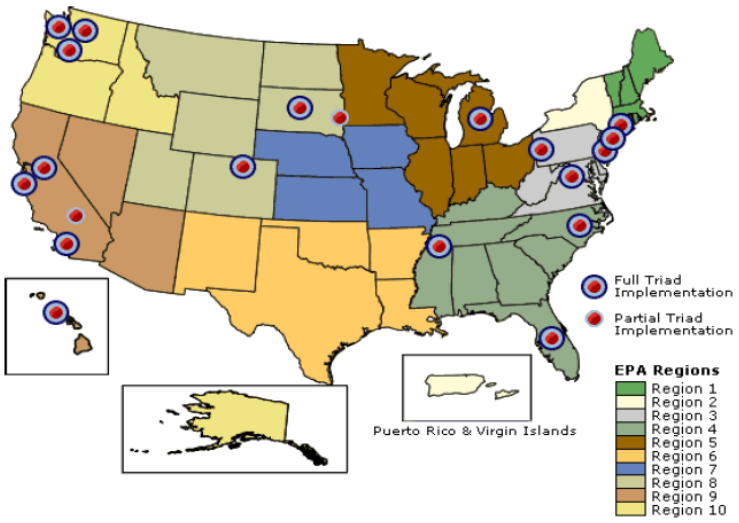
2

TRIAD TO DATE



3

DIRECT Triad BENEFITS

- More certain site decisions
- Lower life-cycle costs
- Faster investigations
- More effective cleanups

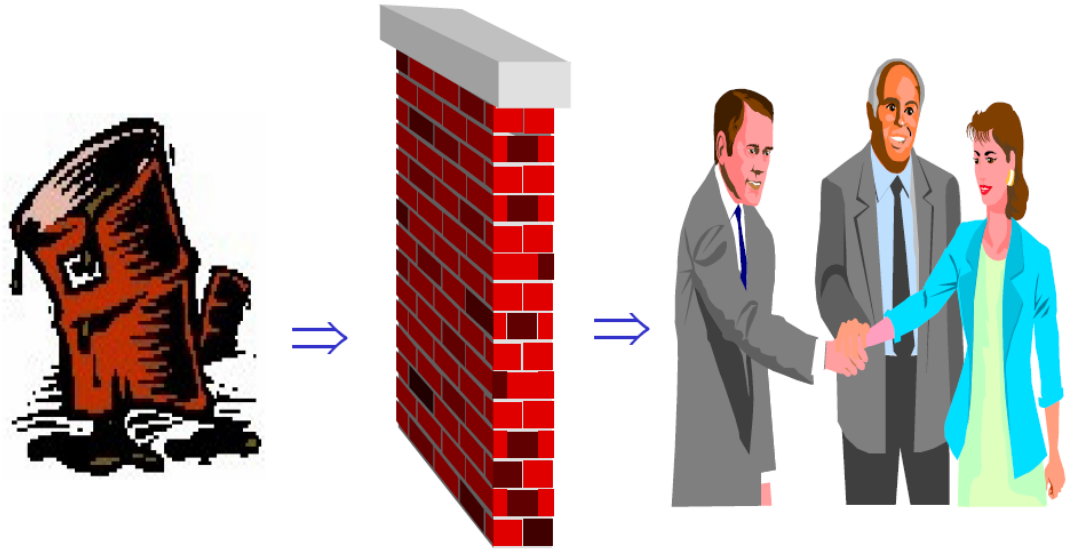
4

INDIRECT Triad BENEFITS

- Better public relations
- More effective communication
- Use of best-available technologies
- Improved morale of staff

5

IF Triad IS SUCH A GOOD IDEA, WHY ISN'T IT USED MORE?



6

TYPES of Triad BARRIERS

- Institutional
- Technical
- Personal

7

INSTITUTIONAL Triad BARRIERS

- Machiavelli designed bureaucracies to be slow to change
- Triad can't replace our current remedial policies
- Mid-level mangers make it happen; most fear failure more than they are excited by success
- Triad is just another fad or re-cycled ideas
- What will my new boss think about Triad?

8

TECHNICAL Triad BARRIERS

- Field data won't stand up in court
- Lab. cert. does not apply to field data
- Field measurements don't use QA
- "Mature" staff do not possess SOTA KSA Triad demands

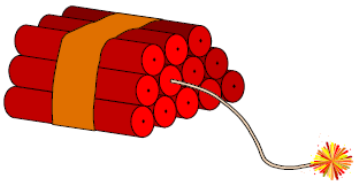
9

PERSONAL Triad BARRIERS

- All the CSM work makes a Triad project cost more
- My staff already has enough to do
- If Triad succeeds, so what? If it fails, I may be demoted.
- Don't bother me!; I get 5 weeks vacation, 16 paid holidays and I'm retiring in 4 years, 3 months and 12 days

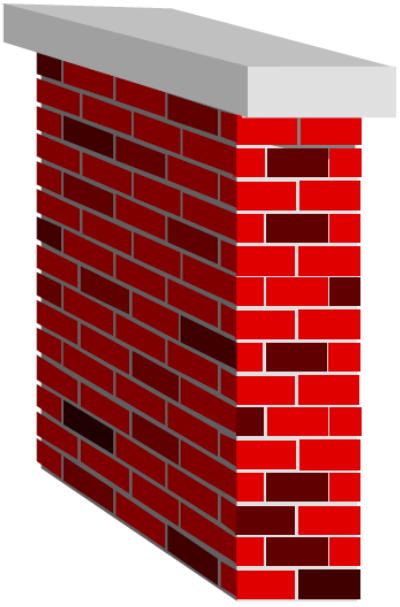
10

SO, HOW DO WE BREAK DOWN THESE BARRIERS???



Institutional

Personal



Technical

11

BREAKING INSTITUTIONAL Triad BARRIERS

- Machiavelli designed bureaucracies to be slow to change
  - But ones that survive do change
- Triad can't replace our current remedial policies
  - Triad's just a case-selective supplement
- Mid-level mangers make it happen; most fear failure much more than they are excited by prospects for success
  - You are not alone and are not breaking new ground
- Triad is just another fad or re-cycled ideas
  - So it really isn't new; it does not make it a bad idea
- What will my new boss think about Triad?
  - If Triad succeeds, they won't care

12

BREAKING TECHNICAL Triad BARRIERS

- Field data won't stand up in court
  - See Daubert & Frye; the "Supremes" disagree
- Only lab. cert. data is any good; field data NG
  - NJDEP and NELAC strongly disagree
- Field measurements don't use QA
  - You may need to repeat 2nd year of college chem.; any analytical measurement has appropriate QA
- "Mature" staff do not possess SOTA KSA Triad demands
  - Find a Triad champion in your agency
  - There is nothing in Triad that a good Jr. scientist/engineer can't handle

13

BREAKING PERSONAL Triad BARRIERS

- All the CSM up-front work makes a Triad project cost more
  - Like brain surgery; the 1st few times are the hardest
- My staff already has enough to do
  - But with Triad, you might actually finish some cases
- If Triad succeeds, so what? If it fails, I may be demoted
  - It has not happened yet
- Don't bother me!; I get 5 weeks vacation, 16 paid holidays and I'm retiring in 4 years, 3 months and 12 days
  - You can learn "Triad 101" in a day or 2; then, turn it over to the "Triad Champion" and coast your way to Florida

14

MY 10 STEP PROGRAM TO Triad SUCCESS

1. Learn something about Triad
2. Survey your internal resources; pick a few of your best staff to be involved
3. Get Triad training from EPA & USGS
4. Develop an implementation plan
5. Engage your upper management
6. Start small with a "low-hanging fruit"
7. Get FAMs certified so field data is OK
8. Feign interest in outcomes
9. Document project outcomes, both technical and financial
10. Expand Triad application very slowly

15

WHAT ARE FUTURE MARKERS FOR Triad SUCCESS

- More states get involved
- Brownsfields projects predominate
- Triad becomes a State-driven initiative, and not viewed as an EPA idea
- Field data become as acceptable as data from fixed-based labs.
- Triad is no longer a “new” concept

Estimation of Uncertainty Based on QC Data: Nested Hierarchical Approach

William S. Ingersoll
NAVSEA Programs Field Office (SEA 04XQ LABS)

ABSTRACT

The concept of analytical measurement uncertainty is widely recognized in analytical chemistry. Uncertainty is usually estimated from replicate preparation and testing of a sample resulting in a range of measurements. This variability of measurements represents the analytical measurement uncertainty. However, routine replicate preparation and testing of environmental samples is not practical. Most environmental samples are prepared and tested only once. For this reason, quantification of the analytical measurement uncertainty is usually not performed in environmental testing laboratories.

An approach for estimating uncertainty was developed based on quality control data. Conceptually, the components of uncertainty can be modeled as being nested within the quality control samples and standards in a hierarchical structure. The data from routine quality control samples and standards are used to "back out" the uncertainty associated with the components of the analytical process and then component uncertainties are combined. The combined uncertainty can then be expanded to a particular level of statistical confidence.

INTRODUCTION

The International Organization of Standardization (ISO) and the International Electrotechnical Commission (IEC) have developed the ISO/IEC 17025 standard, "General Requirements for the Competence of Testing and Calibration Laboratories," December 1999. This standard is used by accrediting bodies worldwide when assessing laboratory capability to generate quality data. In addition, this standard is being integrated into the NELAC Quality Systems Standard. According to ISO/IEC 17025, a laboratory "shall have and shall apply procedures for estimating uncertainty of measurement." (Section 5.4.6.2) As a consequence, environmental laboratories will be required to demonstrate the quality of their analytical measurement data. Documentation of analytical measurement uncertainty is a valuable demonstration of data quality.

The estimation of analytical measurement uncertainty is formalized in the "U.S. Guide to the Expression of Uncertainty in Measurement,"(US GUM), published by American National Standards Institute (ANSI) in 1997. The US GUM is the ANSI adoption of the ISO "Guide to the Expression of Uncertainty in Measurement," (GUM), published in 1993, and it establishes general rules to evaluate and express uncertainty for quantitative analytical measurements. This internationally recognized approach requires evaluating, expressing, and reporting the uncertainty associated with analytical measurement results. The US GUM approach establishes a uniform presentation of data that promotes data comparability and data quality evaluation in which the estimated uncertainty is the confidence interval centered on the analytical measurement result. The interval envelops the variability of the analytical measurement and provides a realistic level of confidence when making a decision using the result.

Most current environmental programs do not define the process for determining and reporting analytical measurement uncertainty. The overall analytical measurement uncertainty includes both field sampling and laboratory activities. Therefore the definition and determination of measurement uncertainty required by the decision-maker is not exclusively a laboratory-generated quantity. The laboratory provides the data for calculating the uncertainty associated with laboratory activities, but the decision-maker must also incorporate the uncertainty associated with field activities into the uncertainty equation for environmental decisions. The nested approach described in this paper provides a comprehensive procedure for reporting the laboratory contribution to the variability in the field sampling and laboratory testing data used for environmental regulatory programs.

ESTIMATING AND EXPRESSING UNCERTAINTY

The general rules for evaluating and expressing analytical measurement uncertainty are simple in concept. According to the US GUM, the general rules are not "detailed, technology-specific instruction." (US GUM, Section 1.4)

The steps for estimating uncertainty are incorporated into the following conceptual algorithm:

- Specify the analyte of interest that is to be quantified
- Identify the sources of analytical measurement uncertainty
- Quantify the components of analytical measurement uncertainty
- Calculate the combined and expanded analytical measurement uncertainty

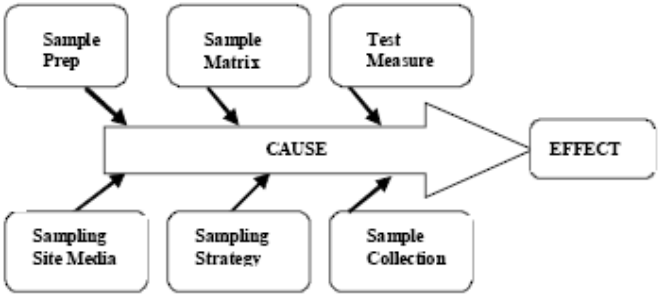
The first step is to state what is to be quantified (the analyte of interest). For environmental analytical measurements, the analytes of interest include inorganic, organic, and radioactive parameters. In addition, a specified sequence of activities is required to collect, prepare, and quantify the analyte of interest. A summary of the preparation and testing method with statements concerning the activities required to analyze the analyte of interest in the sample should be included in the quantification statements (laboratory report). Method performance in real-world matrices should also be quantified.

The second step is to identify the sources of analytical measurement variability or uncertainty. The sources of uncertainty can be partitioned into the following general components:

- Sampling site media
- Sampling strategy
- Sample collection
- Sample prep
- Sample matrix
- Test measure

Each component contributes or "causes" the uncertainty "effect" on the measurement. This is represented in the following figure (Figure 1):

Figure 1: "Cause-and-Effect" Diagram



Environmental laboratories control subsampling, sample preparation, and sample testing, and must estimate the uncertainties associated with these components. The sources of uncertainty include sample compositional and distributional heterogeneity, chemical digestion or extraction, instrument response, calibration and standardization, and sample matrix interference.

The third step is to quantify the components of analytical measurement uncertainty. A frequent approach to evaluating and expressing uncertainty of a measurement is the use of the statistical concept of the confidence interval. The confidence interval is the range of results that reasonably captures the analyte concentration with a specified probability. When the confidence interval is constructed by the statistical analysis of replicate results, the approach is a type A evaluation of standard uncertainty (US GUM, Section 4.2). When the confidence interval is not constructed by statistical analysis of replicate results, the approach is a type B evaluation of standard uncertainty (US GUM, Section 4.3).

The fourth step is to combine the individual uncertainties and then apply a "coverage factor" which is chosen on the basis of the desired level of confidence to be associated with the interval around the measurement. Typical coverage factors are 2 and 3, corresponding to intervals with levels of confidence of approximately 95% and 99%, respectively.

Less rigorous approaches such as the use of laboratory control samples (LCS) quality control limits or the use of proficiency testing (PT) study acceptance limits misrepresent the uncertainty associated with analytical measurement of real-world environmental samples. The LCS approach does not capture matrix interferences on subsampling, sample preparation, and sample testing associated with real-world environmental samples. The PT approach uses the pooled results of laboratories that participate in the studies and does not represent the analytical measurement uncertainty associated with a particular laboratory.

THE NESTED APPROACH

Environmental samples are routinely prepared and tested only once per sample. Thus any rigorous statistical determination of uncertainty is not possible. However, readily available laboratory quality control standard and sample replicate data are available, and these data can be used to estimate the analytical measurement uncertainty for single test results. Using these quality control limits, a mathematical model can be constructed to systematically "back-out"

component uncertainties. The mathematical model is based on summing in quadrature or square root sum of the squares equation.

Quality control standards and samples included the following:

- Instrument standardization (calibration) standard (ICAL)
- Instrument independent calibration verification (ICV)
- Instrument continuing calibration verification (CCV)
- Laboratory control sample (LCS)
- Matrix spike sample (MS)
- Duplicate matrix spike sample (MSD) or duplicate sample (Dup)

The relative standard deviation for each quality control standard or sample is calculated by dividing the acceptable deviation of the quality control standard or sample by 3 (assuming a 3σ control limit). For example, if the quality control limits are 95-105% recovery for the ICAL, then the acceptable relative deviation from the reference value is ± 5%. This 5% is divided by 3 for a standard deviation of 1.67%. The other standard deviations are calculated in a similar fashion. The following table (Table 1) presents example control limits and relative standard deviations for the quality control standards and samples.

Table 1: Example Quality Control Data

Quality Control Standard or Sample	Quality Control Limits in Percent	Percent Relative Standard Deviation in Percent
Instrument Standardization (Calibration) Standard (ICAL)	95-105	1.67
Instrument Independent Calibration Verification (ICV)	90-110	3.33
Laboratory Control Sample (LCS)	80-120	6.67
Matrix Spike Sample (MS)	70-130	10

The ICAL standard variability is the result of the instrumental variability or repeatability. The ICV variability is a result of a combination of the testing variability and the spike preparation variability. The LCS variability is a result of a combination of the testing variability, the spike preparation variability, and the sample preparation variability. The MS variability is a result of a combination of the testing variability, the spike preparation variability, the sample preparation variability, subsampling variability, and the matrix effects on sample preparation and testing variability. These individual component uncertainties can be partitioned by the "backing-out" approach. Backing-out means working backwards from the quantified relative standard uncertainties of quality control limits to estimate the relative uncertainties of the general components of the analytical measurement procedures. This procedure can be simplified by using standard computer programs such as Excel. By including matrix spike data, the nested approach can provide a comprehensive procedure for reporting the variability in the field sampling and laboratory testing data used for environmental regulatory programs.

Once the relative standard uncertainties associated with the laboratory contribution to analytical measurement uncertainty, including the contributions from subsampling, matrix interference,

sample preparation, and sample testing, have been determined, they are combined into the relative standard uncertainty for routine environmental samples. This combined relative standard uncertainty can be expanded to a specified confidence level. Thus, when reporting analytical measurement results, an estimation of uncertainty is required to fully quantify the results. For example, if the analytical measurement result is 100 µg/L and the combined relative standard uncertainty is 9.5%, the analytical measurement is reported with a confidence interval of ± 19% of the analytical measurement at the 95% level of confidence:

Equation 1: Calculation of Uncertainty

$$\textit{Reported Analytical Measurement} = 100\ \mu g/L \pm (100\ \mu g/L * 0.19) = 100 \pm 19\ \mu g/L$$

CONCLUSION

The QC-based nested approach for estimating analytical measurement uncertainty is capable of capturing the matrix interferences on specific laboratory subsampling, sample preparation, and sample testing of real-world environmental samples. It was specifically designed to estimate analytical measurement uncertainty for single test results of environmental samples. The nested approach promotes a uniform expression of the environmental data that is consistent with international definitions. It is a useful tool for identifying, quantifying, and comparing components of uncertainty. Ultimately, the environmental decision-maker must evaluate the significance of these sources of uncertainty and determine the acceptability data variability from these components.

REFERENCES

1. American National Standards Institute, ANSI/NCSL Z540-2-1997, *American National Standard for Expressing Uncertainty-U.S. Guide to the Expression of Uncertainty in Measurement*, National Conference of Standards Laboratories, 1997.

2. Defense Technical Information Center, DTIC #AD396946, Distribution A, 2001, *Environmental Analytical Measurement Uncertainty Estimation: Nested Hierarchical Approach.*

3. The International Organization of Standardization and the International Electrotechnical Commission, ISO/IEC 17025, 2005, *General Requirements for the Competence of Testing and Calibration Laboratories*.

4. National Environmental Laboratory Accreditation Conference, 2003, *Quality Systems, Chapter 5.*

Estimation of Analytical Measurement Uncertainty

William Ingersoll

Introduction

- Analytical measurement uncertainty
  - ISO 17025 requirements
- Rationale for estimating uncertainty
  - Guide to the Expression of Uncertainty in Measurement (ISO GUM)
- QC-based Nested approach
  - Based on quality control data

National Environmental Laboratory Accreditation Conference

- NELAC Chapter 5 based on ISO/IEC 17025
- ISO/IEC 17025 replaces ISO Guide 25
- General Requirements for the Competence of Testing and Calibration Laboratories
- International Version
  - Guide to the Expression of Uncertainty in Measurement (ISO GUM)
- American Version
  - American National Standard Institute for Expressing Uncertainty (ANSI GUM)

ISO 17025 References to Uncertainty

- References uncertainty in:
- 4.12.2.1
- 5.1.2
- 5.4.1
- 5.4.6.1
- 5.4.6.2
- 5.4.6.3
- 5.6.2.1.1
- 5.6.2.2.1
- 5.10.3.1

ISO 17025 References to Uncertainty

- Where applicable, include a statement on the estimation of uncertainty of measurement with results
- Instead of reporting:

  10 mg/L
- Now report:

  10 +/- 2 mg/L @ 95% CL

Measurement Without Uncertainty Estimation

- Laboratory A
- Laboratory B
- Laboratory C

- 10 ppm
- 10 ppm
- < 20 ppm

Measurement Without Uncertainty Estimation

• Laboratory A	• 10 ppm
• Laboratory B	• 10 ppm
• Laboratory C	• < 20 ppm

Measurement With Uncertainty Estimation

• Laboratory A	• 10 +/- 2 ppm
• Laboratory B	• 10 +/- 10 ppm
• Laboratory C	• < 20 ppm

Measurement With Uncertainty Estimation

• Laboratory A	• 10 +/- 2 ppm
• Laboratory B	• 10 +/- 10 ppm
• Laboratory C	• < 20 ppm

GUM: Systematic Estimation of Measurement Uncertainty

- Identify the analytical components of uncertainty
- Represent the standard uncertainties by the standard deviations of the components
- Evaluate the covariance of the components that contribute to uncertainty
- Combine the standard uncertainties of the analytical components
- Expand the combined standard uncertainty

Components of Total Study Variability

- Study population
- Sampling strategy
- Sample collection
- Sample preparation
- Matrix interference
- Laboratory testing

Population Effects

- The natural variability inherent in the contaminant distribution of the sampling site
- Cannot be reduced, but can be estimated
- Estimated natural variability confounded by sampling and testing uncertainty

Analytical Measurement Variability

QC Sample/Standard	Field Variability	Strategy Variability	Collection Variability	Matrix Variability	Preparation Variability	Spike Variability	Instrument Variability
Routine Field Sample	X	X	X	X	X		X
Co-located Sample		X	X	X	X		X
Duplicate Field Sample			X	X	X		X
Matrix Spike Sample				X	X	X	X
Laboratory Control Sample					X	X	X
Calibration Verification						X	X
Calibration Standard							X

Sampling Strategy Effects

- Design
  - Number of samples
  - Location of samples
- Simple random sampling
- Stratified random sampling
- Systematic grid sampling
- Composite sampling
- Representativeness of sampling

Sample Collection Effects

- Sample collector efficiency
  - % Recovery of analytes
  - Bias is controlled when every particle has the same probability of being selected
- Sample collector decontamination
  - Cross-contamination from one sample location to the next
- Sample preservation
  - Degradation or precipitation of analytes

Sample Preparation Effects

- Extraction, separation, and concentration
- Percent recovery of analytes from each preparation process

Matrix Interference Effects

- Homogenization, particle size reduction, and subsampling
- Refractory matrices
  - Inhibit extraction of analytes
- Co-precipitation of interferents
  - Swamps analytes during concentration and separation processes
- Co-elution of interferents
  - Impacts analytical method selectivity

Test Measurement Effects

- Carryover between sample tests
- Instrumental drift
- Intrinsic instrumental repeatability

Mathematical Model For Estimating Uncertainty

Data Uncertainty, ^{D}S

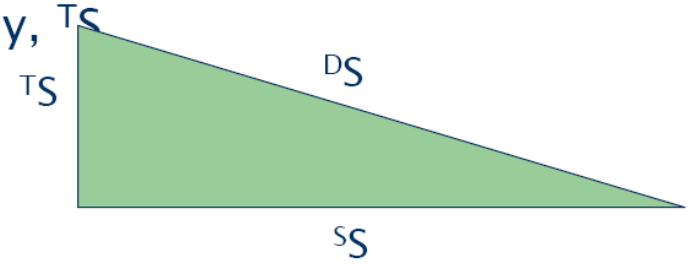
Subsampling Variability, ^{S}S

Chemical Preparation and Instrumental Analysis Variability, ^{T}S

$$^{D}S^2 = {}^{S}S^2 + {}^{T}S^2$$

$$^{D}S^2 = 30^2 + 10^2$$

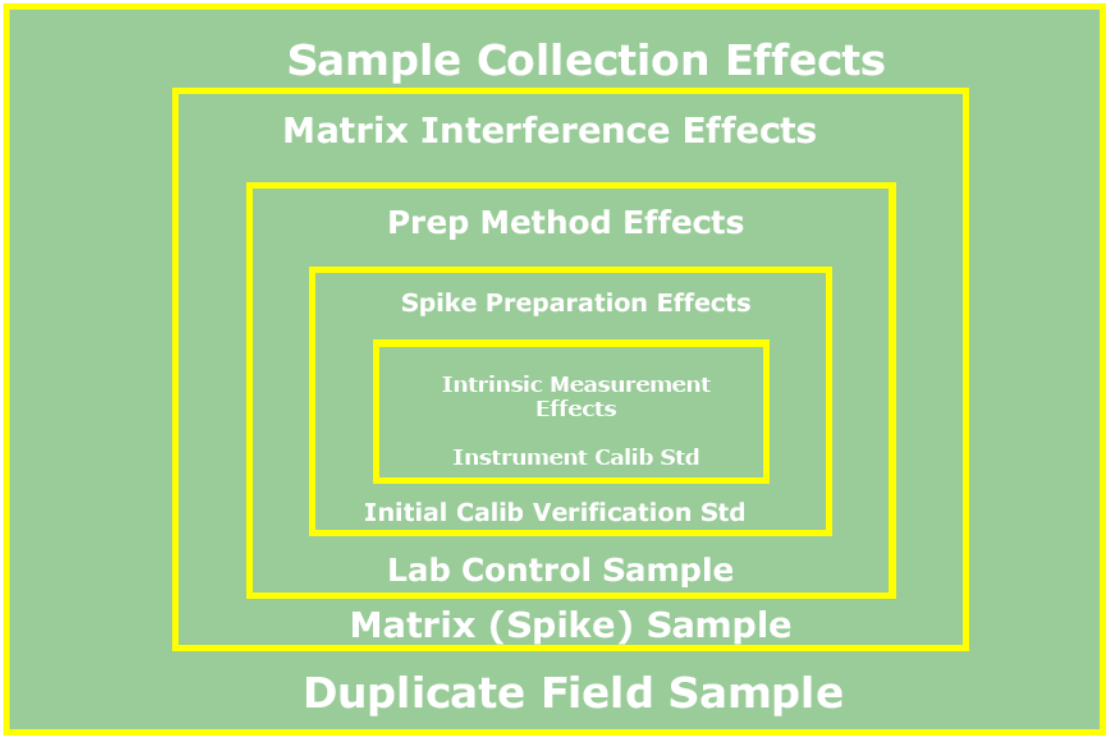
$$^{D}S = 32$$



QC-Based Nested Hierarchical Approach

- Identifies sources of uncertainty from field sampling to laboratory testing
- Works backward
  - Backs-out component standard uncertainties from combined uncertainties of quality control samples
- Models uncertainty as nested components

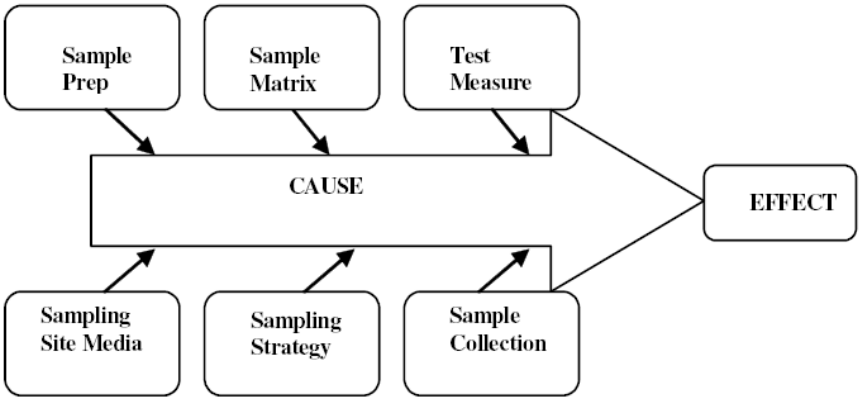
Conceptual Model



Uncertainty Calculator

- Uses readily available QC data
  - ICS, ICV, LCS, MIS (MS/MSD)
- Calculates individual contributions to measurement uncertainty
  - Excel based
- Specify confidence level and enter measurement
- Calculates relative uncertainty and uncertainty interval
  - Provides bias corrected values (if required)

Uncertainty Cause-Effect Diagram



Reference Value Calculation

- $(X_i - R)/R$
  - X_i - Individual analytical measurement
  - R - Reference value
- Relative deviation of analytical measurement from analyte concentration
  - Multiply by 100 for % deviation

Duplicate Sample Calculation

- $(X_i - X_j)/[(X_i + X_j)/2]$
  - X_i - Initial sample analytical measurement
  - X_j – Duplicate sample analytical measurement
- Relative difference between replicate analytical measurements
  - Multiply by 100 for % deviation as Relative Percent Difference

QC-based Nested Analytical Measurement Uncertainty Page 1

What are the analyte/matrix/technology? Copper in Wastewater by ICP

Enter 20 replicate results for the following quality control samples as percent deviation (%):
ICS - Instrument calibration standard
ICV - Second source calibration verification standard
LCS - Laboratory control sample
MIS - Matrix interference sample (matrix spike, organic surrogate, radiochemical tracer)
FDS - Field-split duplicate sample
CLS - Co-located duplicate sample

	ICS	ICV	LCS	MIS	FDS	CLS
	1.1	0.5	4.0	12.0	0.0	0.0
	0.8	0.1	0.5	1.4	0.0	0.0
	0.4	1.0	1.5	8.0	0.0	0.0
	2.0	1.2	1.7	3.7	0.0	0.0
	1.0	0.2	0.1	12.0	0.0	0.0
	1.2	0.4	2.2	0.4	0.0	0.0
	1.7	1.2	0.4	3.6	0.0	0.0
	3.7	0.9	0.3	0.1	0.0	0.0
	1.1	0.1	0.5	2.7	0.0	0.0
	3.1	1.3	15.0	17.0	0.0	0.0
	2.0	0.9	20.0	30.0	0.0	0.0
	0.7	1.0	0.4	3.7	0.0	0.0
	0.4	2.0	4.0	1.5	0.0	0.0
	0.9	0.2	0.6	5.0	0.0	0.0
	1.4	1.0	1.5	1.4	0.0	0.0
	1.9	1.4	5.0	20.0	0.0	0.0
	2.0	1.5	24.0	3.5	0.0	0.0
	1.5	1.7	3.0	5.0	0.0	0.0
	1.6	3.0	13.0	-24.0	0.0	0.0
	1.1	3.1	11.0	-13.0	0.0	0.0
Std. Dev.	0.84	0.85	7.2	11.1	0.0	0.0
Bias	1.5	1.1	5.4	4.7		
Recovery	101.5	101.1	105.4	104.7		

Select Confidence Level

- Two-tailed distribution
- 20 data points
  - 19 degrees of freedom
  - Student's *t*-value
- 95% Confidence Level is usual
- Can also select
  - 80%
  - 90%
  - 99%

Confidence Levels and Coverage Factors

Confidence Level	Coverage Factor
80%	1.328
90%	1.729
95%	2.093
99%	2.981

QC-based Nested Approach *Copper in Wastewater by ICP* **Page 2**

Components of Analytical Uncertainty
IME - Intrinsic instrumental measurement effects
SPE - Spike preparation effects
PME - Preparation method effects
MIE - Matrix interference effects
SCE- Sample collection effects
SLE - Sample location effects

Component	Percent Standard Uncertainty		Component	Percent Recovery	Component	Systematic Error	
IME	~ 0.8	% relative standard deviation	IME	~ 101	IME	~ 1	percent
SPE	~ 0.1	% relative standard deviation	SPE	~ 100	SPE	~ 0	percent
PME	~ 7.1	% relative standard deviation	PME	~ 104	PME	~ 4	percent
MIE	~ 8.5	% relative standard deviation	MIE	~ 99	MIE	~ -1	percent
SCE	~ 0.0	% relative standard deviation					
SLE	~ 0.0	% relative standard deviation					

What is the Confidence Level (CL)? Enter ONLY one of these percentages: 80, 90, 95, 99 95 %
Your specified t-value is 2.093 for a Two-Tailed Normal Distribution Confidence Interval

Relative Analytical Measurement Uncertainty for routine field samples
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)
23.3 % relative uncertainty

Relative Systematic Error associated with the measurement of routine field samples
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)
5.1 % relative systematic error

QC-based Nested Approach *Copper in Wastewater by ICP* **Page 2**

Components of Analytical Uncertainty
IME - Intrinsic instrumental measurement effects
SPE - Spike preparation effects
PME - Preparation method effects
MIE - Matrix interference effects
SCE- Sample collection effects
SLE - Sample location effects

Component	Percent Standard Uncertainty		Component	Percent Recovery	Component	Systematic Error	
IME	~ 0.8	% relative standard deviation	IME	~ 101	IME	~ 1	percent
SPE	~ 0.1	% relative standard deviation	SPE	~ 100	SPE	~ 0	percent
PME	~ 7.1	% relative standard deviation	PME	~ 104	PME	~ 4	percent
MIE	~ 8.5	% relative standard deviation	MIE	~ 99	MIE	~ -1	percent
SCE	~ 0.0	% relative standard deviation					
SLE	~ 0.0	% relative standard deviation					

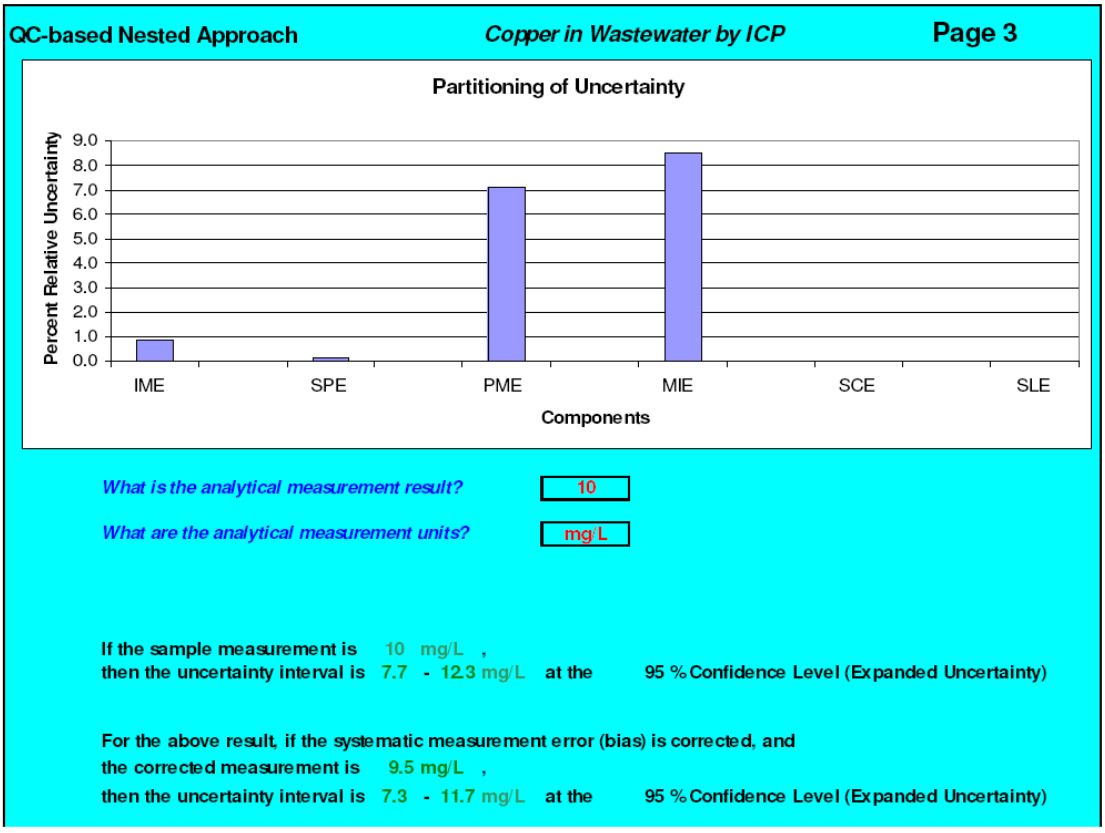
What is the Confidence Level (CL)? Enter ONLY one of these percentages: 80, 90, 95, 99 99 %
Your specified t-value is 2.861 for a Two-Tailed Normal Distribution Confidence Interval

Relative Analytical Measurement Uncertainty for routine field samples
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)
31.9 % relative uncertainty

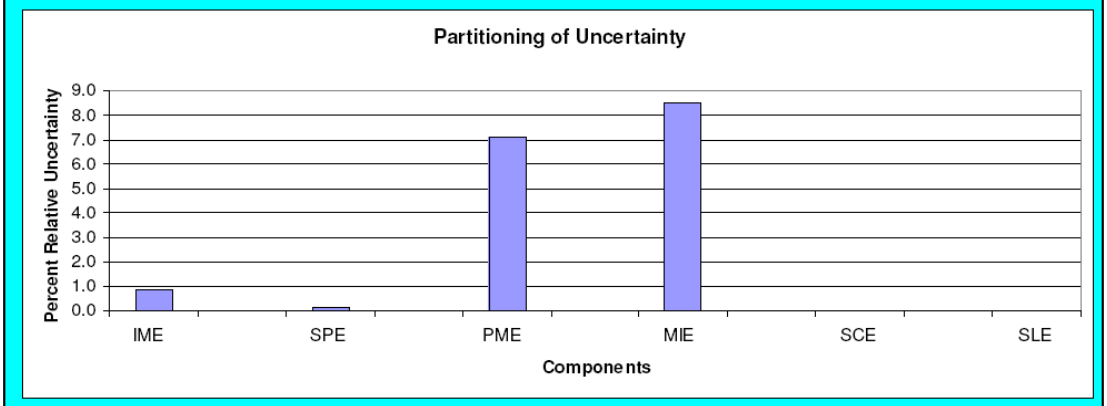
Relative Systematic Error associated with the measurement of routine field samples
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)
5.1 % relative systematic error

Analytical Measurement

- Presents histogram of uncertainty components
- Enter the analytical measurement result
- Enter the units
- Automatically calculates the uncertainty interval associated with the analytical measurement
- Automatically corrects for bias



QC-based Nested Approach *Copper in Wastewater by ICP* **Page 3**



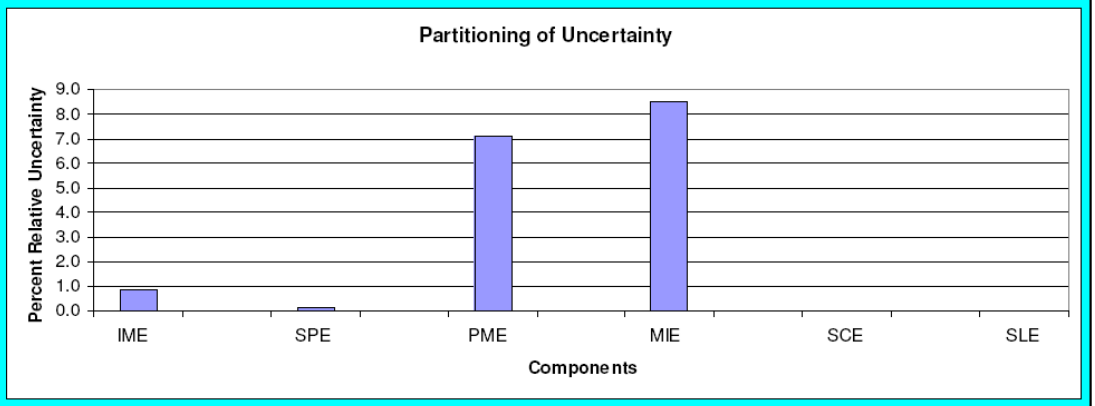
What is the analytical measurement result? 20

What are the analytical measurement units? mg/L

If the sample measurement is 20 mg/L ,
then the uncertainty interval is 15.3 - 24.7 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

For the above result, if the systematic measurement error (bias) is corrected, and
the corrected measurement is 19.0 mg/L ,
then the uncertainty interval is 14.6 - 23.5 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

QC-based Nested Approach *Copper in Wastewater by ICP* **Page 3**



What is the analytical measurement result? 5

What are the analytical measurement units? mg/L

If the sample measurement is 5 mg/L ,
then the uncertainty interval is 3.8 - 6.2 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

For the above result, if the systematic measurement error (bias) is corrected, and
the corrected measurement is 4.8 mg/L ,
then the uncertainty interval is 3.6 - 5.9 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

Summary

- Analytical measurement uncertainty
- Nested approach
- Partitioning components of uncertainty
- Propagation of analytical measurement uncertainty
- Uncertainty calculator

Improving Environmental Data Quality
Because the Right Decision Requires Quality Data

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www.navylabs.navy.mil
www.denix.osd.mil/denix/DOD/Working/EDQW/edqw.html

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MAKING A DECISION WITH VARIABLE DATA

Moore, Marlene; Advanced Sytems, Inc.

Data usability is the report on the adequacy of data for making decisions, performed after completion of the report on the results of validation and verification. The usability step involves assessing whether the process execution and resulting data meet project quality objectives documented in the Quality Assurance Project Plan (QAPP).

A usability determination considers whether data meet project quality objectives as they relate to the decision to be made, and evaluates whether data are suitable for making the decision. All types of data (e.g., sampling, on-site analytical, off-site laboratory) are relevant to the data usability determination. The decision maker uses this information in order to make decisions with variable data.

Data usability is the last step in the data review process. Data review is the process which data are examined and evaluated to varying levels of detail and specificity by a variety of personnel who have different responsibilities within the data management process. It includes verification, validation, and usability assessment.

The project team at the start of the project defines the data usability assessment process. The items to consider for the usability assessment:

- The usability assessment must follow the verification (completeness of sampling and testing records) and validation (compliance with method and project requirements for sampling and testing). (See Table 8 from the UFP-QAPP Reference 2).

- Summarize the usability assessment process and all usability assessment procedures, including interim steps and any statistics, equations, and computer algorithms that will be used to assess data.

- Describe the documentation to be generated during the usability assessment.

- Identify the personnel (by title and organizational affiliation) responsible for performing the usability assessment. Define the qualification of the personnel to perform and review the assessment.

- Describe how usability assessment results are to be presented in order to identify trends, relationships (correlations), and anomalies.

- Describe the evaluative procedures used to assess overall measurement error associated with the project and include the data quality indicators (DQIs) or measurement quality objectives (MQOs) as defined for the project.

In the past, the only formal data review was limited to the contract laboratory program test data as defined in the EPA contract requirements for data validation (CLP). These data validation

protocols included a section for "Overall Assessment". This assessment is described as "a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data".

To develop this narrative, the data validator uses "professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed". However this was limited only to the laboratory data and does not address the sample collection or sampling design.

The CLP provides a series of contract specifications in the form of a statement of work that covers laboratory services purchased under specific contracts for Superfund sites. The CLP also provides guidelines for evaluating laboratory conformance to its contract specifications; however, it does not address any of the data usability requirements and therefore does not provide assurance that collected data are appropriate for their intended uses. There are many environmental programs not covered by CLP, and many aspects of environmental data collection outside its scope (e.g., the systematic planning process, sampling activities, QA oversight). The CLP does not address the assessment of the overall quality system for the project. Any deviations that affect the quality of the data must be presented in the data usability report.

A data usability assessment requires a review of the QAPP and sufficient communication with the data user(s) to develop a clear understanding of the intended use and desired quality of the data. It requires the validator to obtain a more complete record of the sampling and laboratory's activities, including logs for sample collection, handling, preparation, calibration, and instrument performance; instrument printouts; and raw data. The extent to which data validators have access to these types of information depends on the project management team.

Data usability is a detailed investigation of particular data records that need special interpretation or review. The purpose of the data usability is to answer questions about the data that arise as a result of the data user's review of the data verification and data validation report. The inputs to the data review include the planning documents, data validation report, hard-copy data package, the validated data set, and a general knowledge of the environmental problem and its history. As the information is reviewed, the data user is looking at whether the data appears to be appropriate and sufficient to support decision-making based on the original project needs. The data user may also identify errors or omissions in the data or data validation report that need to be corrected. The report should include items such as a list of the samples collected, field information about how the samples were collected, the analysis performed on the samples, and the quality of the reported data. The data reviewer should attempt to document anything out of the ordinary that is noticed about the data during their review. Examples of data validation and data suitability are presented in Table 9 (EPA/QA G-8 Reference 1).

The data usability assessment completes the data review activities used to ensure that only scientifically sound data that are of known and documented quality and meet project quality objectives (PQOs) are used in making environmental decisions. The approach used for data review of a project must be appropriate to the project requirements.

Table 8. Data Review Process Summary

Process Term	Objective	Scope	Data Review Step	Output
Verification	Review to see if data required for the project are available.	– Sampling* – Analysis	I. Completeness check	Verification Report – May be checklist form – Package includes all documentation
Validation	– Assess and document the performance of the field sample collection process. – Assess and document the performance of the analytical process.	– Sampling* – Analysis	IIa. Check compliance with method, procedure, and contract requirements IIb. Compare with measurement performance criteria from the QAPP*	Validation Report – Includes qualified data – May be part of other report such as RI/FS
Usability Assessment*	Assess and document usability to meet project quality objectives.	- Sampling - Analysis	III. Assess usability of data by considering project quality objectives and the decision to be made*	Usability Report – May be part of other report such as RI/FS

*The scope of the term or the step involved is an expansion of current practice.

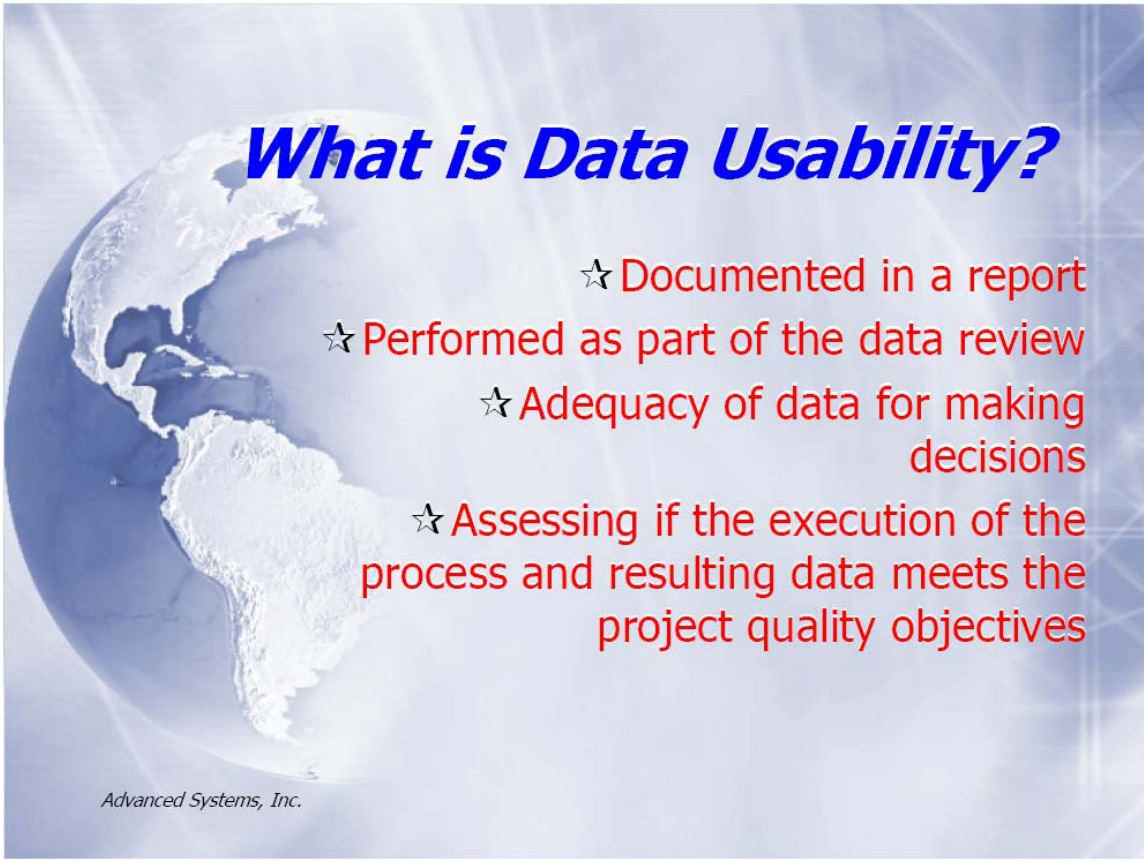
Table 9. Data Validation Versus Data Suitability

Data Validation Question	Data Suitability Question	Examples
Have the analytical methods been followed properly?	Now that data are available, do we still think that these were the appropriate analytical methods?	Were there extreme matrix interferences? Were matrix spike/matrix spike duplicate recoveries unusually low using these methods?
Have the detection limits been calculated properly?	Are these detection limits adequate for the goals of this project?	Were detection limits appropriate (do they cover the threshold of concern for each compound)? Were the technical basis for calculation of detection limits documented correctly?
Have MQO goals, such as precision and bias, been achieved?	Based on the available data, do these MQO goals still seem reasonable?	Were the initial calibration criteria (response factors, precision, correlation coefficient) appropriate for these analytes?
Are the appropriate data points flagged with qualifiers?	What do patterns in the qualified data suggest about the overall data set?	For data that fall between the detection limit and the quantitation limit, has the laboratory provided numeric values rather than flags only? How do you interpret flags indicating contaminated blanks when the real samples have the same contaminants?

References:

Guidance on Environmental Data Validation and Verification, QA/G-8, Final, November 2002, EPA//240/R-02/004, Office of Environmental Information, Quality Staff, U.S. Environmental Protection Agency, Washington, DC. ***Uniform Federal Policy for Quality Assurance Project Plans,*** Intergovernmental Data Quality Task Force, Part 1, Final, Version 1, March 2005. ***Workbook for Federal Policy for Quality Assurance Project Plans,*** Intergovernmental Data Quality Task Force. Part 2A, Final, Version 1, March 2005. ***Quality Assurance/Quality Control Compendium: Minimum QA/QC Activities,*** Intergovernmental Data Quality Task Force, Part 2B, Final, Version 1, March 2005.


Data Usability
Making a Decision with Variable Data


What is Data Usability?
☆ Documented in a report
☆ Performed as part of the data review
☆ Adequacy of data for making decisions
☆ Assessing if the execution of the process and resulting data meets the project quality objectives
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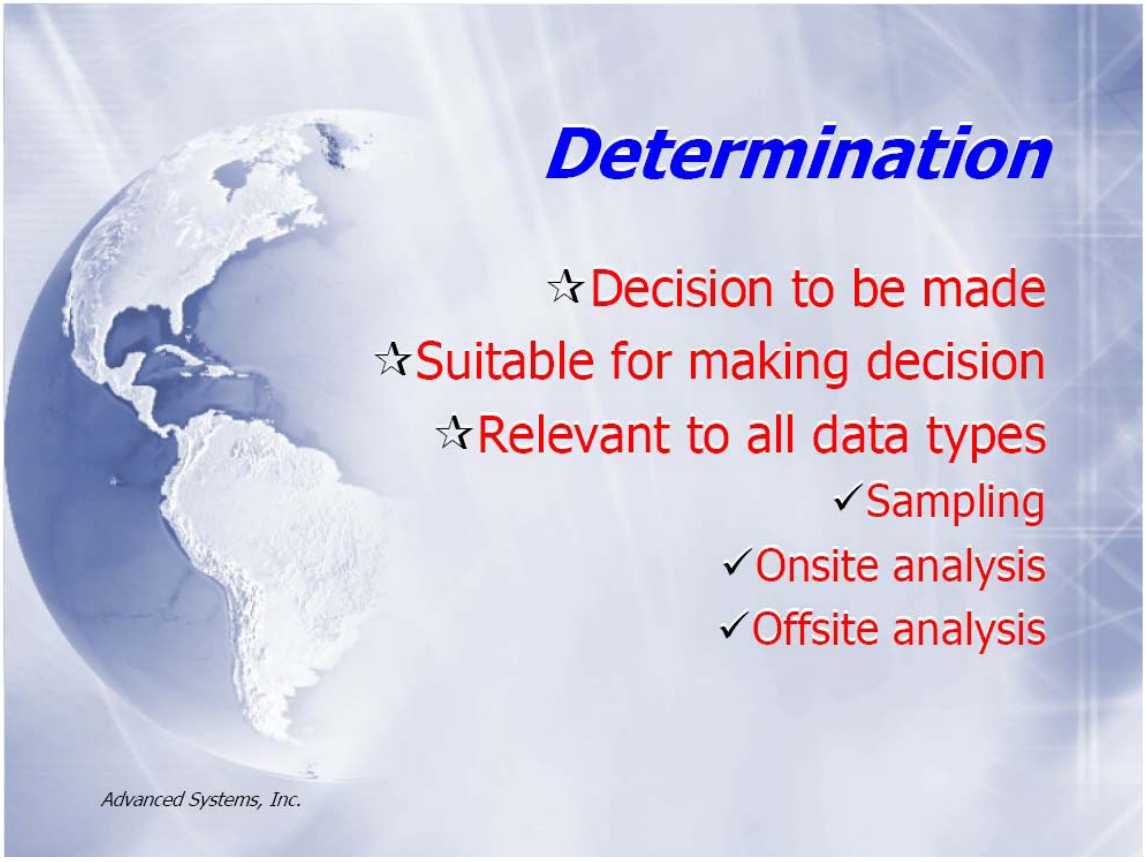
Determination
☆Decision to be made
☆Suitable for making decision
☆Relevant to all data types
✓Sampling
✓Onsite analysis
✓Offsite analysis
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Unique to each Project
☆Defined at start of project
☆Personnel identified
☆Responsibilities defined
☆Process documented
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History
☆Contract requirements for data validation
☆"A brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data"
Advanced Systems, Inc.


History
☆Data validator uses
✓"professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed."
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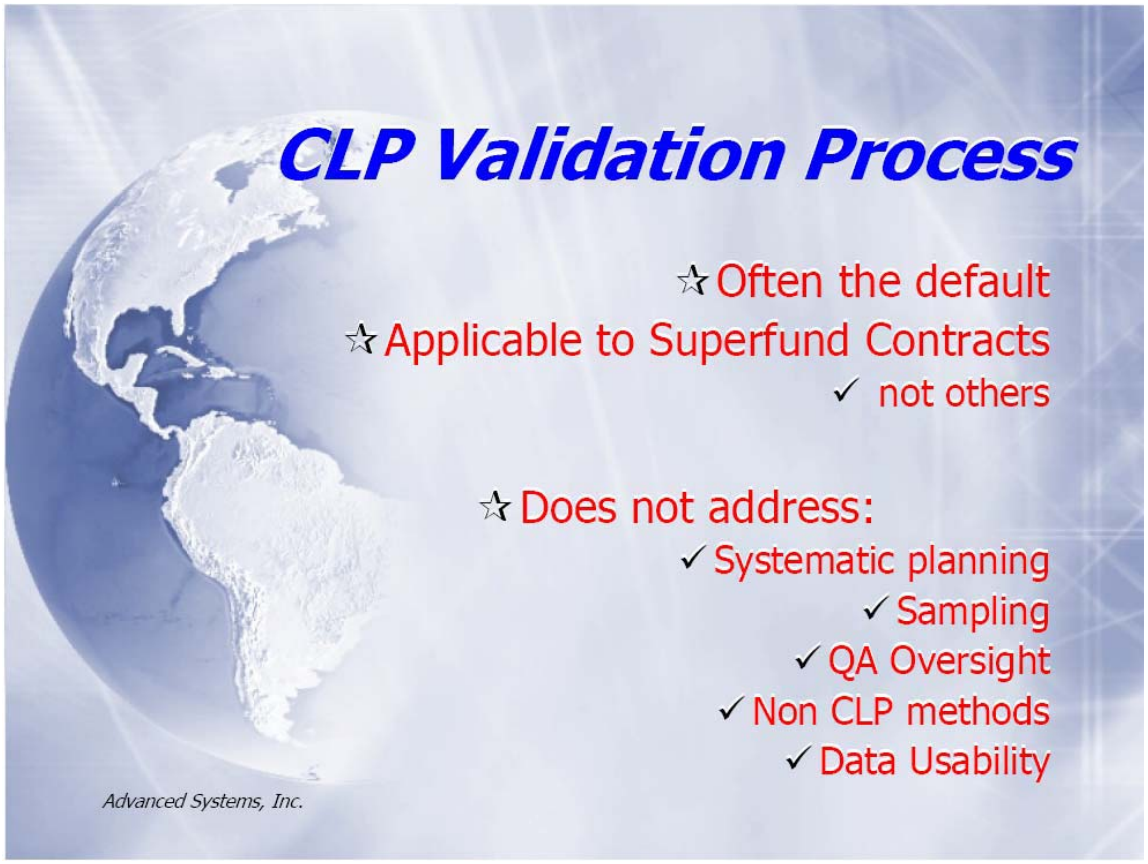
CLP Validation Process
☆Often the default
☆Applicable to Superfund Contracts
✓ not others
☆Does not address:
✓Systematic planning
✓Sampling
✓QA Oversight
✓Non CLP methods
✓Data Usability
Advanced Systems, Inc.


Data Review Today
☆Verification/Validation/Usability
☆Detailed investigation of particular data records that need special interpretation
☆Appropriate to meet project requirements
☆Does the data support the decision?
✓What are the limitations on the data use?
✓How confident is the decision based on the available data?
Advanced Systems, Inc.


Items to Consider
☆Usability follows verification/validation
☆Process defined
☆Documentation defined
☆Personnel qualification defined
☆Trends, relationships, and anomalies presented
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Items to Consider
☆Evaluative Procedures to Assess
✓Overall measurement error
✓Data quality indicators
✓Measurement quality objectives
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Data Review Process

IDQTF UFP-QAPP Manual
Page: 109 of 149

Table 8. Data Review Process Summary

Process Term	Objective	Scope	Data Review Step	Output
Verification	Review to see if data required for the project are available.	– Sampling* – Analysis	I. Completeness check	Verification Report – May be checklist form – Package includes all documentation
Validation	– Assess and document the performance of the field sample collection process. – Assess and document the performance of the analytical process.	– Sampling* – Analysis	IIa. Check compliance with method, procedure, and contract requirements IIb. Compare with measurement performance criteria from the QAPP*	Validation Report – Includes qualified data – May be part of other report such as RI/FS
Usability Assessment*	Assess and document usability to meet project quality objectives.	- Sampling - Analysis	III. Assess usability of data by considering project quality objectives and the decision to be made*	Usability Report – May be part of other report such as RI/FS

*The scope of the term or the step involved is an expansion of current practice.

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Questions

- ☆ Were extreme matrix interferences identified?
- ☆ Validation: Have the analytical methods been followed properly to minimize interferences?
- ☆ Usability: Are these the appropriate analytical methods?
- ☆ How do these extremes affect the decision?

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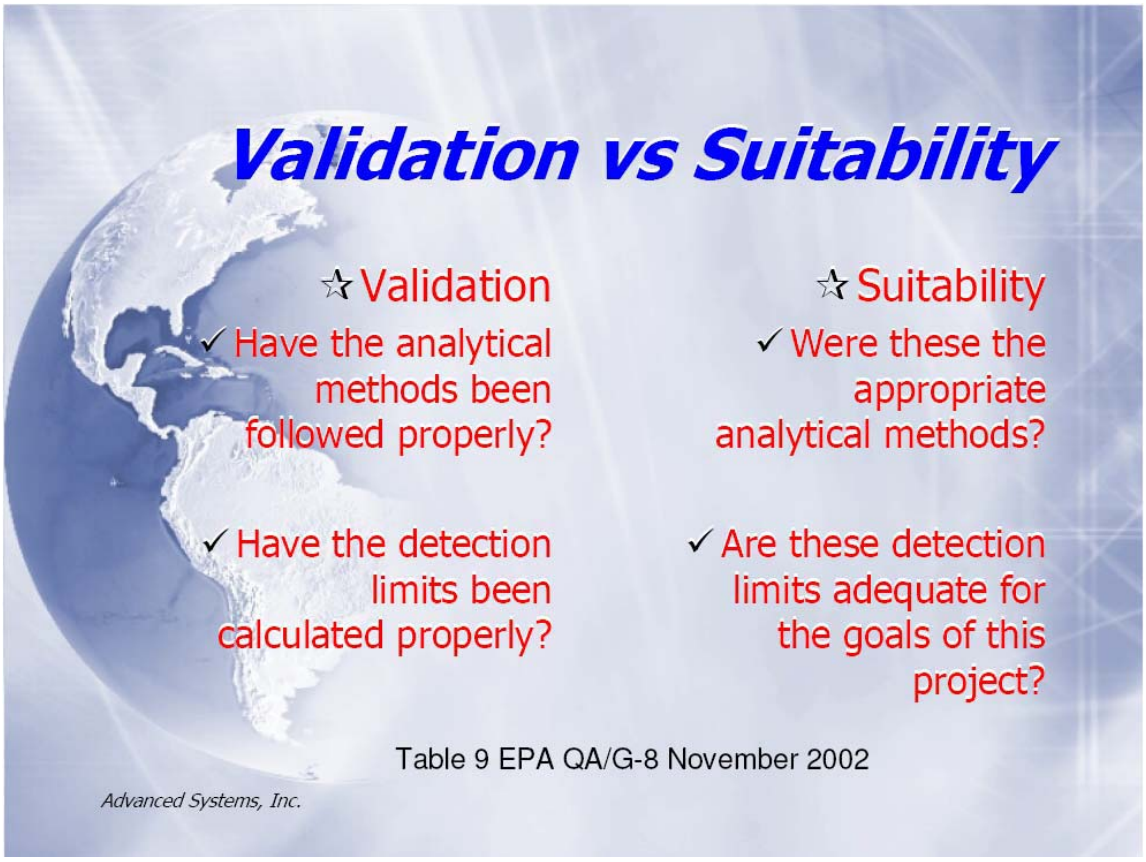
Validation vs Suitability
☆ Validation
✓ Have the analytical methods been followed properly?
✓ Have the detection limits been calculated properly?
☆ Suitability
✓ Were these the appropriate analytical methods?
✓ Are these detection limits adequate for the goals of this project?
Table 9 EPA QA/G-8 November 2002
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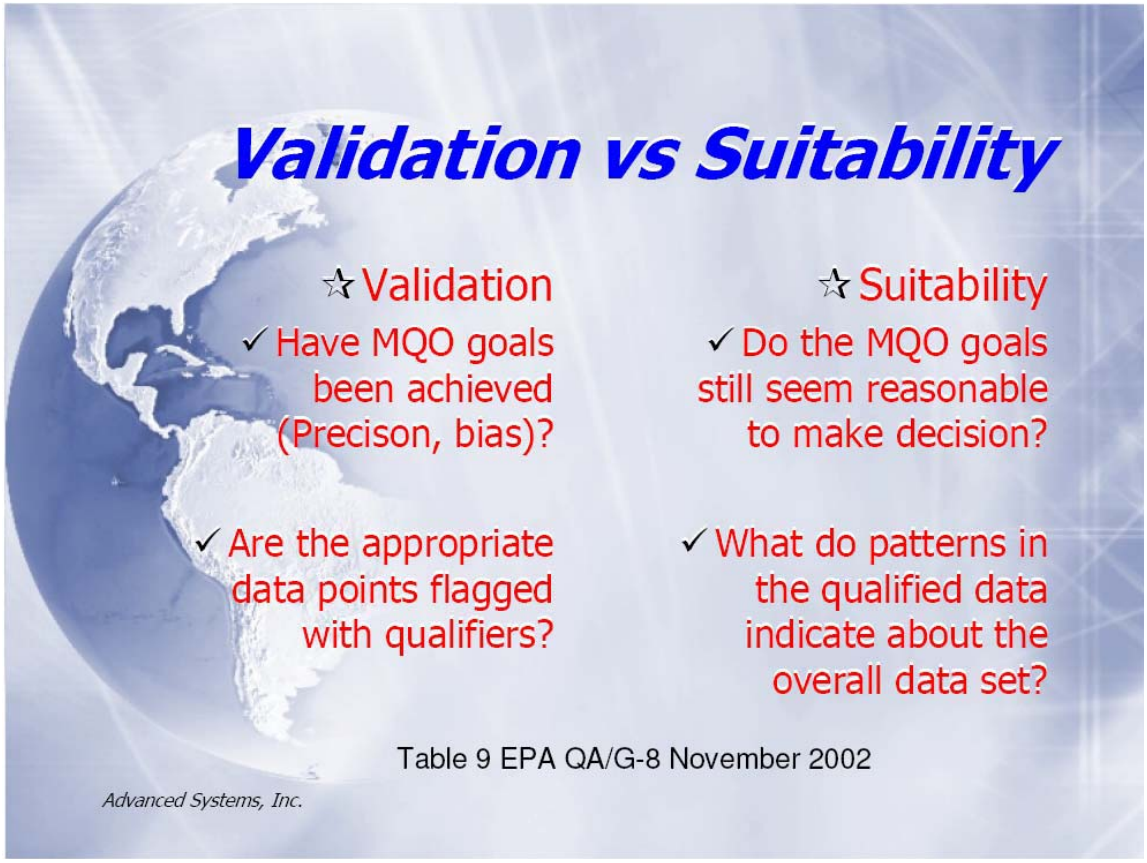
Validation vs Suitability
☆ Validation
✓ Have MQO goals been achieved (Precison, bias)?
✓ Are the appropriate data points flagged with qualifiers?
☆ Suitability
✓ Do the MQO goals still seem reasonable to make decision?
✓ What do patterns in the qualified data indicate about the overall data set?
Table 9 EPA QA/G-8 November 2002
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Summary

☆Data usability provides the decision maker with summary of:

✓How good is the data

✓How variable is the data

✓Has the data variability data been minimized to allow the appropriate decision

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References

☆ ***Guidance on Environmental Data Validation and Verification,*** QA/G-8, EPA//240/R-02/004, Office of Environmental Information, Quality Staff, U.S. EPA, Final, November 2002

☆ ***Uniform Federal Policy for Quality Assurance Project Plans,*** Intergovernmental Data Quality Task Force, Part 1, Final, Version 1, March 2005

☆ ***Workbook for Federal Policy for Quality Assurance Project Plans,*** Intergovernmental Data Quality Task Force. Part 2A, Final, Version 1, March 2005

☆ ***Quality Assurance/Quality Control Compendium: Minimum QA/QC Activities,*** Intergovernmental Data Quality Task Force, Part 2B, Final, Version 1, March 2005

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Questions??
Contact the Speaker:
Marlene Moore
Advanced Systems, Inc.
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(302 368 1211)
Advanced Systems, Inc.

WEB-EDMS SYSTEM

Garrison, Grant E.; Integrated Environmental Services, Inc.
Young, Michael Dr.; Integrated Environmental Services, Inc.

Complex site cleanups involve massive amounts of data, often gathered at a large cost. Despite the investment in the data, uncertainties remain as to the actual characteristics of the site due to the real world constraints of limited resources for investigations. Dynamic sampling strategies that allow real time changes in sampling plans in response sampling results offer significant promise of the ability to save time and money while reducing uncertainty associated with limited data gathering. However, achieving those objectives requires a real-time data management system that can easily handle both the challenges of database management and data analysis to support decisions to modify sampling plans on-the-fly. This paper will describe one such system developed for the private sector that is now in use on Department of Energy facilities.

Integrated Environmental Services, Inc., in managing large scale, complex site cleanups for aerospace and defense, oil and gas, and real estate clients, recognized the need for an all-in-one, intuitive and user friendly system. Working with experts in GIS, 3D data visualization, health risk assessment, environmental engineering and computer programming fields, Integrated developed web-based Environmental Data Management System (webEDMS). This patented software is able to seamlessly integrate the components of the RI/FS process. The webEDMS application provides a cradle-to-grave data management solution for investigation and cleanup of DOE sites. The system stores and organizes project data from a variety of sources (real-time monitoring devices; electronic databases including laboratory reports; hardcopy; maps; photographs; schedules, budgets, etc.).

WebEDMS provides team members the ability to convert hard-earned massive amounts of site data to valuable information without searching through hardcopy libraries of project reports and re-keying the information. The project team gains insight from the data by understanding the nature, extent and changes of site contamination over time, via 3-D visualization. All site information is linked and searchable through one single application. As it is a web-based system, this wealth of information is available to all relevant project team members located throughout the country. This transparency and access is important not only to allow the entire project team to participate in the dynamic sampling strategy decision making process, but also to building trust in the site conceptual model that allows decisions to be reached with the confidence of all parties.

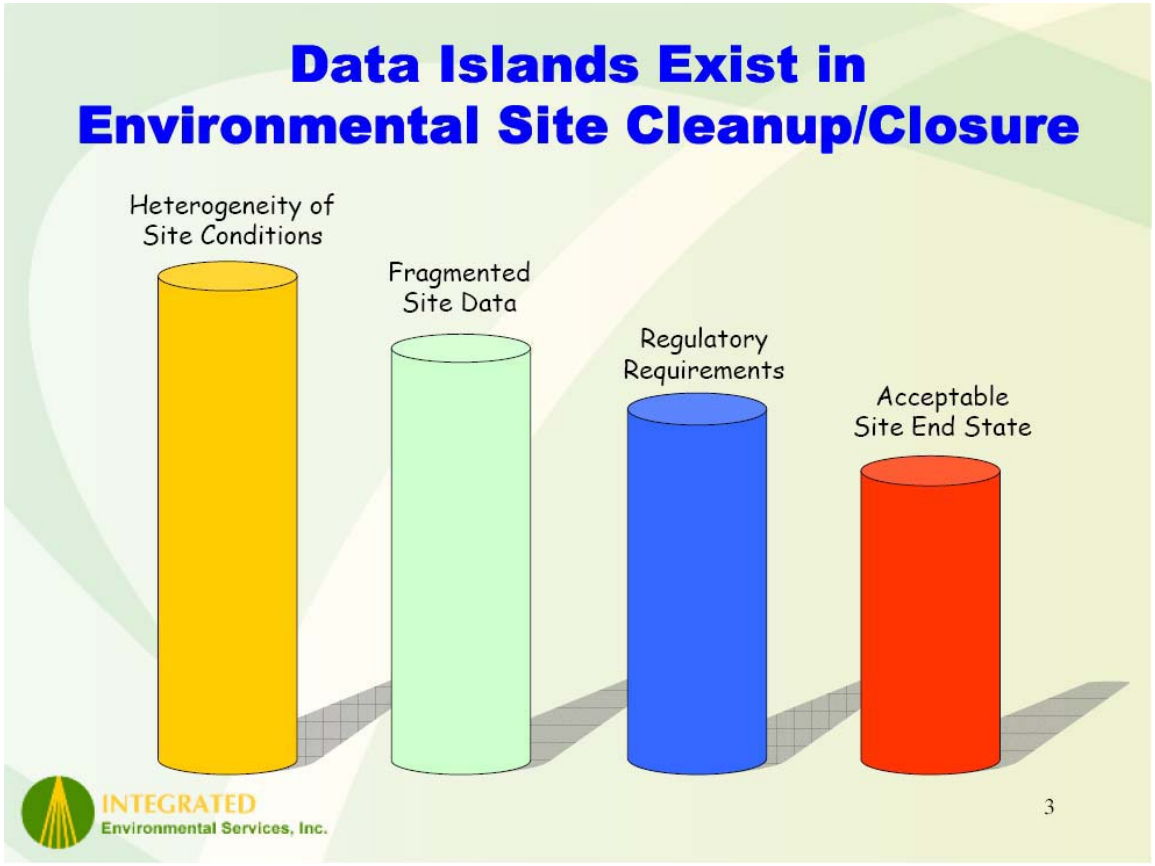
WebEDMS goes even further by automating the risk assessment process and allows the user to conduct human health risk assessments with just a few clicks of the mouse. Consequently, sampling decisions can be made rapidly with a full understanding of site conditions. The user can choose the appropriate media type and the contaminants of concern. The user also can chose Federal or State-specific toxicity criteria, specific receptors associated with the land use scenarios, and the applicable exposure pathways. The health risk assessment module of the webEDMS is designed based on USEPA default parameters; however, modifications to these parameter are allowed. The user can conduct risk assessments that result in site specific Health Based Remedial Goals (HBRGs) or calculate the site-specific cumulative incremental lifetime cancer risk.

Web-based Environmental Data Management System – A System for Real Time Environmental Data Management and Risk Assessment

Objectives

- Introduce and Demonstrate Patented webEDMS software
- Discuss Advantages of Real-Time Risk Assessment in Reducing Uncertainty
- Discuss Synergies between Triad & webEDMS

2


Data Islands Exist in Environmental Site Cleanup/Closure
Heterogeneity of Site Conditions
Fragmented Site Data
Regulatory Requirements
Acceptable Site End State
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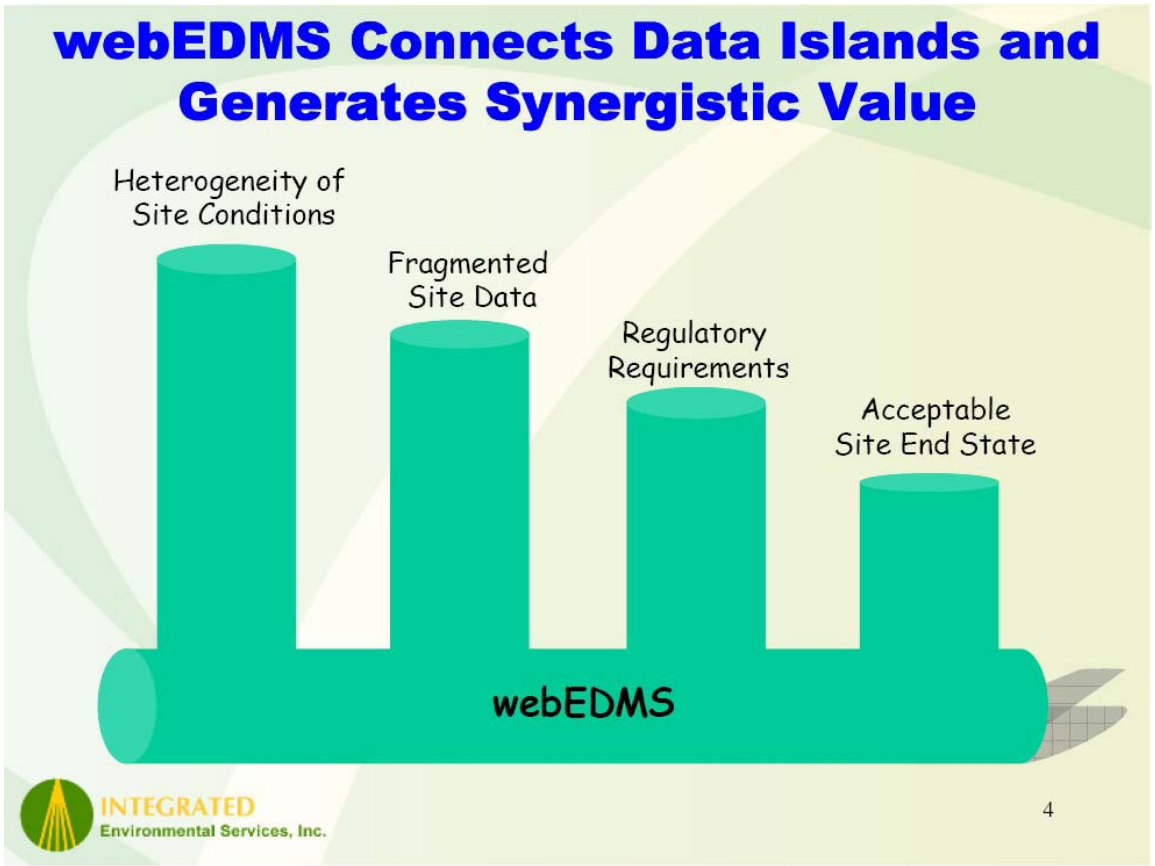
3


webEDMS Connects Data Islands and Generates Synergistic Value
Heterogeneity of Site Conditions
Fragmented Site Data
Regulatory Requirements
Acceptable Site End State
webEDMS
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Overview of webEDMS

- The most powerful, integrated, proven and user-friendly system on the market with real-time "Informatics" (integrated and seamless data acquisition, analysis, warning, reporting, collaboration and decision support) capabilities
- The only web-based, cradle-to-grave, real-time data sharing and communication tool that empowers the user to make scientifically defensible decisions based on complete, up-to-the-minute site information

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Benefits of webEDMS

- Provides transparency to the entire RI/FS process, thus enhances project quality and streamlines regulatory reviews and approvals
- 3D data visualization helps the user understand complex site conditions, identify impediments to site closure and design the most cost-effective remedial plan
- Performs real-time health risk assessments to guide site activities and ensure acceptance of the site end state/desired outcome
- All these lead to cheaper, quicker and safer site cleanup and closure

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Applications of webEDMS (a Click & Show System)

"Converts Data → Information → Knowledge → Solutions/Trust on the Fly"

Real-Time Sensors

PDAs

Data Entry

GIS-based Data Central

- GIS
- Databases
- Documents
- Data analysis
- Data charting
- Project management

Risk

- Site Risk
- Cleanup Levels

3-D

- Visualize Data in 3D
- 3D Plume Maps
- 3D Cutaway Views

Fate & Transport*

- Plume modeling

What-Ifs

- Plan before acting
- Compare alternatives
- Identify "+" and "-"
- Build consensus
- Define end state
- Develop best path

Decision

- Based on complete info
- Avoid costly mistakes
- Save time and $$
- Earn trust

* Desktop Application

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2D Data Analysis & Trending Interpretation

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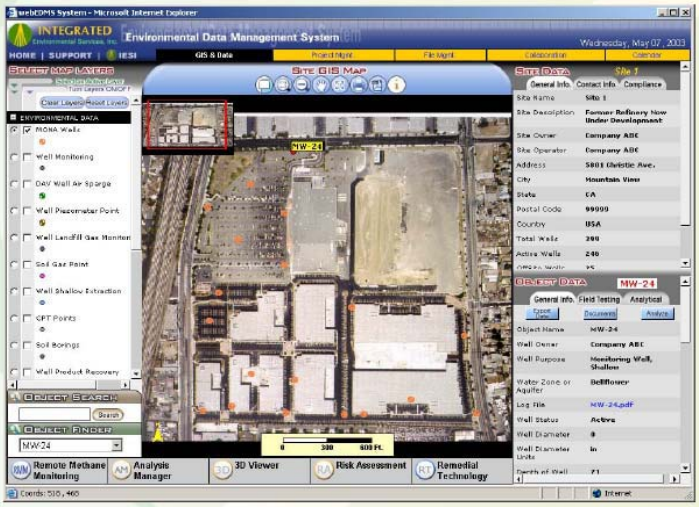
*web*EDMS: GIS Maps



- *web*EDMS links site data, documents and related information to its unique (x,y,z)
- User simply clicks an object on the map and its related data is shown (i.e. object analysis)

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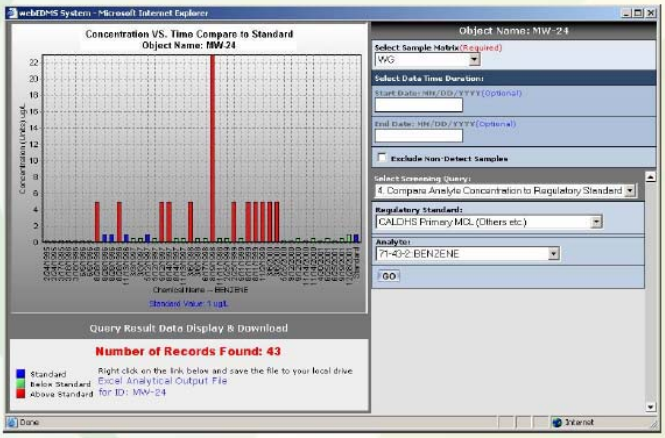
*web*EDMS: Object Analysis (1)



- Perform analysis on individual objects on the fly
- Compare to regulatory standards
- View results in a chart or spreadsheet
- Trend plots created dynamically

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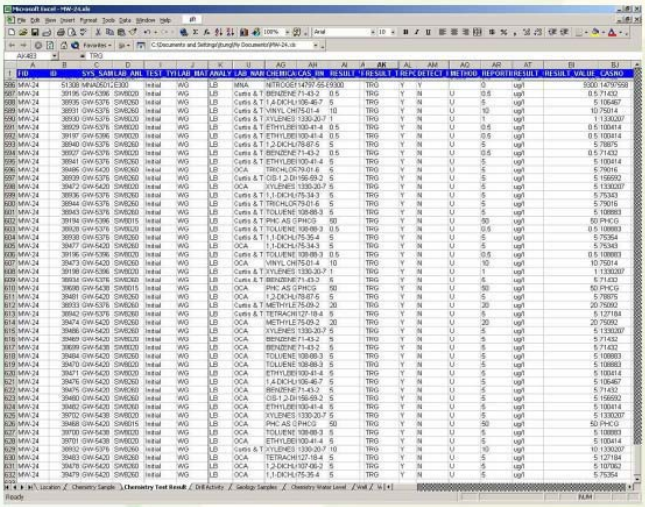
webEDMS: Object Analysis (2)



- View results in a spreadsheet
- All collected data on an object is indexed and exported in seconds for report preparation

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web-EDMS: Object Analysis (3)

- Compare site data to regulatory standards or user-defined values
- Display query results (> threshold levels) spatially on site maps
- Color-coded results on map for easy trending interpretation
- This photo shows hot spots are all within site boundaries

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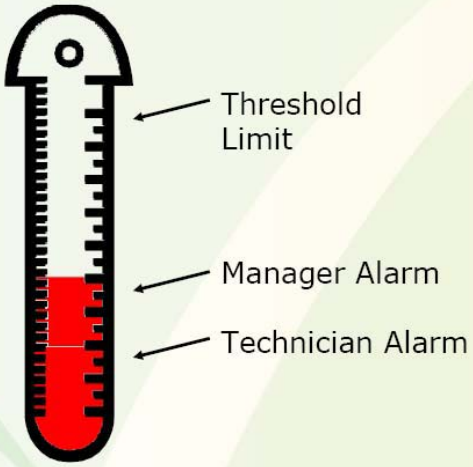
Multiple Levels of Notification



- Keep responders fully informed
- Email, voice, and/or text notification
- Continuous alerts until acknowledged or mitigated

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3D Visualization of Site Conditions

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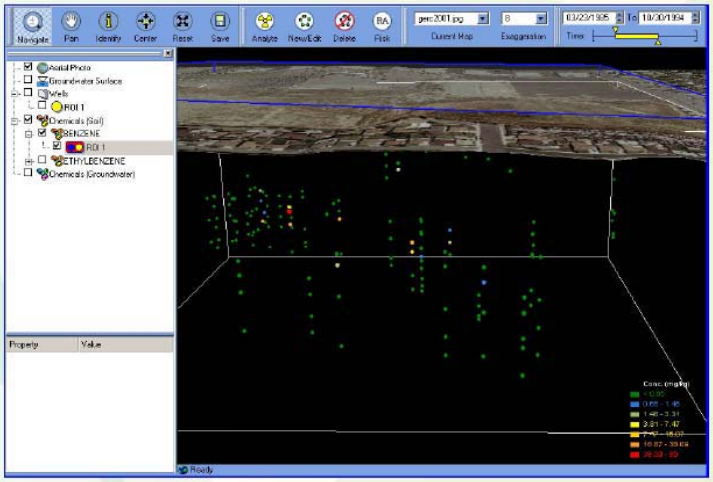
All Data Can Be Shown Visually



- Build common ground within the project team
- Time periods of sampling results can be specified
- This shows a limited time frame of samples

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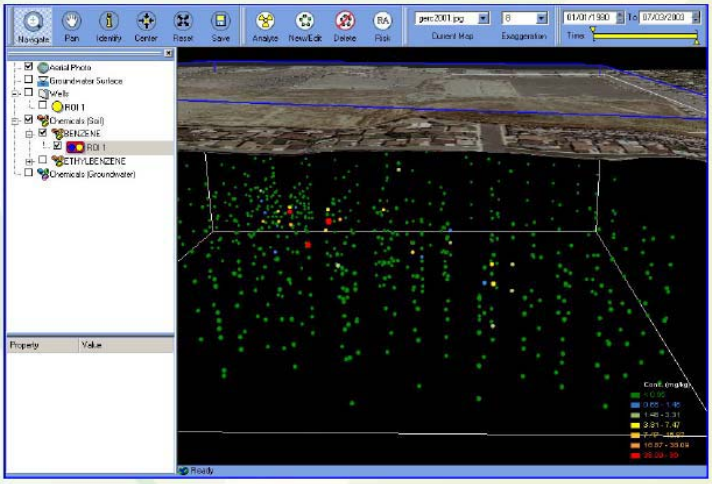
*web*EDMS Allows Easy Partitioning of Site Data by Time and Geographic Area



- Here is a much longer time frame of sampling
- Much more data is shown here
- Data related to any selected geographic areas can be selected for analysis

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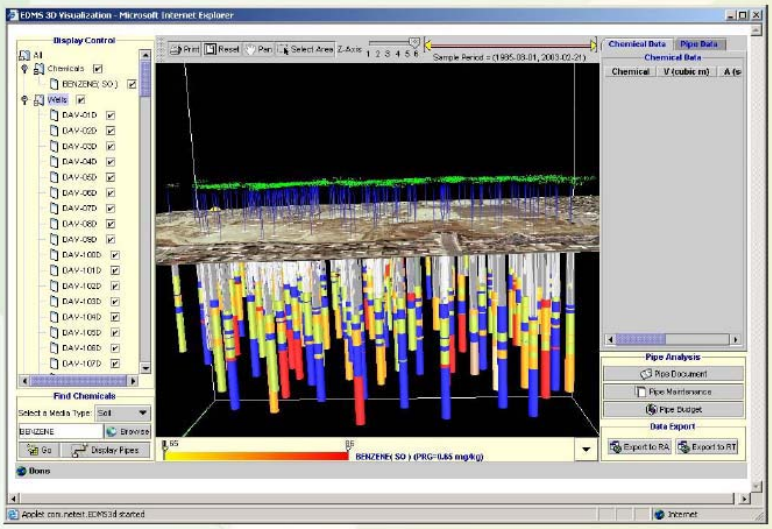
webEDMS: 3D Visualization



- Visualize site conditions in 3D
- View well casing, soil lithology
- View sample concentrations

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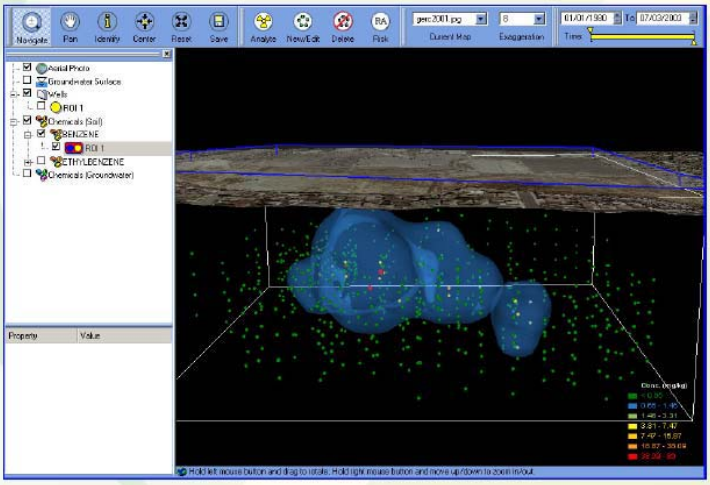
webEDMS: Plume Conditions (1)



- Display plume conditions based on area, cleanup level selected
- Calculate size, volume of impacted area
- New threshold conc. renders new shape of plume

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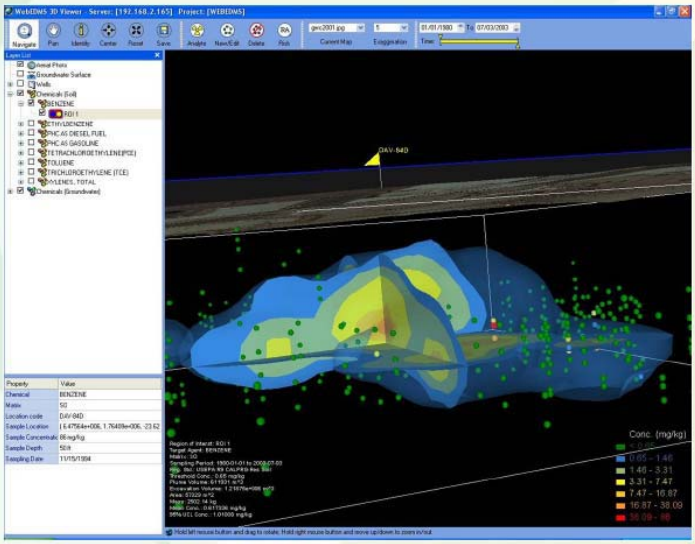
webEDMS: Plume Conditions (2)



- Dissecting plume vertically and horizontally to identify impediments to site closure and see effects of the hot spots
- Calculate size, volume of impacted area
- New cross section renders new impacted areas

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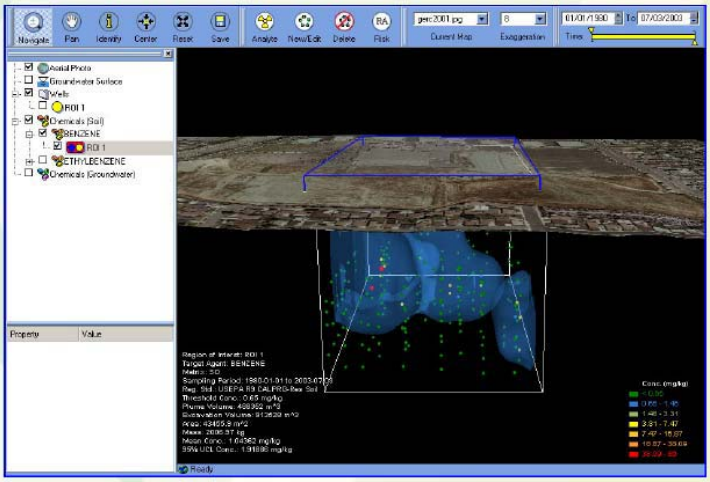
webEDMS: Region of Interest



- Create Region of Interest (ROI) of any shape
- Perform analysis on ROI (plume size, shape, risk assessment) on the fly

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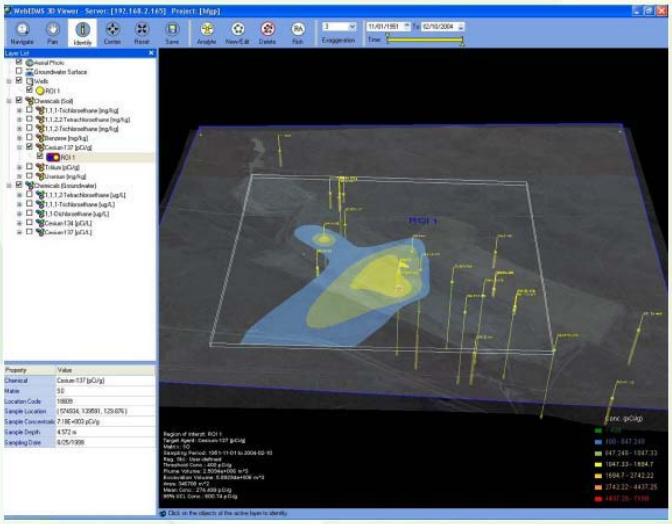
webEDMS: Aerial View of GW Contamination



- Create transparent view of plume by COC (compound of concern)
- Critical in understanding site conditions (plume size, shape, risk assessment) on the fly

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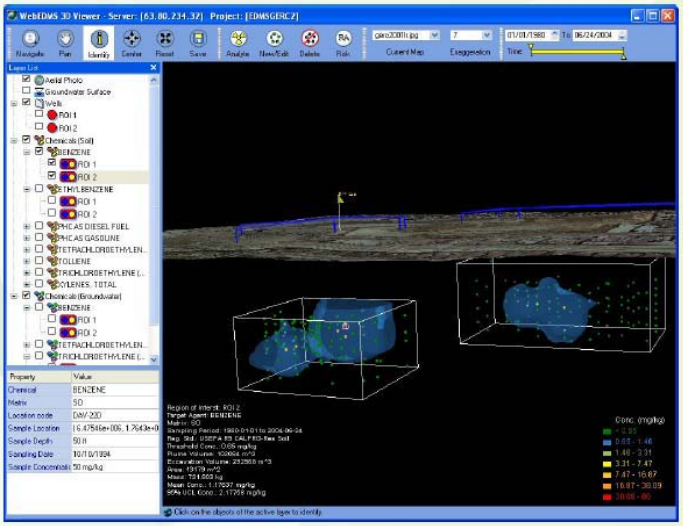
Select Multiple Regions of Interest



- Create multiple ROIs
- View, compare subsurface conditions simultaneously
- View plume extents relative to individual ROI

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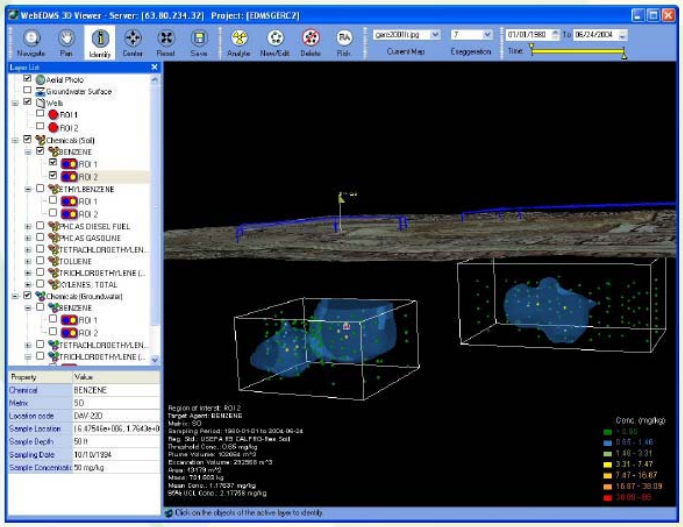
Regions of Interest (Cont.)



- Display individual ROI attributes
- Instantly calculate health risk associated with ROI selected
- Identify impediments to site closure (major risk drivers) instantly

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Automated Risk Assessment

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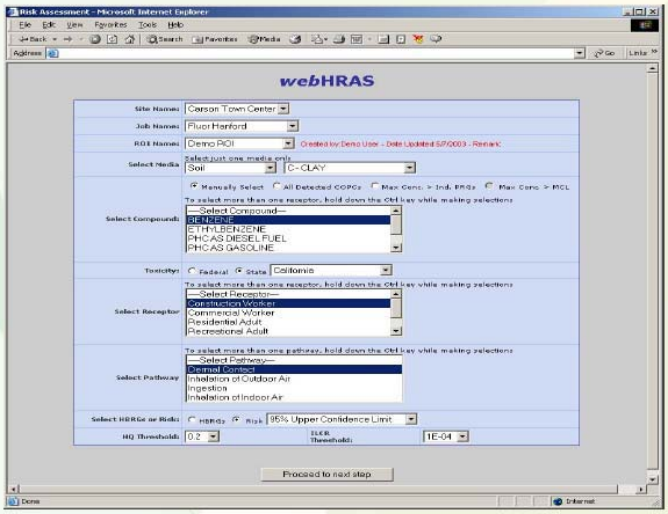
The *web*EDMS Risk Assessment Provides a Tool to Assess Site End State on the Fly



- The Risk Assessment is directly linked to central database
- Evaluates user-specified site and receptor conditions
- User can identify any geographic area for focused risk assessment
- User can specify the medium of impacted and time frame of interest

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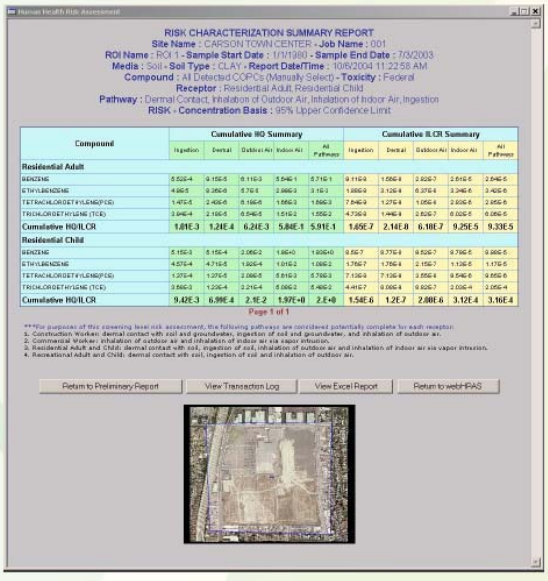
The *web*EDMS Risk Assessment Identifies the Acceptable Site End State on the Fly



- Health risks associated with user defined conditions are calculated real time
- User can identify major risk drivers in the hot spot areas and
- Develop the best remedial approach accordingly

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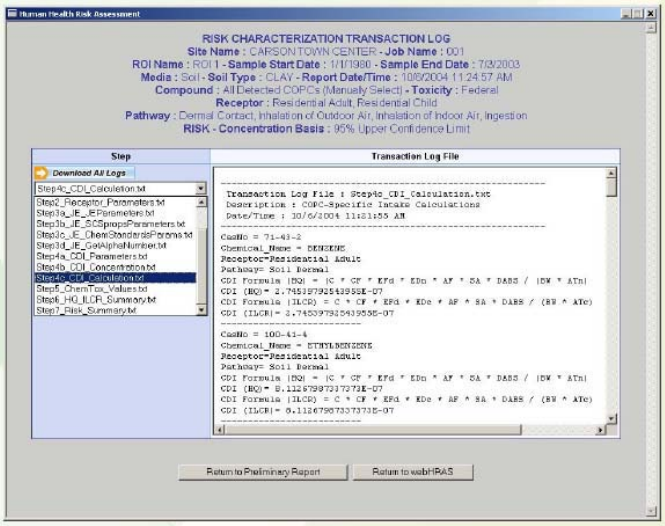
Details of Risk Calculation Are Saved Electronically for Paper Report



- It makes risk calculations transparent to laymen
- It builds trust with stakeholders
- Real time risk calculation saves time and money
- It provides much needed what-if management tools to the team

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Triad and webEDMS

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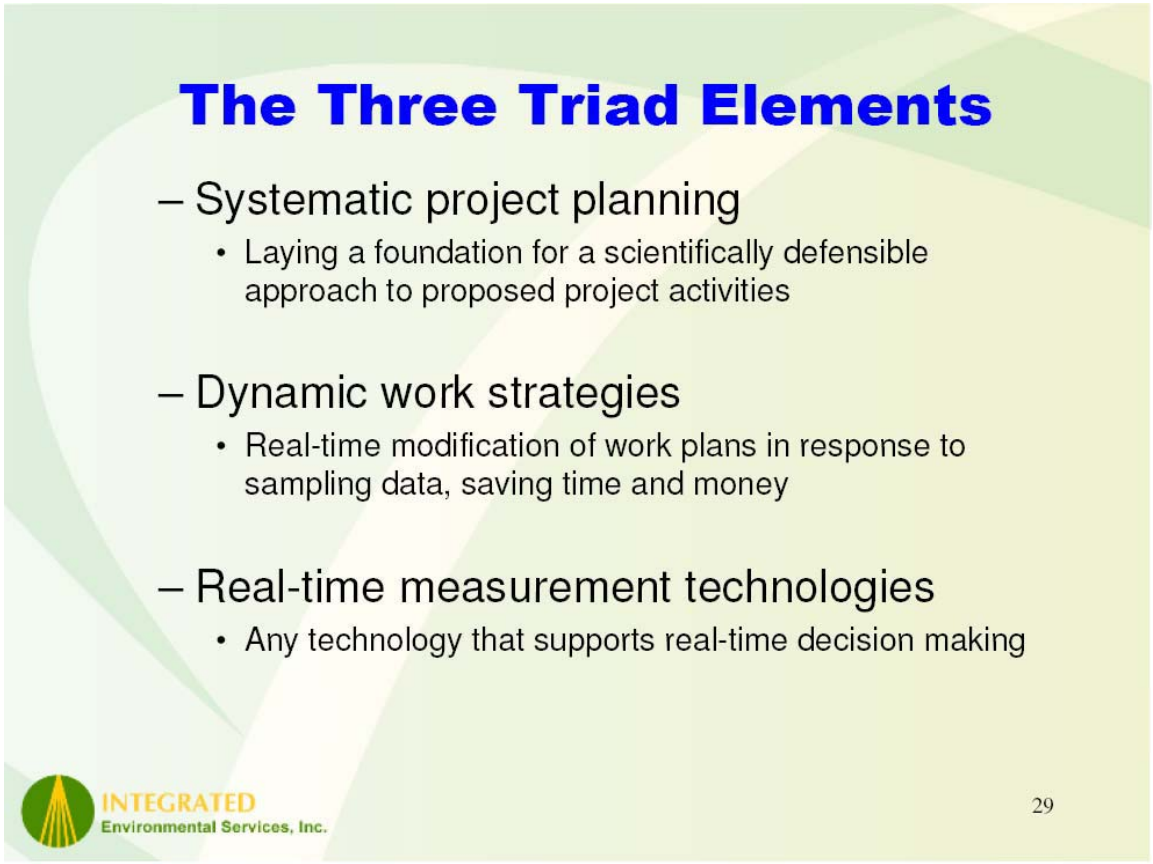
The Three Triad Elements
– Systematic project planning
• Laying a foundation for a scientifically defensible approach to proposed project activities
– Dynamic work strategies
• Real-time modification of work plans in response to sampling data, saving time and money
– Real-time measurement technologies
• Any technology that supports real-time decision making
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TRIAD TO INCREASE CERTAINTY IN REMEDIATION DESIGN

Mack, James; New Jersey Institute of Technology

For a site cleanup project in New Jersey, real-time analytics played a key role in filling the data gaps creating large uncertainties when estimating the volume of petroleum material in the subsurface, a critical input to successful site cleanup. The contaminants consisted of TPH, PCBs, and chlorinated solvents. The analytical techniques used included in situ petroleum detection and characterization using a fuel fluorescence detector (FFD), PetroFlag test kit and routine laboratory analysis for TPH, and mobile laboratory GC-MS for Aroclors and chlorinated VOCs.

A demonstration of methods applicability (DMA) was used to establish a predictive relationship between the complex FFD's fluorescent response and site-specific petroleum fingerprints. This predictive relationship permitted real-time, semi-quantitative, in situ, high vertical and areal sampling density logging of the subsurface to locate and bound quantities of separate and mixed "pools" of fuels and oils for appropriate remedial design.

This project's dynamic work strategy (which was supported by real-time, high-density analytics) was able to resolve in 3 weeks of field time data gaps that had been unsuccessfully addressed for over 10 years.

Triad and Remediation Design

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Newark, New Jersey
(973) 596 5857
mack@adm.njit.edu

Remediation & Uncertainty

- Converting Investigation Information Into Hard Remediation Design Is Fraught With Peril
- Do You Know The Following:
  - Volumes Of Impacted Material
  - Contaminate Concentrations/Mass Requiring Treatment
  - Application Location (Is It In The Right Place)
  - Performance Predictions
  - Operating Timeframe
- It All Comes Down to One Thing: Can You Predict the Remediation Cost With Confidence

Triad & Uncertainty Management

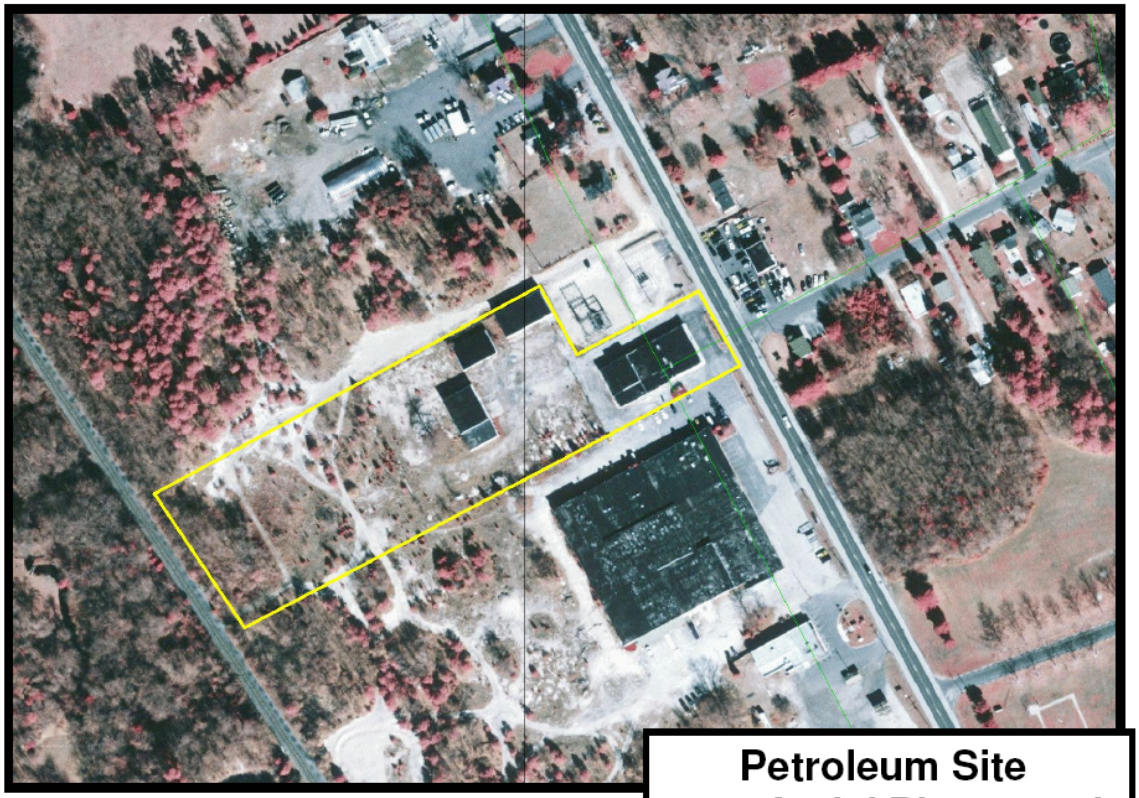
- Triad Focuses On Systematically Improving The CSM, Than Simple Regulatory Compliance
- Sample Representativeness Is As Important As Analytical Data Quality
- Collaborative Data Sets Increase Sample Density And Accuracy
- Data Imaging/Visualization Improves Communications & Agreement On Remediation Objectives
- **All Leads To**: Increased Confidence In Remediation Design, Implementation & Costing

Case Examples:

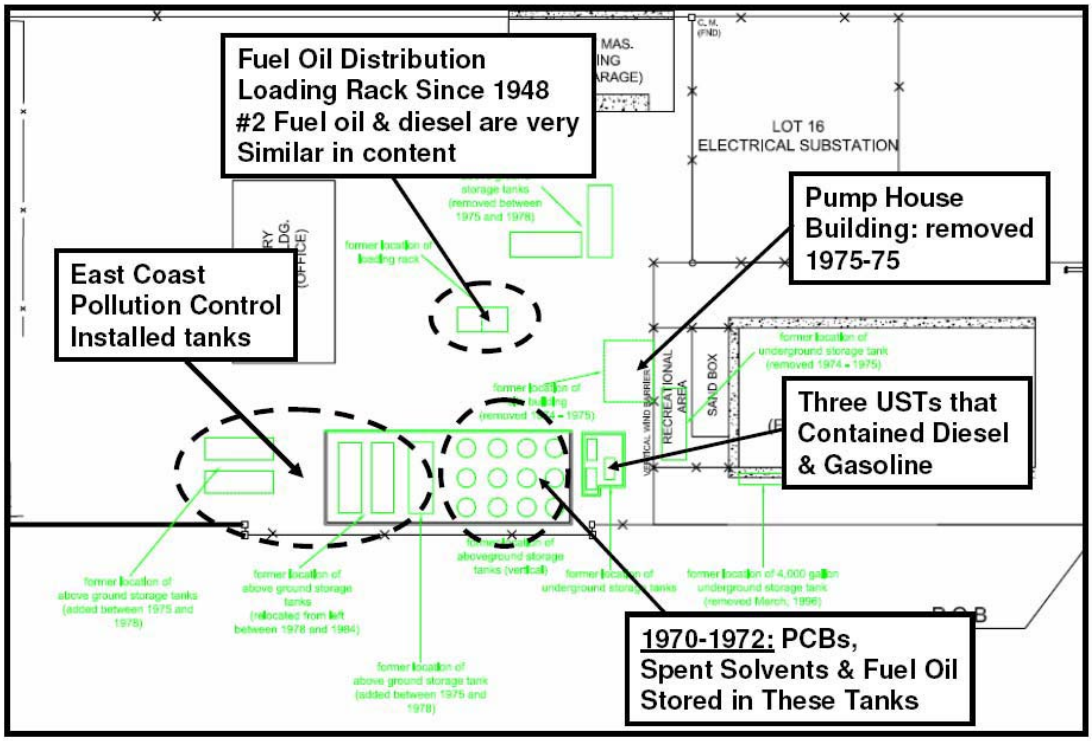
1. Petroleum Distribution Facility
2. Former Chemical Manufacturing Facility

Site Background

- Located in Franklinville, New Jersey
- Site size: Approximately 10 ac
- Long History of Petroleum Product Handling (Since 1940's)
- Also Was a Waste Oil Management Facility in Mid-70's
- Very Poor House Keeping Resulted in Extensive Releases by Various Hydrocarbons



Petroleum Site
2002 Aerial Photograph



Site Historical Operations Relative to COCs & Source Areas

Initial Conceptual Site Model

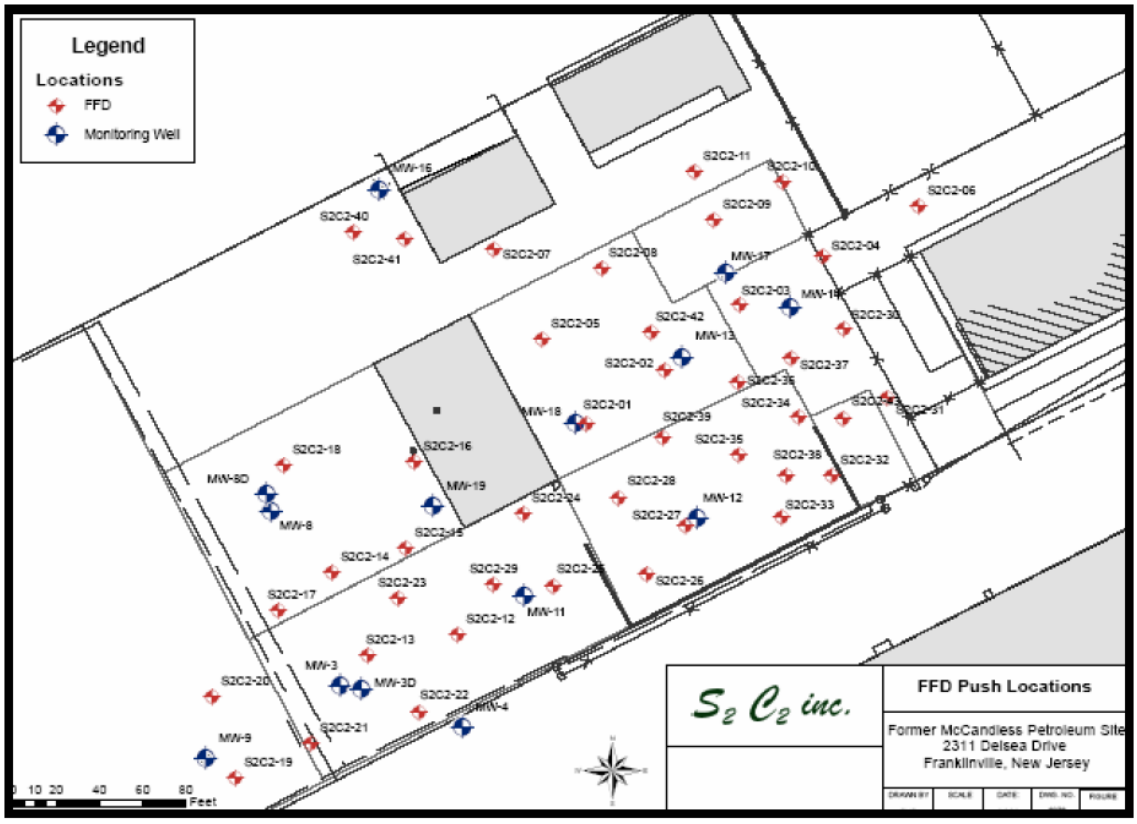
- Oil was released at site during past operations
  - From 1947 to 1972: home heating oil (No. 2 oil)
- PCBs & solvents were dissolved in waste oils brought to site in 1972-1974 which released to environment
- Oil (w/PCBs & solvents) migrated downward to water table and accumulated on top of watertable
- PCBs & VOCs in the oil begin to mix with and VOCs dissolve into groundwater (VOCs dissolve; PCBs mix w/ top of water table)
- Oil layer becomes an important interval to clearly delineate because it is likely the source of PCB & TCE in groundwater

Basic Field Activities Sequence

- **Step 1:** FFD profiles & modeling to rapidly define oil layers & create 3-D image
- **Step 2:** VOC in groundwater to confirm no site DNAPL source
- **Step 3:** Soil sampling to delineate PCBs in vadose zone & PCBs/oil in the saturated zone
- **Step 4:** Bulk sampling in 3 areas (bulk density, porosity, natural oxidant demand; permeability; grain size distribution, etc.) to evaluate potential for in-site treatment

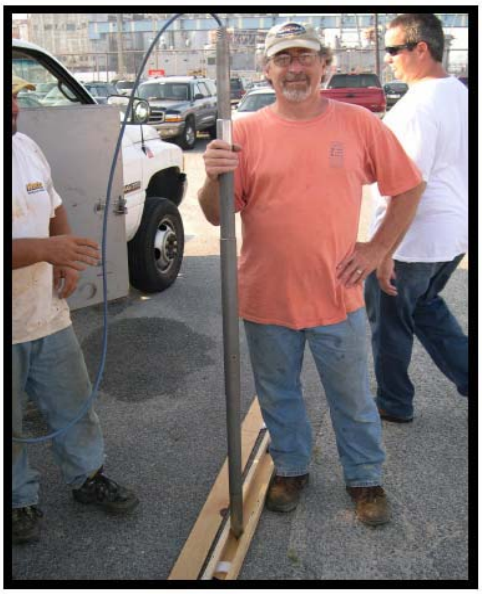
Field Activities

- Three weeks of field work in March 2006
- 43 FFD depth profiling locations
- 66 groundwater samples tested on-site for VOCs at 18 locations (variable depths)
- PDB in three existing monitoring wells
- 37 soil borings
- 85 soil samples for PCBs
  - Most samples analyzed in the field using mobile lab
  - Select group of samples sent to off-site lab to verify field analyses (five PCB & seven TPH)
- 3 treatability samples

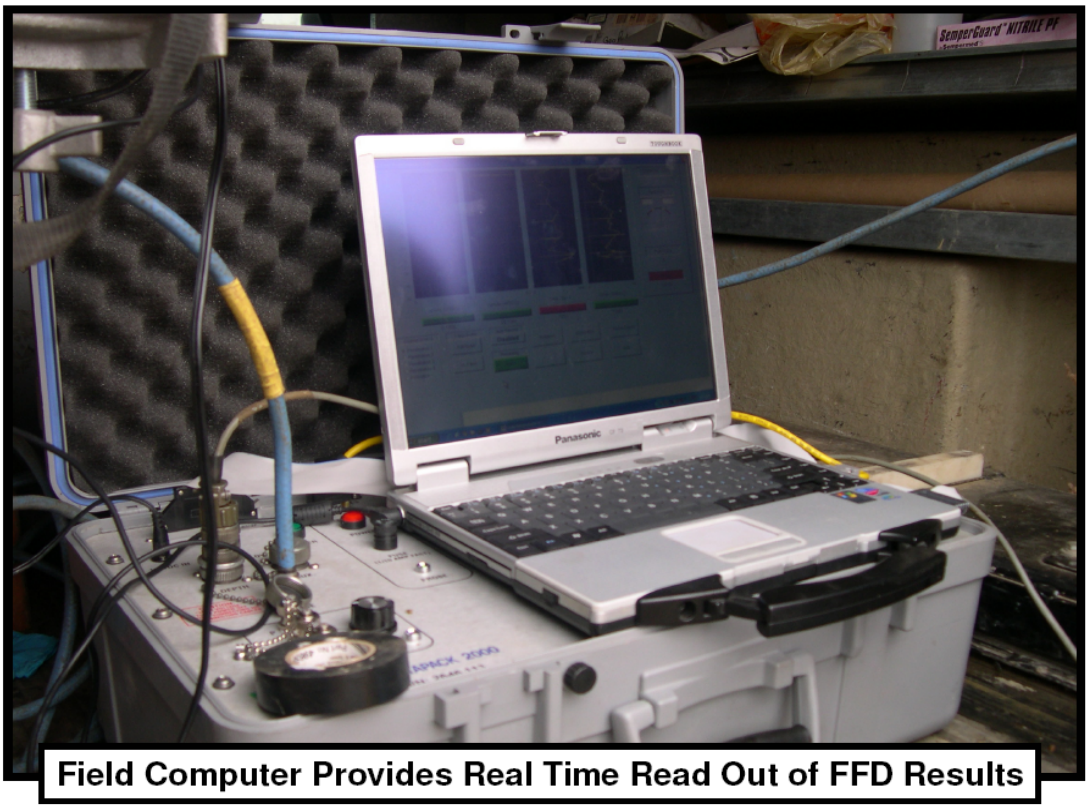


Fuel Florescence Detector (FFD)

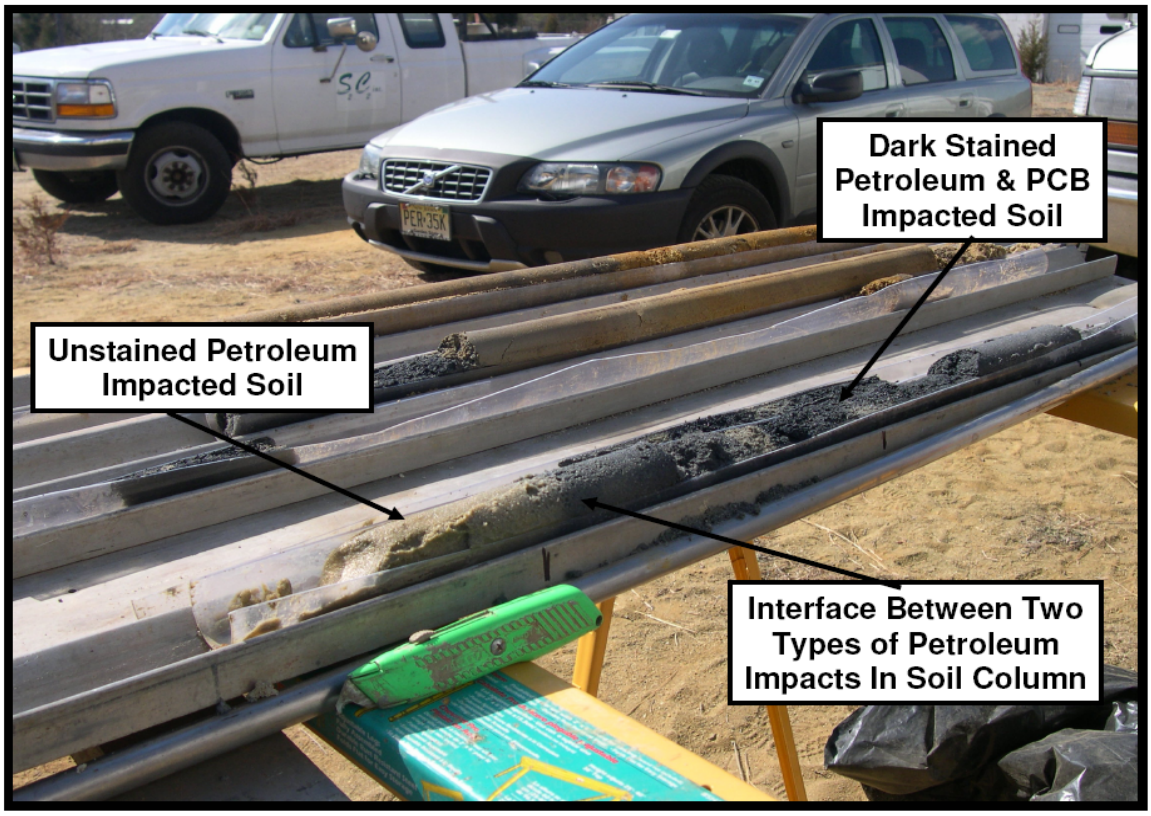
- Primarily for petroleum hydrocarbon delineation
- Direct push Ultraviolet Florescence (UVF) probe (push only)
- UV lamp in probe causes hydrocarbons to fluoresce
- Fluorescence captured by probe and converted to electronic signal
- Continuous log of electronic signal created
- Signal strength corresponds to concentration and can be imported to ArcGIS
- Impact area can be imaged by classifying according to signal strength

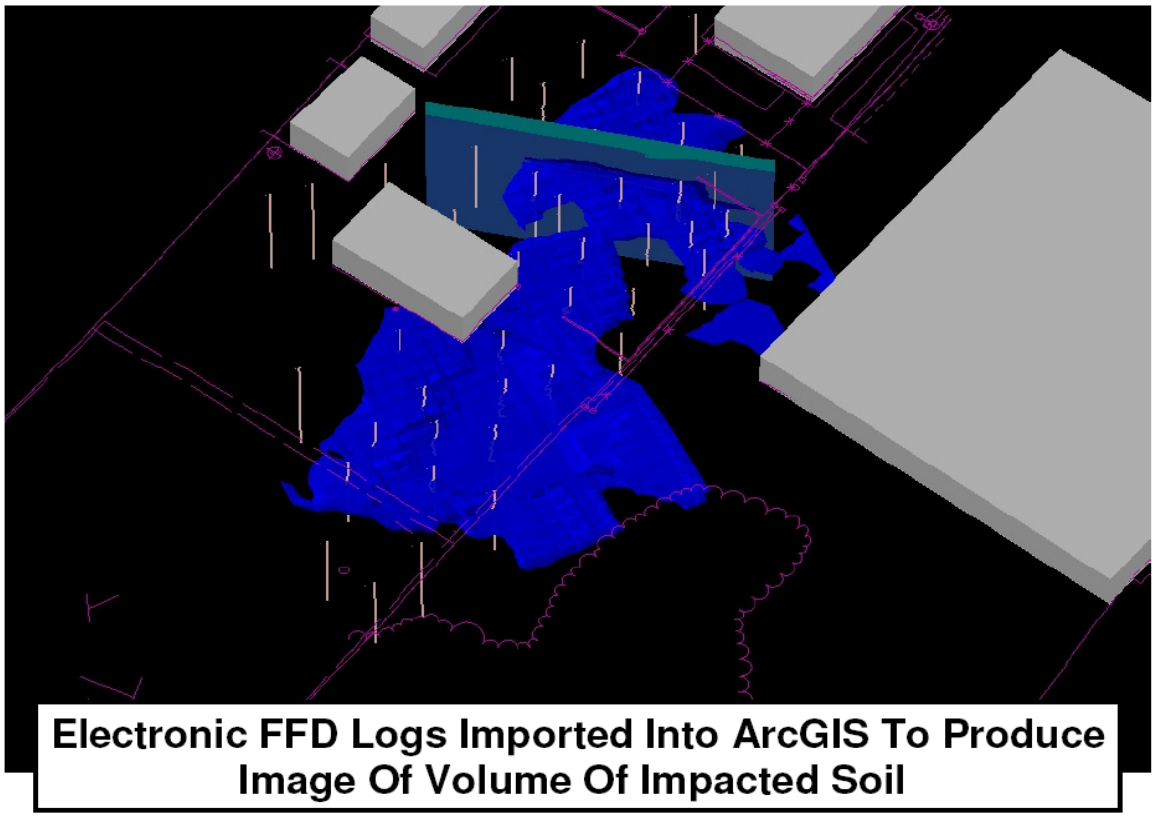


Fuel Fluorescence Detector

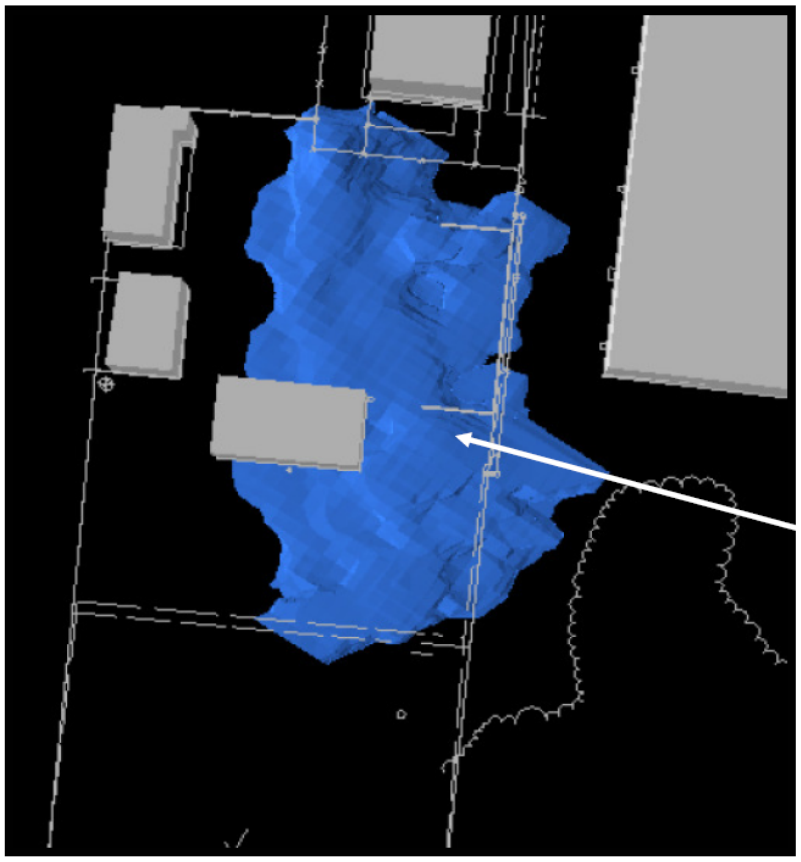


Field Computer Provides Real Time Read Out of FFD Results





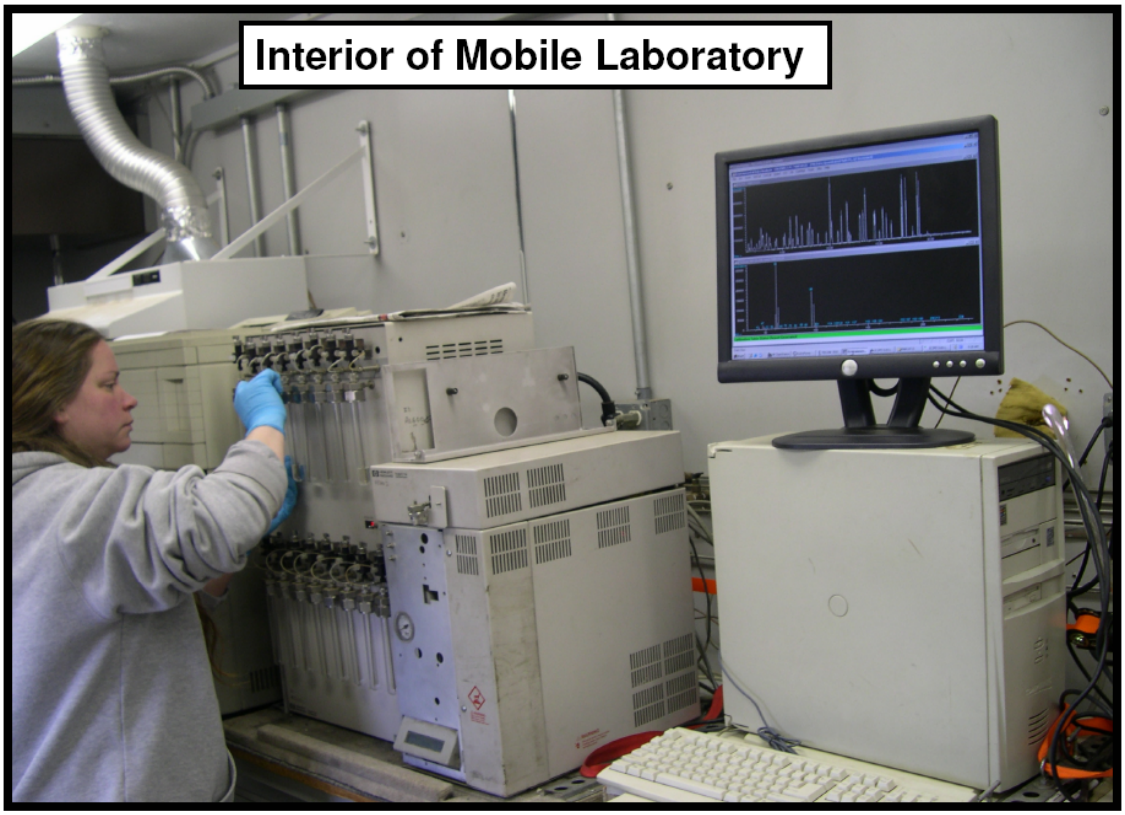
Electronic FFD Logs Imported Into ArcGIS To Produce Image Of Volume Of Impacted Soil

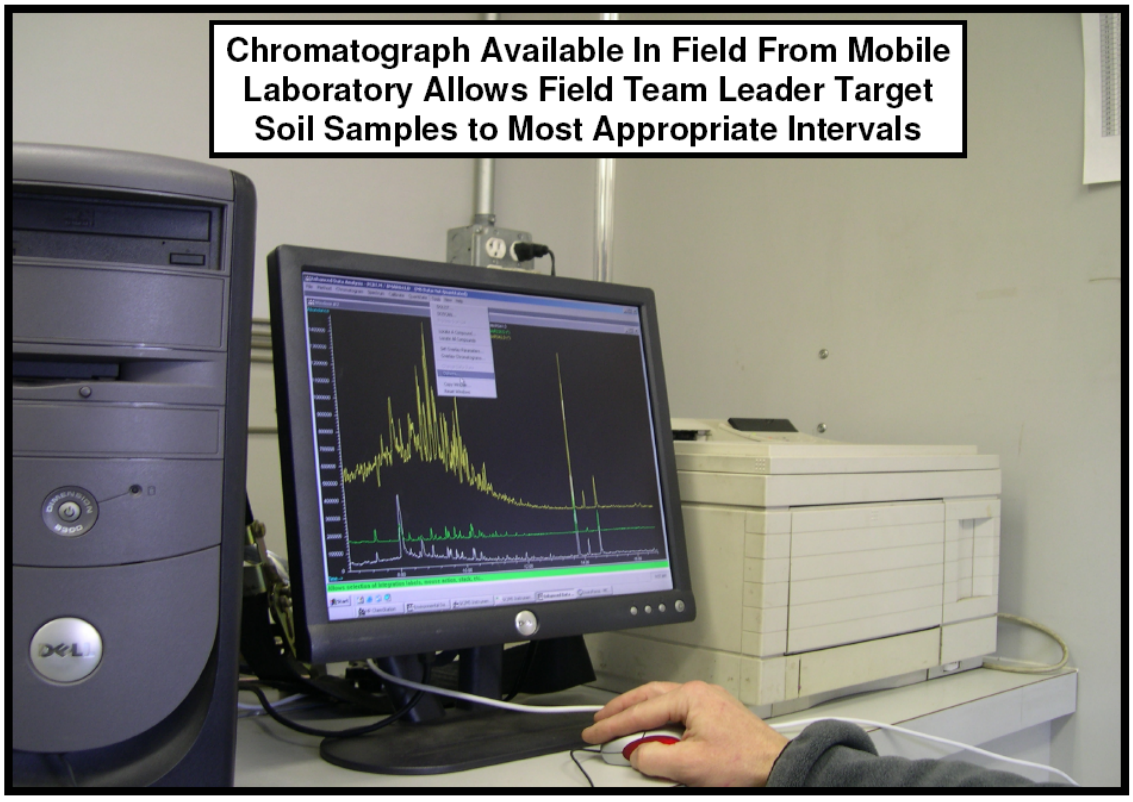


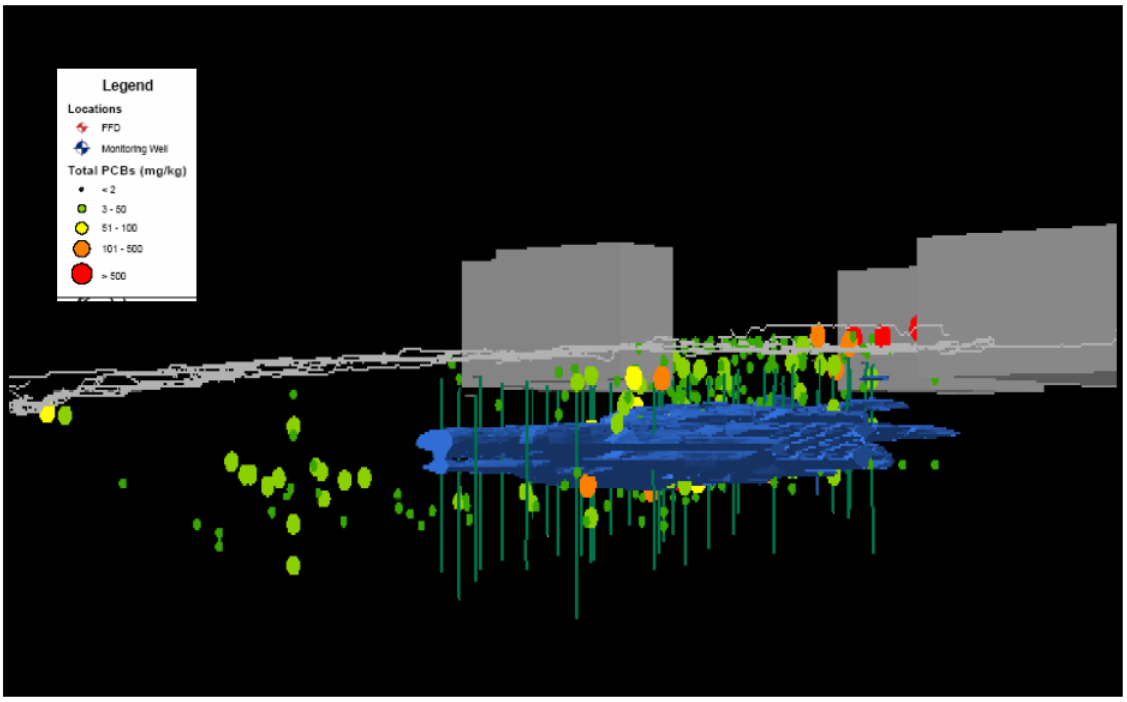
Plan View of Oil Impact Area Mapped By FFD

Oil Impact Layer Between 7 to 12 Feet Below Land Surface

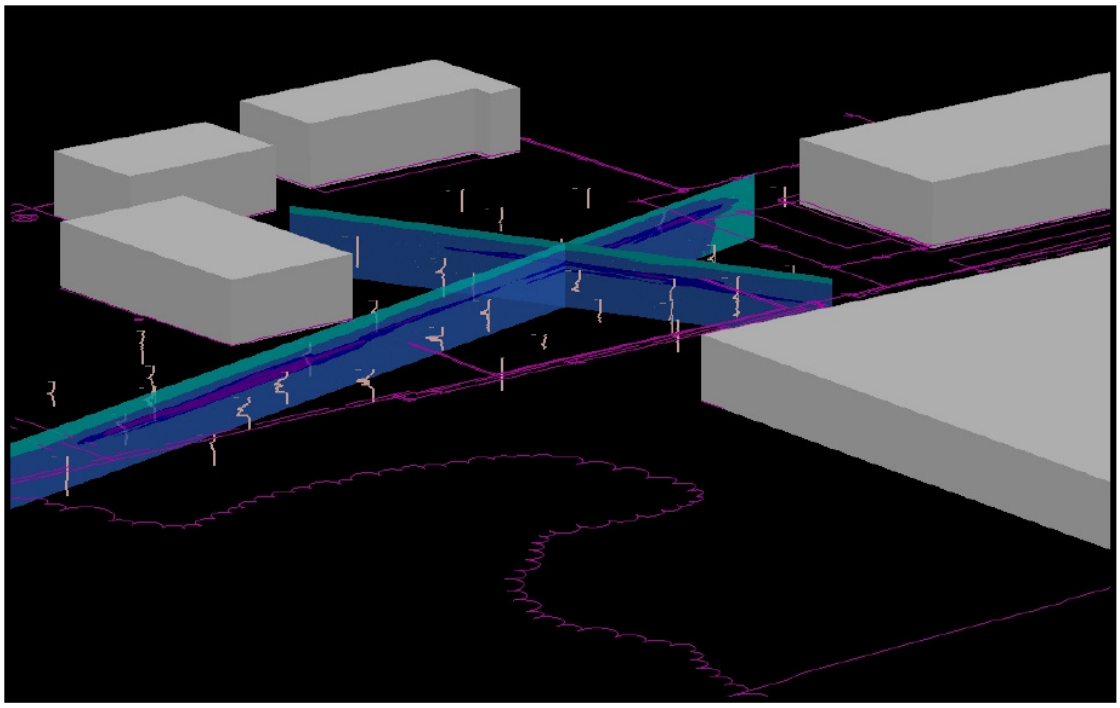
Soil Sample Extraction Set Up In Field For PCB Analysis In Mobile Lab


Interior of Mobile Laboratory

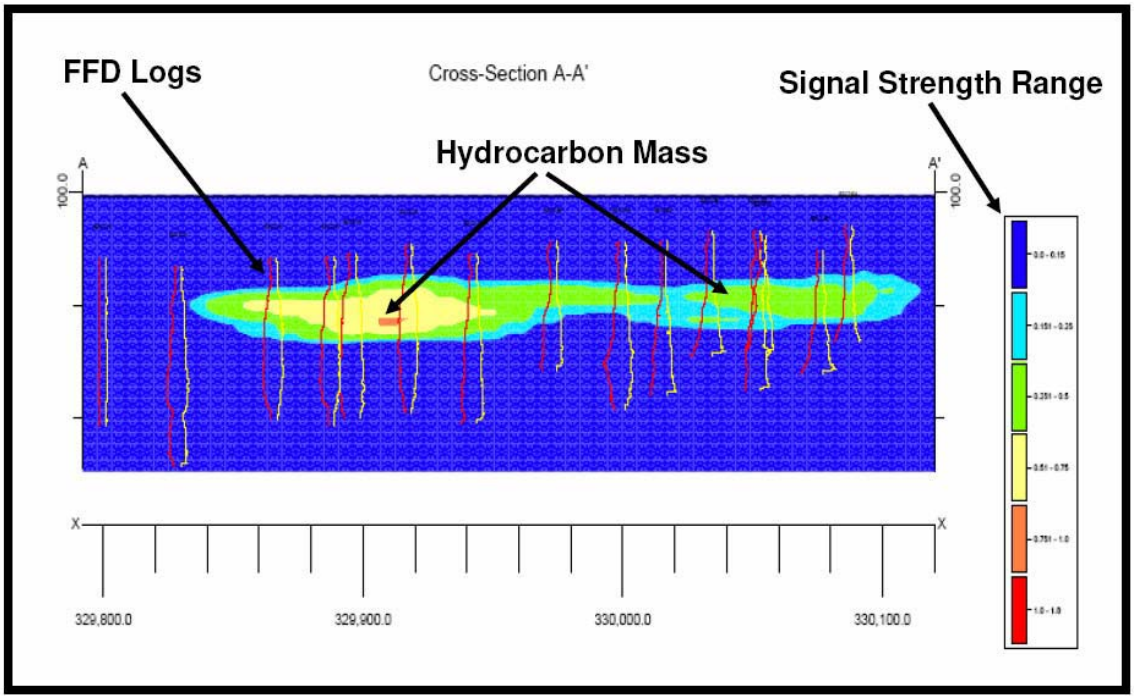

Chromatograph Available In Field From Mobile Laboratory Allows Field Team Leader Target Soil Samples to Most Appropriate Intervals



Cross Section Of the Oil Impact Layer With PCB Soil Sample Results Illustrated as Colored Circles

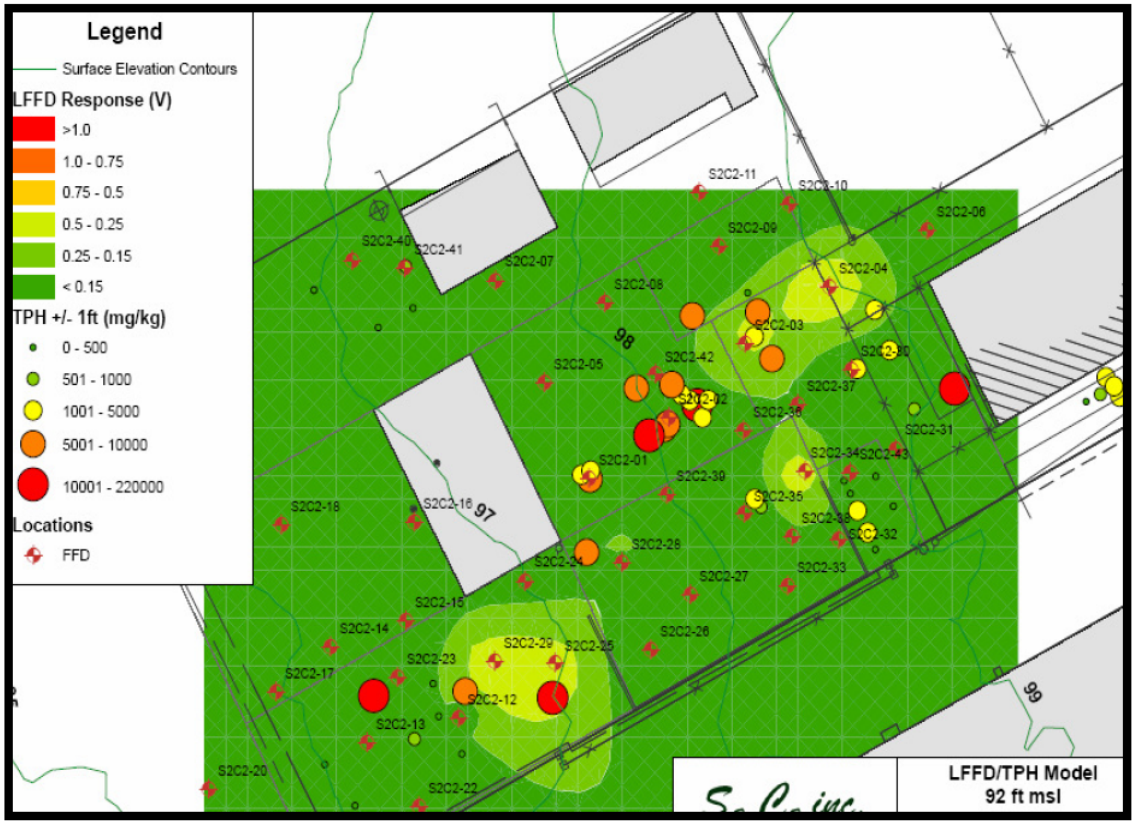


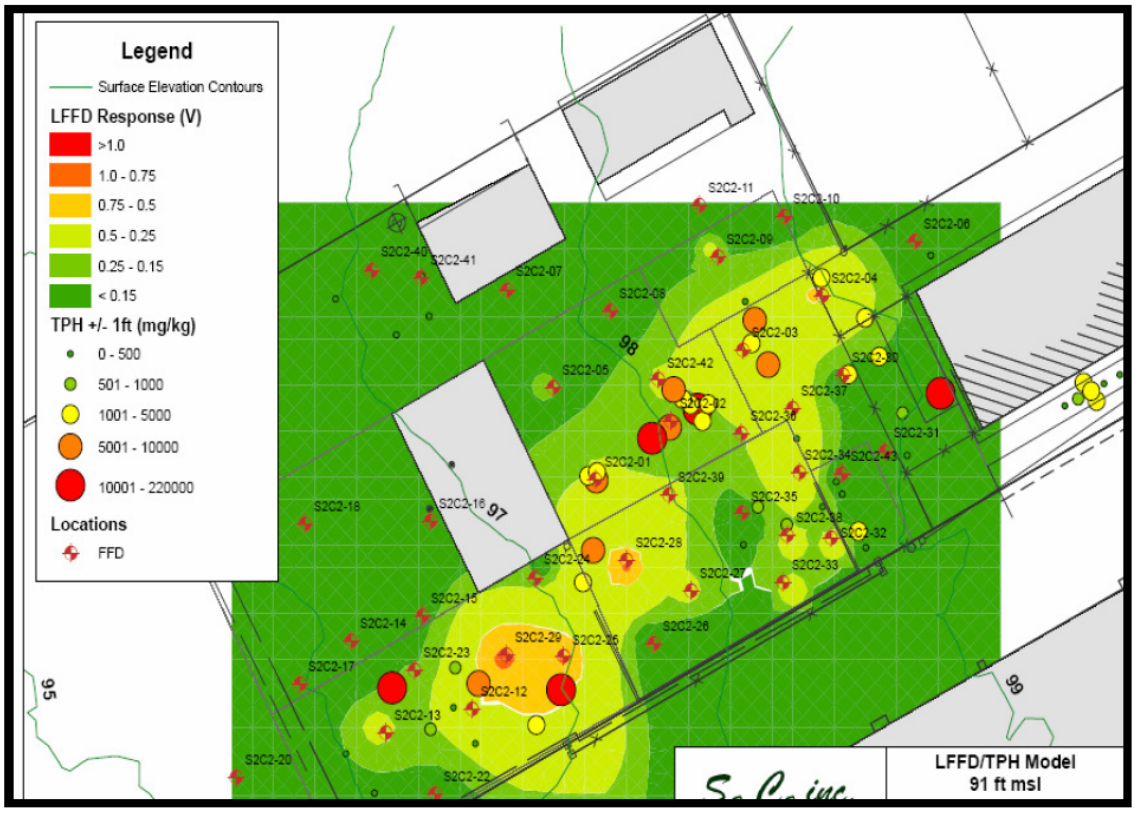
Fence Diagram Through the Hydrocarbon Mass: First Step in Converting Investigation Information & Images into Engineering Diagrams

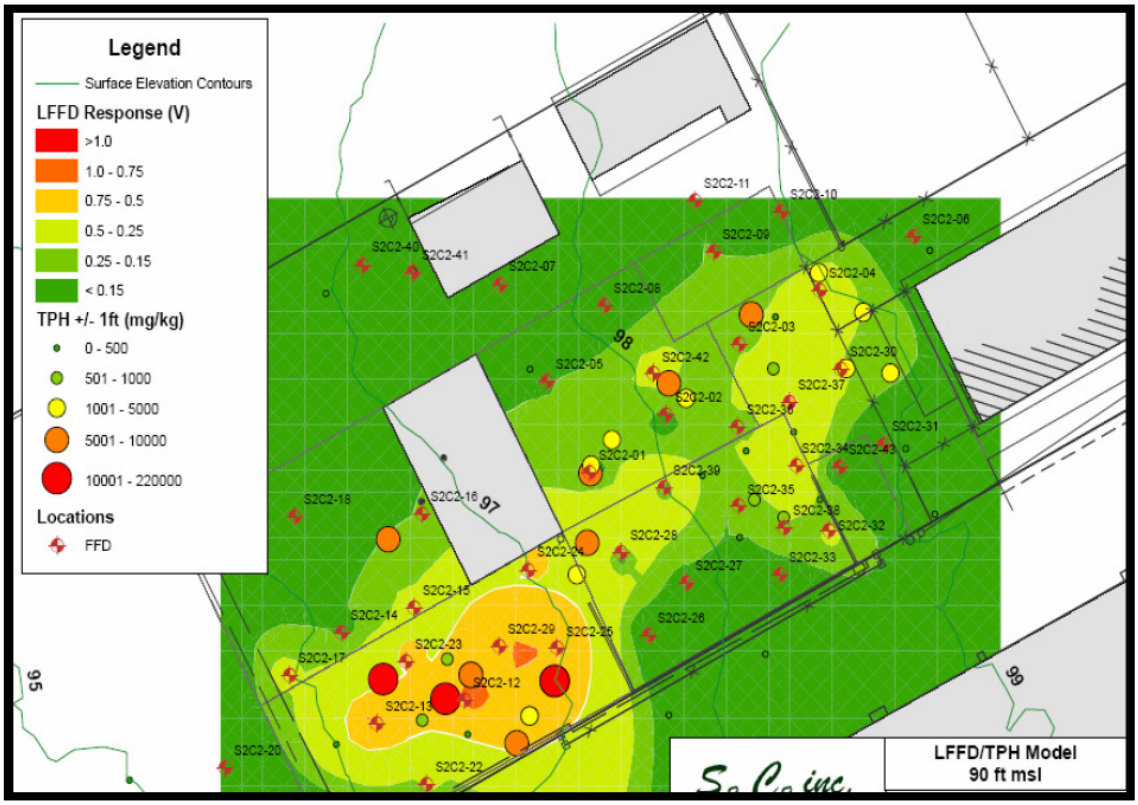


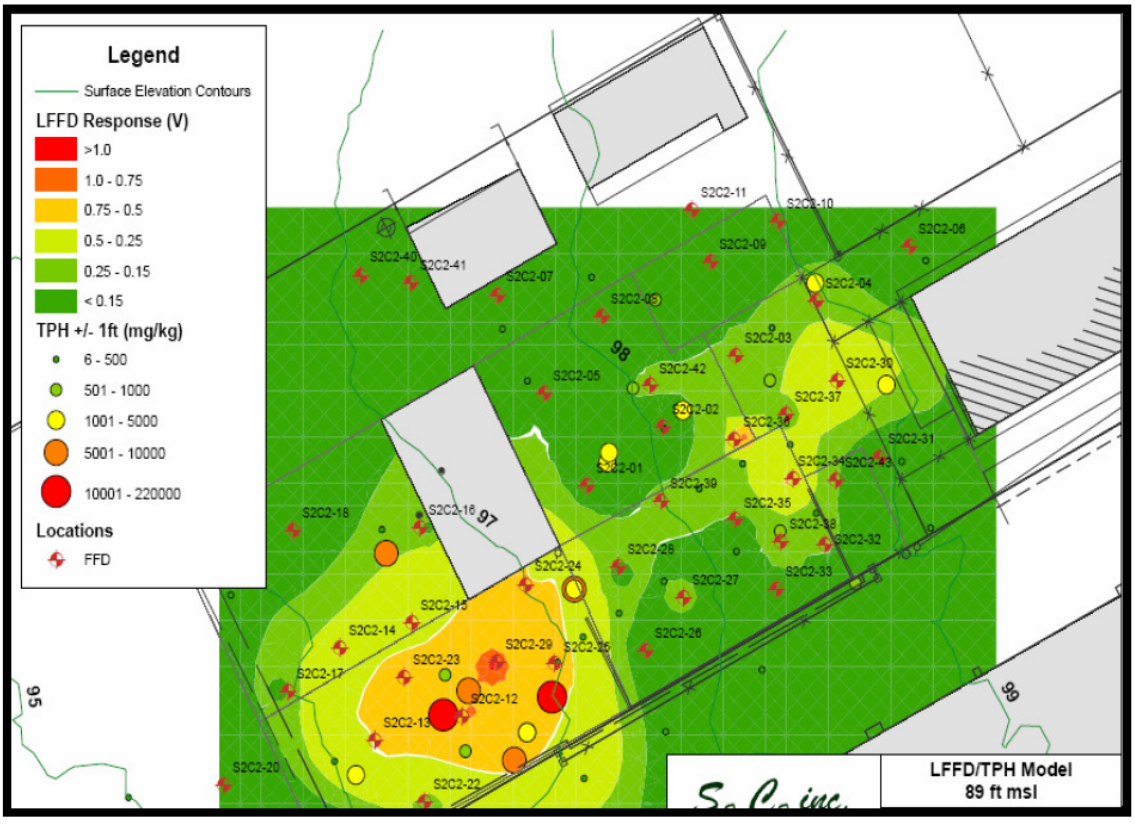
Cross Section Through The Hydrocarbon Mass Mapped By The FFD: Starting Basis for Ozone Sparging System Layout

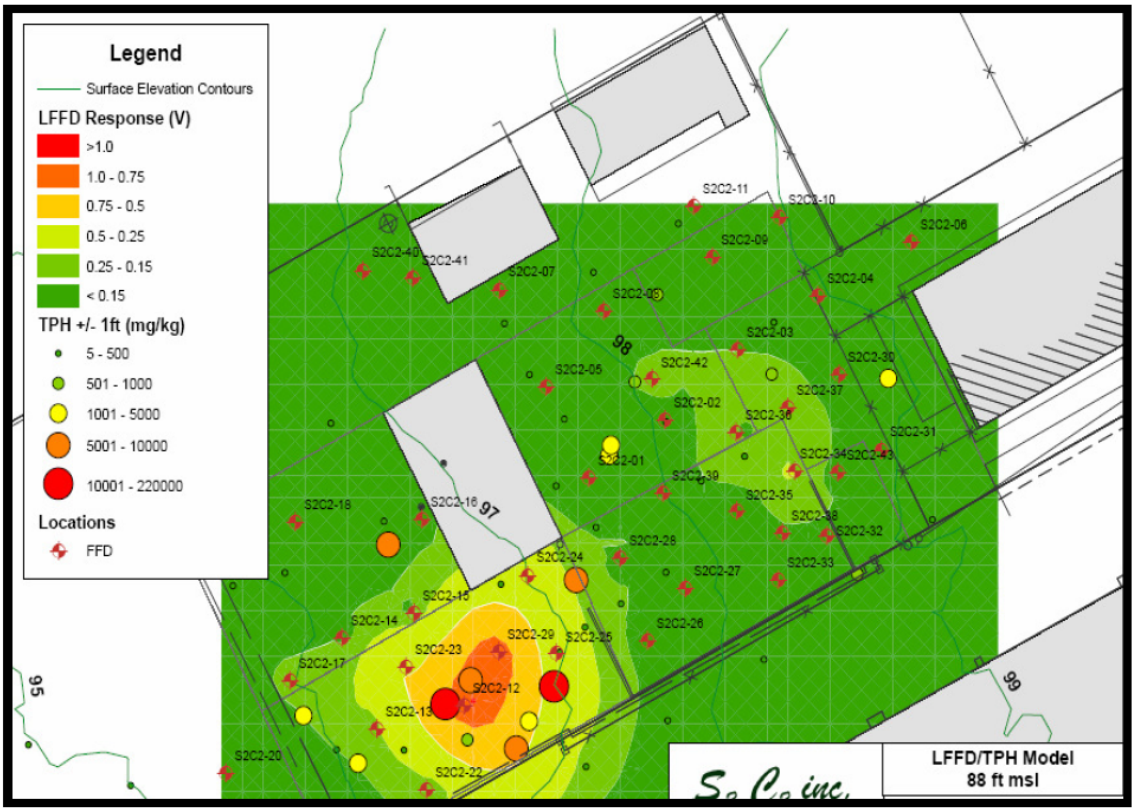
Horizontal One Foot Slices Through the 3D Imaged Hydrocarbon Impact Zone: Moving Downward Through Model

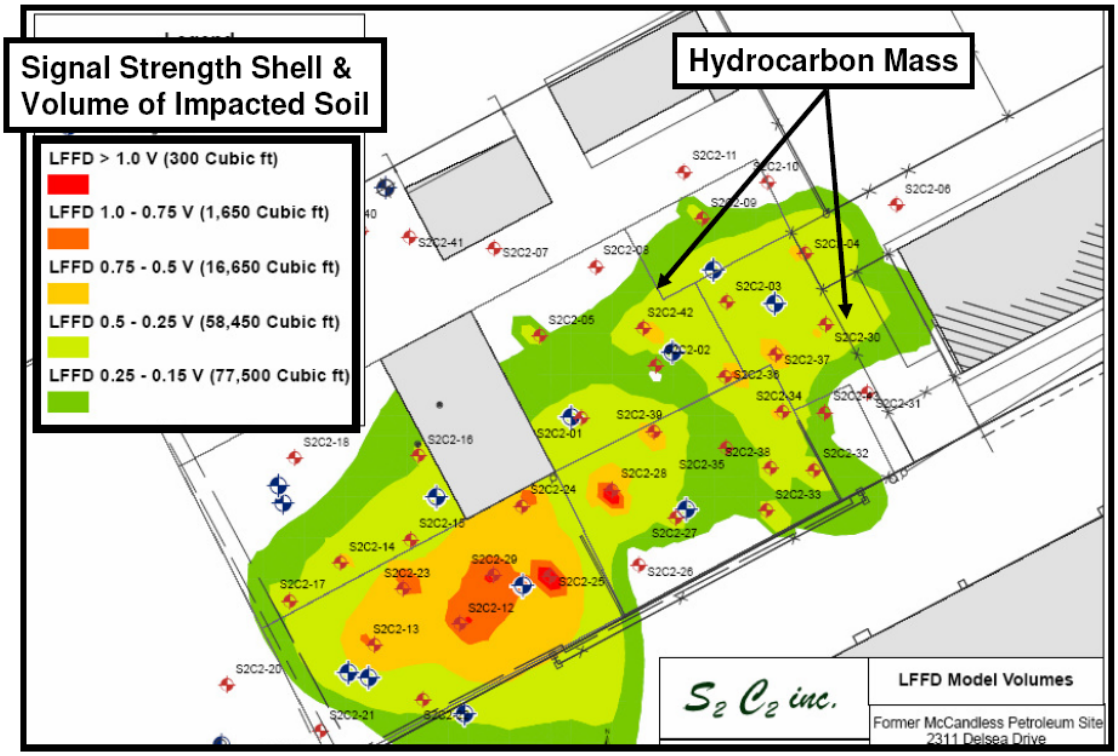

Legend
Surface Elevation Contours
LFFD Response (V)
>1.0
1.0 - 0.75
0.75 - 0.5
0.5 - 0.25
0.25 - 0.15
< 0.15
TPH +/- 1ft (mg/kg)
0 - 500
501 - 1000
1001 - 5000
5001 - 10000
10001 - 220000
Locations
FFD
LFFD/TPH Model
92 ft msl


Legend
Surface Elevation Contours
LFFD Response (V)
>1.0
1.0 - 0.75
0.75 - 0.5
0.5 - 0.25
0.25 - 0.15
< 0.15
TPH +/- 1ft (mg/kg)
0 - 500
501 - 1000
1001 - 5000
5001 - 10000
10001 - 220000
Locations
FFD
LFFD/TPH Model
91 ft msl

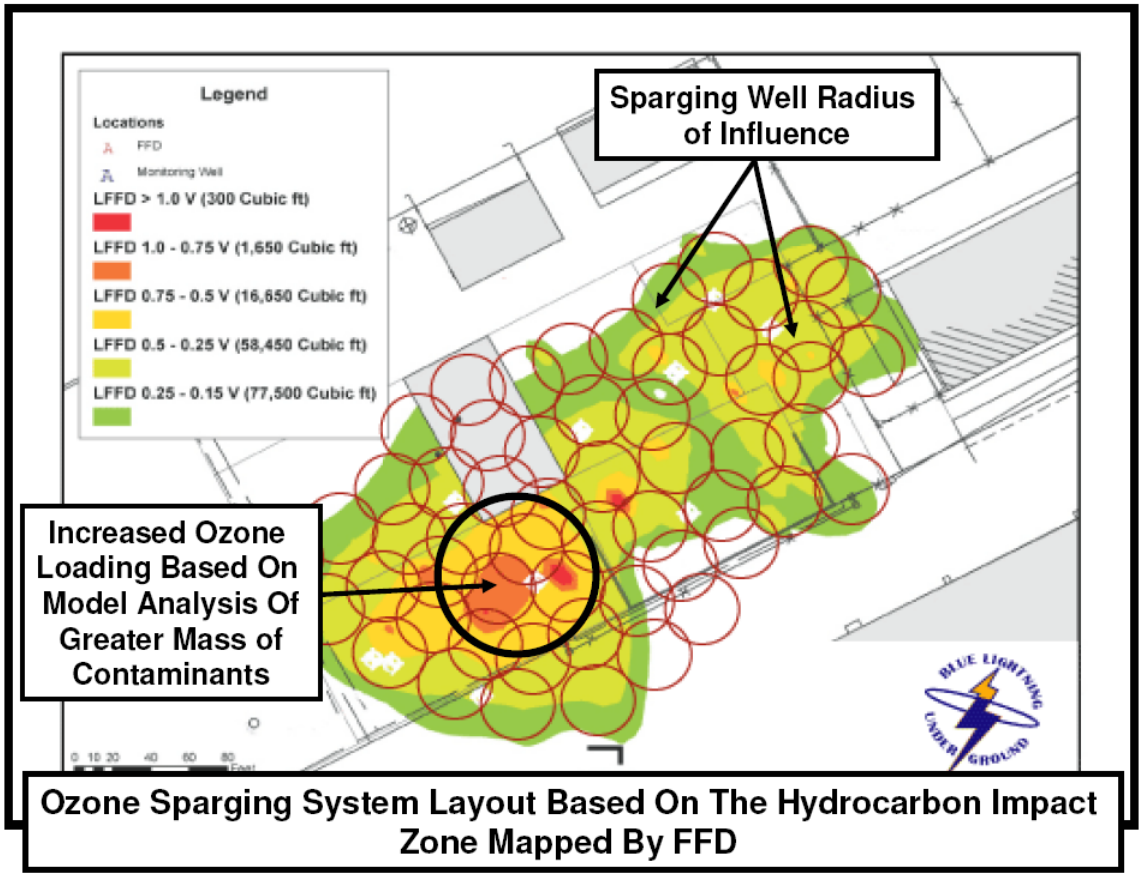

Legend
Surface Elevation Contours
LFFD Response (V)
>1.0
1.0 - 0.75
0.75 - 0.5
0.5 - 0.25
0.25 - 0.15
< 0.15
TPH +/- 1ft (mg/kg)
0 - 500
501 - 1000
1001 - 5000
5001 - 10000
10001 - 220000
Locations
FFD
LFFD/TPH Model
90 ft msl


Legend
Surface Elevation Contours
LFFD Response (V)
>1.0
1.0 - 0.75
0.75 - 0.5
0.5 - 0.25
0.25 - 0.15
< 0.15
TPH +/- 1ft (mg/kg)
6 - 500
501 - 1000
1001 - 5000
5001 - 10000
10001 - 220000
Locations
FFD
LFFD/TPH Model
89 ft msl

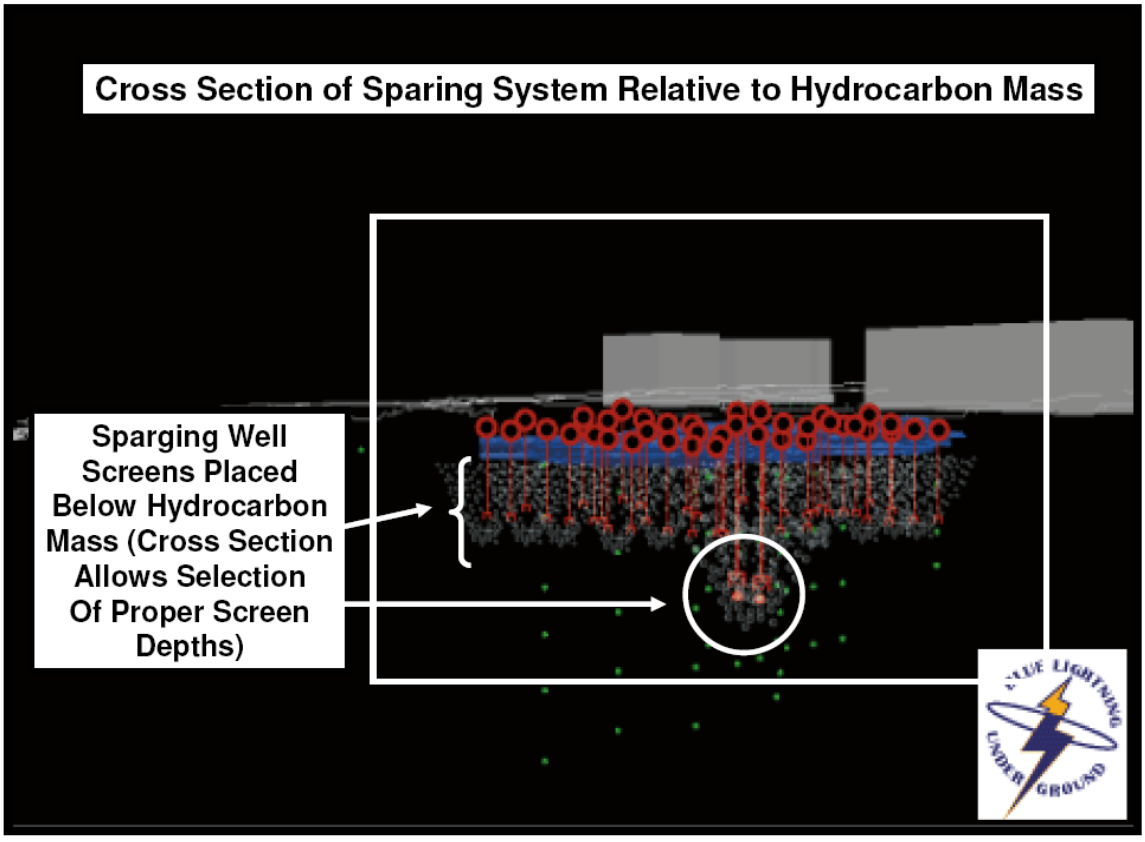




Horizontal Slices Are "Stacked" To Determine The Volume of Impacted Soil Within Each Signal Strength Shell, Which Is Then Converted to Mass In Place



Ozone Sparging System Layout Based On The Hydrocarbon Impact Zone Mapped By FFD



Summary: Converting Investigation Imaging to Hard Engineering

- Investigation Images Depict Findings Relative To Objectives Such As Impact Area, Migration & Exposure
- Remediation Design Requires Images To Be Converted To Engineering Data Such As Mass, Volumes & Dimensions
- Triad Provides The Sampling & Analytical Density To Develop Detailed Remedial Designs
- Process:
  - Convert 3D Images To Plan & Cross Section Views
  - Correlate Image Shells W/ Concentrations To Obtain Mass & Volume Estimates
  - Develop Layouts Using Plan & Cross Section Views
  - Adjust Treatment Material Loading Based On Mass Distributions

Overall Summary

- Collaborative Data Sets Consisting Of Information From Multiple Testing Methods Provides Increased Detail Of Impact Area
- Increased Detail Enables Engineers To Design Remediation Applications With Greater Confidence
- Transition From Investigation To Hard Design Quicker And Easier Using Triad Based Computer Imaging

TUESDAY, AUGUST 29, 2006

CONCURRENT SESSIONS

Air

NATIONAL PICTURE OF AMBIENT AIR TOXICS

Hafner, Hilary R.; Sonoma Technology, Inc.
McCarthy, Michael C.; Sonoma Technology, Inc.

Ambient air toxics measurements for hazardous air pollutants collected in the United States from 1990 to 2003 were analyzed for diurnal, seasonal, and/or annual variability and trends. Visual and statistical analyses were used to identify and quantify temporal variations in air toxics at national and regional levels. A major issue with air toxics data that affect our ability to identify and quantify trends is that much of the data is below method detection limits (MDLs). Of the 39 air toxics included in this study, about 40% of the measurements were reported as a substituted value (e.g., MDL, MDL/2, zero). Also, some of the data that appear to be below MDL are not indicated as such. Furthermore, many of the species MDLs are above the cancer benchmark for that specie which makes it difficult for analysts to assess risk. In this study, data that were clearly substituted were considered invalid; we set data completeness criteria for inclusion of data in an analysis.

Four different diurnal variation-patterns were identified for fourteen air toxics and three different seasonal patterns were identified for thirty-four air toxics. Sufficient data exist to quantitatively assess long-term trends of 15 air toxics. Urban concentrations of o-xylene, benzene, 1,3-butadiene, chloroform, carbon tetrachloride, cadmium (tsp) and lead (tsp) were shown to have declined. Urban concentrations of tetrachloroethylene, trichloroethylene, and acetaldehyde concentrations declined on average, but were not statistically significant; formaldehyde, chromium (tsp), and arsenic (tsp) concentrations increased on average, but were not statistically significant. Urban concentrations of methylene chloride, and manganese (tsp) showed a mix of increasing and decreasing trends, with no clear national trend. This presentation will show a National view of ambient air toxics concentrations in the United States, put these concentrations in perspective relative to health benchmarks, and discuss data needs as the National Air Toxics Trends Site (NATTS) program matures.

What Is the National Picture of Air Toxics Concentrations?

Hilary R. Hafner
Michael C. McCarthy

Presented at the
National Environmental Monitoring Conference
Arlington, VA

August 29, 2006

STI

STI-2992

Background

- Air toxics have been measured at several hundred sites since 1960 by state, local, and tribal air pollution control agencies, but little exploration of the data at a national scale had been performed prior to 2000.
- In 2000, a long-term data analysis project was initiated to guide development of a national air toxics monitoring program and subsequently to investigate national-scale air toxics trends.
- Since 2000, the EPA and the states have worked together to establish the National Air Toxics Trend Sites (NATTS) program, numerous community-scale monitoring studies, and a multi-year data analysis project.

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What Are the Most Important Air Toxics?

- They are based on National Air Toxics Assessment 1999 (NATA99) risk-weighted rankings of people exposed to air toxics.
- Top 10 rankings are for number of people exposed to cancer risk greater than 10^{-6}, 10^{-5}, and 10^{-4}.

Pollutant	10^{-4}	10^{-5}	10^{-6}
Benzene	3	1	3
Chromium VI	2	6	10
Coke Oven Emissions	1	3	-
Naphthalene	10	4	8
1,3-Butadiene	-	2	7
Carbon Tetrachloride	-	8	2
Particulate Organic Matter (total)	5	7	-
Hydrazine (?)	4	9	-
Tetrachloroethene	-	5	9
Ethylene Dibromide	-	10	6
Bis(2-ethylhexyl)phthalate	-	-	1
Acetaldehyde	-	-	4
1,1,2,2-Tetrachloroethane	-	-	5
Arsenic	6	-	-
Ethylene Oxide	7	-	-
Cadmium	8	-	-
Benzidine	9	-	-

3

Number of Measurement Sites for Key Toxics

Measurements from 2000-2005* at

>100 sites

=20 sites

<20 sites

Not available

* Data in AQS

Pollutant	10^{-4}	10^{-5}	10^{-6}
Benzene	3	1	3
Chromium VI	2	6	10
Coke Oven Emissions	1	3	-
Naphthalene	10	4	8
1,3-Butadiene	-	2	7
Carbon Tetrachloride	-	8	2
Particulate Organic Matter (total)	5	7	-
Hydrazine	4	9	-
Tetrachloroethene	-	5	9
Ethylene Dibromide	-	10	6
Bis(2-ethylhexyl)phthalate	-	-	1
Acetaldehyde	-	-	4
1,1,2,2-Tetrachloroethane	-	-	5
Arsenic	6	-	-
Ethylene Oxide	7	-	-
Cadmium	8	-	-
Benzidine	9	-	-

4

Measurements above Detection Limits

Measurements from 2000-2005*

>75%

>50%

>25%

<25%

Not available

* Data in AQS

Pollutant	10^{-4}	10^{-5}	10^{-6}
Benzene	3	1	3
Chromium VI	2	6	10
Coke Oven Emissions	1	3	-
Naphthalene	10	4	8
1,3-Butadiene	-	2	7
Carbon Tetrachloride	-	8	2
Particulate Organic Matter (total)	5	7	-
Hydrazine	4	9	-
Tetrachloroethene	-	5	9
Ethylene Dibromide	-	10	6
Bis(2-ethylhexyl)phthalate	-	-	1
Acetaldehyde	-	-	4
1,1,2,2-Tetrachloroethane	-	-	5
Arsenic (all size fractions)	6	-	-
Ethylene Oxide	7	-	-
Cadmium (all size fractions)	8	-	-
Benzidine	9	-	-

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Risk Assessment Suitability: National Perspective

	Cancer Benchmark/MDL <1	Cancer Benchmark/MDL = 1 to 10	Cancer Benchmark/MDL >10
Median/MDL <1	Lower MDL is needed to be able to quantify annual average and qualitatively assess risk.	Upper limit of cancer risk is 10^{-6}. MDL is sufficient to estimate maximum risk.	Upper limit of risk is 10^{-7}. MDL is sufficient to determine that upper limit of risk is negligible.
Median/MDL = 1 to 10	Cancer risk is on the order of 1 in 10^{-5}. MDL is sufficient to estimate risk.	Cancer risk is on the order of 10^{-6}. MDL is sufficient to estimate risk.	Cancer risk is $<10^{-6}$. MDL is sufficient to determine that upper limit of risk is small.
Median/MDL >10	Cancer risk is quantifiable and $>10^{-5}$. MDL is sufficient to quantify risk.	Cancer risk is quantifiable and $>10^{-6}$. MDL is sufficient to quantify risk.	Cancer risk is quantifiable and on the order of 10^{-6}. MDL is sufficient to quantify risk.

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Risk Assessment Suitability: National Perspective (2000-2005)

	Cancer Benchmark/MDL <1	Cancer Benchmark/MDL = 1 to 10	Cancer Benchmark/MDL >10
Median/MDL <1	1,1,2,2-Tetrachloroethane 1,1,2-Trichloroethane 1,2-Dichloropropane 1,3-Butadiene Acrylonitrile Arsenic $PM_{2.5}$ Cadmium $PM_{2.5}$ Chromium VI Chromium $PM_{2.5}$ Ethylene dibromide Ethylene dichloride Hexachlorobutadiene Tetrachloroethene Vinyl Chloride	Bromoform 1,1-Dichloroethane 1,4-Dichlorobenzene Trichloroethene	Naphthalene
Median/MDL = 1 to 10	Carbon Tetrachloride Ethylene oxide	Nickel $PM_{2.5}$	
Median/MDL >10		Acetaldehyde Benzene	Formaldehyde

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Spatial Suitability

Key Toxics		Data Quality % data above MDL and/or other issues Unacceptable <20% above MDL or other issues * denotes species with other issues	Poor >20% above MDL	Moderate >40% above MDL	Good >60% above MDL	Very good >80% above MDL
Data Quantity # of cities with annual averages	Insufficient <10		Naphthalene		Ethylene Oxide	
	Low <40		Chromium VI			
	Medium <80	Acrolein*				
	High < 120					Acetaldehyde Formaldehyde
	Very High >120	1,1,2,2-Tetrachloroethane Bromomethane Chromium $PM_{2.5}$* Ethylene dibromide Cadmium $PM_{2.5}$ Nickel $PM_{2.5}$* Trichloroethene Vinyl chloride	1,4-Dichlorobenzene Chloroform Arsenic $PM_{2.5}$ Lead $PM_{2.5}$ Tetrachloroethene	1,3-Butadiene Carbon tetrachloride Dichloromethane Manganese $PM_{2.5}$	Lead (TSP)	Benzene *Ozone* *$PM_{2.5}$*

MDL = method detection limit, often calculated as the analytical blank + three times the standard instrument error (noise), yielding a value where concentrations are detectable with 99% confidence.

* Indicates pollutant's data quality was downgraded due to known measurement or risk estimation issues. Acrolein had measurement issues prior to 2005, and its data quality ranking was downgraded from moderate (based on data above MDL) to unacceptable. Chromium $PM_{2.5}$ and Nickel $PM_{2.5}$ do not measure the toxic component directly (Chromium VI or Nickel subsulfide) and therefore data quality was downgraded from poor (based on data above MDL) to unacceptable.

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Detection Limits are Too High!

- The monitoring community has done a great job of getting spatial coverage at hundreds of sites in the United States.
- Unfortunately, the data being collected are not very useful for risk analyses (except for identifying upper limits on some concentrations) or spatial variability analyses for most species.
- Better detection limits are needed.
  - Should we spend more money on better detection limits rather than on routine monitoring?
  - How can we improve collection or analysis methods to acquire more useful data?
    - Longer sampling times?
    - Improved analytical methods?
    - More pollutant-specific methods?

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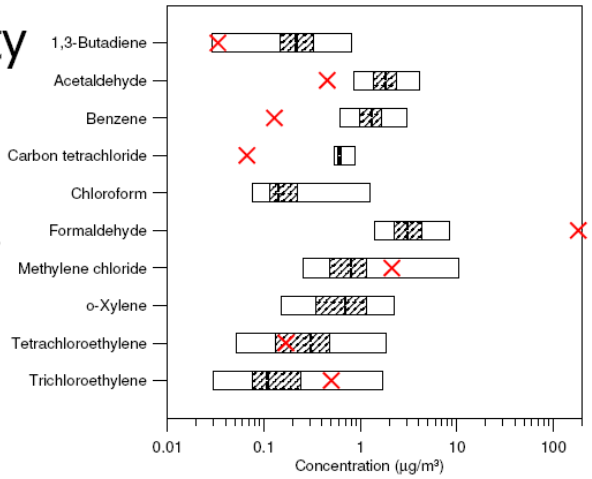
What Can We Do With the Data?

- Temporal variability
  - Diurnal
  - Seasonal
  - Interannual trends
- Spatial variability
  - Between cities
  - Within cities



x = 10^{-6} cancer benchmark
5th, 25th, 50th, 75th, 95th percentiles
of national urban concentrations shown

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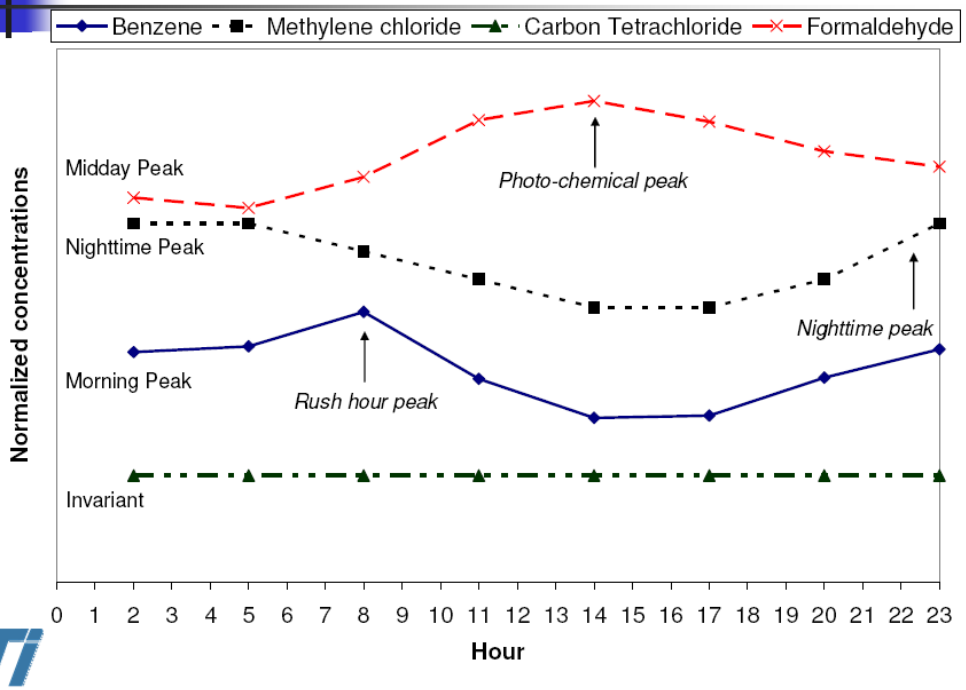
Diurnal Variability



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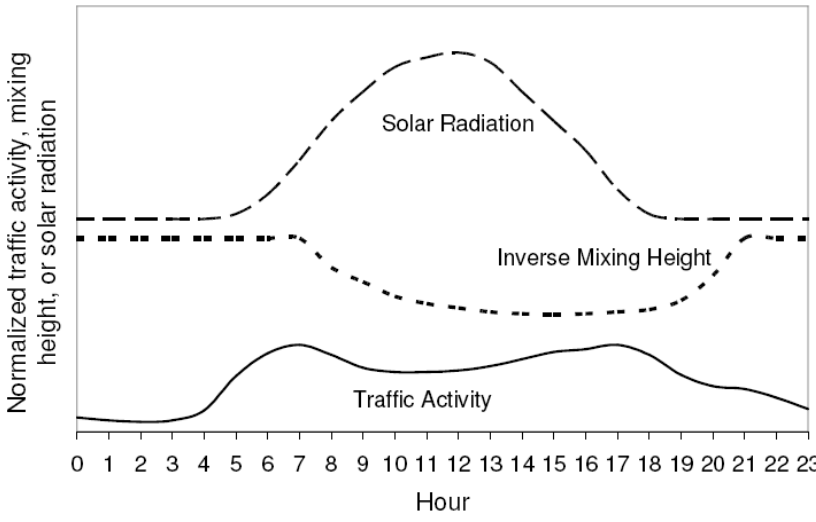
Diurnal Variability: What Is Causing the Observed Differences?



- Nighttime peak pollutants are dominated by ventilation from mixing heights
- Midday peak pollutants are dominated by the increased production driven by solar radiation
- Morning peak pollutants are a combination of traffic emissions and inverse mixing heights.

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Diurnal Variability Summary

Mobile Source	Mixing Height	Secondary Production
Benzene	Methylene chloride	Formaldehyde
o-Xylene	Chloroform	Acetaldehyde
1,3-Butadiene	Trichloroethylene	
m-Xylene		**Invariant**
Toluene		Carbon tetrachloride
Ethylbenzene		

? Tetrachloroethylene ?

Mobile source-dominated
Carbonyl compounds
Chlorinated
Metals
PAHs

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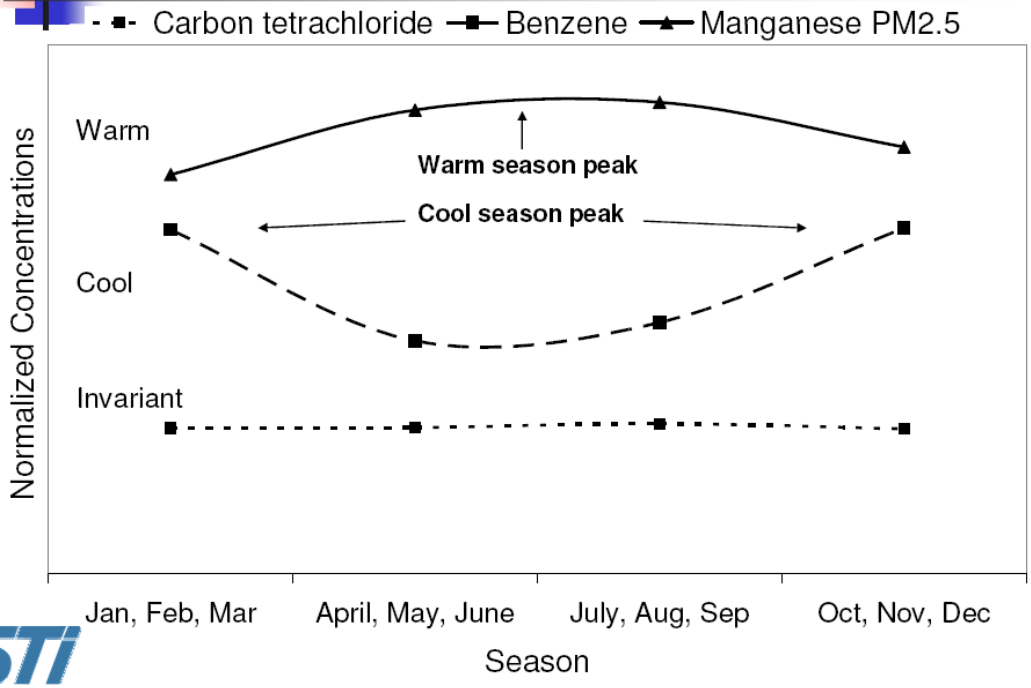
Seasonal Variability



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Seasonal Variability Summary

Cool Pattern	Warm Pattern	Invariant Pattern
Carbon monoxide	Ozone	Carbon tetrachloride
Sulfur dioxide	PM_{10}	Dichlorodifluoromethane
Nitrogen oxides	$PM_{2.5}$ – Crustal component	Trichlorofluoromethane
$PM_{2.5}$ elemental carbon	$PM_{2.5}$ sulfate	
$PM_{2.5}$ nitrate	$PM_{2.5}$ Organic carbon	
Benzene	Formaldehyde	
Toluene	Acetaldehyde	
1,3-Butadiene		
Methane		
Mostly primary	Secondary or higher emissions in summer	Background, not emitted locally or regionally

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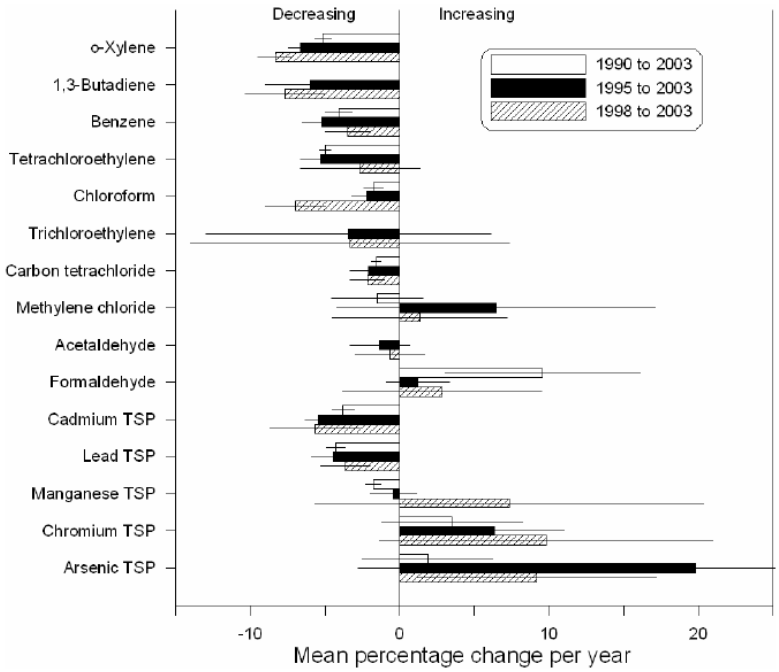
Trends in Air Toxics



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Trend Categories

Significant Decrease

o-Xylene
Benzene
1,3-Butadiene
Chloroform
Carbon tetrachloride
Cadmium (tsp)
Lead (tsp)

Decreased on Average

Acetaldehyde
Tetrachloroethylene
Trichloroethylene

Increased on Average

Formaldehyde
Chromium (tsp)
Arsenic (tsp)

Mixed Trends

Methylene chloride
Manganese (tsp)

Mobile source-dominated
Carbonyl compounds
Chlorinated
Metals
PAHs

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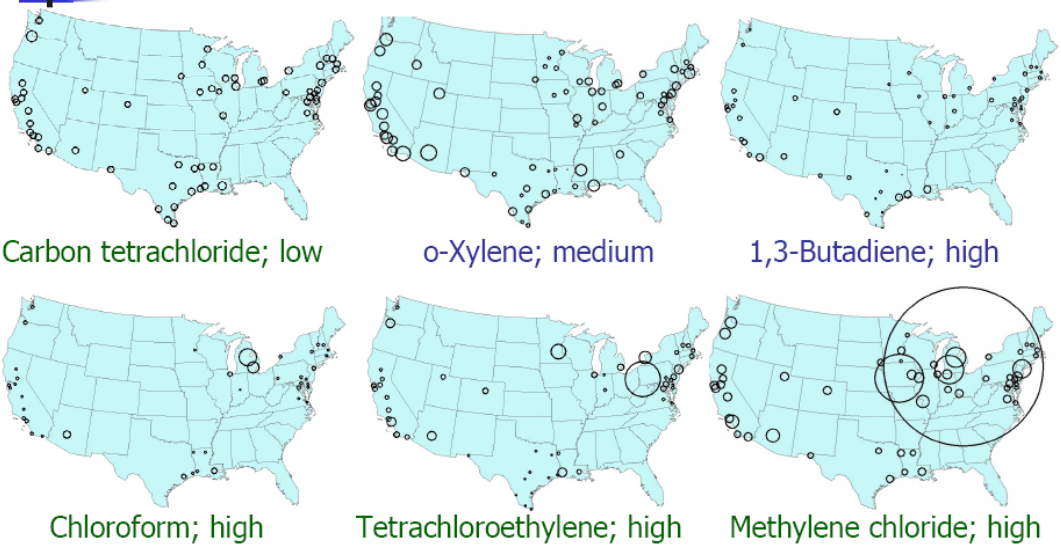
Spatial Variability in Citywide Average Concentrations of Gases



Carbon tetrachloride; low
o-Xylene; medium
1,3-Butadiene; high
Chloroform; high
Tetrachloroethylene; high
Methylene chloride; high

Note, circles on all maps represent the same concentration scale.

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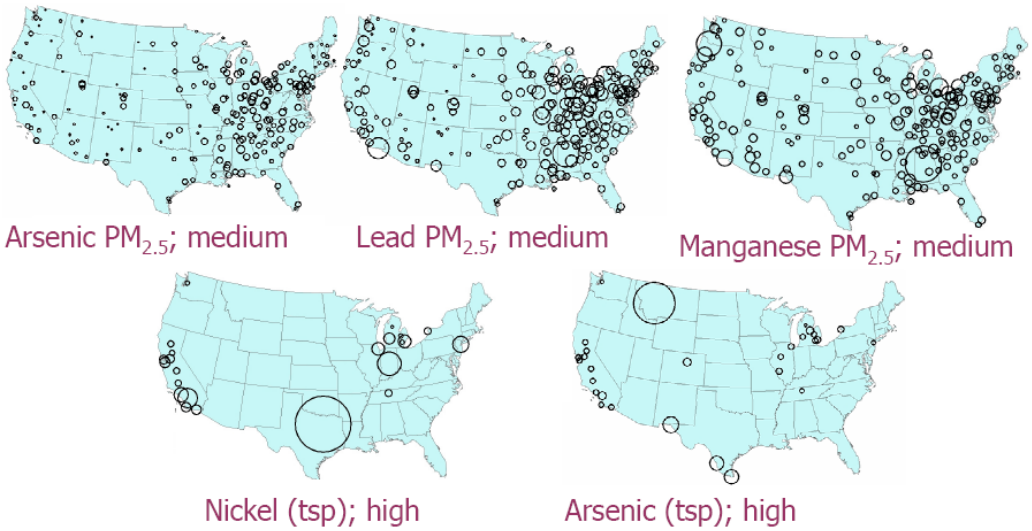
Spatial Variability in Citywide Average Concentrations of PM Metals



Arsenic $PM_{2.5}$; medium

Lead $PM_{2.5}$; medium

Manganese $PM_{2.5}$; medium

Nickel (tsp); high

Arsenic (tsp); high

Note, circles on all maps represent the same concentration scale.

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Between-city Spatial Variability Categories

Low	Medium	High
Carbon Tetrachloride	Formaldehyde	Chloroform
Benzene	Arsenic $PM_{2.5}$	Lead (tsp)
	Chromium (tsp) and $PM_{2.5}$	Nickel (tsp)
	Acetaldehyde	Arsenic (tsp)
	o-Xylene	Tetrachloroethylene
	Lead $PM_{2.5}$	Trichloroethylene
	Manganese (tsp) and $PM_{2.5}$	Methylene Chloride
	Nickel $PM_{2.5}$	
	1,3-Butadiene	

Note, pollutants are arranged in order of increasing spatial variability (i.e., Methylene Chloride had the highest variability).

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Conclusions

- Better detection limits are needed!
- Air toxics data are adequate to investigate national spatial and temporal trends.
- Air toxics are much more complicated than ozone and $PM_{2.5}$ with respect to diurnal, seasonal, annual, and spatial trends.

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Acknowledgments and References

- Thanks to the U.S. Environmental Protection Agency Office of Air Quality Policy and Standards for funding air toxics analyses
- References:
  - Kenski D., Koerber M., Hafner H.R., McCarthy M.C., and Wheeler N. (2005) Lessons learned from air toxics data: a national perspective. *Environ. Man. J.*, 19-22.
  - McCarthy M.C., Hafner H.R., and Chinkin L.R. (2006) Temporal variability of selected air toxics: a national perspective. (Submitted).
  - McCarthy M.C., Hafner H.R., and Chinkin L.R. (2006) Spatial variability of selected air toxics: a national perspective. (Submitted).

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Trends in Air Toxics

	1990 – 2003			1995 - 2003			1998 - 2003		
Pollutant	Median 1990 Concentration (µg/m³)	Mean % change and CI	# of sites (# with significant decrease)	Median 1995 Concentration (µg/m³)	Mean % change and CI	# of sites (# with significant decrease)	Median 1998 Concentration (µg/m³)	Mean % change and CI	# of sites (# with significant decrease)
o-Xylene	2.4	-72 ± 8	4 (3)	1.3	-60 ± 7	12 (10)	0.92	-50 ± 7	20 (6)
1,3-Butadiene	No Data			0.18	-54 ± 27	8 (4)	0.28	-46 ± 16	22 (7)
Benzene	3.7	-57 ± 13	8 (3)	2.4	-47 ± 12	24 (12)	1.9	-21 ± 9	33 (6)
Tetrachloroethylene	1.1	-70 ± 5	6 (6)	0.42	-48 ± 12	18 (4)	0.14	-16 ± 24	28 (3)
Chloroform	0.28	-25 ± 9	3 (0)	0.24	-20 ± 9	6 (0)	0.31	-42 ± 12	7 (4)
Trichloroethylene	No Data			0.11	-31 ± 86	9 (3)	0.082	-20 ± 64	21 (1)
Carbon tetrachloride	0.76	-22 ± 4	2 (0)	0.71	-19 ± 11	5 (0)	0.68	-13 ± 7	10 (0)
Methylene chloride	1.2	-21 ± 43	2 (1)	0.79	58 ± 96	5 (0)	0.69	8 ± 35	9 (0)
Acetaldehyde	No Data			1.6	-12 ± 18	9 (1)	1.7	-4 ± 14	12 (0)
Formaldehyde	1.0	134 ± 91	6 (0)	2.5	11 ± 19	16 (0)	2.4	17 ± 40	18 (1)
Cadmium TSP	0.0072	-53 ± 10	6 (4)	0.0030	-49 ± 8	6 (6)	0.0022	-34 ± 18	6 (1)
Lead TSP	0.20	-60 ± 9	85 (58)	0.096	-40 ± 13	72 (24)	0.073	-22 ± 10	61 (8)
Manganese TSP	0.033	-25 ± 7	20 (10)	0.029	-4 ± 14	22 (4)	0.027	44 ± 78	20 (2)
Chromium TSP	0.0066	49 ± 66	8 (2)	0.0043	57 ± 42	9 (0)	0.0051	59 ± 67	12 (0)
Arsenic TSP	0.0016	26 ± 61	15 (7)	0.0014	178 ± 203	15 (1)	0.0018	55 ± 48	16 (0)

Mean percentage change and confidence interval (CI) in air toxics concentrations from 1990, 1995, or 1998 through 2003 at all sites. The number of sites and number of sites with decreasing trends are also shown.

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Collection and Analysis of Acrolein using Compendium Method TO-15

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ABSTRACT
Acrolein, because of its polarity and reactivity, is recovered more efficiently in canister samples using EPA Compendium Method TO-15 with Gas Chromatography/Mass Spectroscopy (GC/MS) and selective ion monitoring (SIM) than the previously used Compendium Method TO-11A. Determination of acrolein by Method TO-11A is less accurate because of the low acrolein capture efficiency and the tautomerization of the acrolein hydrazone derivative on acidified 2, 4-dinitrophenylhydrazine (DNPH) cartridges. Eastern Research Group (ERG) has demonstrated this superior performance of canister sampling through the results of a study that introduced a gaseous acrolein standard, representative of "real world" samples, concurrently into DNPH cartridges and canisters. A field study comparison of the collection efficiency of acrolein using Method TO-15 and Method TO-11A will be presented for samples simultaneously collected throughout the country for one year in canister and cartridge samples. Data using Method TO-15 collection and analysis of ambient air across the United States will be presented to show the recovery of acrolein in canister samples. Audit results will be presented proving the accuracy of acrolein from canister samples using Method TO-15.

INTRODUCTION
Acrolein is listed as one of the four core compounds for the National Air Toxics Trends System (NATTS) throughout the country. Because of this, and because of the reactivity and toxicity of acrolein in ambient air, ERG has been studying new techniques to collect and analyze acrolein more accurately. Method TO-11A has been the standard method the analysis of aldehydes in ambient air. ERG has not reported analytical results for the measurement of acrolein since 1999 because of its unstable retention on the adsorbent cartridges used for Compendium Method TO-11A. An Addendum to Method TO-11A was issued March, 1999 to remove acrolein from the analyte list. Recently, ERG has determined that acrolein can be analyzed more accurately using Compendium Method TO-15 from air samples in canisters. Method TO-15 is an analytical method currently used for the sampling and analytical procedures for the measurement of subsets of volatile organic compounds that are included in the 1989 hazardous air pollutants (HAPs) listed in the Title III of the Clean Air Act Amendments of 1990.

The following data present the comparison of two compendium methods as well as the precision and accuracy following Method TO-15.

Methodology
DNPH treated cartridges and SUMMA canisters were used to collect ambient samples at the same sampling site. These samples are taken at the same time on the same sampling systems. The canisters and cartridges were collected for 24 hours. Canisters collect 6L of whole air, whereas the carbonyl tubes concentrate and stabilize carbonyl compounds from a volume of air. ERG collects and analyzes all canister samples at a vacuum from 1 to 12 inches of Hg to

ensure volatile organic compounds remain in the vapor phase. If the canister is pressurized, condensation of water from high-humidity samples may cause fractional losses of polar, water-soluble compounds.

Method Development – Method TO-11A

Method TO-11A, the standard method for the analysis of aldehydes in ambient air, demonstrates low recovery for acrolein. A recent study conducted by ERG used a certified standard of gaseous acrolein rather than liquid DNPH derivative spikes to simulate a real world sample. The certified cylinder was used to sample underivatized acrolein through a sampling system onto the DNPH cartridges.

Four sample sets (i.e., duplicate paired carbonyl cartridges) were collected from a common test manifold, one set every 24 hours over a period of 4 days. After the samples were collected, the cartridges were extracted within 7 days of sampling and analyzed within 30 days of extraction. Table 1 presents the sample recovery results. Because the recovery was consistently below acceptable limits, ERG decided to evaluate acrolein analysis by TO-15.

Table 1: Carbonyl Recovery Data -Modified Method TO-11A, Gaseous Samples

Sample	Acrolein[a] (two peaks)	
	Conc. Recovered (ppbv)	Percent Recovery
Sample Run 1 – Primary	2.55	43%
Sample Run 1 – Duplicate	2.18	37%
Sample Run 2 – Primary	2.59	44%
Sample Run 2 – Duplicate	2.33	39%
Sample Run 3 – Primary	2.47	42%
Sample Run 3 – Duplicate	2.32	39%
Mean ± Standard Deviation	2.41 ± 0.16	41% ± 3%

[a] Acrolein nominal concentration is 5.92 ppbv.

Method Development – Method TO-15

Acrolein was measured using Method TO-15 without altering the analytical method currently used to determine the toxics compounds reported to the EPA for the Urban Air Toxics Monitoring Program (UATMP). Acrolein was stable in calibration standards and could be separated from other Method TO-15 compounds using conditions recommended in the method.

The goal was to try to determine acrolein at low enough concentrations (at or below risk levels) without major modifications to the current method. Reaching low detection limits required the use of Gas Chromatography/Mass Spectroscopy (GC/MS) with selective ion monitoring (SIM). MDLs are determined at the ERG analytical laboratory using 40 CFR, Part 136 procedures. ERG's experimentally determined MDL for acrolein is 0.10 ppbv (0.23 $\mu g/m^3$) for 2006.

To evaluate field sample collection, a canister sample was collected through a NATTS TO-15 sampler spiked with gaseous acrolein. Results from the analysis of this single sample showed acceptable recovery for acrolein of ± 10 percent.

ERG then examined acrolein recovery and stability using Method TO-15. Multiple canisters from different manufacturers were spiked with know amounts of acrolein and analyzed several times over a period of 4 weeks. The relative percent difference (RPD) between time zero (Week 1) and subsequent analysis for this study is shown in Table 2.

Table 2: Acrolein Stability in Canisters Expressed in RPD

Sample ID	Relative humidity	Concentration (ppbv)	RPD		
			Week 2	Week 3	Week 4
1-1	10%	Low – 0.5	10.5%	ND	ND
1-2		High – 10	5.04%	-4.47%	9.68%
1-3	80%	Low – 0.5	0%	ND	ND
1-4		High – 10	0%	-2.05%	-0.79%
2-1	10%	Low – 0.5	2.74%	-2.67%	-2.67%
2-2		High – 10	NA	8.76%	14.8%
2-3	80%	Low – 0.5	8.89%	-2.11%	**-27.5%**
2-4		High – 10	0.29%	-0.66%	13.9%
3-1	10%	Low – 0.5	2.99%	-2.90%	-16.2%
3-2		High – 10	7.50%	16.2%	**27.1%**
3-3	80%	Low – 0.5	-8.00%	**40.0%**	ND
3-4		High – 10	-10.2%	-16.7%	10.1%
4-1	10%	Low – 0.5	**-26.2%**	**-36.9%**	**-43.0%**
4-2		High – 10	3.65%	5.56%	3.56%
4-3	80%	Low – 0.5	7.06%	-6.59%	-16.7%
4-4		High – 10	-0.35%	-9.67%	12.5%

NA = Not applicable – analytical malfunction.
ND = Not detected.
NOTE: Results listed in **bold** are outside the required RPD of 25%.

Acrolein recovery over four weeks was within acceptable range. The stability at the low concentration and humidity is less than the high concentration and humidity. This study supports the ability to report acrolein concentrations for NATTS and UATMP sites across the country.

After the stability study was completed, the Rhode Island Department of Health Laboratory reported acrolein concentrations increased in ambient air canisters within a short period of time after collection. To investigate the Rhode Island observation, ERG performed a short-term stability study. Grab samples were taken on an overpass above a heavily traveled highway. This

allowed elevated levels of acrolein from mobile sources emissions to be present in the canisters. Table 3 presents the results of this study. Because of the close chemical structure of acrolein and 1,3-butadiene, recoveries for both compounds are presented. Results are presented for the analysis performed directly after sampling, 24 hours after sampling, and pressurized samples. As shown, there was no statistical differences in the results with the exception of Canister 2080, which had variance over the NMP data guidelines of 25%.

Table 3: Ambient Air Stability Study

ANALYZED IMMEDIATELY AFTER COLLECTION				
Canister ID 068				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**% RPD**
6/23/2006 13:04	0.29		2.15	
6/23/2006 15:27	0.27	7.1%	2.05	4.8%
6/23/2006 17:49	0.23	23.1%	2.02	6.2%
Canister ID EP0763				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**RPD**
6/23/2006 14:15	0.55		3.18	
6/23/2006 16:38	0.51	7.5%	3.10	2.5%
6/23/2006 18:59	0.51	7.5%	3.07	3.5%
ANALYZED 24 HOURS AFTER COLLECTION				
Canister ID 2080				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**RPD**
6/2/2006 21:12	0.37		2.95	
6/3/2006 4:05	0.51	**31.8%**	2.99	1.3%
6/3/2006 20:48	0.56	**40.9%**	2.99	1.3%
6/4/2006 1:30	0.55	**39.1%**	2.76	6.7%
6/4/2006 18:13	0.46	21.7%	2.8	5.2%
Canister ID ER019				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**RPD**
6/2/2006 22:22	0.33		1.69	
6/3/2006 5:16	0.31	6.3%	1.66	1.8%
6/3/2006 21:58	0.32	3.1%	1.67	1.2%
6/4/2006 2:41	0.32	3.1%	1.61	4.8%
6/4/2006 19:23	0.35	5.9%	1.66	1.8%

ANALYZED 24 HOURS AFTER COLLECTION – INITIALLY PRESSURIZED				
Canister ID TX007				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**RPD**
6/5/2006 10:24 2.5 psi	1.18		6.2	
6/6/2006 13:45 (0" Hg)	1.23	4.1%	5.84	6.0%
6/6/2006 18:29 (<0 "Hg)	1.28	8.1%	6.85	10.0%
6/6/2006 23:12 (<0 "Hg)	1.18	0.0%	5.58	10.5%
6/7/2006 3:56 (<0" Hg)	1.18	0.0%	5.59	10.3%
6/7/2006 8:41 (< 0" Hg)	1.23	4.1%	5.67	8.9%
Canister ID 2240				
Time	**Acrolein (ppbv)**	**RPD**	**1,3-Butadiene (ppbv)**	**RPD**
6/5/2006 9:11 (2.5 psi)	1.85		8.87	
6/6/2006 14:56 (0" Hg)	1.9	2.7%	8.33	6.3%
6/6/2006 19:39 (<0 "Hg)	1.83	1.1%	8.35	6.0%
6/7/2006 0:23 (<0 "Hg)	1.88	1.6%	8.2	7.9%
6/7/2006 5:07 (<0" Hg)	1.86	0.5%	8.26	7.1%
6/7/2006 9:52 (<0 "Hg)	1.77	4.4%	7.76	13.3%

NOTE: Results listed in **bold** are outside the required RPD of 25%.

Compendium Method Comparison

ERG has collected acrolein from the National Monitoring Program sites (NMP) since July 2005 following Method TO-15. To demonstrate the percent differences between the two methods, Table 4 presents results for Method TO-11A versus TO-15. Percent recovery of Method TO11A assumes the Method TO-15 results represent acrolein concentration in these ambient air samples.

Table 4: Method TO-11A versus Method TO-15

Site	Date	TO-11A (ppbv)	TO-15 (ppbv)	% Recovery of TO-11A
Bountiful, UT	9/13/05	0.114	3.17	3.6%
Loudon, TN	10/13/05	0.040	1.10	3.6%
Providence, AL	10/19/05	0.059	1.20	4.9%
Birmingham, AL	10/19/05	0.137	1.46	9.4%
Shillar Park, Chicago, IL	10/31/05	0.085	1.08	7.9%
Madison, WI	11/12/05	0.049	0.47	10.4%
Barceloneta, Puerto Rico	11/12/05	0.024	0.84	2.9%
Minneapolis, MN	11/18/05	0.018	1.21	1.5%
Camden, NJ	12/24/05	0.186	0.78	23.8%
New Brunswick, NJ	12/30/05	0.040	1.18	3.4%
Sioux Falls, SD	2/28/06	0.089	0.56	15.9%
Grand Junction, CO	3/24/06	0.099	0.58	17.1%

Site	Date	TO-11A (ppbv)	TO-15 (ppbv)	% Recovery of TO-11A
Austin, TX – site 1	4/23/06	0.054	0.48	11.3%
Austin, TX – site 2	4/23/06	0.037	0.39	9.5%
Austin, TX – site 3	4/23/06	0.035	0.58	6.0%
Austin, TX – site 4	4/23/06	0.036	0.53	6.8%
Austin, TX – site 5	4/23/06	0.089	0.45	19.8%
Custer Park, SD	5/17/06	0.044	0.74	5.9%
Elizabeth, NJ	5/29/06	0.192	0.66	29.1%
Tulsa, OK	5/29/06	0.121	0.82	14.8%

The recoveries of acrolein are clearly much lower for Method TO-11A than for Method TO-15 in a real field samples.

Method TO-15 Field Sample Results for Acrolein

Nineteen NMP sites collected samples from July 2005 to July 2006. Some monitors were placed near the centers of heavily populated cities (e.g., Chicago, IL and St. Louis, MO), while others were placed in moderately populated areas (e.g., Madison, WI and Custer, SD). Acrolein concentrations measured during this time varied significantly from monitoring location to monitoring location. The proximity of the monitoring locations to different emissions sources, especially industrial facilities and heavily traveled roadways, often explains the observed spatial variations in ambient air quality.

A total of 1,450 acrolein measurements (including duplicate and replicate samples) were detected at the 43 NMP sites from July 2005 to July 2006. Five hundred and sixteen of these samples were taken at four sites during the clean-up after Hurricane Katrina. Of the 1,450 acrolein measurements, 54 % of these results were detects and 1.2% of these concentrations were below the MDL. The average acrolein concentration was 1.54 µg/m^3. Table 5 presents the sample count, maximum value, minimum detected value, median, mean for this data set.

Table 5: Analytical Results for Samples Collected Between July 2005 and June 2006

Site ID	Frequency of Detects	Maximum Value (µg/m3)	Minimum Value (µg/m3)	Median (µg/m3)	Average (µg/m3)
Austin, TX (site 1)	90%	13.25	0.71	2.93	4.33
Austin, TX (site 5)	80%	11.64	1.17	3.36	4.09
Austin, TX (site 3)	85%	16.49	0.60	1.73	3.87
Austin, TX (site 4)	80%	12.17	0.35	1.22	3.71
Austin, TX (site 2)	86%	15.85	0.28	1.45	3.34
El Paso, TX	63%	22.57	0.23	0.77	2.57
Dickson, TN	50%	3.54	0.62	2.30	2.26
Tulsa, OK (site 3)	100%	3.20	0.76	1.81	1.92

Site ID	Frequency of Detects	Maximum Value (µg/m3)	Minimum Value (µg/m3)	Median (µg/m3)	Average (µg/m3)
Chester, NJ	89%	5.82	0.12	1.17	1.90
Madison, WI	72%	6.33	0.35	0.67	1.82
Detroit, MI (site 2)	11%	1.81	1.81	1.81	1.81
Custer Park, SD	98%	5.73	0.28	1.29	1.80
Bountiful, UT	88%	7.29	0.37	1.36	1.61
Peterson, NJ (site 3)	100%	3.68	0.35	1.01	1.57
Sioux Falls, SD	98%	5.61	0.44	0.90	1.46
Loudon, TN (site 2)	100%	2.71	0.32	1.45	1.46
Barceloneta, Puerto Rico	84%	6.49	0.16	1.07	1.39
New Brunswick, NJ	90%	2.88	0.30	1.01	1.36
Grand Junction, CO	98%	3.59	0.30	1.28	1.34
Chicago, IL (site 2)	66%	3.57	0.28	0.78	1.34
Detroit, MI (site 3)	20%	1.31	1.31	1.31	1.31
San Juan, Puerto Rico	100%	2.78	0.35	1.12	1.31
Peterson, NJ (site 1)	100%	2.48	0.60	1.05	1.29
Tulsa, OK (site 1)	100%	2.35	0.64	1.06	1.27
Gulf Port, MS	90%	4.23	0.16	1.07	1.21
Pascagoula, MS	61%	3.59	0.14	0.95	1.21
Birmingham, AL (site 2)	76%	3.36	0.23	0.85	1.18
Stennis Airport, MS	60%	5.36	0.16	0.94	1.16
Tupelo, MS	63%	2.39	0.14	0.79	1.03
Minneapolis, MN	91%	2.78	0.18	0.80	1.01
North Birmingham, AL	83%	2.14	0.32	0.76	0.95
Elizabeth, NJ	94%	3.80	0.12	0.58	0.93
Chicago, IL (site 1)	92%	2.94	0.16	0.64	0.90
Kenner, LA	79%	2.70	0.18	0.76	0.89
Birmingham, AL (site 1)	62%	1.99	0.18	0.64	0.89
Peterson, NJ (site 2)	91%	1.77	0.25	0.78	0.83
St. Louis, MO	72%	1.72	0.14	0.63	0.78
Loudon, TN (site 1)	83%	2.53	0.30	0.58	0.77
Camden, NJ	95%	1.79	0.25	0.77	0.76
Detroit, MI (site 1)	83%	2.25	0.18	0.55	0.76
Providence, AL	58%	2.76	0.16	0.23	0.75
Sault Sainte Marie, MI	100%	1.35	0.35	0.40	0.63
Tulsa, OK (site 2)	100%	0.58	0.58	0.58	0.58
Detroit, MI (site 4)	36%	0.58	0.27	0.42	0.42
Average	80%	22.57	0.12	1.08	1.54

Data from the NMP sites are shown in Figure 1. The highest concentration were taken at El Paso, TX, at 9.59 ppbv (22.57 µg/m^3). Because of the large amount of samples taken for Hurricane Katrina, data from these sites are shown separately in Figure 2. These samples were collected on a 1-in-1 and 1-in-3 day schedules. These data are presented in Figure 2 using the same scale as Figure 1. Acrolein results from the NMP and Katrina sites are relatively the same and show similar increases or decreases over time.

Figure 1: Analytical Acrolein Results for Samples Collected Between July 2005 and June 2006

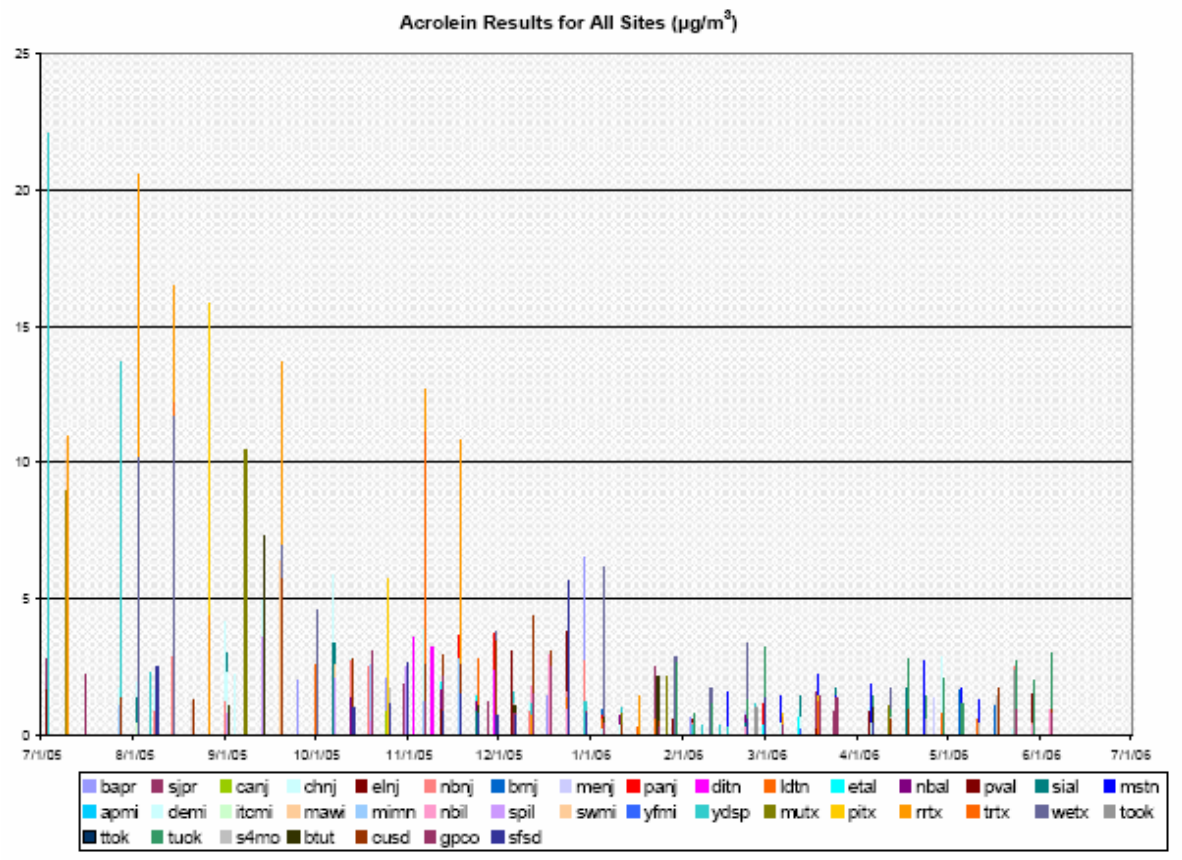
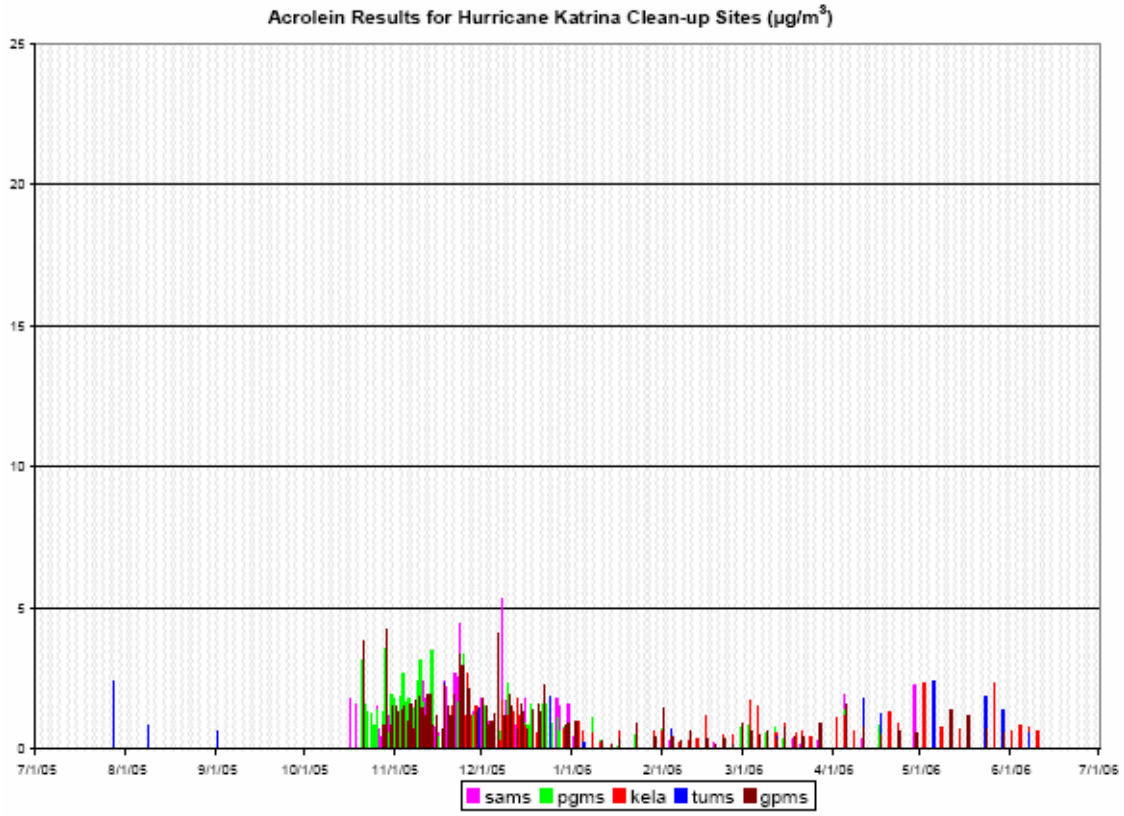


Figure 2: Katrina Acrolein Results for Samples Collected Between July 2005 and June 2006



Data Quality Control and Assurance

An audit containing acrolein was prepared in November, 2005 by US EPA and sent to ERG for analysis. Table 6 presents a summary of the audit report. The acrolein concentration determined by ERG resulted in a 22.3 RPD from the nominal value spiked in the canister. The 'True' value was based on the results of 3 analyses performed by Alion/EPA(ORD).

Table 6: Acrolein Audit Results

Compound	ERG (ppbv)	True (ppbv)	% Difference	Uncertainty
Acrolein	1.48	1.21	22%	± 11.3%
1,3-Butadiene	1.84	1.44	28%	± 0.2%

NOTE: The percent uncertainty is the coefficient of variation for the three replicate analyses.

Precision of the analytical and sampling technique was determined by the analysis of duplicate sampling episodes and replicate analysis. A duplicate sample (i.e., a sample collected simultaneously with a primary sample using the same sampling system) provides information on the potential for analytical variability. The duplicate and replicate analysis results were complied from sites sampling in the NMP from July, 2005 through June, 2006.

The data are presented in Relative Percent Difference (RPD) and the Coefficient of Variation (CV). The RPD expresses average concentration differences relative to the average concentration detected during replicate analyses. The RPD is calculated as follows:

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100 \quad (1)$$

Where:

X_1 is the ambient air concentration of a given compound measured in one sample;
X_2 is the concentration of the same compound measured during duplicate or replicate analysis; and
X is the arithmetic mean of X_1 and X_2.

As this equation shows analyses with low variability have lower RPDs (and better precision), and analyses with high variability have higher RPDs (and poorer precision). The RPD method quality objective for all data from the NMP is 25 percent. The replicate data show very good precision with a few outliers present. As shown in Table 7, the overall compound by compound average shows very good precision for replicate analyses at 5.82 percent.

Table 7: Replicate Analysis Results (July 2005 to June 2006)

Site ID	# of Duplicates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Loudon, TN	7	14%	15%	14%
San Juan, Puerto Rico	6	12%	11%	10%
Dickson, TN	1	11%	11%	0%
Austin, TX (site 2)	1	10%	10%	0%
Kenner, LA	19	10%	14%	22%
Pascagoula, MS	22	7%	7%	7%
Stennis Airport, MS	20	7%	8%	6%
Austin, TX (site 1)	1	6%	6%	0%
Austin, TX (site 3)	1	6%	6%	0%
Birmingham, AL (site 2)	4	6%	7%	7%
Austin, TX (site 4)	1	4%	4%	0%
Peterson, NJ (site 3)	2	4%	4%	2%
North Birmingham, AL	4	4%	7%	9%
Austin, TX (site 5)	28	4%	8%	10%
Peterson, NJ (site 1)	4	3%	4%	4%
Sioux Falls, SD	8	3%	4%	4%
Gulf Port, MS	22	2%	4%	5%

Site ID	# of Duplicates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Grand Junction, CO	14	1%	6%	9%
Custer Park, SD	8	1%	3%	7%
Barceloneta, Puerto Rico	8	0%	5%	8%
Chester, NJ	12	0%	2%	4%
Elizabeth, NJ	14	0%	1%	3%
New Brunswick, NJ	12	0%	3%	4%
Peterson, NJ (site 3)	6	0%	3%	4%
Tupelo, MS	12	0%	3%	9%
Detroit, MI	28	0%	4%	5%
El Paso, TX	29	0%	3%	6%
St. Louis, MO	11	0%	1%	3%
Bountiful, UT	12	0%	5%	9%
Average	11	4%	6%	6%

The duplicate data show method precision that is not as consistent as the replicate analyses. Results outside the 25% RPD objective can be grouped into two sets. Results with few detectable results show high average but low median results. Other sites show one set of duplicates with high RPD which skews the average RPD above the quality objective. For example, San Juan, Puerto Rico presents a high average of 47 percent, but the median is acceptable at 14 percent. Three duplicate sets were taken and only one of those failed, causing the average to exceed the acceptable limit. Bountiful, UT, Peterson, NJ (site 2), and Grand Junction, CO had similar instances. Other factors, such as unknown sampler/operator errors or canister variance, are possible explanations for high average RPD results. Table 8 presents the overall data average results at 32%, which is slightly over the 25% target.

Table 8: Duplicate Statistical Data Results (July 2005 to June 2006)

Site ID	# of Duplicates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Peterson, NJ (site 3)	1	**80%**	**80%**	26%
Sioux Falls, SD	4	**52%**	**61%**	40%
Barceloneta, Puerto Rico	4	**46%**	**68%**	72%
Kenner, LA	10	**37%**	**50%**	67%
Austin, TX (site 5)	12	**33%**	**47%**	68%
Bountiful, UT	5	21%	**60%**	26%
Peterson, NJ (site 2)	3	21%	**49%**	25%
Birmingham, AL (site 2)	2	16%	16%	41%
San Juan, Puerto Rico	3	14%	**47%**	25%
North Birmingham, AL	2	10%	10%	31%
Pascagoula, MS	11	9%	17%	53%

Site ID	# of Duplicates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Stennis Airport, MS	13	6%	21%	58%
Detroit, MI	7	6%	25%	74%
Grand Junction, CO	6	6%	**41%**	23%
Loudon, TN	3	6%	5%	22%
Gulf Port, MS	11	5%	**27%**	59%
Custer Park, SD	4	5%	5%	47%
El Paso, TX	15	4%	17%	0%
New Brunswick, NJ	6	2%	14%	71%
Tupelo, MS	6	1%	12%	14%
Peterson, NJ (site 1)	4	1%	21%	6%
Chester, NJ	5	0%	23%	29%
St. Louis, MO	5	0%	12%	4%
Average	6	16%	**32%**	38%

NOTE: Results listed in **bold** are outside the required RPD of 25%.

SUMMARY

ERG has determined that Method TO-11A results for acrolein show a significant negative bias. ERG's audit recovery and stability testing demonstrate acceptable results using Method TO-15 for the analysis of acrolein. Comparison to Method TO-11A, demonstrated the acceptable recovery of Method TO-15 analysis using Gas Chromatography/Mass Spectrometry/Selected Ion Monitoring (GC/MS/SIM) for analysis of real field samples for acrolein.

ACKNOWLEDGMENTS

The authors would like to express their appreciation for the hard work and dedication shown by the U.S. EPA, OAQPS staff and Eastern Research Group's laboratory.

REFERENCES

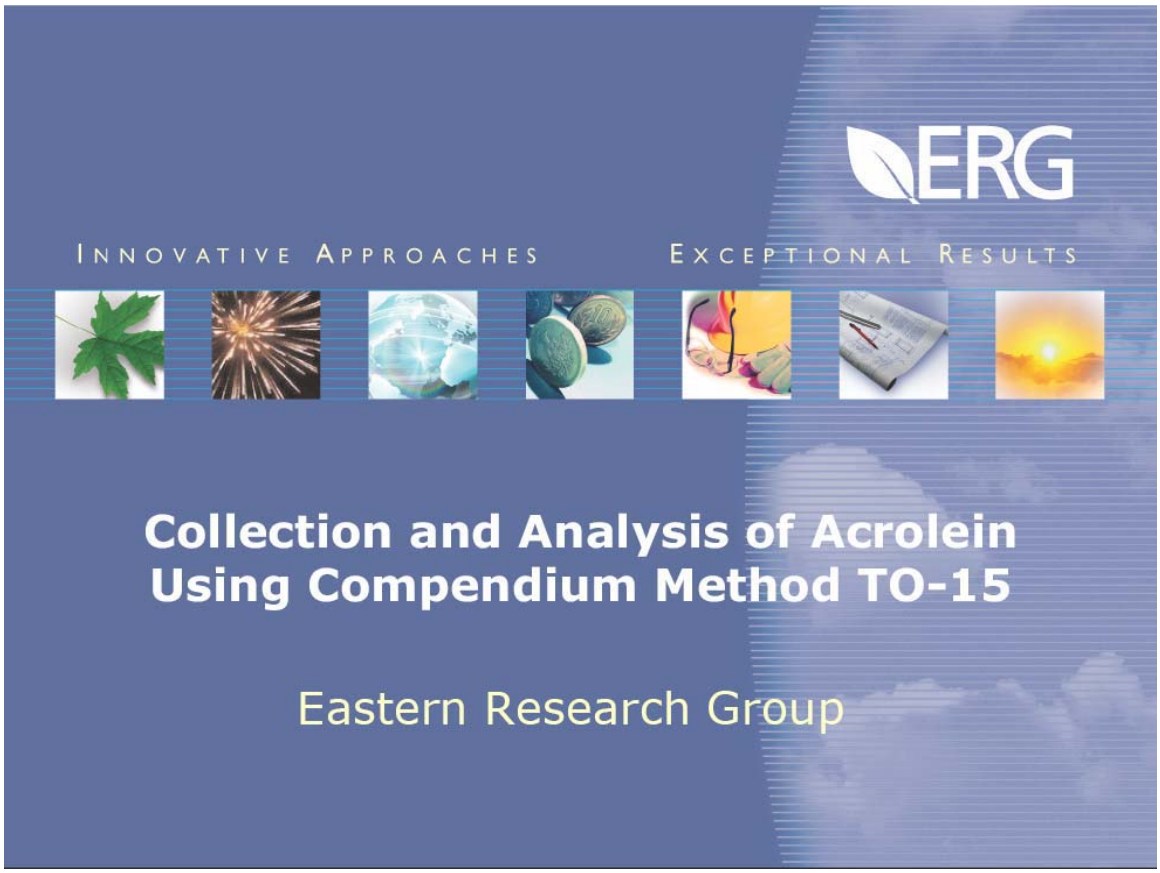
1. U.S. Environmental Protection Agency, 1999. *Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*. EPA-ORD, Cincinnati, Ohio.

2. U.S. Environmental Protection Agency, 1999. *Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)*. EPAORD, Cincinnati, Ohio.

3. U.S. Environmental Protection Agency. *Carbonyl Recovery and Stability Study in Canisters.* Swift, J.; Merrill, R.; Tedder, D. J. Homolya, Delivery Order Manager. Research Triangle Park, NC.

4. U.S. Environmental Protection Agency. *Standard Operating Procedure for the GC/MS Analysis of Acrolein in Canister Air Samples.* Tedder, D.; Swift, J.; Merrill, R.; J. Homolya, Delivery Order Manager. Research Triangle Park, NC.

5. E-mail correspondence from Michael Jones, EPA/OAQPS dated 6/8/06 regarding laboratory work performed by the Rhode Island Department of Health Laboratory.



Introduction

- Acrolein is listed as one of the core NATTS compounds
- Because of its reactivity, acrolein in ambient air samples presents an analytical challenge
- Penetrates biological membranes, strong dermal irritant, inhalation irritant and possible human carcinogen
- Cancer Risk level – 0.018 µg/m^3

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Possible Active Methods of Acrolein Determination

- Air samples collected on Dinitrophenylhydrazine (DNPH) cartridges, analyzed by Method TO-11A on an HPLC
- Air samples collected in stainless steel canisters, analyzed by Method TO-15 on a GC/MS SIM

ERG

3

Acrolein Determination by Method TO-11A

- Method TO-11A is based on a specific reaction of organic carbonyls with the DNPH on the sample cartridges in the presence of a strong acid
- Samples are extracted within 2 weeks of sampling
- Extracts are analyzed within 30 days of sample preparation

ERG

4

Potential Problems with Method TO-11A for Acrolein

- Acrolein appears to break down on the DNPH cartridge to form a second derivative peak after sampling
- The second peak coelutes with a Method TO-11A target peak

ERG

5

Method Development – Method TO-11A

- Simulated "real world" conditions by using a gaseous blend of carbonyls
- Blended a 100 ppv ±10% gas with clean humidified air to a nominal concentration of 5.92 ppbv
- Collected duplicate samples through a carbonyl sampler and analyzed by Method TO-11A adding the two separate acrolein peaks

ERG

6

Acrolein Recovery using TO-11A (Gaseous Standard)

Sample	Acrolein [a] (two peaks)	
	Conc. Recovered (ppbv)	Percent Recovery
Sample Run 1 – Primary	2.55	43%
Sample Run 1 – Duplicate	2.18	37%
Sample Run 2 – Primary	2.59	44%
Sample Run 2 – Duplicate	2.33	39%
Sample Run 3 – Primary	2.47	42%
Sample Run 3 – Duplicate	2.32	39%
Mean ± Standard Deviation	2.41 ± 0.16	41% ± 3%

[a] Acrolein nominal concentration is 5.92 ppbv.

ERG

7

Method Development – Method TO-15

- Simulated "real world" conditions by using a gaseous blend of carbonyls
- Blended a 100 ppv ±10% gas with clean humidified air to a nominal concentration of 5.92 ppbv
- Collected duplicate samples through a canister sampler
- Recovered 90% of acrolein following Method TO-15

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8

Acrolein using Method TO-15 (SIM Mode)

- Monitor Ions 55 and 56
- Acceptable calibration from 0.25 ppbv to 15.0 ppbv
- 2006 Method Detection Limit of 0.10 ppbv (0.23 µg/m^3)

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9

Stability Study of Acrolein in Canister Samples

- Sixteen acrolein samples were prepared in canisters
- Low and high humidity
- Low and high concentration
- Samples were analyzed on Days 0, 7, 14, 21, 28

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10

Method TO-15 Stability Study – Average RPD

Condition	% RPD				
	Week 1	Week 2	Week 3	Week 4	Average
Relative % Humidity					
Low -10%	-3.86%	0.89%	-2.35%	-0.96%	-1.57%
High - 80%	1.00%	-0.29%	0.32%	-1.42%	-0.10%
Concentration (ppbv)					
Low - 0.5 ppbv	-11.15%	-0.25%	-1.86%	-21.21%	-8.62%
High – 10 ppbv	8.29%	0.85%	-0.38%	11.36%	5.03%

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11

Acrolein Initial Stability Study

- Rhode Island Dept of Health Labs reported noticed increase immediately after sampling
- Performed short-term stability study
- Took grab samples on an overpass above a heavily traveled highway
- Recoveries for 1,3-Butadiene is presented also because of its close chemical structure to acrolein
- Canisters with nothing detected held for 1 week with no increase in detection (still not detected).

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12

Ambient Air Stability Study – Part 1 of 3

Analyzed Sample Immediately After Collection

Canister ID 068

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/23/2006 13:04	0.29		2.15	
6/23/2006 15:27	0.27	7.1%	2.05	4.8%
6/23/2006 17:49	0.23	23.1%	2.02	6.2%

Canister ID EP0763

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/23/2006 14:15	0.55		3.18	
6/23/2006 16:38	0.51	7.5%	3.10	2.5%
6/23/2006 18:59	0.51	7.5%	3.07	3.5%

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13

Ambient Air Stability Study – Part 2 of 3

Analyzed Sample 24 Hours After Collection

Canister ID 2080

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/2/2006 21:12	0.37		2.95	
6/3/2006 4:05	0.51	**31.8%**	2.99	1.3%
6/3/2006 20:48	0.56	**40.9%**	2.99	1.3%
6/4/2006 1:30	0.55	**39.1%**	2.76	6.7%
6/4/2006 18:13	0.46	21.7%	2.8	5.2%

Canister ID ER019

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/2/2006 22:22	0.33		1.69	
6/3/2006 5:16	0.31	6.3%	1.66	1.8%
6/3/2006 21:58	0.32	3.1%	1.67	1.2%
6/4/2006 2:41	0.32	3.1%	1.61	4.8%
6/4/2006 19:23	0.35	5.9%	1.66	1.8%

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NOTE: Results listed in **bold** are outside the required RPD of 25%.

14

Ambient Air Stability Study – Part 3 of 3

Analyzed Sample 24 Hours After Collection – Initially Pressurized

Canister ID TX007

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/5/2006 10:24 2.5 psi	1.18		6.20	
6/6/2006 13:45 (0" Hg)	1.23	4.1%	5.84	6.0%
6/6/2006 18:29 (<0 "Hg)	1.28	8.1%	6.85	10.0%
6/6/2006 23:12 (<0 "Hg)	1.18	0.0%	5.58	10.5%
6/7/2006 3:56 (<0" Hg)	1.18	0.0%	5.59	10.3%
6/7/2006 8:41 (< 0" Hg)	1.23	4.1%	5.67	8.9%

Canister ID 2240

Time	Acrolein	% RPD	1,3-Butadiene	% RPD
6/5/2006 9:11 (2.5 psi)	1.85		8.87	
6/6/2006 14:56 (0" Hg)	1.90	2.7%	8.33	6.3%
6/6/2006 19:39 (<0 "Hg)	1.83	1.1%	8.35	6.0%
6/7/2006 0:23 (<0 "Hg)	1.88	1.6%	8.20	7.9%
6/7/2006 5:07 (<0" Hg)	1.86	0.5%	8.26	7.1%
6/7/2006 9:52 (<0 "Hg)	1.77	4.4%	7.76	13.3%

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15

Compendium Method Comparison

- Comparison of Methods TO-15 and TO-11A using actual NMP samples from across the country
- Acrolein recoveries are clearly much higher for Method TO-15 than Method TO-11A

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16

Compendium Method Comparison (1 of 2)

Site	Date	TO-11A (ppbv)	TO-15 (ppbv)	% Recovery
Bountiful, UT	9/13/05	0.114	3.17	3.6%
Loudon, TN	10/13/05	0.040	1.10	3.6%
Providence, AL	10/19/05	0.059	1.20	4.9%
Birmingham, AL	10/19/05	0.137	1.46	9.4%
Shillar Park, Chicago, IL	10/31/05	0.085	1.08	7.9%
Madison, WI	11/12/05	0.049	0.47	10.4%
Barceloneta, Puerto Rico	11/12/05	0.024	0.84	2.9%
Minneapolis, MN	11/18/05	0.018	1.21	1.5%
Camden, NJ	12/24/05	0.186	0.78	23.8%
New Brunswick, NJ	12/30/05	0.040	1.18	3.4%

Note: % Recovery of TO-11A represents the TO-11A versus TO-15 measurements.

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17

Compendium Method Comparison (2 of 2)

Site	Date	TO-11A (ppbv)	TO-15 (ppbv)	% Recovery
Sioux Falls, SD	2/28/06	0.089	0.56	15.9%
Grand Junction, CO	3/24/06	0.099	0.58	17.1%
Austin, TX – site 1	4/23/06	0.054	0.48	11.3%
Austin, TX – site 2	4/23/06	0.037	0.39	9.5%
Austin, TX – site 3	4/23/06	0.035	0.58	6.0%
Austin, TX – site 4	4/23/06	0.036	0.53	6.8%
Austin, TX – site 5	4/23/06	0.089	0.45	19.8%
Custer Park, SD	5/17/06	0.044	0.74	5.9%
Elizabeth, NJ	5/29/06	0.192	0.66	29.1%
Tulsa, OK	5/29/06	0.121	0.82	14.8%
			Average	10.4%

Note: % Recovery of TO-11A represents the TO-11A versus TO-15 measurements.

ERG

18

Method TO-15 Field Sample Results for Acrolein

- 19 Sites from July '05 to July '06
- 1,450 acrolein measurements
- 516 of these were from samples during Hurricane Katrina clean-up
- 54% of the 1,450 were detects
- 1.2% of the 1,450 were under the MDL
- Average concentration was 1.54 µg/m^3
- Median concentration was 1.08 µg/m^3

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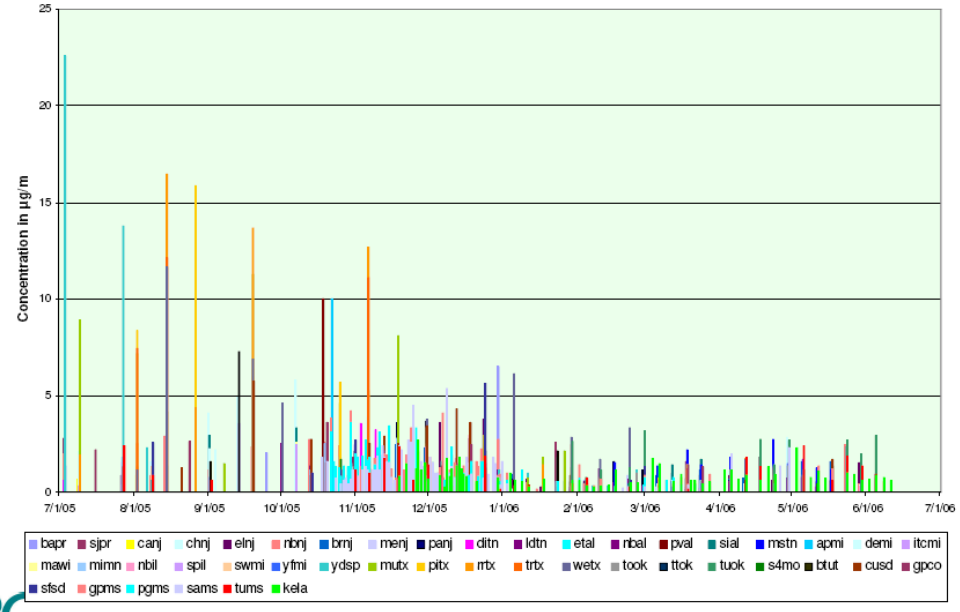
19

Analytical Acrolein Results including Katrina (7/05 to 7/06)



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Data Quality Control and Assurance

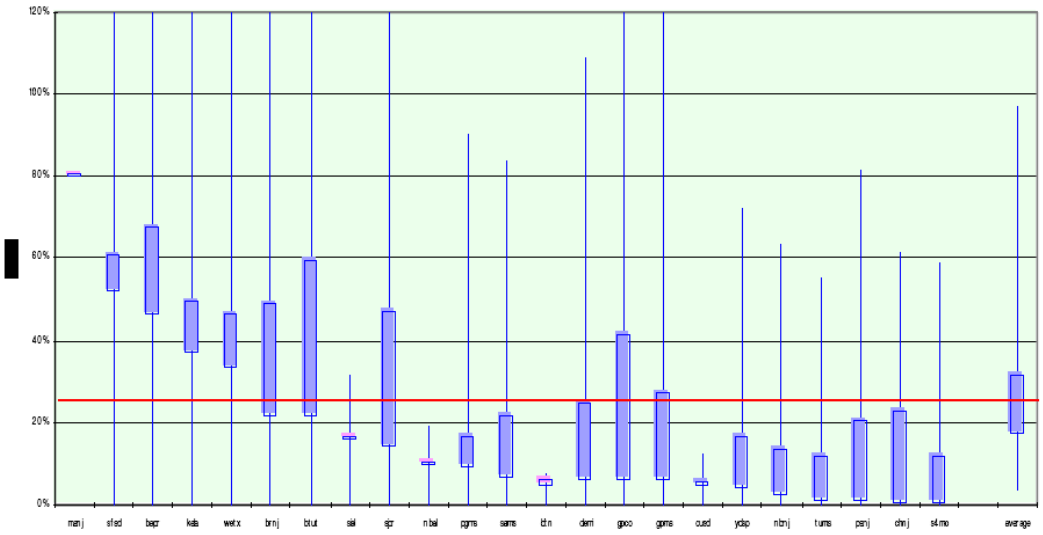
Compound	ERG (ppbv)	True (ppbv)	% Difference	Uncertainty
Acrolein	1.48	1.21	22.3	± 11.3%
1,3-Butadiene	1.84	1.44	27.8	± 0.2%

- True value was based on results of 3 analyses performed by Alion/EPA (ORD).
- The percent uncertainty is the coefficient of variation for the three replicate analyses.

ERG

21

Duplicate Analysis Results (July '05 to June '06)



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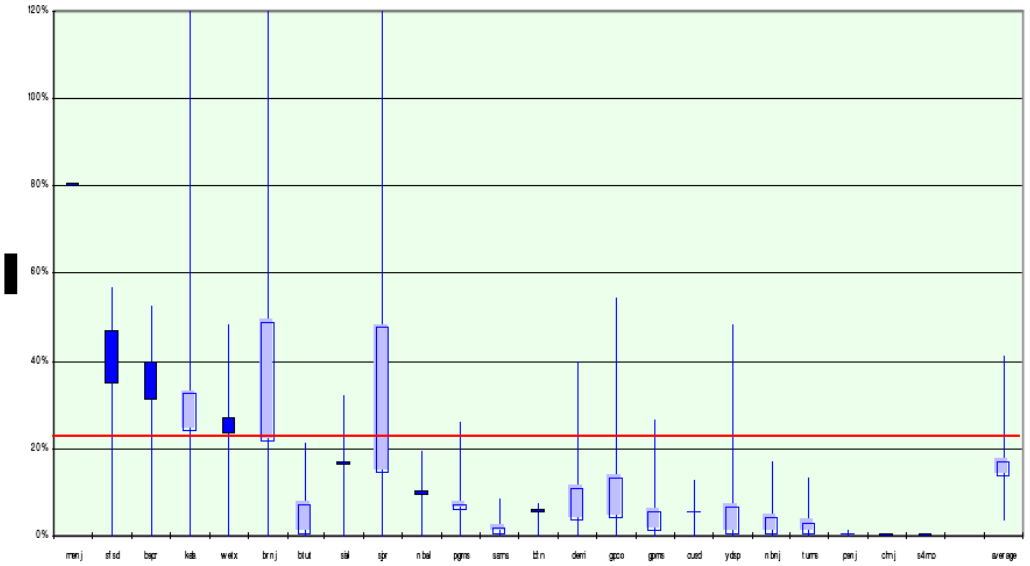
22

Duplicate Analysis Results –Outliers Omitted (July '05 to June '06)



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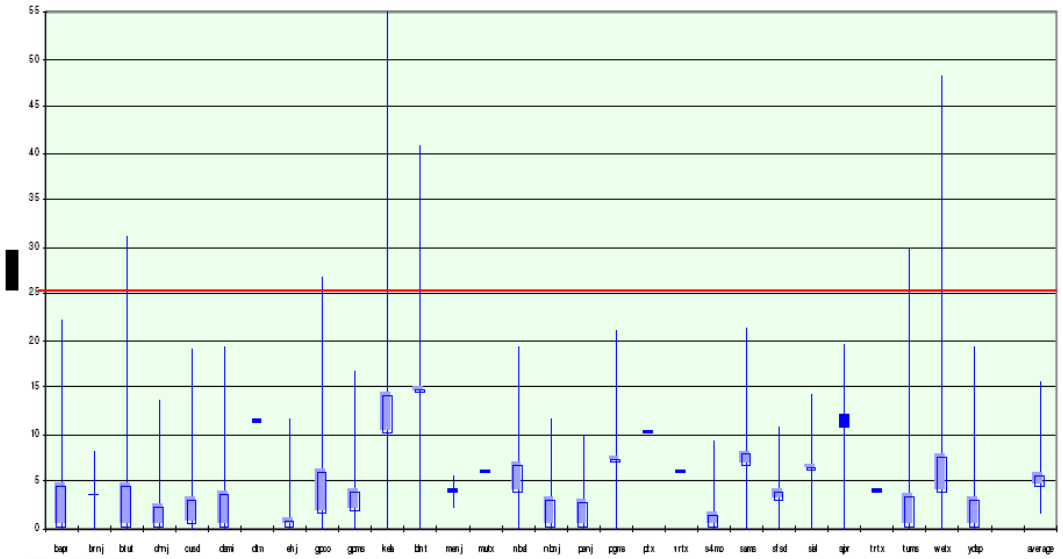
23

Replicate Analysis Results (July '05 to June '06)



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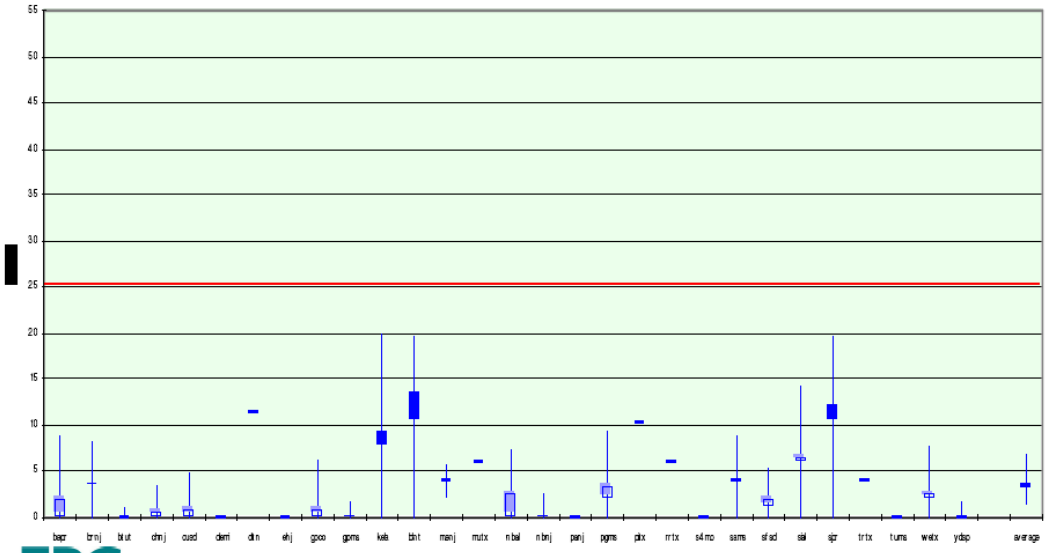
24

Replicate Analysis without Outliers (July '05 to June '06)



ERG

Conclusions

- Higher acrolein recovery using Method TO-15
- Audit, collocate, duplicate, and replicate samples pass NATTS daily quality objectives
- Results from NMP and Katrina are relatively the same and show similar trends
- Need another years data to see if trends are consistent

ERG

Acknowledgments

- US EPA, OAQPS
  - Jim Homolya
  - Mike Jones
  - Dennis Mikel
- ERG
  - Donna Tedder
  - Mitchell Howell
  - Ray Merrill

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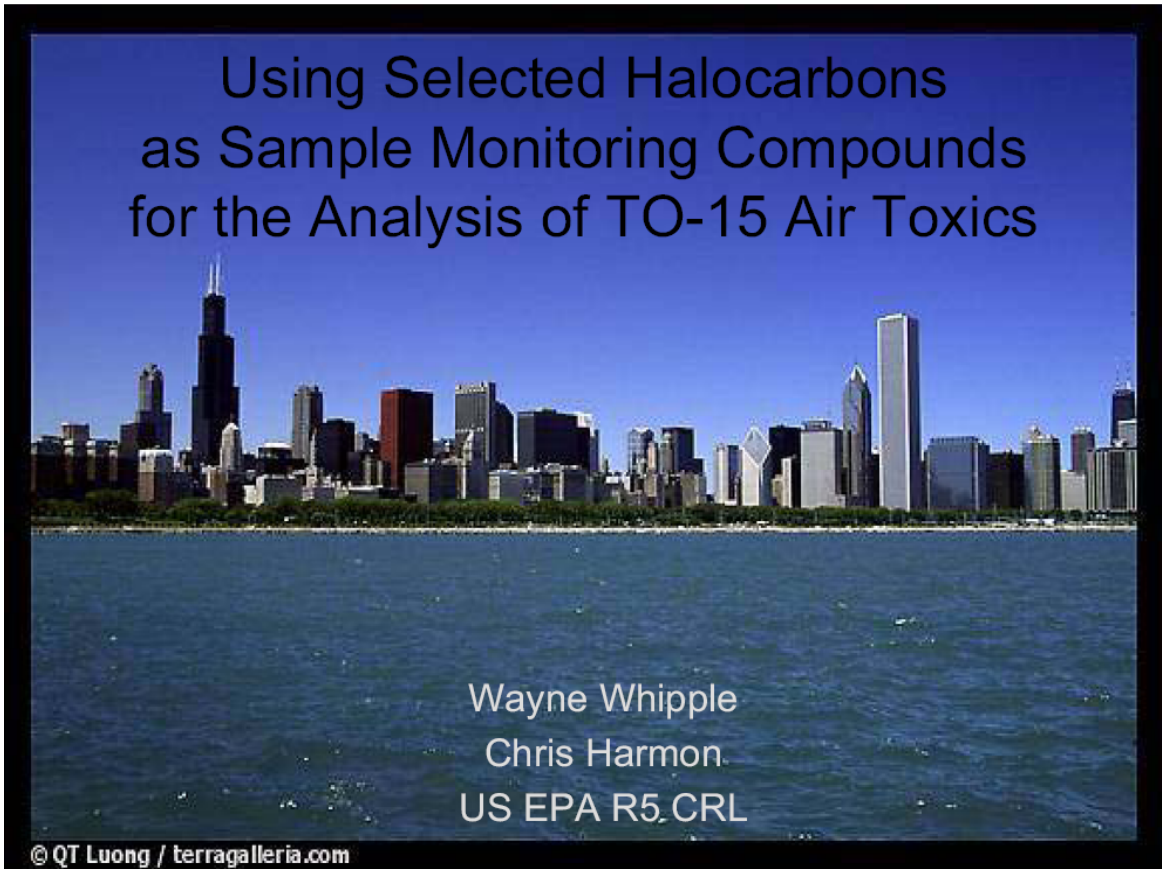
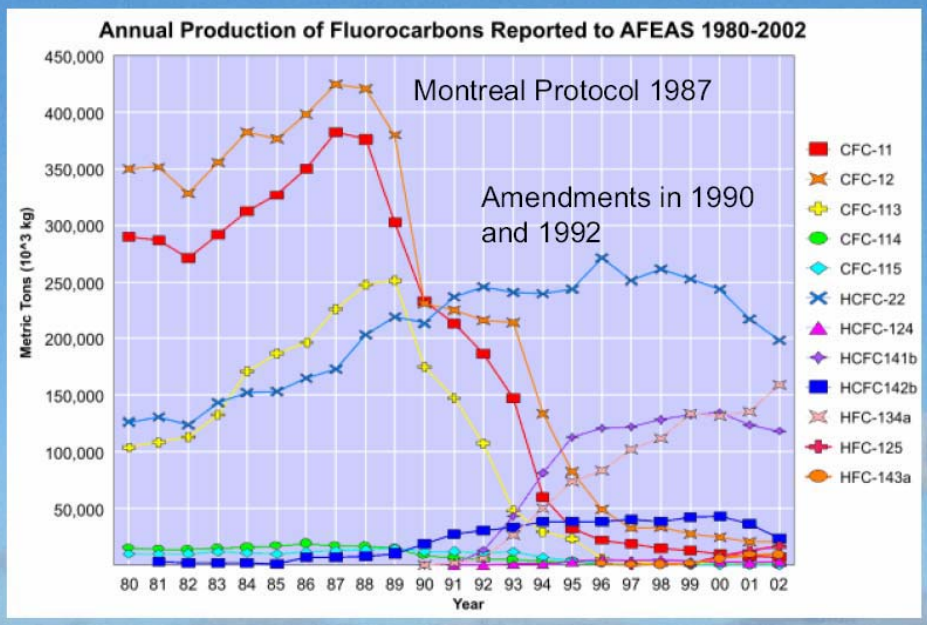


Outline

- Purpose
  - To demonstrate that the use of using selected halocarbons as sample monitoring compounds improves confidence in data
    - Ensure ambient samples are analyzed properly
    - Track the performance of the system
- Theory
  - Source and Sinks of Halocarbons
    - Production and Usage
    - Montreal Protocol and accords
    - Lifetime in Atmosphere
  - Global Distribution
    - Background Measurements
- Data
  - Chicago Measurements from October through May 2005
    - Stability of measurements
    - Histograms
    - Mobile Alabama Study
- Results
  - Use a suite of halocarbons to track each sample for proper analysis
  - Track performance of system and limits of data

Reason why this works

- CFCs are only man made
- Halocarbons persist for a extremely long time in the troposphere
- Were globally banned
  - Proven to cause stratospheric ozone depletion
  - Montreal Protocol
  - discovery of the ozone hole over Antarctica
  - subsequent accords in 1990 and 1992
- They now have consistent concentrations throughout the planet at detectable levels



http://www.afeas.org/production_and_sales.html
Alternative Fluorocarbons Environmental Acceptability Study

Sinks for VOCs

Troposphere

reactions

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $\lambda < 300$ nm or $O(^3P)$

$H_2O + O(^1D) \rightarrow 2 \cdot OH$

$RX + \cdot OH \rightarrow ROH + \cdot X$ (X = ·Cl, ·Br ...)

$RX + \cdot OH \rightarrow R\cdot + H_2O$ (X = H)

deposition (ocean, ground, lakes, aerosol)

Stratosphere

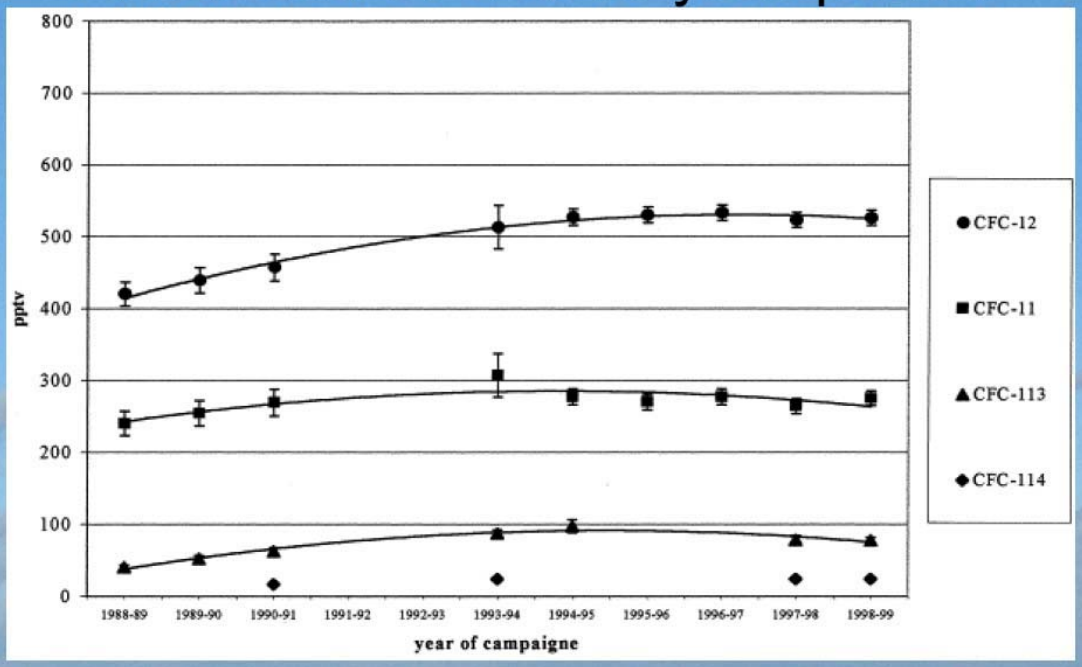
$RX + h\nu \rightarrow R + X$ (stratosphere for CFCs)

Tropospheric Lifetime of Halocarbons

Halocarbon	Lifetime	Sinks
CCl_2F_2 (F12)	~150 years	Photolysis in stratosphere
$CFCl_3$ (F11)	65 years	Photolysis in stratosphere
$C_2Cl_3F_3$ (F113)	~ 100 years	Photolysis in stratosphere
$C_2Cl_2F_4$ (F114)	200 years	Photolysis in stratosphere
CCl_4	40 years	Photolysis in stratosphere and ocean uptake
CH_3CCl_3 (methylchloroform)	8 years	Reactions with OH

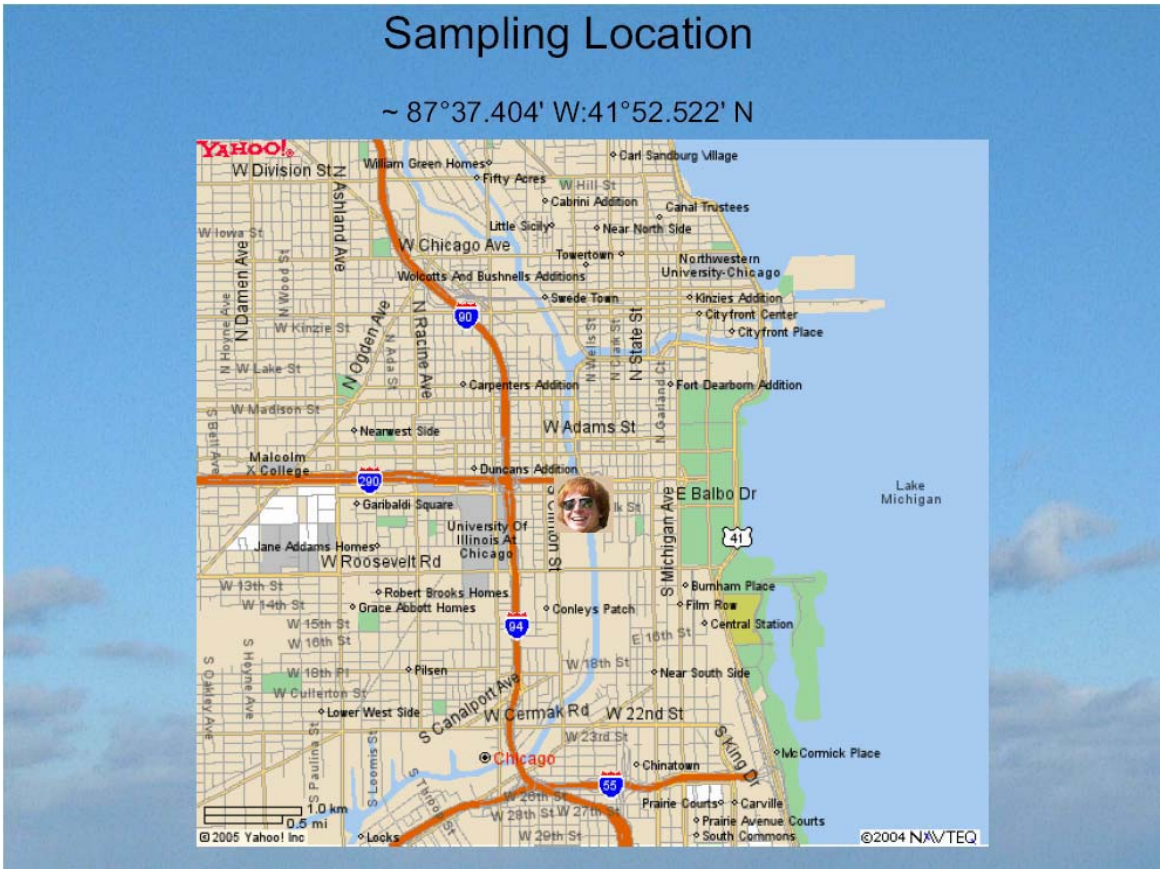
Warnek, Peter; Chemistry of the Natural Atmosphere, 1988 pp 270, 271

CFC concentration levels measured in Antarctica over a 10-year period

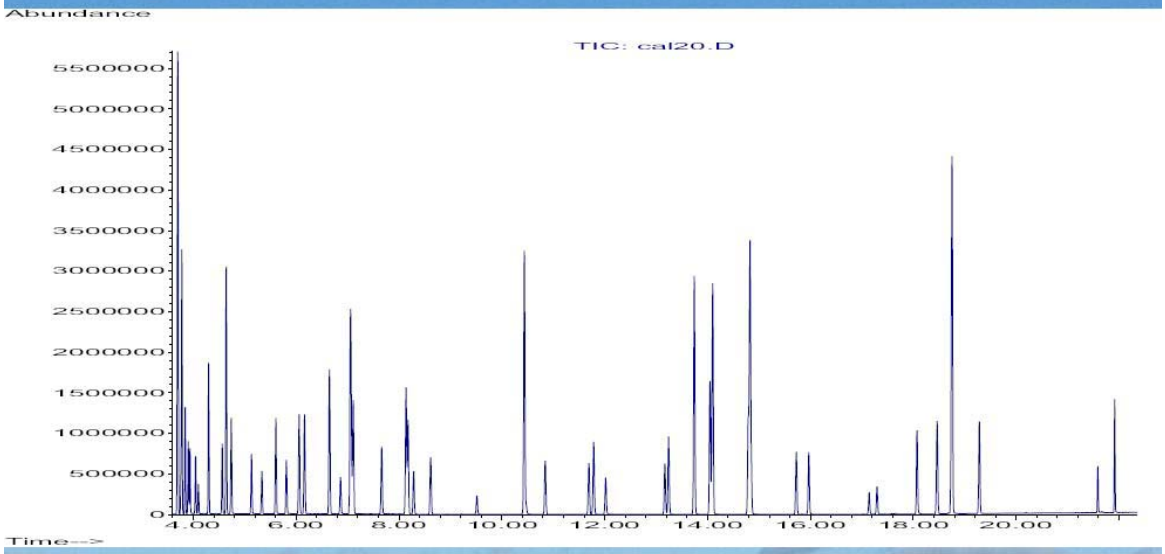


Analysis

- Samples taken almost every workday from October 2004 through May 2005
- In small park close to major freeways in downtown
- 2.7 L Canisters
- Analyzed using auto sampler and preconcentrator
- Quad GC/MS EI

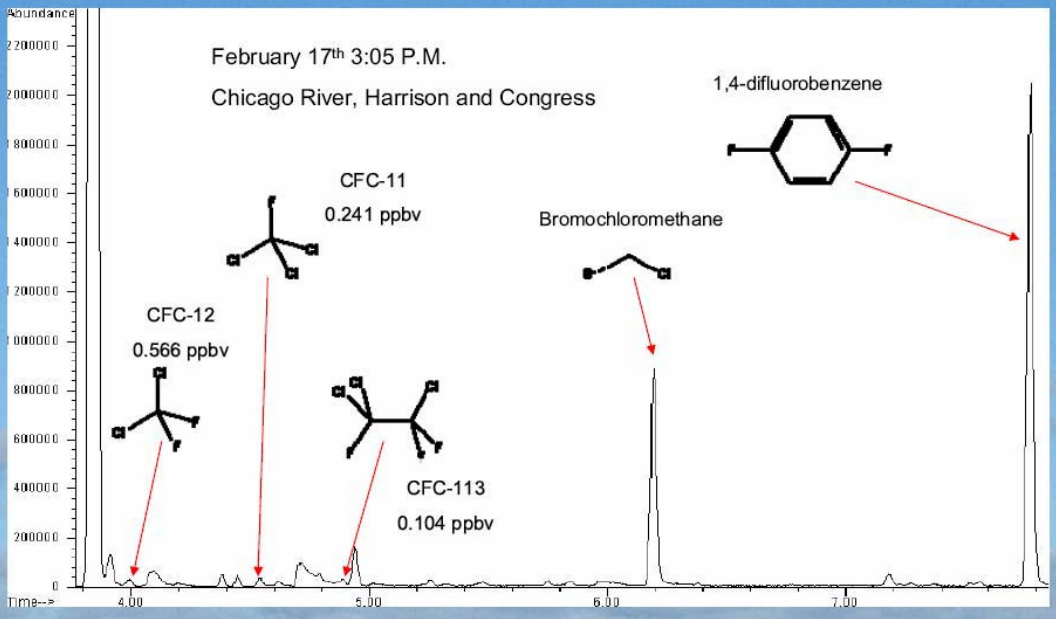

Sampling Location
~ 87°37.404' W:41°52.522' N
YAHOO!
W Division St
William Green Homes
Fifty Acres
Carl Sandburg Village
W Hill St
Cabrini Addition
Canal Trustees
Little Sicily
Near North Side
W Chicago Ave
Towertown
Northwestern University-Chicago
Wolcotts And Bushnells Additions
Kinzies Addition
Cityfront Center
Cityfront Place
Carpenters Addition
Fort Dearborn Addition
Nearwest Side
W Adams St
Malcolm X College
Duncans Addition
Garibaldi Square
University Of Illinois At Chicago
E Balbo Dr
Lake Michigan
Jane Addams Homes
W Roosevelt Rd
Robert Brooks Homes
Grace Abbott Homes
Conleys Patch
Burnham Place
Film Row
Central Station
Pilsen
Near South Side
W Cermak Rd
W 22nd St
Lower West Side
S Canalport Ave
Chicago
Chinatown
McCormick Place
Prairie Courts
Carville
Prairie Avenue Courts
South Commons
1.0 km
0.5 mi
© 2005 Yahoo! Inc
Locks
©2004 NAVTEQ

Agilent 6890/5973 Entech 7200

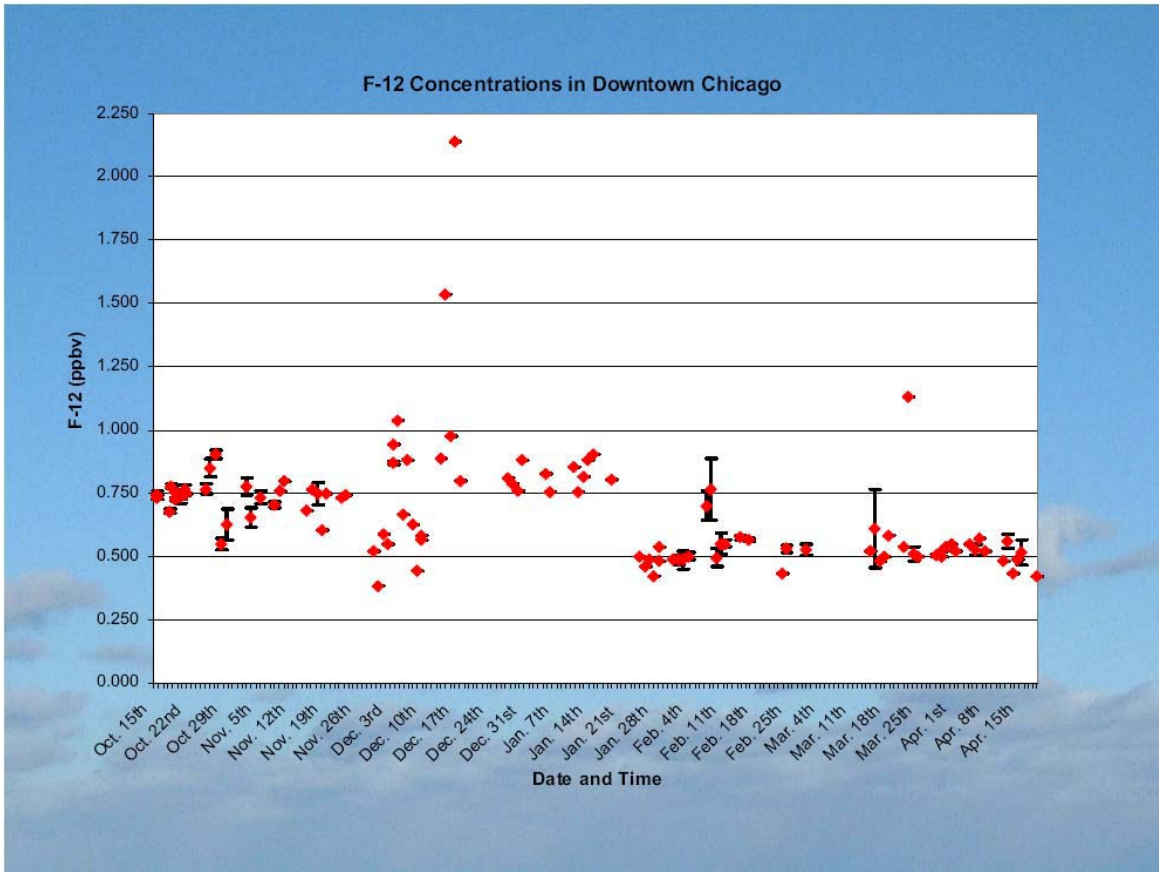


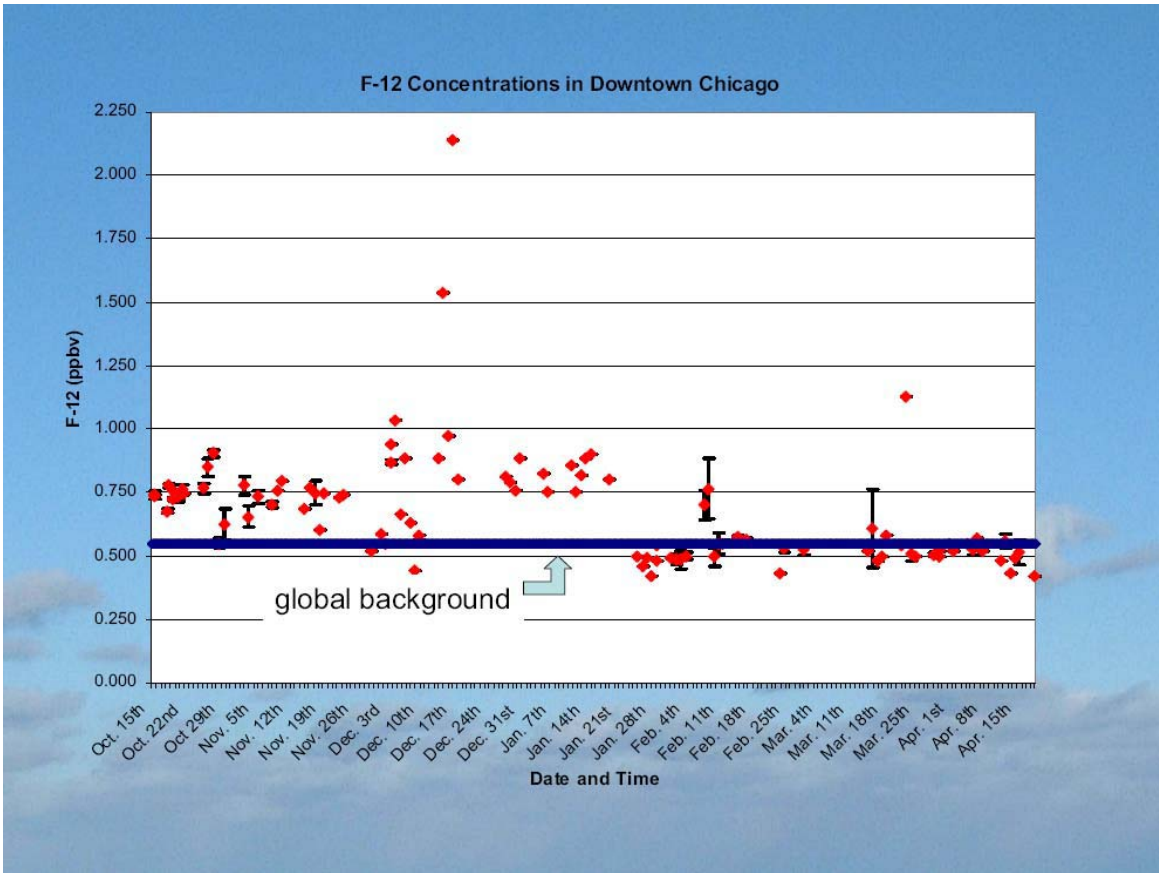
~ 20 ppbv cal standard - VRX 0.25 x 0.25 Column

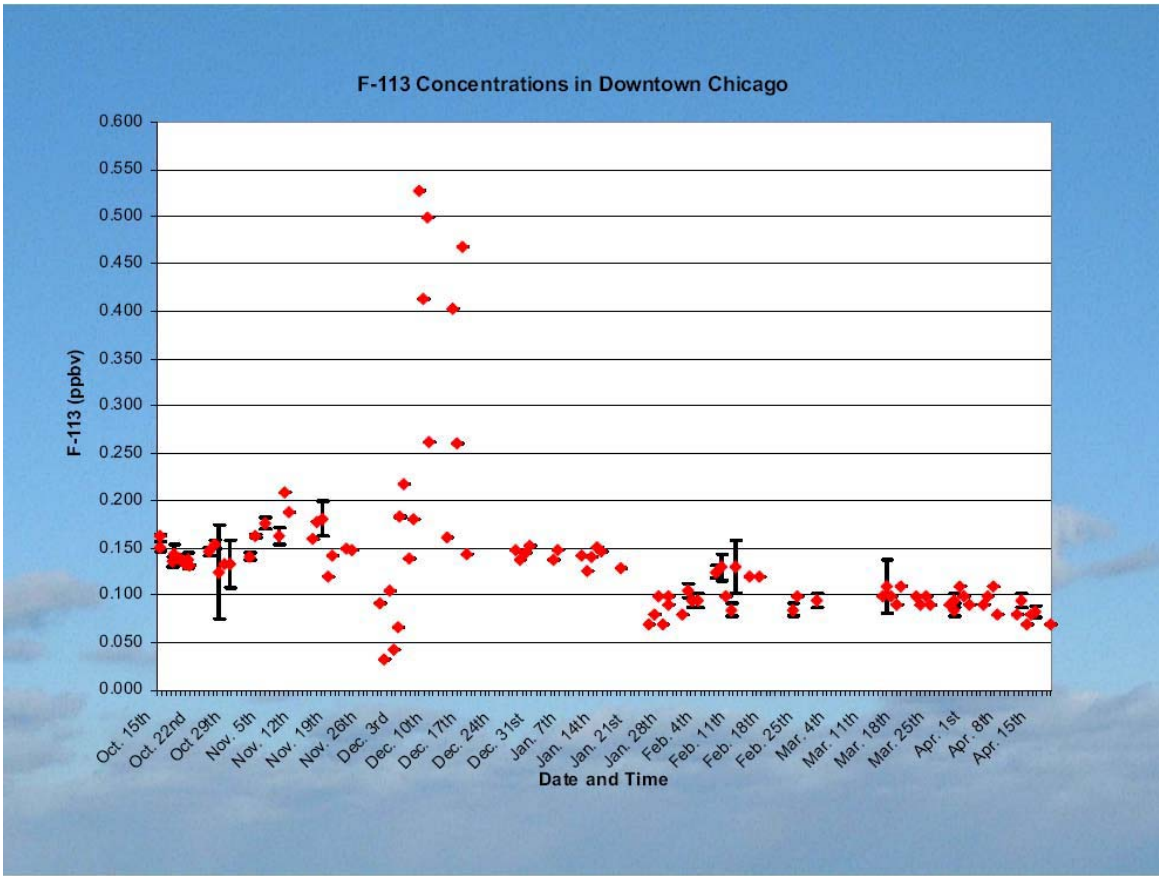
System Monitoring Compounds

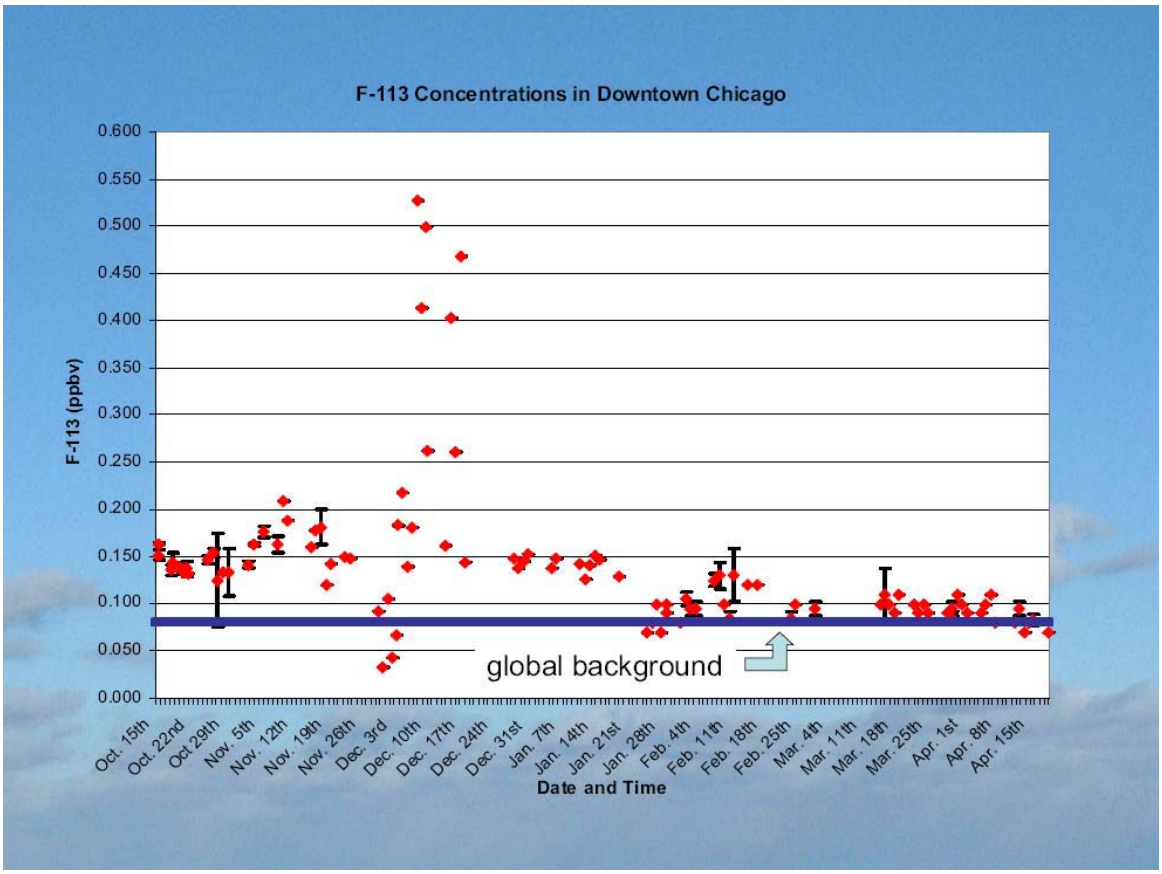


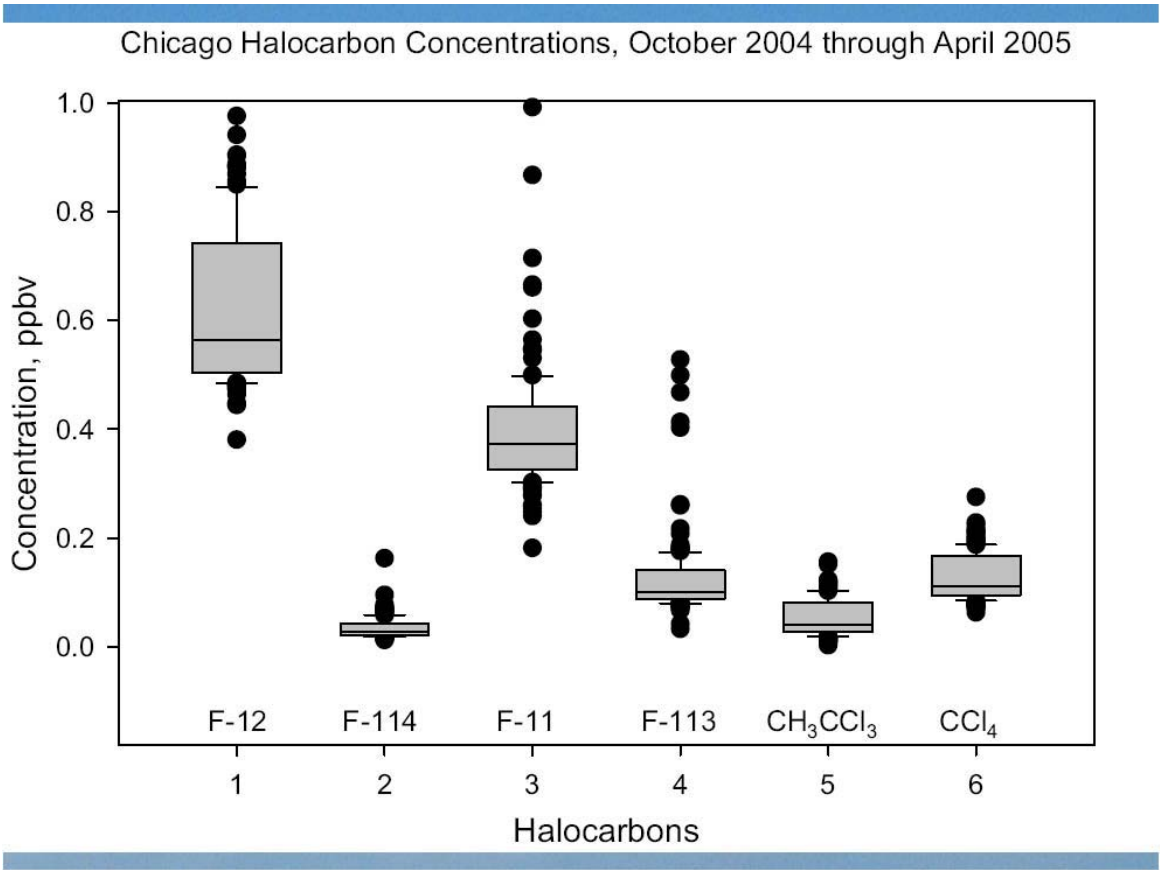
0.32 mm id DB 5 MS

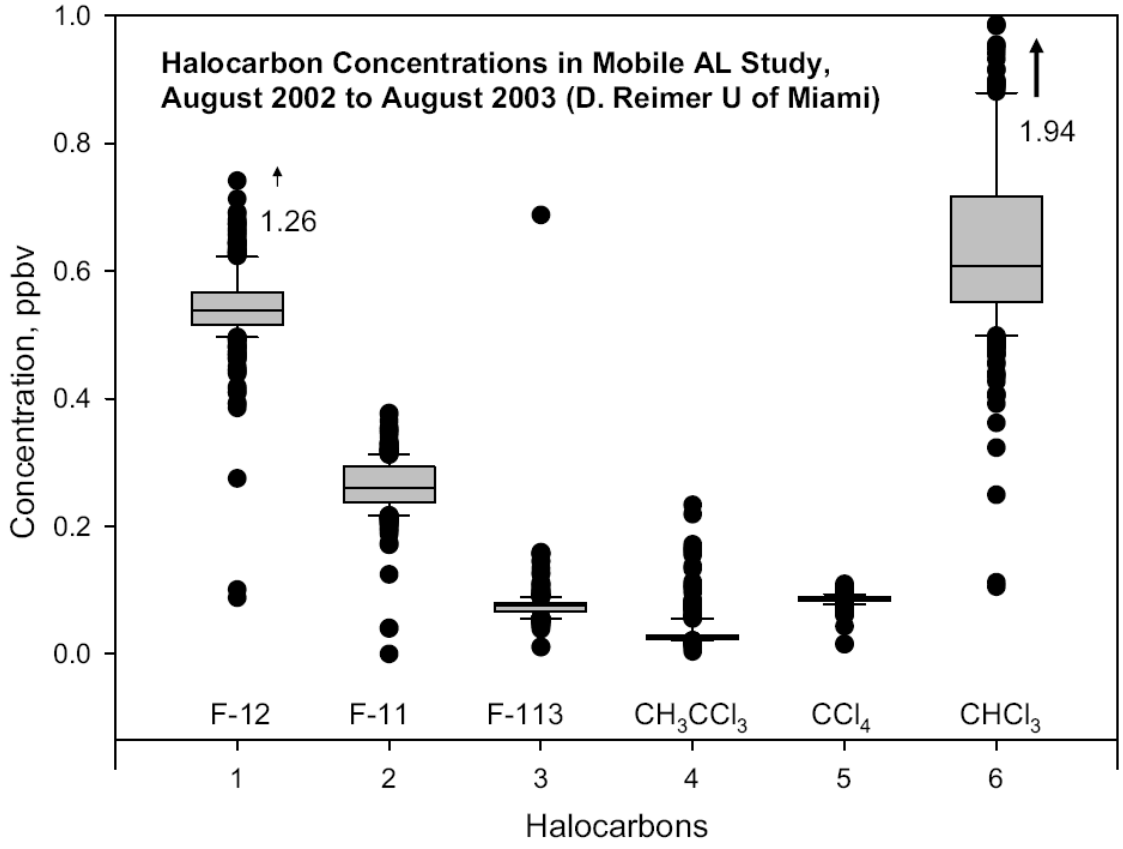

F-12 Concentrations in Downtown Chicago
F-12 (ppbv)
2.250
2.000
1.750
1.500
1.250
1.000
0.750
0.500
0.250
0.000
Oct. 15th
Oct. 22nd
Oct 29th
Nov. 5th
Nov. 12th
Nov. 19th
Nov. 26th
Dec. 3rd
Dec. 10th
Dec. 17th
Dec. 24th
Dec. 31st
Jan. 7th
Jan. 14th
Jan. 21st
Jan. 28th
Feb. 4th
Feb. 11th
Feb. 18th
Feb. 25th
Mar. 4th
Mar. 11th
Mar. 18th
Mar. 25th
Apr. 1st
Apr. 8th
Apr. 15th
Date and Time


F-12 Concentrations in Downtown Chicago
F-12 (ppbv)
2.250
2.000
1.750
1.500
1.250
1.000
0.750
0.500
0.250
0.000
global background
Oct. 15th
Oct. 22nd
Oct 29th
Nov. 5th
Nov. 12th
Nov. 19th
Nov. 26th
Dec. 3rd
Dec. 10th
Dec. 17th
Dec. 24th
Dec. 31st
Jan. 7th
Jan. 14th
Jan. 21st
Jan. 28th
Feb. 4th
Feb. 11th
Feb. 18th
Feb. 25th
Mar. 4th
Mar. 11th
Mar. 18th
Mar. 25th
Apr. 1st
Apr. 8th
Apr. 15th
Date and Time


F-113 Concentrations in Downtown Chicago
F-113 (ppbv)
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Oct. 15th
Oct. 22nd
Oct 29th
Nov. 5th
Nov. 12th
Nov. 19th
Nov. 26th
Dec. 3rd
Dec. 10th
Dec. 17th
Dec. 24th
Dec. 31st
Jan. 7th
Jan. 14th
Jan. 21st
Jan. 28th
Feb. 4th
Feb. 11th
Feb. 18th
Feb. 25th
Mar. 4th
Mar. 11th
Mar. 18th
Mar. 25th
Apr. 1st
Apr. 8th
Apr. 15th
Date and Time


F-113 Concentrations in Downtown Chicago
F-113 (ppbv)
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
global background
Oct. 15th
Oct. 22nd
Oct 29th
Nov. 5th
Nov. 12th
Nov. 19th
Nov. 26th
Dec. 3rd
Dec. 10th
Dec. 17th
Dec. 24th
Dec. 31st
Jan. 7th
Jan. 14th
Jan. 21st
Jan. 28th
Feb. 4th
Feb. 11th
Feb. 18th
Feb. 25th
Mar. 4th
Mar. 11th
Mar. 18th
Mar. 25th
Apr. 1st
Apr. 8th
Apr. 15th
Date and Time


Chicago Halocarbon Concentrations, October 2004 through April 2005
Concentration, ppbv
1.0
0.8
0.6
0.4
0.2
0.0
F-12
F-114
F-11
F-113
CH3CCl3
CCl4
1
2
3
4
5
6
Halocarbons


Halocarbon Concentrations in Mobile AL Study,
August 2002 to August 2003 (D. Reimer U of Miami)
Concentration, ppbv
1.0
0.8
0.6
0.4
0.2
0.0
1.26
1.94
F-12
F-11
F-113
CH3CCl3
CCl4
CHCl3
1
2
3
4
5
6
Halocarbons

Acceptance Limits in the CRL SOP

Compound	Lower Limit Warning Range (ppbv)	Normal Range (ppbv)	Upper Limit Warning Range (ppbv)
Dichorodifluoromethane (F-12)	0.506 – 0.538	0.538 – 0.885	0.885 – 1.060
Dichlorotetrafluoroethane (F-114)	0.010 – 0.015	0.015 – 0.077	0.077 – 0.086
Trichlorofluoromethane (F-11)	0.232 – 0.253	0.253 – 0.589	0.589 – 0.623
1,1,2-Trichloro1,2,2-Trifluoroethene (F-113)	0.074 – 0.080	0.080 – 0.228	0.228 – 0.306
1,1,1-Trichloroethane (methylchloroform)	0.036 – 0.040	0.040 – 0.126	0.126 – 0.159
CCl_4 (carbon tetrachloride)	0.105 – 0.110	0.110 – 0.214	0.214 – 0.262

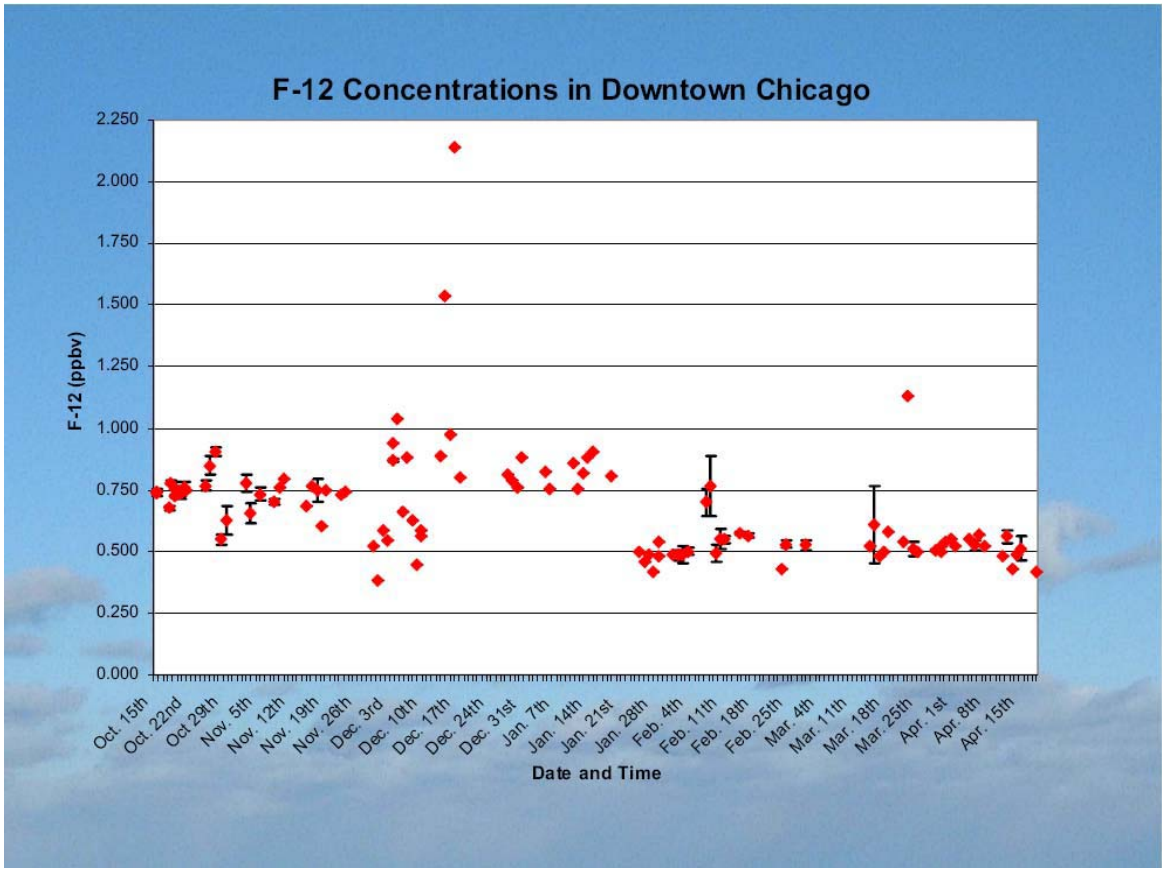
- Limits derived from whole data set ± 3σ, warning limits set at 2σ of set
- Three out of the six must be within the acceptance range
- Knowledge of the sample may help if limits are exceeded

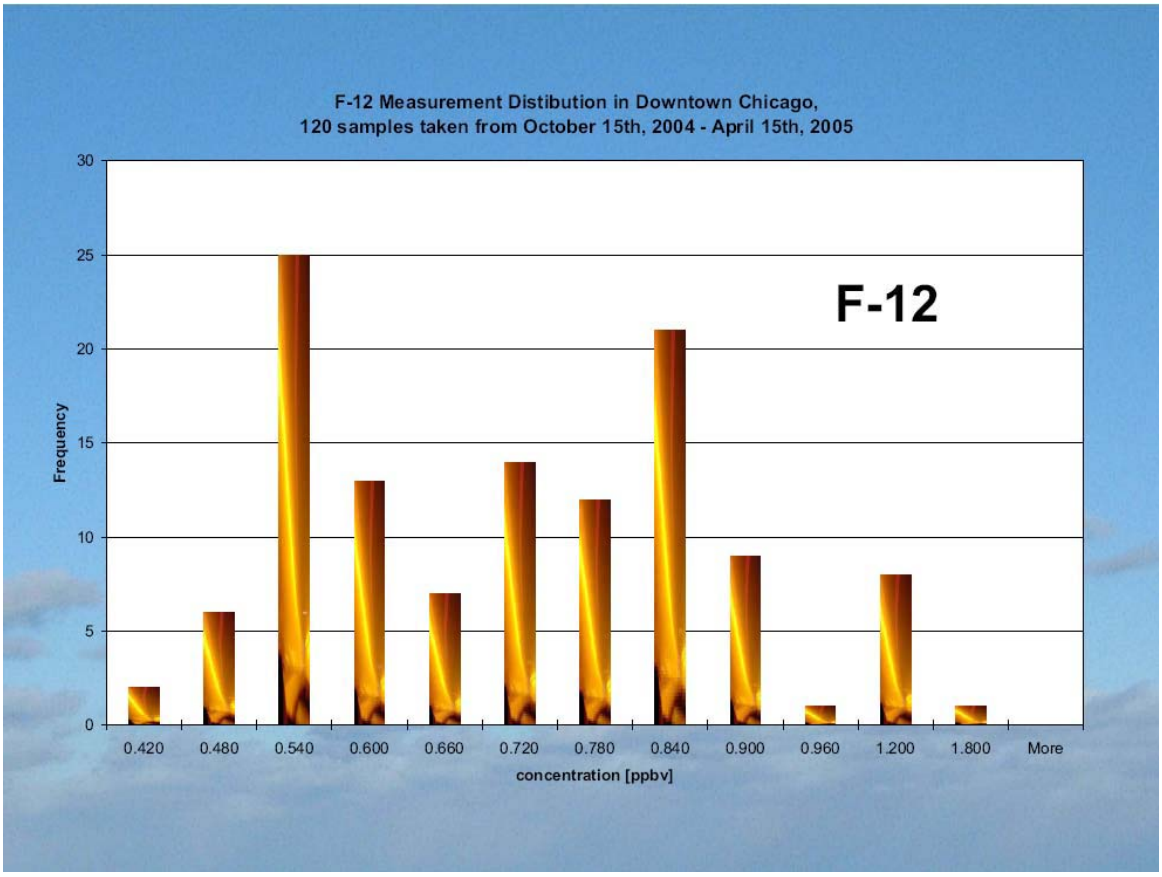
What causes out of limits?

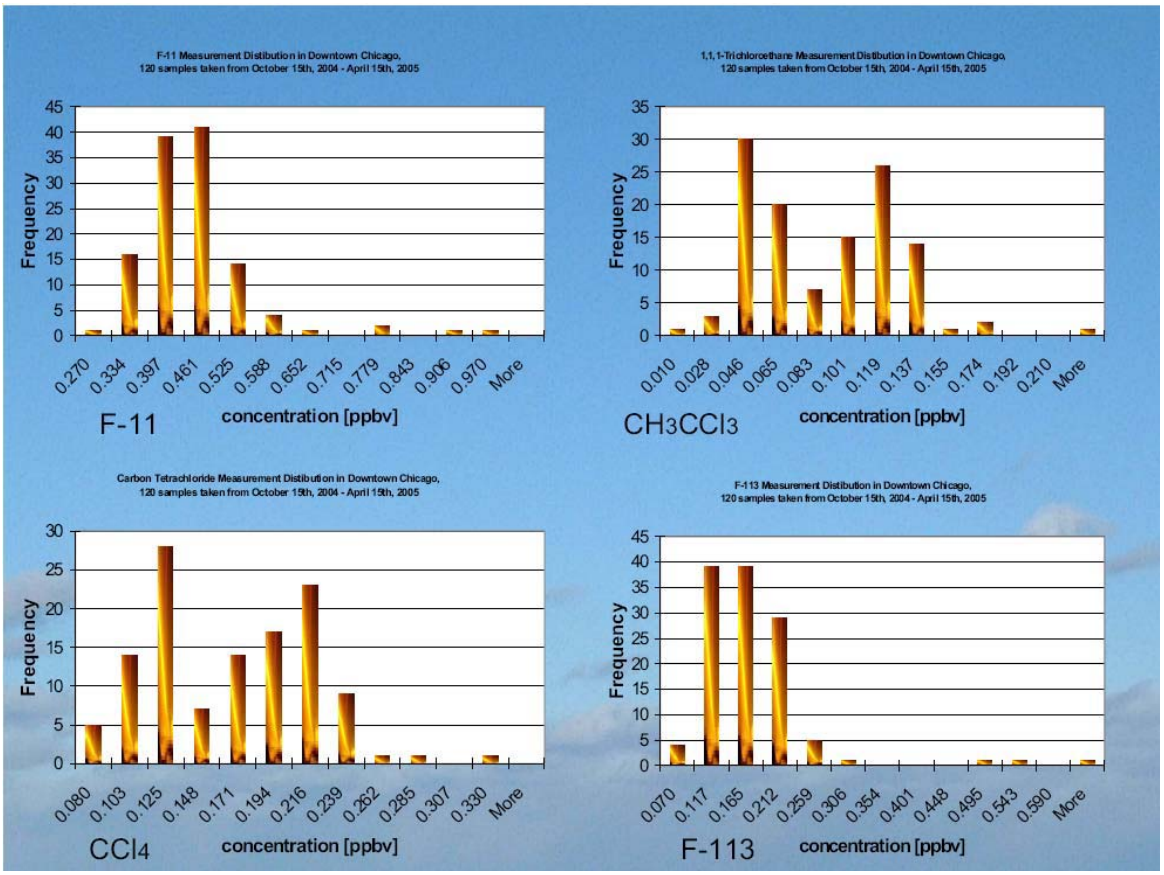
- If compounds are low most causes are:
  - Not enough sample trapped on loop
  - Dilution incorrect
  - Not an ambient sample of tropospheric air
- If samples are too high most causes are:
  - If all compounds high, dilution error
  - If one or two are high, may be real measurement
  - Sample may still be real measurement if all are high but need to investigate where sample came from

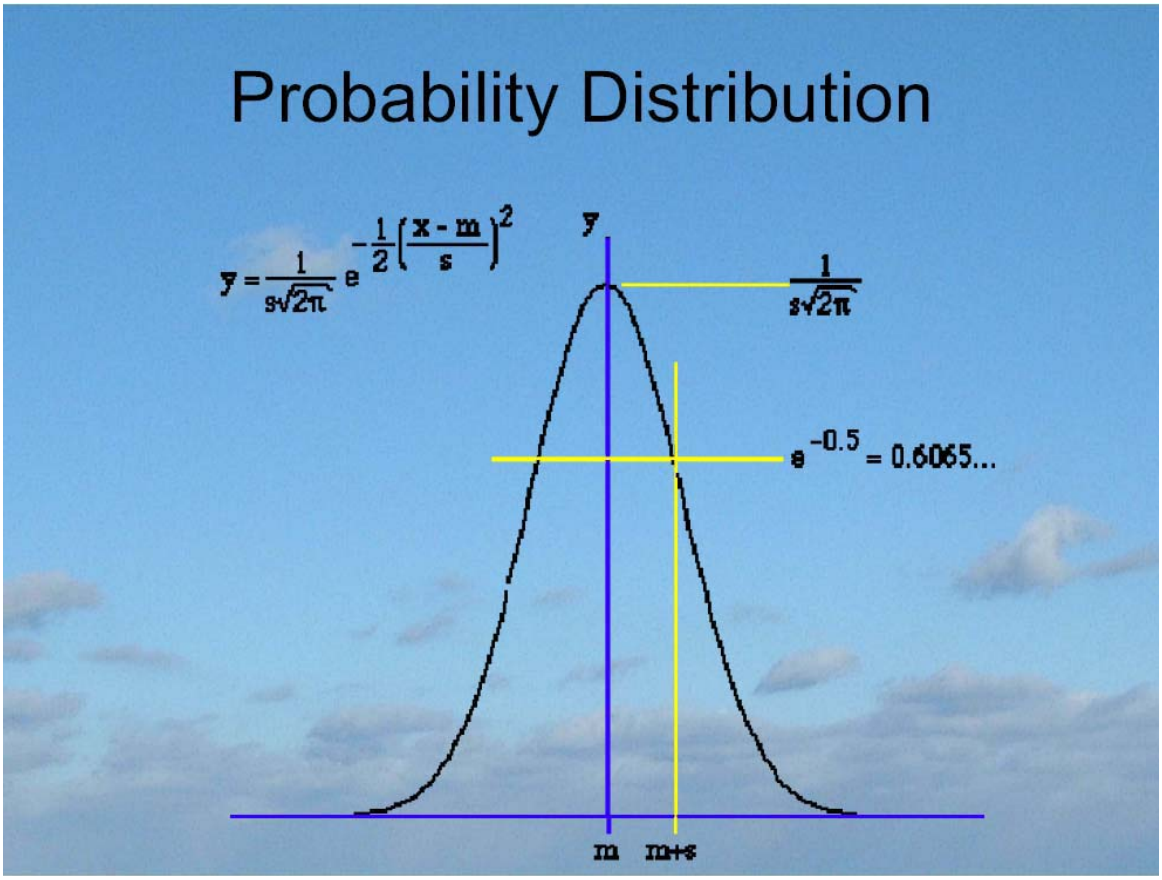
Data Analysis

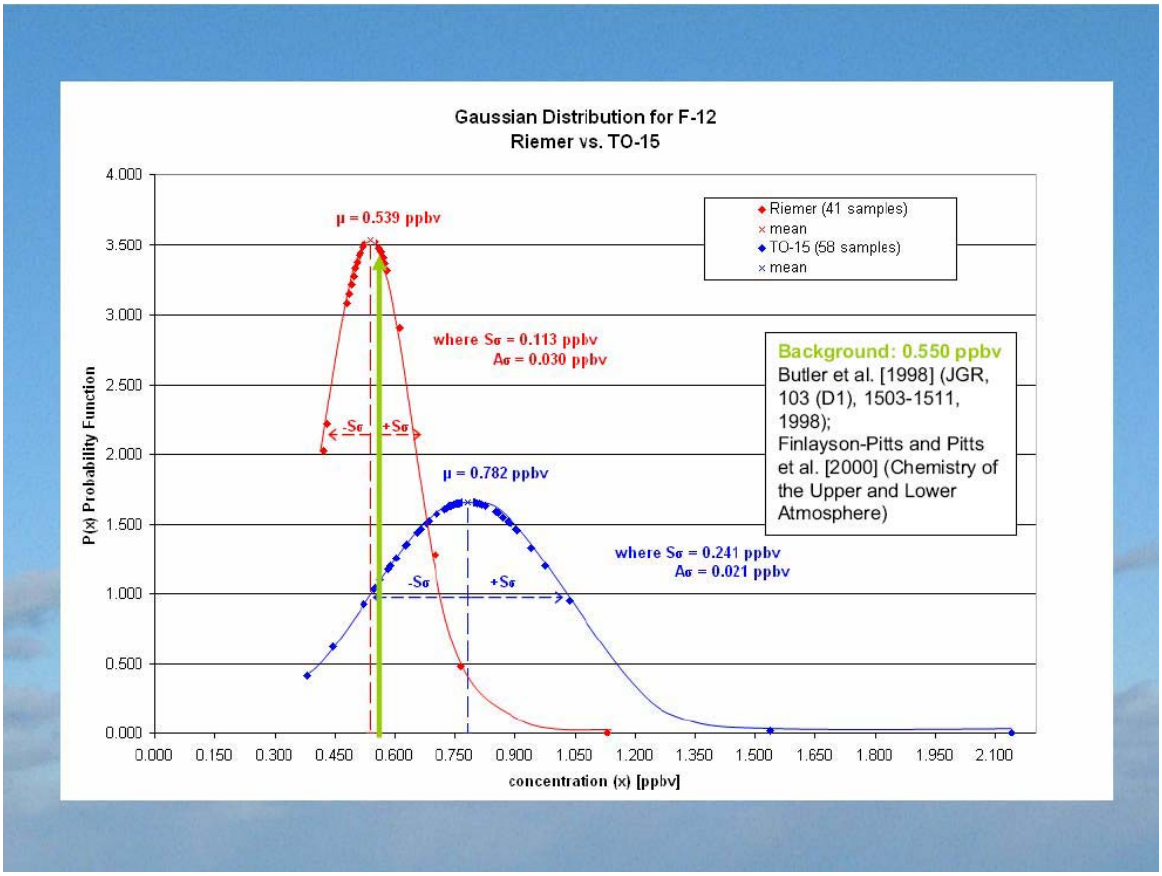
- Accuracy of standards, if only for the exact compounds
- Helps understand the limitations of the analysis
  - Trends in data (correlation analysis)
  - Compliance

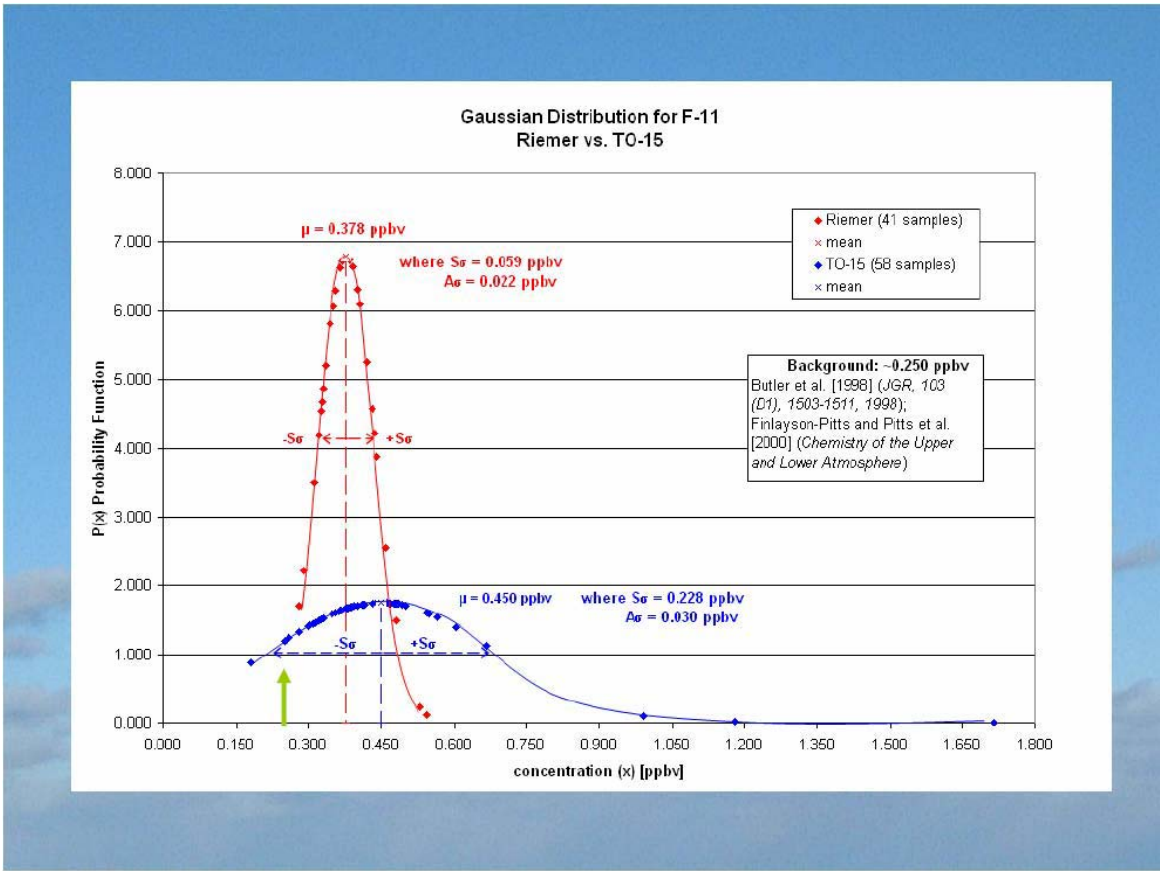


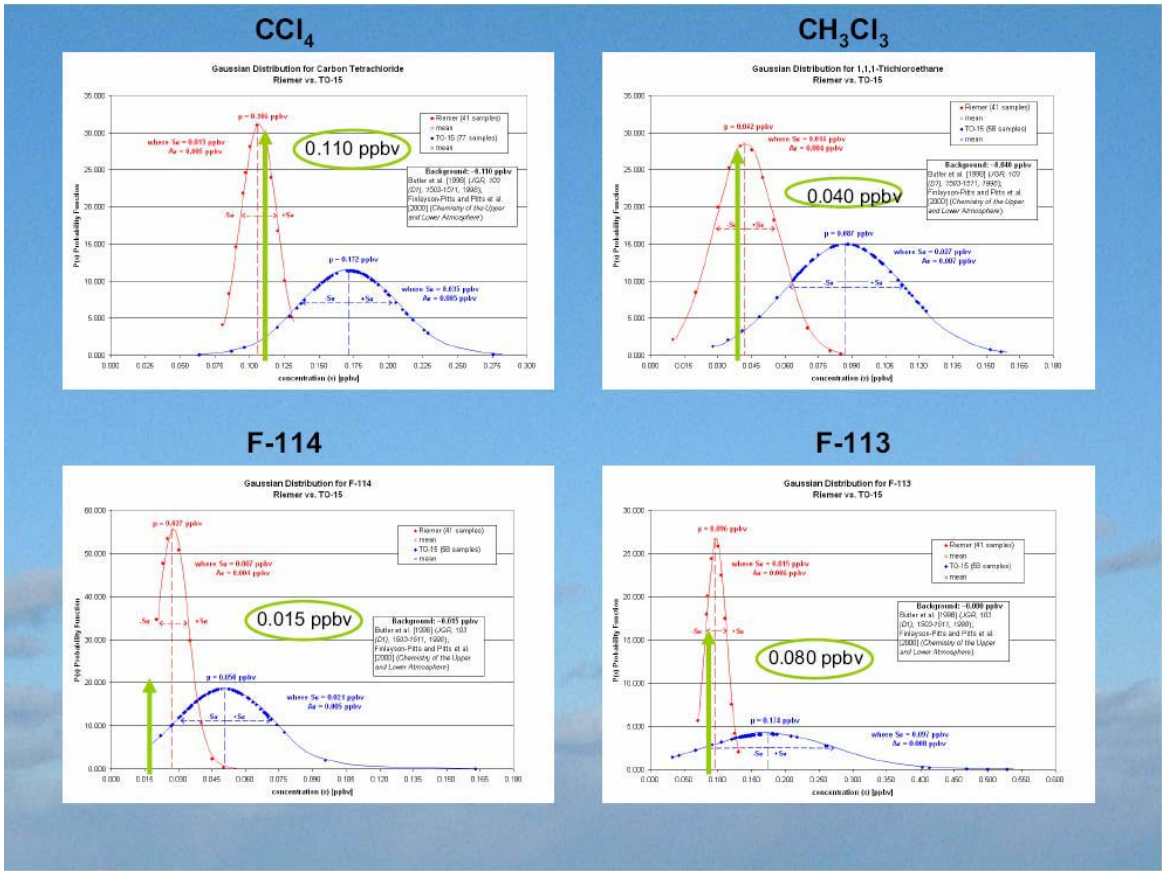

F-12 Measurement Distibution in Downtown Chicago,
120 samples taken from October 15th, 2004 - April 15th, 2005
F-12
Frequency
0
5
10
15
20
25
30
0.420
0.480
0.540
0.600
0.660
0.720
0.780
0.840
0.900
0.960
1.200
1.800
More
concentration [ppbv]


F-11 Measurement Distibution in Downtown Chicago,
120 samples taken from October 15th, 2004 - April 15th, 2005
Frequency
0.270
0.334
0.397
0.461
0.525
0.588
0.652
0.715
0.779
0.843
0.906
0.970
More
F-11
concentration [ppbv]
1,1,1-Trichloroethane Measurement Distibution in Downtown Chicago,
120 samples taken from October 15th, 2004 - April 15th, 2005
Frequency
0.010
0.028
0.046
0.065
0.083
0.101
0.119
0.137
0.155
0.174
0.192
0.210
More
CH3CCl3
concentration [ppbv]
Carbon Tetrachloride Measurement Distibution in Downtown Chicago,
120 samples taken from October 15th, 2004 - April 15th, 2005
Frequency
0.080
0.103
0.125
0.148
0.171
0.194
0.216
0.239
0.262
0.285
0.307
0.330
More
CCl4
concentration [ppbv]
F-113 Measurement Distibution in Downtown Chicago,
120 samples taken from October 15th, 2004 - April 15th, 2005
Frequency
0.070
0.117
0.165
0.212
0.259
0.306
0.354
0.401
0.448
0.495
0.543
0.590
More
F-113
concentration [ppbv]


Probability Distribution
$y = \frac{1}{s\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-m}{s}\right)^2}$
y
$\frac{1}{s\sqrt{2\pi}}$
$e^{-0.5} = 0.6065...$
m
m+s


Gaussian Distribution for F-12
Riemer vs. TO-15
P(x) Probability Function
concentration (x) [ppbv]
Riemer (41 samples)
mean
TO-15 (58 samples)
mean
μ = 0.539 ppbv
where Sσ = 0.113 ppbv
Aσ = 0.030 ppbv
-Sσ
+Sσ
μ = 0.782 ppbv
where Sσ = 0.241 ppbv
Aσ = 0.021 ppbv
-Sσ
+Sσ
Background: 0.550 ppbv
Butler et al. [1998] (JGR, 103 (D1), 1503-1511, 1998);
Finlayson-Pitts and Pitts et al. [2000] (Chemistry of the Upper and Lower Atmosphere)


Gaussian Distribution for F-11
Riemer vs. TO-15
P(x) Probability Function
concentration (x) [ppbv]
μ = 0.378 ppbv
where Sσ = 0.059 ppbv
Aσ = 0.022 ppbv
-Sσ
+Sσ
μ = 0.450 ppbv
where Sσ = 0.228 ppbv
Aσ = 0.030 ppbv
-Sσ
+Sσ
Riemer (41 samples)
mean
TO-15 (58 samples)
mean
Background: ~0.250 ppbv
Butler et al. [1998] (JGR, 103 (D1), 1503-1511, 1998); Finlayson-Pitts and Pitts et al. [2000] (Chemistry of the Upper and Lower Atmosphere)


CCl4
Gaussian Distribution for Carbon Tetrachloride
Riemer vs. TO-15
0.110 ppbv
CH3Cl3
Gaussian Distribution for 1,1,1-Trichloroethane
Riemer vs. TO-15
0.040 ppbv
F-114
Gaussian Distribution for F-114
Riemer vs. TO-15
0.015 ppbv
F-113
Gaussian Distribution for F-113
Riemer vs. TO-15
0.080 ppbv

Conclusion

- Demonstrated that CFCs and selected halocarbons are consistent throughout most of troposphere
  - Why they are consistent (sources and sinks)
  - That they are consistent (global and local data)
- Limits can be set on historical data which are within instrument detection limits, although low.
  - F-12 can be diluted 5 times and detectable
- Using these limits has led to understanding both accuracy and precision of data produced by our system

Appreciation

- Region 5 Chicago Regional Laboratory for support
- Chris Harmon for energetic work
- R5 Air Division for financial support for standards and Chris
- LTIG Airheads for help in solving problems
- US Taxpayer (always worth remembering)
- The countries of the world for stopping the production of CFCs, a monumental and unparalleled accomplishment, The world is truly a better and safer place as a result

Collection and Analysis of Hexavalent Chromium in Ambient Air

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Eastern Research Group, 601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

ABSTRACT

Hexavalent chromium (Cr^{6+}) is one of the top four pollutants of concern in the EPA National Air Toxics Trends Stations (NATTS) Program. The Environmental Protection Agency (EPA) worked in conjunction with Eastern Research Group (ERG) to improve the California Air Resource Board (CARB) Method 039 for Cr^{6+} monitoring. Attempts to sample and analyze Cr^{6+} at NATTS with improved sensitivity uncovered challenges in the sampling procedures. Issues with background contamination on filters and stability of field samples were the most important contributors to bias and imprecision. Different filters and filter preparations were studied to minimize background Cr^{6+} on filters. A standardized method for media preparation and storage will be discussed. A stability study was performed was performed to determine the best storage conditions to maintain Cr^{6+} stability with less than 30 Relative Percent Difference (RPD). The stability of Cr^{6+} was also evaluated using collocated samplers with spiked and blank filters. Data, using improvements to the Cr^{6+} sampling and analysis procedure for the NATTS, will be presented to show the recent history of Cr^{6+} recovery from field samples.

INTRODUCTION

Chromium is a natural constituent of the earth's crust and is present in several oxidation states. Trivalent chromium (Cr^{3+}) is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium is anthropogenic from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxic and cancer substance. Hexavalent chromium is a known inhalation irritant and associated with respiratory cancer. Exposure occurs primarily in the chrome plating and anodizing process, and emissions from chromate treated cooling towers.

METHOD DEVELOPMENT

Previous sampling and analysis studies for Cr^{6+} at NATTS have shown a variety of issues including filter contamination and storage stability issues. High filter background concentrations are due to manufacturing processes or contamination in storage. Background contamination results in small differences between measured and blank values, which make data interpretation at low concentrations less confident.

Determining the Sampling Media

Four types of filter media were examined to determine which performed best in terms of background contamination and stability. These filters were prepared using the standard CARB Standard Operating Procedure (SOP) 039 to determine if the chromium leaching off the filters at ambient temperatures would cause contamination. The filters used in this study were:

- Cellulose;
- Binderless Quartz;
- Teflon®; and
- Polyvinyl Chloride (PVC).

The results of this study show that the best media is the cellulose filters. The Teflon® filter results are questionable because the coating solution does not adhere to these filters. The results for all of the filters are presented in Table 1 below.

Table 1: Chromium Filter Background Contamination – Assessing the Filter Media

	Filter Media Concentrations (total ng)			
Sample Name	Cellulose	Binderless Quartz	PVC	Teflon®
Day 0 – 1	Not Detected	8.42	2.43	0.320
Day 0 – 2	Not Detected	6.95	2.03	0.370
Day 0 – 3	Not Detected	8.22	3.00	0.400
Day 6 – 1	Not Available	21.91	Not Available	Not Available
Day 6 – 2	Not Available	47.72	Not Available	Not Available
Day 6 – 3	Not Available	28.33	Not Available	Not Available
Day 12 – 1	1.44	Not needed	15.9	0.430
Day 12 – 2	1.12	Not needed	14.6	ND
Day 12 – 3	0.760	Not needed	14.4	ND

ERG treated the cellulose filters selected from initial evaluation of filter media in an attempt to reduce the background below the detection limit of the analysis method. Filters were cleaned with nitric acid to remove hexavalent chromium prior to filter preparation before sampling. Once cleaned, hexavalent chromium was not detected on any unspiked filters. Recovery on spiked filters was from 92 to 100 percent. Based on these results, the acid washed filters are determined to have no associated chromium contamination.

Temporal Stability Study

A temporal study was performed on cellulose and Teflon filters because of the low recovery of background Cr^{6+} in the background contamination study. To determine if the preferred filter preparation method would interfere with recovery of Cr^{6+} samples, 32 bicarbonate coated cellulose and 32 Teflon filters were prepared and spiked. All filters were spiked with 2.5 total ng $^{6+}$ and placed on the laboratory countertop. The experimental design for each filter media included:

- Four spiked filters were analyzed the day they were spiked and four were placed in the freezer.

- Four spiked filters were analyzed the day after spiking (Day 2) and four were placed in the freezer.
- Four spiked filters were analyzed two days after spiking (Day 3) and four were placed in the freezer.
- Four spiked filters were analyzed three days after spiking (Day 4) and four were placed in the freezer.

Table 2 shows the spiked filter results.

Spiked Samples	Cellulose Filters		Teflon Filters	
	Average Concentration (total ng)	Percent Recovery	Average Concentration (total ng)	Percent Recovery
Stored at Room Temperature				
Day 1	2.21	96.03 ± 4%	2.05	88.93 ± 5%
Day 2	1.84	80.14 ± 8%	2.25	97.83 ± 6%
Day 3	1.64	71.2 ± 8%	2.27	98.8 ± 35%
Day 4	1.04	36.1 ± 21%	2.53	110 ± 3%
Stored at -18°C				
Day 1	1.72	74.9 ± 8%	NA	NA
Day 2	1.71	74.2 ± 9%	NA	NA
Day 3	1.32	57.2 ± 3%	2.46	108 ± 8%
Day 4	1.13	49.2 ± 14%	NA	NA
Blanks	ND	NA	ND	NA

Table 2: Cr^{6+} Filter Stability Study

One of the purposes of this study is to determine whether it is feasible to have the filters stored in the field for more than one day after sampling. The cellulose filters stored at room temperature had a significantly reduced recovery from 96 percent on Day 1 to 36 percent on Day 4. The recoveries for the Teflon filters stored at room temperature varied from Day 1 to Day 4 by approximately 15 percent. Similarly, the results for the cellulose filters that were stored at -18°C before analysis ranged from 75 percent on Day 1 to 49 percent on Day 4. Because only one set of Teflon filters was frozen for the stability study, limited data is available for conclusions; however, the recovery for Day 3 is 108 percent. This study shows that the cellulose filters would need to be recovered within 1 day to determine the best recovery, whereas the Teflon filter could be recovered up to 4 days without any significant loss.

Interfering Element Check

Possible interfering compounds were added to the filters and to determine if there were any positive or negative interference when analyzing for Cr^{6+}. All filters were spiked with 10 total ng of Cr^{6+}. Four separate sets of filters were spiked with 10 total ng of Cr^{3+}, Fe, and Mg. All

recoveries were within 95.3% ± 13%, indicating that these elements do not pose any interference for the analysis of Cr^{6+}.

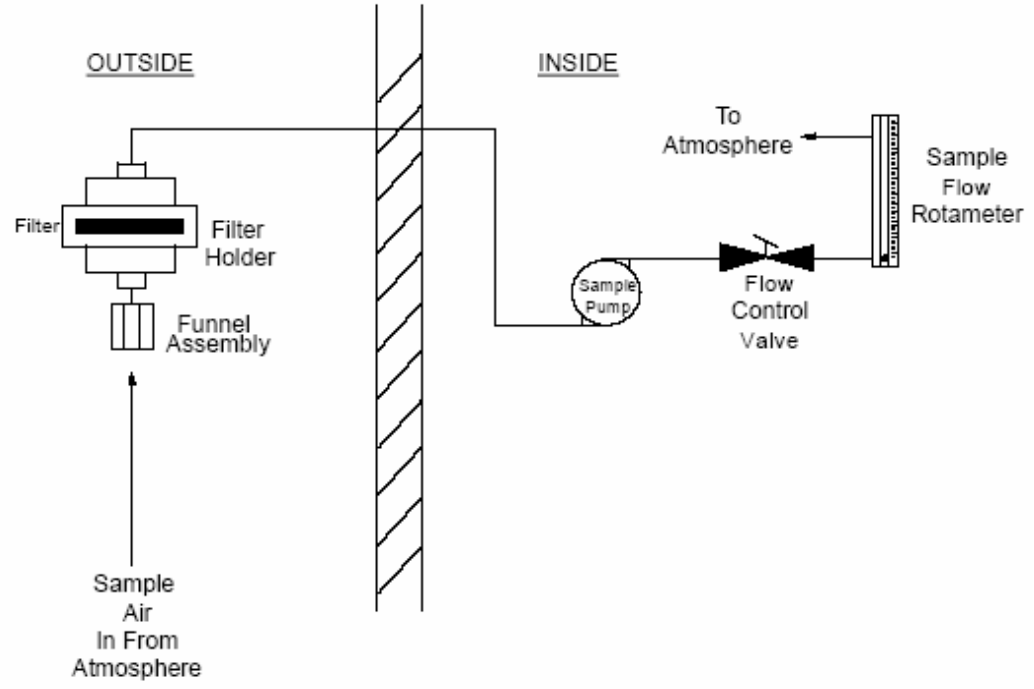
Method Validation

Field studies were performed to validate the filter preparation and storage study determined acceptable under laboratory conditions.

Cr^{6+} Sampling Study

A hexavalent chromium sample is collected by pulling ambient air through the prepared filter at a known flow rate for a period of 24 hours. The hexavalent chromium sampling system is designed to automatically perform a 24-hour filter collection and is automated using a digital timer to initiate sample collection at a flow rate of 15 Lpm. The prepared filter assembly is attached to the inlet of the probe, and the funnel is attached to the inlet of the filter assembly. At the end of the 24-hour collection period, the filter assembly containing the exposed filter is removed from the sampler. The Teflon rod stock plugs are reinserted into the inlet and outlet. Figure 1 presents a standard Cr6+ sampling layout.

Figure 1: Cr^{6+} Sampler Layout



To validate the preparation and stability of the cellulose and Teflon filters, a sampling study was performed. The sampling site chosen for the study included collocated samplers loaded with either spiked or unspiked filters. For the initial study, each sample sets collected the following cellulose filters:

- One filter unspiked. (Background Sample)

- One filter spiked at 2.5 total ng. Total spiked amount in a 21.6 m^3 sample is 0.12 ng/m^3. This value is 10 times the current detection limit, but is assumed an appropriate average result from samples collected in the field. (Spike)
- One trip blank (stored in cooler during sampling period). (Trip Blank)

- One filter spiked at 2.5 total ng and left in the filter container. This filter was stored in the freezer while the samples were taken to the field. It was taken out of the freezer immediately before analysis. (Matrix Spike)

All samples were analyzed the day after collection. The results are presented in Table 3 below. All passive and trip blank samples had no detectable hexavalent chromium. The recoveries of spiked samples are slightly better during cold, wet days.

Table 3: Ambient Monitoring Study – Cellulose Filters

	Conditions					
Sample Set	**Sample Volume (m^3)**	**Humidity**	**Temperature**	**Comments**	**RPD**	**% Recovery**
1	21.57	88% (58% - 96%)	48.8°F (44.1°F - 57.9°F)	Rain	**28**	72%
MS – 1					3.2	103%
2	21.66	81% (38% - 100%)	41.3°F (37°F - 59°F)	Rain	6.4	94%
MS – 2					4.0	96%
3	21.7	76% (37% - 100%)	37.8°F (34°F – 42.1°F)	Overcast to Clear	**73**	27%
MS – 3					9.1	109%
4	21.7	42% (24% - 61%)	35.3°F (27°F – 45°F)	Cloudy to Clear	**58**	42%
MS - 4					0	100%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.
MS = Matrix Spike

The cellulose filters showed varying recoveries on the samples taken. Two of the 8 spiked filters recovered under 70%, with a total average recovery at 80.4%. A comparison study was performed to reproduce the sampling completed on the cellulose filters. This study is presented in Table 4 and is described below:

- Teflon Set 1 through 3 followed same procedures as the cellulose study (spiked at 2.5 total ng),

- Teflon Set 4 through 7 collected using a lower flow rate at 8 L/min (spiked at 2.5 total ng for 4 and 5, 5.0 total ng for 6 and 7),

- Teflon Set 8 and 9 collected at 15 L/min with a particulate filter before the spiked filter (spiked at 2.5 and 5.0 total ng, respectively),

- Teflon Set 10 and 11 collected using an ozone scrubber cartridge (used for TO-11A sampling) that would take out ozone as well as particulate (spiked at 2.5 total ng).

Table 4: Spiked Teflon Filter Study (with rough polypropylene support)

Sample Set	Setup	RPD	% Recovery
Teflon Set 1	Standard conditions at 15 L/min	**24**	76%
Teflon Set 2		**64**	**36%**
Teflon Set 3		4.0	96%
Teflon Set 4	Flow at 8 L/min	1.2	101%
Teflon Set 5		**83**	**17%**
Teflon Set 6		9.0	109%
Teflon Set 7		**60**	**41%**
Teflon Set 8	Collected a particulate filter before spiked filter	1.9	98%
Teflon Set 9		5.6	94%
Teflon Set 10	Collected using an ozone scrubber before spiked filter	13	113%
Teflon Set 11		6.3	94%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%. The Teflon also showed varying recoveries. Three of the 11 spiked filters recovered under 70%, with a total averaged recovery at 79.5%. This indicated a close comparison of the Teflon to the cellulose filter Cr^{6+} collection.

In order to distinguish other possible interferants, another set of experiments were preformed:

- Volume Check -the rate of collection was too high by reducing the overall sample volume to 11.5 m^3,
- Particulate Check -the particulate reacted with the Cr^{6+} to reduce it to Cr^{3+} by having a Teflon filter inline before the spiked filter, and
- Ozone Check – ozone reacts to oxidize other agents that could reduce the Cr^{6+} to Cr^{3+}. As presented in Table 5, the Cr^{6+} recovery was not affected by changing any of these parameters

As presented in Table 5, the Cr^{6+} recovery was not affected by changing any of these parameters (volume, particulate and ozone).

Table 5: Physical Interferants Check for Cr^{6+} Sampling

Sample	Spiked in total ng	Results in total ng	Percent Recovery
Volume Check – collected at 11.5 m^3 (instead of standard 21.6 m^3)			
Run 1	2.5	2.53	101%
Run 2	5.0	5.45	109%
Particulate Check – collected particulate before ambient air crossed spiked filter			
Run 1	2.5	2.45	98.1%
Run 2	5.0	4.72	94.4%
Ozone Check – scrubbed ozone and particulate before ambient air crossed spiked filter			
Run 1	2.5	2.82	113%
Run 2	5.0	4.68	93.7%

Comparison Sampling Using Cellulose and Teflon Filters

The optimal way to confirm the performance using either filter is to collect collocated sets of cellulose and Teflon filters. ERG sent five different NATTS sites the standard cellulose and Teflon filters as a means to evaluate the performance of the Teflon filters. These sites were selected based on recent history of Cr^{6+} in their samples. The results are presented in Table 6 below.

Table 6: Comparison of Cr^{6+} Recovery on Cellulose and Teflon Filters

Site	Total # of Samples	Similar Results on Cellulose and Teflon (±30% RPD)	Cellulose Concentration Higher (>30% RPD)	Teflon Concentration Higher (>30% RPD)
Boston, MA	3	0%	100%	0%
Detroit, MI	5	20%	80%	0%
Seattle, WA	4	75%	25%	0%
Tampa, FL	5	0%	80%	20%
Washington, DC	4	0%	75%	25%
Average	4	19%	72%	9%

Note: Sampling was conducted from June to August 2005.

This table shows the total number of samples collected at each site and compares the Cr^{6+} recoveries of the cellulose to the Teflon filters. For example, the site in Detroit sampled 5 sets of filters (one cellulose and one Teflon filter) during the same sampling period. One of these filter sets had similar recoveries for the cellulose and Teflon filters, and the other 4 filter sets had higher Cr^{6+} recoveries with the cellulose filters. The lower recovery on the Teflon filters could be due to other reducing compounds in the ambient air that would convert the Cr^{6+} to Cr^{3+}. This is prevented from occurring on the cellulose filters because of the sodium bicarbonate coating. In

Seattle, WA, the air stream is being blown from the west, off the Pacific Ocean. Because of the lower interference from mobile and emission sources, the difference between the cellulose and Teflon filters is minimal. The other 4 sites (Boston, Detroit, Tampa, and Washington, DC) are in highly populated areas where these emissions could reduce the Cr^{6+} significantly. Based on the results of this sampling study, ERG determined that collection on the acid washed, sodium bicarbonate coated cellulose filters would recover the Cr^{6+} more efficiently for real-world ambient samples.

FIELD SAMPLE RESULTS FOR HEXAVALENT CHROMIUM

Twenty-two National Monitoring Program (NMP) sites collected Cr^{6+} samples from January 2005 to December 2005. Some monitors were placed near the centers of heavily populated cities (e.g., Chicago, IL and Detroit, MI), while others were placed in moderately populated areas (e.g., Madison, WI and Hazard, KY). Hexavalent Chromium concentrations measured during this time varied significantly from monitoring location to monitoring location. The proximity of the monitoring locations to different emissions sources, especially industrial facilities and heavily traveled roadways, often explains the observed spatial variations in ambient air quality. Table 7 presents the frequency of detects, maximum value, minimum detected value, median, and average.

Table 7: Analytical Results for Samples Collected Between January 2005 and December 2005

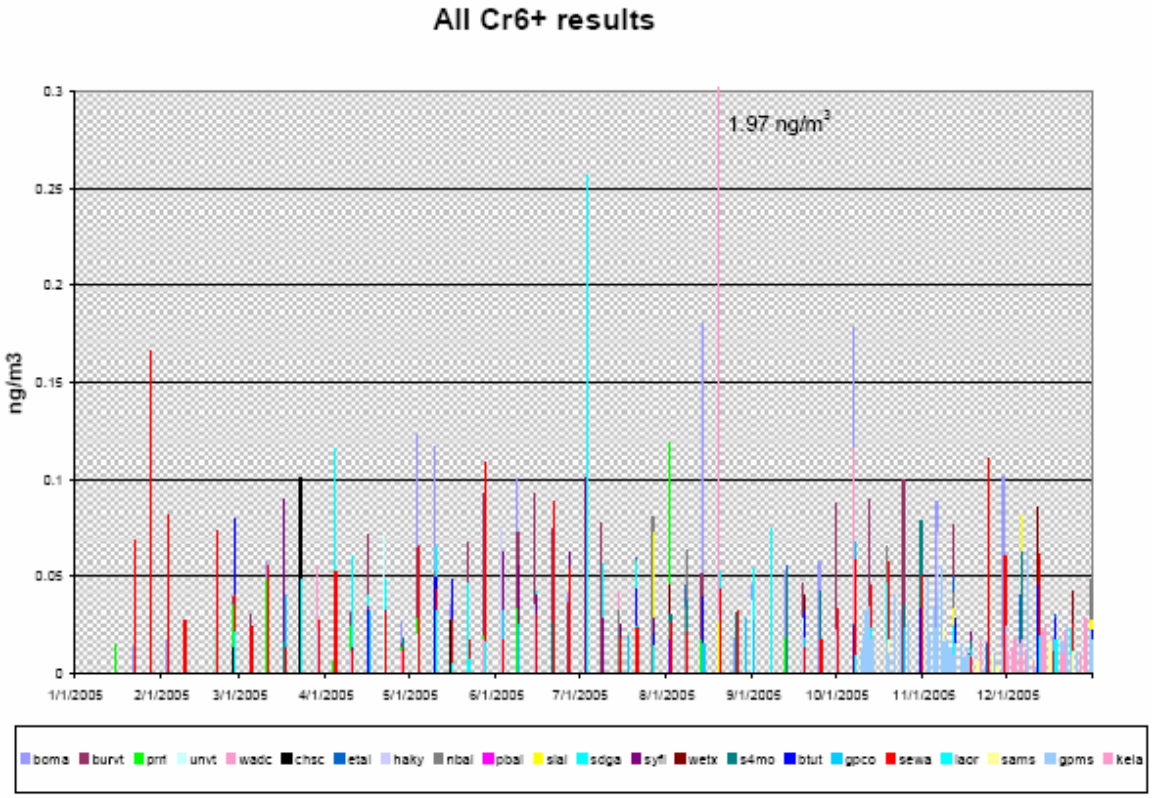
Site	Frequency of Detects	Maximum Value (ng/m^3)	Minimum Value (ng/m^3)	Median (ng/m^3)	Average (ng/m^3)
Roxbury, MA	78%	0.180	0.011	0.032	0.048
Burlington, VA	74%	0.099	0.011	0.039	0.047
Providence, RI	60%	0.119	0.006	0.023	0.028
Underhill, VT	29%	0.071	0.003	0.021	0.025
Washington, DC	52%	1.970	0.007	0.018	0.103
Chesterfield, SC	41%	0.101	0.004	0.017	0.023
Birmingham, AL (site 1)	79%	0.059	0.015	0.030	0.036
Hazard, KY	41%	0.076	0.008	0.022	0.027
North Birmingham, AL	69%	0.080	0.013	0.041	0.041
Providence, AL	50%	0.020	0.003	0.015	0.012
Birmingham, AL (site 2)	56%	0.082	0.023	0.034	0.041
S. Dekalb Co., GA	71%	0.116	0.010	0.039	0.039
Tampa, FL	53%	0.101	0.005	0.025	0.033
Detroit, MI	83%	0.093	0.016	0.042	0.043
Madison, WI	48%	0.108	0.007	0.018	0.026
Chicago, IL	69%	0.086	0.004	0.023	0.027
Austin, TX	85%	0.086	0.010	0.029	0.034

Site	Frequency of Detects	Maximum Value (ng/m^3)	Minimum Value (ng/m^3)	Median (ng/m^3)	Average (ng/m^3)
St. Louis, MO	71%	0.078	0.011	0.026	0.029
Bountiful, UT	67%	0.079	0.004	0.027	0.030
Grand Junction, CO	61%	0.067	0.001	0.021	0.022
Seattle, WA	83%	0.166	0.007	0.031	0.041
La Grande, OR	30%	0.256	0.005	0.017	0.034
Kenner, LA	47%	0.028	0.001	0.017	0.016
Gulf Port, MS	33%	0.026	0.001	0.009	0.011
Stennis Airport, MS	56%	0.062	0.002	0.015	0.020
Average	58%	0.168	0.007	0.025	0.034

A total of 1,209 Cr^{6+} measurements were detected at the 22 NMP sites from January 2005 to December 2005. Two hundred and nine of these were taken at three sites during the clean up after Hurricane Katrina. Of the 1,209 Cr^{6+} measurements, 58% of these results were detects and 12% of these concentrations were below the MDL. The average Cr^{6+} concentration was 0.034 ng/m^3.

Data from the NMP sites is presented in Figure 2. The highest concentration was taken at Washington, DC, at 1.97 ng/m^3. The samples taken for Katrina were collected on a 1-in-1 schedule starting October 10, 2005. Hexavalent chromium results at Katrina monitoring sites were similar or slightly lower than other sites in the program.

Figure 2: Analytical Cr^{6+} Results for Samples Collected Between January 2005 and December 2005



DATA QUALITY CONTROL AND ASSURANCE

Precision of the analytical and sampling technique was determined using the analysis of collocated sampling episodes. A collocated sample (i.e., a sample collected simultaneously with the primary and collocated sample using separate sampling systems) provides information on the potential for sampling variability. ERG was not able to perform replicate analyses because the final sample instrument injection volume did not allow the replicate analyses. Method spikes were analyzed, however, and give an acceptable range of 80-120% recovery. The collocated results were compiled from sites sampling in the NMP from January 2005 through December 2005.

The collocated data is presented in Relative Percent Difference (RPD). The RPD expresses average concentration differences relative to the average concentrations detected during collocated analyses. The RPD is calculated as follows:

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100 \qquad (1)$$

Where:

X_1 is the ambient air concentration of given compound measured in one sample;

X_2 is the concentration of the same compound measured during collocated analysis; and
X is the arithmetic mean of X_1 and X_2.

As this equation shows analyses with low variability have lower RPDs (and better precision), and analyses with high variability have higher RPDs (and poorer precision). The RPD method quality objective for all data from the NMP is 25 percent.

Collocated results outside the 25% RPD objective can be grouped into two sets. Results with few detectable results show high average RPD but low median RPD results. Other sites show one set of collocates with high RPD, which skews the average RPD above the quality objective. For example, Seattle, Washington presents a high average of 28 percent, but the median is acceptable at 6.1 percent. Seven collocated sets were taken and only one of those failed, causing the average to exceed the acceptable limit. Table 10 presents the collocated data results.

Table 10: Collocate Statistical Data Results (January 2005 to December 2005)

Site ID	# of Collocates	Median (RPD)	Average (RPD)	Percent Standard Deviation
S. Dekalb Co., GA	3	**89.0%**	**89.0%**	6.1%
Austin, TX	1	**30.5%**	**30.5%**	0.0%
Detroit, MI	4	20.3%	19.1%	12.6%
Roxbury, MA	7	19.0%	22.1%	19.3%
Birmingham, AL (site 1)	1	16.6%	16.6%	0.0%
Gulf Port, MS	8	16.3%	21.9%	26.0%
St. Louis, MO	3	14.4%	15.0%	15.3%
Providence, RI	7	14.3%	29.9%	45.2%
Kenner, LA	5	12.1%	**28.1%**	40.6%
Grand Junction, CO	4	9.6%	16.9%	22.9%
Madison, WI	4	8.8%	12.3%	15.3%
Burlington, VA	12	8.1%	16.2%	30.3%
Seattle, WA	7	6.1%	**27.9%**	52.1%
Washington, DC	4	4.1%	9.0%	13.1%
Chicago, IL	4	2.8%	6.4%	9.6%
Underhill, VT	7	0.0%	5.5%	9.5%
Chesterfield, SC	6	0.0%	10.1%	24.8%
Hazard, KY	6	0.0%	5.6%	11.2%
North Birmingham, AL	2	0.0%	0.0%	0.0%
Providence, AL	2	0.0%	0.0%	0.0%
Birmingham, AL (site 2)	2	0.0%	0.0%	0.0%
Tampa, FL	5	0.0%	4.0%	8.9%
Stennis Airport, MS	11	0.0%	2.6%	8.8%
Average	5	11.8%	16.9%	16.2%

The overall data average RPD result is 16.9%, which is within the 25% target. The S. Dekalb Co., GA site is a notable exception to this group of results. This location has a sampler that requires the filters to be installed on site instead. The normal practice is to place them in a filter holder under controlled laboratory conditions to prevent Cr^{6+} contamination. All of the collocated results from S. Dekalb Co. ranged from 82 to 91% RPD.

CONCLUSIONS

Based on the results of this study, ERG concludes Teflon filters do not collect the Cr^{6+} more efficiently then cellulose. Reducing agents in the ambient air seem to be converting the Cr^{6+} to $^{3+}$ and the filter media must stabilize and protect the Cr^{6+} from these reducing agents. The Teflon filters do not have the buffer coating (sodium bicarbonate) to stabilize the Cr^{6+} on the filter when reducing agents, such as acid gases.

ERG laboratory's detection limit for acrolein is 0.012 ng/m^3 (experimentally determined using 40 CFR, Part 136 procedures) which is lower than the cancer and noncancer health risk threshold concentration. Based on the results of this study, sample collection using the sodium bicarbonate coated cellulose filters is recommended. There are certain preservation procedures that must be followed before acceptable sample results should be reported, including:

- The filters must be acid washed and rinsed before coating them with the sodium bicarbonate to prevent Cr^{6+} background. Using this method however, does not lengthen the collection or storage hold time.

- All samples must be retrieved from the field one day after the sample has been collected to prevent Cr^{6+} negative bias (loss) (up to 20% on the first day).

- All samples must be frozen after collection to reduce the risk of Cr^{6+} loss.

Analysis of sodium bicarbonate coated cellulose filters containing known concentrations of Cr^{6+} demonstrated acceptable recoveries, if the samples are recovered as soon as possible after sampling ends.

ERG has determined that this modified method shows consistent recovery for Cr^{6+} over time throughout the country. The collocated sample recoveries meet the method quality objectives set by the EPA for the NATTS program, however there does seem to be limitations on sample recovery for loading filters outside of the controlled laboratory conditions.

ACKNOWLEDGMENTS

The authors would like to express their appreciation for the hard work and dedication shown by the U.S. EPA, OAQPS staff and Eastern Research Group's laboratory.

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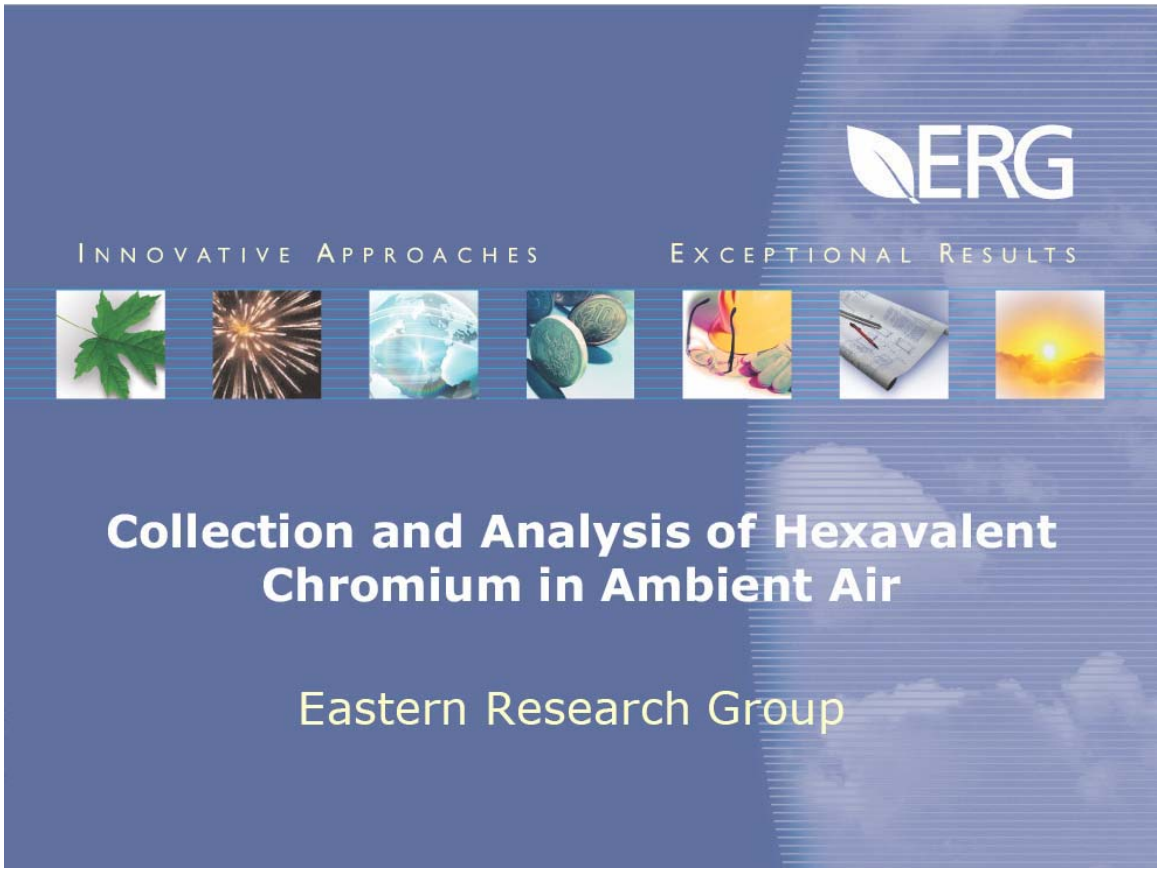
1. California Air Resources Board, March 2002. *Standard Operating Procedure for the Analysis of Hexavalent Chromium at Ambient Atmospheric Levels by Ion Chromatography, MLD039, Revision 3*.

2. U.S. Environmental Protection Agency. *Hexavalent Chromium Method Development.* Swift, J.; Merrill, R.; Tedder, D.; J. Homolya, Work Assignment Manager. Research Triangle Park, NC.

3. U.S. Environmental Protection Agency. *Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC).* Swift, J.; Merrill, R.; J. Homolya, Work Assignment Manager. Research Triangle Park, NC.



Introduction

- Chromium is present in several oxidation states
- Cr^{3+} is naturally occurring, environmentally pervasive and a trace element in man and animals
- Cr^{6+} is anthropogenic from a number of commercial and industrial sources

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2

Hexavalent Chromium Health Effects

- Penetrates biological membranes
- Identified as an industrial toxic and cancer substance
- Inhalation irritant and associated with respiratory cancer
- Cancer Risk Level – 0.084 ng/m^3
- Non-Cancer Risk Level – 0.00011 ng/m^3
- ERG MDL Level – 0.011 ng/m^3, assuming 21.6 total m^3 sampled

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Method Development

- Provide cleanest filter media
- Provide filter media that does not affect background
- Stabilize the Cr^{6+} on the filter
- Recover spike Cr^{6+} on recommended filter media

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Quality Control Criteria

- Relative Percent Difference (RPD) ± 25%
- Coefficient of Variation (CV) ±15%
- Analyzed 4 sets to statistically achieve QA controls

All results shown outside of this criteria will be highlighted in **red**

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Filter Media Determination

- Cellulose
- Binderless Quartz
- Teflon®
- Polyvinyl Chloride (PVC)

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Assessing the Blank Filter Media

Sample Name	Filter Concentrations (total ng)			
	Cellulose	Binderless Quartz	PVC	Teflon®
Day 0 – 1	Not Detected	8.42	2.43	0.32
Day 0 – 2	Not Detected	6.95	2.03	0.37
Day 0 – 3	Not Detected	8.22	3.00	0.40
Day 6 – 1	Not Available	21.91	Not Available	Not Available
Day 6 – 2	Not Available	47.72	Not Available	Not Available
Day 6 – 3	Not Available	28.33	Not Available	Not Available
Day 12 – 1	1.44	Not needed	15.9	0.43
Day 12 – 2	1.12	Not needed	14.6	ND
Day 12 – 3	0.76	Not needed	14.4	ND

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Cr6+ Filter Stability Study

Spiked Samples	Cellulose Filters		Teflon Filters	
	Average Concentration (total ng)	Percent Recovery	Average Concentration (total ng)	Percent Recovery
Stored at Room Temperature				
Day 1	2.21	96.03 ± 4%	2.05	88.93 ± 5%
Day 2	1.84	80.14 ± 8%	2.25	97.83 ± 6%
Day 3	1.64	**71.2** ± 8%	2.27	98.8 ± 35%
Day 4	1.04	**36.1** ± 21%	2.53	110 ± 3%
Stored at -18°C				
Day 1	1.72	**74.9** ± 8%	NA	NA
Day 2	1.71	**74.2** ± 9%	NA	NA
Day 3	1.32	**57.2** ± 3%	2.46	108 ± 8%
Day 4	1.13	**49.2** ± 14%	NA	NA
Blanks	ND	NA	ND	NA

All results shown outside of this criteria will be highlighted in **red**

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Cellulose Filter Freezer Study (Spiked 2.5ng Cr^{6+})

Sample	Analyzed - Not Frozen			Frozen before Analyzed		
	Date Analyzed	RPD	CV	Date Analyzed	RPD	CV
Day 0 AVERAGE	8-Mar	4	2.46	11-Mar	5	6.15
Day 2 AVERAGE	9-Mar	20	7.10	11-Mar	**26**	12.21
Day 3 AVERAGE	10-Mar	**29**	11.37	11-Mar	**43**	6.47
Day 4 AVERAGE	11-Mar	**66**	11.68	11-Mar	**51**	**27.59**

All results shown outside of this criteria will be highlighted in **red**

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Interfering Element Check

- Filters were spiked with 10 total ng of Cr^{6+}.
- Four sets of filters were spiked with 10 total ng of Cr^{3+}, Fe, and Mg.
- Recoveries were within 95.3% ± 13%.
- These elements do not pose any interference for the analysis of Cr^{6+}.

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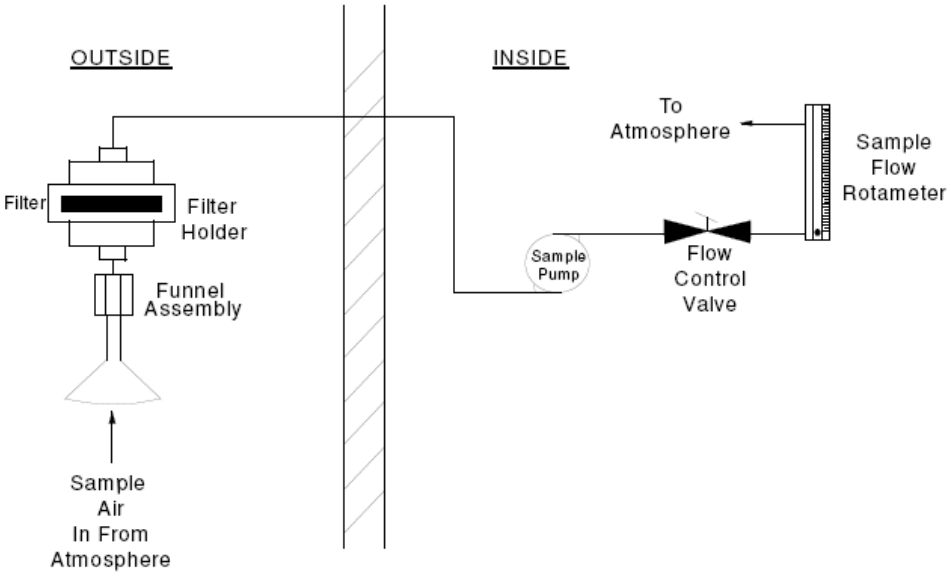
ERG Cr6+ Sampling System



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Sampling Setup

- One filter unspiked (Sample)
- One filter spiked at 2.5 ng
- One trip blank
- One filter spiked at 2.5 ng and left in the filter container - Method Spike

All Samples collected had no Cr^{6+} detected

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Cellulose Filter (Standard Bicarbonate Solution)

Sample Set	Conditions				% Recovery
	Sample Volume (m^3)	Humidity	Temperature	Comments	
1	21.57	88% (58% - 96%)	48.8°F (44.1°F - 57.9°F)	Rain	72%
MS – 1					103%
2	21.66	81% (38% - 100%)	41.3°F (37°F - 59°F)	Rain	94%
MS – 2					96%
3	21.7	76% (37% - 100%)	37.8°F (34°F – 42.1°F)	Overcast to Clear	27%
MS – 3					109%
4	21.7	42% (24% - 61%)	35.3°F (27°F – 45°F)	Cloudy to Clear	42%
MS - 4					100%

All results shown outside of this criteria will be highlighted in **red**

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Spiked Teflon Filter Study (w/rough polypropylene support)

Sample Set	Setup	% Recovery
Teflon Set 1	Standard conditions at 15 L/min	76%
Teflon Set 2		36%
Teflon Set 3		96%
Teflon Set 4	Flow at 8 L/min	101%
Teflon Set 5		17%
Teflon Set 6		109%
Teflon Set 7		41%
Teflon Set 8	Collected a particulate filter before spiked filter	98%
Teflon Set 9		94%
Teflon Set 10	Collected using an ozone scrubber before spiked filter	113%
Teflon Set 11		94%

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All results shown outside of this criteria will be highlighted in **red**

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Comparison of Cr6+ Recovery on Cellulose and Teflon Filters

Site	Total # of Samples	Similar Results on Teflon & Cellulose	Cellulose Concentration Higher (>25% RPD)	Teflon Concentration Higher (>25% RPD)
Boston, MA	3	0	3	0
Detroit, MI	5	1	4	0
Seattle, WA	4	3	1	0
Tampa, FL	5	0	4	1
Washington, DC	4	0	3	1
Average	4.2	0.8	3	0.4

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2005 Field Site Sample Results

- 1,209 Cr^{6+} measurements were detected at the 22 NMP
- 209 of these were taken at 3 sites during the clean up after Hurricane Katrina
- Of the 1,209 Cr^{6+} measurements, 58% of these results were detects and 12% of these concentrations were below the MDL
- Average Cr^{6+} concentration was 0.034 ng/m3.

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Analytical Results for samples collected between 1/05 to 12/05 (1 of 2)

Sorted by Frequency – highest 3 & lowest 3

Site	Frequency of Detects	Maximum Value (ng/m³)	Minimum Value (ng/m³)	Median (ng/m³)	Average (ng/m³)
Austin, TX	85%	0.086	0.01	0.029	0.034
Detroit, MI	83%	0.093	0.016	0.042	0.043
Seattle, WA	83%	0.166	0.007	0.031	0.041
Gulf Port, MS	33%	0.026	0.001	0.009	0.011
La Grande, OR	30%	0.256	0.005	0.017	0.034
Underhill, VT	29%	0.071	0.003	0.021	0.025

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Analytical Results for samples collected between 1/05 to 12/05 (2 of 2)

Sorted by Average – highest 3 & lowest 3

Site	Frequency of Detects	Maximum Value (ng/m³)	Minimum Value (ng/m³)	Median (ng/m³)	Average (ng/m³)
Washington, DC	52%	1.97	0.007	0.018	0.103
Roxbury, MA	78%	0.18	0.011	0.032	0.048
Burlington, VT	74%	0.099	0.011	0.039	0.047
Kenner, LA	47%	0.028	0.001	0.017	0.016
Providence, AL	50%	0.02	0.003	0.015	0.012
Gulf Port, MS	33%	0.026	0.001	0.009	0.011

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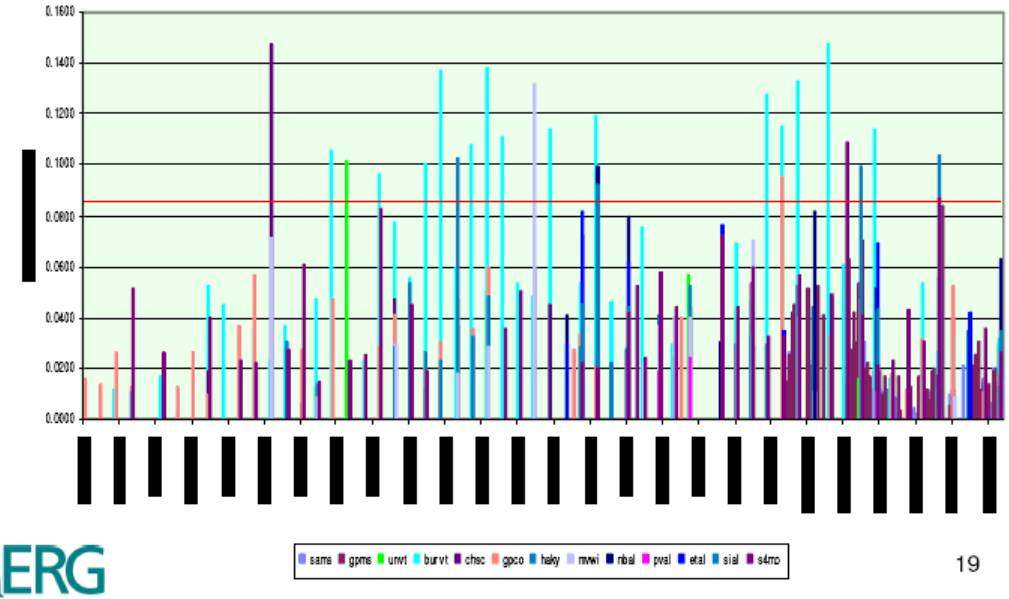
Figure of Analytical Cr6+ Results between 1/05 to 12/05



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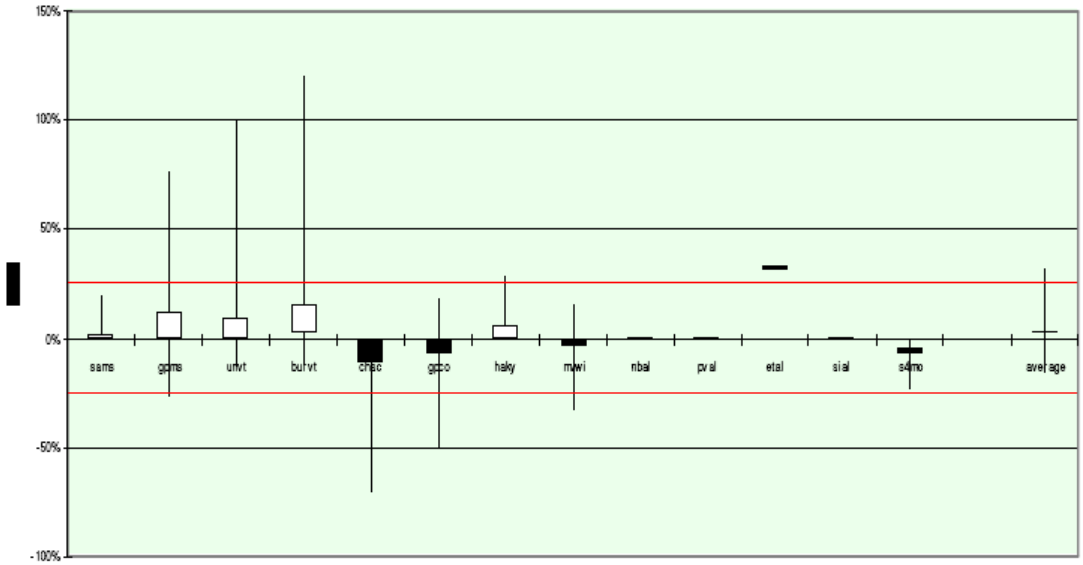
Duplicate Analysis Results (Jan'05 to Dec'05)



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Duplicate Analysis Results (Jan'05 to Dec'05)

Site	1	2	3	4	5	6	7	8	9	10	11	Average	Absolute Value Average
sams	19%	0%	0%	0%	0%	0%	0%	0%	0%			2%	2%
gpms	-27%	32%	77%	-11%	0%	-5%	36%	0%	4%			12%	21%
unvt	0%	0%	0%	100%	-10%	-13%	0%	0%				10%	15%
burvt	0%	0%	0%	-12%	7%	6%	34%	19%	2%	120%	2%	16%	18%
chsc	0%	0%	-70%	0%	0%	0%						-12%	12%
gpco	18%	-50%	0%	-1%								-8%	17%
haky	0%	0%	0%	29%	0%							6%	6%
mvwi	-33%	0%	16%	0%								-4%	12%
nbal	0%											0%	0%
pval	0%											0%	0%
etal	32%											32%	32%
sial	0%											0%	0%
s4mo	0%	-9%	0%	-23%								-8%	8%

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All results shown outside of this criteria will be highlighted in **red**

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Conclusions

- Teflon filters do not collect the Cr^{6+} more efficiently then cellulose
- Sample collection using sodium bicarbonate coated cellulose filters is recommended
- Filters must be acid washed before coating them with sodium bicarbonate to prevent Cr^{6+} background

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Conclusions, Cont.

- Samples must be retrieved from the field one day after the sample has been collected to prevent Cr^{6+} loss
- Samples must be frozen after collection to reduce the risk of Cr^{6+} loss

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Acknowledgments

- **US EPA, OAQPS**
  - **Jim Homolya**
  - **Mike Jones**
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  - **Julie Swift**

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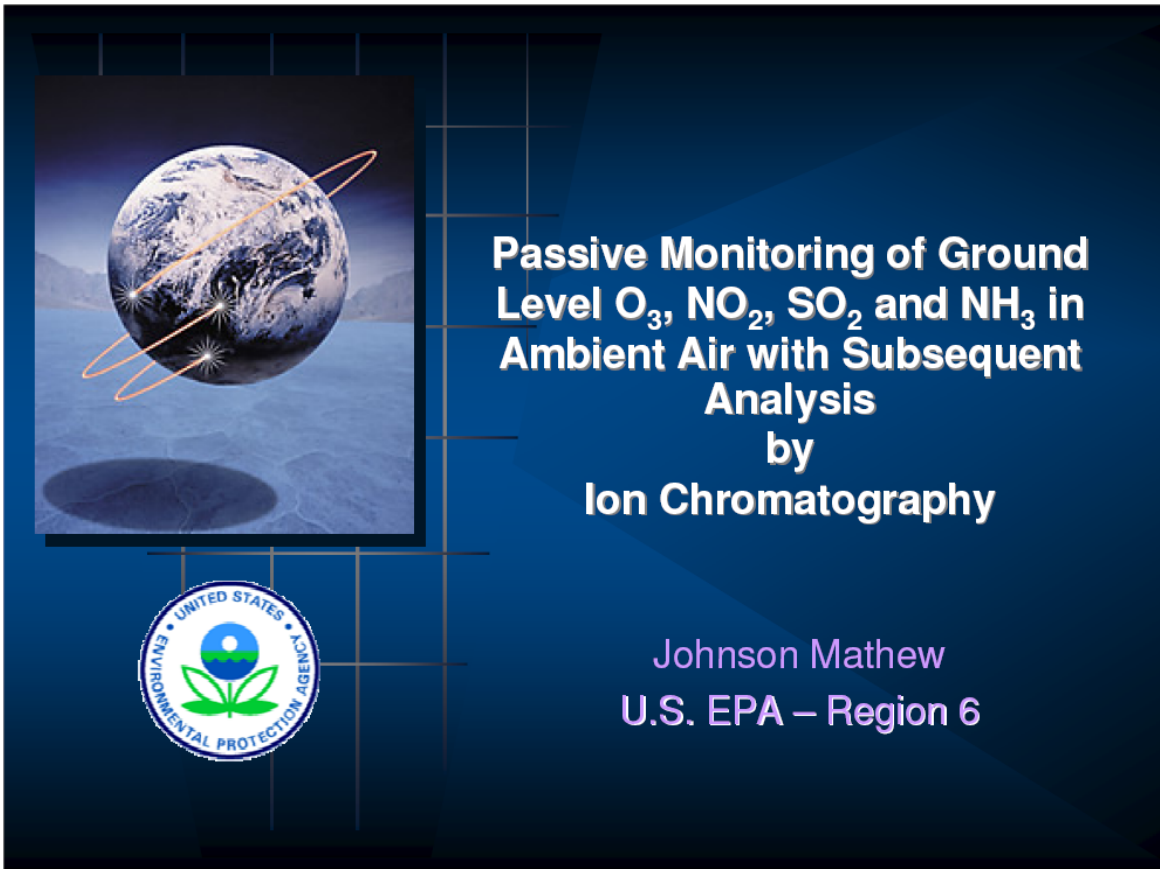
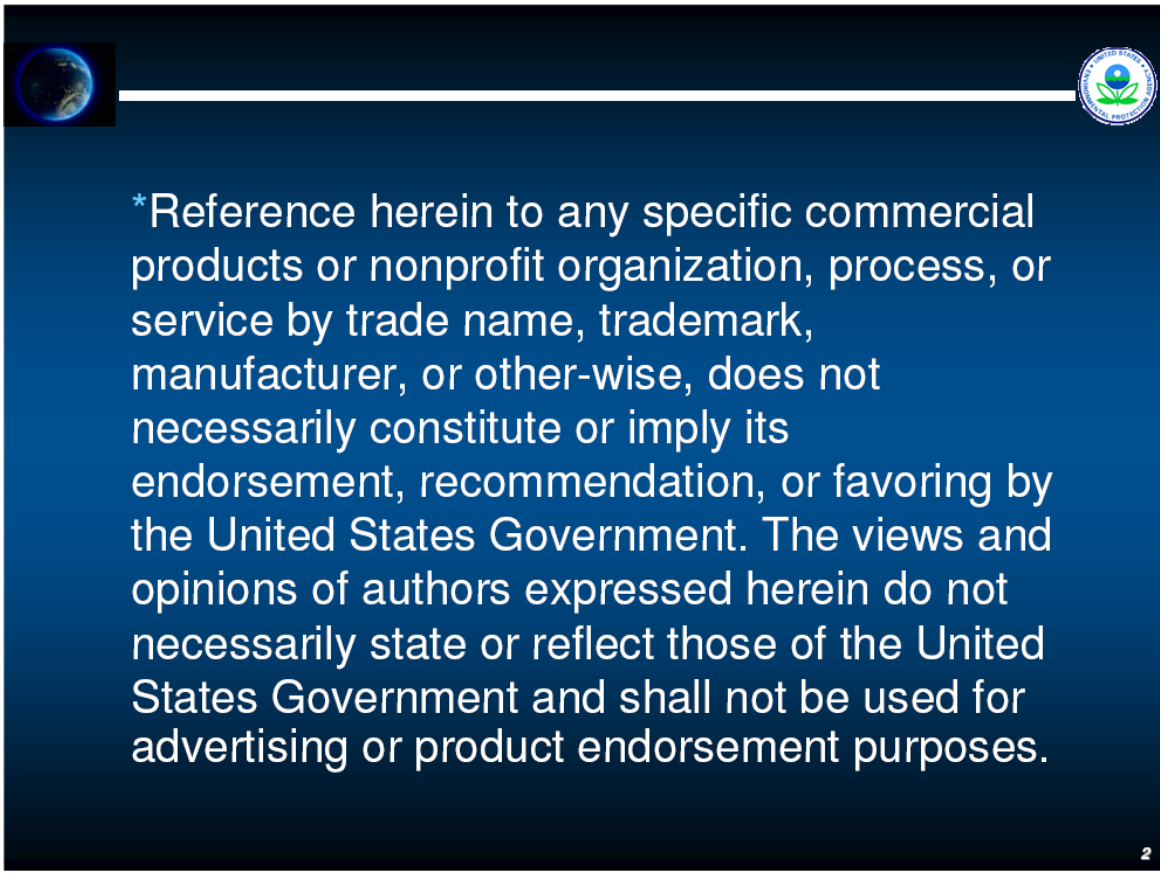
PASSIVE MONITORING OF GROUND LEVEL OZONE

Matthew, Johnson; United States EPA

Chemically impregnated filters are used to passively monitor ground level ozone, nitrogen dioxide, sulfur dioxide and ammonia in ambient air. Contaminant in air reacts with chemical on the filter to form respective complex. Using Ion Chromatography instrument we can determine the reacted species. This presentation will demonstrate use of Ion Chromatography instruments to monitor and calculate ground level Ozone, Nitrogen dioxide, Sulfur dioxide and Ammonia in ambient air.


Passive Monitoring of Ground Level O_3, NO_2, SO_2 and NH_3 in Ambient Air with Subsequent Analysis by Ion Chromatography
Johnson Mathew
U.S. EPA – Region 6


*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.
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Outline

- Air Standard
- Continuous monitoring
- Passive monitoring
- Composition of filters
- Extraction and Analysis
- QC
- Passive Ammonia
- Conclusion

3

National Ambient Air Quality Standard

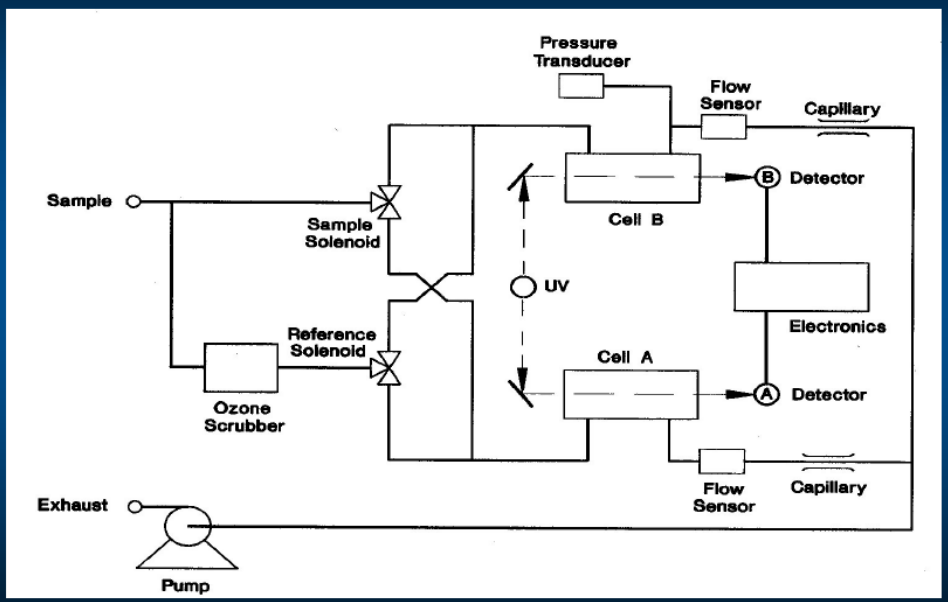
- US ENVIRONMENTAL PROTECTION AGENCY HAS ESTABLISHED NATIONAL AMBIENT AIR QUALITY STANDARD FOR SIX AIR POLLUTANTS;
  - OZONE
  - NITROGEN DIOXIDE
  - SULFUR DIOXIDE
  - CARDON MONOOXIDE
  - LEAD
  - RESPIRABLE PARTICULATE MATTER

4

Basic Monitoring

5

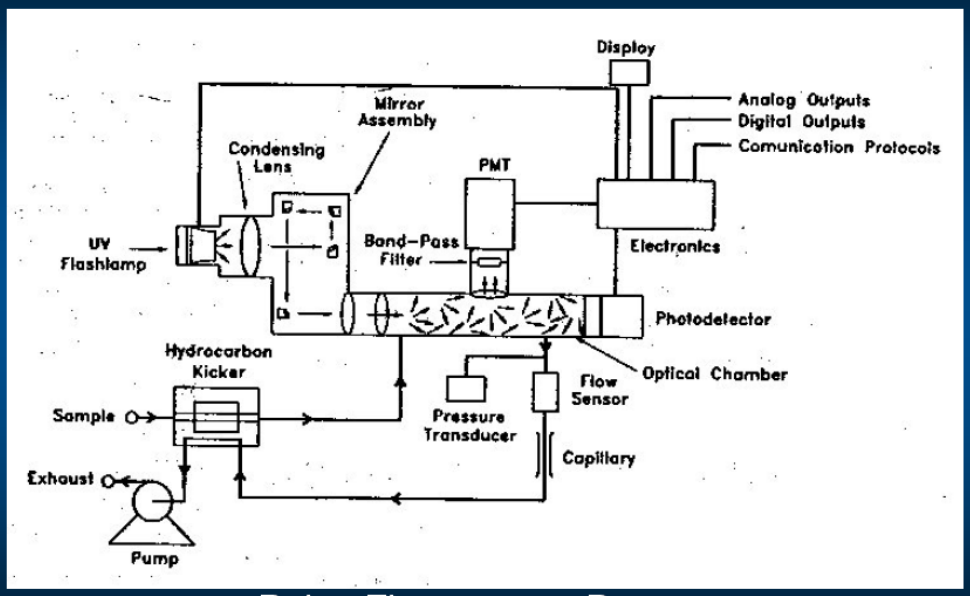
Continuous Monitor - Ozone



UV Detector

6

Continuous Monitor – SO_2

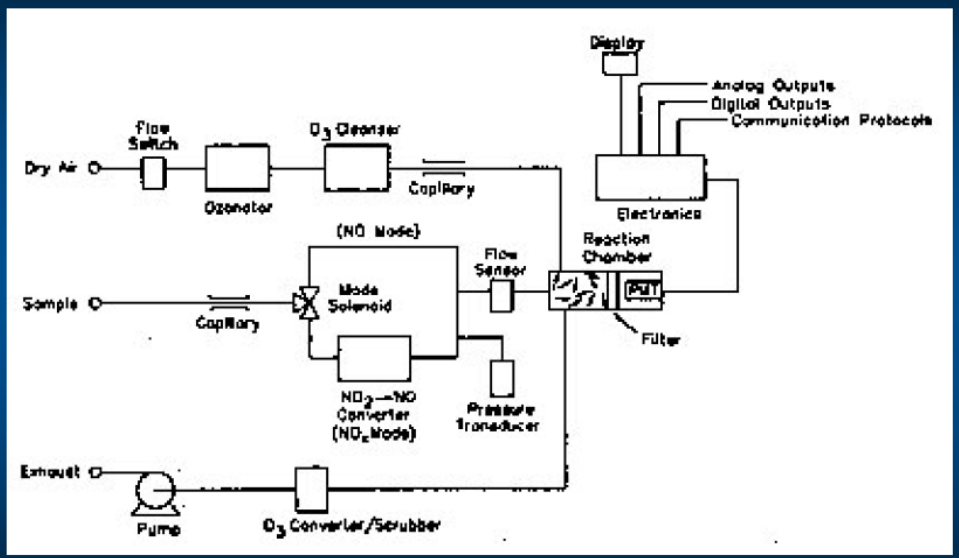


- Pulse Florescence Detector

$$SO_2 + h\nu_1 \longrightarrow SO_2^* \longrightarrow SO_2 + h\nu_2$$

7

Continuous Monitor – $NO/NO_2/NO_x$

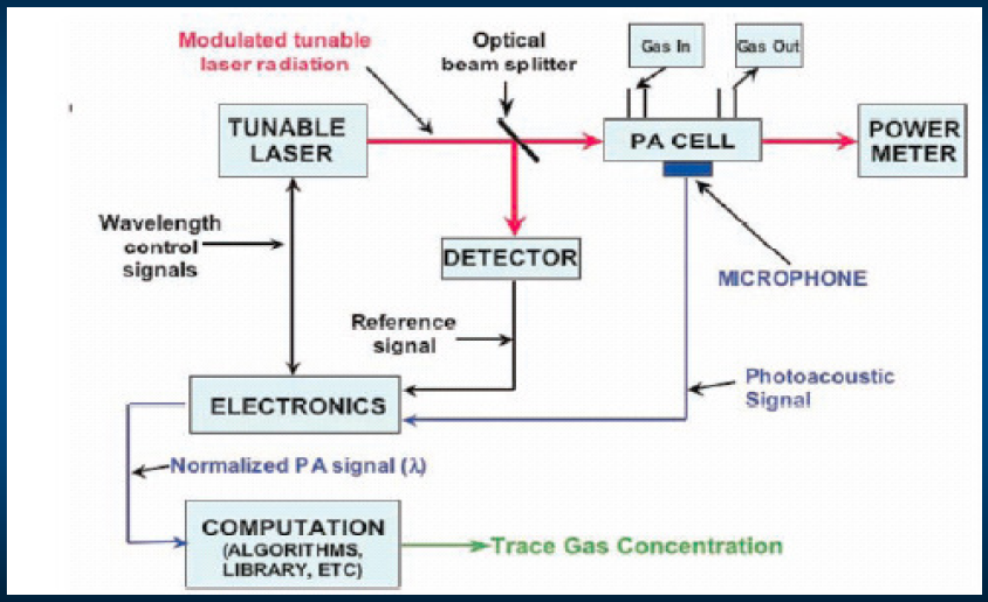


- Florescence Detector

$$NO + O_3 \longrightarrow NO_2 + O_2 + h\nu$$

8

Continuous Monitor - Ammonia



- Photoacoustic spectroscopy

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Passive Sampling Device -Schematic

ASSEMBLING THE MONITORS

10

Application

- Collection of ground level ANALYTES in ambient air using Passive Sampling Devices(PSDs) (Ogawa Inc., USA) and subsequent analysis by Ion Chromatography.

11

Composition of filters

- For Passive O_3
  - 14.5 mm Ø collection filter
  - Coated with Sodium Nitrite ($NaNO_2$)
  - $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$
- For Passive SO_2
  - 14.5 mm Ø collection filter
  - Coated with Triethanolamine (TEA)

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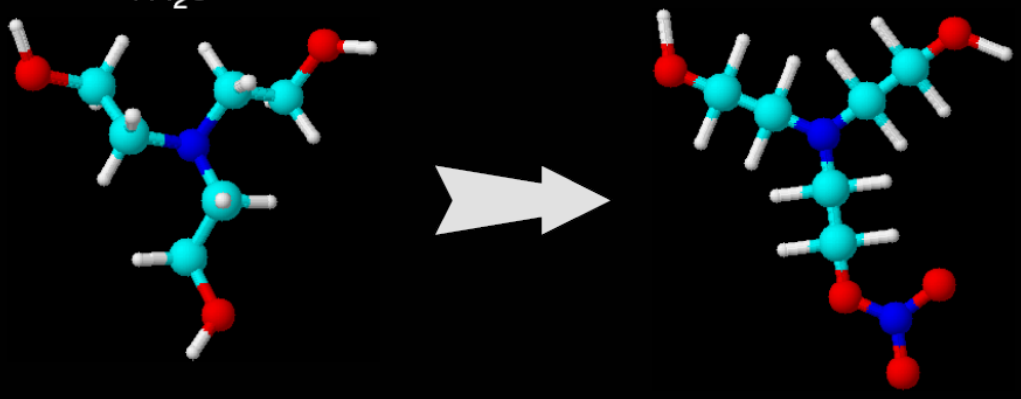
Composition of filters

- For Passive NO_2
  - Coated with Triethanolamine (TEA)
  - $2NO_2+2N(CH_2CH_2OH)_3 \longrightarrow N(CH_2CH_2OH)_2(CH_2CH_2ONO) + N(CH_2CH_2OH)_2(CH_2CH_2ONO_2) + H_2O$



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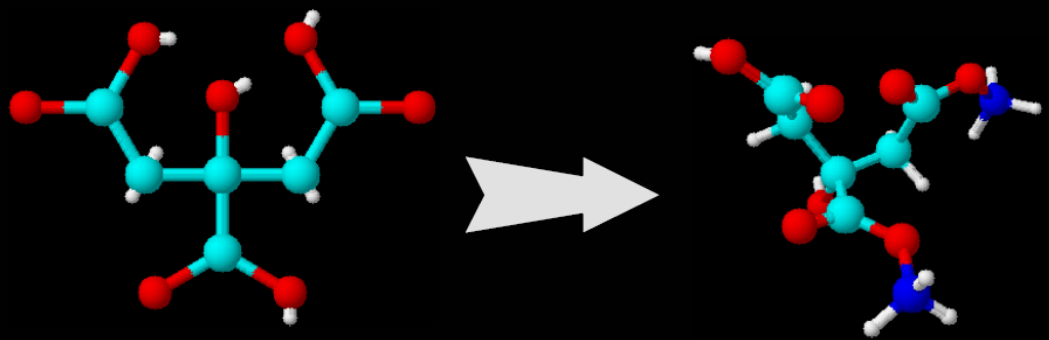
Composition of filters

- For Passive NH_3
  - Coated with Citric Acid
  - $NH_3 + H_3C_6H_5O_7 \longrightarrow NH_4H_2C_6H_5O_7 / (NH_4)_2HC_6H_5O_7 / (NH_4)_3C_6H_5O_7$



14

Assembly & shipping

- Assembly & shipping Room
- Support team with Branch Chief

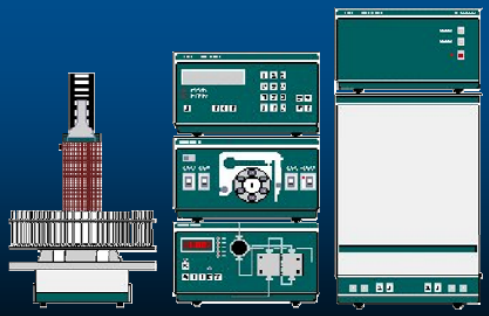
15

Extraction

- Ozone analysis(O_3)
  - Both Filters are extracted with 5 mL of ultra pure water
  - Sonicating for 20 min, ready for IC analysis
- Nitrogen Dioxide analysis(NO_2)
  - One Filter is extracted with 8 mL of ultra pure water
  - Sonicating for 20 min, ready for IC analysis
- Sulfur Dioxide analysis(SO_2)
  - One Filter is extracted with 8 mL of ultra pure water
  - Sonicating for 30 min
  - Add a drop of 30% H_2O_2, wait 1 hr before IC analysis
- Ammonia analysis (NH_3)
  - Two Filter is extracted with 8 mL of ultra pure water
  - Sonicating for 15 min
- * occasional shaking at all steps is required

16

Ion Chromatography
Modular System



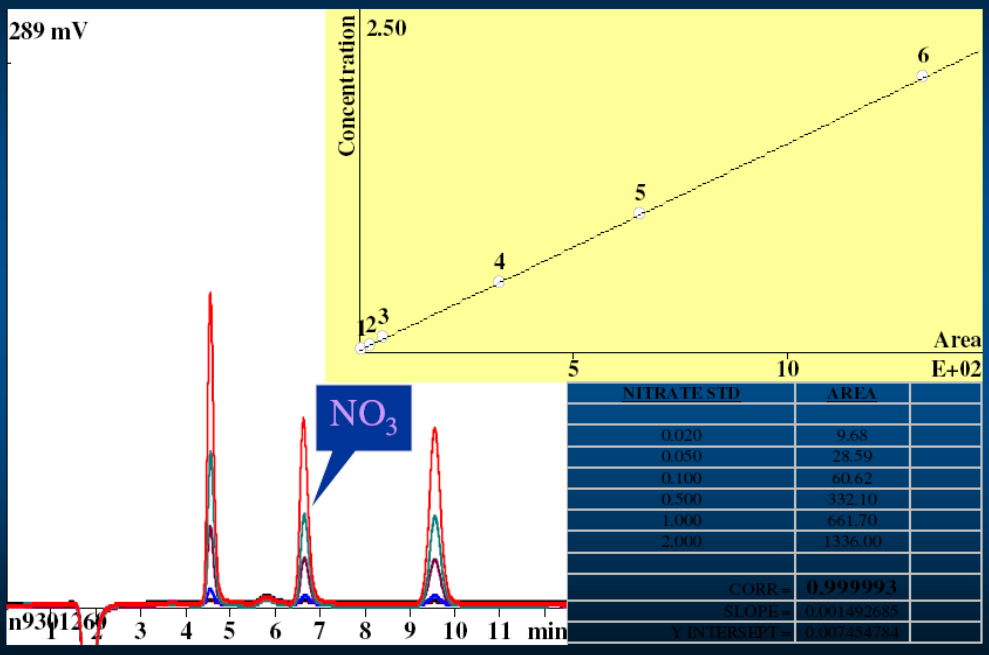
17

Experimental Conditions

- For O_3, NO_2 and SO_2
  - Metrohm Modular IC system
    - Eluent: 3.5 mM sodium carbonate
    - Sample loop size: 25 µL
    - Flow rate: 0.7 mL/min
    - Column
      - Analytical Column: MetroSep ASUPP 5 (4mm x 100 mm)
      - Guard: RP guard disk

18

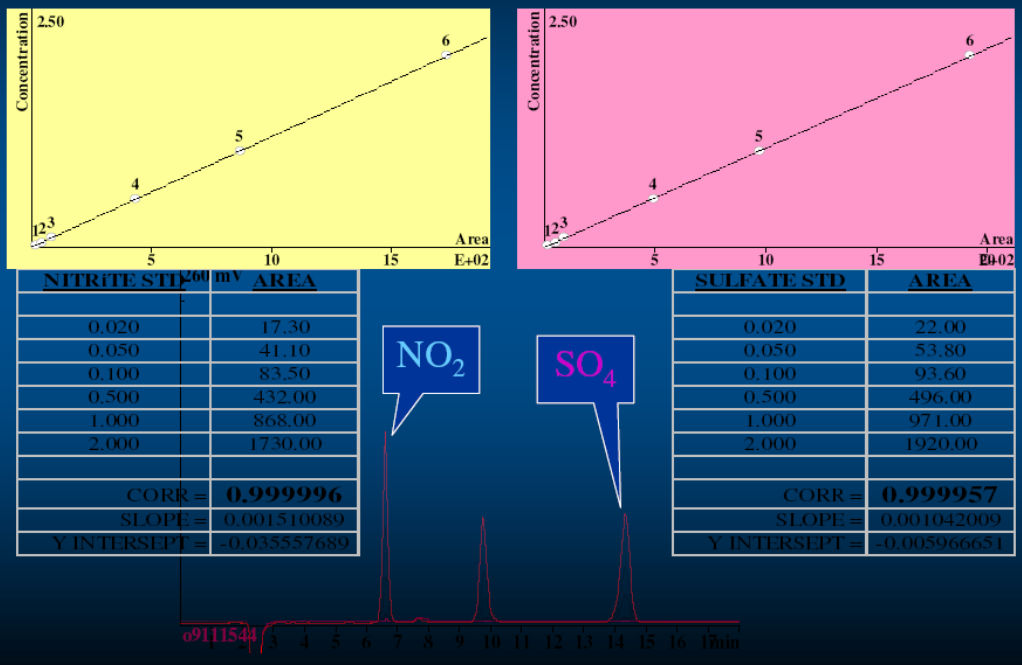
Calibration and Curve for O_3



NITRATE STD	AREA
0.020	9.68
0.050	28.59
0.100	60.62
0.500	332.10
1.000	661.70
2.000	1336.00
CORR =	0.999993
SLOPE =	0.001492685
Y INTERSEPT =	-0.007454784

19

Calibration and Curve for NO_2 & SO_2



NITRITE STD	AREA
0.020	17.30
0.050	41.10
0.100	83.50
0.500	432.00
1.000	868.00
2.000	1730.00
CORR =	0.999996
SLOPE =	0.001510089
Y INTERSEPT =	-0.035557689

SULFATE STD	AREA
0.020	22.00
0.050	53.80
0.100	93.60
0.500	496.00
1.000	971.00
2.000	1920.00
CORR =	0.999957
SLOPE =	0.001042009
Y INTERSEPT =	-0.005966651

20

Sampling Site Locations

- The sites were located in a variety of areas including high populated areas, downwind rural areas, and different areas of complex terrain (e.g. on mesas/mountains or in valleys)

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Analysis Sequence

Queue Editor 1.01 - C:\Program Files\Metrohm\IC Net 2.2\IC Net\Systems\USEPA_NO2_NO3_SO4_051403\090403_PO3week6.que

File Edit Help

	System	Ident	Vial	Volume	Dilution	Amount	Internal Standard Amount	Level	Injections	Done
1	USEPA_NO2_NO3_SO4_051403.smt	BLANK	2	25.0	1.0	1.0	100.0	0	1	0
2	USEPA_NO2_NO3_SO4_051403.smt	BLANK	2	25.0	1.0	1.0	100.0	0	1	0
3	USEPA_NO2_NO3_SO4_051403.smt	ICC-0.5PPM	3	25.0	1.0	1.0	100.0	0	1	0
4	USEPA_NO2_NO3_SO4_051403.smt	IPC-1	4	25.0	1.0	1.0	100.0	0	1	0
5	USEPA_NO2_NO3_SO4_051403.smt	0309001-10	5	25.0	1.0	1.0	100.0	0	1	0
6	USEPA_NO2_NO3_SO4_051403.smt	0309001-11	6	25.0	1.0	1.0	100.0	0	1	0
7	USEPA_NO2_NO3_SO4_051403.smt	0309001-1	7	25.0	1.0	1.0	100.0	0	1	0
8	USEPA_NO2_NO3_SO4_051403.smt	0309001-1 MS	8	25.0	1.0	1.0	100.0	0	1	0
9	USEPA_NO2_NO3_SO4_051403.smt	0309001-1 MSD	9	25.0	1.0	1.0	100.0	0	1	0
10	USEPA_NO2_NO3_SO4_051403.smt	0309001-2	10	25.0	1.0	1.0	100.0	0	1	0
11	USEPA_NO2_NO3_SO4_051403.smt	0309001-3	11	25.0	1.0	1.0	100.0	0	1	0
12	USEPA_NO2_NO3_SO4_051403.smt	0309001-4	12	25.0	1.0	1.0	100.0	0	1	0
13	USEPA_NO2_NO3_SO4_051403.smt	0309001-5	13	25.0	1.0	1.0	100.0	0	1	0
14	USEPA_NO2_NO3_SO4_051403.smt	BLANK	14	25.0	1.0	1.0	100.0	0	1	0
15	USEPA_NO2_NO3_SO4_051403.smt	ICC-0.5PPM	3	25.0	1.0	1.0	100.0	0	1	0
16	USEPA_NO2_NO3_SO4_051403.smt	0309001-6	16	25.0	1.0	1.0	100.0	0	1	0
17	USEPA_NO2_NO3_SO4_051403.smt	0309001-6 DUP	17	25.0	1.0	1.0	100.0	0	1	0
18	USEPA_NO2_NO3_SO4_051403.smt	0309001-7	18	25.0	1.0	1.0	100.0	0	1	0
19	USEPA_NO2_NO3_SO4_051403.smt	0309001-8	19	25.0	1.0	1.0	100.0	0	1	0
20	USEPA_NO2_NO3_SO4_051403.smt	0308015-9	20	25.0	1.0	1.0	100.0	0	1	0
21	USEPA_NO2_NO3_SO4_051403.smt	LRB SITE 5	21	25.0	1.0	1.0	100.0	0	1	0
22	USEPA_NO2_NO3_SO4_051403.smt	0309001-21	22	25.0	1.0	1.0	100.0	0	1	0
23	USEPA_NO2_NO3_SO4_051403.smt	0309001-22	23	25.0	1.0	1.0	100.0	0	1	0
24	USEPA_NO2_NO3_SO4_051403.smt	0309001-13	24	25.0	1.0	1.0	100.0	0	1	0
25	USEPA_NO2_NO3_SO4_051403.smt	BLANK	14	25.0	1.0	1.0	100.0	0	1	0
26	USEPA_NO2_NO3_SO4_051403.smt	ICC-0.5PPM	26	25.0	1.0	1.0	100.0	0	1	0
27	USEPA_NO2_NO3_SO4_051403.smt	0309001-12 MS	27	25.0	1.0	1.0	100.0	0	1	0
28	USEPA_NO2_NO3_SO4_051403.smt	0309001-12 MSD	28	25.0	1.0	1.0	100.0	0	1	0
29	USEPA_NO2_NO3_SO4_051403.smt	0309001-13	29	25.0	1.0	1.0	100.0	0	1	0
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31	USEPA_NO2_NO3_SO4_051403.smt	0309001-15	31	25.0	1.0	1.0	100.0	0	1	0
32	USEPA_NO2_NO3_SO4_051403.smt	0309001-16	32	25.0	1.0	1.0	100.0	0	1	0
33	USEPA_NO2_NO3_SO4_051403.smt	0309001-17	33	25.0	1.0	1.0	100.0	0	1	0
34	USEPA_NO2_NO3_SO4_051403.smt	0309001-17 DUP	34	25.0	1.0	1.0	100.0	0	1	0
35	USEPA_NO2_NO3_SO4_051403.smt	0309001-18	35	25.0	1.0	1.0	100.0	0	1	0
36	USEPA_NO2_NO3_SO4_051403.smt	0309001-19	36	25.0	1.0	1.0	100.0	0	1	0

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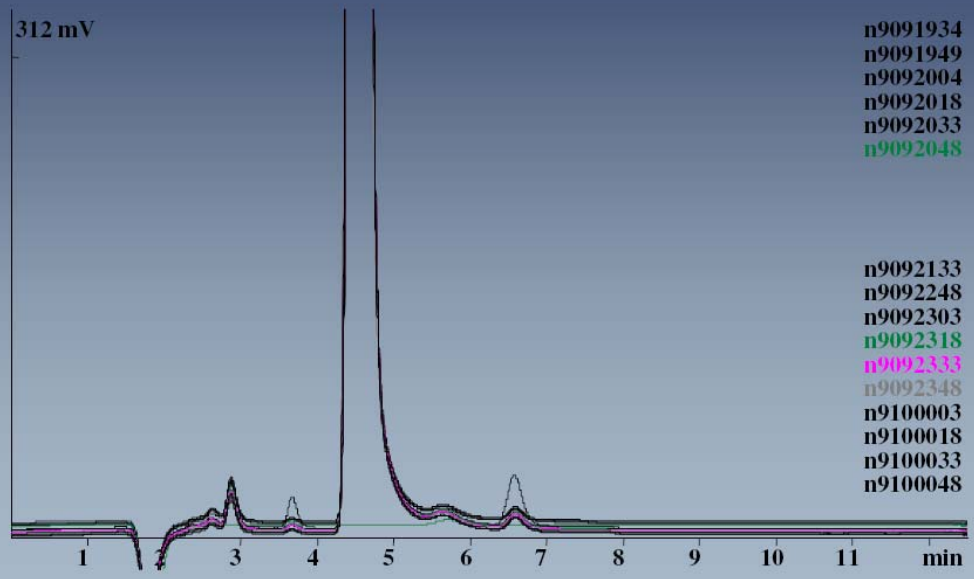
SUPER-IMPOSED 16 Sample Chromatogram - Ozone



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Calculations for Ozone

O_3 concentration (ppb) = ConNO_3(ug/mL)* X

- (example 0.7104 ug NO_3/ml) for 24 hr sampling
  - The ozone concentration is calculated from the following equation:
  - 0.7104 ug NO_3/ml*5 ml
  - 3.552 ug
  - Sampling rate = 21.8ml/min
  - O_3 ppm= (3.552 ug NO3/ (21.8ml/min * 1440) *1u mole NO_3/62 ug NO_3 * 1 u mole O_3/1 u mole NO_3 *24.5ul O_3/1 u mole O_3 * 10^{-6} (m^3) O_3/1000 ul O_3 * 1/0.03139 m^3)
  - 0.045ppm O_3

24

Concentration calculation for NO_2

- PPB $NO_2=(\alpha_{NO2})*ng\ NO_2$
  $=(\alpha_{NO2})*ugNO_2*1000$
  ug NO_2 is determined by IC

$\alpha_{NO2}=1000/(0.677*P*RH)+(2.009*T)+89.8$
where $P=\{2P_N/(P_T+P_N)\}^{2/3}$

T=Ambient temperature in ^0C
RH= Relative humidity
P_N=17.535 (water vapor pressure @20 ^0C)
P_T=vapor pressure at ambient temperature

25

Concentration calculation for SO_2

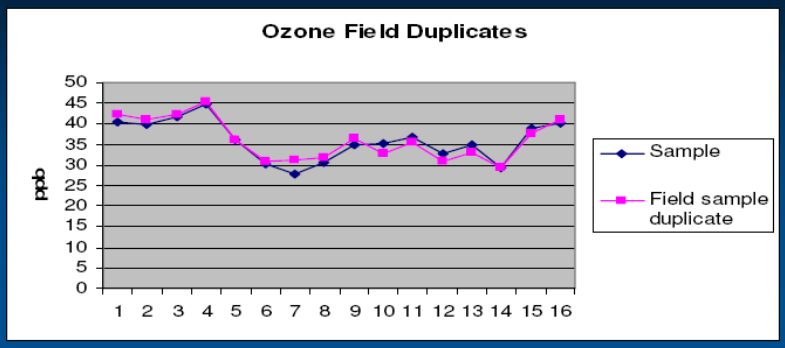
- PPB $SO_2=(\alpha_{NO2})*ng\ SO_4$
  $=(\alpha_{NO2})*ugSO_4*1000$
  ug SO_4 is determined by IC

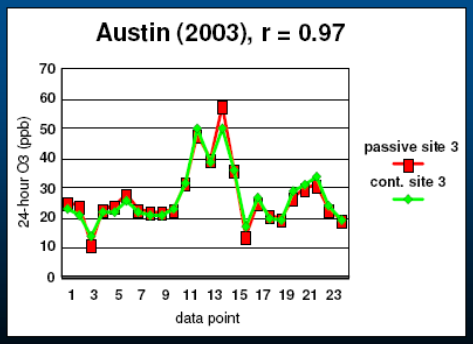
$\alpha_{SO2}=1000/(0.677*P*RH)+(2.009*T)+89.8$
where $P=\{2P_N/(P_T+P_N)\}^{2/3}$
At 20 °C the value of α^{SO2} = 39

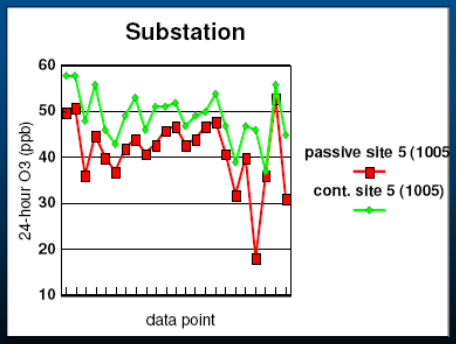
T=Ambient temperature in ^0C
RH= Relative humidity
P_N=17.535 (water vapor pressure @20 ^0C)
P_T=vapor pressure at ambient temperature

26

COMPARISION OF PASSIVE TO CONTINIOUS SAMPLING - Ozone







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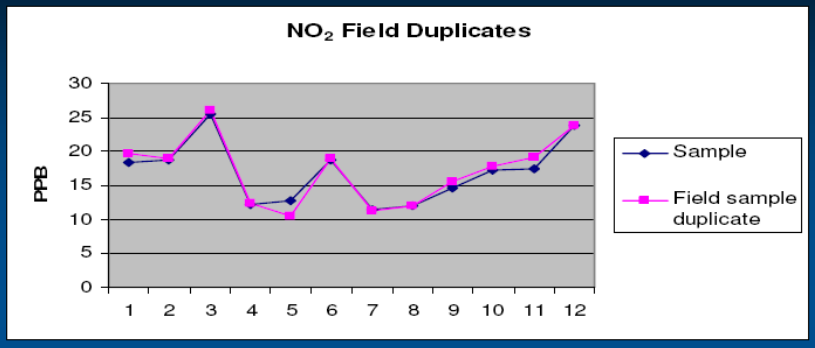
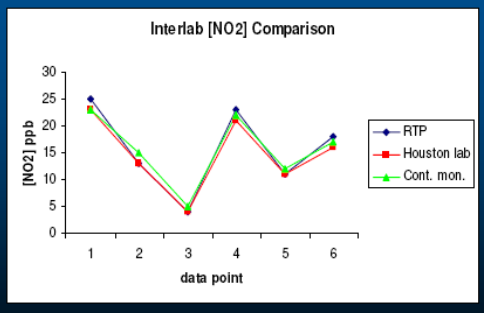
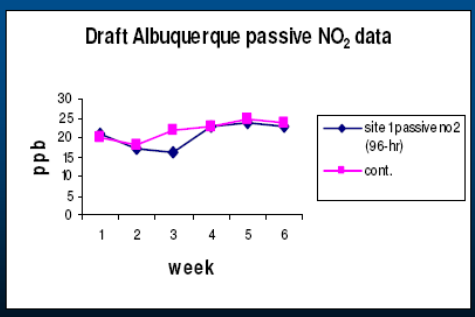
COMPARISION OF PASSIVE TO CONTINIOUS SAMPLING – NO_2







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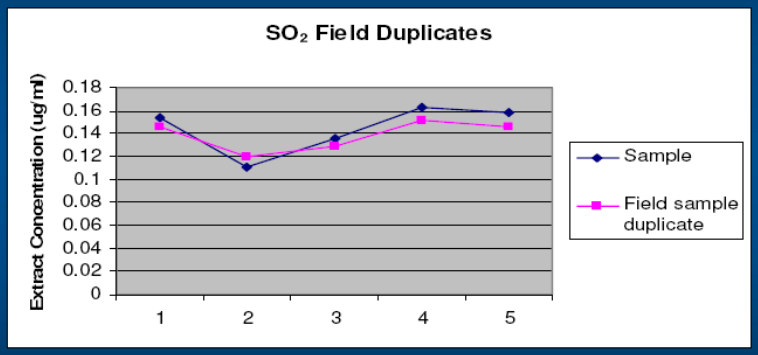
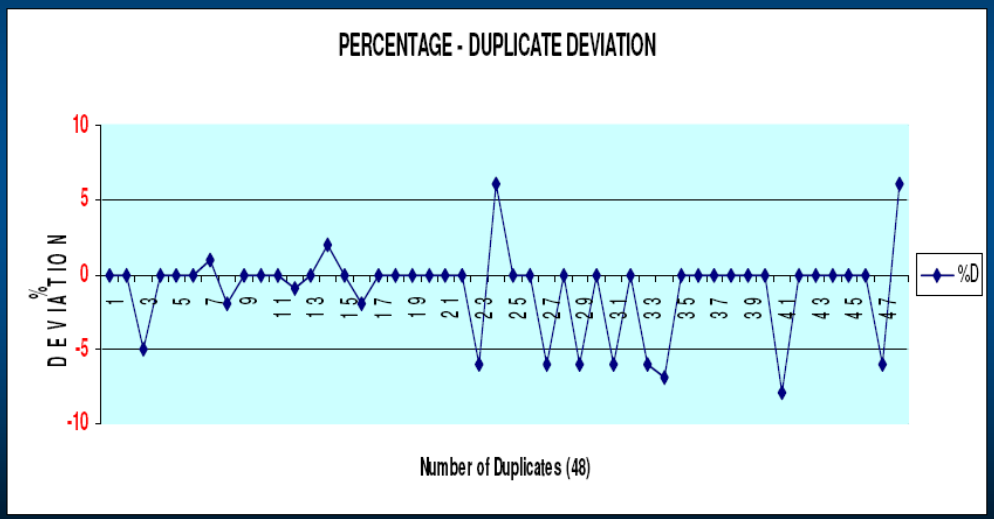
COMPARISION OF PASSIVE TO CONTINIOUS SAMPLING – SO_2



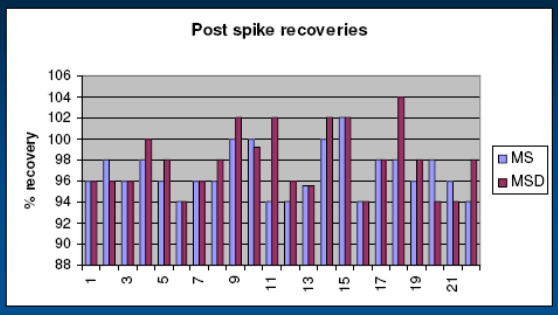
29

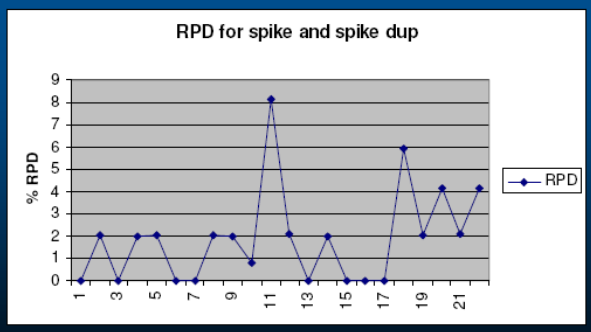
Duplicate Deviation (Analysis)



30

Spike Recovery and RPD





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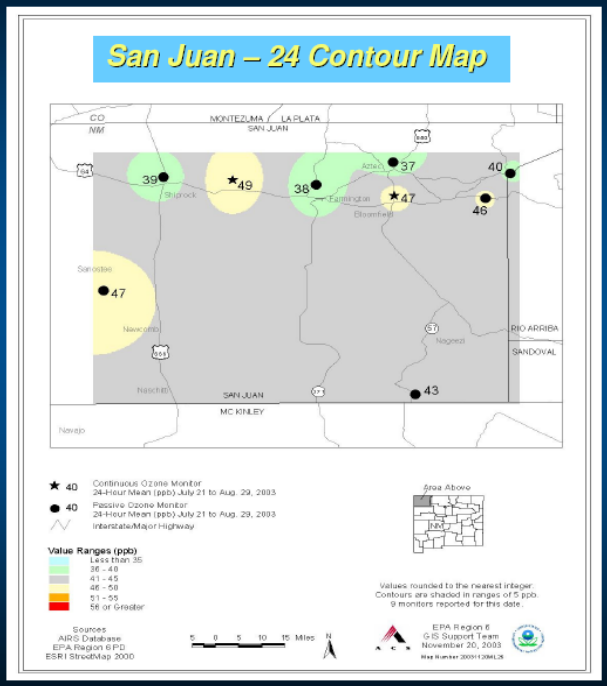
Example: Why was this monitoring study conducted? & Conclusion



To get a better picture of the distribution of high ozone concentrations in San Juan County (New Mexico, US) beyond the two existing continuous ozone monitoring stations at Substation and Bloomfield, both located in the north central part of the county.

Monitoring results showed significantly high ozone concentrations in the western and northeastern areas of San Juan Co, NM in addition to the high ozone concentrations already found in the north central area of the county

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Development of Passive NH_3 Monitoring

- Where does the ammonia come from?
  - Enzymatic oxidative hydrolysis of uric acid excreted by poultry and hydrolysis of urea by urease

    1) $C_2(NH)_4(CO)_3 + 2H_2O + 1.5O_2 \longrightarrow 2(NH_2)_2CO + 3CO_2$

    2) $(NH_2)_2CO + H_2O \longrightarrow 2NH_3 + CO_2$
  - Other major agriculture sources include:
    - decomposition of animal excreta, spray fertilization of crops, and release from agricultural soils fertilized with composted manure and litter

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Environmental impacts (ammonia)

- Ammonia is most prevalent alkaline gas in atmosphere and readily combines with acidic species
  - SO_2
  - HNO_3
  - H_2SO_4
- to form aerosols such as
  - Ammonium nitrate
  - Ammonium sulfate and other compounds
- These aerosols may cause **haze and impair visibility** characteristics in the atmosphere.

34

Methods to measure ammonia emissions from animal houses: the case of the Netherlands

J. Mosquera[1], G.-J Monteny[1] and J.W. Erisman[2]

[1] Wageningen University & Research Centrum
[2] Energy Research Centre of the Netherlands

Transport and reaction

NH_4HSO_4
$(NH_4)_2SO_4$
NH_4NO_3

NH_3

Emission

Deposition

NH_3
NH_4^+

Effects
- Acidification
- Eutrophication
- Loss of biodiversity

AGROTECHNOLOGY & FOOD INNOVATIONS
WAGENINGEN UR

35

Experimental Conditions

- For NH_3
  - **Metrohm Modular IC system**
    - **Eluent: C2 eluent (Tartaric acid-dipicolinic acid)**
    - **Sample loop size: 100 µL**
    - **Flow rate: 1.0 mL/min**
    - **Column**
      - **Analytical Column: Cation Column Metrosep C2 (4mm x 250/100 mm)**
      - **Guard: RP guard disk**

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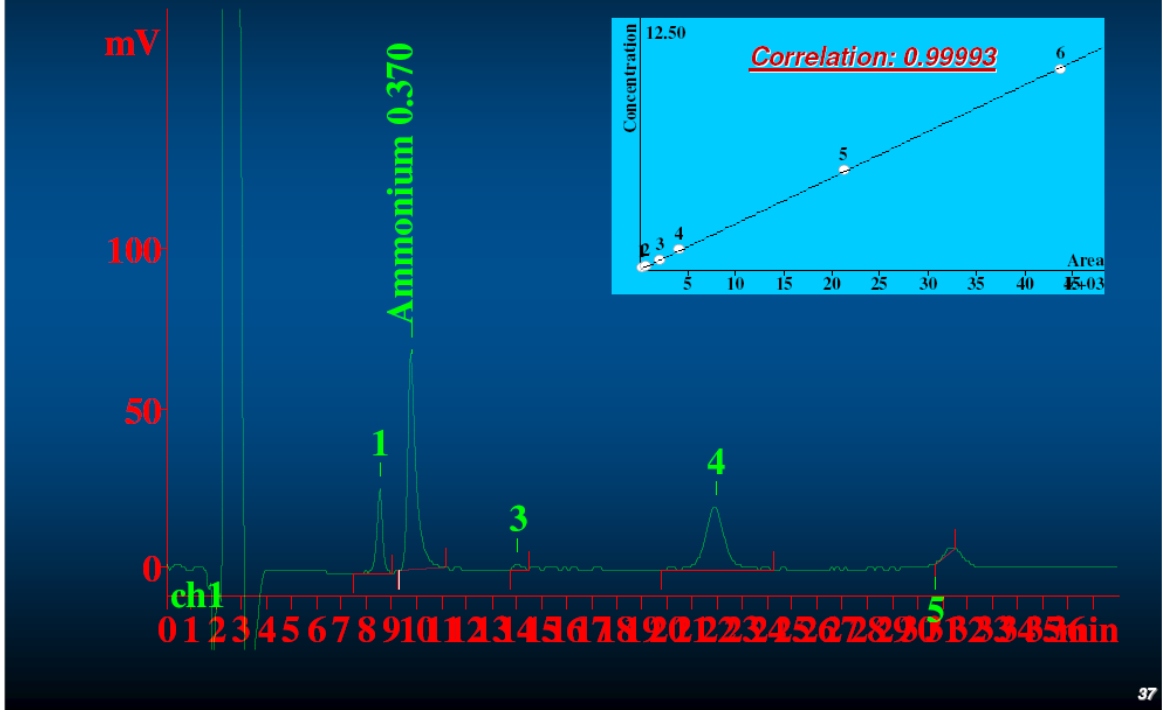
Chromatogram and calibration



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Concentration calculation for NH_3

- NH_3 concentration (ppb) = ($ConNH_3$(ng)*α^{NH_3})/ t
  - where :
    - $ConNH_3$ = the ammonia quantity (in ng)
    - α^{NH_3} is the ppb concentration conversion coefficients (ppb - min/ng).
    - α^{NH_3} = 43.8
    - t is sample collection time in minutes

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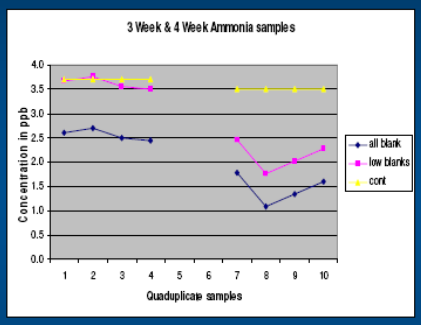
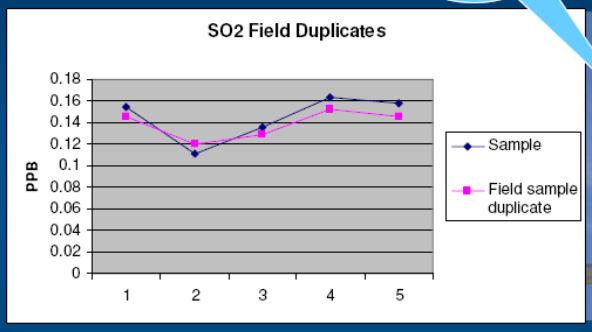
Ammonia samples

Different orientation of psd - similar value





3 week **4 week** **3 week**

Blank values

0.046

0.205

0.060

0.239

All blanks : includes all 4 blanks

Low blanks : includes only two low values

Cont : continuous monitor value

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Conclusions

- Benefits of passive sampling
  - Very easy to use
  - No power required
  - Ogawa Sampler is reusable countless times
  - Same sampler is used for diffrent gases.
  - Where cost is an issue passive sampling provides an inexpensive alternative to continuous sampling
  - Usually used for 24-hour or longer sampling, although for ozone it can be successfully used for time intervals as short as 8 hours
  - Can provide credible monitoring data to help fill in data gaps and to screen new areas, including remote rural areas.

40

Two papers published (6MD and 6PD)

- "***Evaluation of short-term Ogawa passive, photolytic, and federal reference method sampling devices for nitrogen oxides in El Paso and Houston, Texas***": *Journal of Environmental Monitoring (Royal Society of Chemistry publication).*
- "***Evaluation of Ogawa Passive Sampling Devices as an Alternative Measurement Method for the Nitrogen Dioxide Annual Standard in El Paso, Texas*** "**:***Journal of Environmental Monitoring (Royal Society of Chemistry publication).*

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Acknowledgements

- Dr. Doug Lipka: Branch Chief, EPA
- Rick McMillin: Lab Manager, EPA
- Dr. Melvin Ritter : Team Leader, EPA
- Mark Sather : Project Lead, EPA
- Jerry Varns: Scientist, EPA (RTP)
- Jim Mulick: Former EPA Scientist
- Dr. Mike Wolfson: Professor (Harvard university)
- John Lay and Neal Nguyen, EPA

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WEDNESDAY A.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Organic Methods

ENHANCEMENTS OF EPA METHOD 535

Krol, Jim Sr.; Waters Corporation

EPA Method 535, ver 1.1, authored in April 2005 discusses a method limitation with the identification and quantification of alachor ESA from acetochor ESA. These analytes are structurally similar having the same molecular weight and MSMS transitions, and requires chromatographic resolution prior to MSMS. Because of this limitation, 2 possible candidates are within the same retention time window, and the identification of these analytes must be manually checked; a time consuming task.

The method calls for an ammonium acetate/methanol gradient using a 5 µm, 2.1 x 100 mm, dC18 column at 60°C. These chromatographic conditions are optimize for efficiency necessary to resolve alachlor EAS from acetochlor EAS. However, the trade off is high backpressure due to MeOH viscosity. Because of stated MS suppression effects of sample TOC on analyte response, this chromatographic mobile phase cannot be modified, but the column selectivity can be changed.

This presentation will discuss the applicability of other LC column chemistries to achieve the required resolution. Concurrently, other mobile phase types may improve resolution and MSMS sensitivity without sacrificing TOC suppression.

Waters

Aisling M. O'Connor
Sr. Applications Chemist

Enhancements to EPA Method 535

NEMC 2006

For Complete Confidence

Waters

Chloroacetanilide / Acetamide Herbicides

- U.S. Registered
  Alachlor, Acetochlor, Metolachlor, Propachlor, Flufenacet and Dimethenamid
- Control of broadleaf & annual grasses on crops
- ESA (Ethane Sulfonic Acid) & OA (Oxanilic Acid) Metabolites
- Metabolites are more water soluble and have increased mobility than parent herbicide
- USGS reported higher conc. & occurrence of metabolites than parent compounds in ground & surface water

Waters

UCMR 2

- Unregulated Contaminant Monitoring Rule
- 26 contaminants,9 analytical methods,07-11
- Assessment monitoring & screening survey lists
- Public water systems serving > 100,000 people to conduct screening survey
- Acetochlor ESA / OA, Alachlor ESA / OA and Metolachlor ESA/OA on the screening survey list
- Data will be used to determine if these contaminants should be regulated

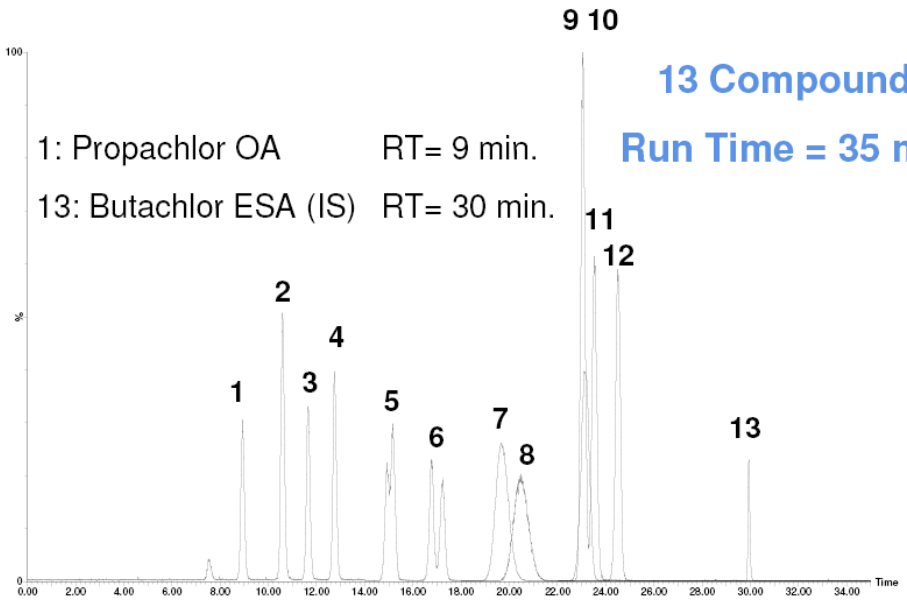
Waters

EPA 535 Methodology

- 250 mL sample extracted and conc. through a graphitized carbon SPE cartridge, dried and made up to 1 mL
- Sample injected on C_{18} column at 65ºC and analyzed by LC/MS/MS, negative ion mode, multiple reaction monitoring (MRM)
- Mobile phase 5 mM ammonium acetate & methanol
- Concentration determined by use of chromatographic internal standard calibration
- Waters Alliance HPLC or Waters ACQUITY UPLC with Quattro Micro API Tandem Quadropole Mass Spectrometer used in this study

Waters

HPLC/MS/MS Chromatogram



Waters

Enhancing the Method

- Increase throughput
  - EPA Mth. HPLC / Tandem Quad runtime = 35 min.
  - EPA Mth. HPLC / Ion Trap runtime = 60 min.
- Resolution
  - Alachlor ESA and Acetachlor ESA are structural isomers, same MRM channel; 314 → 80
  - Required resolution, Rs > 1.0

Acquity™
Ultra Performance LC

Waters

UPLC Conditions

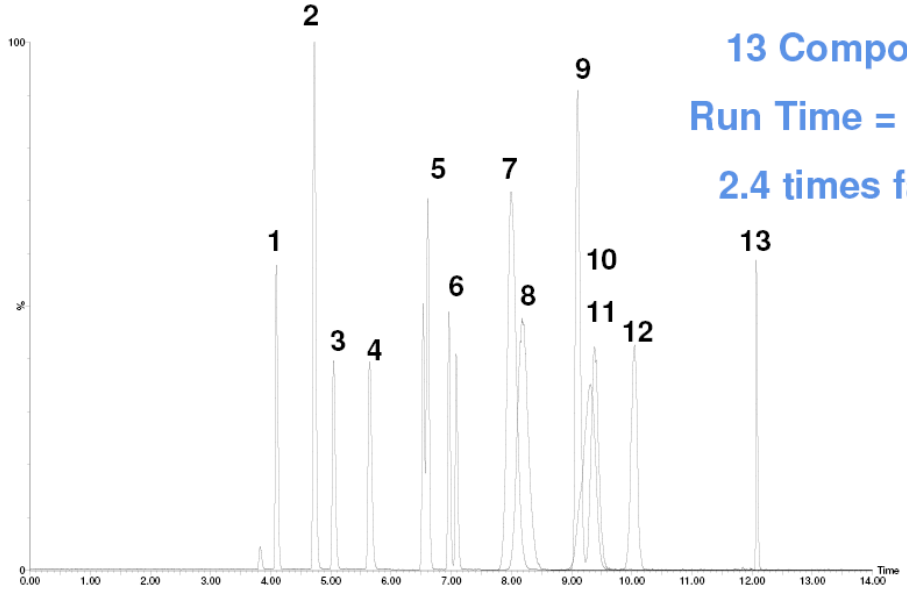
- ACQUITY UPLC™ BEH C_{18} Column, 2.1 x 150 mm, 1.7 µm at 65°C
- Flow Rate = 0.45 mL/min
- Gradient
  - Solvent A: 5mM Ammonium Acetate
  - Solvent B: Methanol
- Injection vol.= 30 µL

	% A	%B
Initial	90	10
5.0	75	25
7.5	66	34
10.5	65	35
11.0	10	90

- Pressure = 7,500 psi at initial conditions

Waters

UPLC/MS/MS Chromatogram



13 Compounds

Run Time = 14 min.

2.4 times faster!

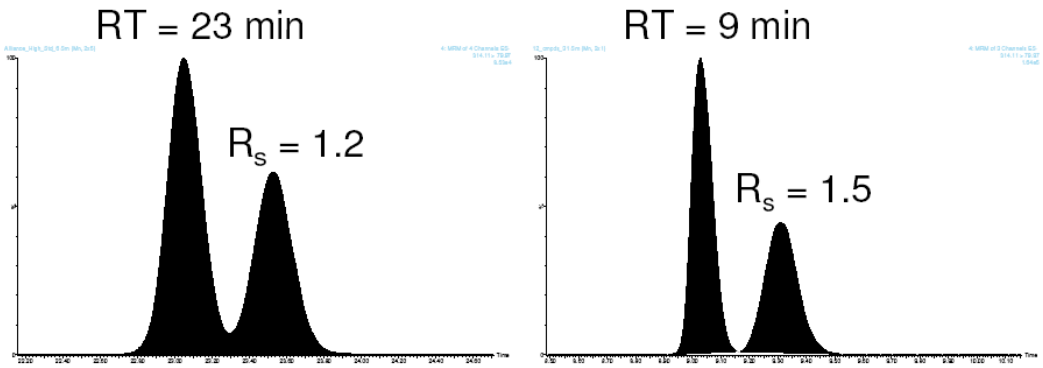
1: Propachlor OA RT= 4.1 min.

13: Butachlor ESA (IS) RT= 12.1 min.

Waters

Improved Resolution

Alachlor ESA & Acetachlor ESA (314 → 80)



HPLC

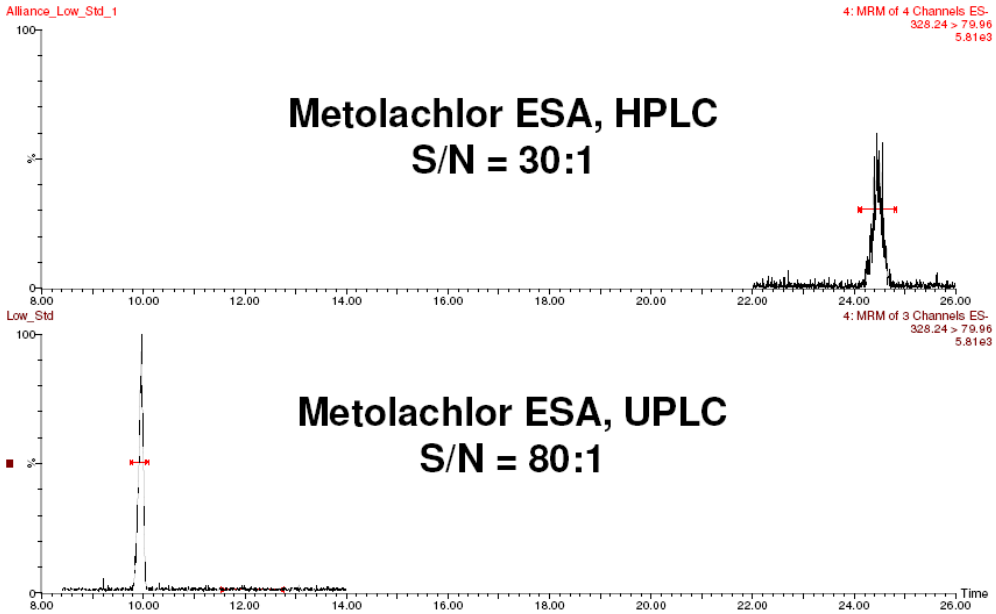
2.1 x 100 mm, 5µm column

UPLC

2.1 x 150 mm, 1.7µm column

Waters

Sensitivity HPLC vs. UPLC



Waters

Improved Sensitivity

- 0.05 µg/L standard
- 2 – 4 X improvement in sensitivity using UPLC

Compound	UPLC S/N	HPLC S/N
Acetochlor ESA	**50:1**	25:1
Acetochlor OA	**65:1**	20:1
Alachlor ESA	**95:1**	45:1
Alachlor OA	**80:1**	20:1
Metolachlor ESA	**80:1**	30:1
Metolachlor OA	**50:1**	25:1

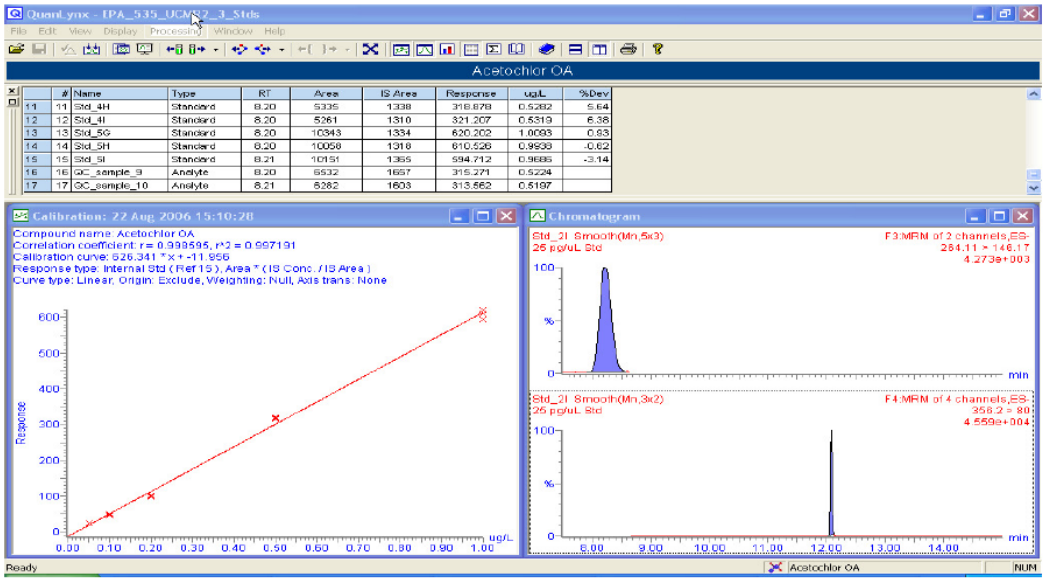
Waters

Linearity

- Calibration curves were constructed using an internal standard method
- Concentration of standards was 0.05 µg/L to 1.00 µg/L for 250 mL of extracted sample
- Correlation coefficients > 0.997 were obtained for all 6 metabolites on UCMR2 list
- Processing carried out using QuanLynx software

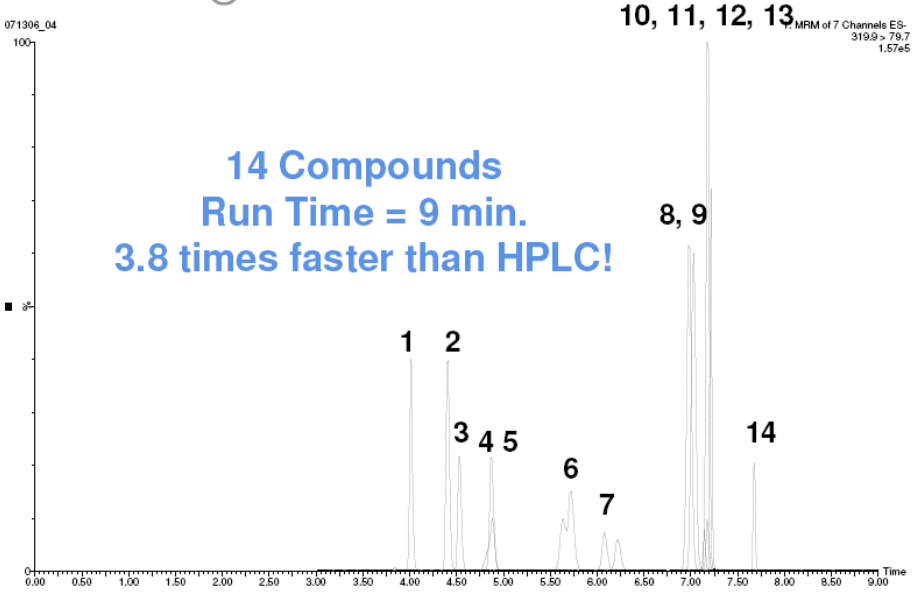
Waters

QuanLynx Sample Report



Waters

Alternative UPLC/MS/MS Approach (Suffolk County Water Authority)

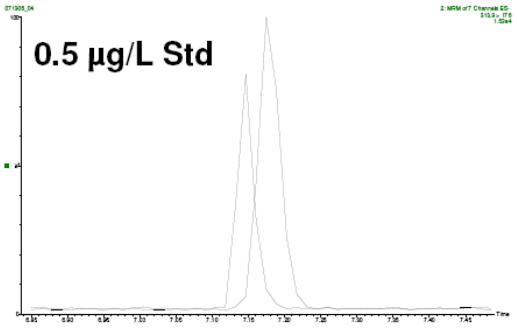


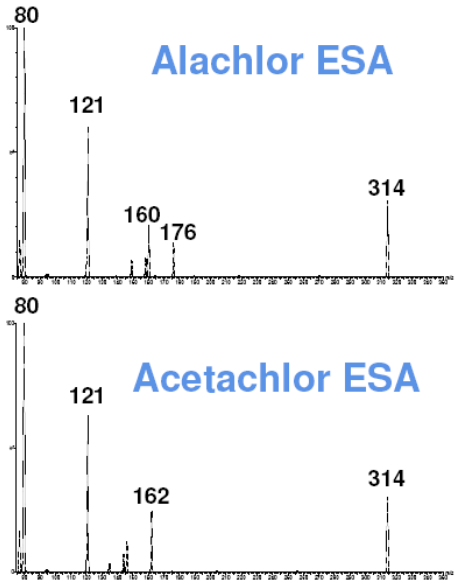
1: Propachlor OA RT= 4.1 min.

14: Butachlor ESA (IS) RT= 7.6 min.

Alternative Approach 2 (SCWA)

- Less sensitive product ions
- Alachlor ESA, 314 → 176
- Acetachlor ESA, 314 → 162





Alternative Approach, Sensitivity

Analyte Name	Fortification Conc. (µg/L)	Mean Conc. (µg/L)	Standard Dev. (µg/L)	MDL (µg/L)
Metolachlor ESA	0.20	0.19	0.02	0.06
Alachlor ESA	0.20	0.20	0.02	0.06
Acetochlor ESA	0.20	0.19	0.02	0.06
Alachlor OA	0.20	0.18	0.02	0.06
Acetochlor OA	0.20	0.18	0.01	0.05
Metolachlor OA	0.20	0.20	0.02	0.05

Notes: 250 mL of sample extracted using an automated system

Detection Limits determined by analyzing 7 replicates

Waters

Conclusions

Advantages of UPLC for EPA Method 535 Include:

- Increased Throughput
  - EPA method runtimes reported are up to 60 mins, runtimes of 9 minutes were achieved by UPLC
- Better Resolution
  - Improved Rs values for Alachlor ESA and Acetachlor ESA
- Sensitivity
  - ≥ 2X increase in sensitivity over HPLC
  - Increase in sensitivity allowed use of less sensitive product ions for Alachlor ESA and Acetachlor ESA

Waters

Acknowledgements

- Suffolk County Water Authority
  - Karen Randazzo, Laboratory Director
  - Christine Lasher, Chromatography Supervisor
  - Christopher Conte, Chemist

STIR BAR SORPTIVE EXTRACTION (SBSE) SAMPLE PREPARATION FOR AQUEOUS ENVIRONMENTAL SAMPLES: AN OVERVIEW

Pfannkoch, E. A.; Stuff, J. R.; and Whitecavage, J. A. – GERSTEL, Inc.

The determination of volatile and semivolatile analytes in aqueous solutions using stir bar sorptive extraction (SBSE) as the extraction step is gaining acceptance in a wide variety of application areas including water and wastewater analysis, foods and beverages, and other consumer products. SBSE uses a high capacity polydimethylsiloxane (PDMS) phase on a stir bar to simultaneously stir and concentrate nonpolar analytes from polar matrices, eliminating organic solvent extraction. Analytes are transferred to the GC by thermal desorption, typically achieving sub-ppb detection limits from sample sizes of 20mL or less.

This presentation will provide an overview of SBSE method optimization and illustrate the technique with examples including semivolatile organics (EPA Method 8270), PAH's, pesticides, and other applications of environmental interest.

GERSTEL Twister

Stir Bar Sorptive Extraction
Environmental Applications

GERSTEL

Outline

- SBSE introduction
- Environmental Applications
  - Water odor
  - Semivolatile organics
  - Pesticides
  - Pharmaceutical and personal care products (PPCP)
  - Endocrine disrupting compounds (EDC)
  - Other

GERSTEL

Technique is called SBSE Stir Bar Sorptive Extraction

- Same principle as liquid/liquid extraction
  - But with a low amount of immobilized „solvent“ (PDMS)
- Extraction is based on sorption
  - Predictable recovery due to proportionality with log $K_{o/w}$
  - No displacement effects
- PDMS
  - Very inert
  - Retains no water
  - Selectivity eliminates polar matrix interferences
- Desorption with TDS or TDU
  - Fast and mild
  - Extremely low detection limits (ppq to ppt)

GERSTEL

GERSTEL-Twister Design

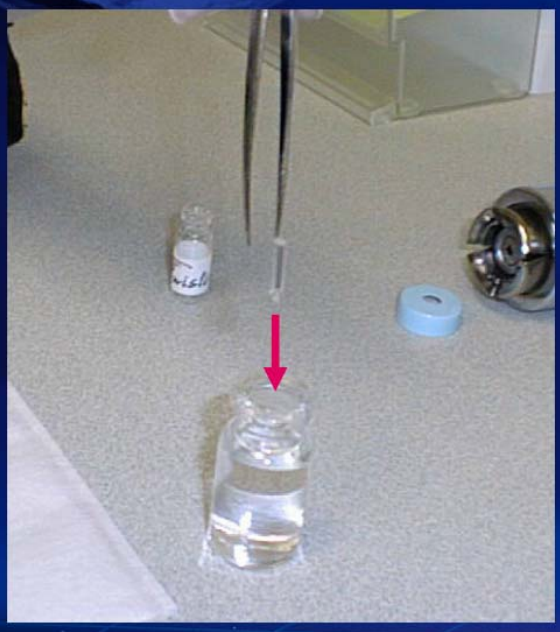
Magnetic core, sealed in glass and coated with PDMS

l = 10 mm, df = 0.5 mm ⟶ 24 µl
df = 1.0 mm ⟶ 63 µl
l = 20 mm, df = 0.5 mm ⟶ 47 µl
df = 1.0 mm ⟶ 126 µl

SPME : max. 0.5 µl

GERSTEL

Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)



- A PDMS-coated stir bar (GERSTEL Twister) is added to the vial

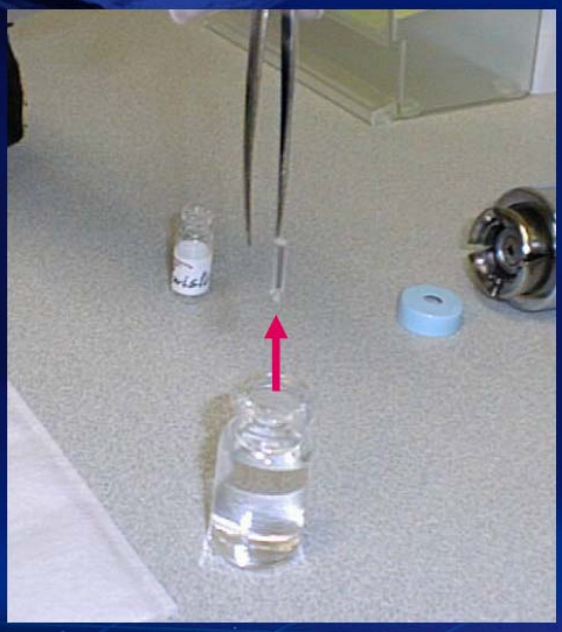
GERSTEL

Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)

- A PDMS-coated stir bar (GERSTEL Twister) is added to the vial
- Stirred for 60 min

GERSTEL

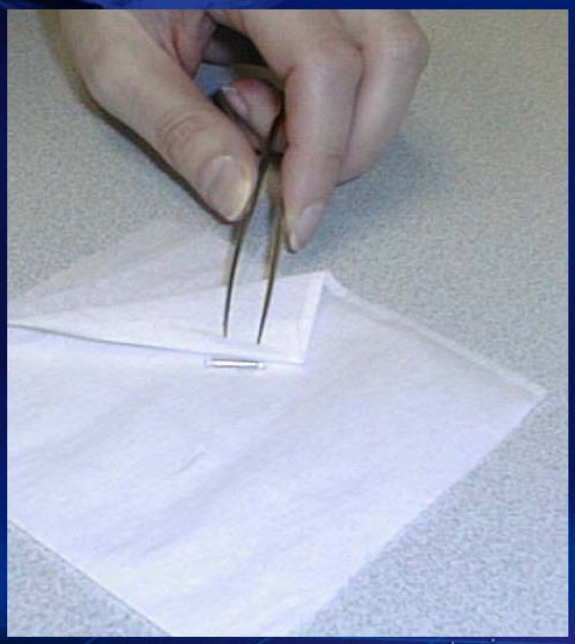
Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)



- A PDMS-coated stir bar (GERSTEL Twister) is added to the vial
- Stirred for 60 min
- Removed with forceps and rinsed briefly in distilled water

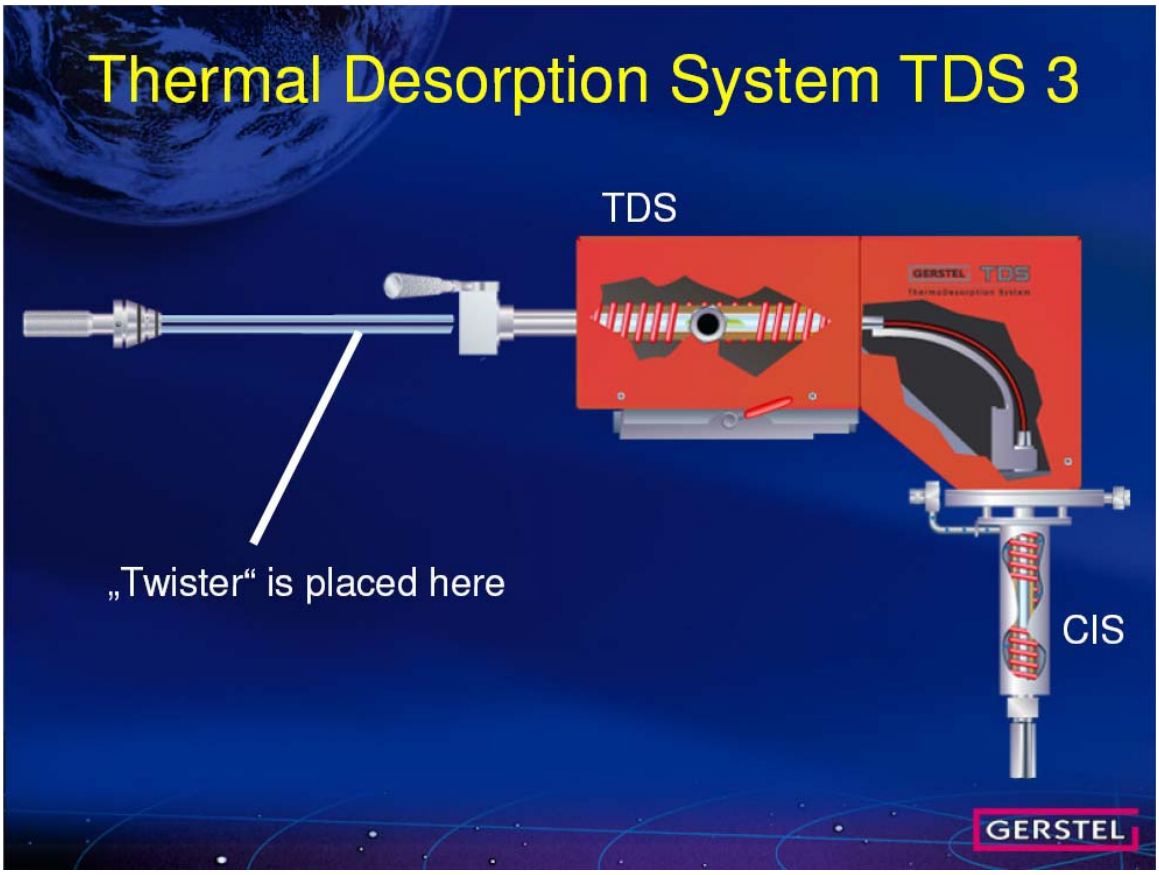
GERSTEL

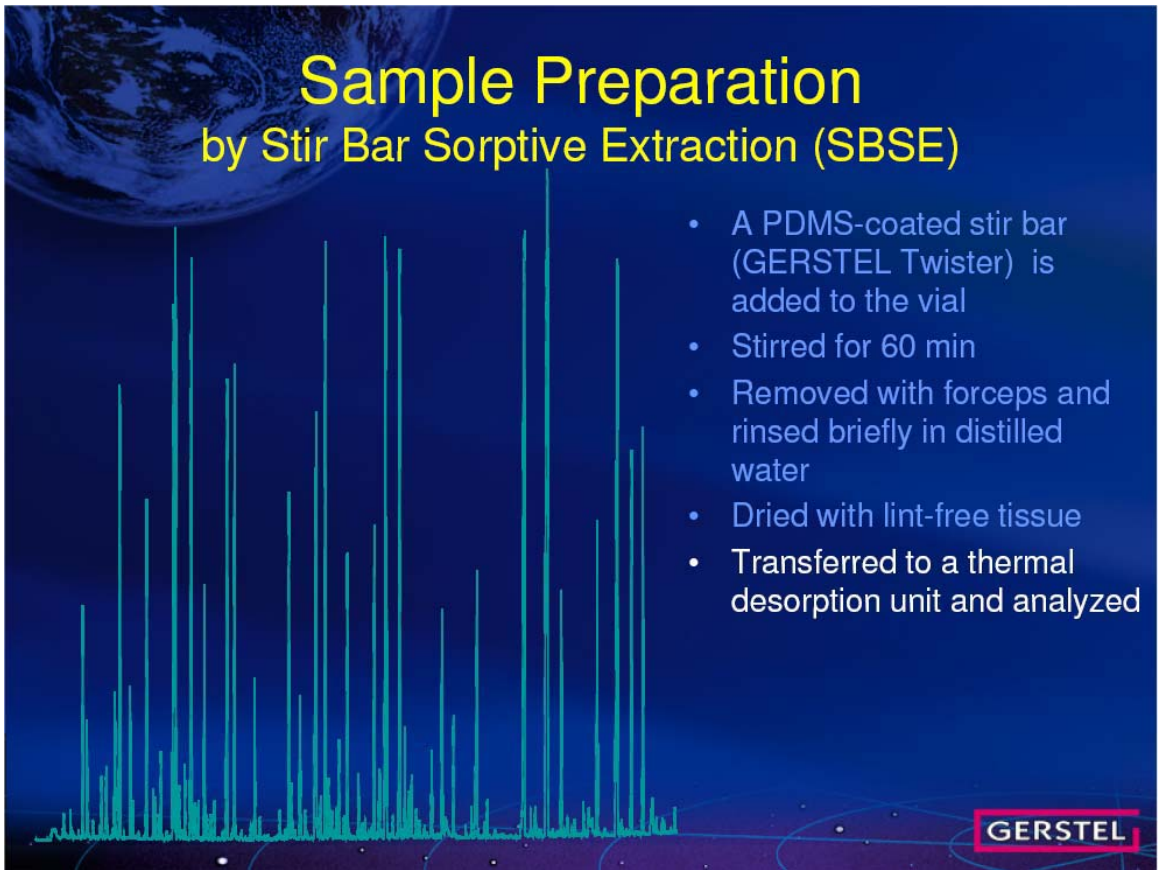
Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)



- A PDMS-coated stir bar (GERSTEL Twister) is added to the vial
- Stirred for 60 min
- Removed with forceps and rinsed briefly in distilled water
- Dried with lint-free tissue

GERSTEL


Thermal Desorption System TDS 3
TDS
„Twister“ is placed here
CIS
GERSTEL


Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)
• A PDMS-coated stir bar (GERSTEL Twister) is added to the vial
• Stirred for 60 min
• Removed with forceps and rinsed briefly in distilled water
• Dried with lint-free tissue
• Transferred to a thermal desorption unit and analyzed
GERSTEL

Outline

- SBSE Introduction
- Environmental Applications
  - Water odor
    - Geosmin/MIB/TCA
    - Haloanisoles
  - Semivolatile organics
  - Pesticides
  - Pharmaceutical and personal care products (PPCP)
  - Endocrine disrupting compounds (EDC)
  - Other

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ODOROUS COMPOUNDS

	Odor threshold	Odor type	Molecular mass
2-MIB (2-methyl isoborneol)	5-10 ng/l	earthy	152
Geosmin	1 - 10 ng/l	musty	182
2,4,6-TCA (2,4,6-trichloroanisole)	0,1 - 2 ng/l	musty	212
2,3,6-TCA (2,4,6-trichloroanisole)	0,1 - 2 ng/l	musty	212
2,3,4-TCA (2,4,6-trichloroanisole)	0,2 - 2 ng/l	musty	212
2,4,6-TBA (2,4,6-tribromoanisole)	0,15 - 2 ng/l	musty	346

From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy

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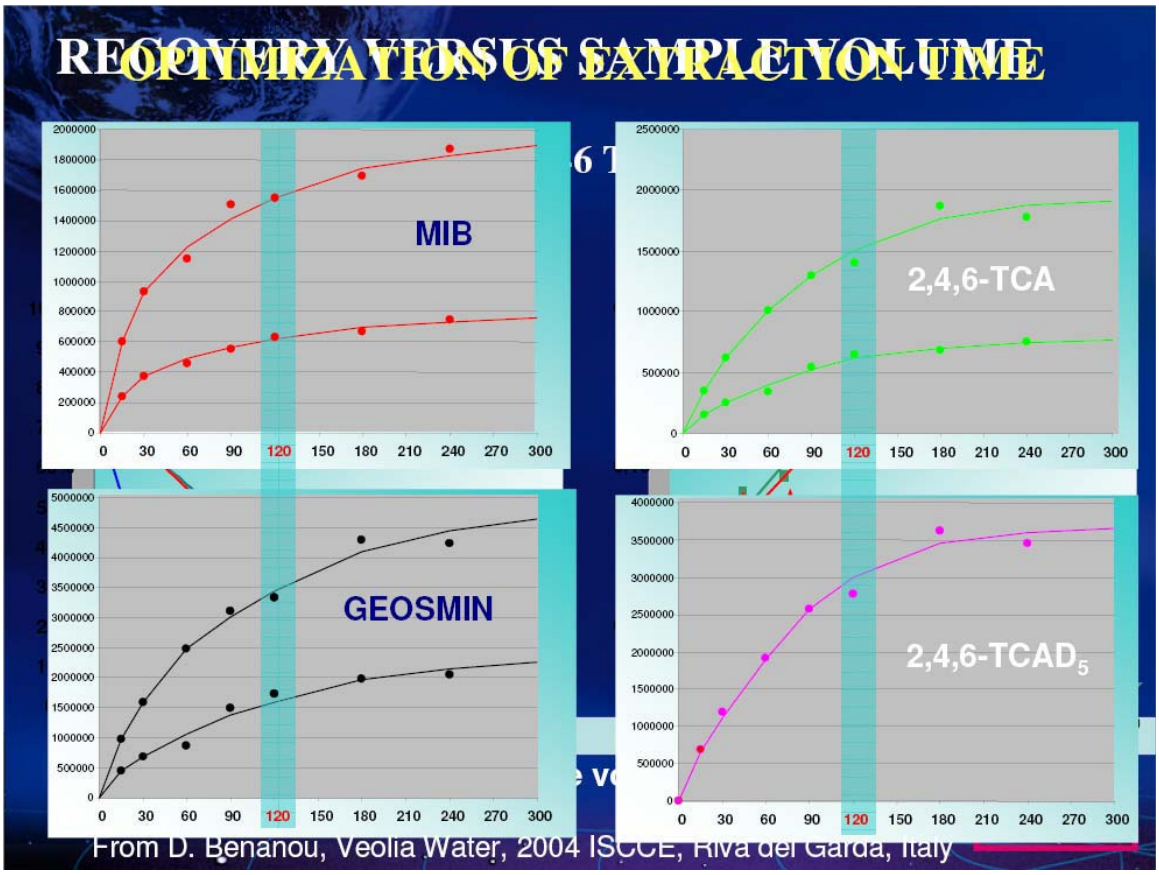
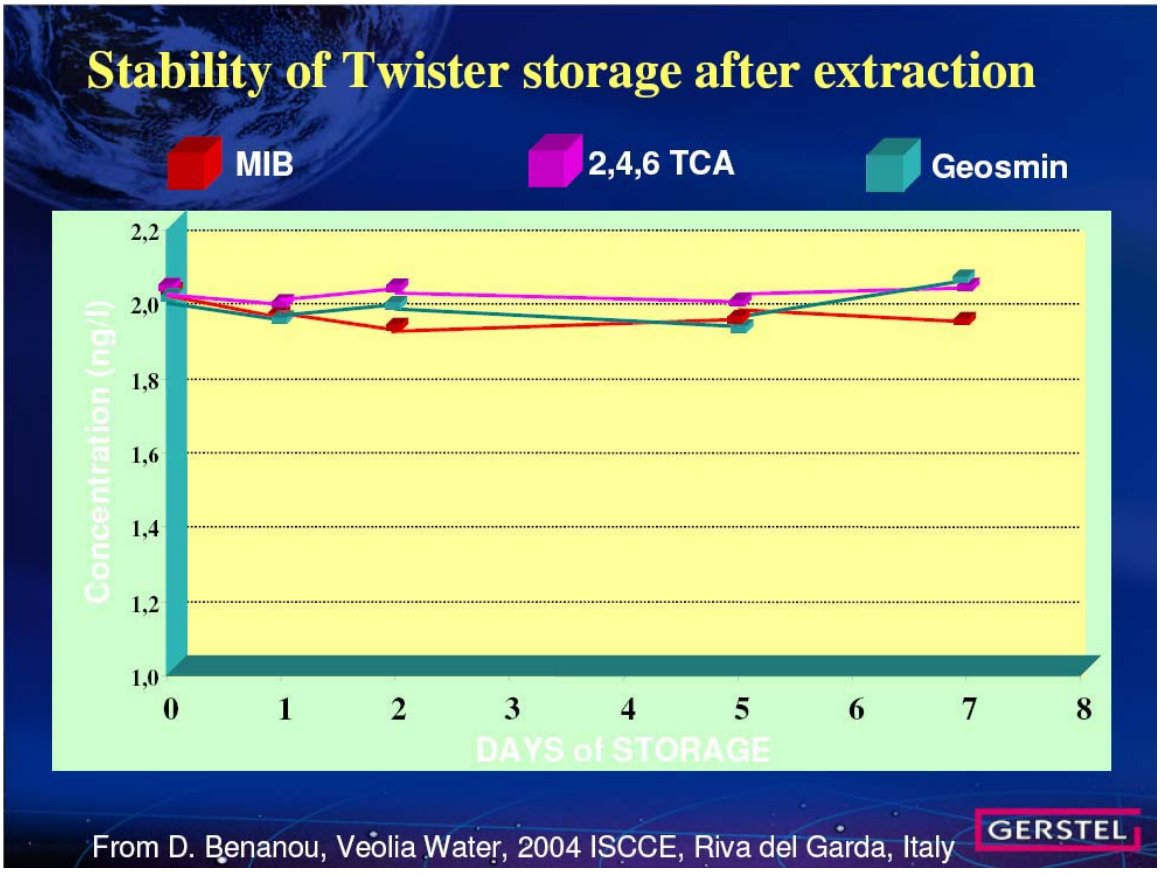
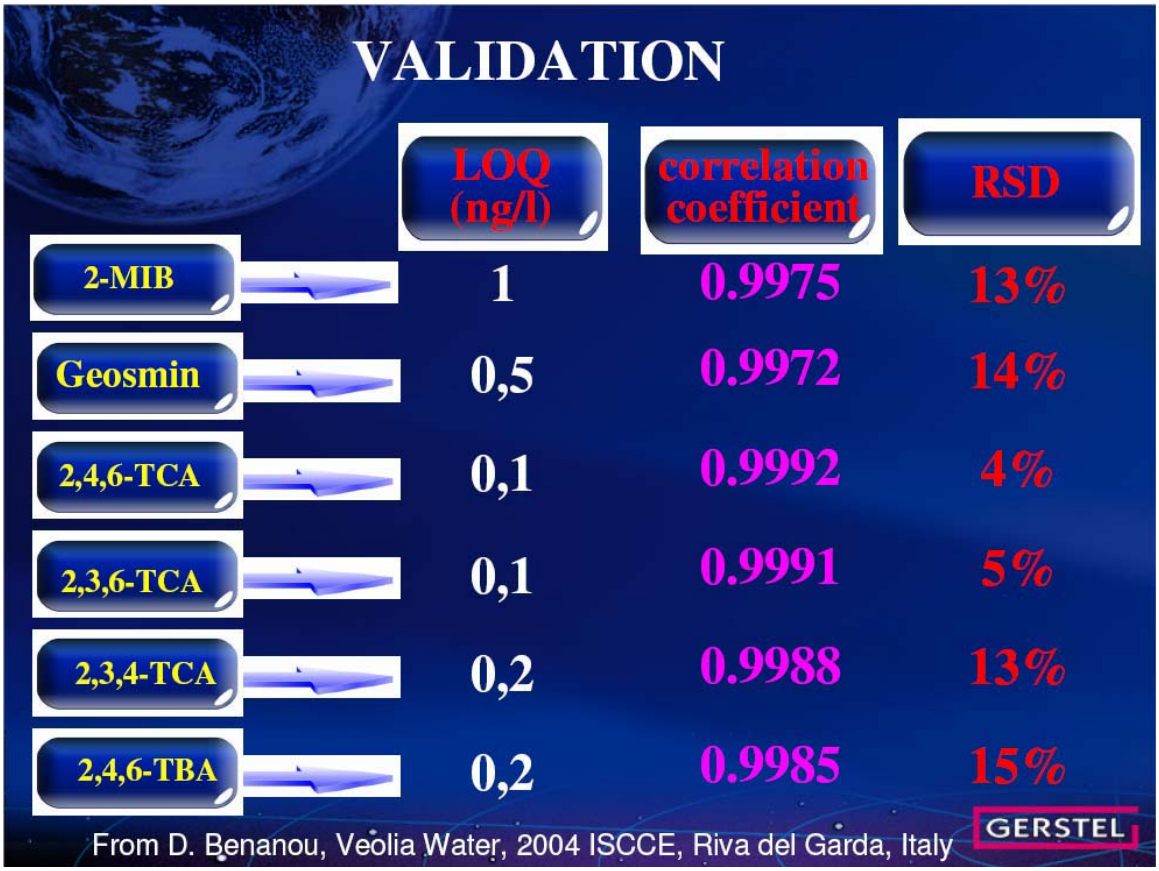

RECOVERY VERSUS SAMPLE VOLUME
OPTIMIZATION OF EXTRACTION TIME
MIB
2,4,6-TCA
GEOSMIN
2,4,6-TCAD5
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy


Stability of Twister storage after extraction
MIB
2,4,6 TCA
Geosmin
Concentration (ng/l)
DAYS of STORAGE
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy
GERSTEL


VALIDATION
LOQ (ng/l)
correlation coefficient
RSD
2-MIB
1
0.9975
13%
Geosmin
0,5
0.9972
14%
2,4,6-TCA
0,1
0.9992
4%
2,3,6-TCA
0,1
0.9991
5%
2,3,4-TCA
0,2
0.9988
13%
2,4,6-TBA
0,2
0.9985
15%
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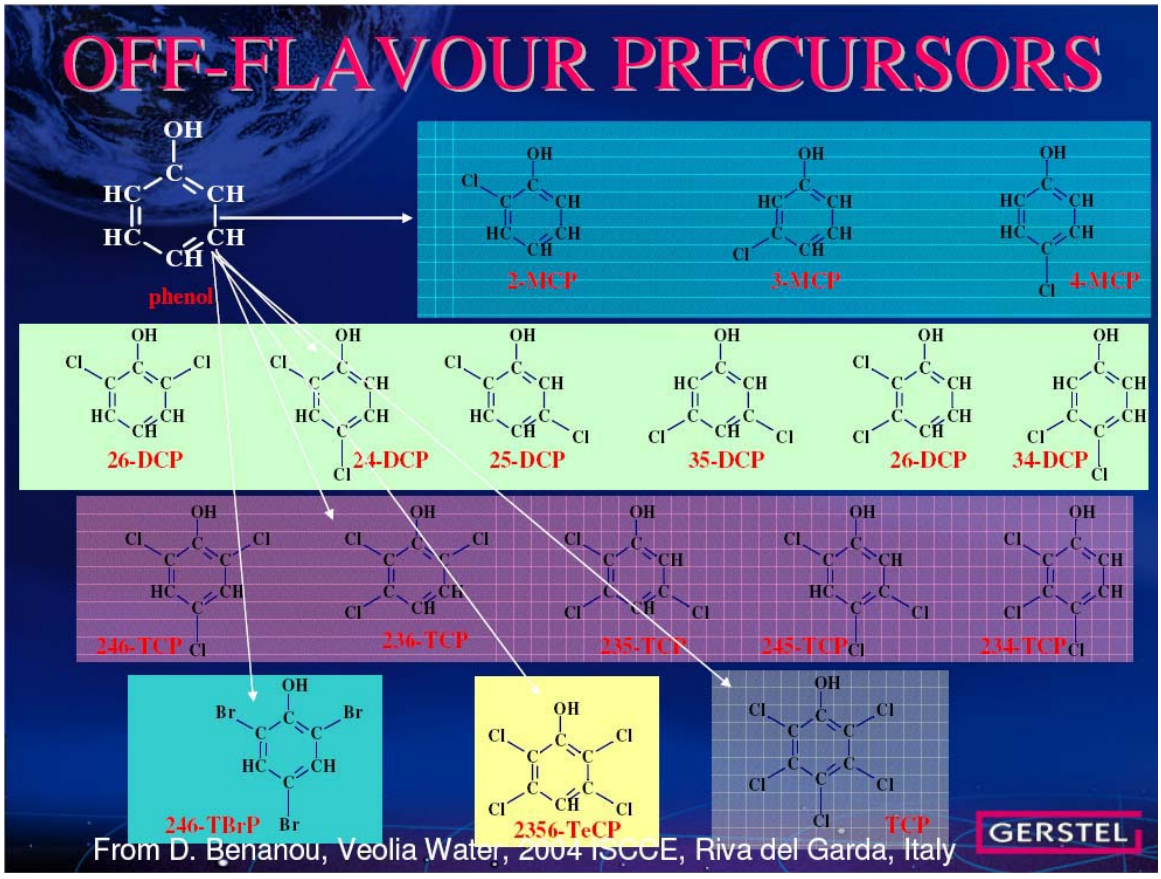
GERSTEL


OFF-FLAVOUR PRECURSORS
phenol
2-MCP
3-MCP
4-MCP
26-DCP
24-DCP
25-DCP
35-DCP
26-DCP
34-DCP
246-TCP
236-TCP
235-TCP
245-TCP
234-TCP
246-TBrP
2356-TeCP
TCP
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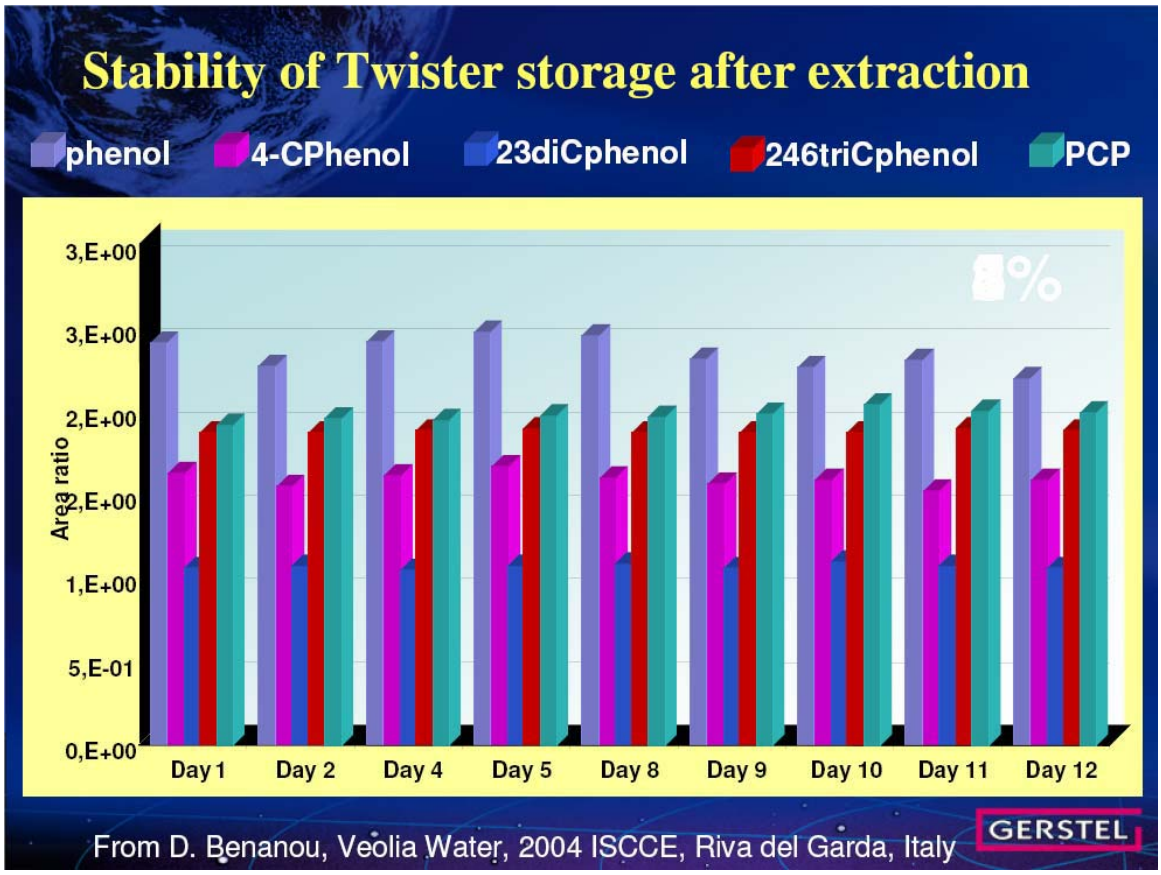
GERSTEL


Stability of Twister storage after extraction
phenol
4-CPhenol
23diCphenol
246triCphenol
PCP
Area ratio
3,E+00
3,E+00
2,E+00
2,E+00
1,E+00
5,E-01
0,E+00
Day 1
Day 2
Day 4
Day 5
Day 8
Day 9
Day 10
Day 11
Day 12
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy
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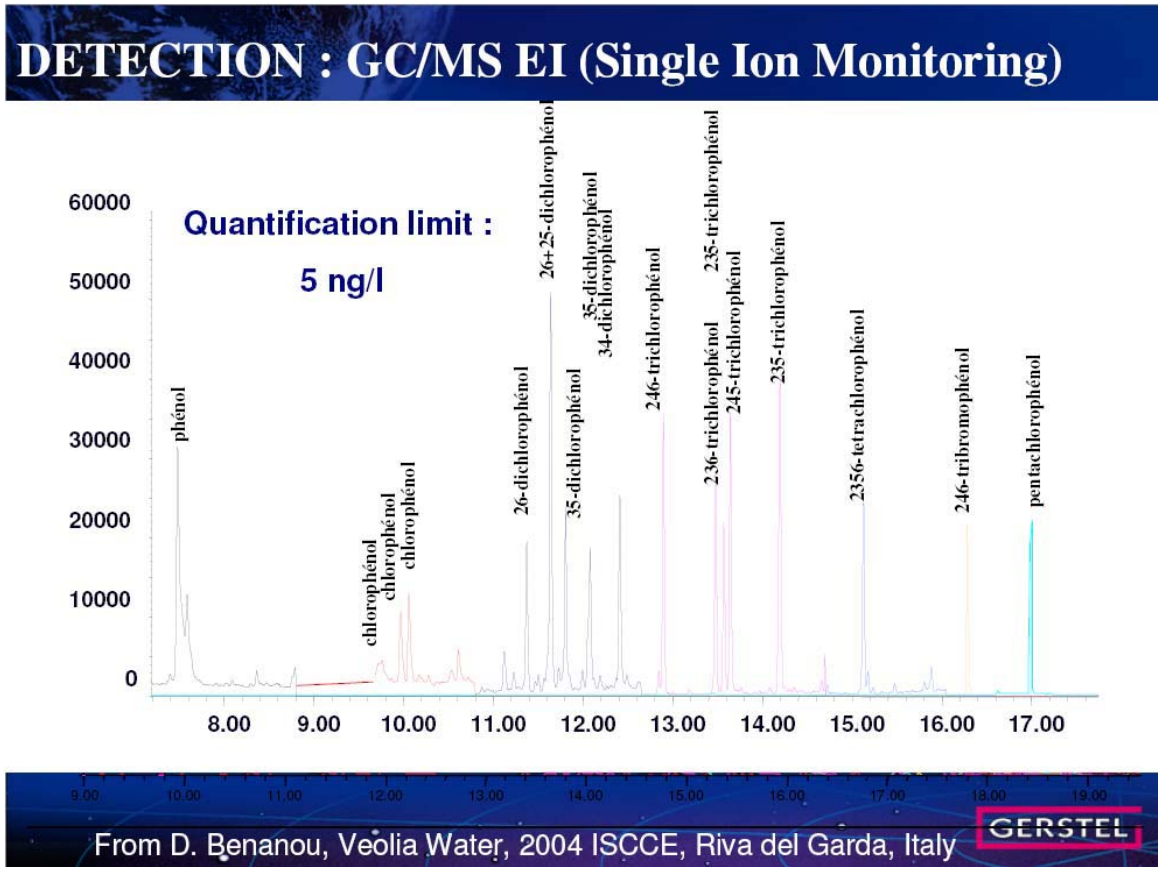
DETECTION : GC/MS EI (Single Ion Monitoring)
Quantification limit :
5 ng/l
60000
50000
40000
30000
20000
10000
0
phénol
chlorophénol
chlorophénol
chlorophénol
26-dichlorophénol
26+25-dichlorophénol
35-dichlorophénol
34-dichlorophénol
35-dichlorophénol
246-trichlorophénol
236-trichlorophénol
235-trichlorophénol
245-trichlorophénol
235-trichlorophénol
2356-tetrachlorophénol
246-tribromophénol
pentachlorophénol
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
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Outline

- SBSE Introduction
- Environmental Applications
  - Water odor
  - Semivolatile organics
    - PAH
    - EPA 8270
    - Organotin
  - Pesticides
  - Pharmaceutical and personal care products (PPCP)
  - Endocrine disrupting compounds (EDC)
  - Other

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PAH extraction from water by SBSE

Compound	%RSD 10 ng/l	%RSD 50ng/l	Linearity	Sensitivity area/(ng/l)	Detection Limit (ng/l)
Naphthalene	12	9	0.98782	165	0.5
a-Methylnaphthalene	7	4	0.99219	114	0.6
2-Methylnaphthalene	5	4	0.9941	114	0.8
Acenaphthylene	8	5	0.9978	182	0.3
Acenaphthene	10	3	0.99707	135	1.5
Fluorene	9	4	0.99872	178	2
Phenanthrene	11	5	0.99948	303	0.8
Anthracene	15	6	0.99865	207	1.2
Fluoranthene	10	4	0.99946	260	0.1
Pyrene	9	3	0.99971	256	0.7
Benz(a)anthracene	8	5	0.9786	103	0.2
Chrysene	6	5	0.98527	137	0.2
Benzo(b)fluoranthene	10	5	0.92903	55	0.3
Benzo(k)fluoranthene	6	4	0.97357	96	0.5
Benzo(a)pyrene	10	6	0.92543	54	1.2
Indeno(1,2,3-cd)pyrene	12	9	0.99894	22	1.4
Dibenz(a,h)anthracene	14	7	0.99995	89	0.3
Benzo(g,h,i)perylene	14	7	0.99848	74	0.2

Kolahgar, B., Hoffmann, A., Heiden, A. J. Chromatogr., 963, (2002), 225

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Peak	Compound	Log Kow	15mL %Rec	Peak	Compound	Log Kow	15mL %Rec
16	Bis(2-chloroethoxy)methane	1.3	3.3	25	2,4,6-Trichlorophenol	3.45	83.0
10	n-nitrosodi-n-propylamine	1.33	3.6	26	2,4,5-Trichlorophenol	3.45	83.0
37	3-Nitroaniline	1.47	4.9	35	Dibenzofuran	3.71	89.9
41	4-Nitroaniline	1.47	4.9	23	2-Methylnaphthalene	3.72	90.1
1	Phenol	1.51	5.3	27	2-Chloronaphthalene	3.81	91.8
S2	Phenol-d6	1.51	5.3	18	1,2,4-Trichlorobenzene	3.93	93.7
2	Bis(2-chloroethyl)ether	1.56	5.9	30	Acenaphthylene	3.94	93.8
29	Dimethyl phthalate	1.66	7.3	S4	2-Fluorobiphenyl	3.96	94.1
S1	2-Fluorophenol	1.71	8.2	39	Fluorene	4.02	94.8
20	4-Chloroaniline	1.72	8.3	11	Hexachloroethane	4.03	94.9
34	2,4-Dinitrophenol	1.73	8.5	33	Acenaphthene	4.15	96.1
12	Nitrobenzene	1.81	10.1	S5	2,4,6-Tribromophenol	4.18	96.3
S3	Nitrobenzene-d5	1.81	10.1	47	Phenanthrene	4.35	97.5
14	2-Nitrophenol	1.91	12.3	48	Anthracene	4.35	97.5
36	4-Nitrophenol	1.91	12.3	49	di-n-butyl phthalate	4.61	98.6
28	2-Nitroaniline	2.02	15.4	24	Hexachlorocyclopentadiene	4.63	98.7
7	2-Methylphenol	2.06	16.6	40	4-Chlorophenylphenylether	4.69	98.8
9	m/p-mehtylphenol	2.06	16.6	21	Hexachlorobutadiene	4.72	98.9
3	2-Chlorophenol	2.16	20.0	46	Pentachlorophenol	4.74	99.0
31	2,6-Dinitrotoluene	2.18	20.8	52	Butyl Benzyl Phthalate	4.84	99.2
32	2,4-Dinitrotoluene	2.18	20.8	50	Fluoranthene	4.93	99.3
43	2-Methyl-4,6-dinitrophenol	2.27	24.4	51	Pyrene	4.93	99.3
8	Bis(2-chloroisopropyl)ether	2.39	29.8	44	4-Bromophenylphenylether	4.94	99.3
15	2,4-Dimethylphenol	2.61	41.4	53	Benz(a)anthracene	5.52	99.8
13	Isophorone	2.62	41.9	55	Chrysene	5.52	99.8
38	Diethyl phthalate	2.65	43.6	S6	Terphenyl-d14	5.52	99.8
22	4-Chloro-3-Methylphenol	2.7	46.5	45	Hexachlorobenzene	5.86	99.9
17	2,4-Dichlorophenol	2.8	52.2	58	Benzo(b)fluoranthene	6.11	100.0
19	Naphthalene	3.17	71.9	59	Benzo(a)pyrene	6.11	100.0
42	n-Nitrosodiphenylamine	3.17	71.9	60	Indeno(1,2,3-cd)pyrene	6.7	100.0
54	3-3-Dichlorobenzidine	3.21	73.8	61	Dibenz(a,h)anthracene	6.7	100.0
4	1,3-Dichlorobenzene	3.28	76.8	62	Benzo(g,h,i)perylene	6.7	100.0
5	1,4-Dichlorobenzene	3.28	76.8	56	Bis(2-ethylhexyl) phthalate	8.39	100.0
6	1,2-Dichlorobenzene	3.28	76.8	57	di-n-octyl phthalate	8.54	100.0

Twister Recovery Estimates

8270

Compounds and Surrogates

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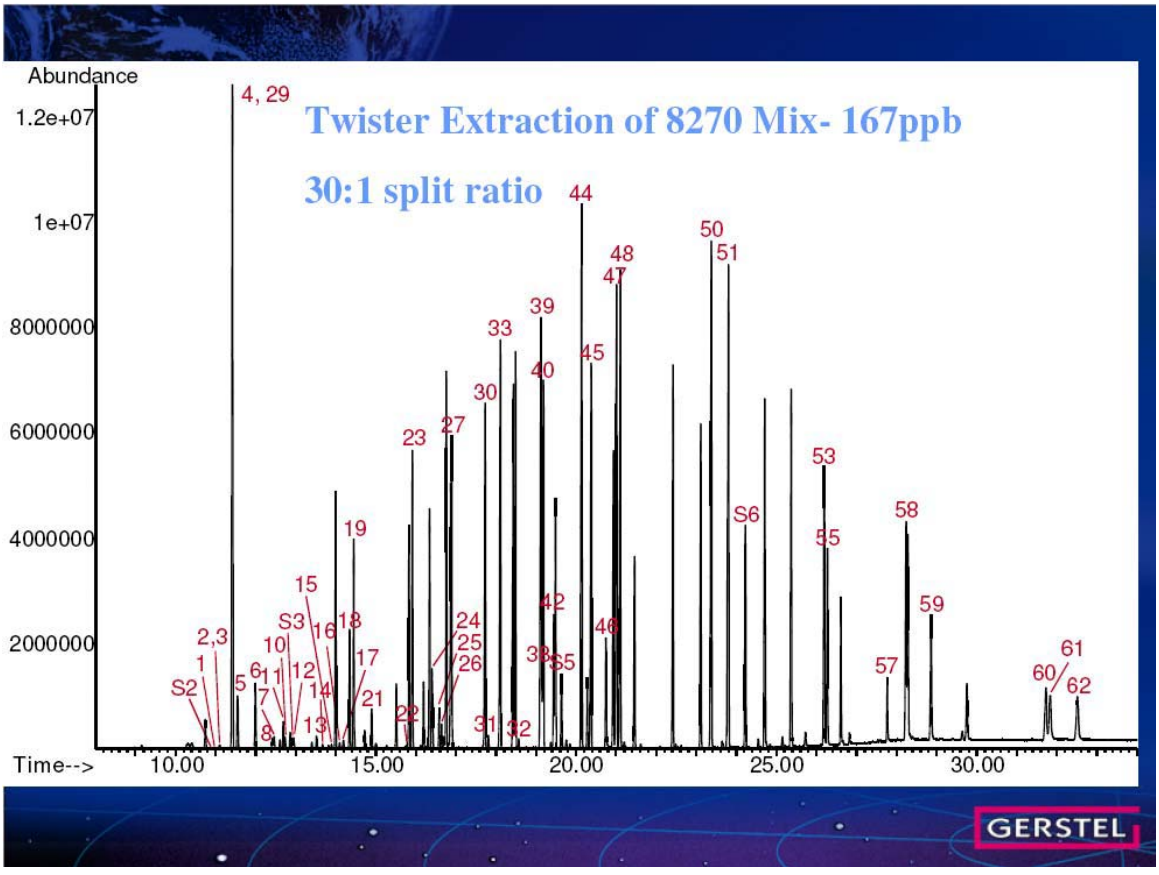
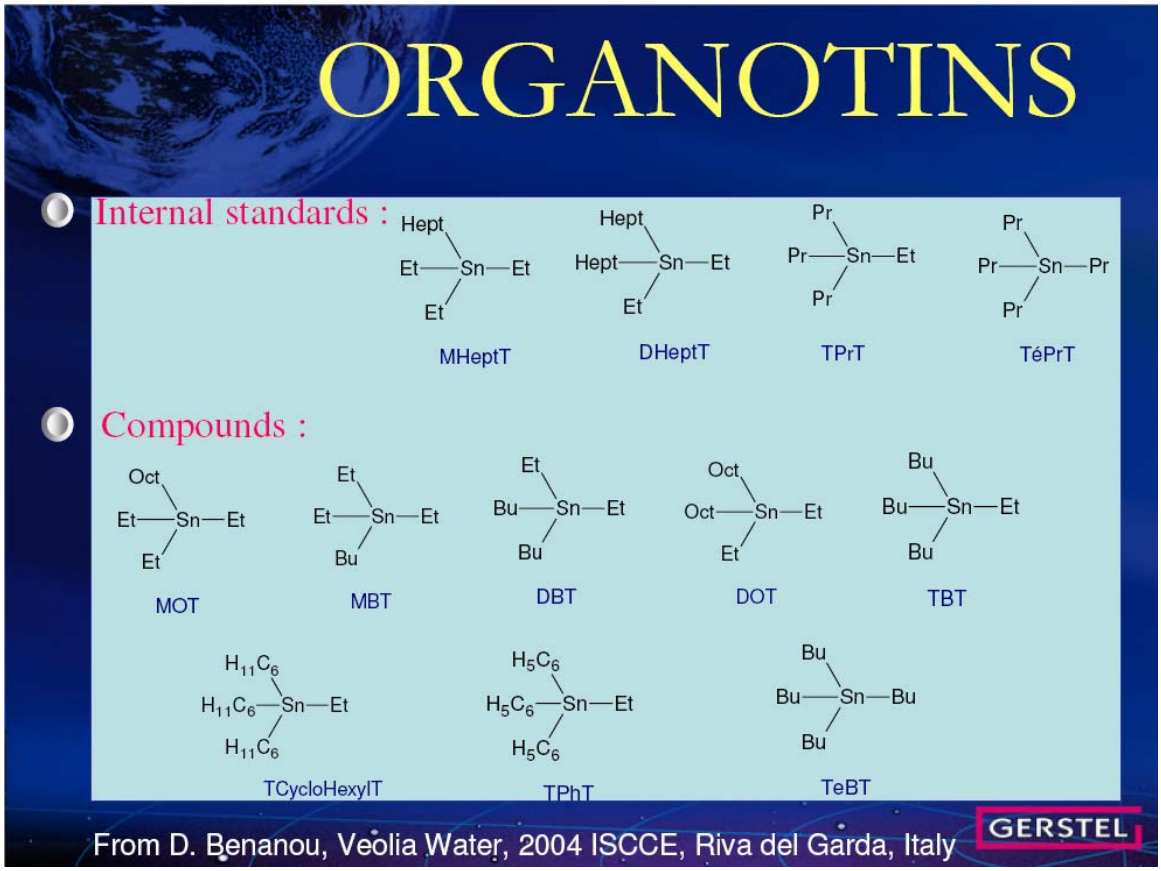
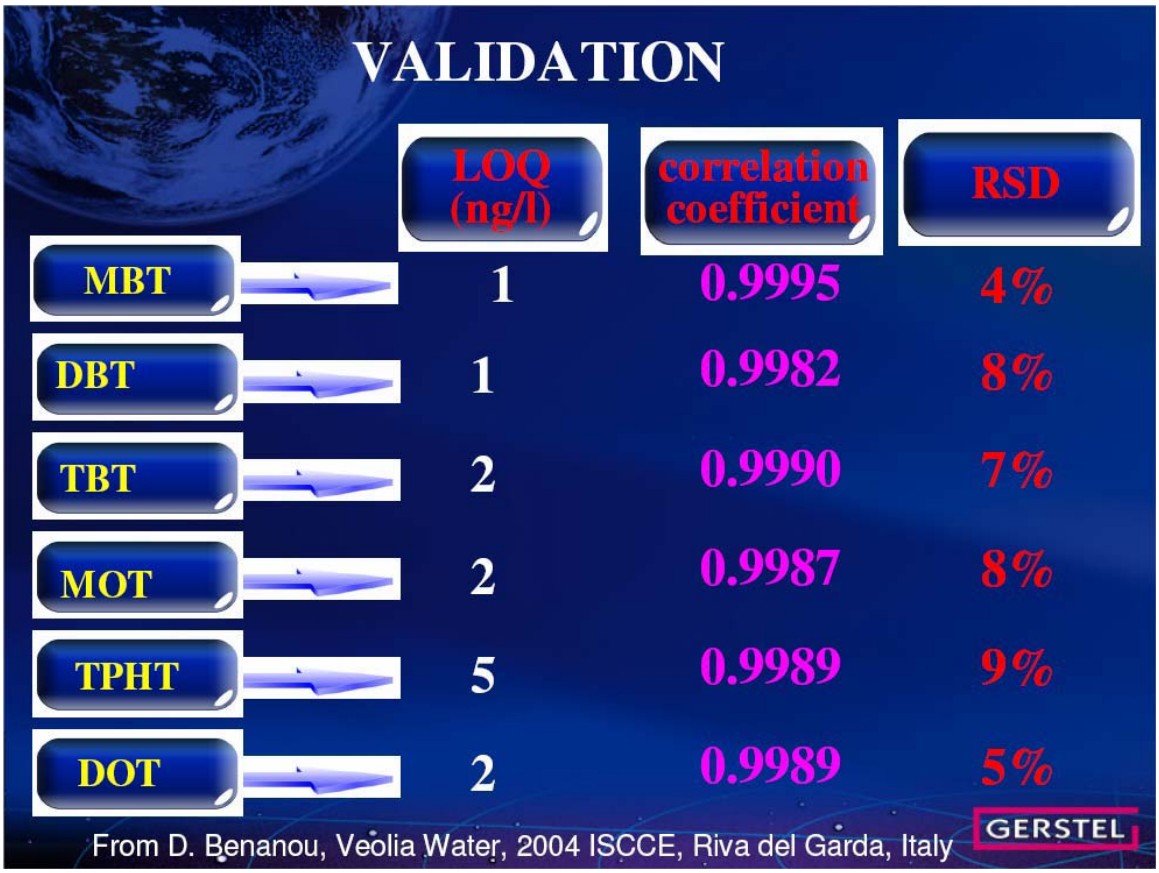


GERSTEL


ORGANOTINS
Internal standards :
MHeptT
DHeptT
TPrT
TéPrT
Compounds :
MOT
MBT
DBT
DOT
TBT
TCycloHexylT
TPhT
TeBT
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy
GERSTEL


VALIDATION
LOQ (ng/l)
correlation coefficient
RSD
MBT 1 0.9995 4%
DBT 1 0.9982 8%
TBT 2 0.9990 7%
MOT 2 0.9987 8%
TPHT 5 0.9989 9%
DOT 2 0.9989 5%
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy
GERSTEL

Outline

- SBSE Introduction
- Environmental Applications
  - Water odor
  - Semivolatile organics
  - Pesticides
    - Water
    - Food
  - Pharmaceutical and personal care products (PPCP)
  - Endocrine disrupting compounds (EDC)
  - Other

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Trends in Residue Analysis

- MS becoming standard detector
- Moving from target compound analysis to multi-residue methods (MRM)
- Lower detection limits (< 10 ppb)
- Miniaturization of sample preparation
  - reduction of solvent consumption (500mL/sample)
  - automation (multi-step labor intensive)
  - higher sample throughput

GERSTEL

Sample Preparation
by Stir Bar Sorptive Extraction (SBSE)

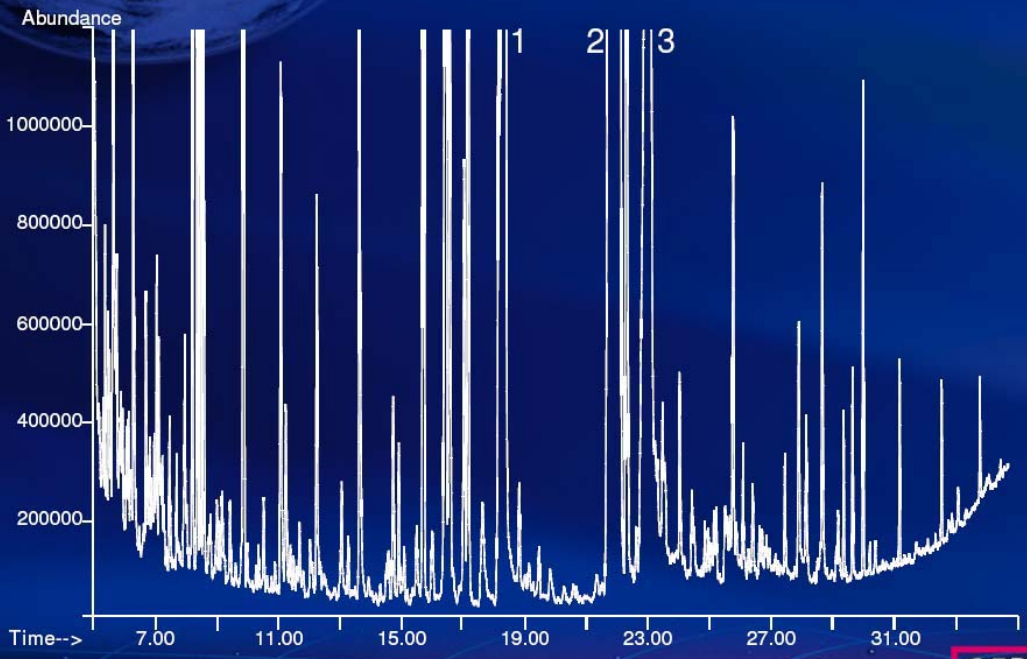
- 15 g sample is homogenized with 30 mL methanol (5 min ultraturrax + 15 min ultrasonic bath)
- Centrifuge
- 1 mL extract is diluted with 10 mL water
- Stir Bar Sorptive Extraction is performed
- => 440 (out of ~500) GC-amenable pesticides

Examples: Lettuce and Baby food

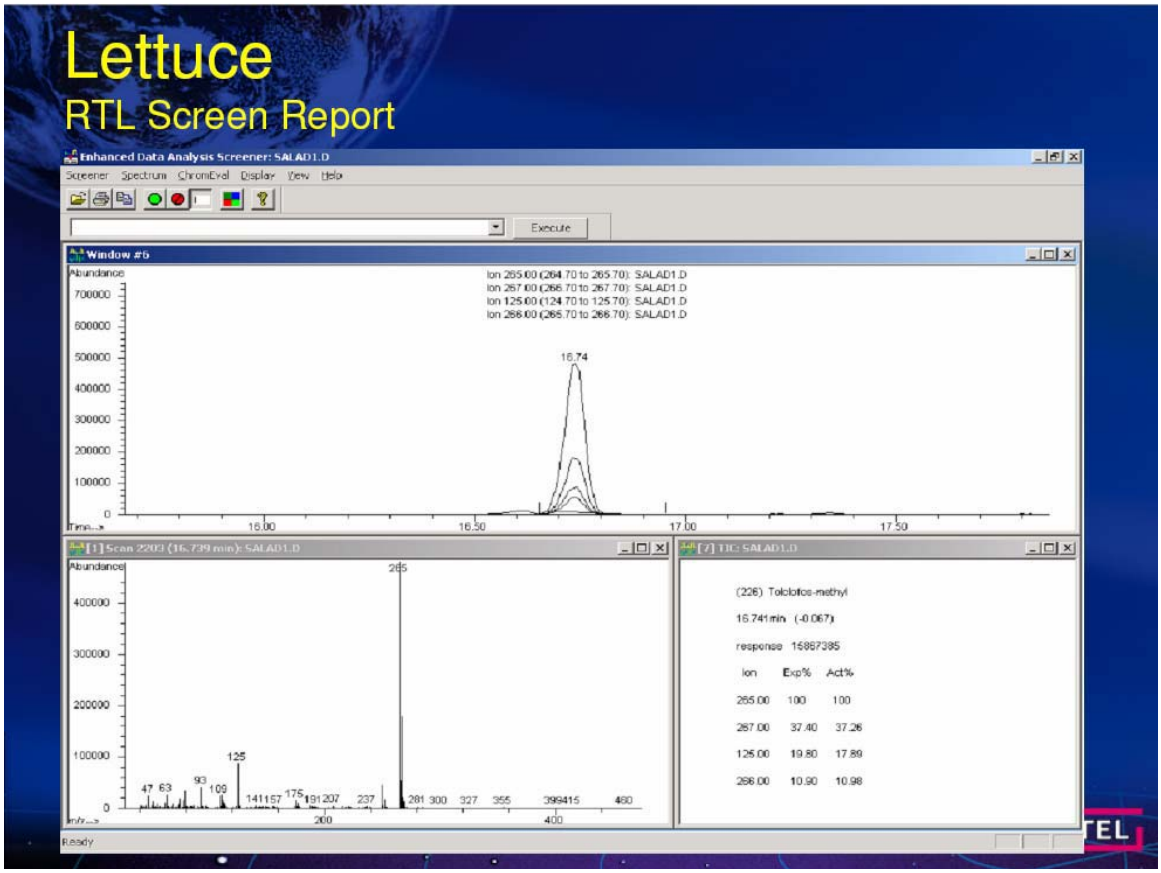
GERSTEL

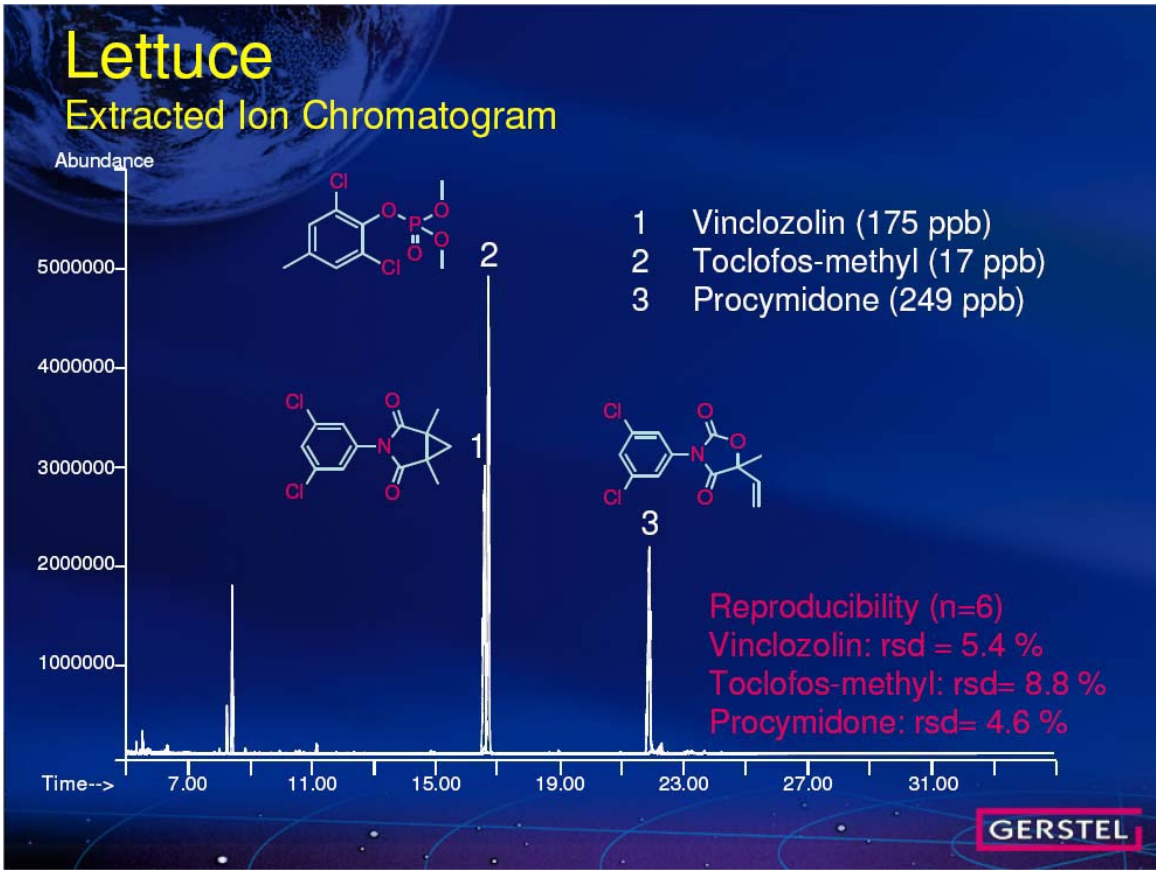
Lettuce
Total Ion Chromatogram

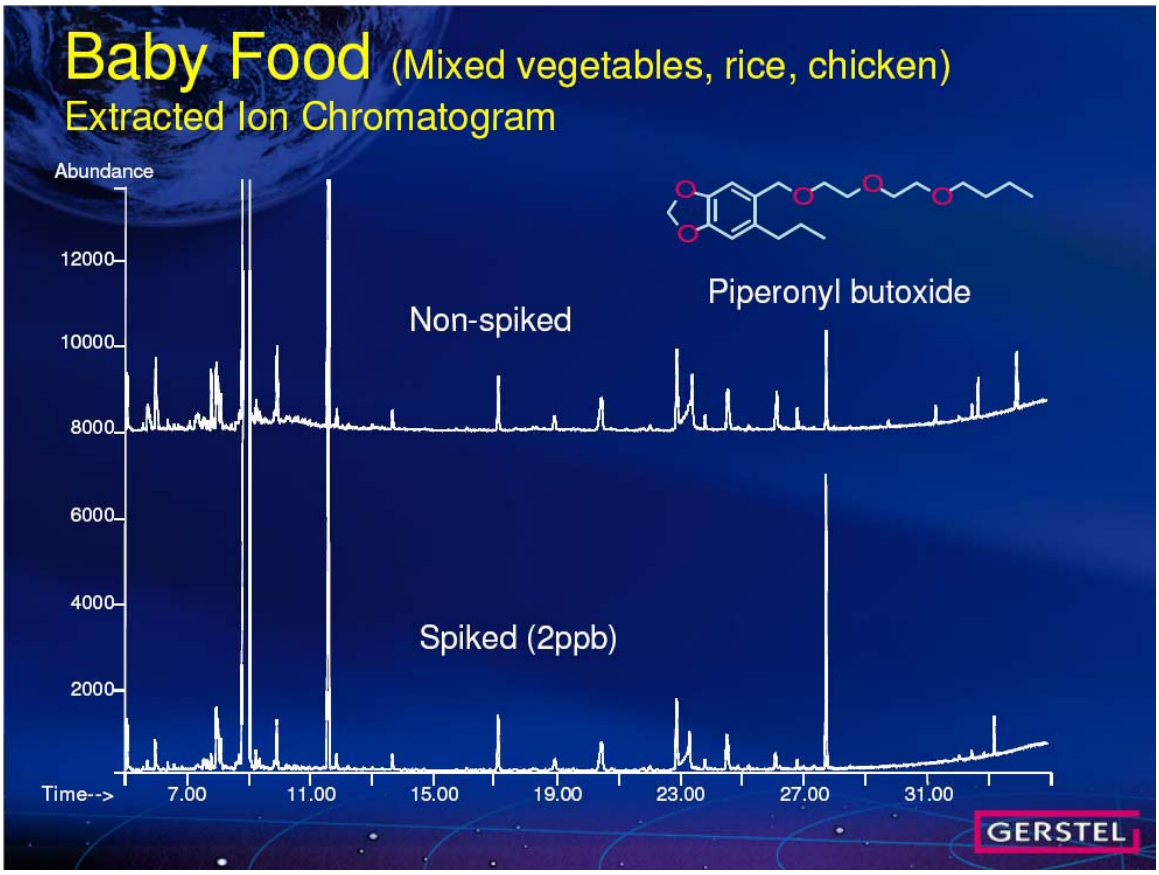
1 Palmitic Acid
2 Oleic Acid
3 Stearic Acid

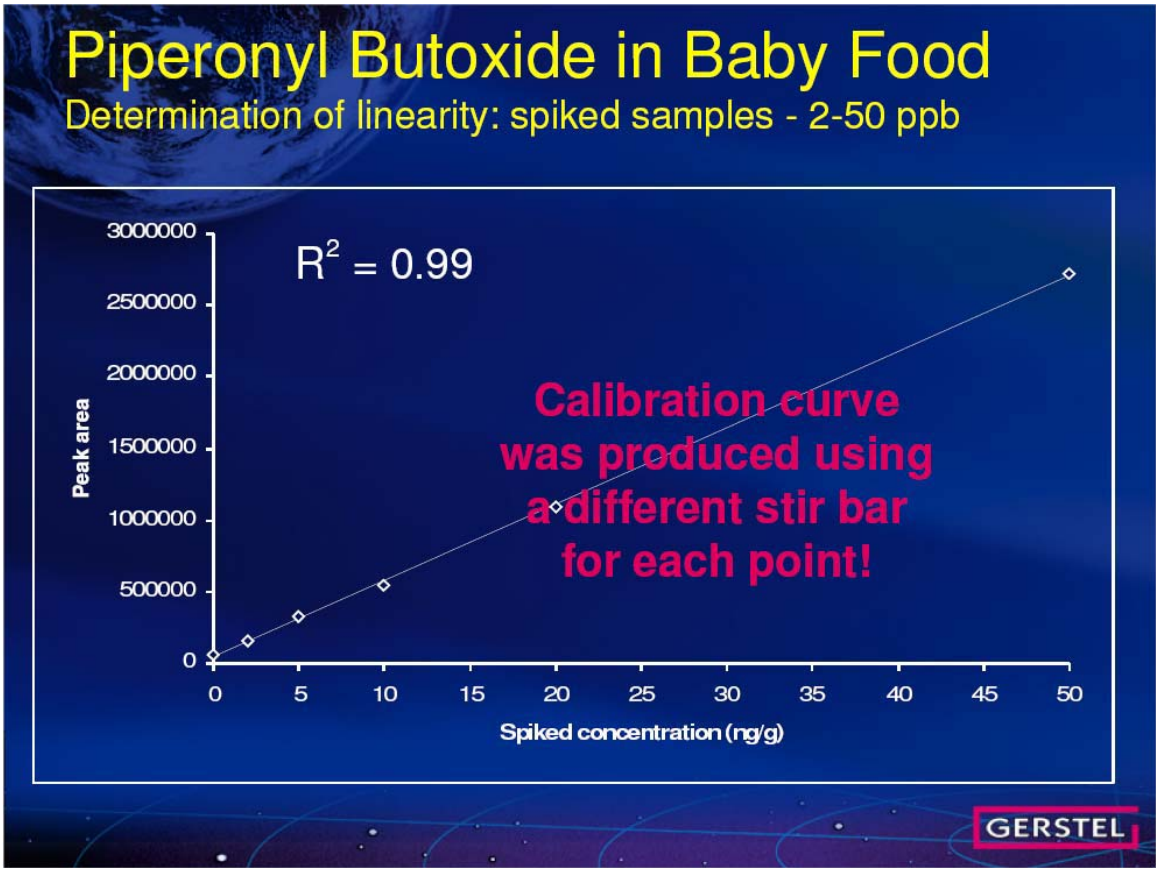


GERSTEL


Lettuce
RTL Screen Report
Enhanced Data Analysis Screener: SALAD1.D
Screener Spectrum ChromEval Display View Help
Execute
Window #6
Abundance
Ion 265.00 (264.70 to 265.70): SALAD1.D
Ion 267.00 (266.70 to 267.70): SALAD1.D
Ion 125.00 (124.70 to 125.70): SALAD1.D
Ion 268.00 (265.70 to 268.70): SALAD1.D
16.74
Time-->
16.00
16.50
17.00
17.50
[1] Scan 2203 (16.739 min): SALAD1.D
265
125
[7] TIC: SALAD1.D
(226) Toclofos-methyl
16.741 min (-0.067)
response 15867385
Ion Exp% Act%
265.00 100 100
267.00 37.40 37.26
125.00 19.80 17.89
268.00 10.90 10.98
Ready


Lettuce
Extracted Ion Chromatogram
Abundance
5000000
4000000
3000000
2000000
1000000
Time-->
7.00
11.00
15.00
19.00
23.00
27.00
31.00
1 Vinclozolin (175 ppb)
2 Toclofos-methyl (17 ppb)
3 Procymidone (249 ppb)
Reproducibility (n=6)
Vinclozolin: rsd = 5.4 %
Toclofos-methyl: rsd= 8.8 %
Procymidone: rsd= 4.6 %
GERSTEL


Baby Food (Mixed vegetables, rice, chicken)
Extracted Ion Chromatogram
Abundance
12000
10000
8000
6000
4000
2000
Non-spiked
Piperonyl butoxide
Spiked (2ppb)
Time-->
7.00
11.00
15.00
19.00
23.00
27.00
31.00
GERSTEL


Piperonyl Butoxide in Baby Food
Determination of linearity: spiked samples - 2-50 ppb
R2 = 0.99
Calibration curve
was produced using
a different stir bar
for each point!
Peak area
3000000
2500000
2000000
1500000
1000000
500000
0
0
5
10
15
20
25
30
35
40
45
50
Spiked concentration (ng/g)
GERSTEL

Determination of Pesticide Residues in Food

from Classical to Novel Techniques

Aniko Kende, Tamas Rikker, Kornel Torkos

EKOL – Separation Science Research and Training Laboratory

Budapest, Hungary

Method Comparison

- LLE with GPC cleanup (Method DFG S19)

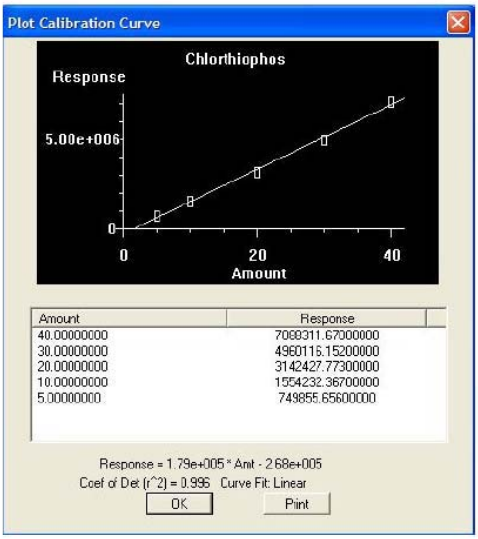
After 42 sample injections

- SBSE after methanol extraction

After 42 sample injections

Stir Bar Sorptive Extraction

Calibration curve of Chlorthiophos



Recovery and RSD results of 10 ppb spiked apple sample

	DFG S19 analogue		SBSE	
	Recovery%	RSD%	Recovery%	RSD%
Butylate	47.4	7.6	85.9	6.1
Quintozene	29.7	12.9	100.1	1.4
2,4,5-T	62.1	8.5	92.5	11.8
Methyl parathion	77.4	12.6	86.9	28.2
Malathion	78.6	10.0	73.2	33.9
Chlorpyriphos	66.0	30.6	95.3	6.1
Isodrin	121.5	55.7	59.7	10.2
Prothiophos	50.7	19.5	63.3	6.9
Chlorbenzilate	41.7	21.5	94.0	4.4
Ethion	64.6	18.5	90.6	7.2
Bifenthrin	31.7	29.1	16.6	13.0
Leptophos	38.5	24.2	28.0	22.3
Pirimiphos-methyl	90.3	11.2	85.2	7.0
Metolachlor	39.4	12.7	85.9	20.9
Average	60.0	19.6	75.5	12.8

Stir Bar Sorptive Extraction

- Suitable for vegetable and fruit samples (non-fatty matrices)
- Target compounds: log $K_{octanol/water} \geq 2$
- Scan LOQ ≤ 10 µg/kg
- Retention Time Locking (RTL) Pesticide Database – qualitative analysis of 567 compounds
- Quantitation Database for 150 pesticides

- Awaiting accreditation in the contract laboratory

Outline

- SBSE Introduction
- Environmental Applications
  - Water odor
  - Semivolatile organics
  - Pesticides
  - Pharmaceutical and personal care products (PPCP)
    - Human and veterinary drugs
    - Musks
    - Fragrances
  - Endocrine disrupting compounds (EDC)
  - Other

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SBSE of Pharmaceutical Compounds

Performance evaluation of thermal desorption system (TDS) for detection of basic drugs in forensic samples by GC-MS

J.A. Crifasi et.al. J. Anal. Toxicology v30 (in press)

- SBSE of over 140 pharmaceutical compounds in biological fluids and tissues
- Detection limits of 1 mg/L or less
- Demonstrated equivalence vs. more cumbersome standard methods

SBSE thermal desorption GC/MS for profiling and target component analysis of pharmaceutical drugs in urine

B. Tienpont et. al., J. Pharma. and Biomed. Anal. 32 (2003) 569-579.

- Demonstrated in-situ derivatization + SBSE for over 20 drugs
- Quantified barbiturates in urine with LOD to 10ng/L (SIM)

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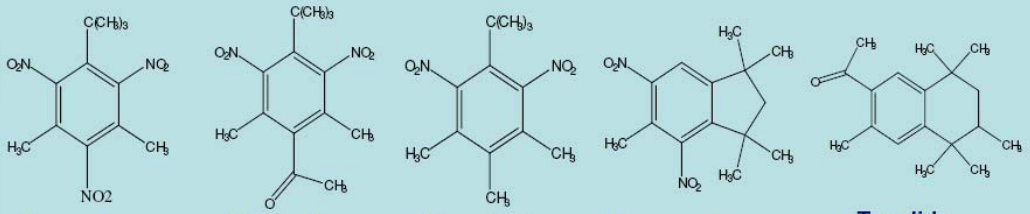
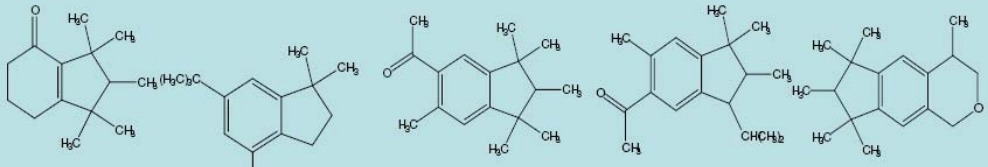
MUSKS



Musc xylene MX | Musc cétone MK | Musc tibetene MT | Musc moskene MM | Tonalide AHTN



Cashmeran DPMI | Celestolide ADBI | Phantolide AHMI | Traseolide ATII | Galaxolide HHCB

From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy

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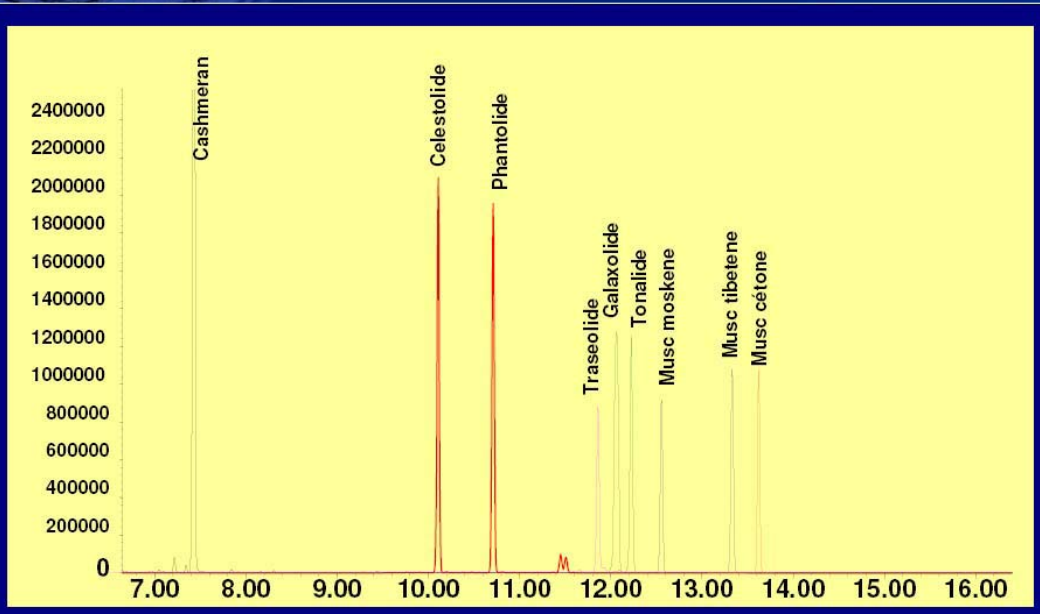
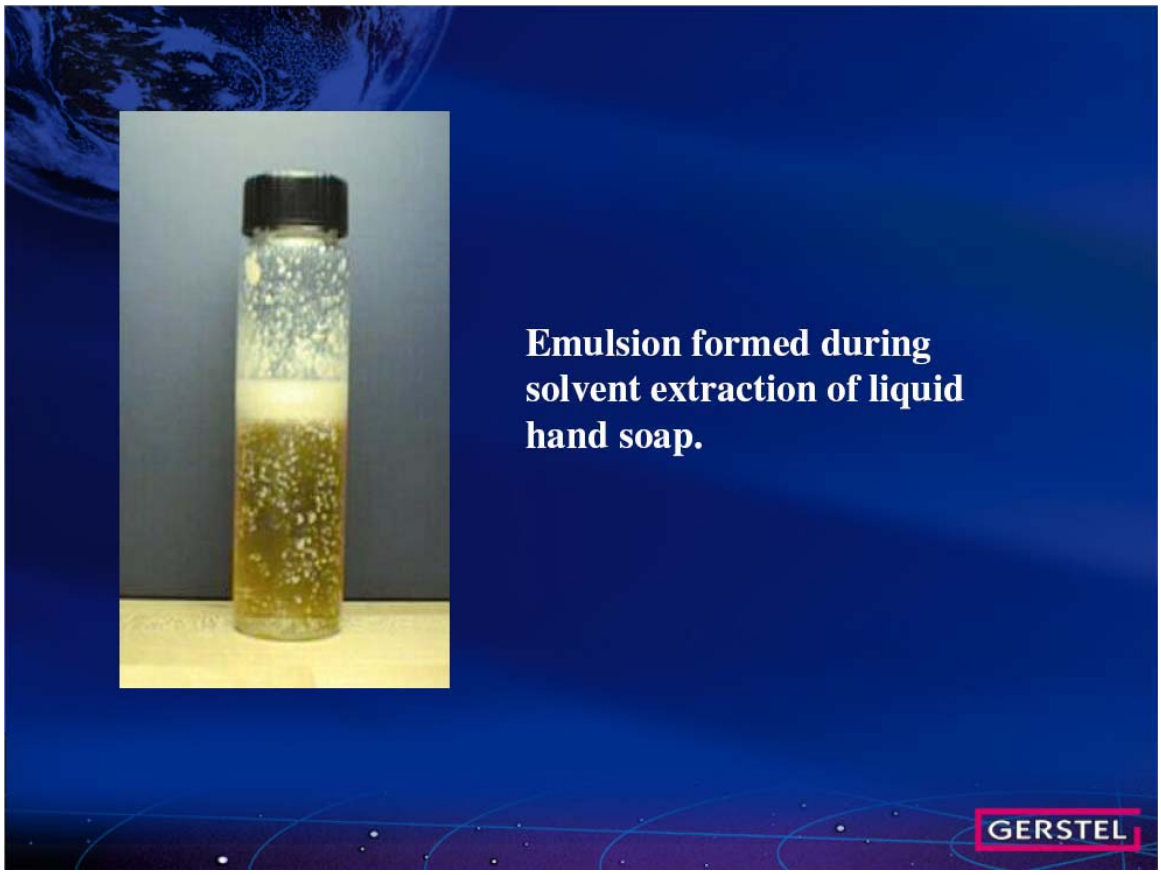
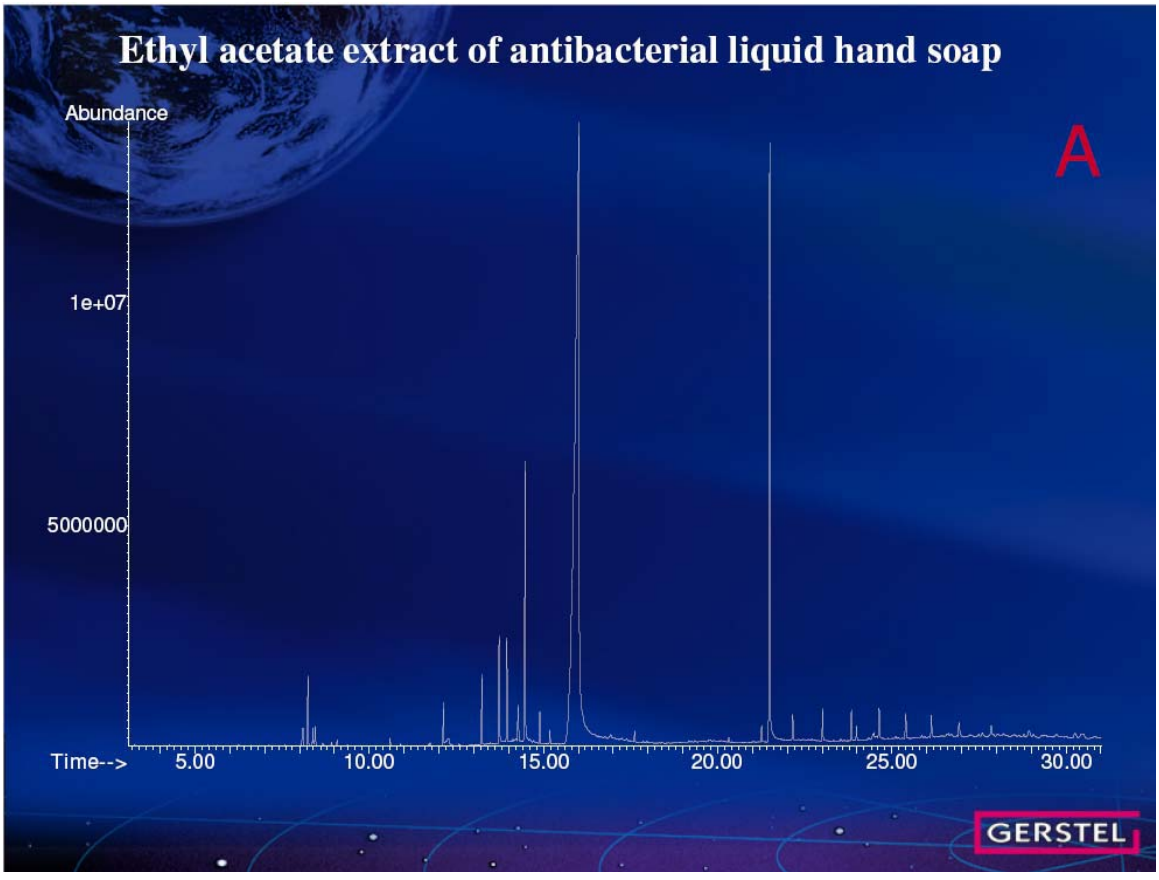
MUSKS IN SLUDGE (30 ng/g dm)

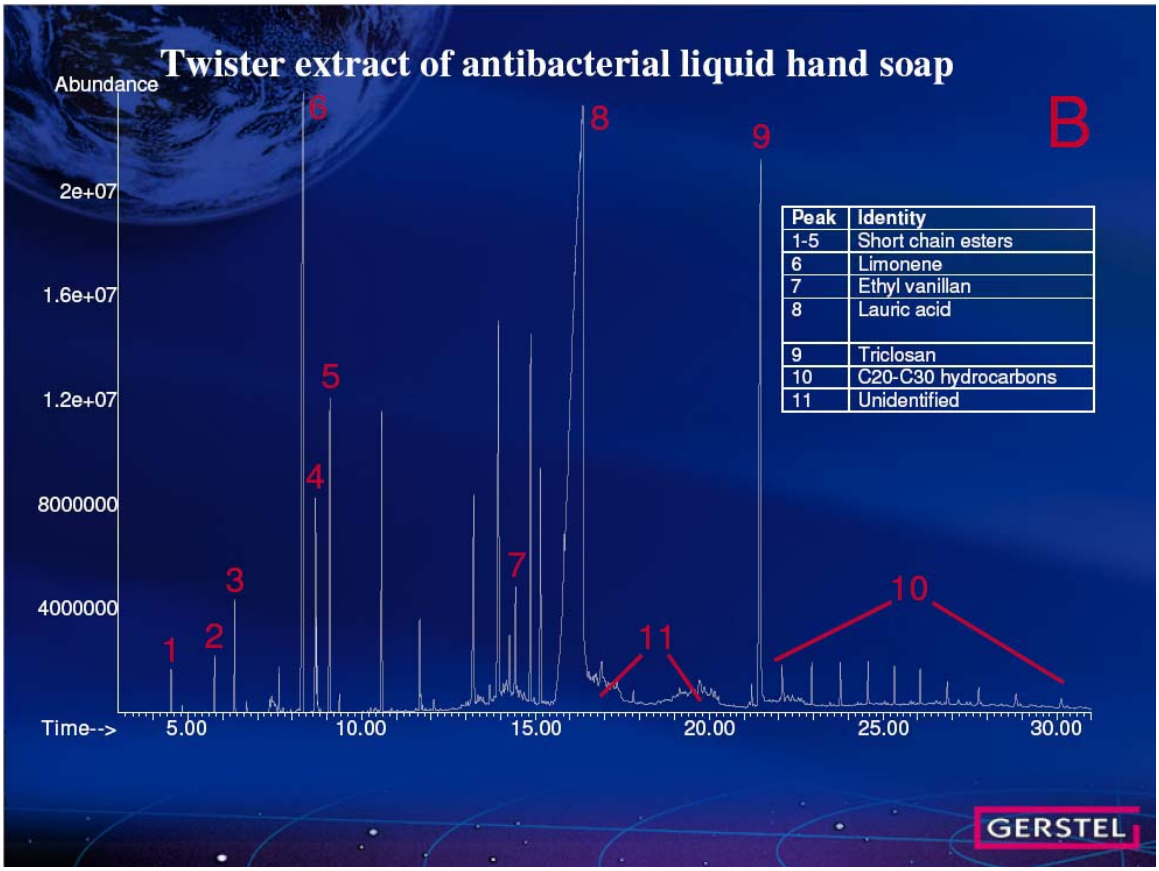


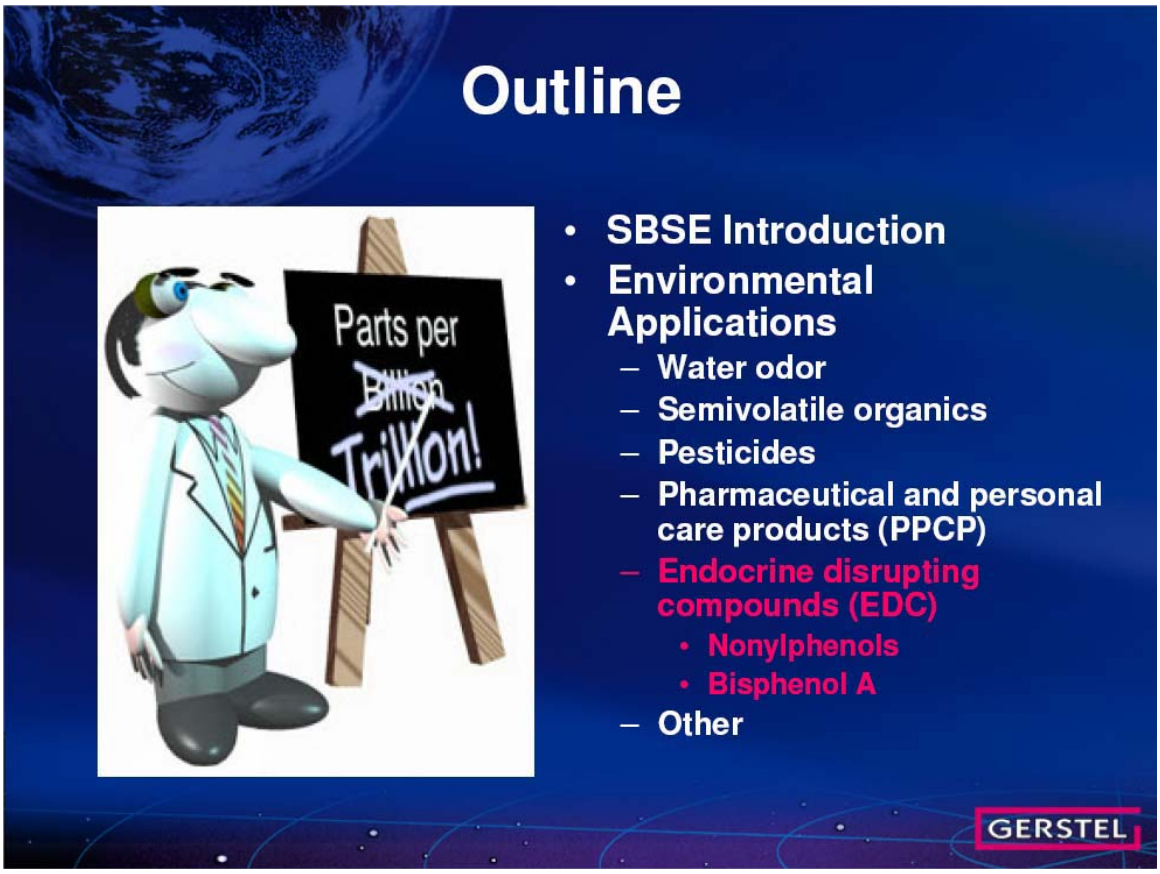
From D. Benanou, Veolia Water, 2004 ISCCE, Riva del Garda, Italy

GERSTEL


Emulsion formed during solvent extraction of liquid hand soap.
GERSTEL


Ethyl acetate extract of antibacterial liquid hand soap
Abundance
A
1e+07
5000000
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
GERSTEL


Twister extract of antibacterial liquid hand soap
Abundance
B
2e+07
1.6e+07
1.2e+07
8000000
4000000
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
1
2
3
4
5
6
7
8
9
10
11
Peak | Identity
1-5 | Short chain esters
6 | Limonene
7 | Ethyl vanillan
8 | Lauric acid
9 | Triclosan
10 | C20-C30 hydrocarbons
11 | Unidentified
GERSTEL


Outline
Parts per Billion Trillion!
• SBSE Introduction
• Environmental Applications
– Water odor
– Semivolatile organics
– Pesticides
– Pharmaceutical and personal care products (PPCP)
– Endocrine disrupting compounds (EDC)
• Nonylphenols
• Bisphenol A
– Other
GERSTEL

SBSE of Endocrine Disrupting Compounds

Trace analysis of phenolic xenoestrogens in water samples by SBSE with in-situ derivatization and TD-GC-MS

M. Kawaguchi et.al. J. Chrom. A 1041 (2004) 19-26.

- SBSE of several chloro- and alkylphenols and bisphenol A with >90% recovery
- LOD for these compounds was 0.5-5.0 ng/L

Multiresidue screening of endocrine disrupter chemicals in water by SBSE-liquid desorption- GC/MS

P. Serodio and J.M.F. Nogueira Anal. Chim. Acta 517 (2004) 21-32.

- Screened over 60 EDC (pesticides/herbicides, PAH, PCB, biocides, phthalates, alkylphenols) in water at sub- ug/L levels

GERSTEL

Outline

- SBSE Introduction
- Environmental Applications
  - Water odor
  - Semivolatile organics
  - Pesticides
  - Pharmaceutical and personal care products (PPCP)
  - Endocrine disrupting compounds (EDC)
  - Other
    - PBDPE fire retardants
    - Explosives
    - Chemical warfare agents

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SBSE of fire retardants and explosives

Analysis of nine PBDPE fire retardants in water by SBSE-TD-GC/MS

J. Llorca-Porcel et.al. Anal. Chim. Acta 569 (2006) 113-118

- SBSE of tri- to hexabromodiphenylethers with near 100% recovery
- LOD for these compounds was 0.3-10.0 ng/L

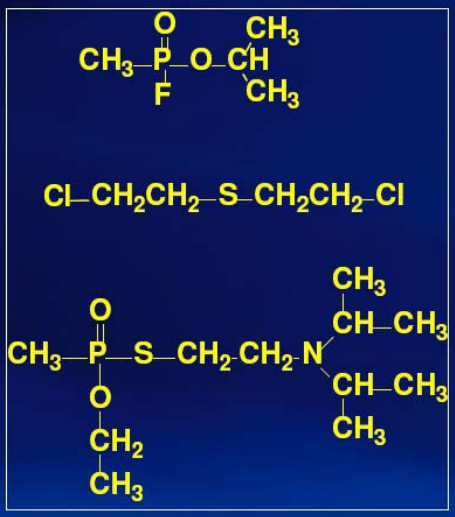
SBSE with thermal desorption ion-mobility spectrometry for the determination of TNT and RDX in water samples

J. K. Lokhnauth and N. H. Snow J. Chrom. A. 1105 (2006) 33-38

- SBSE of explosives at 0.1-2 ng/mL LOD with 1 min analysis time

GERSTEL

Chemical Warfare Agents



GB

HD

VX

GERSTEL

CW Precision Study

- Five 20 mL Samples of HD and VX in DI Water
- Samples Spiked at 750 ppt
- pH = 11.2, 4.0 g KCl Added
- 90 Minute Stir Time

AGENT	Average Recovery (%)	RSD (%)
HD	46.4	9.0
VX	18.0	16

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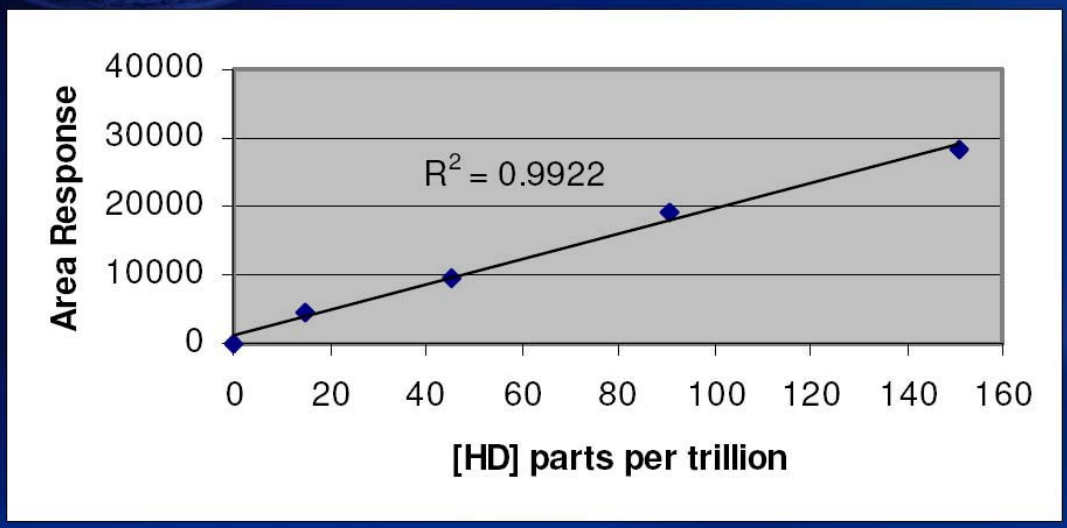
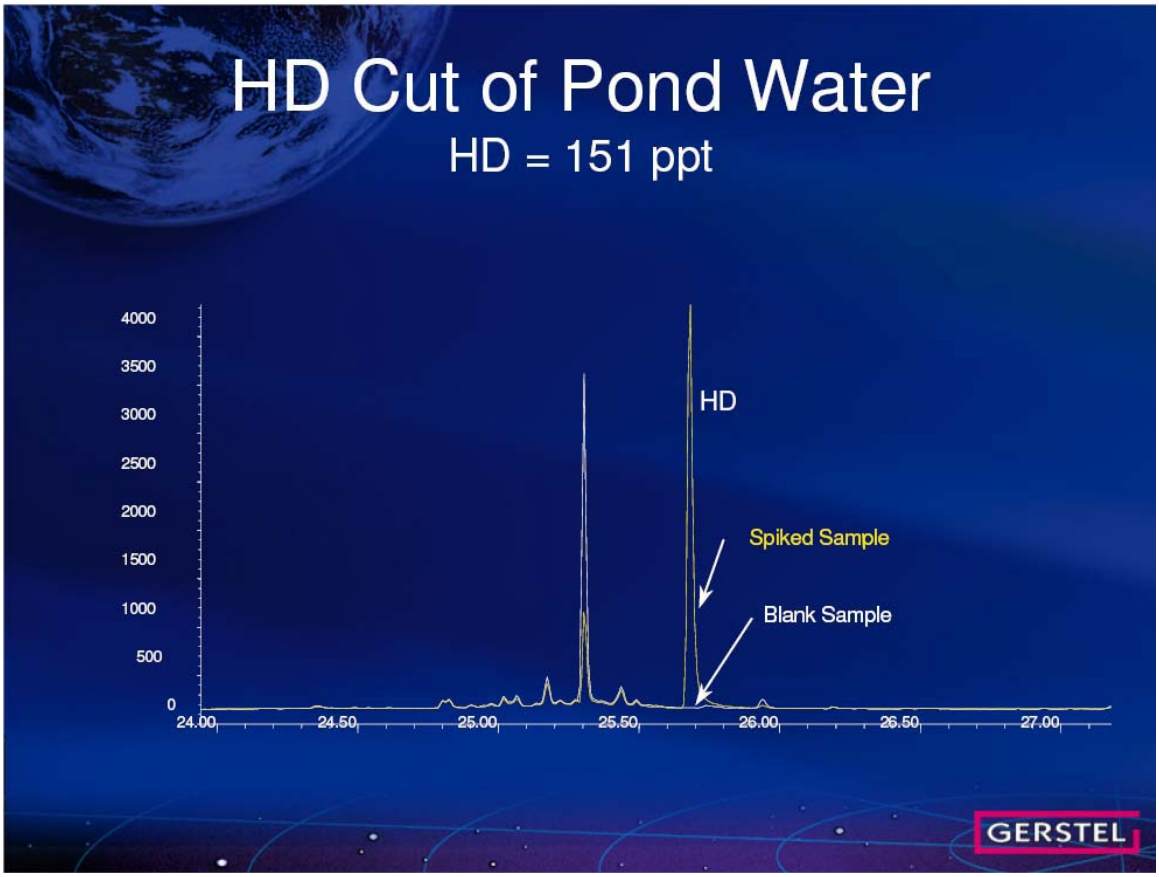
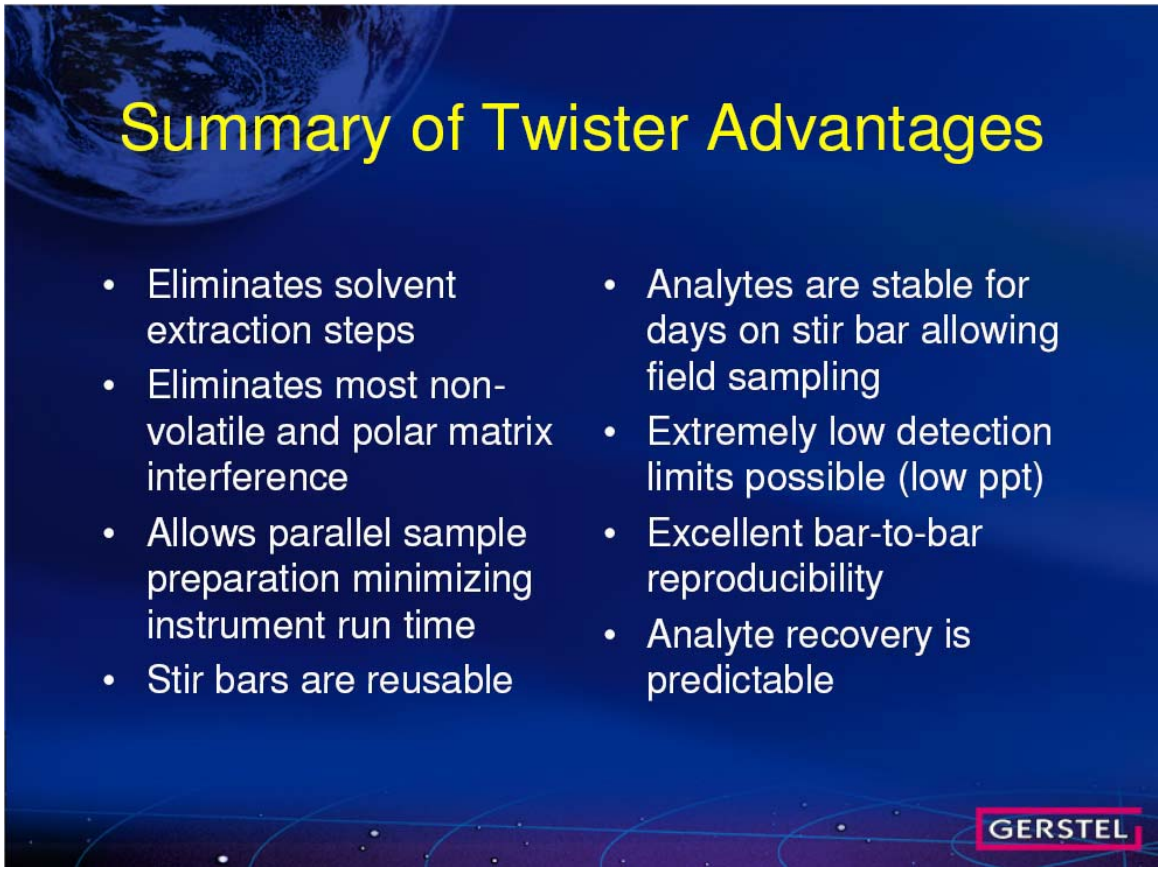
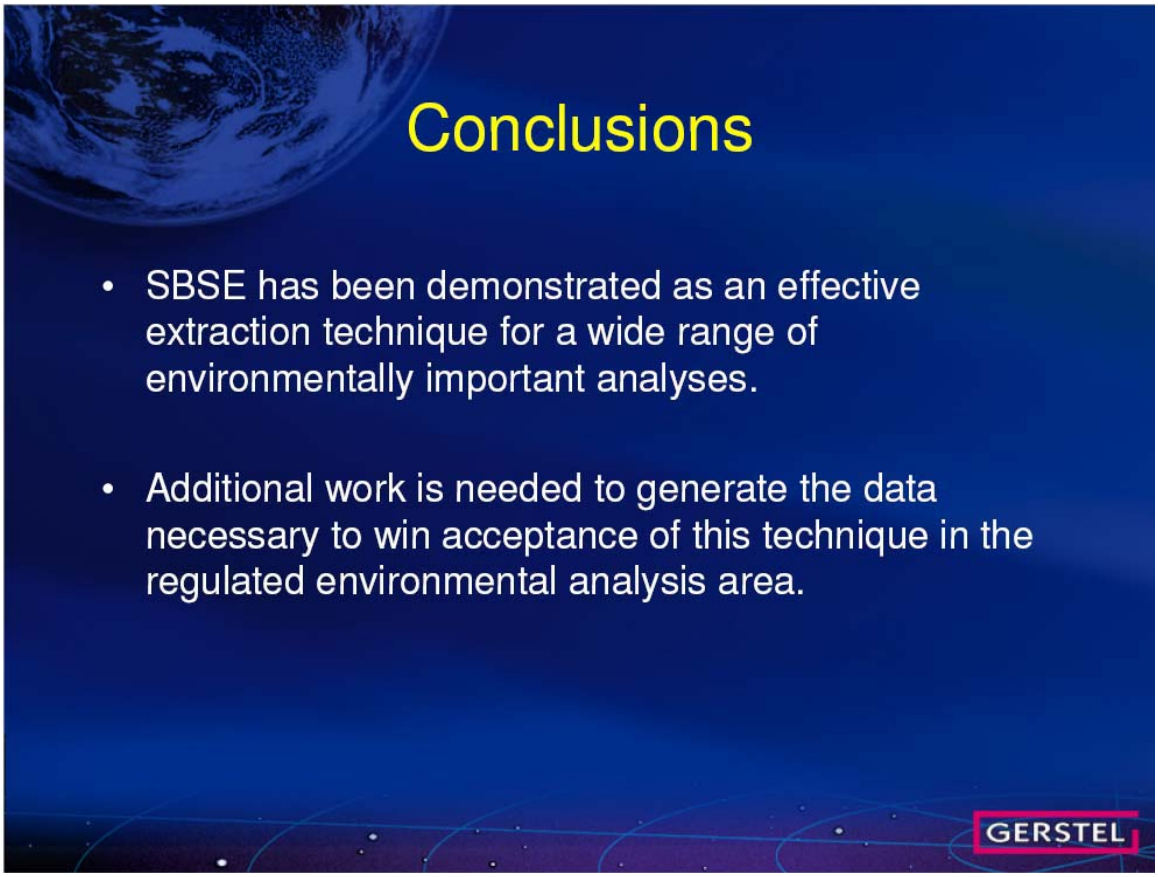
HD Calibration



GERSTEL


HD Cut of Pond Water
HD = 151 ppt
4000
3500
3000
2500
2000
1500
1000
500
0
24.00
24.50
25.00
25.50
26.00
26.50
27.00
HD
Spiked Sample
Blank Sample
GERSTEL


Summary of Twister Advantages
• Eliminates solvent extraction steps
• Eliminates most non-volatile and polar matrix interference
• Allows parallel sample preparation minimizing instrument run time
• Stir bars are reusable
• Analytes are stable for days on stir bar allowing field sampling
• Extremely low detection limits possible (low ppt)
• Excellent bar-to-bar reproducibility
• Analyte recovery is predictable
GERSTEL


Conclusions
• SBSE has been demonstrated as an effective extraction technique for a wide range of environmentally important analyses.
• Additional work is needed to generate the data necessary to win acceptance of this technique in the regulated environmental analysis area.
GERSTEL

METHAMPHETAMINE AND BEYOND

Di Rienzo, Robert P.; DataChem Laboratories, Inc.
Reynolds, John M.; DataChem Laboratories, Inc.
Wade, Richard W.; DataChem Laboratories, Inc.

Newsweek magazine (August 8, 2005) calls methamphetamine America's most dangerous drug. "It creates a potent, long-lasting high - until the user crashes and too often, literally burns…." Newsweek calls attention to the dramatic surge in methamphetamine use which is no longer geographically isolated to the West but is used all across the United States. Methamphetamine use has also spread across the socioeconomic ladder and is no longer used primarily by the poor.

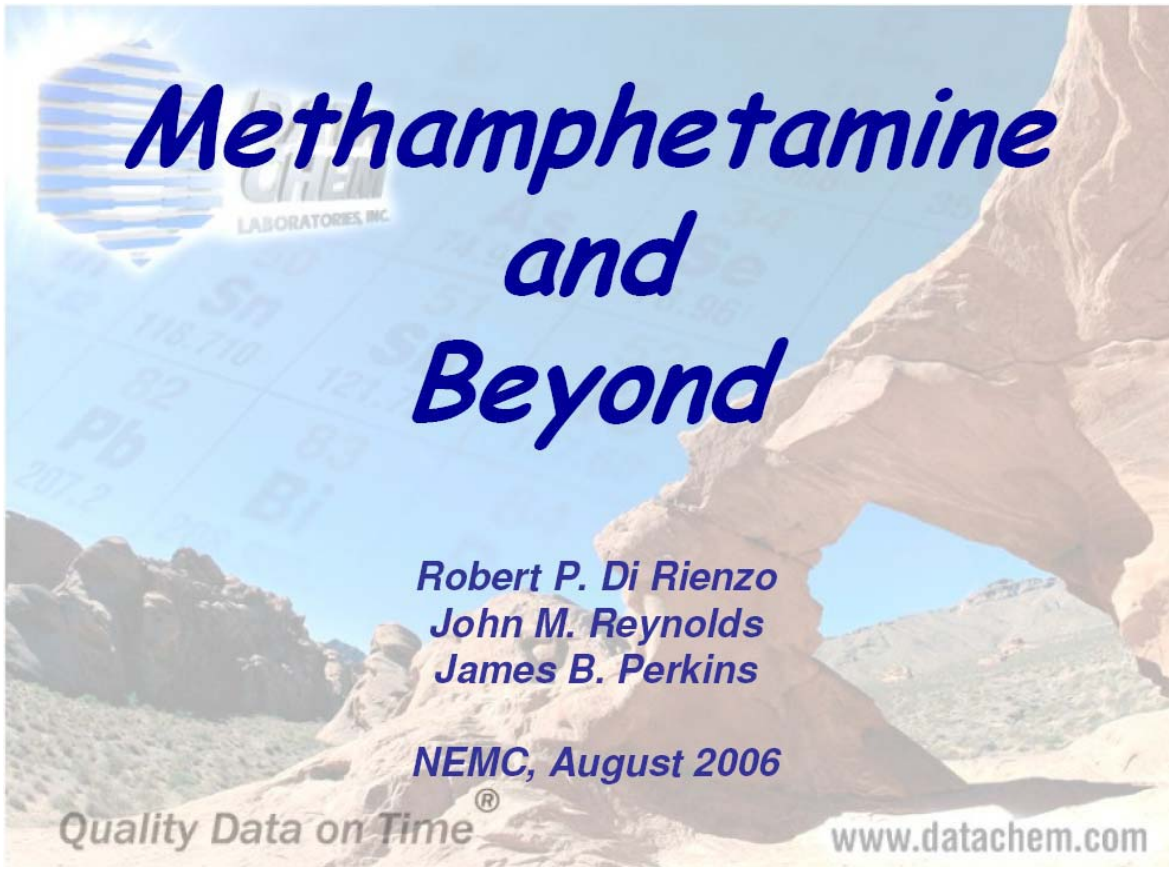
Health and hazardous safety concerns for illicit drug labs extend beyond methamphetamine.

Contamination and exposure may be from a number of other drugs, precursors, contaminants or adulterants. Identification and analysis of these compounds may be important depending on the information needed for the sampling site.

It may be desirable to identify precursors used for the process of drug synthesis. As various drugs become harder to manufacture from certain precursors due to tighter restrictions, new synthetic procedures, new precursors, and new drugs appear in order to meet demand.

Adulterants are substances intentionally or unintentionally added to illicit drugs in the process of production or distribution. Adulterants may exist as "impurities" which are unintentional by-products from manufacture or from impure starting material. Such impurities may help identify the nature or source of the starting material or the process being used to create the illicit drug. The identification of starting material may be important in obtaining convictions and in shutting down such sources.

To protect human health and safety, to identify contamination and to monitor cleanup of clandestine drug labs, methods for analysis of methamphetamine and other illicit drugs have been developed for this rapidly growing concern.


Methamphetamine
and
Beyond
Robert P. Di Rienzo
John M. Reynolds
James B. Perkins
NEMC, August 2006
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Agenda
Problem
Compounds of Interest
Other Drug Lab Contaminants
New Methods
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Methamphetamine Problem

- Increasing Use
- Health and Safety
- Precursors
- Contamination and Exposure
- Clandestine Laboratory Production
  - 20,000 Meth Labs busted in 2004

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Dump site contaminates creek

Fish found dead in South Canal Creek near Highway 59

By MIKE DE LA CRUZ
Staff Writer

A Caltrans worker found what could be a methamphetamine lab dump site, said sheriff's Deputy Wayne Hutton.

The worker was sweeping the shoulder of Highway 59 north of Oakdale Road Wednesday shortly before noon when he noticed empty industrial-size cans and dead fish in South Canal Creek, where it intersects the highway, and immediately reported the incident.

Soon a Merced County Sheriff's Department deputy, the California Highway Patrol, and officials from the state Department of Forestry, county Health Department, and state Department of Fish and Game, responded.

Sheriff Tom Sawyer, on scene, said any hazardous materials are treated very seriously because of the unknown levels of toxicity. "So we always have a full-blown response until we analyze the contents," he said.

Sheriff's Deputy Wayne Hutton, investigating the incident, said 12 empty 5-gallon alcohol cans, 57 empty 1-gallon alcohol cans, and 10 gray 5-gallon cans without labels, were found. Alcohol is one of the ingredients in methamphetamine, also known as crank, the deputy said.

The cans were crushed and empty and had been transported to the creek in black trash bags, Hutton said. What was originally thought to be a major hazardous spill was downgraded when the cans were found to be empty and crushed.

It is now believed the cans could come from a minor dump site for chemical containers from an illegal methamphetamine laboratory, Hutton said. Hutton said numerous large dead fish were found floating in the slow-moving creek near the dumped cans.

"However, fish farther up the creek on either side were alive and swimming," Hutton said.

But the water will be tested to determine if it is safe for the cattle grazing on both sides of the highway.

The land on the west side of the highway is owned and the land on the opposite side is leased by the Bert Crane Ranch.

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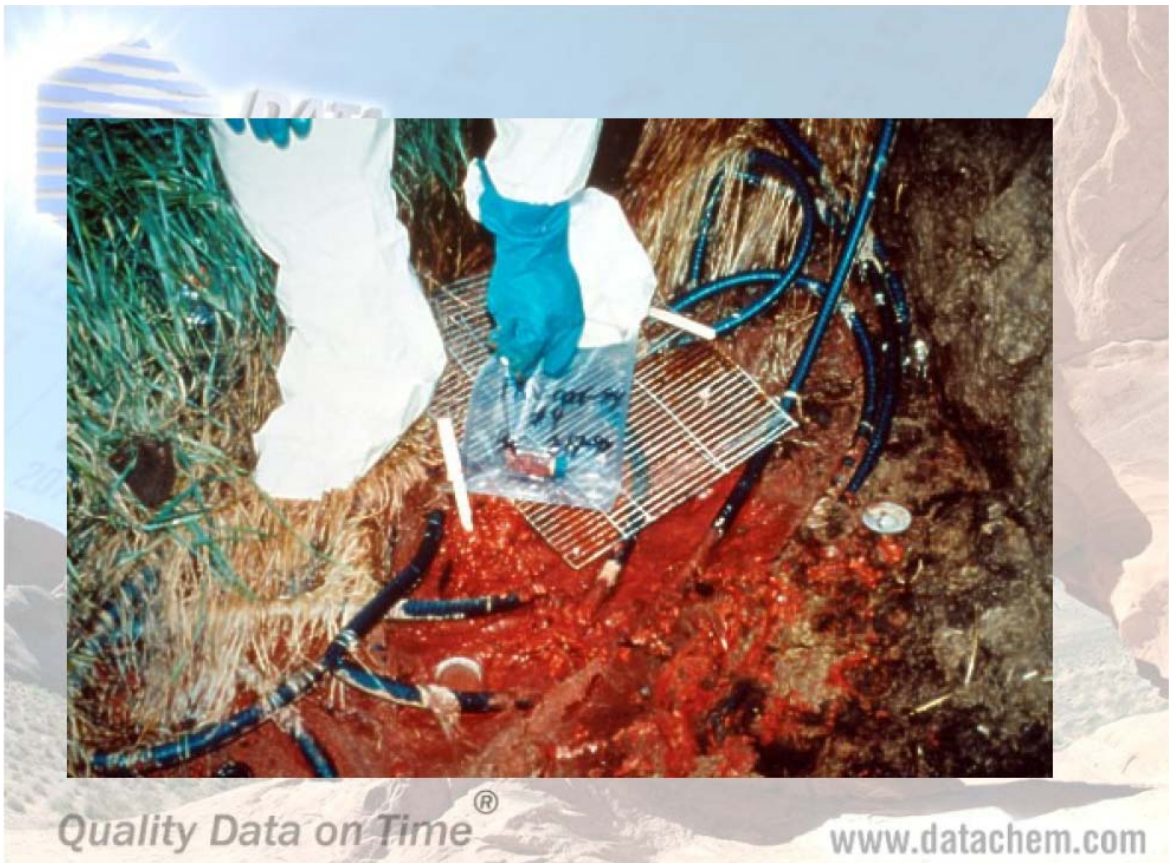
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INSTANT
STARTING FLUID
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HEET
HEET
HEET
Takes the
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DATA CHEM
Quality Data on Time®
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DATA
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BY MARK T. SULLIVAN

METH WARS

[IN DEER COUNTRY]

As its cost in dollars and lives mounts, the fight against methamphetamine now involves sportsmen to a degree no one predicted a handful of years ago. Across the rural countryside, meth labs and meth users have invaded the lands where we fish and hunt–with dangerous consequences

One December evening in 2004, Wildlife Officer Amy Snyder heard shots after legal shooting hours in a popular duck-hunting area in Madison County, Tenn. She put on hip boots and set out into the marsh. But when she arrived at the blind where she thought the shooting had occurred, she found it unoccupied.

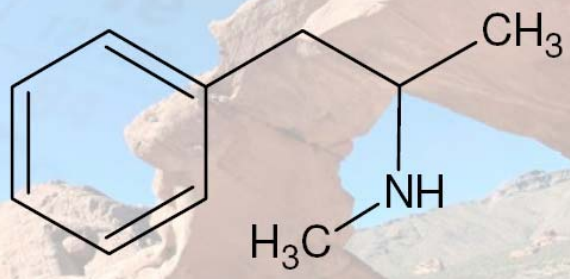
Then Officer Snyder noticed a chemical odor in the air. She shined her light around and in the grass saw a large glass mason jar filled with what looked like corn hominy. She kicked over the jar, saw rubber hoses coming out of the top and panicked.

"It was a meth lab, actively cooking," Snyder recalls. "What I'd done was extremely dangerous. The stuff could have exploded, not to mention what might have happened if I'd surprised the cookers at work."

Snyder had reason to be unnerved. The February before in Greene County, Ind., Conservation Officer Mike Gregg got a report of suspi-

Compound of Interest

Methamphetamine



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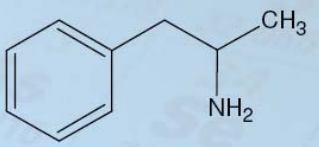
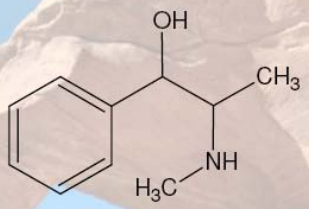
Other Possible Drugs of Interest

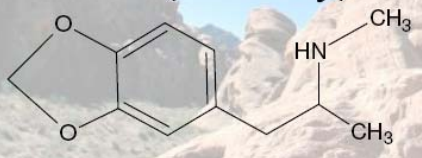
- Amphetamine

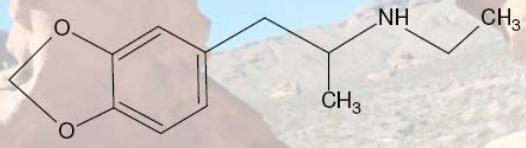


- Ephedrine and Pseudophedrine



- MDMA (Ecstasy)





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Manufacture

Hydrogenation of hydroxyl group

Red Phosphorus/Iodine Method (Most Common)

- Phosphorus + Iodine = Hydroiodic Acid

Birch Reduction

- Lithium and Ammonia

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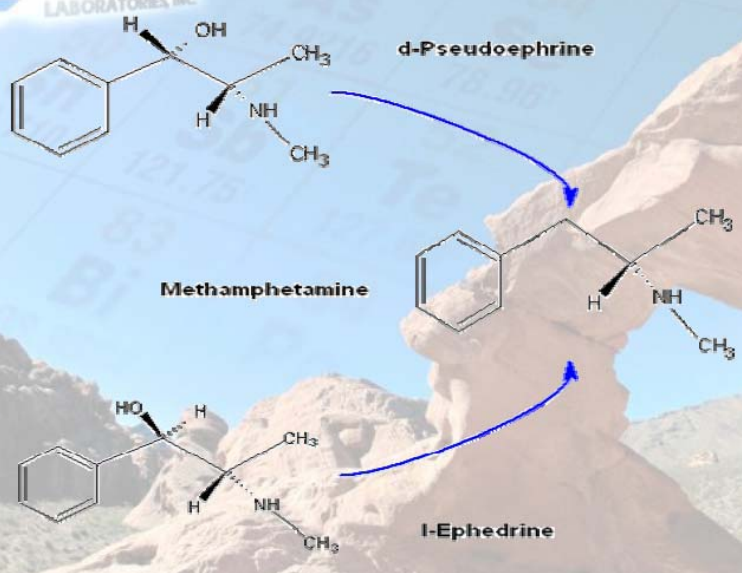
Hydrogenation of Hydroxyl Group



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Commercial Products in the Manufacture of Methamphetamine

Acetone	MSM (nutritional supplement)
Alcohol (isopropyl or rubbing)	Pseudoephedrine (cold medications)
Anhydrous ammonia (fertilizer)	Red phosphorus (matches or road flares)
Ephedrine (cold medications)	Salt (table or rock)
Ether (engine starter)	Sodium hydroxide (lye)
Hydrochloric acid (pool supply)	Sodium metal
Iodine (flakes or crystal)	Sulfuric acid (drain cleaner)
Kitty litter	Toluene (brake cleaner)
Lithium (batteries)	Trichloroethane (gun cleaner)
Methanol (gasoline additive)	

Metamphetamine Laboratory Hazards

Chemical	Hazards
Pseudoephedrine	Ingestion of doses greater than 240 mg causes hypertension, arrhythmia, anxiety, dizziness, and vomiting. Ingestion of doses greater than 600 mg can lead to renal failure and seizures.
Acetone/ ethyl alcohol	Extremely flammable, posing a fire risk in and around the laboratory. Inhalation or ingestion of these solvents causes severe gastric irritation, narcosis, or coma.
Freon	Inhalation can cause sudden cardiac arrest or severe lung damage. It is corrosive if ingested.
Anhydrous ammonia	A colorless gas with a pungent, suffocating odor. Inhalation causes edema of the respiratory tract and asphyxia. Contact with vapors damages eyes and mucous membranes.
Red phosphorus	May explode as a result of contact or friction. Ignites if heated above 260° C. Vapor from ignited phosphorus severely irritates the nose, throat, lungs, and eyes.

Source: DEA Office of Diversion Control.

Methamphetamine Laboratory Hazards

Chemical	Hazards
Hypophosphorous acid	Extremely dangerous substitute for red phosphorus. If overheated, deadly phosphine gas is released. Poses a serious fire and explosion hazard.
Lithium metal	Extremely caustic to all body tissues. Reacts violently with water and poses a fire or explosion hazard.
Hydriodic acid	A corrosive acid with vapors that are irritating to the respiratory system, eyes, and skin. If ingested, causes severe internal irritation and damage that may cause death.
Iodine crystals	Give off vapor that is irritating to respiratory system and eyes. Solid form irritates the eyes and may burn skin. If ingested, cause severe internal damage.
Phenylpropanolamine	Ingestion of doses greater than 75 mg causes hypertension, arrhythmia, anxiety, and dizziness. Quantities greater than 300 mg can lead to renal failure, seizures, stroke, and death.

Source: DEA Office of Diversion Control.

Other Drug Lab Contaminants

Contaminant	Use
Inorganics Acids	Hydroiodic Acid used in Red Phosphorous-Iodine method
Solvents	Used to extract Pseudoephedrine and Ephedrine
Phosphorus/Metals	Red Phosporus used to make Hydroic Acid/ Litium used in Birch Reduction
Iodine	Iodine used to make Hydro Iodic Acid
Phosphine	By product of Red Phosporus-Iodine Method
Ammonia	Birch Reduction

Other Drug Lab Contaminants

Contaminant	Analysis Methods
Inorganics Acids	USEPA 300.0 (Modified for HI)
Solvents	TO-15 or 8021/8260B
Phosphorus/Metals	6010B or 6020A
Iodine	NMAM 6005
Phosphine	OSHA 1003
Ammonia	USEPA 350.1

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Analysis Methods

NMAM Method	Analysis Type
NMAM 9106 Draft	GC/MS with Liquid-Liquid Extraction
NMAM 9109 Draft	GC/MS with Solid-Phase Extraction
NMAM 9111 Draft	LC/MS – Direct Injection

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Analysis Methods

- Accurate quantitation
- Extensive List of qualitative compounds
- Easy Sampling Procedures
- Extensive Validation
- Analytical Challenges associated with closely related compounds

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Qualitative Identification

Nicotine	Norephedrine
Fenfluramine	Methcathinone
Phenylethylamine	Norspseudoephedrine
Phentermine	Aminorex
Cathinone	Acetoaminophen
Bupropion	Methyl phenidate
N-Ethyl amphetamine	Merperidine
Ecgonine-methyl ester	Atropine

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Qualitative Identification

Caffeine	Phencyclidine (PCP)
N,N-Dimethyltryptamine	MDEA
BDB	MBDB
Ketamine	Theophylline
Lidocaine	Mescaline
Trifluoromethylphenyl piperarazine	Chlorpheniramine
Benzyl piperazine	Methyl phenidate
	4-Bromo-2,5-DMPEA

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Qualitative Identification

4-Methylaminorex	Morphine
Dextromethorphan	Codiene
Methaqualone	Oxycodone
Cocaine	Hydromorphone
Atropine	Flunitrazepam
Diazepam	Fentanyl
Hydrocodone	Hydromorphone

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Method Selectivity

- Internal Standard – Methamphetamine-d14
- Retention Time
- Mass Spectra
- Derivatization (GC/MS Methods Only)

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Method Sensitivity

	NMAM 9106	NMAM 9109	NMAM 9111
Limit of Quantitation µg/sample	0.06	0.06	0.06

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Method Summaries

- NMAM 9106 Draft
  - Useful as a drug screen
  - Add Solvent/Internal Standard and mix
  - Liquid-Liquid Extraction
  - Derivatize with perfluorinated acid anhydride
  - Solvent exchange to acetone-toluene
  - Analysis by GC/MS
  - Internal Standard Calibration
  - Wipes or Bulks

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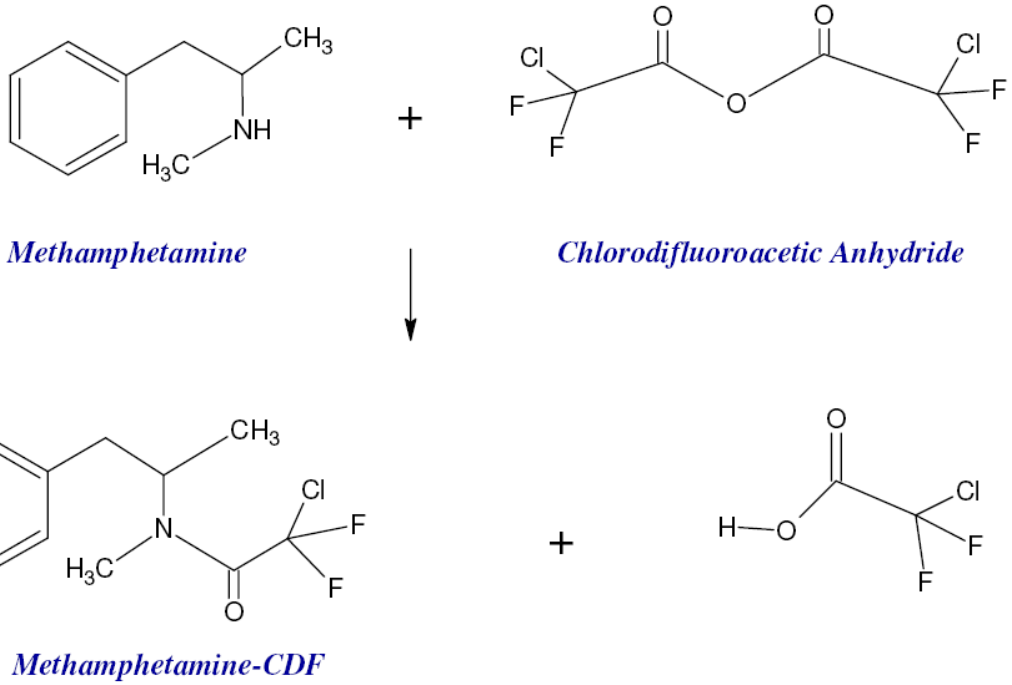
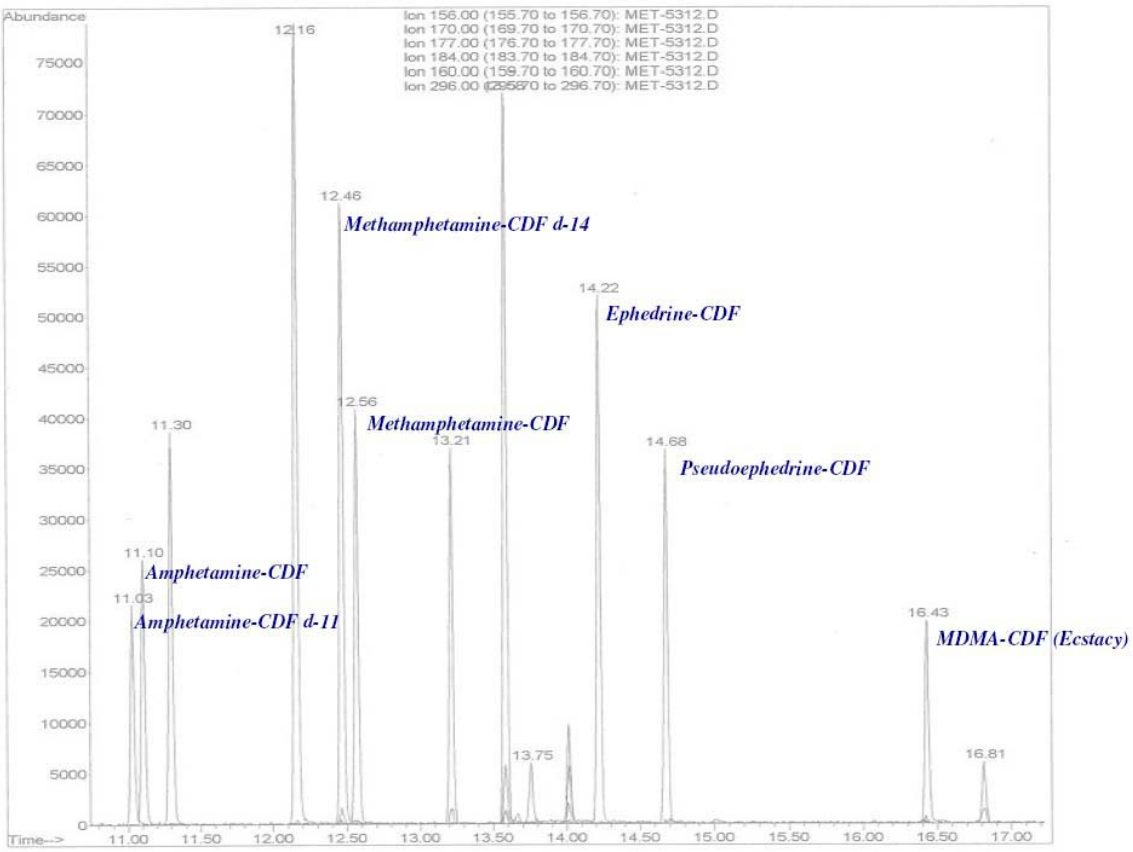
Derivative RXN 9106



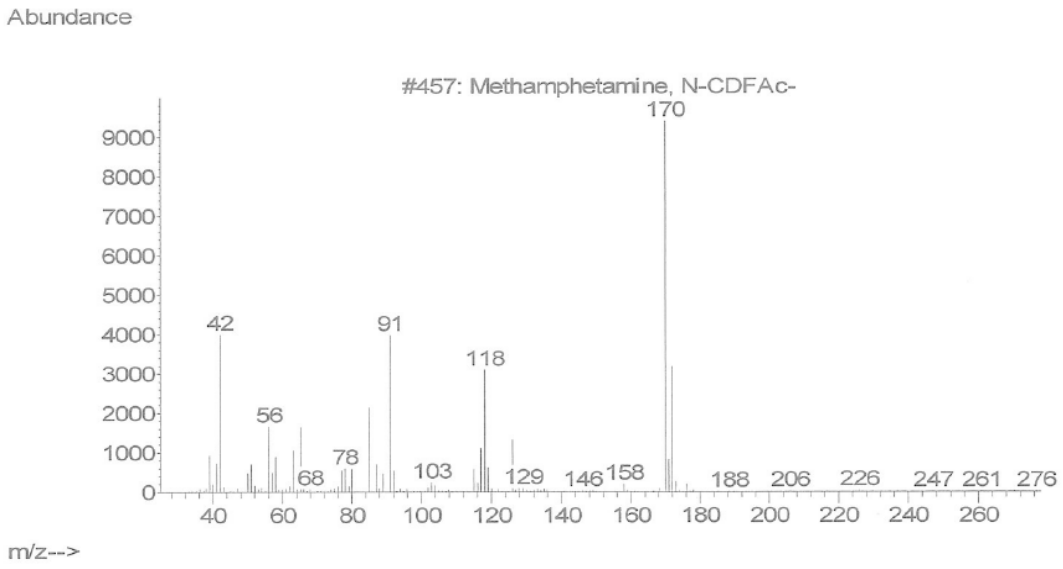
Methamphetamine

Chlorodifluoroacetic Anhydride

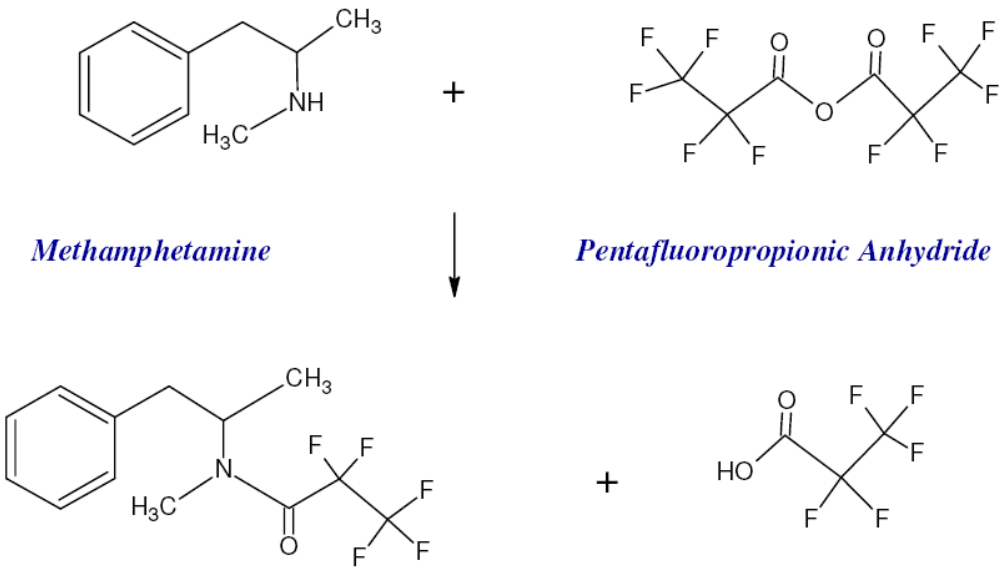
Methamphetamine-CDF

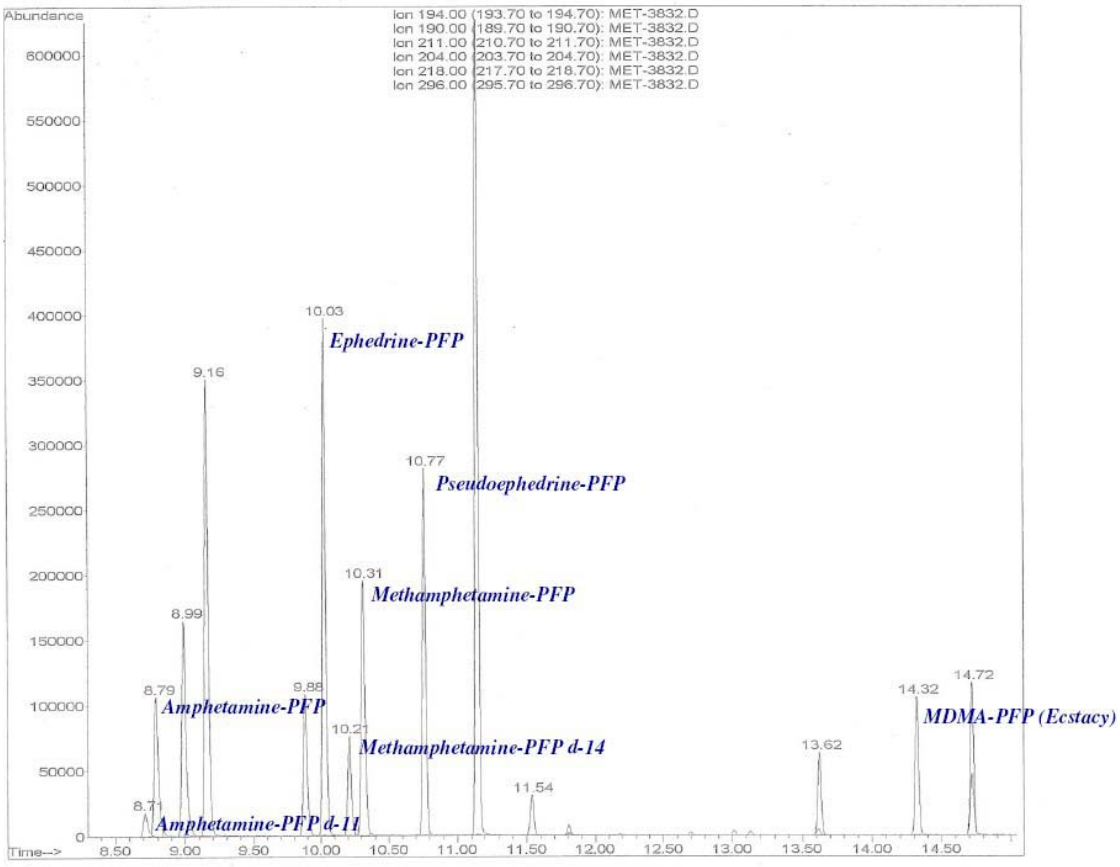


Methamphetamine-CDF Spectra

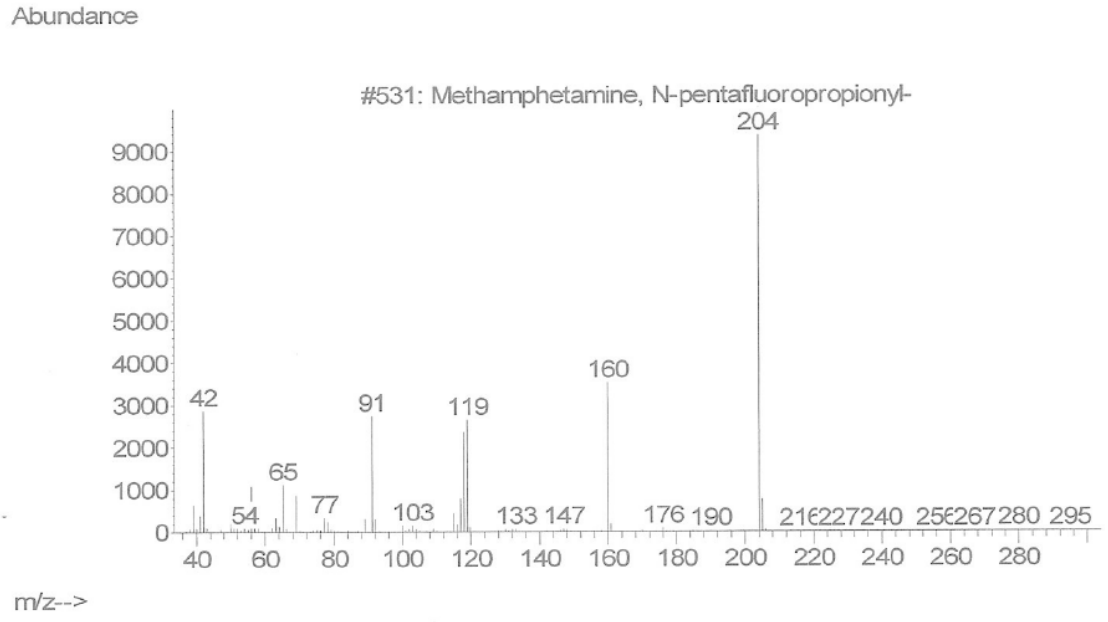


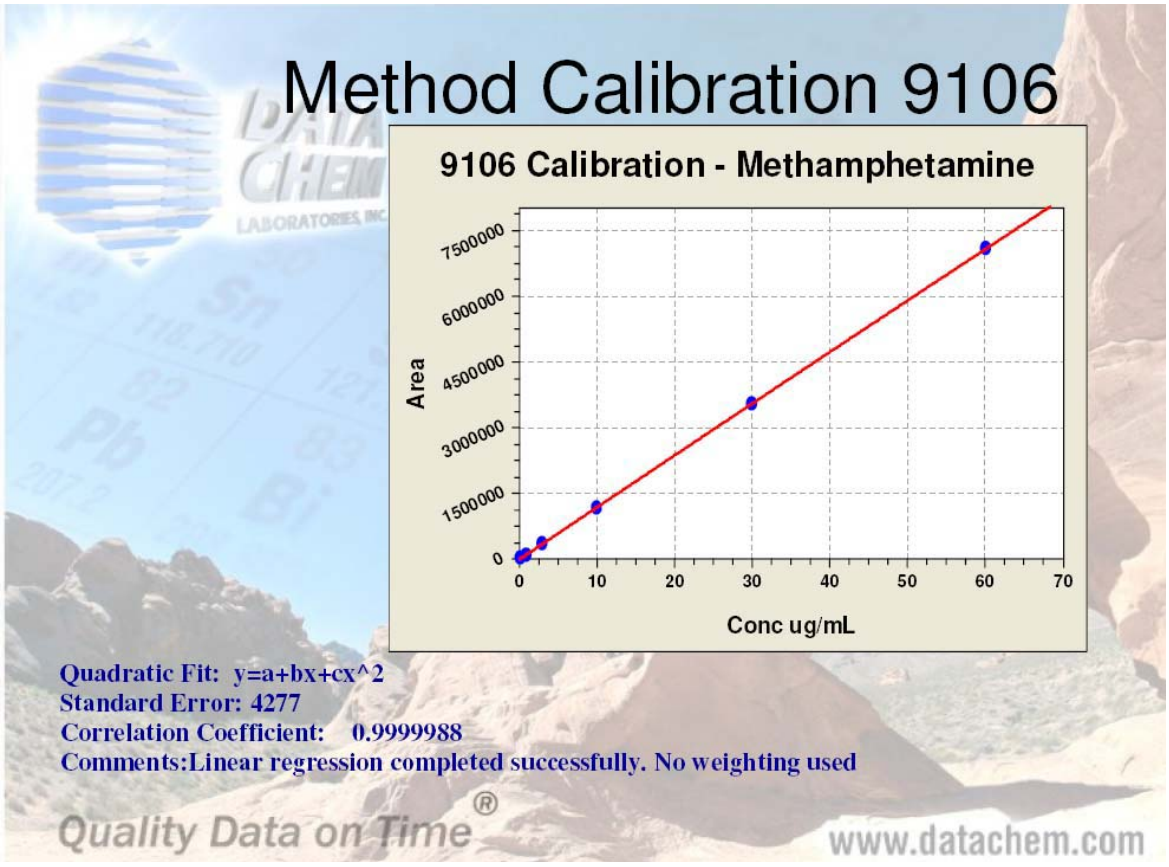
Derivative RXN 9106 Alt



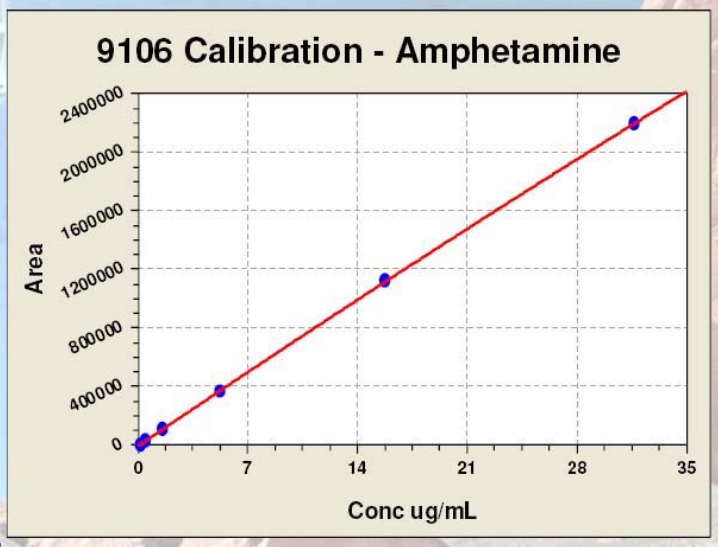


Methamphetamine-PFP Spectra





Method Calibration 9106



Quadratic Fit: y=a+bx+cx^2
Standard Error: 5591
Correlation Coefficient: 0.9999796
Comments:Linear regression completed successfully. No weighting used

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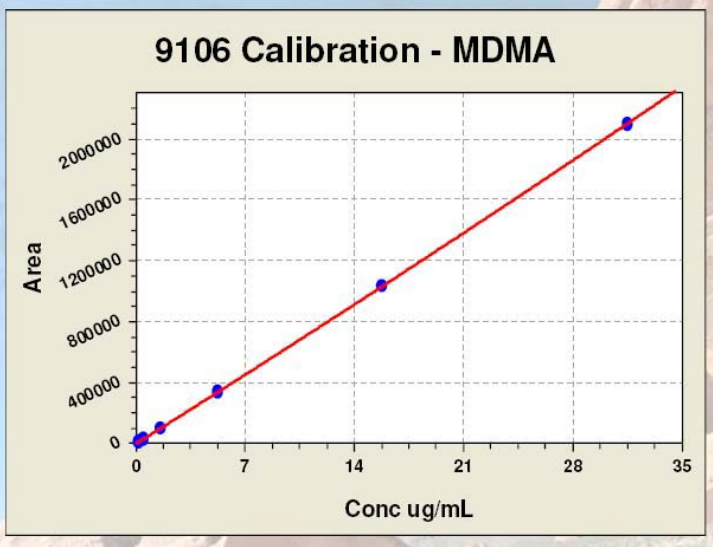
Method Calibration 9106



Quadratic Fit: y=a+bx+cx^2
Standard Error: 2014
Correlation Coefficient: 0.9999971
Comments:Linear regression completed successfully. No weighting used

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Method Summaries

- NMAM 9109 Draft
  - Useful for testing of known targets
  - Add Solvent/Internal Standard and mix
  - Solid Phase Extraction (Remove interference)
  - Elute with $MeCl_2$/IPA/NH_4OH
  - Derivatize with Acetonitrile, MBHFBA and MSTFA
  - Analysis by GC/MS
  - Internal Standard Calibration
  - Wipes or Bulks

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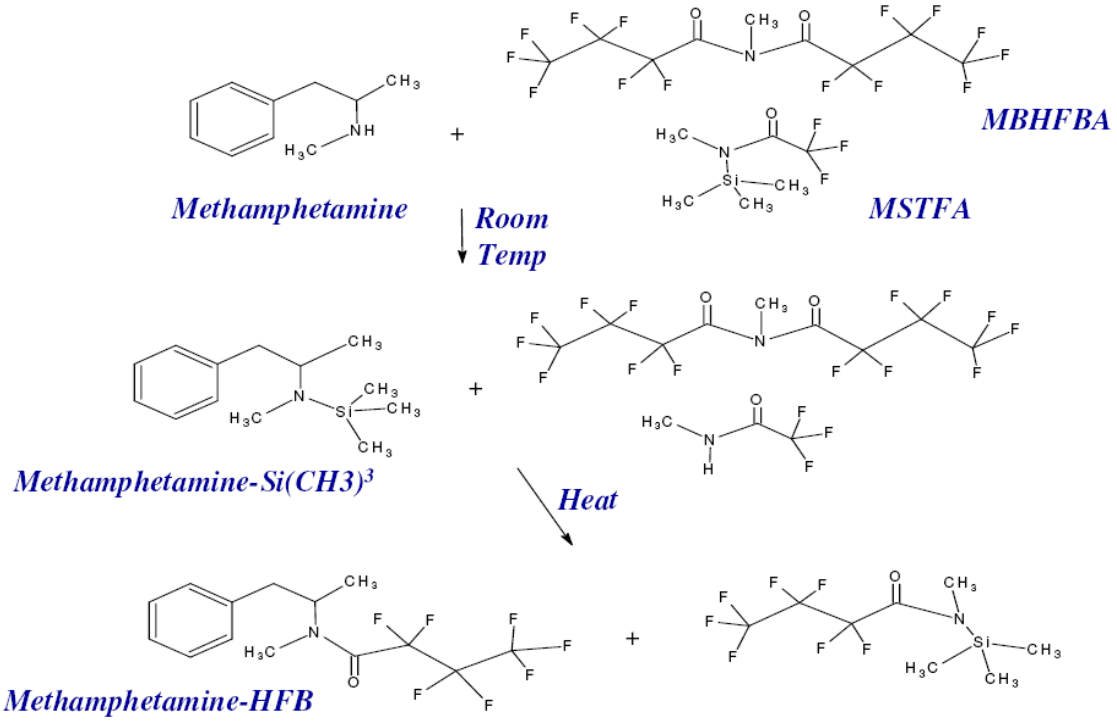
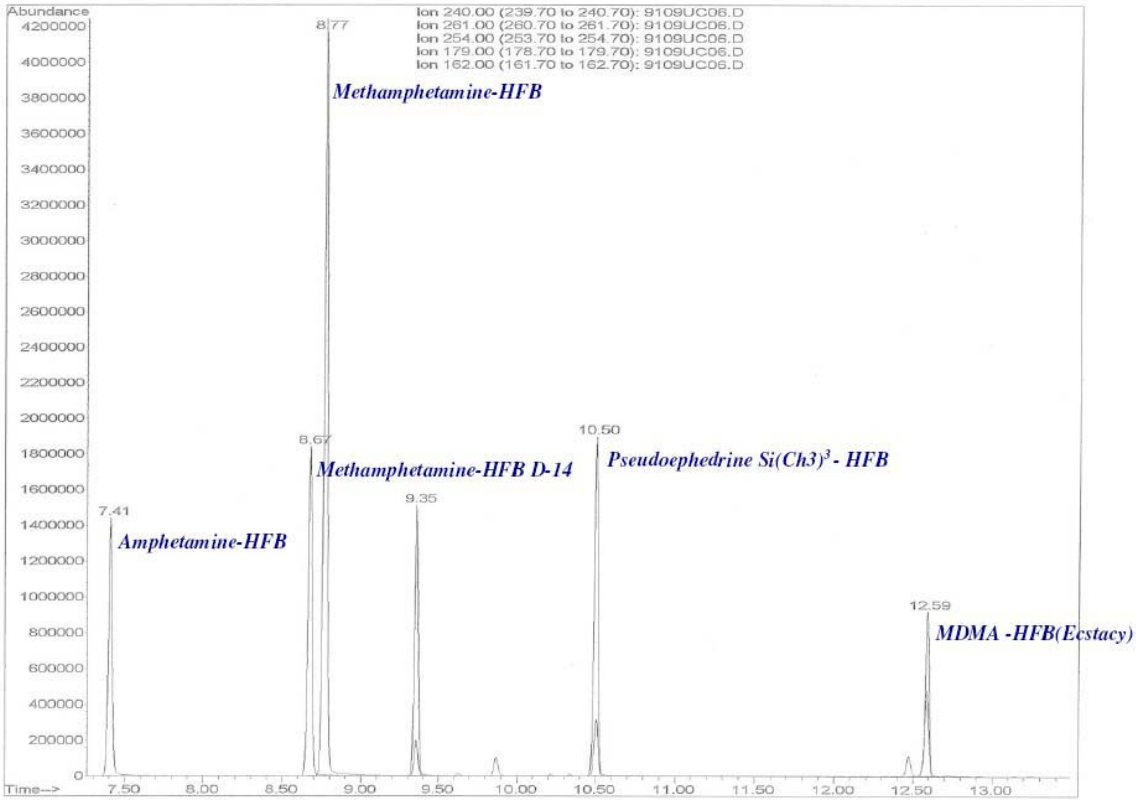
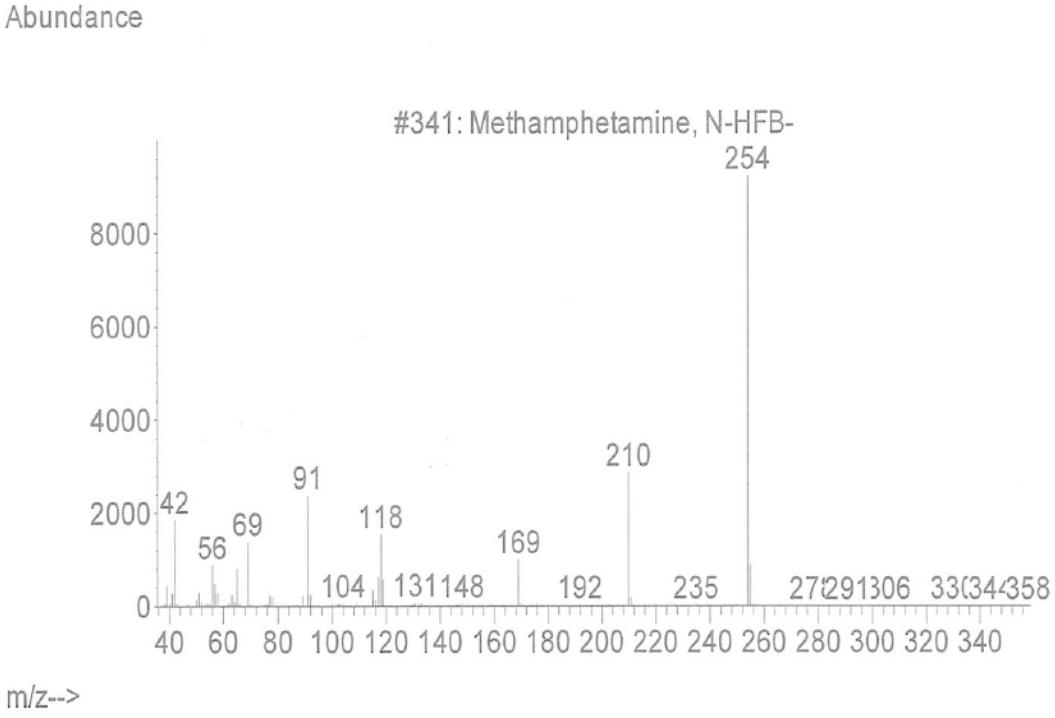
Derivative RXN 9109

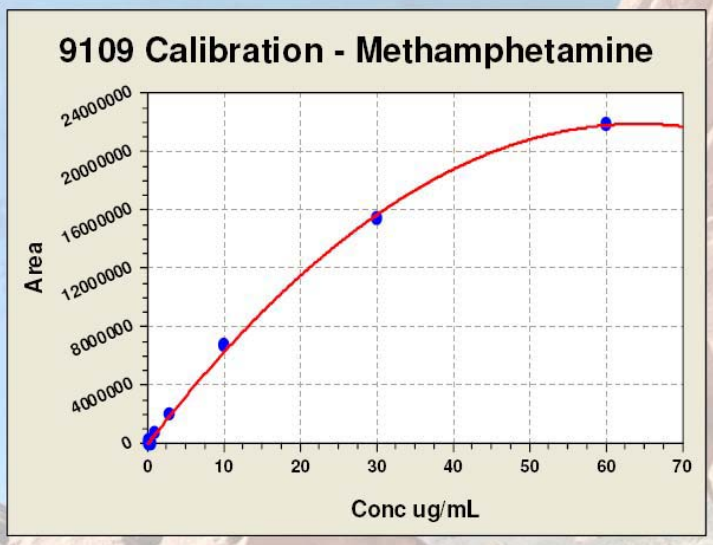




Methamphetamine-HFB Spectra



Method Calibration 9109



Quadratic Fit: y=a+bx+cx^2
Standard Error: 264452
Correlation Coefficient: 0.9995969
Comments:Linear regression completed successfully. No weighting used

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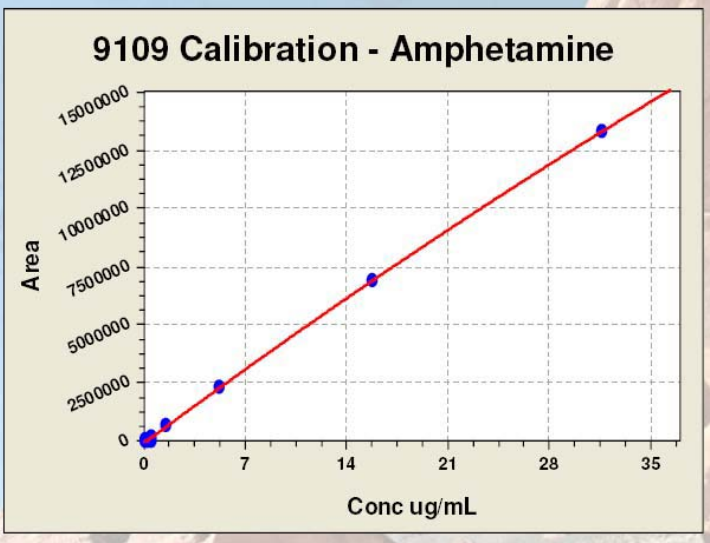
Method Calibration 9109



Quadratic Fit: y=a+bx+cx^2
Standard Error: 76704
Correlation Coefficient: 0.9998957
Comments:Linear regression completed successfully. No weighting used

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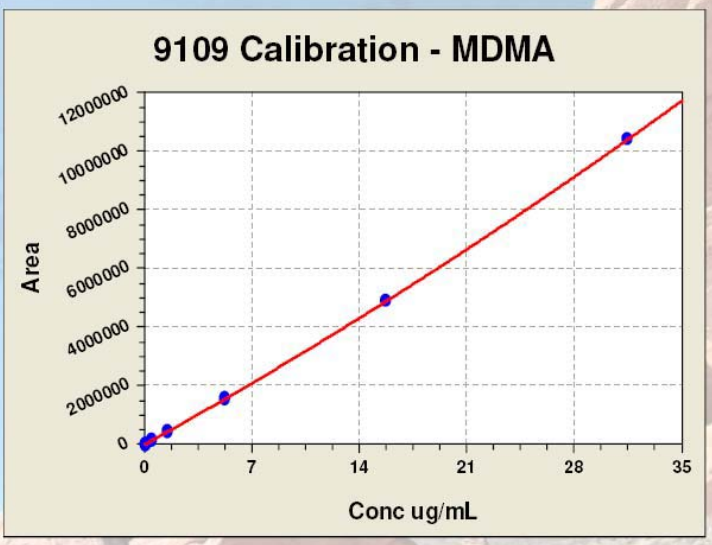
Method Calibration 9109



Quadratic Fit: y=a+bx+cx^2
Standard Error: 20550
Correlation Coefficient: 0.9999874
Comments:Linear regression completed successfully. No weighting used

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Method Summaries

- NMAM 9111 Draft
  - Useful as fast, accurate and cost effective test
  - Add Solvent/Internal Standard and mix
  - Analysis by LC/MS SIM
  - Internal Standard Calibration
  - Wipes or Bulks

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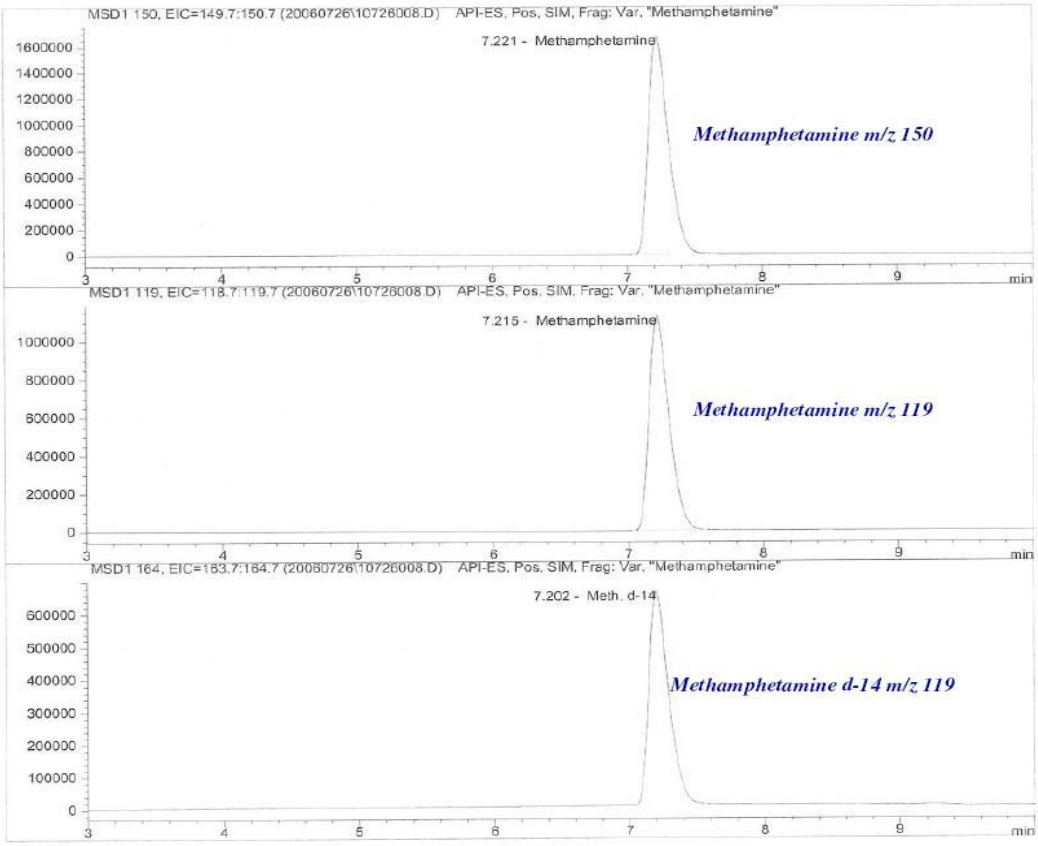
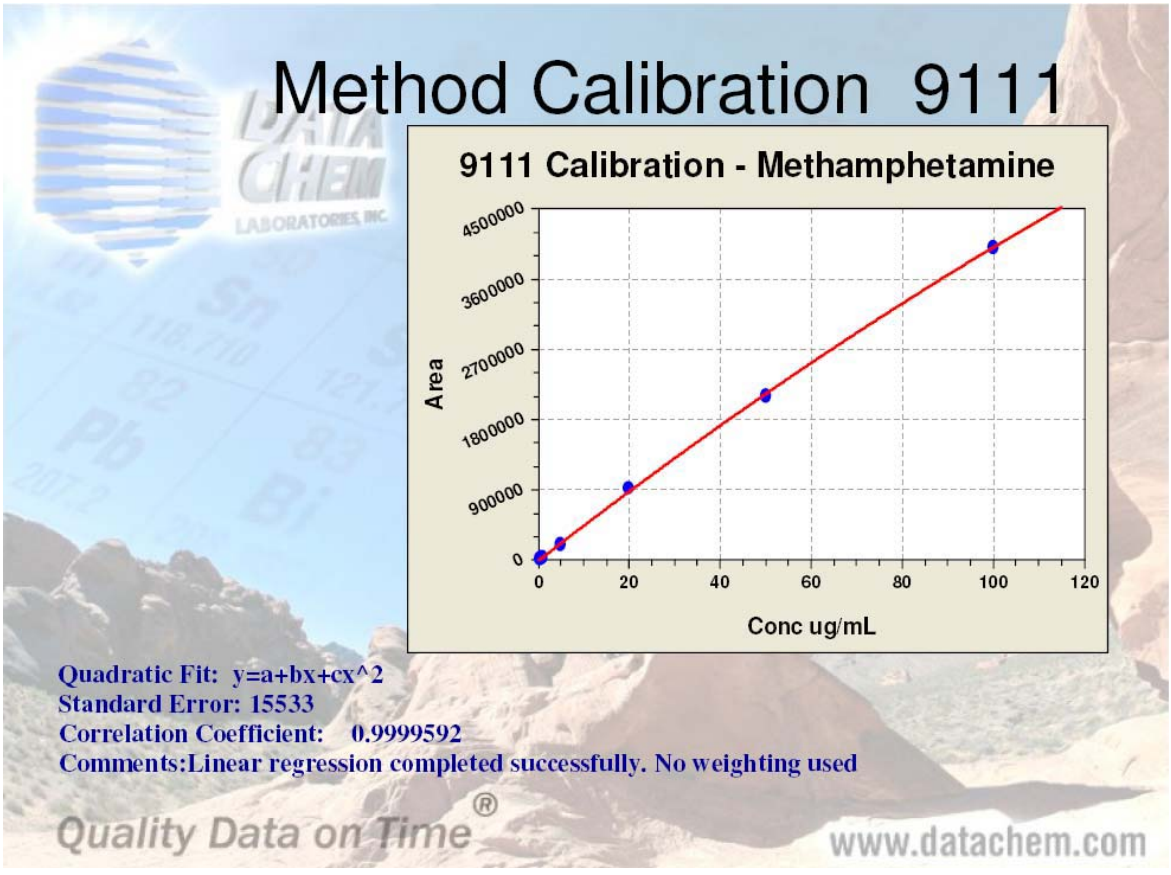

MSD1 150, EIC=149.7:150.7 (20060726\10726008.D) API-ES, Pos, SIM, Frag: Var, "Methamphetamine"
7.221 - Methamphetamine
Methamphetamine m/z 150
MSD1 119, EIC=118.7:119.7 (20060726\10726008.D) API-ES, Pos, SIM, Frag: Var, "Methamphetamine"
7.215 - Methamphetamine
Methamphetamine m/z 119
MSD1 164, EIC=163.7:164.7 (20060726\10726008.D) API-ES, Pos, SIM, Frag: Var, "Methamphetamine"
7.202 - Meth, d-14
Methamphetamine d-14 m/z 119
min


Method Calibration 9111
9111 Calibration - Methamphetamine
Area
Conc ug/mL
Quadratic Fit: y=a+bx+cx^2
Standard Error: 15533
Correlation Coefficient: 0.9999592
Comments:Linear regression completed successfully. No weighting used
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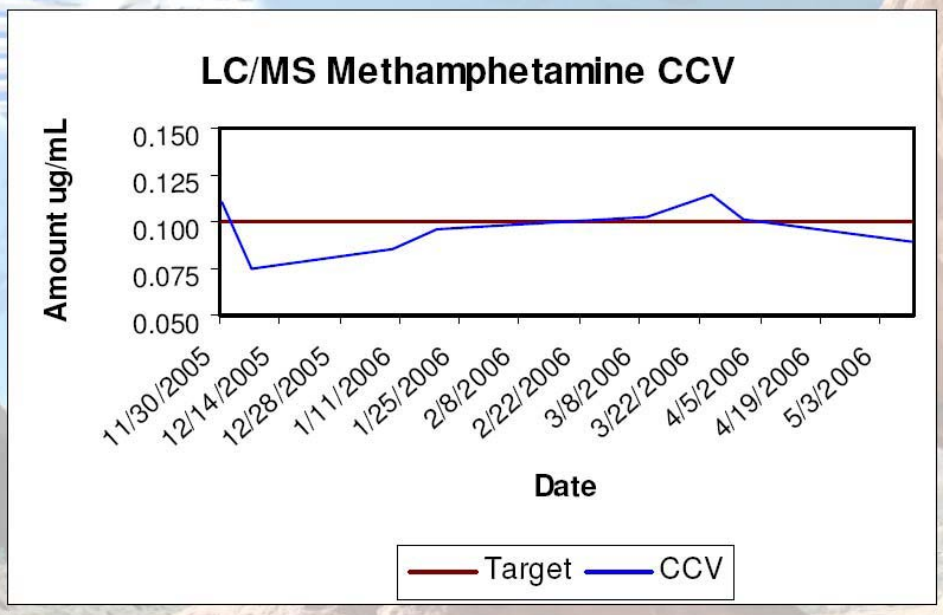
Method Robustness 9111



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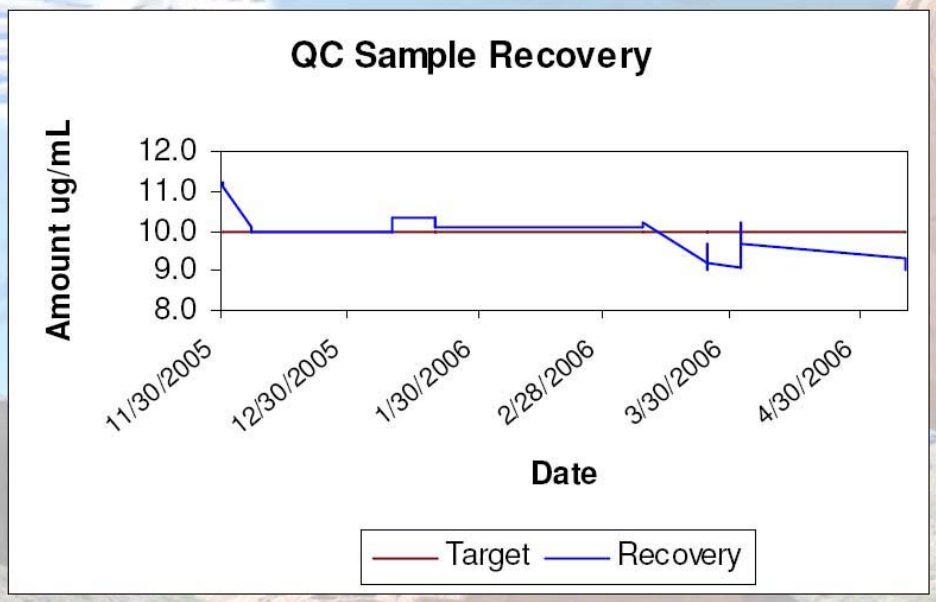
Method Robustness 9111



Control Limits: 81.7% to 115.0%

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Method Comparison

	NMAM 9106	NMAM 9109	NMAM 9111
Cotton Gauze and Methanol	√	√	√
Desorption	√	√	√
Derivatization/Extraction	√	√	NA
Internal Standard	√	√	√
GC/MS	√	√	
LC/MS			√
Additional Analytes	√	√	√
Analysis Time			√
Cost			√

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Two Novel Reversed Phase HPLC Columns for the Baseline Resolution of Explosives Compound of Environmental Interest

Douglas Later, Xiaodong Liu, Andrea Heckenberg, Ilze Birznieks, and C. Pohl

The 22nd Annual National Environmental Monitoring Conference
Arlington, Virginia
August 28—31, 2006

DIONEX

Overview

- Background
  - Explosives and the Environment
  - Explosives Analysis by HPLC (U.S. EPA Method 8330)
  - Current State of the Art
- Acclaim® Explosives E1 Column – A Primary Column
- Acclaim Explosives E2 Column – A Confirmatory Column
- Summary
- Acknowledgements

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Explosives and the Environment

- Explosives – **toxic, mutagenic**
- Polluted areas – soil and groundwater
  - Military and civilian firing ranges
  - Munitions and explosives manufacturing plants
  - Commercial explosive-use sites, e.g. mines
- Major explosive contaminants in environment
  - HMX, RDX, Tetryl, and TNT
  - Manufacturing impurities of TNT (DNTs, NTs, TNB, DNB)
  - Degradation products of TNT (e.g., 2-A-4,6-DNT, 4-A-2,6-DNT, etc.)

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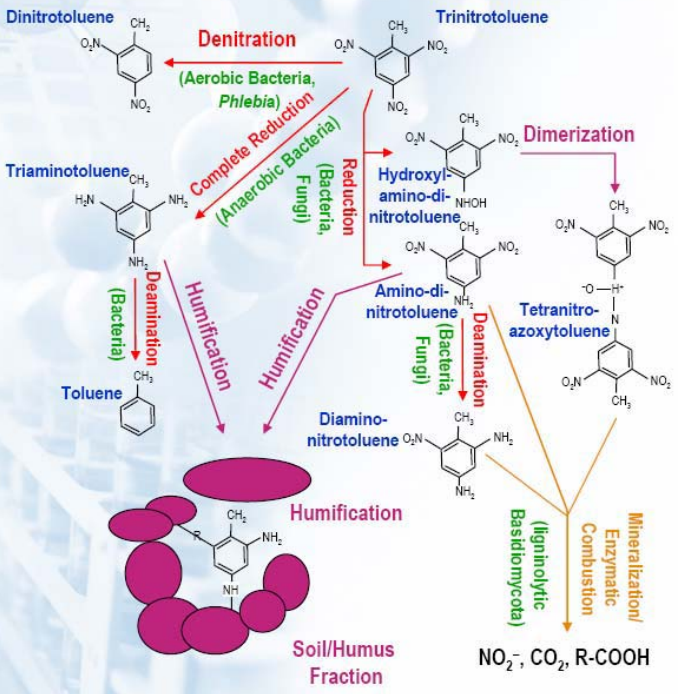
22766

Metabolization of TNT by Soil Microbes



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22767

U.S. EPA Method 8330

- "Method 8330 is intended for the trace analysis of explosives residues by HPLC using a UV detector. This method is used to determine the concentration of 14 target explosives compounds in a water, soil, sediment matrix."
- Primary Column: C18 reversed phase HPLC column, 25-cm x 4.6 mm, 5 µm…"
- Secondary Column: CN reversed phase HPLC column, 25-cm x 4.6 mm, 5 µm…"
- ***"…all positive measurements observed on the C18 column must be confirmed by injection onto the CN column…"***

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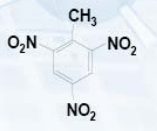
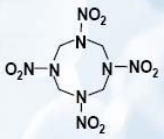
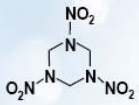
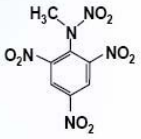
22769

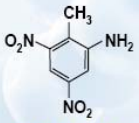
14 Explosives in U.S. EPA Method 8330

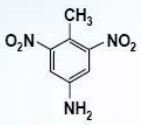

TNT

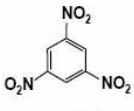

HMX


RDX

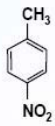

Tetryl


2-A-4,6-DNT


4-A-2,6-DNT


1,3,5-TNB

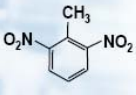

2-NT

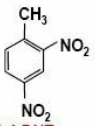

4-NT

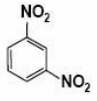

3-NT

Degradation Products of TNT

Manufacturing Impurities of TNT


2,6-DNT


2,4-DNT


1,3-DNB


NB

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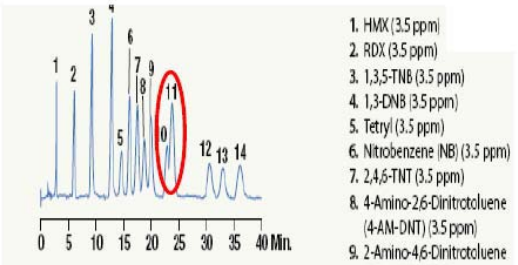
22770

Current Columns for EPA Method 8330

Primary Column - C18 phase

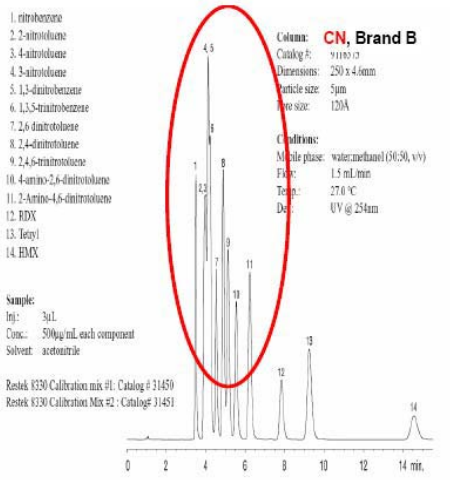


1. HMX (3.5 ppm)
2. RDX (3.5 ppm)
3. 1,3,5-TNB (3.5 ppm)
4. 1,3-DNB (3.5 ppm)
5. Tetryl (3.5 ppm)
6. Nitrobenzene (NB) (3.5 ppm)
7. 2,4,6-TNT (3.5 ppm)
8. 4-Amino-2,6-Dinitrotoluene (4-AM-DNT) (3.5 ppm)
9. 2-Amino-4,6-Dinitrotoluene (2-Am-DNT) (3.5 ppm)
10. 2,6-DNT (3.5 ppm)
11. 2,4-DNT (3.5 ppm)
12. 2-NT (3.5 ppm)
13. 4-NT (3.5 ppm)
14. 3-NT (3.5 ppm)

Column:	C18, Brand A, 4.6 x 150 mm (Part No. 288118)
Mobile Phase:	50/50 Methanol/Water
Flow Rate:	1.0mL/min
Detector:	UV at 254nm
Injection volume:	20µL

http://www.alltechweb.com/literature/brochure/b510p7.pdf

Confirmatory Column - CN phase

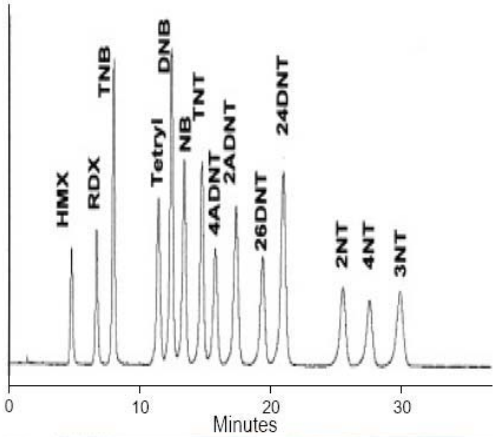


http://www.restek.com/restek/images/external/LC_0193.pdf

DIONEX
22771

Modified Methods for EPA Method 8330

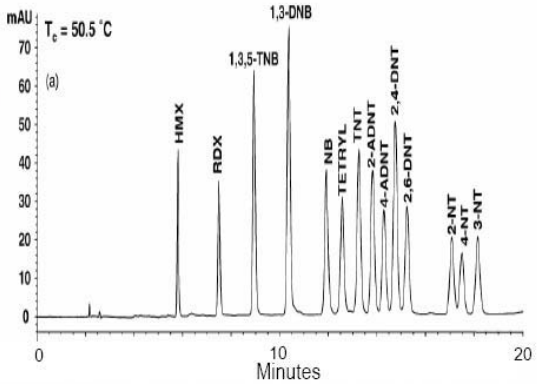
Two-Phase Approach



Columns:	Brand C CN (4.6x30 mm) and C18 (4.6x250 mm), 5 µm
Mobile Phase:	50/50 v/v MeOH/H_2O
Temperature:	20 to 25 °C
Flow Rate:	1.5 mL/min
Inj. Volume:	5 µL
Detection:	UV, 254 nm

M. J. Lang, S. E. Burns, *J. Chromatogr., A. 1999, 849, 381–388*

High Temperature Approach



Columns:	Brand D C8 (4.6x150 mm, 5 µm) with C8 guard (4.6x20 mm)
Mobile Phase:	MeOH/H_2O
Temperature:	50.5 °C
Flow Rate:	1.0 mL/min
Detection:	UV, 254 nm

T. Borch, R. Gerlach, *J. Chromatogr., A. 2004, 1022, 83–94*

DIONEX

Challenge

- To separate 14 explosives compounds in EPA method 8330
  - With superior resolution
  - On a single column
  - Using EPA method 8330
    - » Isocratic method
    - » Moderate temperature (25 to 35 °C)
    - » MeOH/H_2O mobile phase system
  - On a standard HPLC instrument

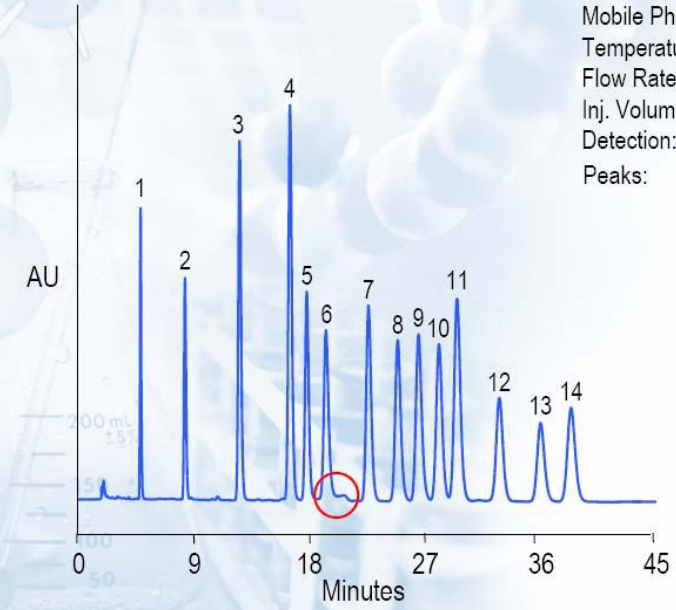
DIONEX
22775

Solution – Acclaim® Explosives E1 & E2 Columns

- **Product Information**
  - **Surface Chemistries:** Proprietary
  - **Silica Substrate:** Spherical, high-purity
  - **Particle size:** 5 µm
  - **Surface area:** 300 m^2/g
  - **Pore size:** 120 Å
  - **Column format:** 4.6 x 250 mm (analytical)
    4.3 x 10 mm (guard)
    2.1 x 250 mm (micro)

DIONEX

Acclaim® Explosives E1 Column



Column: Acclaim Explosives E1, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 43/57 v/v MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks:
1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. Tetryl
7. 2,4,6-Trinitrotoluene
8. 4-Amino-2,6-Dinitrotoluene
9. 2-Amino-4,6-Dinitrotoluene
10. 2,6-Dinitrotoluene
11. 2,4-Dinitrotoluene
12. 2-Nitrotoluene
13. 4-Nitrotoluene
14. 3-Nitrotoluene

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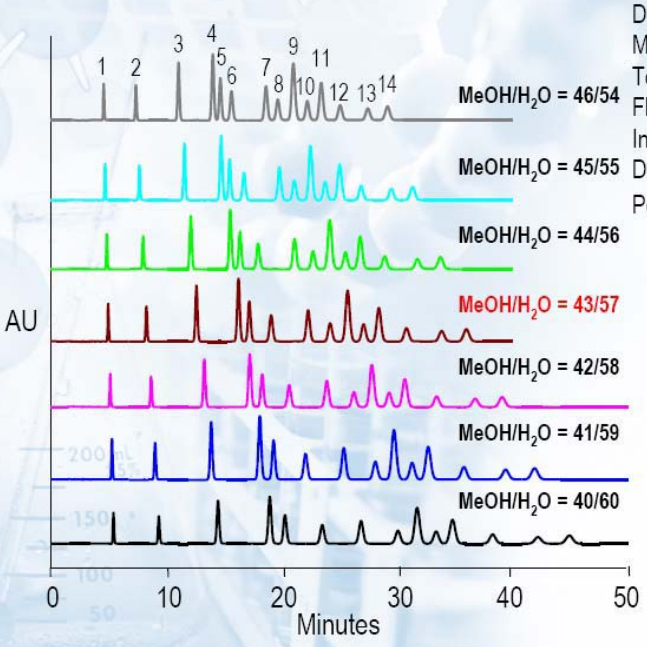
22784

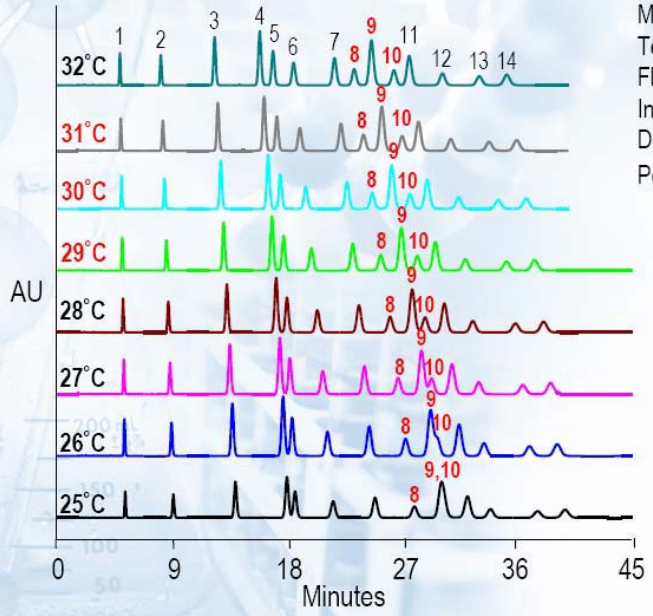
Mobile Phase Organic Content



Column: Acclaim Explosives E1, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks:
1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. Tetryl
7. 2,4,6-Trinitrotoluene
8. 4-Amino-2,6-Dinitrotoluene
9. 2-Amino-4,6-Dinitrotoluene
10. 2,6-Dinitrotoluene
11. 2,4-Dinitrotoluene
12. 2-Nitrotoluene
13. 4-Nitrotoluene
14. 3-Nitrotoluene

DIONEX

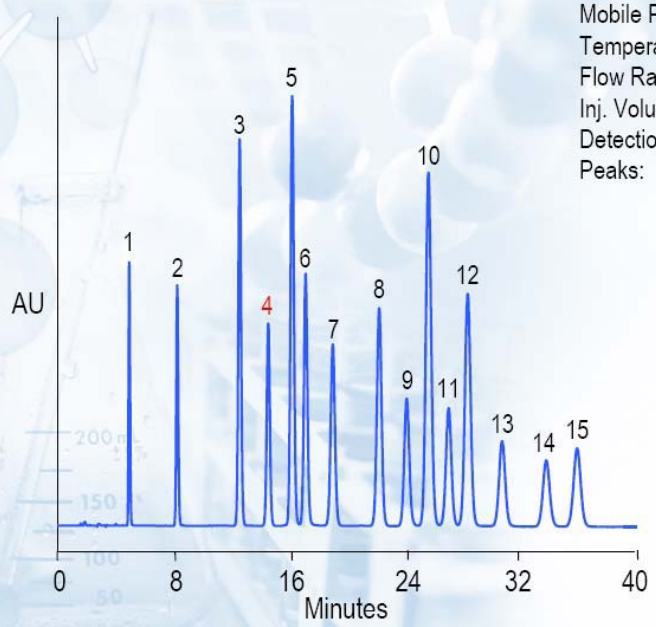
Temperature Effect



Column: Acclaim Explosives E1, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 43/57 v/v MeOH/H_2O
Temperature: 25, 26, 27, 28, 29, 30, 31, 32°C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks:
1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. Tetryl
7. 2,4,6-Trinitrotoluene
8. 4-Amino-2,6-Dinitrotoluene
9. 2-Amino-4,6-Dinitrotoluene
10. 2,6-Dinitrotoluene
11. 2,4-Dinitrotoluene
12. 2-Nitrotoluene
13. 4-Nitrotoluene
14. 3-Nitrotoluene

DIONEX

Acclaim® Explosives E1 Column



Column: Acclaim Explosives E1, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 43/57 v/v MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks:
1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,2-Dinitrobenzene (I.S.)
5. 1,3-Dinitrobenzene
6. Nitrobenzene
7. Tetryl
8. 2,4,6-Trinitrotoluene
9. 4-Amino-2,6-Dinitrotoluene
10. 2-Amino-4,6-Dinitrotoluene
11. 2,6-Dinitrotoluene
12. 2,4-Dinitrotoluene
13. 2-Nitrotoluene
14. 4-Nitrotoluene
15. 3-Nitrotoluene

DIONEX

Chromatographic Performance of Acclaim Explosives E1

Explosives	K'	Resolution	R^2 (peak area)	R^2 (peak height)	LOD (µg/L)
HMX	1.02	12.18	0.9994	0.9999	0.6
RDX	2.37	14.61	1	1	0.2
1,3,5-TNB	4.13	5.43	1	1	0.9
1,3-DNB	5.61	2.15	1	1	0.8
NB	5.99	3.96	0.9999	1	1.3
Tetryl	6.79	3.44	0.9999	1	2.0
2,4,6-TNT	8.08	3.13	1	1	1.5
4-A-2,6-DNT	8.87	2.23	1	1	2.6
2-A-4,6-DNT	9.48	2.02	0.9998	1	1.7
2,6-DNT	10.05	1.82	0.9983	0.9998	2.7
2,4-DNT	10.59	3.15	0.9997	1	1.4
2-NT	11.57	3.67	0.9999	1	3.6
4-NT	12.81	2.38	0.9992	0.9999	4.6
3-NT	13.6	-	0.9994	0.9999	3.8

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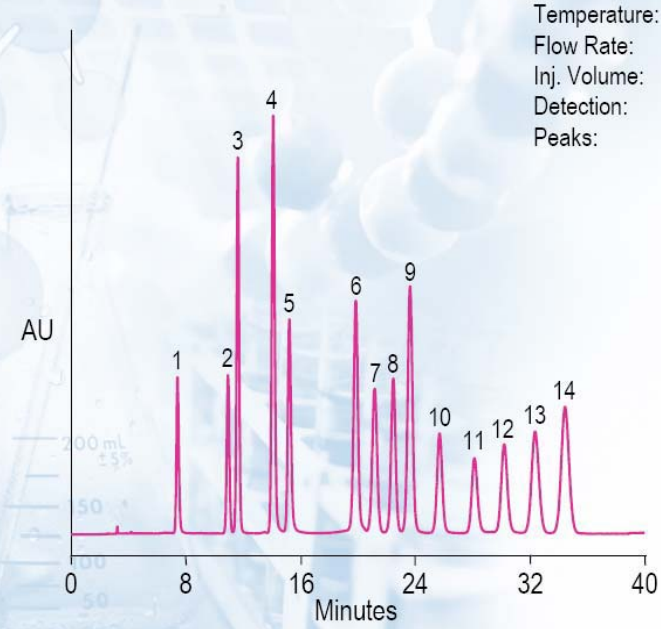
Acclaim® Explosives E2 Column

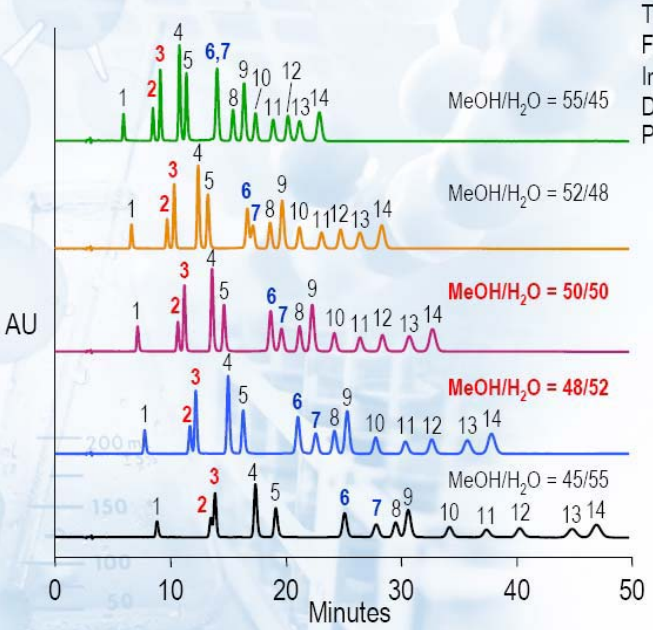
Columns: Acclaim Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 50/50 v/v MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks: (EPA 8330 mix, 50 ppm each)

1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. 2,4,6-Trinitrotoluene
7. Tetryl
8. 2,6-Dinitrotoluene
9. 2,4-Dinitrotoluene
10. 2-Nitrotoluene
11. 4-Nitrotoluene
12. 3-Nitrotoluene
13. 4-Amino-2,6-Dinitrotoluene
14. 2-Amino-4,6-Dinitrotoluene



DIONEX
22779

Mobile Phase Organic Content

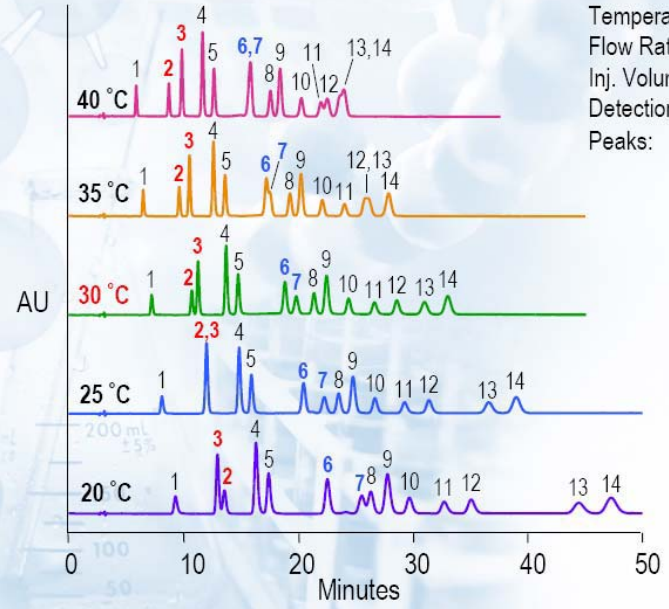


Column: Acclaim® Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks: (EPA 8330 mix, 50 ppm each)

1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. 2,4,6-Trinitrotoluene
7. Tetryl
8. 2,6-Dinitrotoluene
9. 2,4-Dinitrotoluene
10. 2-Nitrotoluene
11. 4-Nitrotoluene
12. 3-Nitrotoluene
13. 4-Amino-2,6-Dinitrotoluene
14. 2-Amino-4,6-Dinitrotoluene

DIONEX
22780

Temperature Effect

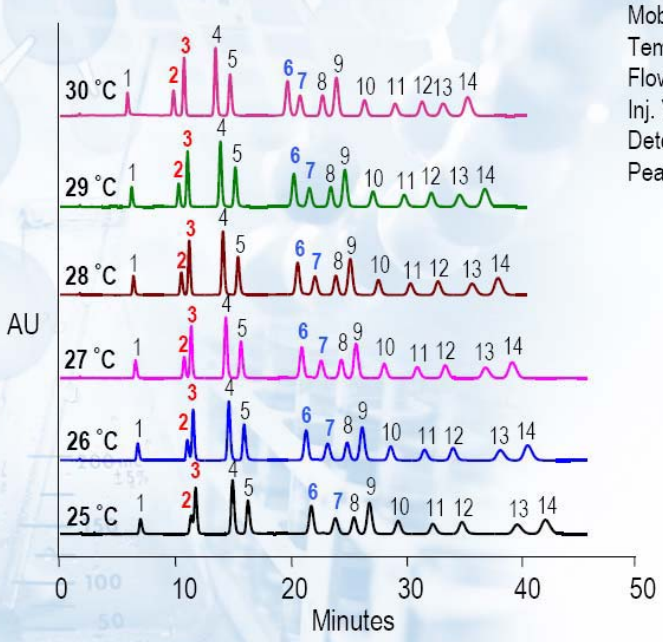


Column: Acclaim® Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 48/52 v/v MeOH/H_2O
Temperature: 20, 25, 30, 35, and 40 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks: (EPA 8330 mix, 50 ppm each)

1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. 2,4,6-Trinitrotoluene
7. Tetryl
8. 2,6-Dinitrotoluene
9. 2,4-Dinitrotoluene
10. 2-Nitrotoluene
11. 4-Nitrotoluene
12. 3-Nitrotoluene
13. 4-Amino-2,6-Dinitrotoluene
14. 2-Amino-4,6-Dinitrotoluene

DIONEX
22781

Temperature

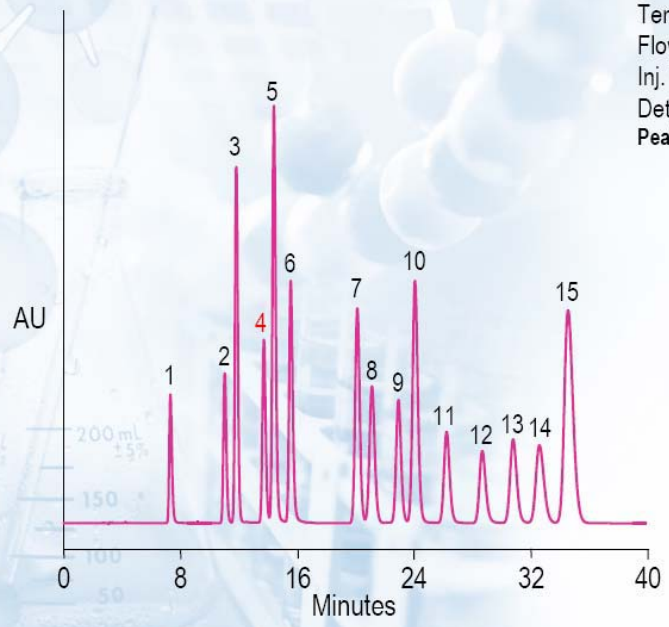


Column: Acclaim® Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 48/52 v/v MeOH/H_2O
Temperature: 25, 26, 27, 28, 29 and 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 1 µL
Detection: UV, 254 nm
Peaks: (EPA 8330 mix, 500 ppm each)

1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. 2,4,6-Trinitrotoluene
7. Tetryl
8. 2,6-Dinitrotoluene
9. 2,4-Dinitrotoluene
10. 2-Nitrotoluene
11. 4-Nitrotoluene
12. 3-Nitrotoluene
13. 4-Amino-2,6-Dinitrotoluene
14. 2-Amino-4,6-Dinitrotoluene

DIONEX

Acclaim® Explosives E2 Column



Columns: Acclaim Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile Phase: 48/52 v/v MeOH/H_2O
Temperature: 29 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm
Peaks: **(EPA 8330 mix, 100 ppm each)**

1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,2-Dinitrobenzene (I.S.)
5. 1,3-Dinitrobenzene
6. Nitrobenzene
7. 2,4,6-Trinitrotoluene
8. Tetryl
9. 2,6-Dinitrotoluene
10. 2,4-Dinitrotoluene
11. 2-Nitrotoluene
12. 4-Nitrotoluene
13. 3-Nitrotoluene
14. 4-Amino-2,6-Dinitrotoluene
15. 2-Amino-4,6-Dinitrotoluene

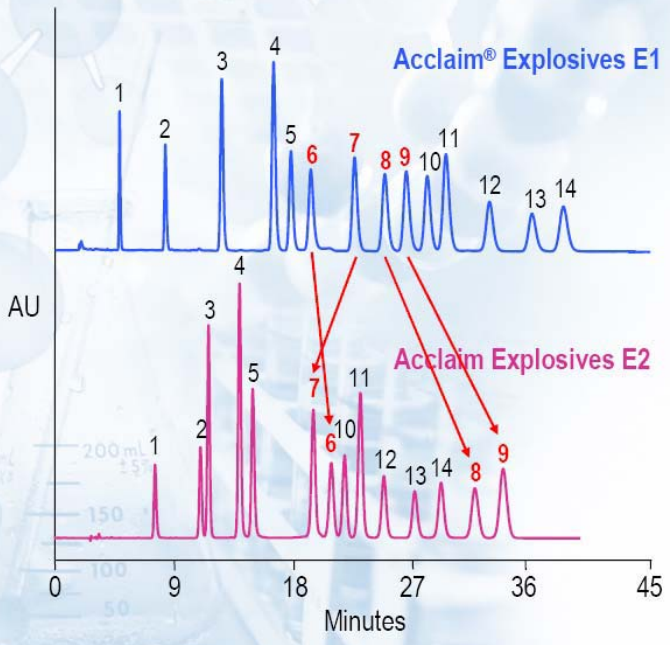
DIONEX

Chromatographic Performance of Acclaim Explosives E2

Explosives	K'	Resolution	R^2 (peak area)	R^2 (peak height)	LOD (µg/L)
HMX	2.03	11.35	1	1	2.5
RDX	3.57	2.08	1	1	2.1
1,3,5-TNB	3.86	7.34	1	1	0.9
1,3-DNB	4.95	4.95	1	1	0.8
NB	5.43	9.57	1	1	1.2
2,4,6-TNT	7.36	2.05	1	1	1.5
Tetryl	7.87	2.73	1	1	2.6
2,6-DNT	8.57	1.81	1	1	2.4
2,4-DNT	9.04	3.38	1	1	1.3
2-NT	9.96	3.46	0.9999	1	3.1
4-NT	10.99	2.74	0.9996	0.9999	4.1
3-NT	11.88	2.49	0.9997	0.9999	3.5
4-A-2,6-DNT	12.81	1.94	0.9993	0.9997	3.9
2-A-4,6-DNT	13.64	-	0.9999	1	2.6

DIONEX

A Total Solution by Dionex



Column: 5 µm, 4.6 x 250 mm
Mobile Phase: MeOH/H_2O
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 5 µL
Detection: UV, 254 nm

Peaks:
1. HMX
2. RDX
3. 1,3,5-Trinitrobenzene
4. 1,3-Dinitrobenzene
5. Nitrobenzene
6. Tetryl
7. 2,4,6-Trinitrotoluene
8. 4-Amino-2,6-Dinitrotoluene
9. 2-Amino-4,6-Dinitrotoluene
10. 2,6-Dinitrotoluene
11. 2,4-Dinitrotoluene
12. 2-Nitrotoluene
13. 4-Nitrotoluene
14. 3-Nitrotoluene

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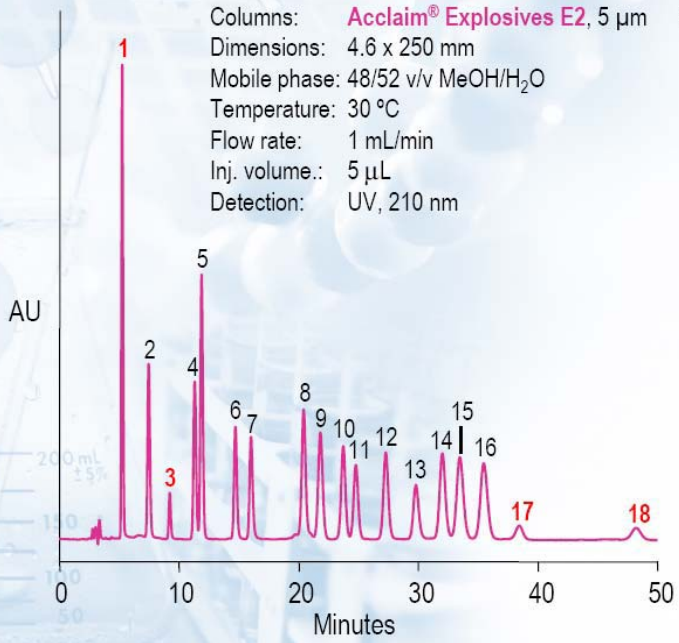
22787

Separation of 18 Explosives

Columns: Acclaim® Explosives E2, 5 µm
Dimensions: 4.6 x 250 mm
Mobile phase: 48/52 v/v MeOH/H_2O
Temperature: 30 °C
Flow rate: 1 mL/min
Inj. volume.: 5 µL
Detection: UV, 210 nm



Peaks: (25 ppm each)
1. 2,4-Di-Amino-6-Nitrotoluene
2. HMX
3. EGDN
4. RDX
5. 1,3,5-Trinitrobenzene
6. 1,3-Dinitrobenzene
7. Nitrobenzene
8. 2,4,6-Trinitrotoluene
9. Tetryl
10. 2,6-Dinitrotoluene
11. 2,4-Dinitrotoluene
12. 2-Nitrotoluene
13. 4-Nitrotoluene
14. 3-Nitrotoluene
15. 4-Amino-2,6-Dinitrotoluene
16. 2-Amino-4,6-Dinitrotoluene
17. DMDNB
18. PETN

DIONEX
22782

Function Comparison

- **Acclaim® Explosives E1**
  - **Superior separation power** for all 14 compounds in EPA 8330
  - **Selectivity similar** to the current primary columns (ODS)
  - An excellent direct replacement for ODS columns
- **Acclaim Explosives E2**
  - **Superior separation power** for all 14 compounds in EPA 8330
  - **Selectivity complementary** to the current primary columns
  - **Ideal selectivity** for separating nitro aromatics, nitramines, and nitrate esters in a single run
  - An unparalleled alternative column

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22789

Conclusion

- **Acclaim® Explosives HPLC columns provide:**
  - Superior capability for separating all 14 explosives in EPA 8330, as well as other explosives of great importance (i.e. PETN, EGDN, etc)
  - Complementary selectivities, providing a complete HPLC solution
  - More accurate results and higher throughput
- **Use for regulatory compliance monitoring?**
  - Barry Lesnik, RCRA National Organic Methods Program Manager, U.S. EPA-OSW/EMRAD has confirmed the following:

    "The Disclaimer language in SW-846 states that the instruments and accessories listed in the methods are those that were used to develop the methods. Other columns can be used provided that they can be demonstrated to perform appropriately for their intended applications."

DIONEX
22790

Acknowledgements

Mark Tracy

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Xiaodong Liu

Chris Pohl

DIONEX

WEDNESDAY A.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Chemical Speciation – Hg, Se, and Br Species

SPECIATION OF MERCURY IN HUMAN HAIR

Fahrenholz, Timothy; Duquesne University
Kingston, Skip H.M.; Duquesne University
Pamuku, Matt; Applied Isotope Technologies, Inc.
Rahman,Mizanur G.M.; Duquesne University

Mercury has been well known as an environmental pollutant for several decades. Generally, human uptake of mercury occurs in the following manners: by consuming methylmercury from fish as a major dietary contaminant; by breathing mercury vapors emitted from various sources as metallic mercury, dental amalgams, and ambient air; and through injection of thimerosal containing vaccines. Hair mercury levels have been found to be indicative of dietary, environmental and occupational exposures to the mercury species. In order to assess the extent of mercury exposure and risk to health, it is essential to determine the levels of inorganic mercury and mercury species such as methylmercury.

To date, the methods for determining mercury species in hair have involved separate extractions and determinations of the inorganic mercury and organomercury species. The methods reported in the literature vary, in that some digest the hair sample while others extract the mercury species from hair without digestion. These methods are susceptible to artifact formation or degradation of mercury species during extraction or digestion processes. As none of these methods can measure and correct for species transformations, such as bi-directional inter-conversions between inorganic mercury to methylmercury, the EPA Method 6800 has been applied as both a diagnostic tool and a determinative technique for species quantitation. During this study, it was found that some methods induced transformation of both mercury species (inorganic mercury and methylmercury) simultaneously. Some other methods induced only demethylation during extraction.

EPA Method 6800, applied as a diagnostic tool, was used in the evaluation of species transformations along with the simultaneous correction of both species shifts. It also provided a reliable and robust means to quantitatively evaluate the accuracy of many literature-reported protocols. Species inter-conversions that occurred after speciated isotopic spiking were quantitatively corrected by monitoring isotope ratios in each species. Method 6800 generated data and comparison of existing methods illustrate potential problem areas with respect to quantitation associated with sample preparation.

Evaluation of Literature Methods Used in Speciation of Mercury in Human Hair: Application of Speciated Isotope Dilution Mass Spectrometry (SIDMS, EPA Method 6800) as a Diagnostic Tool for Accurate Analysis

G M Mizanur Rahman[1], H M 'Skip' Kingston[1], Timothy Fahrenholz[1] and Matt Pamuku[2]

[1]Department of Chemistry & Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA

[2]Applied Isotope Technologies, Inc., 851 Stella Court, Sunnyvale, CA 94087, USA

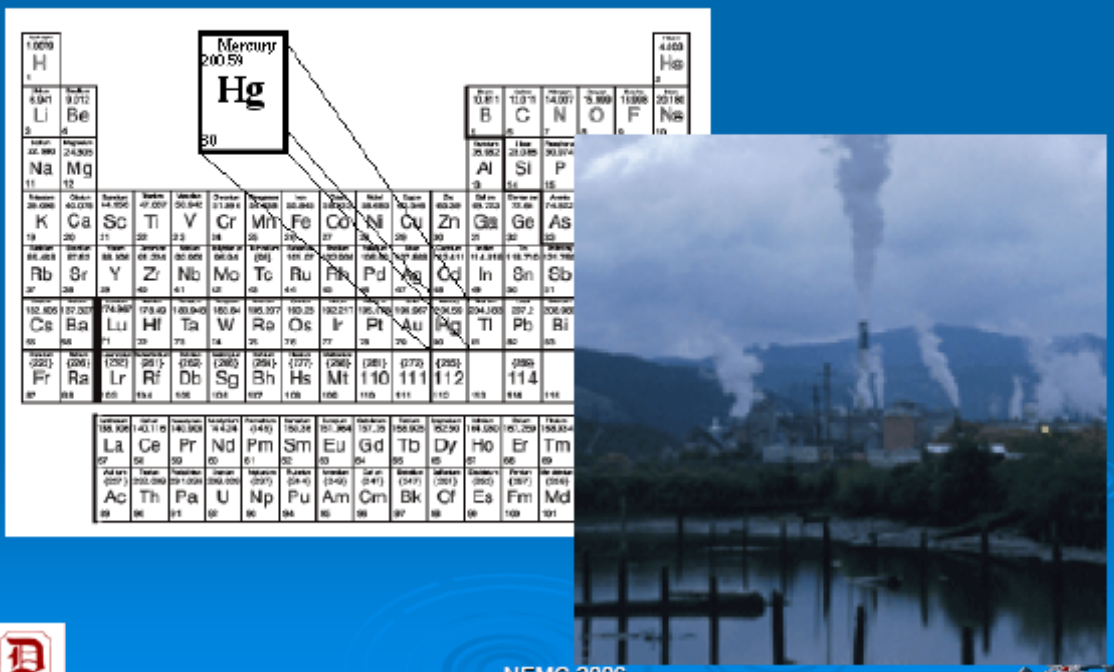
NEMC 2006

Outline

- Background information
- Evaluation of eight (8) literature methods for mercury speciation in human hair
- Introduction to the SIDMS equations and software
- Future directions

NEMC 2006

Mercury: one of the most widely used industrial elements



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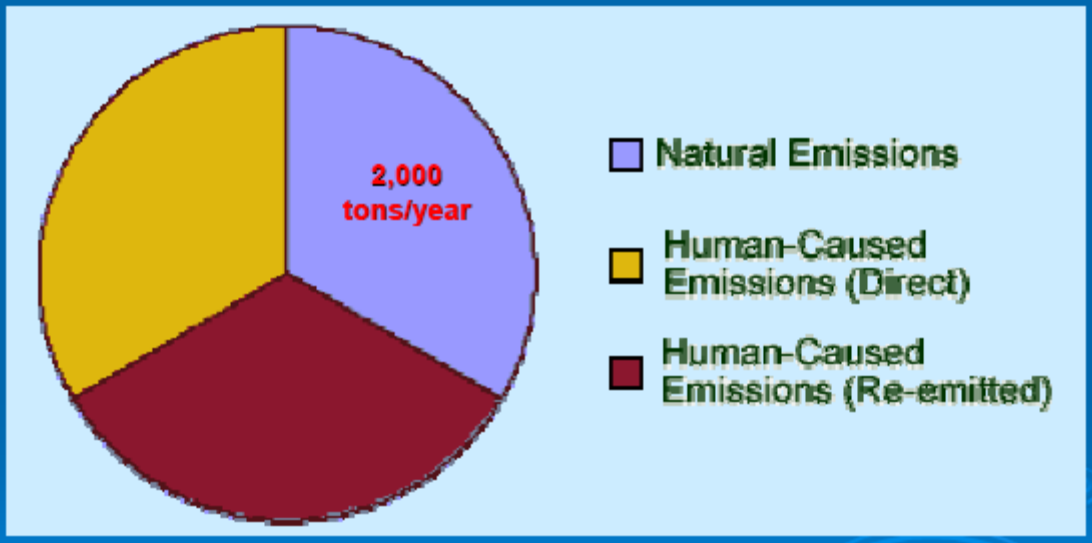
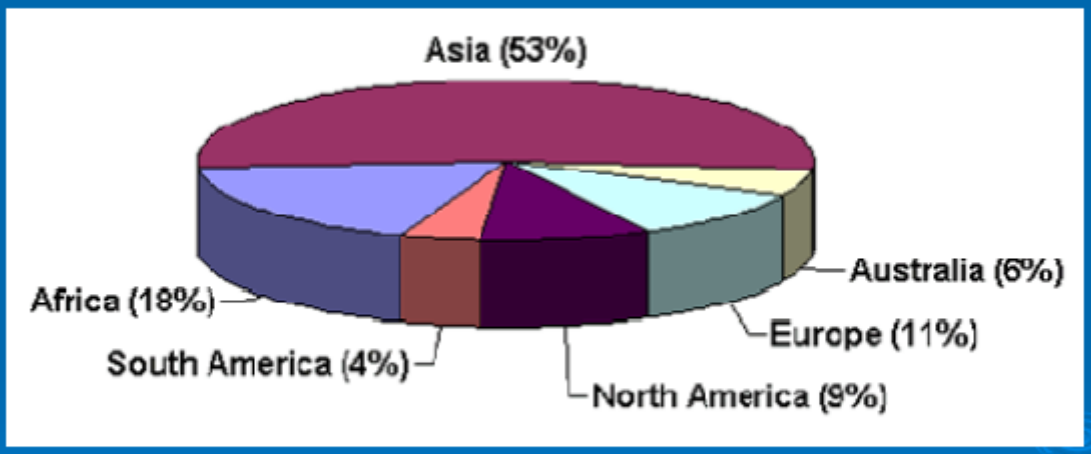
Sources of Mercury into the Environment



2002 data from http://www.epa.gov/cgi-bin/epaprinntonly.cgi; Ref. Jan. 10, 2006

NEMC 2006

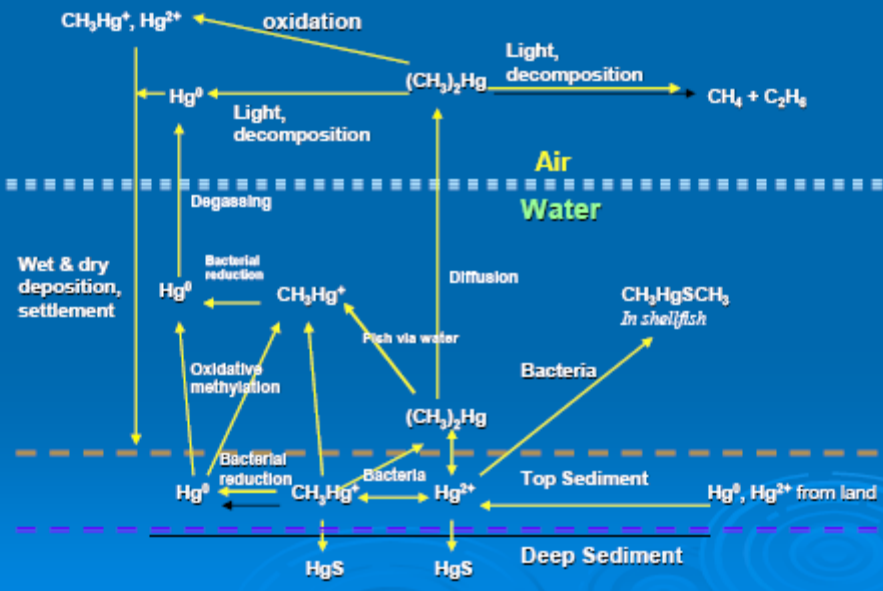
Global Mercury Emissions



2002 data from http://www.epa.gov/cgi-bin/epaprinntonly.cgi; Ref. Jan. 10, 2006

NEMC 2006

Mercury Species Conversion in Nature
Type 1, 2, 3, … species conversion



NEMC 2006

MERCURY EXPOSURE

Inorganic Mercury

- Hg^0 widely used in domestic and industrial applications

Thermometers, thermostats, barometers
Batteries, Fluorescent lights, Electrical switches
Dental fillings and medical equipment
Sold for use in folk medicine in some cultures
Coal burning releases 99% of mercury of all species as Hg^0 into the air (55% of US electric power is coal fired)

Organic Mercury

- Methylmercury is formed in water and soil by bacteria;

Exposure occurs through:
Eating contaminated fish or shellfish
Larger and older fish usually have highest levels of mercury
- Phenylmercury used to control fungus in products before 1991
Exposure occurs through vapors in the air released :
Exterior and oil based paints
Caulks, Cosmetics and toiletries

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Mercury Toxicity

- Potent toxin
  - Methylmercury deteriorates CNS; passes blood/brain barrier, impairs hearing, speech, vision and gait, causes involuntary muscle movements, corrodes skin and mucous membranes, causes chewing and swallowing to become difficult, and in severe cases irreversibly damages areas of brain.
  - Hg^0 passes blood brain membrane and convert into Hg^{2+}.
  - Hg^{2+} damages kidney
  - Fetuses/children more susceptible
- Disasters
  - Japan • 2000 poisonings • 100 deaths (1956)
  - Iraq • 6000 poisonings • 400 deaths (1972)

NEMC 2006

Federal Mercury Limits

- The federal government set human limits of acceptable levels of mercury:
- 2 (ppb) parts of mercury per billion parts of drinking water (set by the EPA)
- 1 (ppm) part of methylmercury in a million parts of seafood (set by the FDA)
- 0.1 milligram of organic mercury per cubic meter of workplace air and 0.05 milligrams per cubic meter of metallic mercury vapor for 8-hour shifts and 40-hour weeks (set by OSHA)
- Methylmercury threshold levels in hair for neurotoxicity set by WHO is 50 ppm and by EPA is 10 ppm.

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Assessment of Human Exposure to Mercury Species

- Body fluid
  - Blood – methylmercury
  - Serum – methylmercury
  - Urine – inorganic mercury
- Tissue
  - Nail – inorganic mercury and methylmercury
  - Hair - Inorganic mercury and methylmercury
    - Total mercury in hair for a normal person is in the range of 0.4 – 6 ppm
    - Hair to blood mercury ratio is 250:1
    - Hair mercury levels found to be a good indicator of dietary, environmental and occupational exposure
    - Concentration of mercury species in hair would be convenient as a biological marker

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Analysis of Mercury Species in Hair

- Digestion
  - Acidic digestion
  - Basic digestion
- Extraction
  - Organic solvents (e.g. benzen, toluene)
  - Solid phase extraction (SPE)
  - Solid phase micro-extraction (SPME)
- Determination
  - Gas chromatography (GC-ECD, GC-MS, GC-AED, GC-CV-AFS)
  - Neutron activation analysis (NAA)
  - Atomic absorption spectrometry (AAS)
  - Inductively coupled plasma mass spectrometry (LC-ICP-MS, GC-ICP-MS)

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Digestion Reagents

- Acidic Digestion
  - $HNO_3 + H_2O_2$
  - 5 M HNO_3
  - 4 M HNO_3
  - 2 M HCl (with or without Ethanol)
  - 4% HCl
  - 50% HCl
  - 4 M KBr + 2 M H_2SO_4
- Basic Digestion
  - 11.2 M NaOH
  - 10 M NaOH
  - 45% NaOH + 10% NaCl + Toluene
  - 7.5 M NaOH
  - 4.5 M KOH

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Current Study Scheme

Mercury species	Extraction/Digestion method	Analytical technique
Total mercury	EPA Method 3052	ICP-MS
Inorganic mercury and methylmercury	Conventional prescribed method	HPLC-ICP-MS SCF-HPLC-ICP-MS SCF-DMA-80A
	SIDMS	HPLC-ICP-MS

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METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

- Sample preparation
  - 100 mg hair sample in microwave vessel
  - Add 10 mL of concentrated HNO_3
  - Seal the microwave vessel
  - Heat at 180 ± 5 °C 10 min
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

Data submitted for publication.
This slide will be updated in future.

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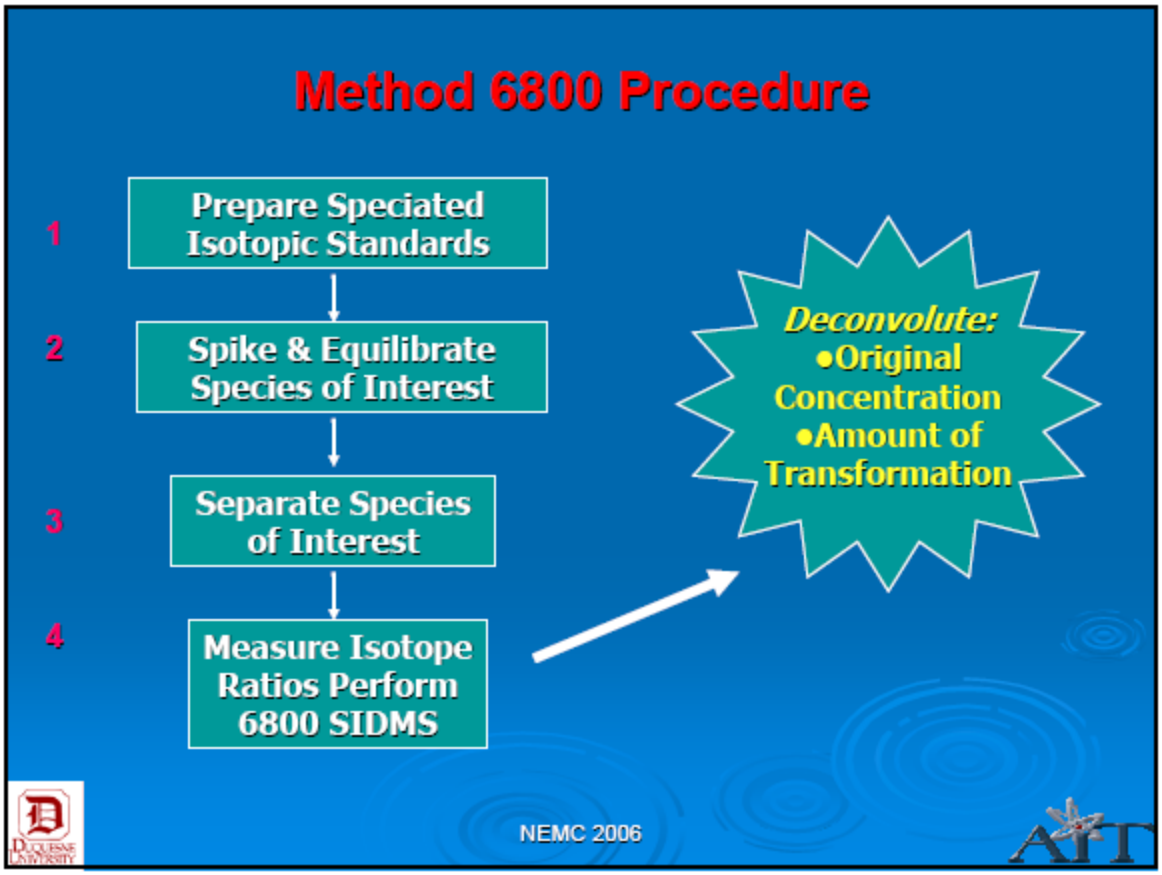
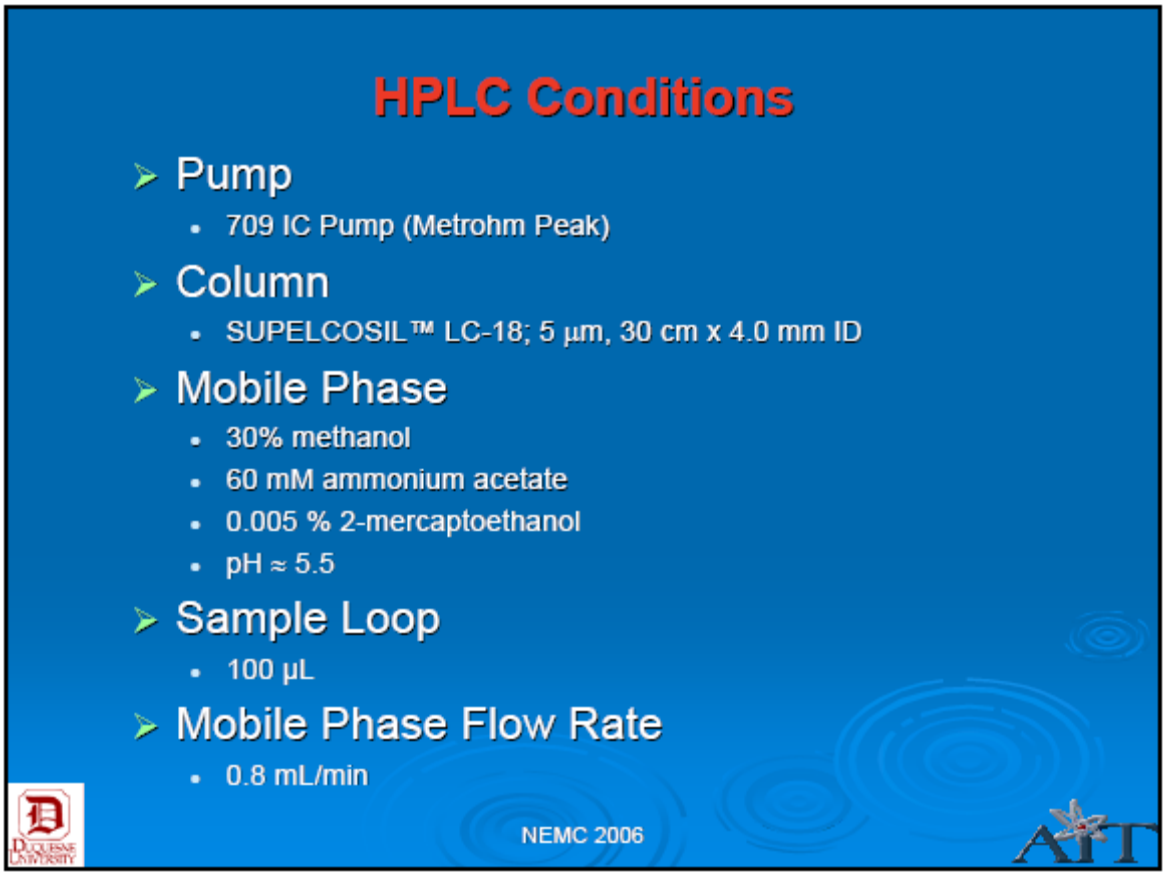

Method 6800 Procedure
1
Prepare Speciated Isotopic Standards
2
Spike & Equilibrate Species of Interest
3
Separate Species of Interest
4
Measure Isotope Ratios Perform 6800 SIDMS
Deconvolute:
•Original Concentration
•Amount of Transformation
NEMC 2006


HPLC Conditions
Pump
709 IC Pump (Metrohm Peak)
Column
SUPELCOSIL™ LC-18; 5 µm, 30 cm x 4.0 mm ID
Mobile Phase
30% methanol
60 mM ammonium acetate
0.005 % 2-mercaptoethanol
pH ≈ 5.5
Sample Loop
100 µL
Mobile Phase Flow Rate
0.8 mL/min
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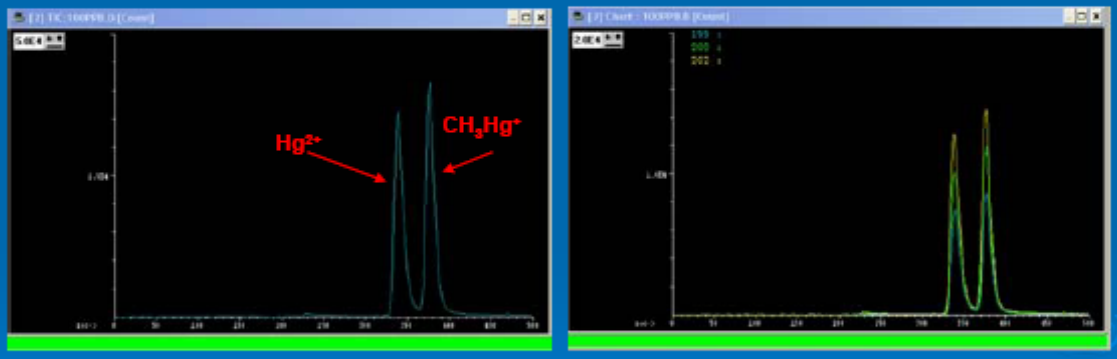
Typical HPLC-ICP-MS Chromatogram for 100 ppb Mixed Mercury Standard



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The Science of the Total Environment 175 (1995) 85–95

the Science of the Total Environment

Methylmercury pollution in the Amazon, Brazil

Hirokatsu Akagi[*a], Olaf Malm[b], Yoshihide Kinjo[a], Masazumi Harada[c], Fernando J.P. Branches[b], Wolfgang C. Pfeiffer[b], Hiroo Kato[a]

[a] National Institute for Minamata Disease, Minamata City, Kumamoto 867, Japan
[b] Laboratorio de Radioisotopos, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil
[c] Faculty of Medicine, Kumamoto University, Kumamoto 862, Japan

- Sample preparation
  - 20 mg hair sample in centrifuge tube
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$)
  - Add 5 mL of 2 M HCl
  - Add 2 drops of ethanol
  - Heat at 100 °C in a water bath for 5 min
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

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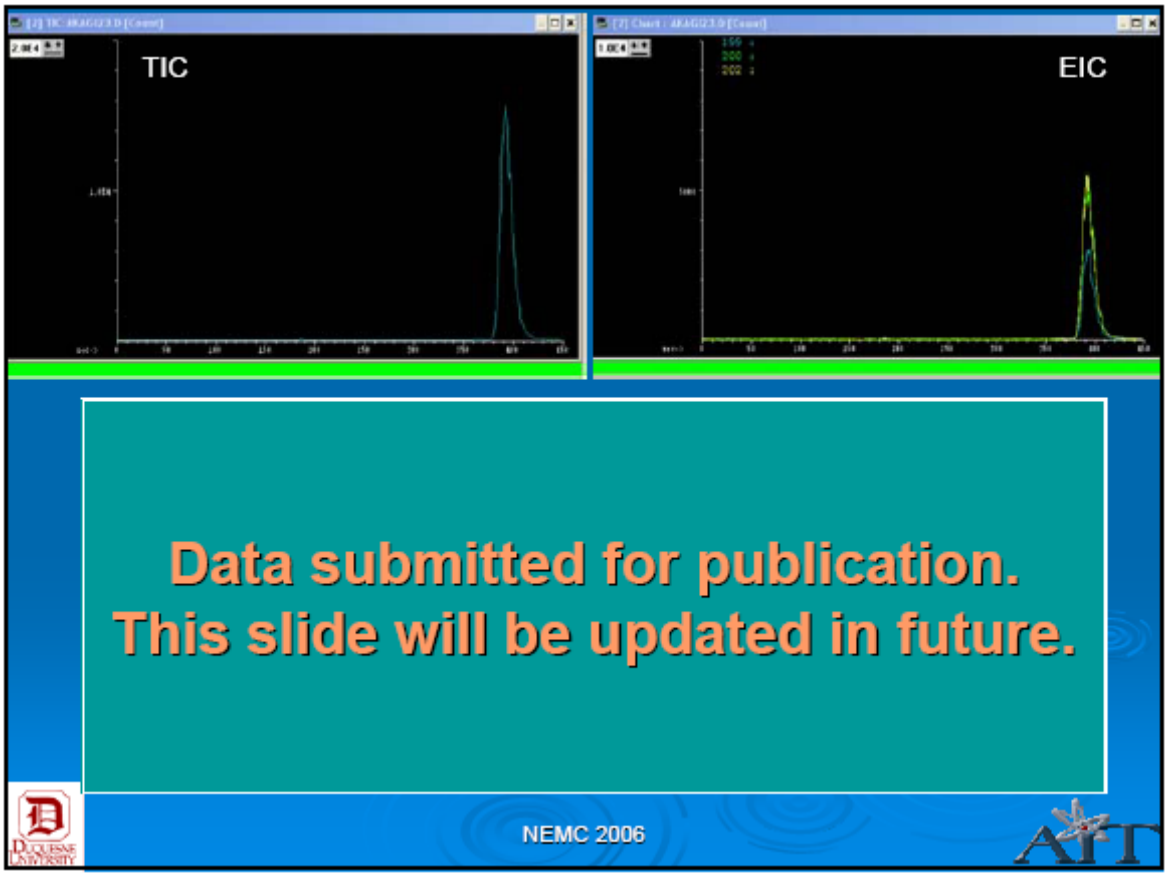
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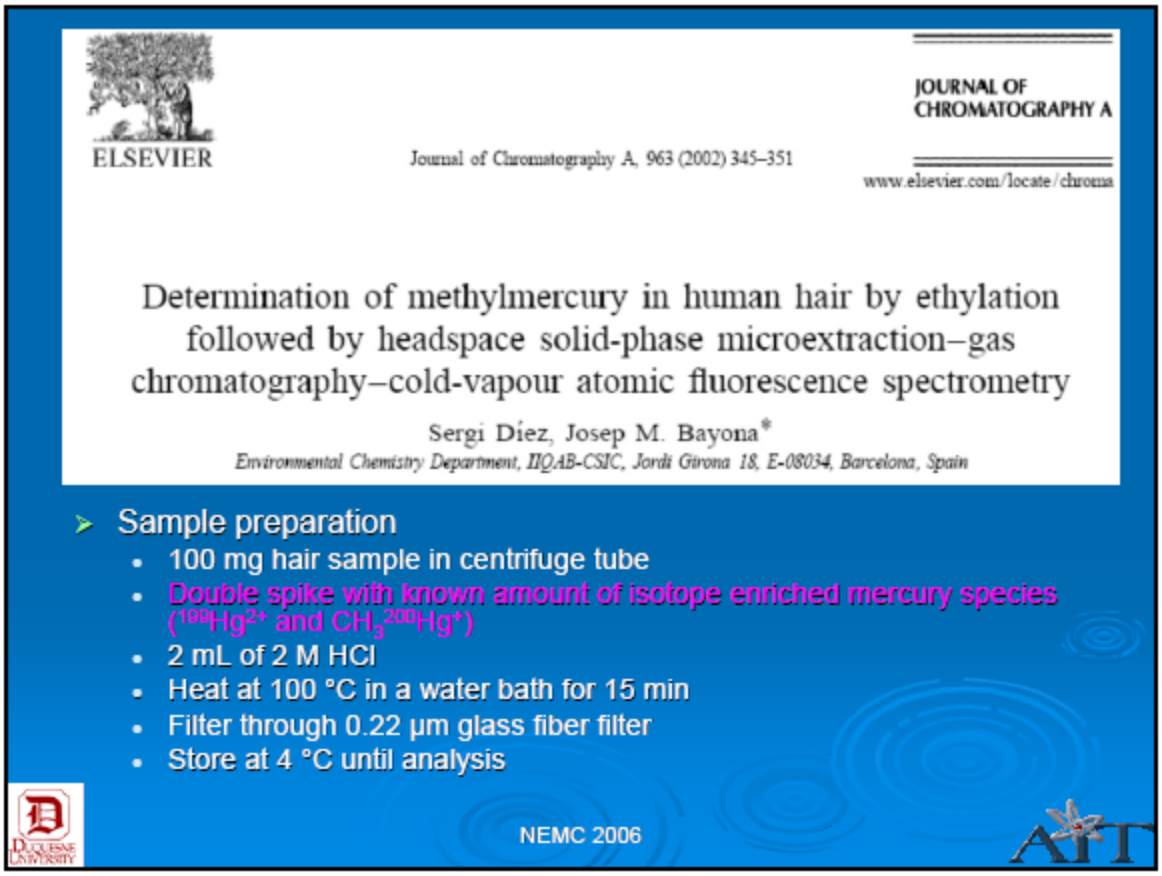
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Journal of Chromatography A, 963 (2002) 345–351
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma
Determination of methylmercury in human hair by ethylation followed by headspace solid-phase microextraction–gas chromatography–cold-vapour atomic fluorescence spectrometry
Sergi Díez, Josep M. Bayona*
Environmental Chemistry Department, IIQAB-CSIC, Jordi Girona 18, E-08034, Barcelona, Spain
Sample preparation
100 mg hair sample in centrifuge tube
Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^{+}$)
2 mL of 2 M HCl
Heat at 100 °C in a water bath for 15 min
Filter through 0.22 μm glass fiber filter
Store at 4 °C until analysis
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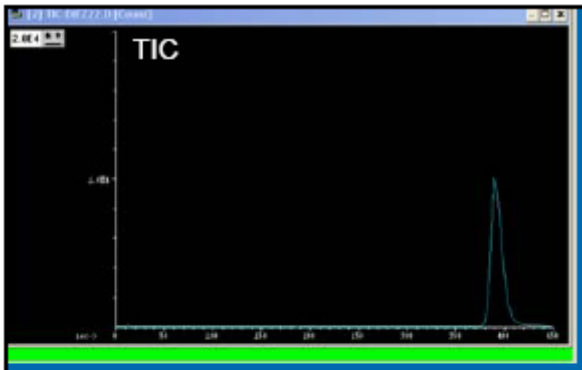

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Analytica Chimica Acta 398 (1999) 265–272

ANALYTICA CHIMICA ACTA

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Rapid acid leaching and slurry sampling procedures for the determination of methyl-mercury and total mercury in human hair by electrothermal atomic absorption spectrometry

Pilar Bermejo-Barrera *, Eva Maria Verdura-Constenla, Antonio Moreda-Piñeiro, Adela Bermejo-Barrera

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Av. das Ciencias s/n. 15706, Santiago de Compostela, Spain

Received 3 February 1999; received in revised form 14 May 1999; accepted 26 May 1999

- Sample preparation
  - 200 mg hair sample in centrifuge tube
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^{+}$)
  - Add 3 mL of 4% (m/m) HCl
  - Mechanical shaking or vortex for 2 min
  - Centrifuge at 2700 rpm for 20 min and separate the supernatant
  - Repeat the extraction process with 2 mL of 4% (m/m) HCl one more time
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

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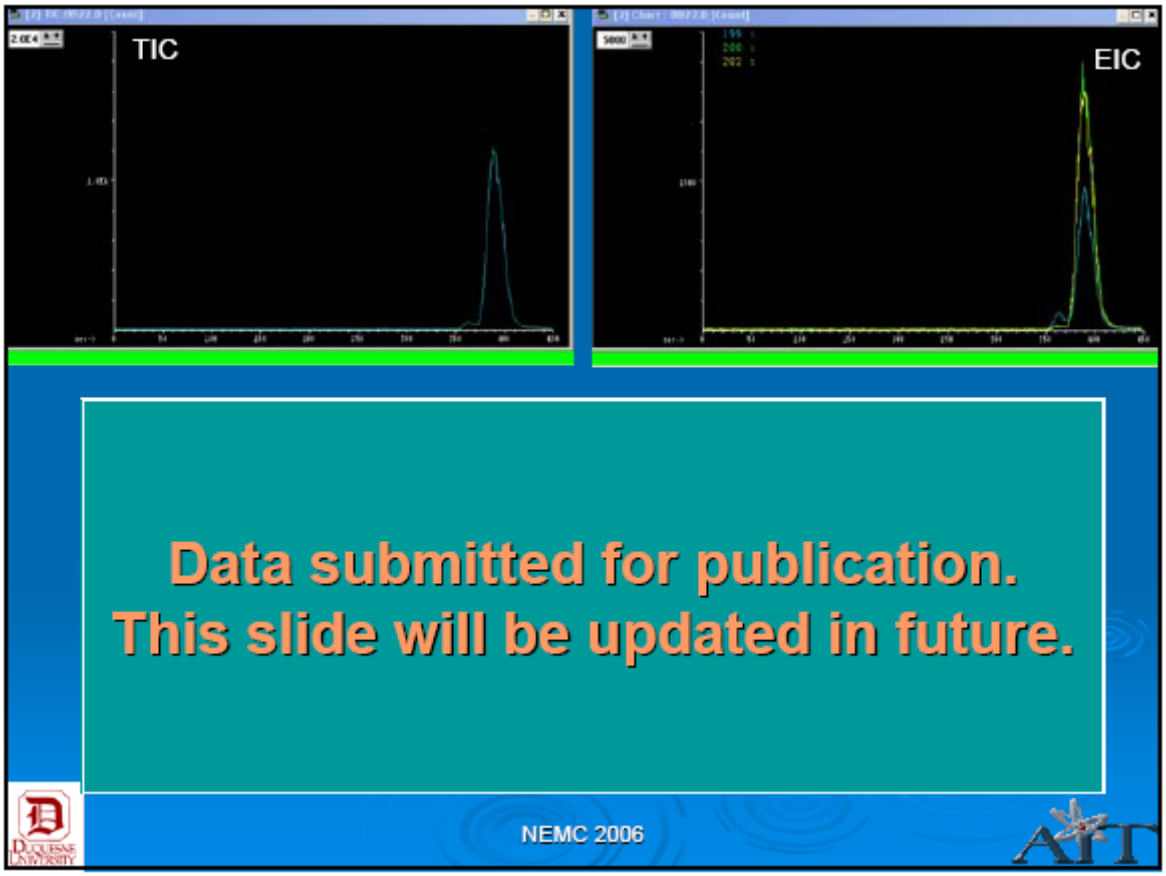
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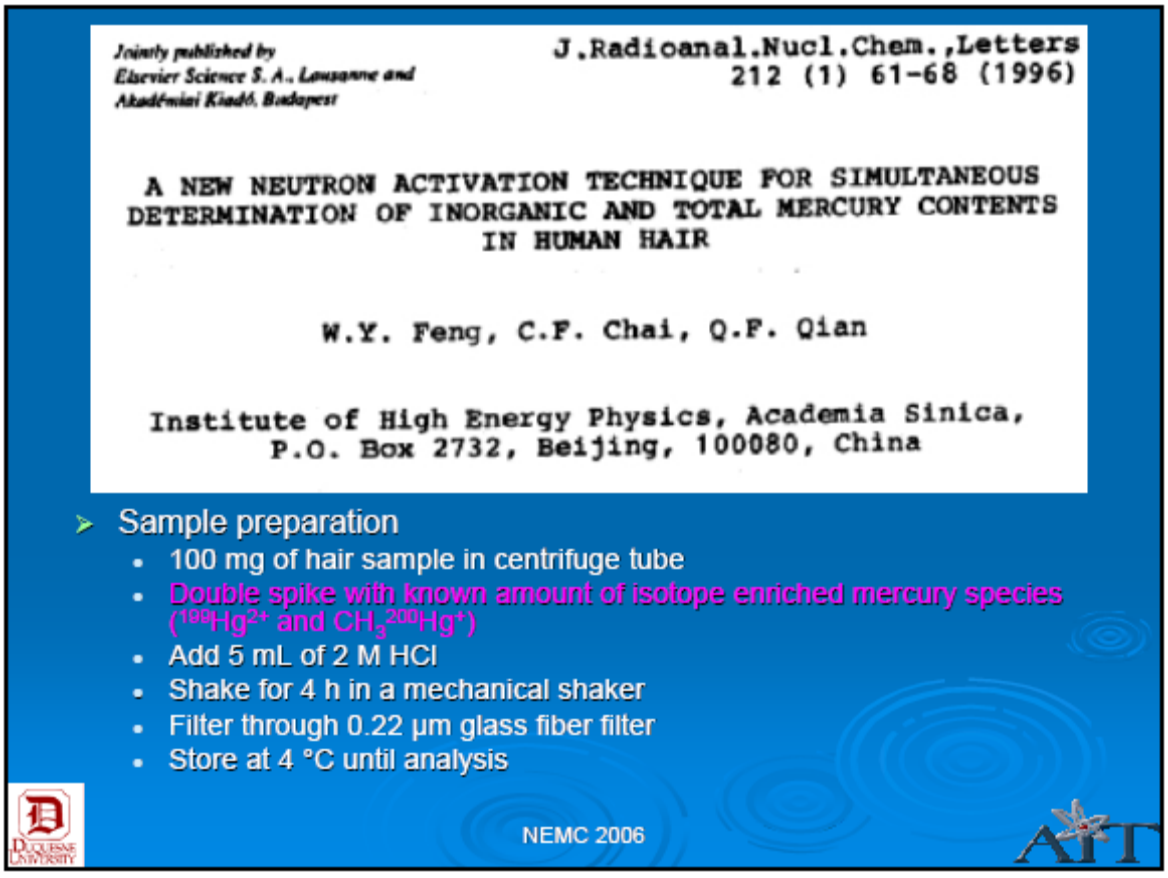
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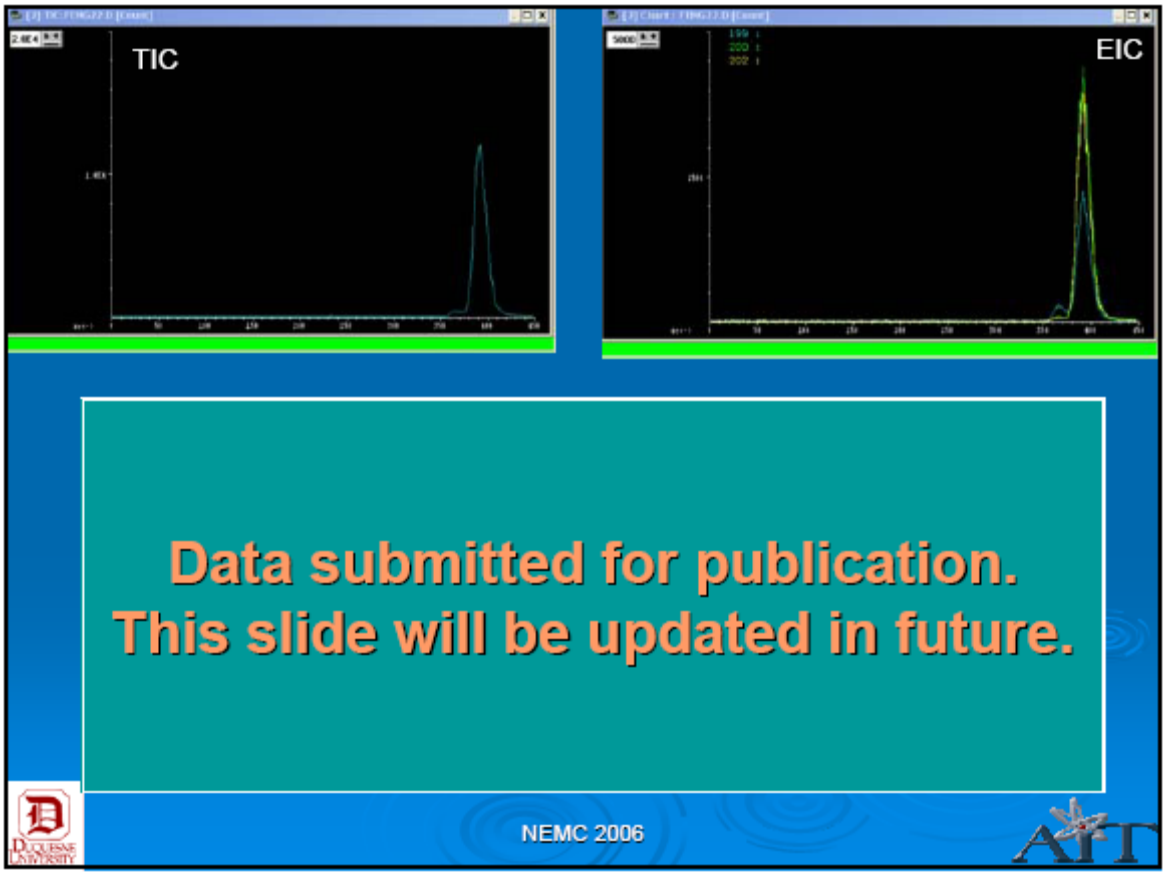
J.Radioanal.Nucl.Chem.,Letters
212 (1) 61-68 (1996)
A NEW NEUTRON ACTIVATION TECHNIQUE FOR SIMULTANEOUS DETERMINATION OF INORGANIC AND TOTAL MERCURY CONTENTS IN HUMAN HAIR
W.Y. Feng, C.F. Chai, Q.F. Qian
Institute of High Energy Physics, Academia Sinica,
P.O. Box 2732, Beijing, 100080, China
Sample preparation
100 mg of hair sample in centrifuge tube
Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$)
Add 5 mL of 2 M HCl
Shake for 4 h in a mechanical shaker
Filter through 0.22 µm glass fiber filter
Store at 4 °C until analysis
NEMC 2006



Total and Methyl Mercury Levels in Human Scalp Hairs of Typical Populations in China by NAA, GC(EC), and Other Techniques

CHIFANG CHAI,*,[1] WEIYUE FENG,[1] QINFANG QIAN,[1] MING GUAN,[2] XINJI LI,[3] YILUN LU,[4] AND XIOUMEI ZHANG[4]

[1]Institute of High Energy Physics and Laboratory of Nuclear Analysis Techniques, Academia Sinica, P.O. Box 2732, Beijing 100080, China; [2]Norman Bethune University of Medical Sciences, Changchun, China; [3]Beijing Environmental Monitoring Station, Beijing, China; and [4]Institute of Geography, Academia Sinica, Beijing, China

- Sample preparation
  - 100 mg of hair sample in centrifuge tube
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$)
  - Add 5 mL of 2 M HCl
  - Keep the mixture on bench top for 24 h
  - Centrifuge and separate the supernatant for analysis
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

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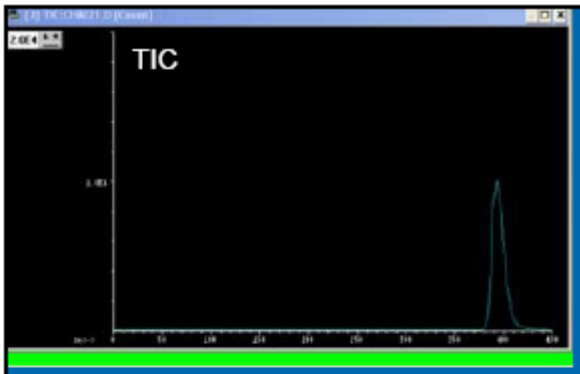

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Journal of Chromatography A, 1025 (2004) 71–75
JOURNAL OF CHROMATOGRAPHY A
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Short communication

Improvements in the methylmercury extraction from human hair by headspace solid-phase microextraction followed by gas-chromatography cold-vapour atomic fluorescence spectrometry

P. Montuori, E. Jover, R. Alzaga, S. Diez, J.M. Bayona*
Environmental Chemistry Department, IIQAB-CSIC, Jordi Girona 18-26, E-08034 Barcelona, Spain

- Sample preparation
  - 20 mg hair sample in centrifuge tube
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$)
  - 350 µL of 5 M HNO_3
  - Heat at 100 °C in a water bath for 2 h
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

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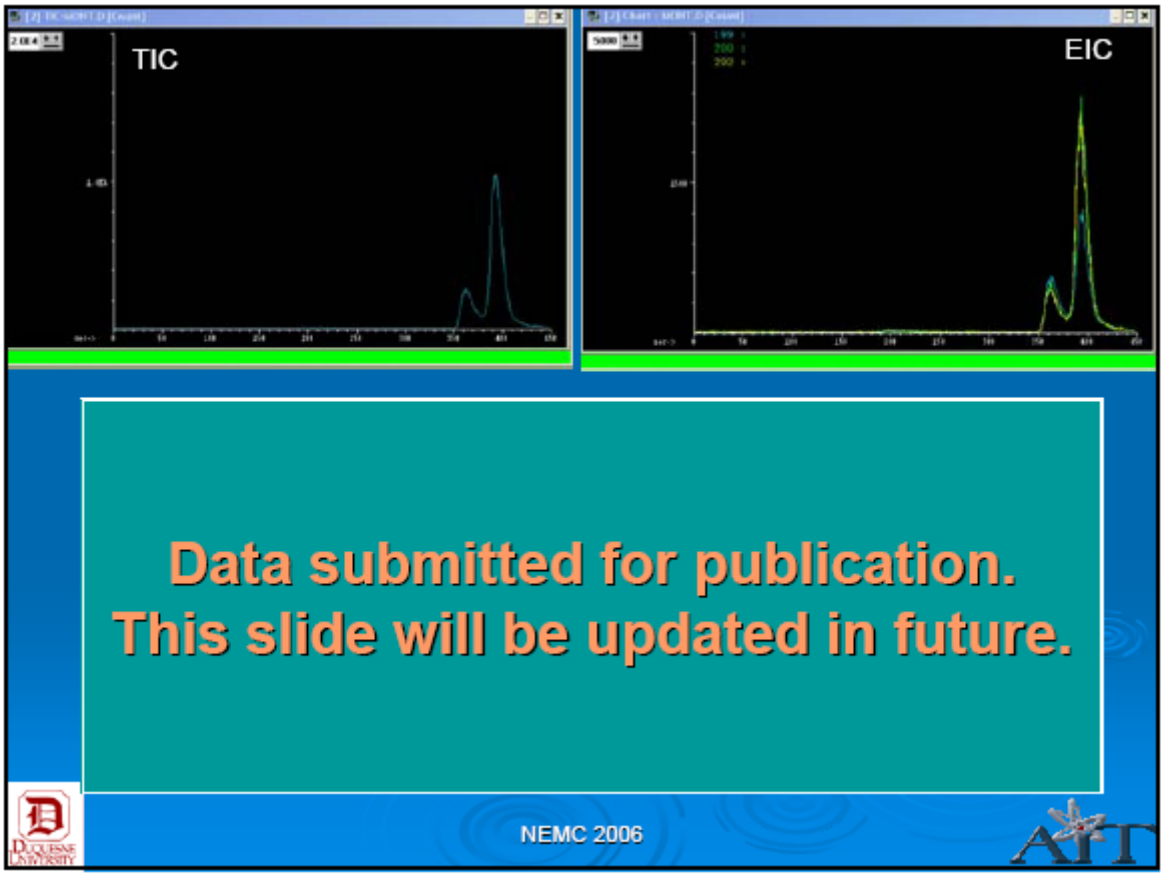
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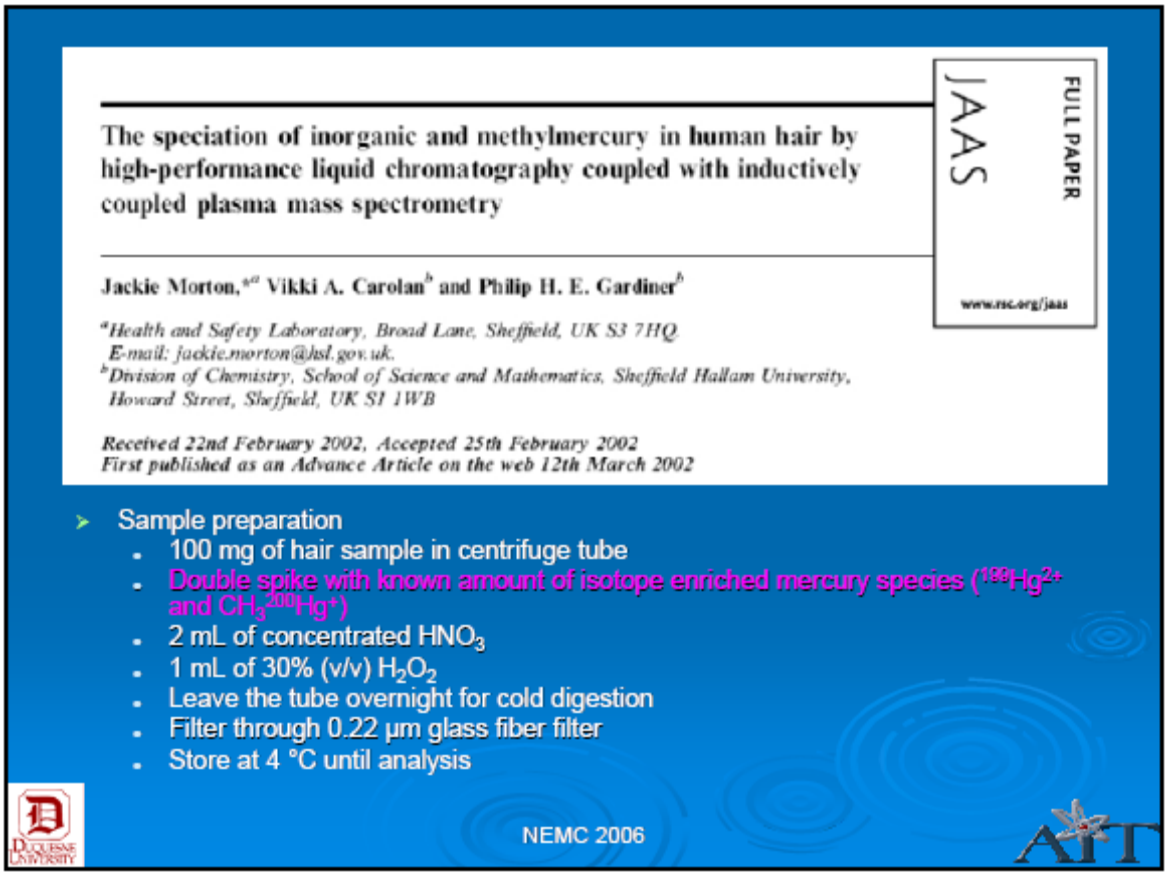
The speciation of inorganic and methylmercury in human hair by high-performance liquid chromatography coupled with inductively coupled plasma mass spectrometry
JAAS
FULL PAPER
www.rsc.org/jaas
Jackie Morton,*[a] Vikki A. Carolan[b] and Philip H. E. Gardiner[b]
[a]Health and Safety Laboratory, Broad Lane, Sheffield, UK S3 7HQ
E-mail: jackie.morton@hsl.gov.uk.
[b]Division of Chemistry, School of Science and Mathematics, Sheffield Hallam University, Howard Street, Sheffield, UK S1 1WB
Received 22nd February 2002, Accepted 25th February 2002
First published as an Advance Article on the web 12th March 2002
Sample preparation
100 mg of hair sample in centrifuge tube
Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$)
2 mL of concentrated HNO_3
1 mL of 30% (v/v) H_2O_2
Leave the tube overnight for cold digestion
Filter through 0.22 µm glass fiber filter
Store at 4 °C until analysis
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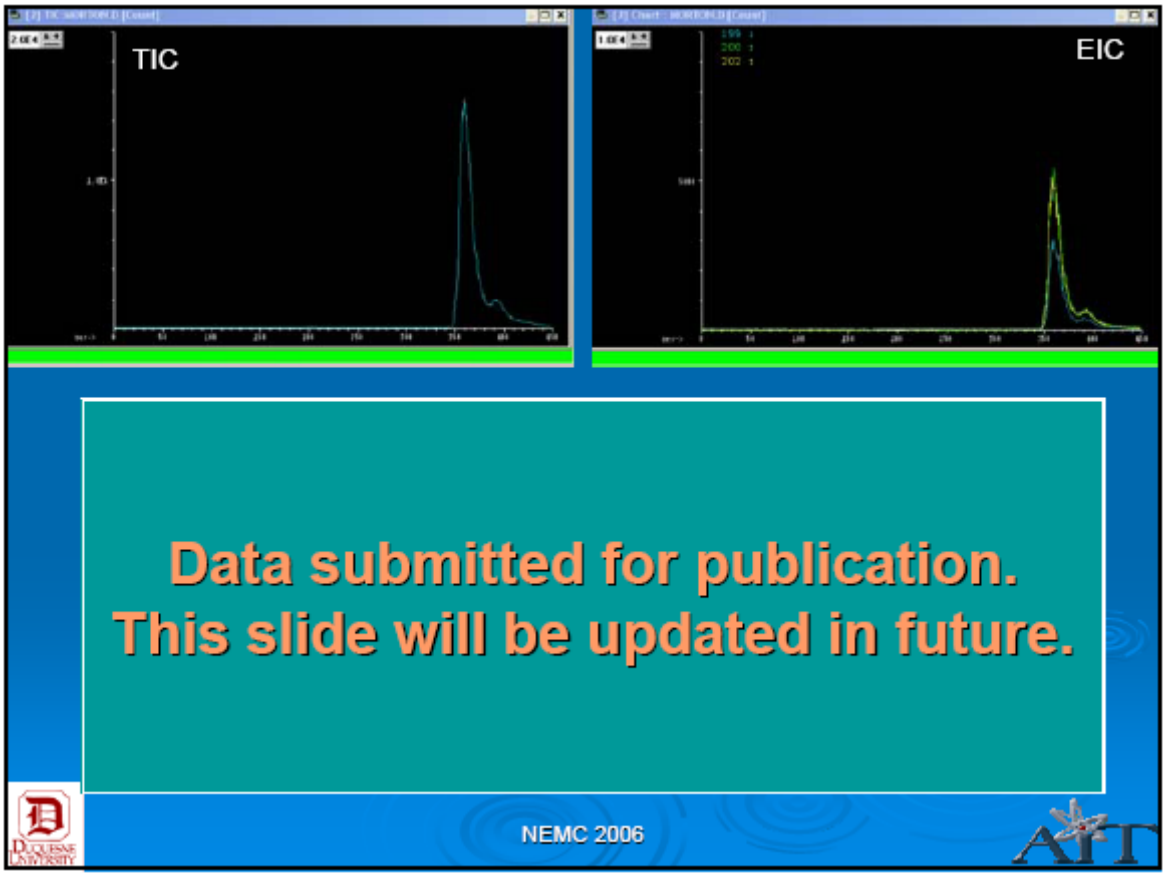

METHOD 3200

MERCURY SPECIES FRACTIONATION AND QUANTIFICATION BY MICROWAVE ASSISTED EXTRACTION, SELECTIVE SOLVENT EXTRACTION AND/OR SOLID PHASE EXTRACTION

ARTICLE

JAAS
www.rsc.org/jaas

Development of a microwave-assisted extraction method and isotopic validation of mercury species in soils and sediments†

G. M. Mizanur Rahman and H. M. 'Skip' Kingston*

Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA. E-mail: kingston@duq.edu; Fax: 412 396 4013 or 412 396 5683; Tel: 412 396 5564

Received 26th March 2004, Accepted 7th January 2005
First published as an Advance Article on the web 4th February 2005

- Sample preparation
  - 100 mg of hair sample in microwave vessel
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^{+}$)
  - 10 mL of 4M HNO_3
  - Extract at 100 °C for 10 min.
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

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HPLC Conditions

- Pump
  - 709 IC Pump (Metrohm Peak)
- Column
  - Novapak™ C18 RP; 4.0 µm, 150 mm x 3.9 mm ID
- Mobile Phase
  - 0.4% (m/v) L-Cysteine
  - pH ≈ 5.0
- Sample Loop
  - 100 µL
- Mobile Phase Flow Rate
  - 1.0 mL/min

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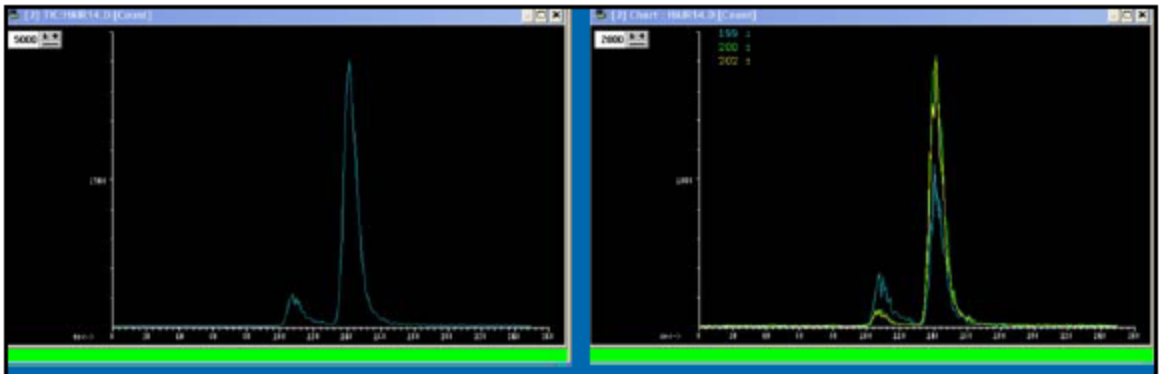

Data submitted for publication.
This slide will be updated in future.

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"Deconvolution" Simplified Equations for Double-Spiking

- For Hg^{2+}

$$R^{In}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

$$R^{In}_{200/202} = \frac{\left({}^{200}A_n N^{In}_n + {}^{200}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{200}A_n N^{Me}_n + {}^{200}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

- For CH_3Hg^+

$$R^{Me}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)\alpha + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

$$R^{In}_{200/202} = \frac{\left({}^{200}A_n N^{In}_n + {}^{200}A^{In}_s N^{In}_s\right)\alpha + \left({}^{200}A_n N^{Me}_n + {}^{200}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

α fraction of Hg^{2+} ⟶ CH_3Hg^+ and β fraction of CH_3Hg^+ ⟶ Hg^{2+}

N^{In} is Concentration of Hg^{2+}, and N^{Me} is Concentration of CH_3Hg^+

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Species Concentration and Species Transformation Correction Simplified for Specific Species Reagents

- For Hg^{2+}

$$R^{In}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

$$R^{In}_{200/202} = \frac{\left({}^{200}A_n N^{In}_n + {}^{200}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{200}A_n N^{Me}_n + {}^{200}A^{Me}_s N^{Me}_s\right)\beta}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)(1-\alpha) + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)\beta}$$

- For CH_3Hg^+

$$R^{Me}_{199/202} = \frac{\left({}^{199}A_n N^{In}_n + {}^{199}A^{In}_s N^{In}_s\right)\alpha + \left({}^{199}A_n N^{Me}_n + {}^{199}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

$$R^{In}_{200/202} = \frac{\left({}^{200}A_n N^{In}_n + {}^{200}A^{In}_s N^{In}_s\right)\alpha + \left({}^{200}A_n N^{Me}_n + {}^{200}A^{Me}_s N^{Me}_s\right)(1-\beta)}{\left({}^{202}A_n N^{In}_n + {}^{202}A^{In}_s N^{In}_s\right)\alpha + \left({}^{202}A_n N^{Me}_n + {}^{202}A^{Me}_s N^{Me}_s\right)(1-\beta)}$$

α fraction of Hg^{2+} ⟶ CH_3Hg^+ and β fraction of CH_3Hg^+ ⟶ Hg^{2+}

N^{In} is Concentration of Hg^{2+}, and N^{Me} is Concentration of CH_3Hg^+

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Species Concentration and Species Transformation Correction Simplified for Specific Species Reagents

- For Hg^{2+}

$$R^{In}_{199/202} = \frac{N^{In}_n}{N^{In}_n} \alpha) \frac{N^{Me}_n}{N^{Me}_n} \beta$$

$$R^{In}_{200/202} = \frac{N^{In}_n}{N^{In}_n} \alpha) \frac{N^{Me}_n}{N^{Me}_n} \beta$$

- For CH_3Hg^+

$$R^{Me}_{199/202} = \frac{N^{In}_n}{N^{In}_n})\alpha \frac{N^{Me}_n}{N^{Me}_n} \beta)$$

$$R^{In}_{200/202} = \frac{N^{In}_n}{N^{In}_n})\alpha \frac{N^{Me}_n}{N^{Me}_n} \beta)$$

α fraction of Hg^{2+} ⟶ CH_3Hg^+ and β fraction of CH_3Hg^+ ⟶ Hg^{2+}

N^{In} is Concentration of Hg^{2+}, and N^{Me} is Concentration of CH_3Hg^+

NEMC 2006

Assay-Keyed Reagent Kits Simplified Equations for SIDMS 6800

- For Hg^{2+}

$$R^{In}_{199/202} =$$

$$R^{In}_{200/202} =$$

= Concentration of Hg^{2+},

- For CH_3Hg^+

$$R^{Me}_{199/202} =$$

$$R^{In}_{200/202} =$$

= Concentration of CH_3Hg^+

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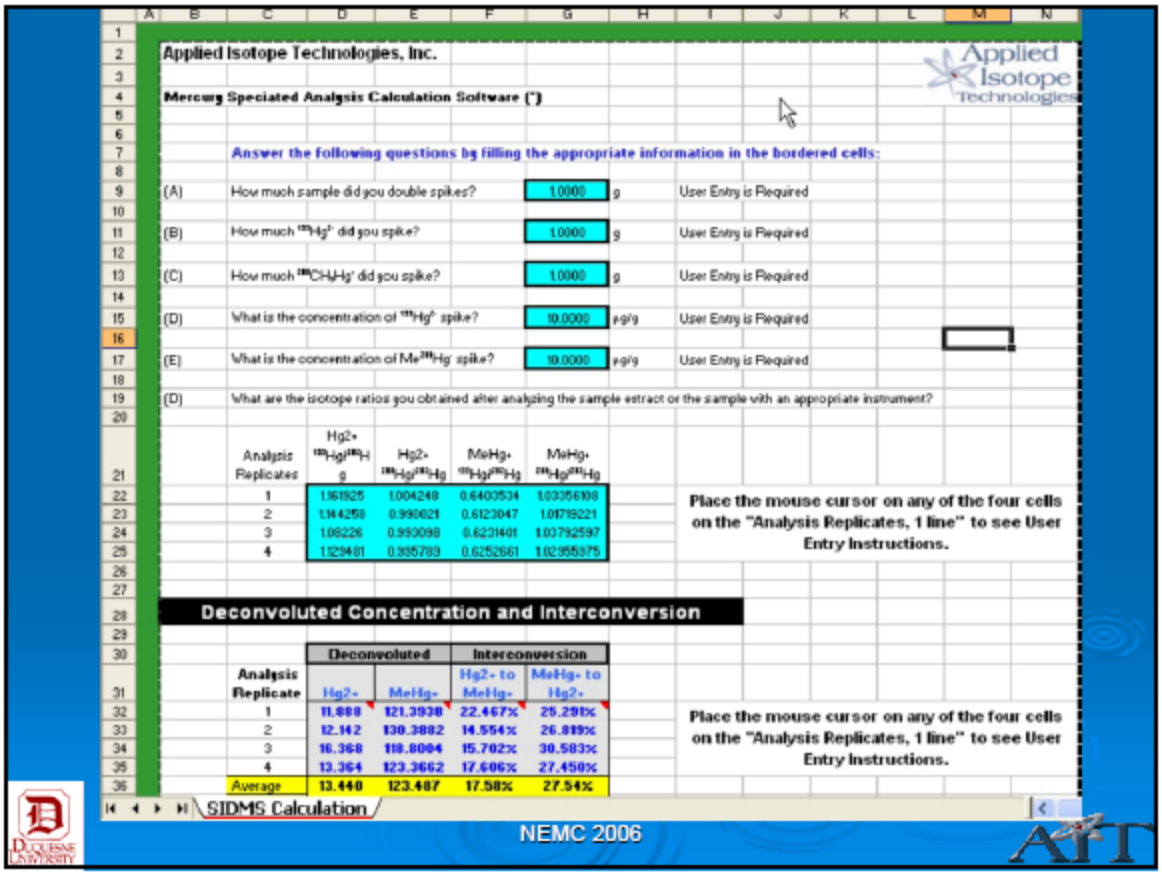

Applied Isotope Technologies, Inc.

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 $Me^{201}Hg^+$ 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	$^{199}Hg/^{202}Hg$	$^{200}Hg/^{202}Hg$	$^{199}Hg/^{202}Hg$	$^{201}Hg/^{202}Hg$
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	1.129461	0.995789	0.6252661	1.02355375

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 Hg^{2+}	Deconvoluted MeHg+	Interconversion Hg^{2+} to MeHg+	Interconversion MeHg+ to Hg^{2+}
1	11.888	121.3938	22.467%	25.28%
2	12.142	130.3882	14.554%	26.819%
3	16.368	118.8004	15.702%	30.583%
4	13.364	123.3662	17.606%	27.450%
Average	13.440	123.487	17.58%	27.54%

Place the mouse cursor on any of the four cells on the "Analysis Replicates, 1 line" to see User Entry Instructions.

SIDMS Calculation

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Future Directions

- Develop a simple and fast extraction method for hair mercury speciation
- Apply the developed method to the real life samples
- Perform EPA Method 6800 (*Elemental and Speciated Isotope Dilution Mass Spectrometry*) as a diagnostic tool to observe if there is any inter-conversion or transformation between mercury species taking place during extraction and/or after extraction

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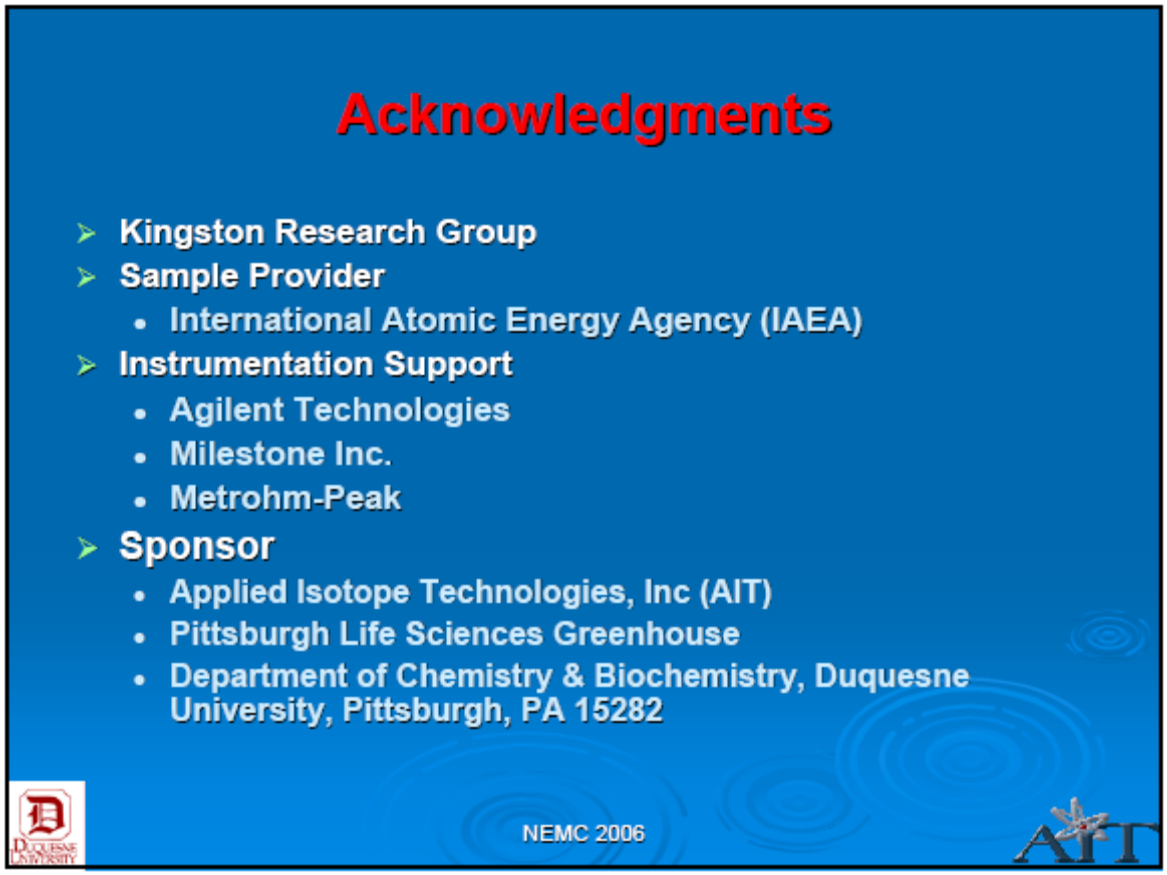
Acknowledgments
Kingston Research Group
Sample Provider
International Atomic Energy Agency (IAEA)
Instrumentation Support
Agilent Technologies
Milestone Inc.
Metrohm-Peak
Sponsor
Applied Isotope Technologies, Inc (AIT)
Pittsburgh Life Sciences Greenhouse
Department of Chemistry & Biochemistry, Duquesne University, Pittsburgh, PA 15282
NEMC 2006

LIQUID CHROMATOGRAPHIC MERCURY SPECIATION: A SUITE OF NEW TECHNIQUES EMPLOYING SOLID-PHASE EXTRACTIONS AND LIQUID-PHASE TRANSFERS AND SEPARATIONS

Shade Ph.D., Christopher W.; Quicksilver Scientific, LLC

In the 1990's, EPA Methods 1630 and 1631 set a new stage for mercury speciation analysis but it has always been a difficult and very expensive endeavor, and this expense arguably has hampered efforts at wide-scale environmental monitoring of methylmercury, the most toxicologically-relevant form of mercury. Though distillation/ethylation/GC/CVAFS (EPA Method 1630) is accurate; it requires extensive labor by a skilled technician and has not been automated, thus keeping the price for such analyses prohibitively high despite the passage of time. To surmount this inherent limitation, a new system for liquid phase transfers, trapping, and separations, centering on ligand-exchange reactions, has been developed.

Soft metals like Hg are almost never in their free-ion state, and thus the best way to manipulate them is to control their speciation with added ligands and then manipulate the formed complexes. Different ligands can be used that span a range of binding strengths and Brønsted basicities in order to effect a series of ligand exchange reactions to trap and/or separate inorganic and methylmercury. Hg/Thiourea - Ion Chromatography is an analytical system for methyl and inorganic mercury (MeHg and Hg^{II}, respectively) that uses an on-line thiol trap to concentrate MeHg and Hg^{II} from prepared sample solutions and then elutes them as charged Hg-Thiourea complexes for sequential separation, oxidation, and reduction to Hg^{0} for Cold Vapor Atomic Fluorescence Spectroscopy detection.

Thiourea's unique nature 1) creates cationic complexes with mercury giving a simple separation strategy, and 2) has very low Brønsted basicity, allowing sorption of mercury species from thiourea solutions onto a thiol resin at medium pH and elution from a thiol resin to the thiourea solution at low pH. The combination of thiourea, with its unique properties, as a ligand and the thiol trap, with its high binding strength, as a preconcentration method allows a greater flexibility in sample preparation chemistries than is permissible by the very condition-sensitive ethylation/purge-and-trap concentration of EPA Method 1630. This flexibility allows the analyst to use thiourea to back-extract solvent extractions (methylene chloride or toluene) or even to replace those solvents with solid-phase extraction media, and has the additional benefit of making the system ideal for simple monitoring of petrochemical products, such as oil or methane gas condensate.

Most importantly, the system features scalable sample preparation methods and automatable sample analysis, creating the potential for steeply reduced pricing of analyses and thus allowing greatly increased monitoring of this important neurotoxin.

Liquid Chromatographic Mercury Speciation:

A suite of new techniques employing solid-phase extractions and liquid-phase transfers and separations

Christopher W. Shade, Ph.D., President
Quicksilver Scientific, LLC - Lafayette, CO

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The Analytical System
Hg-Tu IC/CVAFS

1. On-line Thiol resin preconcentration

2. Charged complex separation

3. Post-Column Cold Vapor Generation/CVAFS

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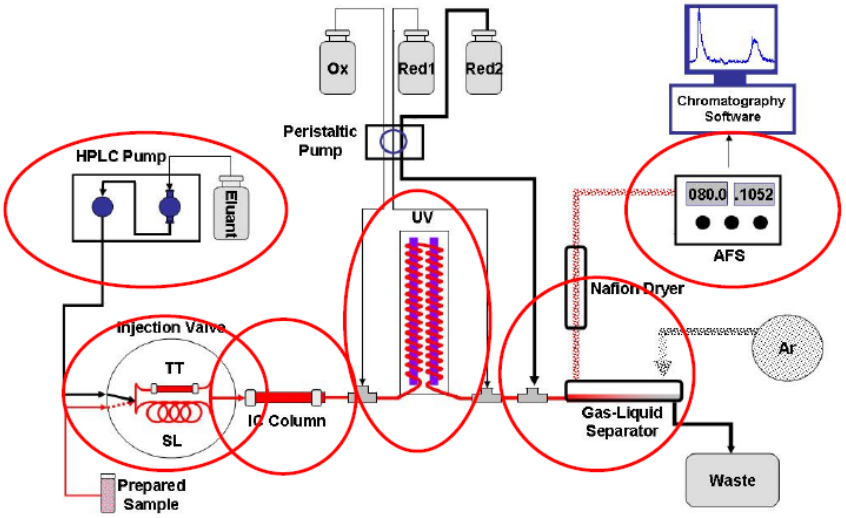
Hg-Thiourea IC/CVAFS



Eluant = 1.0% thiourea, 8.25% HCl, 15% Glacial Acetic Acid – 0.50 mL min^{-1}

Oxidant (Ox) = 5% H_2O_2 – 0.2 mL min^{-1}

Reductant 1 = 15% m/v Na-Ascorbate – 0.2 mL min^{-1}

Reductant 2 = 40% m/v KOH, 6% $SnCl_2$ – 0.8 mL min^{-1}

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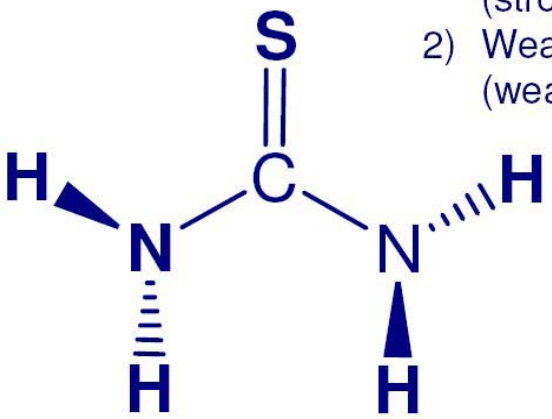
Thiourea

The Ligand of Choice

A Neutral water-soluble ligand

Thione group of thiourea:

1) Strongly binds Hg^{2+} and CH_3Hg^+ (strong Lewis base)
2) Weakly binds H^+ in acid solution (weak Brønsted base)



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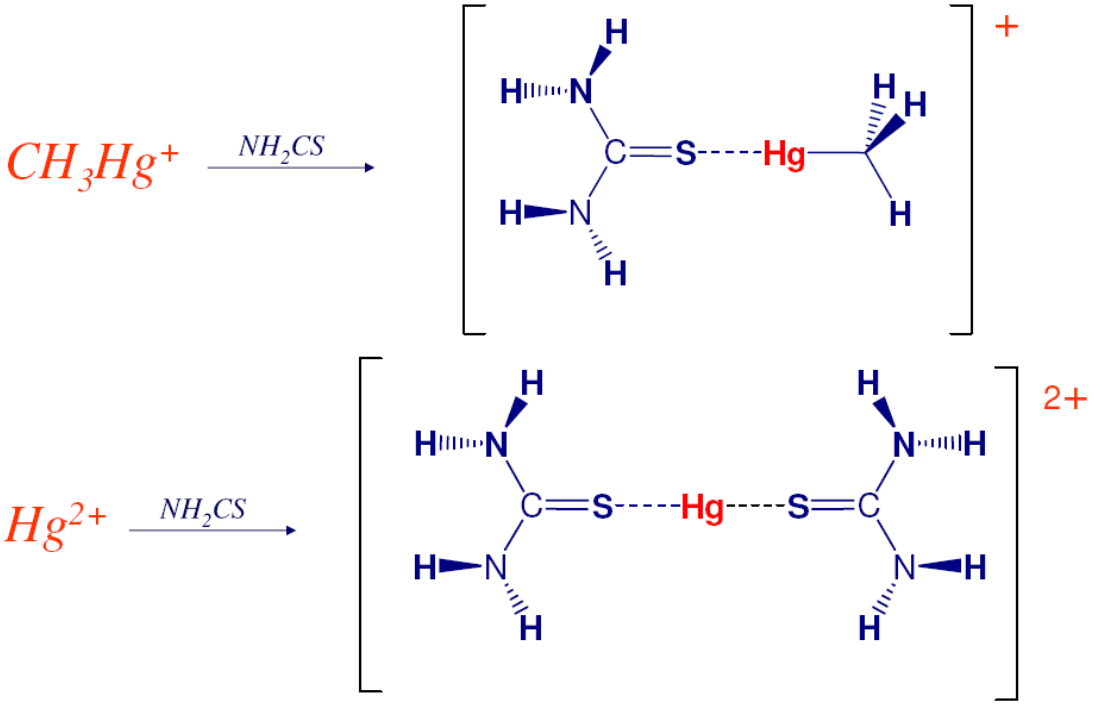
Hg^{2+} and CH_3Hg^+ Thiourea Complexes

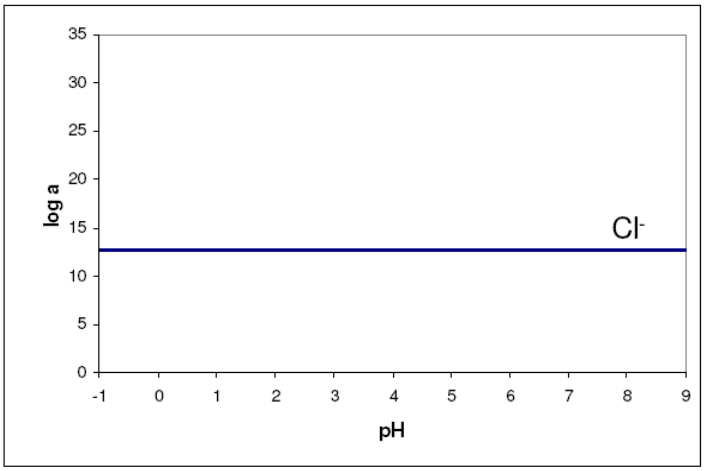


Cation Exchange Separation

Complexation Strengths

The Basis of Ligand Exchange Reactions

Ligand	Log K_1	Log KH
NOM	~22	~10
Tu	11.4	-1.2
OH^-	10.14	14
Br^-	9.07	<<0
Cl^-	6.72	<<0



$\alpha_L \equiv (\sum [Hg^{II}L]/[Hg^{2+}])$ for ligands (L)

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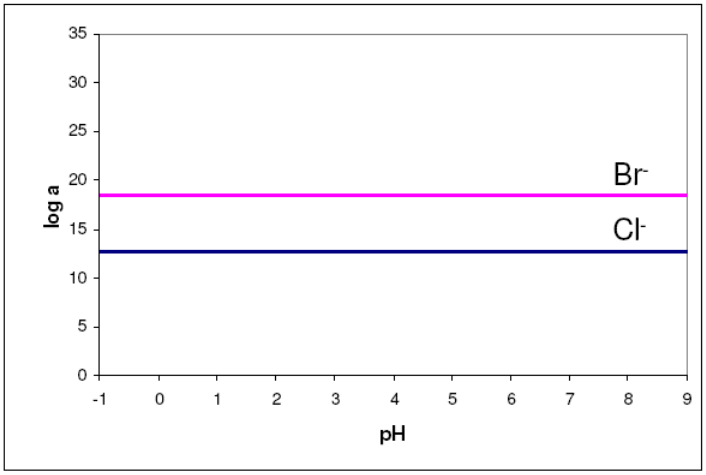

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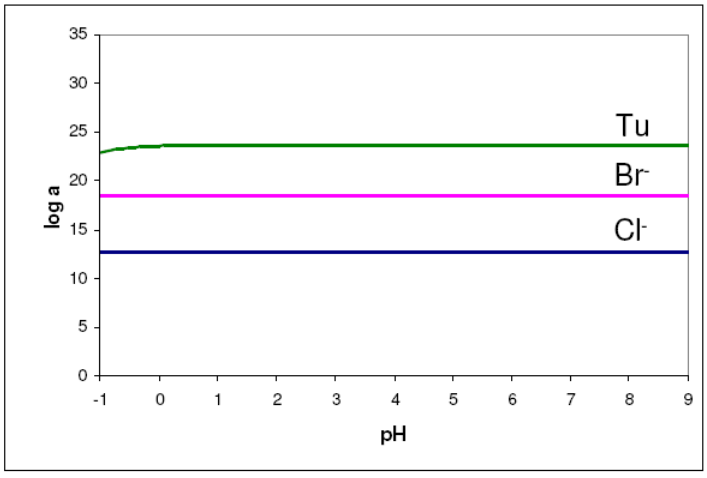

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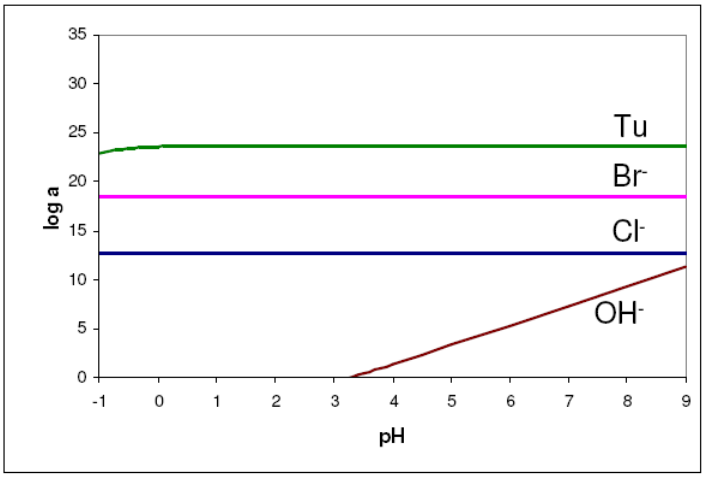

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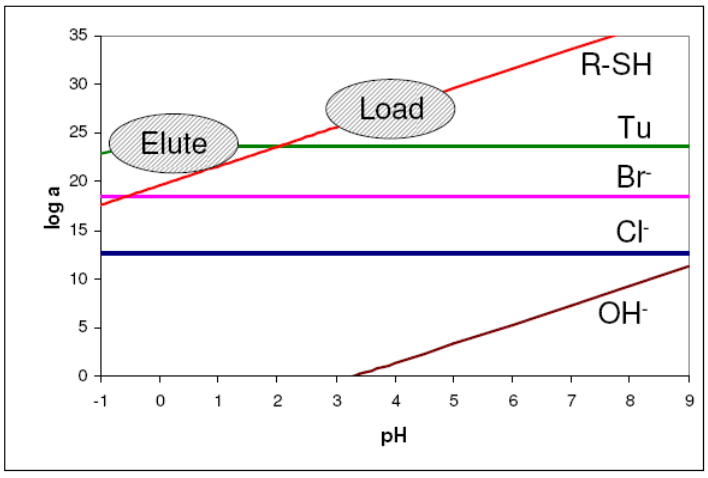

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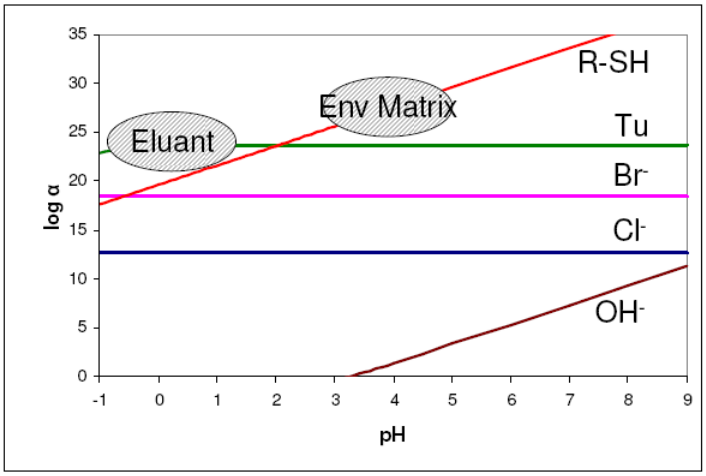

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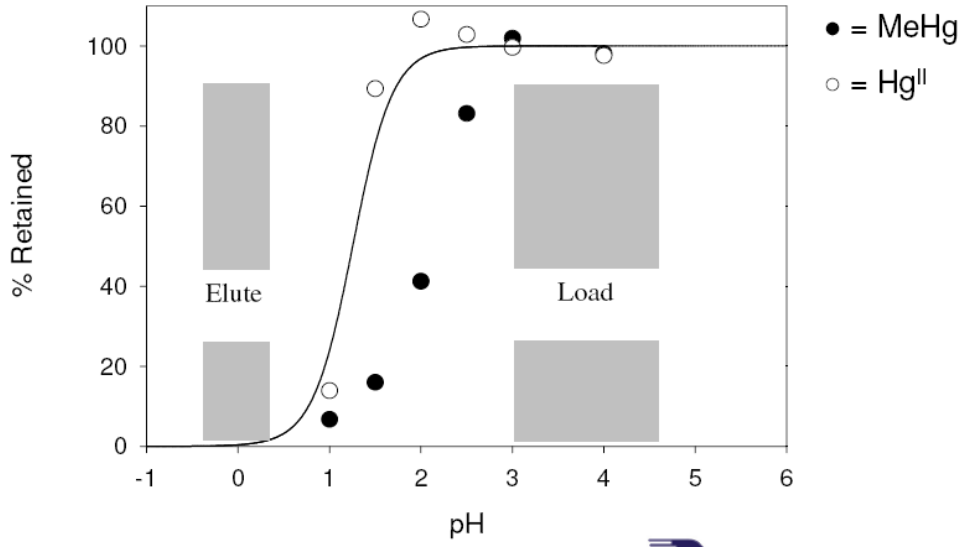
Thiol-Thione pH Dependent Preconcentration/Elution



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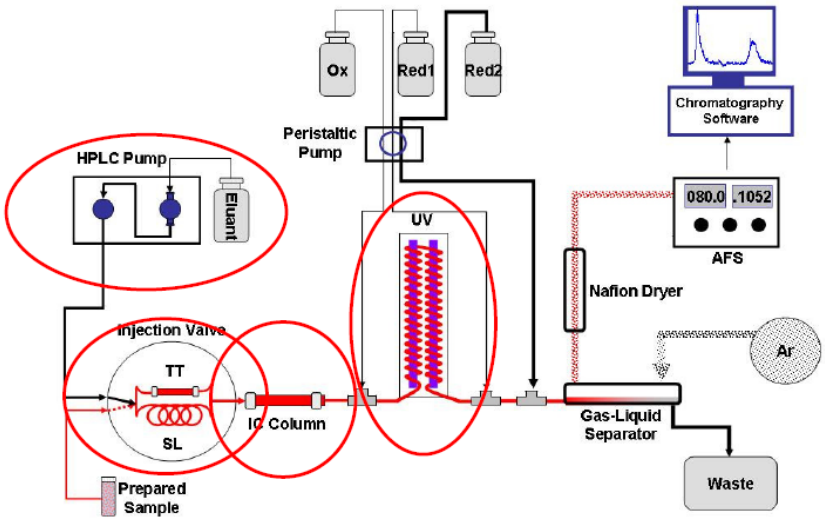
Hg-Thiourea IC/CVAFS



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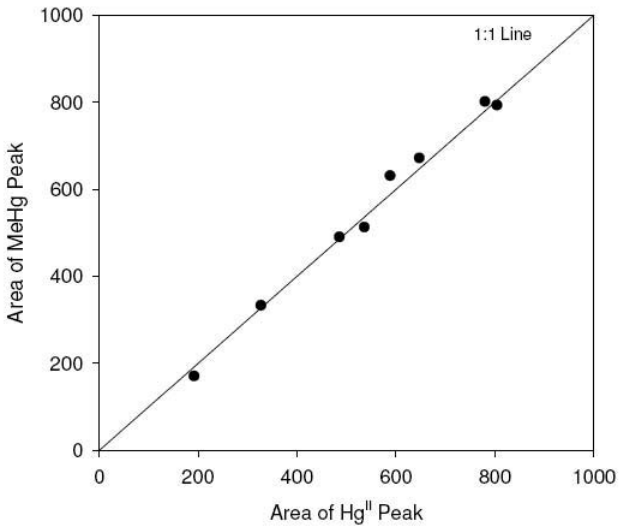
On-line Oxidation Efficiency



- Calibrate with Both MeHg and Hg^{II}, and average values for sensitivity.
- OR if Hg^{II} blank is issue (PC), calibrate with MeHg and get numerous Hg^{II} blank replicates

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Applications

- Biota
- Sediments

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Biota

- Tissue Solubilization/leaching vs. direct leaching
  - Nitric Acid Solubilization / Thiourea leaching
  - Direct Eluant Leaching (no solubilizing)

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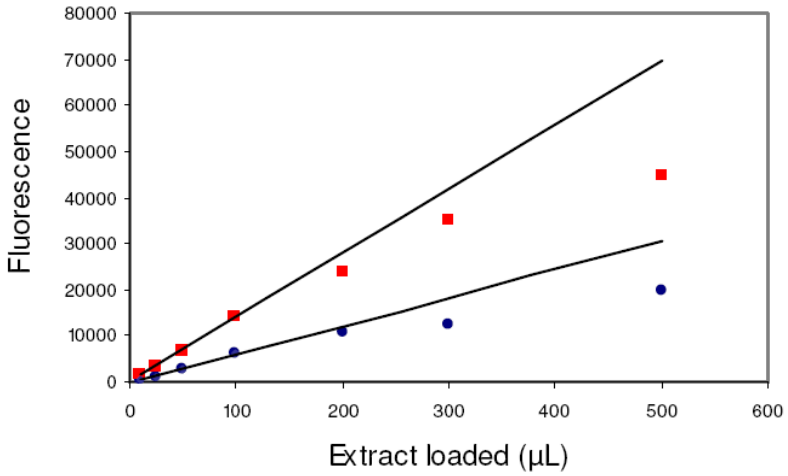
Sample Introduction – Biota/HNO_3

-Levels high enough for direct injection, but matrix prevents it

-Thiol preconcentration



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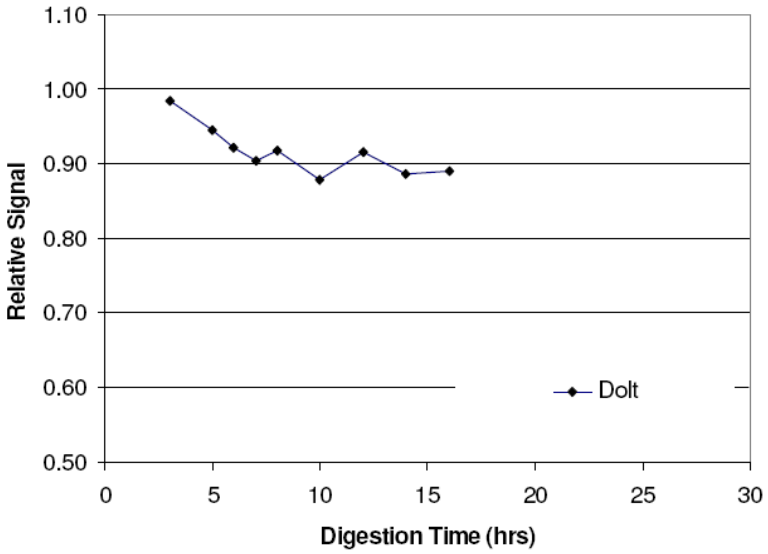
Nitric Acid Solubilization



Data from Hudson Lab Group – UIUC

Wade Wimer and Bob Hudson

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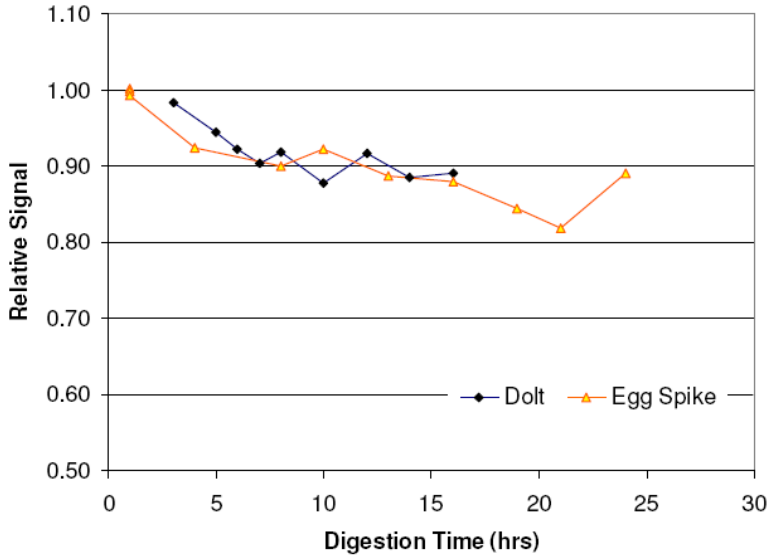
Nitric Acid Solubilization



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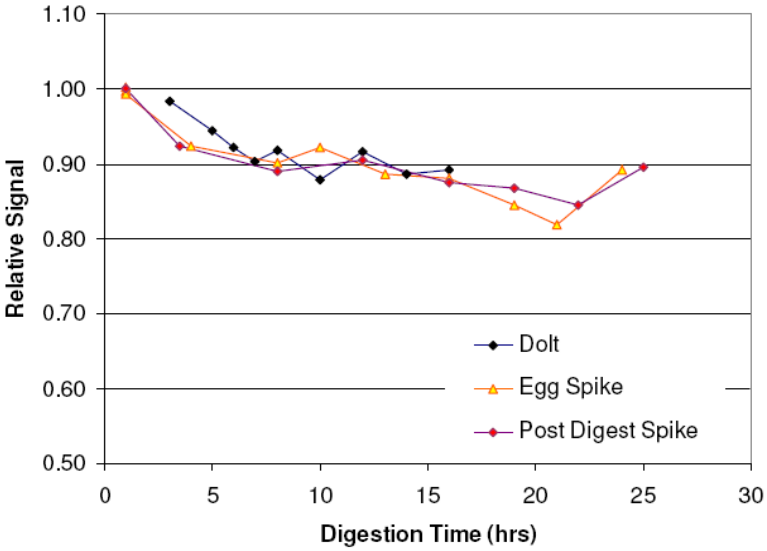

Solubilized Proteins interfering in Preconcentration

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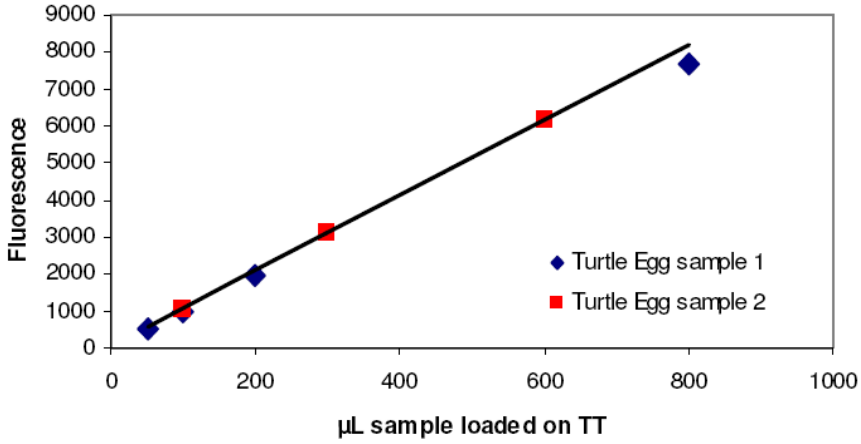
Solid-Phase Extraction(DVB)

-Cleans up sample

-But only getting MeHg now



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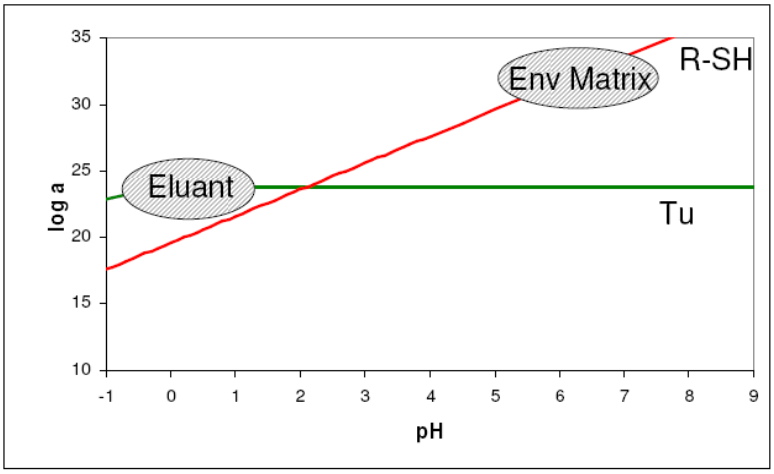
Biota II – The Epiphany

(while staring at a vial of keratin ppt from toenail digestion)



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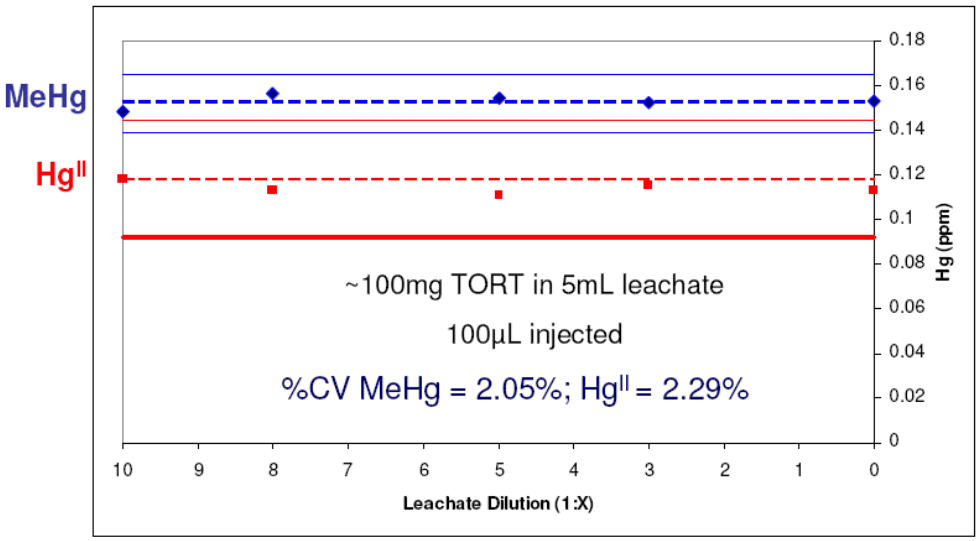
Direct Injection of Leachate



No Solubilization = No matrix problems

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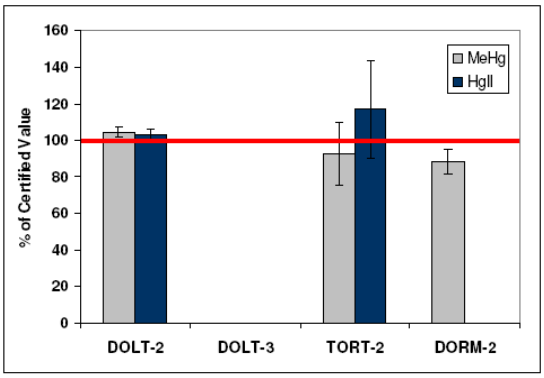
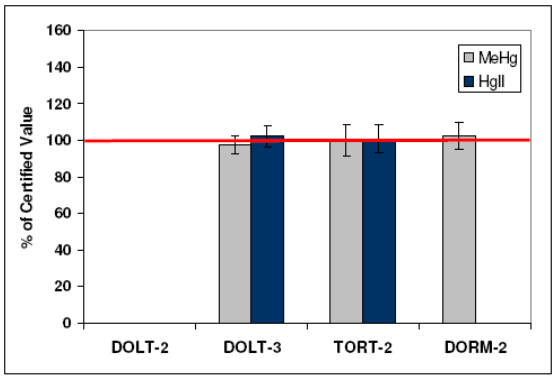
CRM Recoveries



HNO_3



Thiourea Leaching

Human Biomonitoring - Hair

		ppm	Avg ppm	%CV	*Sum MeHg+HgII*	Avg ppm	%CV
LT1	*MeHg*	**1.71**	**1.73**	*2.97*	1.872	**1.882**	*3.30*
	HgII	0.166	**0.156**	*8.74*			
LT2	*MeHg*	**1.69**			1.828		
	HgII	0.141					
LT4	*MeHg*	**1.71**			1.856		
	HgII	0.148					
LT5	*MeHg*	**1.80**			1.970		
	HgII	0.169					
G1	*MeHg*	**0.971**	**0.953**	*3.58*	1.198	**1.236**	*2.92*
	HgII	0.227	**0.283**	*14.33*			
G2	*MeHg*	**0.933**			1.256		
	HgII	0.323					
G3	*MeHg*	**0.918**			1.214		
	HgII	0.297					
G4	*MeHg*	**0.992**			1.276		
	HgII	0.284					

Sediments

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There is a mine full of AVS, a refinery full of oil, a smelter full of Hg, and and 50% OM in my sediments...

What's an analyst to do?

Strong Acid...

and Polymer Resins...

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Background

- Horvat, Liang, and Bloom (1992)
  - incomplete recovery from HCl; better with Cu^{2+}
  - Depression of recovery correlated with LOI
    - worst recovery and no effect of Cu on highest LOI
- We (*Hudson Lab – UIUC*) get weak results with H_2SO_4/KBr/$CuSO_4$ industrially-polluted wetland seds (60-80% recoveries)
- C.M. Tseng et al. microwave HNO_3
- Liang et al. (2003) find HNO_3/$CuSO_4$ ~ distillation > H_2SO_4/KBr/$CuSO_4$ (highly variable recovery)
- Hammerschmidt and Fitzgerald successfully use 2M HNO_3 leaching on LIS

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Acid Leaching/Solvent Extraction

-low artifact/generally good recovery

- Leach in mineral acid and $CuSO_4$
- Toluene Extract (takes neutral MeHg complex and restricts the bulk of anionic Hg^{II})
- Thiourea back-extract
- Load back-extract on thiol trap

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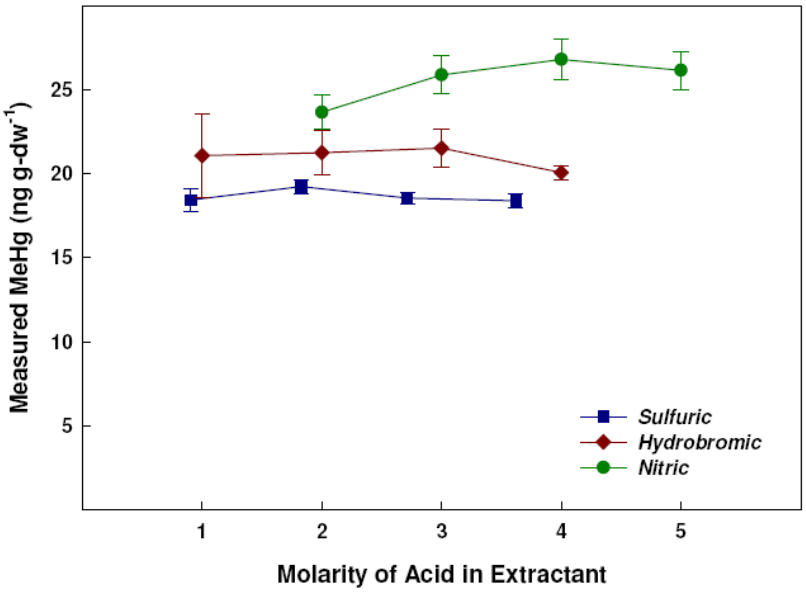
Effects of Acid Types



****Yet, all methods yield certified values of CRM's BCR 580 and DOLT-2****

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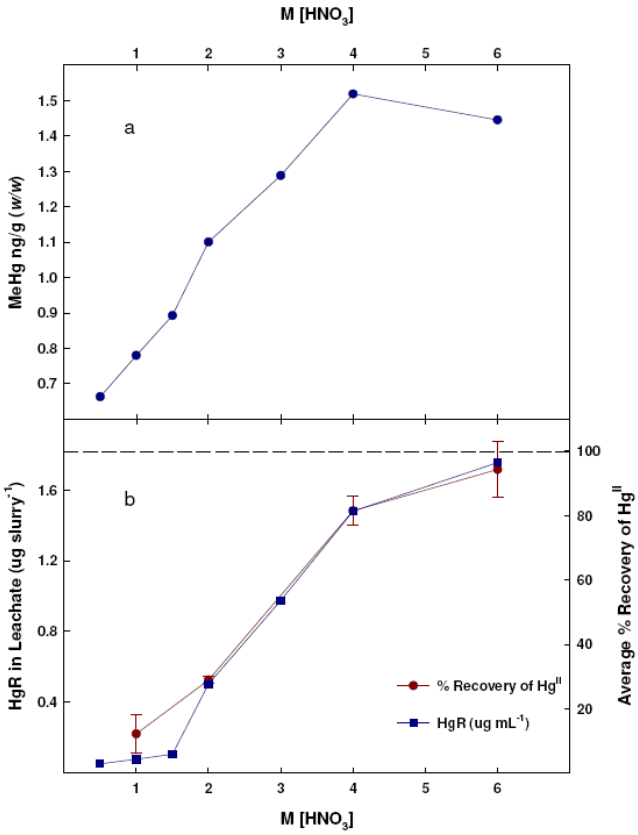

HNO_3 – Titration of sites?

But what are the sites?

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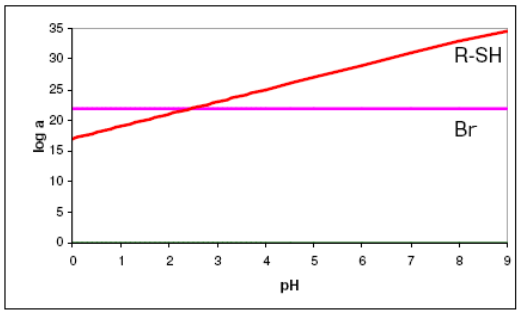
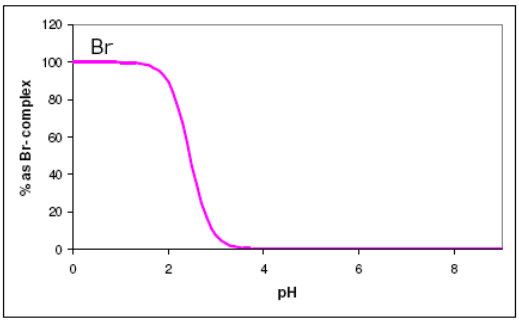
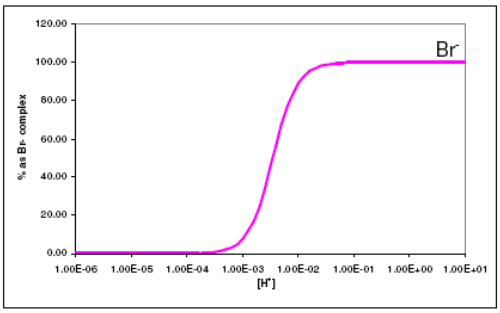
Thiol – Bromide Competition







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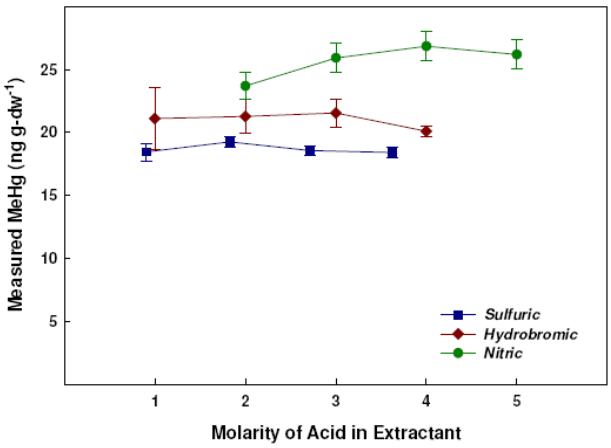

Not related strictly to [H^+]

Not related strictly to [L]

Thus...not thiol competition

What is the key to HNO_3???

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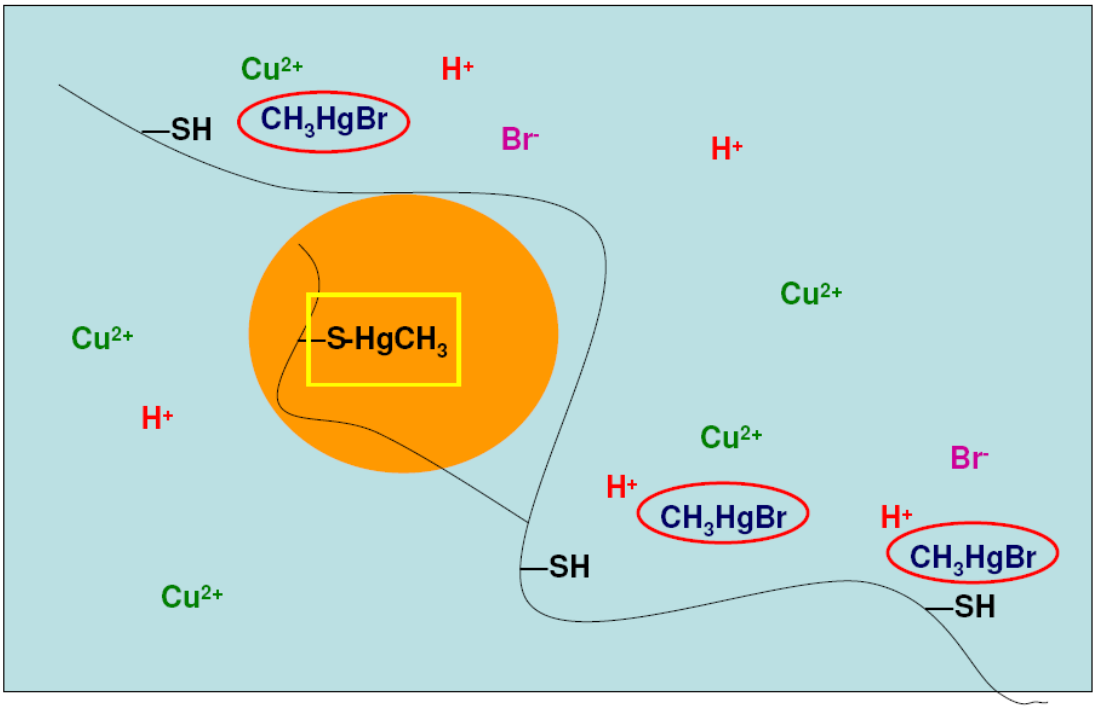
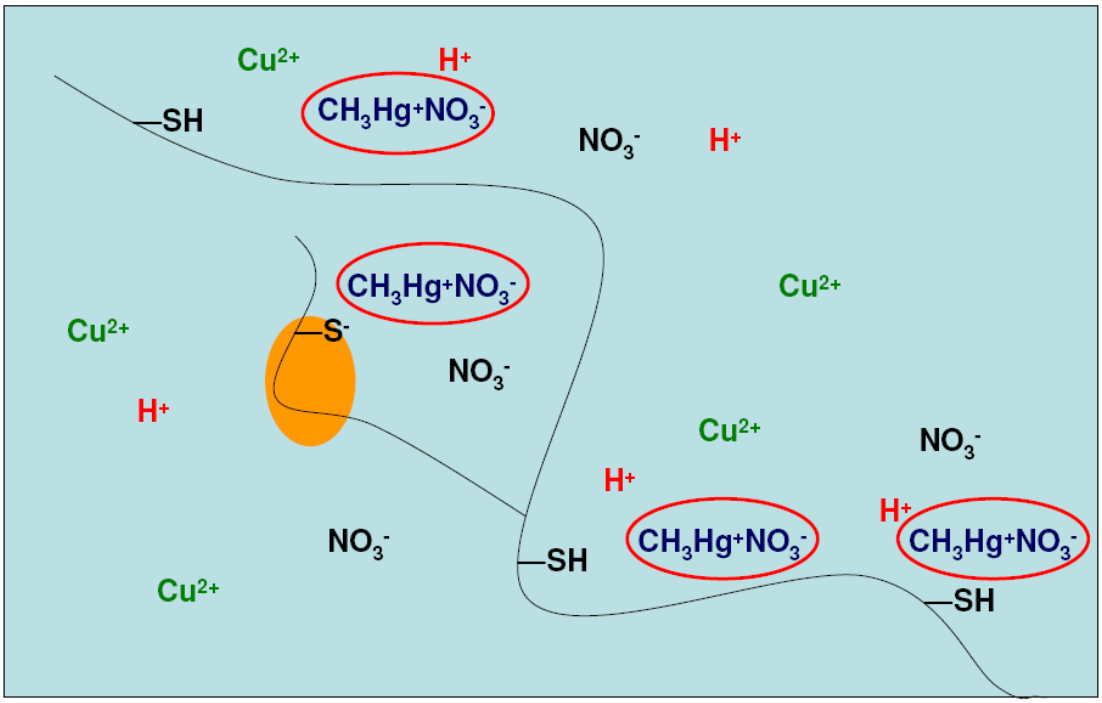
The Hydrophobic Pocket Theory

- Humic material condenses and becomes hydrophobic upon acidification
  - protonation of carboxyl and phenolic groups
- Any hydrophobic compounds in matrix will gather around hydrophic humics
  - natural from flora lipids, waxes
  - anthropogenic petrochemical residues
- Results in humic thiol functionalities being hidden from aqueous acidic extractant
  - both leaving some MeHg behind and giving solbilized MeHgBr a place to partition into and get stuck

Thiol-containing Hydrophobic Pockets - limiting access of aqueous acidic extractant (H_2SO_4/KBr/$CuSO_4$)



Thiol-containing Hydrophobic Pockets – Attacked by HNO_3 (HNO_3/$CuSO_4$)



Take Home Message...

-Highly-Processed Created Samples (e.g. CRM's) do not always reflect the difficult matrix of the real world.

-We need chemistries that can tackle the worst-case scenarios

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PDVB – Polydivinylbenzene "Goodbye to solvents"

- Use SPE cartridges and vacuum extraction manifolds
  - scalable, high-throughput
  - Jordi Associates PDVB – 200mg
- Load with acid leachate (H_2SO_4/KBr, HCl, HNO_3)
  - Sorbs neutral MeHg-Cl,Br complexes and oxoanionic ion-pairs
- Elute with acidic thiourea as cationic MeHg-Tu complex
- Concentrate on thiol trap

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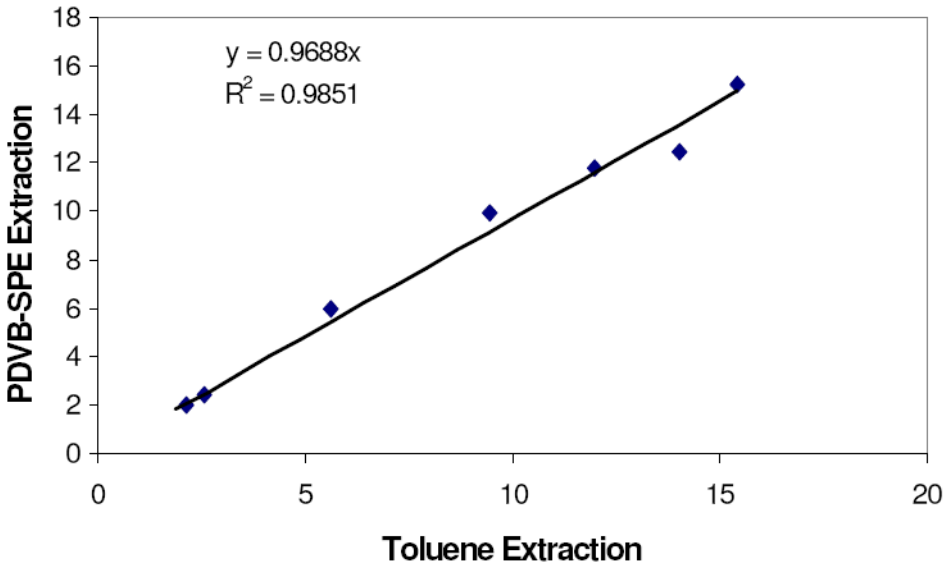
Toluene-PDVB Comparison



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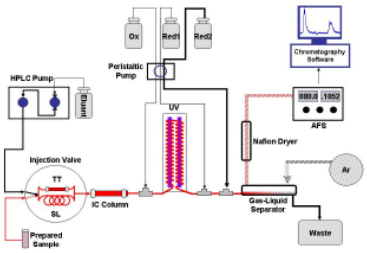
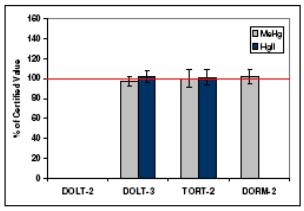
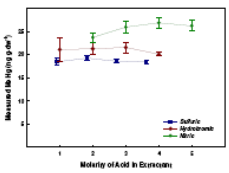


Conclusions

•Hg-Tu IC/CVAFS provides a robust and sensitive, automatable speciation and detection system for MeHg and Hg^{II}

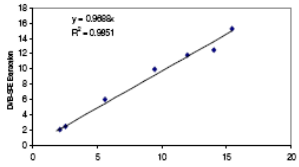


•Eluant leaching provides simple extraction for simulatneous MeHg and Hg^{II} analysis



•$HNO_3/CuSO_4$ provides superior release of MeHg from sediment sites over $H_2SO_4/KBr/CuSO_4$ by accessing sites unavailable to other acid leachants

•PDVB SPE provides scalable solvent-free alternative to MeCl and Toluene



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ANALYTICAL METHODS FOR SELENIUM SPECIATION: THE GOOD, THE BAD, AND THE UGLY

Gerads, Russell and Gürleyük, Hakan; Applied Speciation and Consulting, LLC

The dissemination of information regarding the toxicity associated with different selenium species has significantly increased the demand for selenium speciation analysis. Historically, scientists and industrial experts have relied heavily on older methodologies (hydride generation) which retained considerable interferences and limitations. The facts associated with two different analytical methods for selenium speciation will be presented as they currently apply to real world samples.

ANALYTICAL AND PREPARATORY ISSUES ASSOCIATED WITH TOTAL SELENIUM AND SELENIUM SPECIATION ANALYSIS

Gerads, Russell and Gürleyük, Hakan; Applied Speciation and Consulting, LLC

Many treatment plants are struggling to meet the stringent NPDES permit limits on selenium discharges from their waste streams. While treatment of selenium remains to be a challenging task, different analytical methods can generate inaccurate results for total selenium and selenium speciation analyses compounding the complexity of the problem. Since important treatment decisions are made using these analytical results, the ramifications of generating poor analytical data cannot be understated.

Current EPA methods for the determination of total and dissolved selenium were not designed for the complex waste streams generated by treatment plants. The sample collection container, preservative, digestion technique, selenium species present in solution, and applied analytical method can have significant impacts on the representativeness of the results. In addition, significant biases have been identified with various analytical techniques for selenium speciation which are being applied throughout the industry and consistently fail to provide the necessary information to solve the problem.

Issues associated with various sampling, preservation, digestion, and analytical techniques will be discussed to identify their applicability to many environmental samples. A comparison between different analytical techniques for selenium speciation analysis will be presented and additional information regarding the interaction of certain selenium species will be reviewed to provide a more robust understanding of the complexity of selenium in the environment.

Improved Bromate/Bromide Speciation in Drinking Water by HPLC/ICP-MS

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PerkinElmer Life and Analytical Sciences

ABSTRACT

Water for public consumption must be purified prior to distribution. A number of processes are used for water purification, including treatment with ozone to kill bacteria. While this method is effective, ozonolysis can also convert bromide (a natural component of many waters) into bromate (BrO_3^-), a carcinogen. Therefore, the need exists to measure bromate in drinking waters, which means that it must be measured separately from other forms of bromine. Current methods for measuring bromate and bromide involve separating the bromine-containing components by ion chromatography and using ICP-MS as a detector monitoring bromine at m/z 79; this is the protocol stated in EPA method 321.8.

This work focuses on bromide/bromate speciation by ion chromatography using Dynamic Reaction Cell (DRC) ICP-MS as the detector. Methodology on a new column is developed, speeding up the method by more than a factor of two. Waters from around the world are analyzed, some showing a variety of peaks. Techniques to identify the peaks are explored and a scheme for analysis is presented.

INTRODUCTION

Bromine is a natural component found in waters, most commonly as the bromide ion – Br^-. A common procedure for purifying drinking waters is treatment with ozone to kill bacteria. A byproduct of ozonolysis is the conversion of bromide to bromate (BrO_3^-), a known carcinogen. Therefore, a need exists to measure both bromide and bromate in drinking waters, as opposed to total bromine content.

Our earlier work on bromine speciation focused on separating Br^- and BrO_3^- via anion exchange HPLC, and detecting the species with ICP-MS[1]. The method proved rugged, but required eight minutes per sample. This work focuses on significantly decreasing the analysis time and also explores the possibility of separating other bromine-containing compounds which were found in several water samples.

EXPERIMENTAL

HPLC Conditions

A PerkinElmer Series 200 HPLC system, consisting of a quaternary pump, autosampler (with polypropylene vials), vacuum degasser, and peltier column oven, was used for all analyses. The separation was done with an anion exchange column (ZirChrom®-SAX ; ZirChrom Separations Anoka, MN USA).

Both isocratic and gradient HPLC methods were explored. For samples containing only bromide and bromate, the isocratic method was preferred due to the higher sample throughput. For samples containing additional bromine compounds, the gradient method was used. Details of both methods are shown in Tables 1 and 2, respectively. It should be noted that no pH adjustments were made on the mobile phases; the pHs used were those that resulted from mixing the mobile phase components at the concentrations specified.

Table 1: HPLC Isocratic Method Parameters

HPLC System	Series 200 Quaternary Pump, Autosampler, Vacuum Degasser, Peltier Column Oven
Column	ZirChrom®-SAX (3µm, 100 x 4.6 mm)
Mobile Phase	18 mM NH_4OH + 3 mM HNO_3;
pH	10.2
pH Adjustment	None
Flow Rate	1.5 mL/min
Column Temperature	50°C
Injection Volume	50 µL
Run Time	4 minutes
Total Analysis Time	4 minutes

Table 2: HPLC Gradient Method Parameters

HPLC System	Series 200 Quaternary Pump, Autosampler, Vacuum Degasser, Peltier Column Oven
Column	ZirChrom®-SAX (3µm, 100 x 4.6 mm)
Solvent A	14 mM NH_4OH + 6 mM HNO_3; pH=7.3
Solvent B	18 mM NH_4OH + 3 mM HNO_3; pH=10.2
Gradient Profile	2 min at 100% A Step to 100% B 4 min at 100% B

ICP-MS Conditions

Detection of the HPLC eluent was accomplished with an ELAN DRC II (PerkinElmer/Sciex, Shelton CT, USA). Instrumental conditions are listed in Table 3. All analyses were done in standard mode (i.e., no reaction gas was used) monitoring Br^+ at m/z 79. Those samples which produced chromatograms containing additional peaks were also analyzed in DRC mode, monitoring BrO^+ at m/z 95 and 97. The presence of the same peaks at both bromine isotopes in DRC mode (as well as in standard mode) confirms that the additional peaks contain bromine and are not the result of interferences.

Table 3: ICP-MS Conditions

Instrument	ELAN DRC II
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Dwell Time	250 ms
Analytes	Standard Mode - $^{79}Br^+$ DRC Mode - $^{79,81}BrO^+$ (m/z 95, 97)
Reaction Gas	Standard Mode - None DRC Mode - N_2O = 0.5
RPq	Standard Mode - 0.25 DRC Mode – 0.50

Standards and Samples

Bromide and bromate standards were made daily from 1000 mg/L stock solutions (Spex, Charleston, SC, USA) by dilution in ASTM Type I water.

Samples consisted of bottled waters purchased at local grocery stores from various countries and water collected directly from the tap. No sample preparation or dilutions were used, aside from filtering the waters which contained visible particulates.

Software

All instrument control and data processing and analysis was accomplished with Chromera™ software (PerkinElmer LAS, Shelton, CT USA). Peak areas and external calibration curves were used for quantitative measurements. The calibration standards were diluted with ASTM Type I water, and the concentration levels were chosen to cover the range where the majority of species were found, although occasional samples produced concentrations higher than the highest calibration standard.

RESULTS AND DISCUSSION

Figure 1 shows a chromatogram of a 10 µg/L mixed standard containing both bromate and bromide. The species are separated and baseline-resolved in less than three minutes. Figure 2 displays a chromatogram of a 1 µg/L mixed standard. The intensities of the peaks are about two times baseline noise, signifying the lower level which can be measured. Larger injection volumes would allow lower levels to be measured, but could overload the column at higher concentrations.

Figure 1: Chromatogram (Isocratic LC Method) of a Standard Containing 10 µg/L of Bromide and Bromate

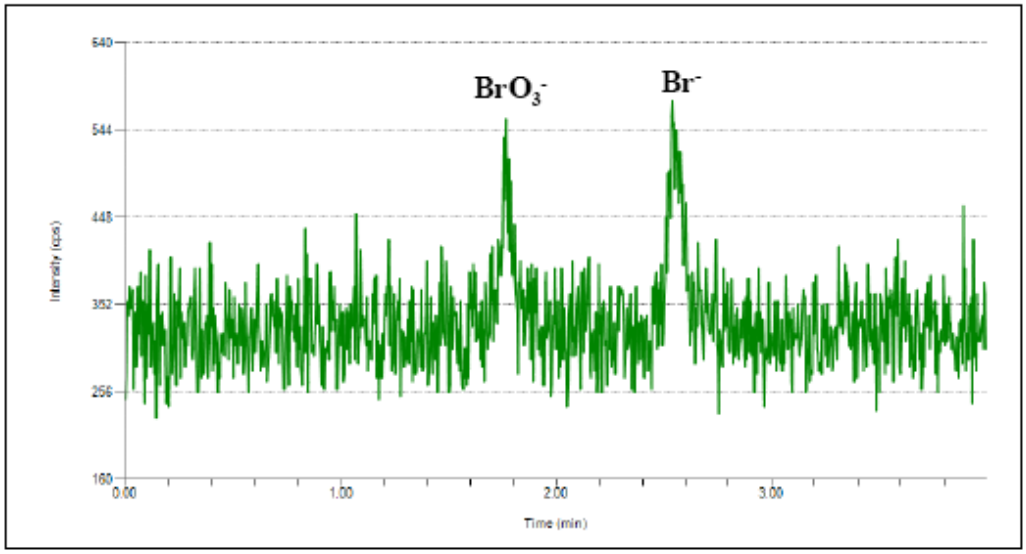

Figure 2: Chromatogram (Isocratic LC Method) of a Standard Containing 1 µg/L of Bromide and Bromate

Once the separation was established, the method was applied to a number of drinking water samples. To determine the reliability of the method, the samples were measured in duplicate on four non-consecutive days; the results appear in Table 4. The small variation in the results indicates the robustness of the method. Additionally, a single sample was analyzed 49 times consecutively over a period of 3.75 hours. Figure 3 shows the chromatograms overlaid from this study, as well as the average concentration and standard deviation of the measurements. Additionally, the relative standard deviation of the retention times for both peaks is 0.5 and 0.4, respectively. Taken together, these tests demonstrate the ruggedness and repeatability of the method.

Table 4: Quantitative Determination of Bromide and Bromate in Water Samples Over Four Days (All units in µg/L)

Sample	Day 1		Day 2		Day 3		Day 4	
	BrO_3^-	Br^-	BrO_3^-	Br^-	BrO_3^-	Br^-	BrO_3^-	Br^-
Australia	---	39.9	---	40.8	---	40.4	---	42.6
Brazil	---	6.91	---	6.53	---	7.02	---	7.40
Spain	---	23.0	---	22.7	---	22.4	---	22.6
Thailand-1	75.2	12.5	82.9	11.3	82.3	9.74	24.4	8.35
Thailand-2	83.6	---	81.1	---	78.1	---	79.3	---
Thailand-3	39.5	10.2	42.8	9.21	42.1	8.79	44.3	8.43
US-1	---	10.7	---	10.0	---	10.1	---	8.36
US-2	---	233	---	237	---	228	---	231
China-1	20.0	6.72	22.9	7.23	22.0	5.14	19.8	6.13
China-2	17.2	12.4	17.2	12.6	17.0	13.4	15.0	12.8
China-3	14.2	416	23.0	422	23.0	400	26.1	421
China-4	99.2	13.9	124	15.4	120	43.4	113	41.5
China-5	---	68.1	---	67.1	---	66.5	---	66.9

All samples are bottled waters, except China 3 and China 5 which are tap waters

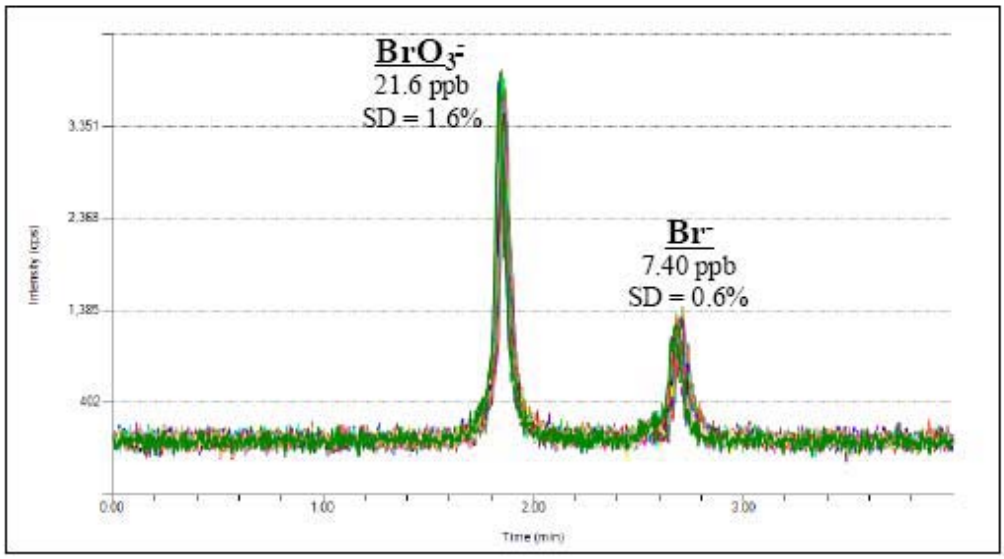

Figure 3: Overlay of 24 Chromatograms (Isocratic LC Method) of a Water Sample Obtained by Consecutive Injections - The average concentrations and standard deviation for each species are shown.

Figure 4 displays chromatograms of two samples which contain peaks in addition to bromate and bromide. To confirm that these peaks are really Br-containing species and not interferences, these samples were analyzed in DRC mode. For this study, BrO^+ was monitored at m/z 95 and 97, representing both bromine isotopes. The conversion of Br^+ to BrO^+ was accomplished by reaction with N_2O in the reaction cell, according to the following gas phase chemical reaction[2]:

$$Br^+ + N_2O \rightarrow BrO^+ + N_2 \quad k = 2.80 \times 10^{-10}\ cm^3s^{-1}$$

The relatively high value of the rate constant k signifies that the reaction occurs rapidly, indicating that it is easily accomplished in the reaction cell.

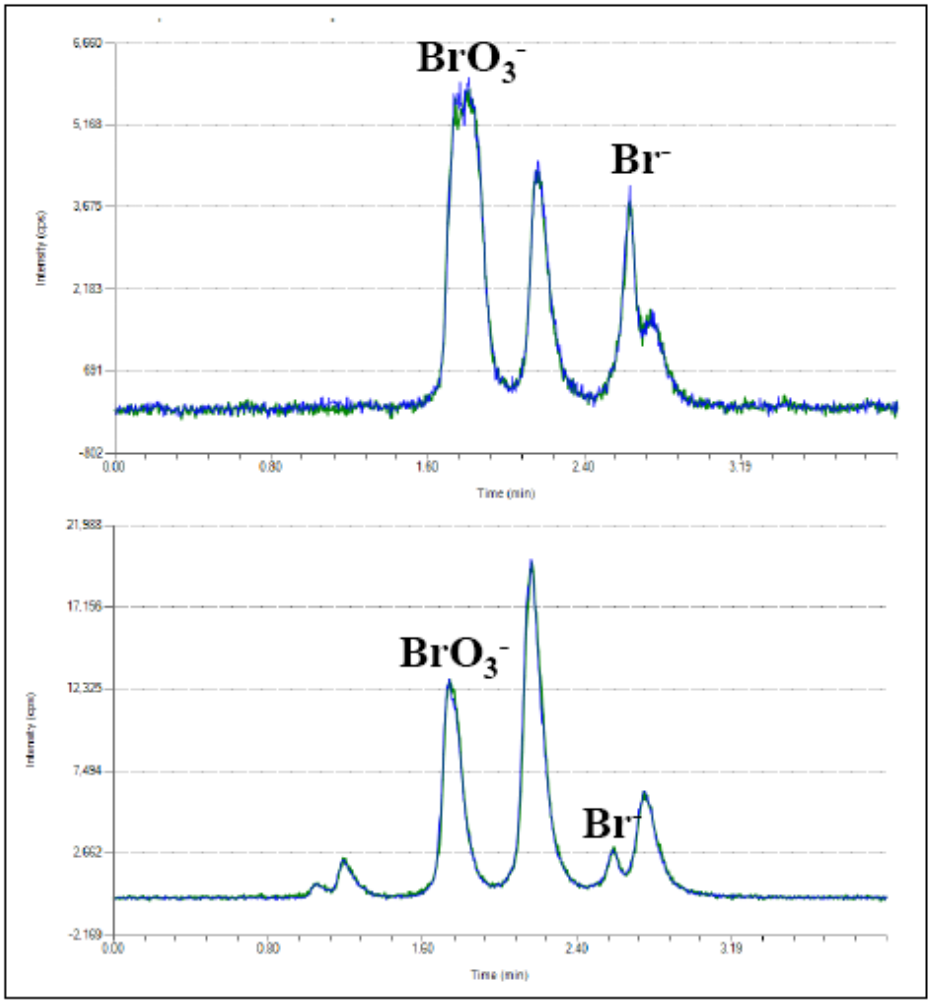

Figure 4: Chromatograms (Isocratic LC Method) of a Water Sample Containing Multiple Peaks: Bromide, Bromate, and Unidentified Species

Figure 5 shows overlaid chromatograms of BrO^- at m/z 95 and 97 for the two samples displayed in Figure 4. Because the chromatograms of both bromine isotopes in DRC mode are the same and match the chromatograms acquired in standard mode (Br 79), it can be concluded that the extra peaks are Br-containing species and not interferences.

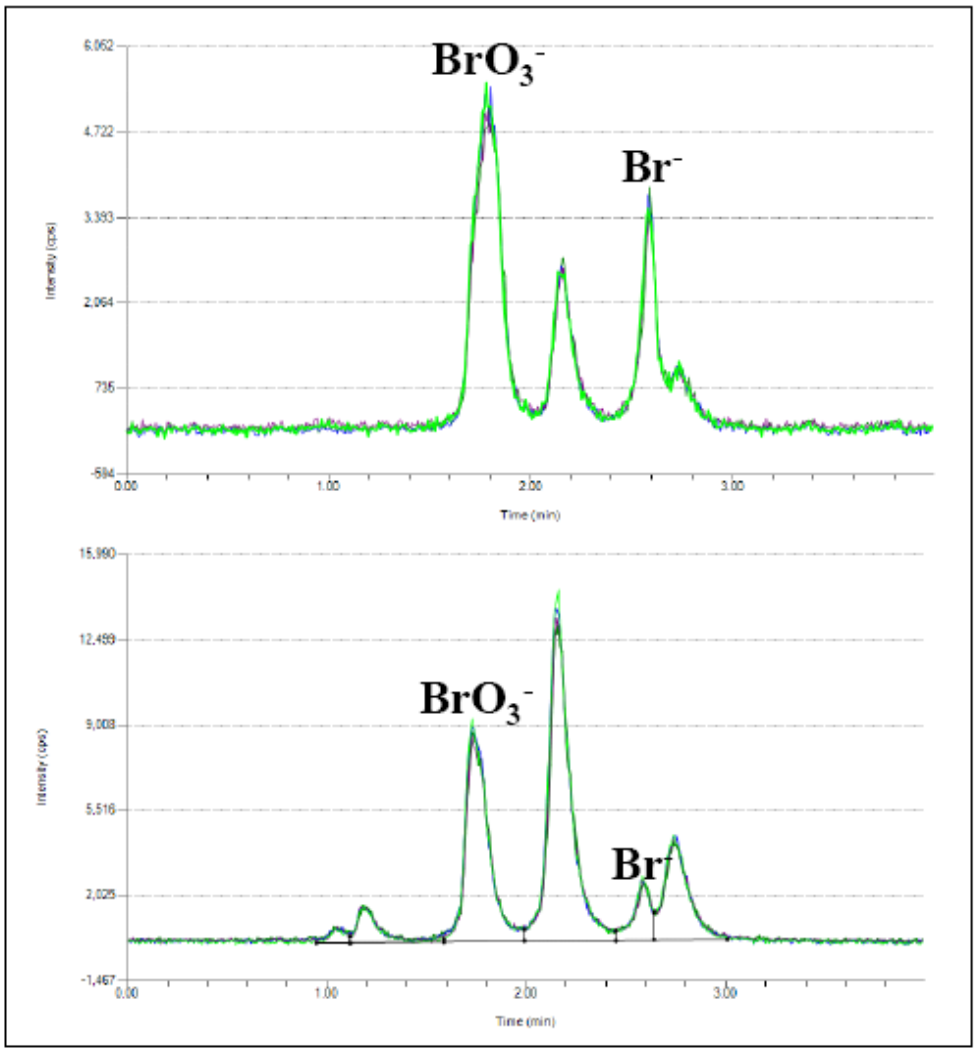

Figure 5: Chromatograms (Isocratic LC Method) of the Same Samples as in Figure 4, but Acquired in DRC Mode - For each sample, 2 chromatograms are overlaid: BrO^+ at m/z 95 and 97

A gradient HPLC separation scheme was then developed to separate the additional compounds. Figure 6 shows chromatograms of the two water samples shown in Figure 4, but with a gradient HPLC method. The additional peaks in Figure 6 (as compared to Figure 4) confirm the presence of additional Br-containing species and indicate the need to perform a gradient separation to obtain true BrO_3^- concentrations. Further confirmation is presented in Figure 7, which shows the DRC-mode chromatograms for the gradient separation of the samples in Figure 6. Table 5 shows the quantitative results of bromate and bromide for the water samples analyzed under the gradient method.

When comparing the results of the isocratic and gradient separations in Tables 4 and 5, a few waters showed higher bromate concentrations with the isocratic method than the gradient method (Thailand 1 and 3, China 3 and 4). The reason for this is incomplete separation of unidentified species which co-elute with bromate with the isocratic method.

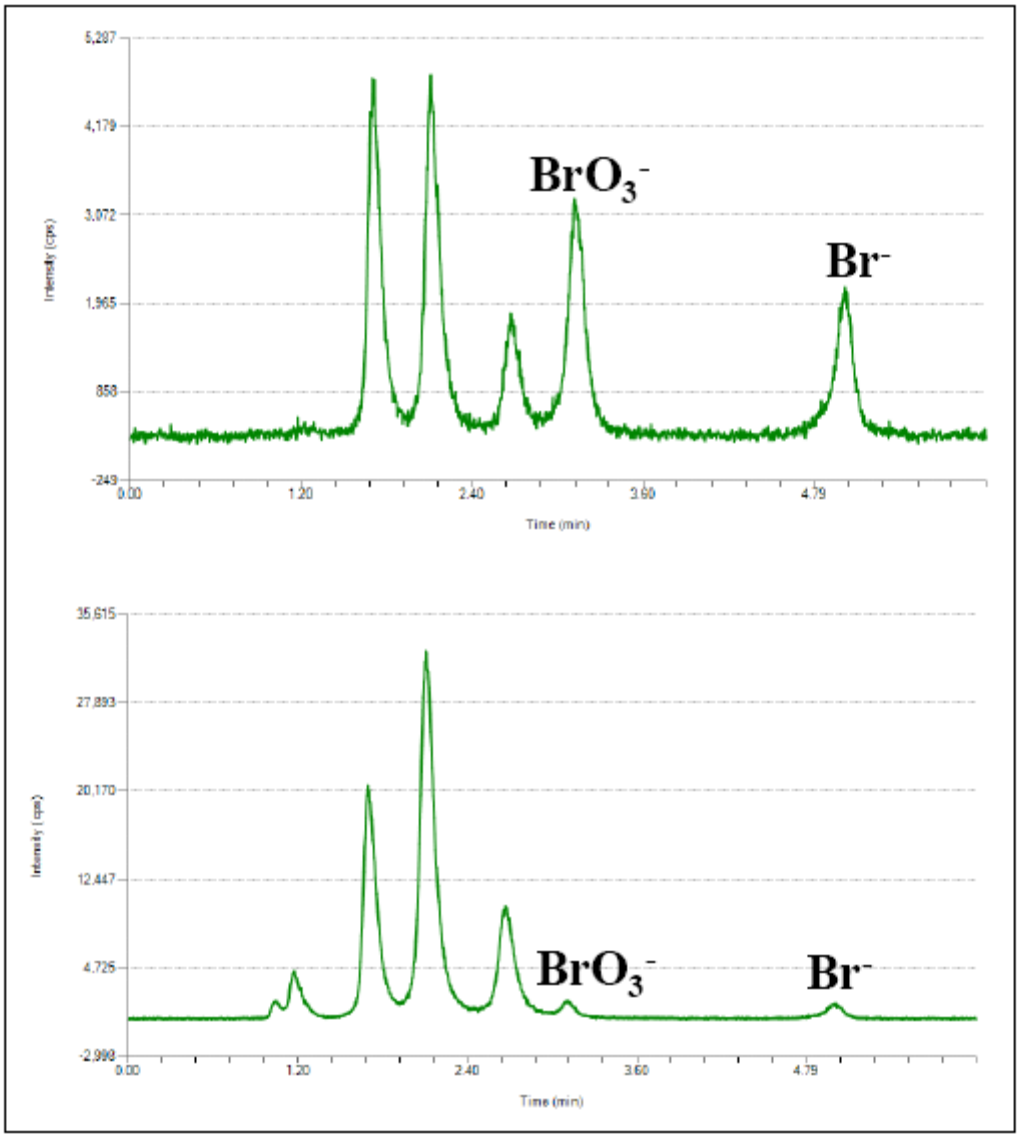

Figure 6: Chromatograms of the Samples in Figure 4, but Obtained with a Gradient LC Method

Although this incomplete separation leads to false high results, the combination of the isocratic and gradient methods could be used in tandem, with the isocratic method used for rapid screening, and the gradient method used for samples showing bromate concentrations above a pre-defined level method with the isocratic method. Since both methods use the same column and mobile phase components, switching between methods is simple.

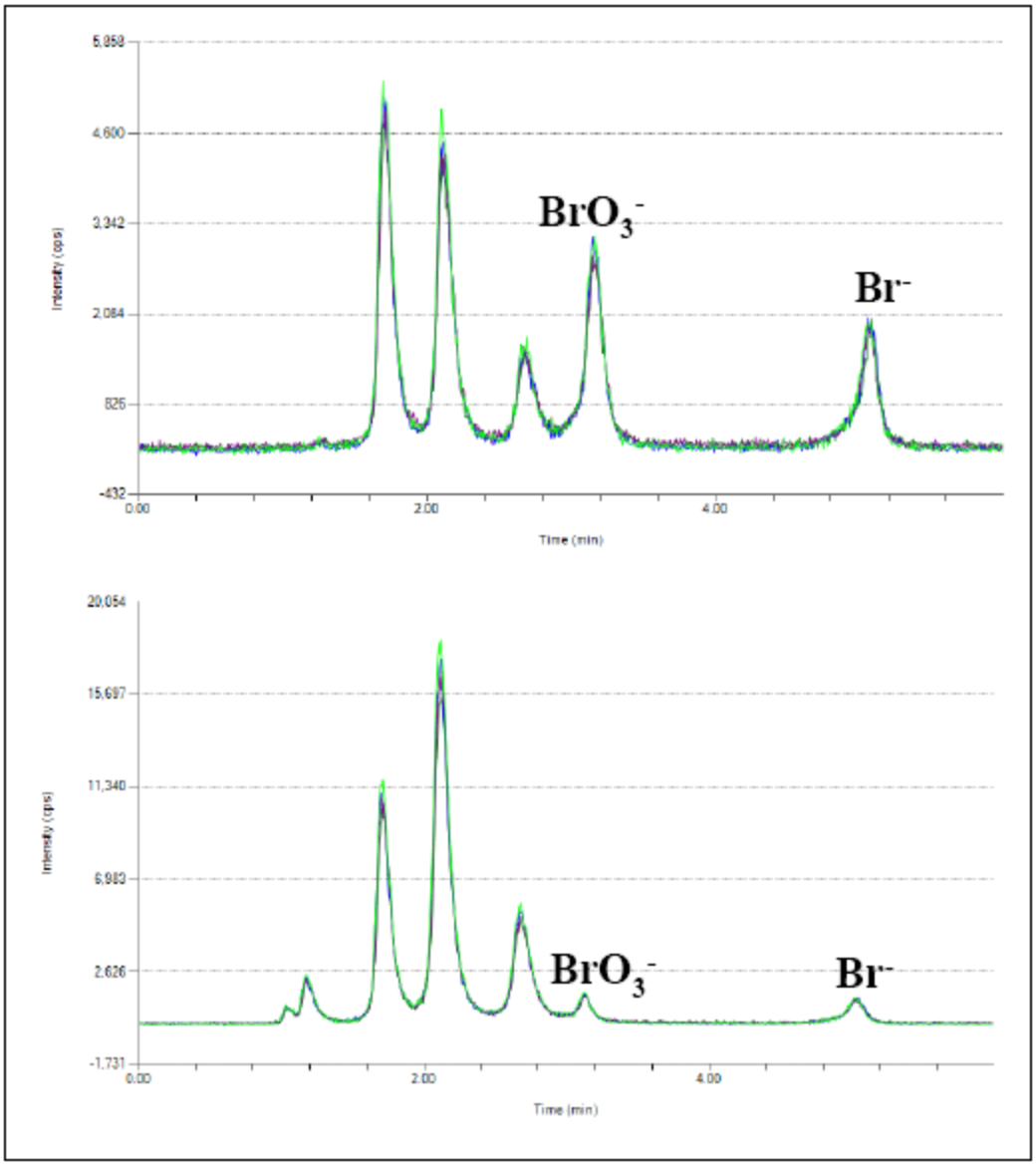

Figure 7: DRC-mode Chromatograms of the Samples in Figure 6, Obtained with a Gradient LC Method

It should be noted that no work was done to identify the additional bromine species. This could be accomplished with HPLC/ICP-MS by analyzing other known bromine-containing compounds and matching retention times with the unidentified bromine compounds. Another option would be to use LC/MS, which might allow the unknown species to be identified by examining the fragmentation pattern of the compounds. However, a main limitation of LC/MS is it's low-sensitivity, relative to LC/ICP-MS.

Table 5: Quantitative Determination of Bromide and Bromate in Water Samples with the Gradient HPLC Method (All units in µg/L)

Sample	BrO_3^-	Br^-
Australia	---	38.1
Brazil	---	7.94
Spain	---	23.5
Thailand-1	37.4	17.3
Thailand-2	76.0	---
Thailand-3	3.03	9.36
US-1	---	8.79
US-2	---	224
China-1	20.8	7.41
China-2	16.1	11.9
China-3	---	380
China-4	14.0	11.8
China-5	---	64.6

All samples are bottled waters, except China 3 and China 5 which are tap waters

CONCLUSION

This work has demonstrated a rapid, robust method for separating and measuring bromide and bromate in drinking waters. The separations are accomplished in less than three minutes and proved to be repeatable from injection to injection and over several days. For those waters containing additional bromine-containing species, a gradient HPLC method was established. Taken together, the isocratic separation scheme can serve as a rapid screening method; those samples which contain additional bromine species can then be analyzed by the longer gradient method. If lower levels need to be measured, the injection volume of the HPLC autosampler can be increased.

REFERENCES

1. Perrone, P.A., Reuter, W.M., Neubauer, K.R., Bosnak, C.P., Hall, G.A., Grosser, Z.A, *Bromine Speciation by HPLC/ICP-MS* (Application Note), 2005, PerkinElmer LAS.

2. Anicich, V.G. *An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics*, 2003, National Aeronautics and Space Administration.

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Improved Bromate/Bromide Speciation in Drinking Water by HPLC/ICP-MS

Pamela A. Perrone, Wilhad M. Reuter, Kenneth R. Neubauer, Zoe A. Grosser

PerkinElmer Life and Analytical Sciences

Shelton, CT USA

Bromate

PerkinElmerSCIEX™

- Bromide (Br^-) is naturally occurring in water, bromate (BrO_3^-) is not
- Bromate forms when water containing bromide is treated with ozone purification
- Bromate is toxic with suspected carcinogenic properties
- Regulated US drinking water MCL is 10 μg/L (FR Dec 16, 1998)
- FDA mandated 10 μg/L limit in bottled water (2002)
- Added to California proposition 65 list

Page 2

US EPA Method 321.8

PerkInElmerSCIEX™

- Developed in 1997 for bromate analysis
- Ion chromatography used for separation
- Five bromine-containing species separated in 12 minutes
- MDL of 0.3 μg/L determined for bromate

- 1997 is a long time ago in speciation development
- Newer information on occurrence and typical levels may aid in refining the method
- The possibility of multielement work may more effectively use the detector

Page 3

Schematic of an HPLC/ICP-MS System

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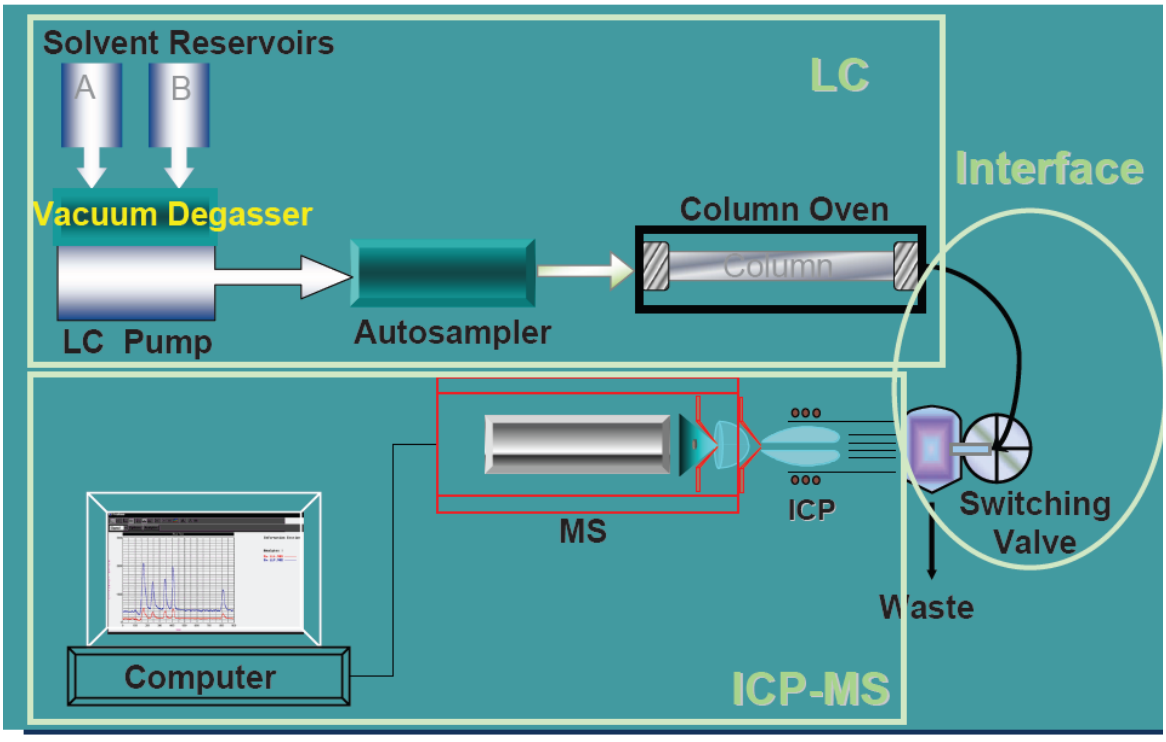

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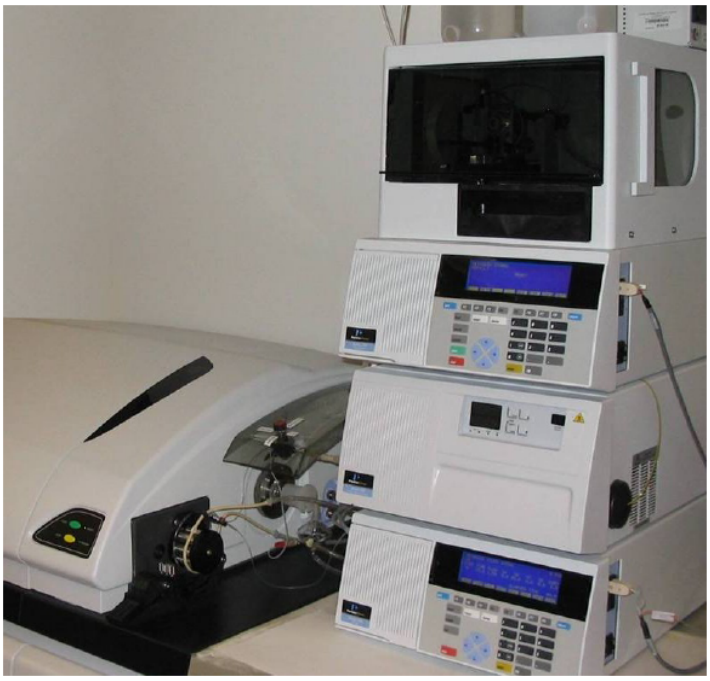
Typical HPLC/ICP-MS system



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Challenges

- Which species are important?
- Developing a chromatographic method to separate the various species of interest
- Understanding the effects of different matrices on the chromatography

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Previous Work - Ion Exchange Chromatography

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- Method developed to separate two species most often found in drinking water, Br^- and BrO_3^-
- Use Hamilton PRP-x100, 5 µm x 15 cm column (anion exchange)
  - Same column as for As speciation in urine
  - Different mobile phase
- Advantages
  - Achieves good separation
  - Simple mobile phase (HNO_3 + NH_4OH)
  - Clean mobile phase components
- Disadvantages
  - Longer chromatography than desired

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Ion Exchange Chromatography

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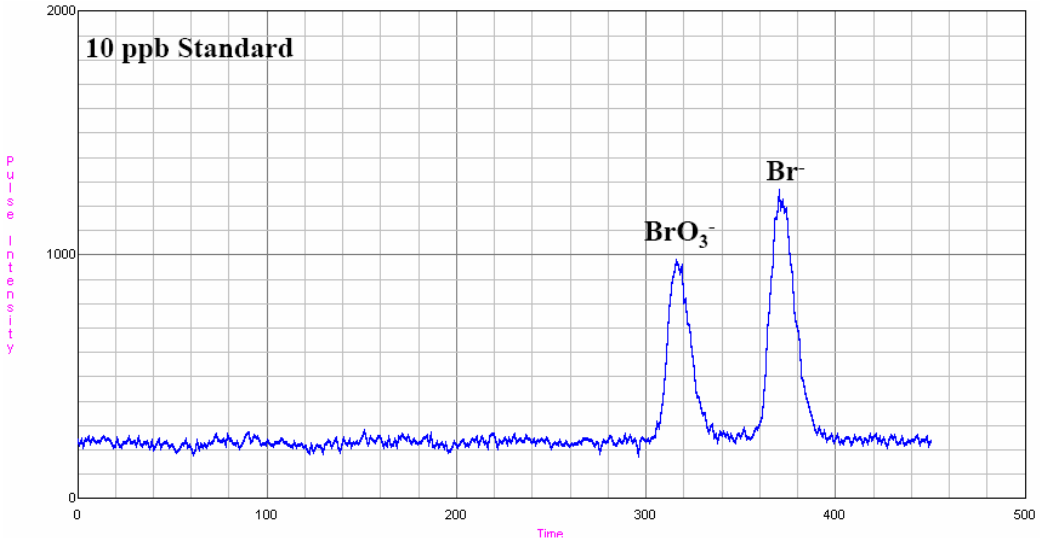
Good separation of the components of interest!



Bromine Speciation by HPLC/ICP-MS, Application Note 007303_01, PerkinElmer Life and Analytical Sciences, Shelton, CT USA

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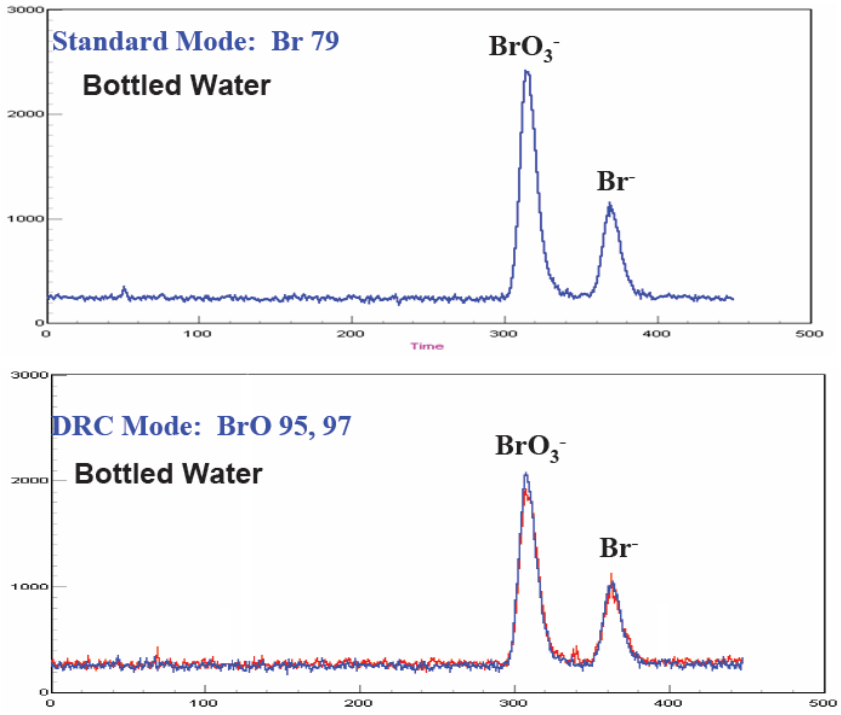
Comparison of Std and DRC Modes



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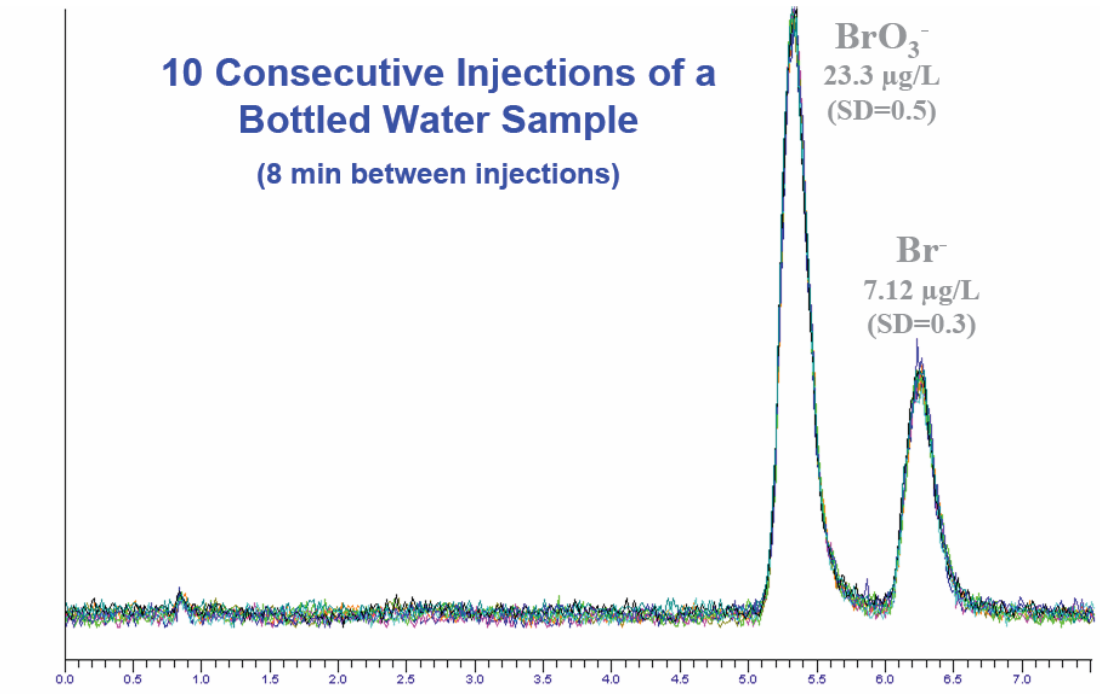
Injection Stability



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Low Concentrations

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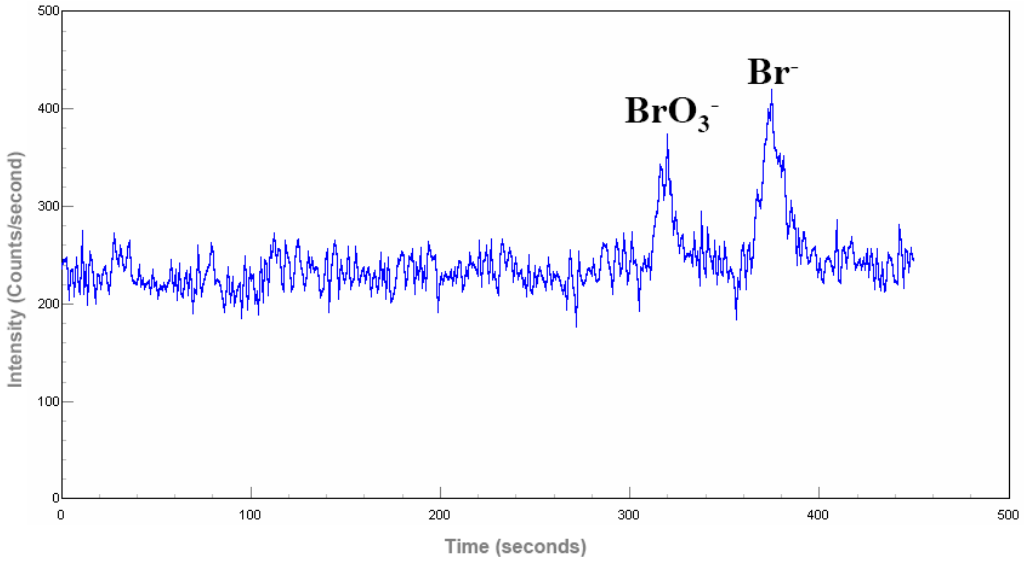
Chromatogram of a standard containing 1 µg/L each of bromate and bromide.



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Improvements

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- The original method takes 8 minutes for the chromatography to occur
- Faster chromatography would provide a better match to the detector (ICP-MS) and provide better throughput

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HPLC Conditions: Br Speciation Improved

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HPLC System	PerkinElmer Model 200 Quaternary Pump, Column Oven, and Autosampler
Column	3μm x 10 cm ZirChrom - SAX
Mobile Phase	18 mM NH_4OH + 3 mM HNO_3
Flow Rate	1.5 mL/min
pH	10.2
pH Adjustment	None
Injection Volume	50 μL
Sample Preparation	None
Samples	Various waters (non-acidified)

Different column used, isocratic method

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ICP-MS Conditions: Br Speciation

PerkinElmer SCIEX

Instrument	ELAN DRC II
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Analytes	Br^+ (m/z 79)
Dwell Time	250 ms

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Calibration – 5, 10, 50, 100 ppb

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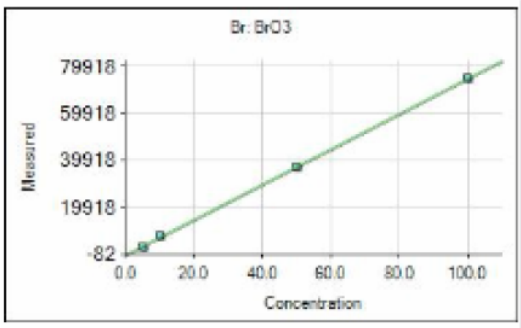
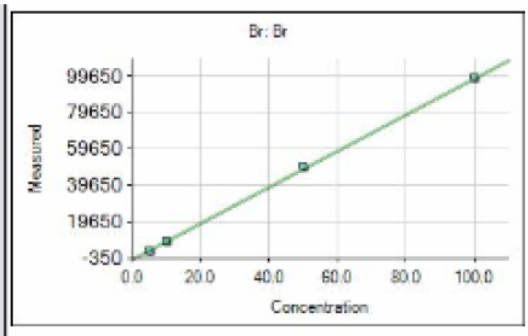
BrO_3^-



y = 751.1874x + -82.0279

R-Squared: 0.999959

Br^-



y = 991.7658x + -349.6351

R-Squared: 0.999872

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Brazil – Indaia – 2 Injections

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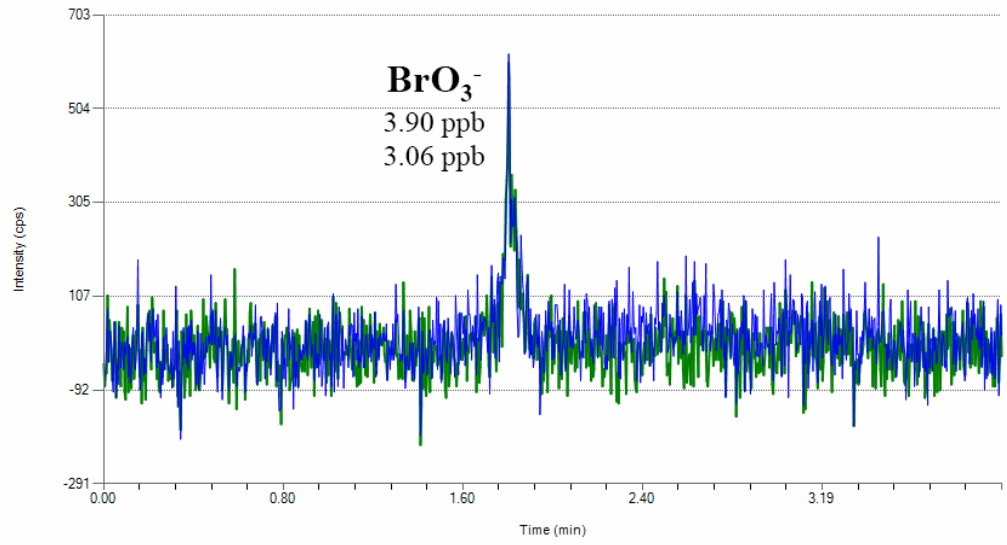

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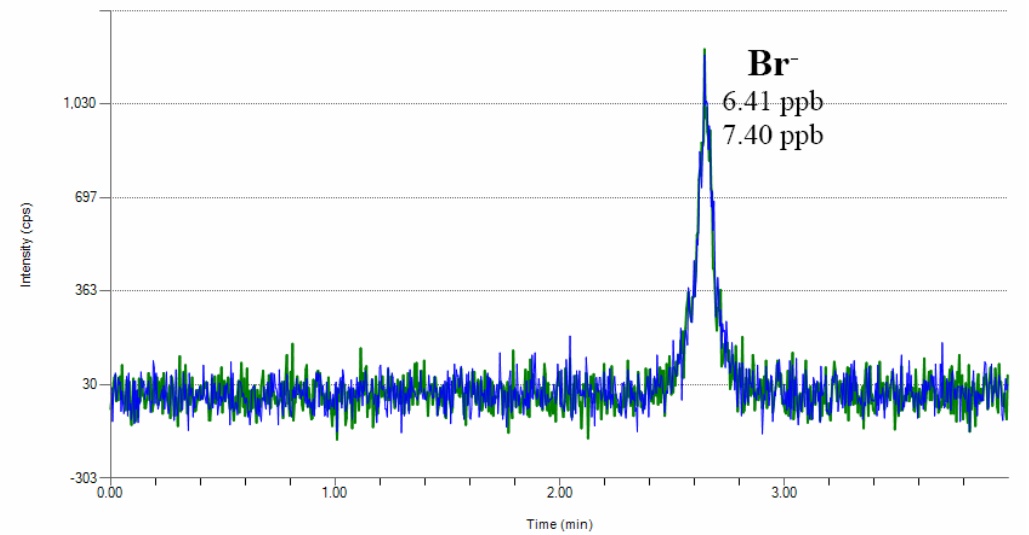
Brazil – Crystal Spa – 2 Injections



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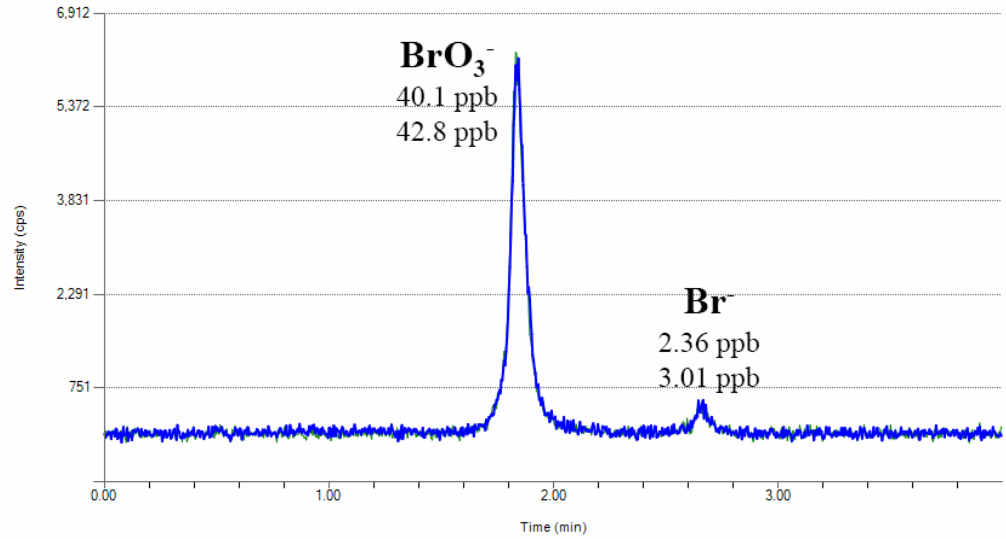
Mexico – Bonafont – 2 Injections



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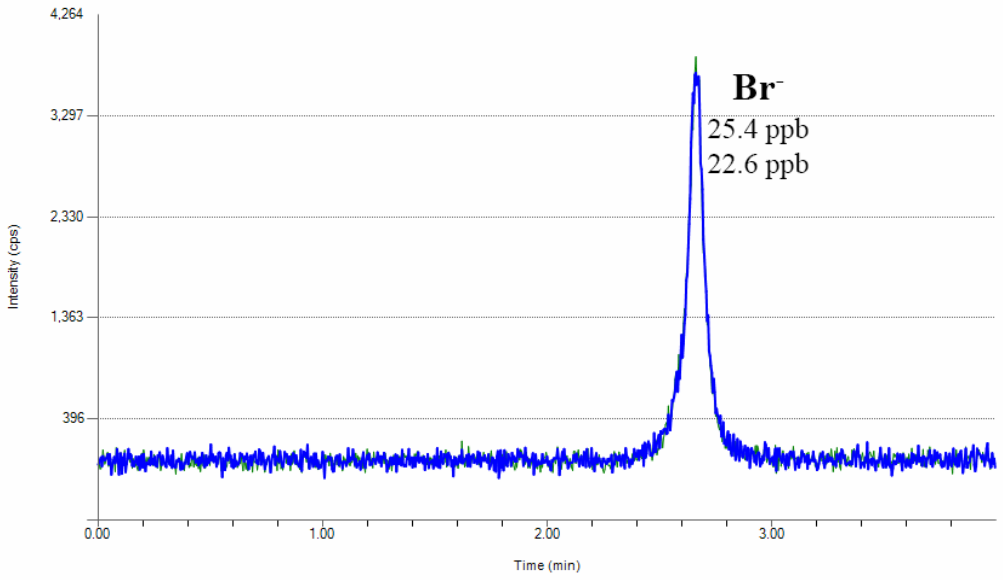
Spain – Font Vella – 2 Injections



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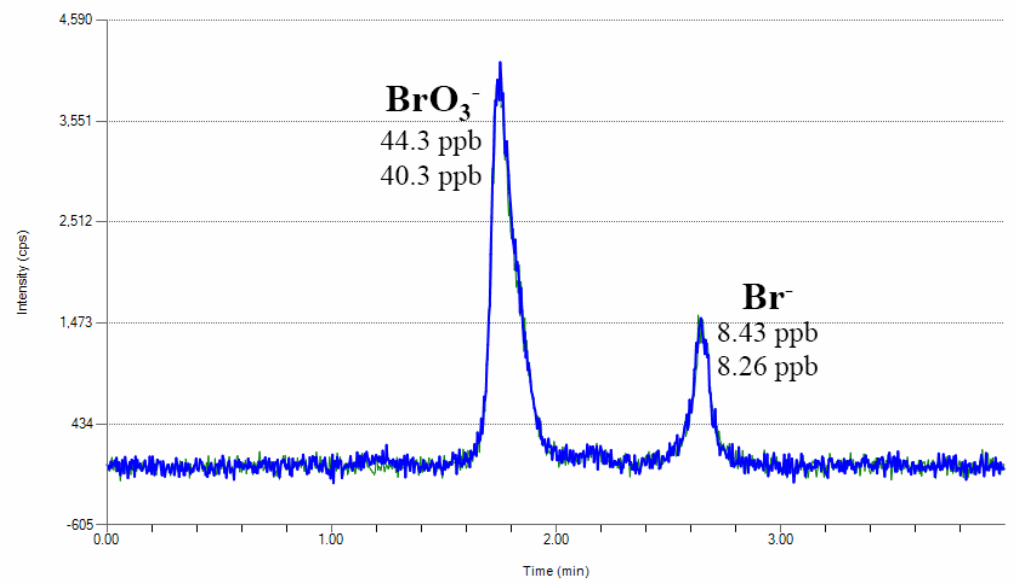
Thailand – Namthip – 2 Injections



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China – Qingchun – 49 Injections – 3 hrs 45 min

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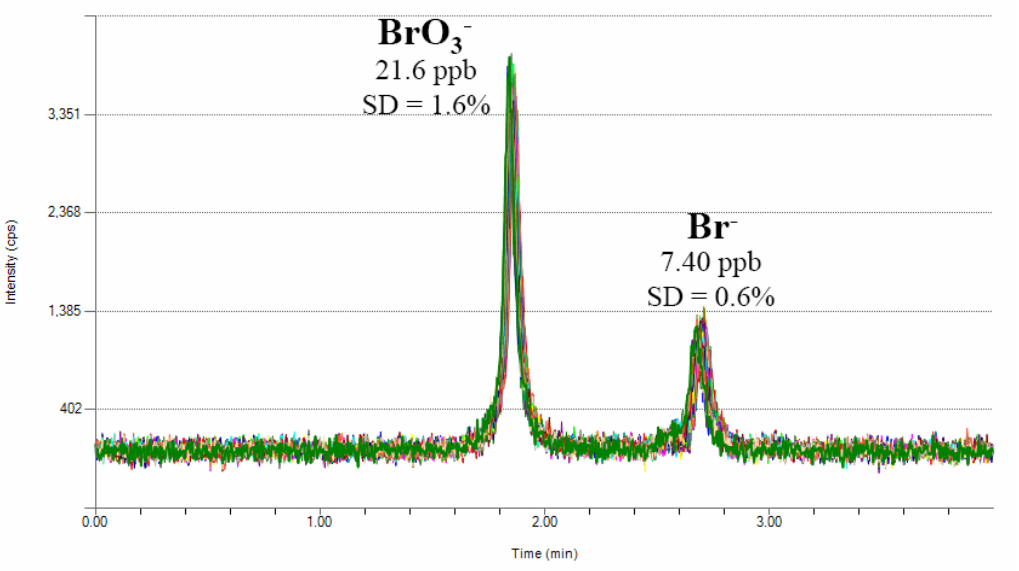

Good short-term precision

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Three-day (nonconsecutive) Reproducibility

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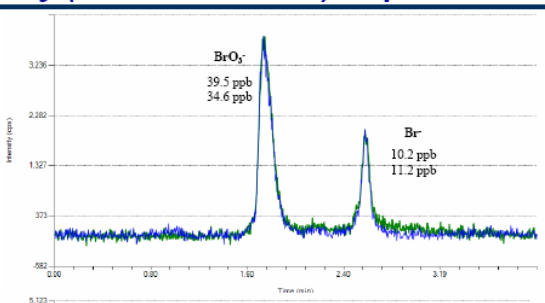
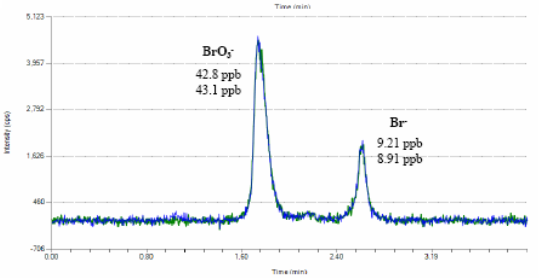
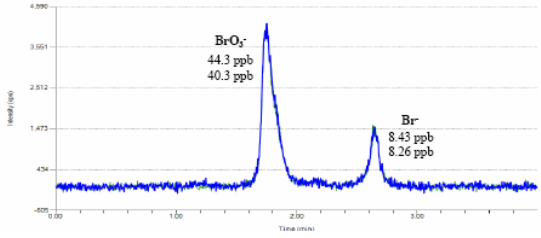
Day 1



Day 2



Day 4



Compound	Average (µg/L) ppb	SD (µg/L)
BrO_3^-	40.8	3.5
Br^-	9.4	1.1

Good longer-term precision

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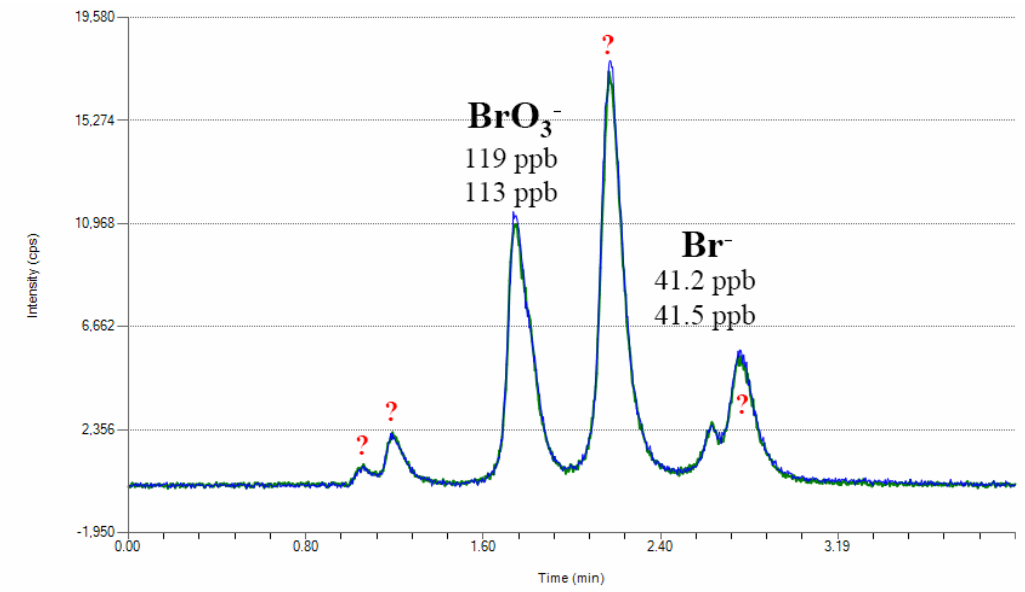
China – Waterman – 2 Injections



Page 23

Summary – New Column

- Separation of species of interest good
- Precision of replicate injections within 20%
- Precision over several days excellent
- Detection capability estimated to be <0.5 ppb bromate

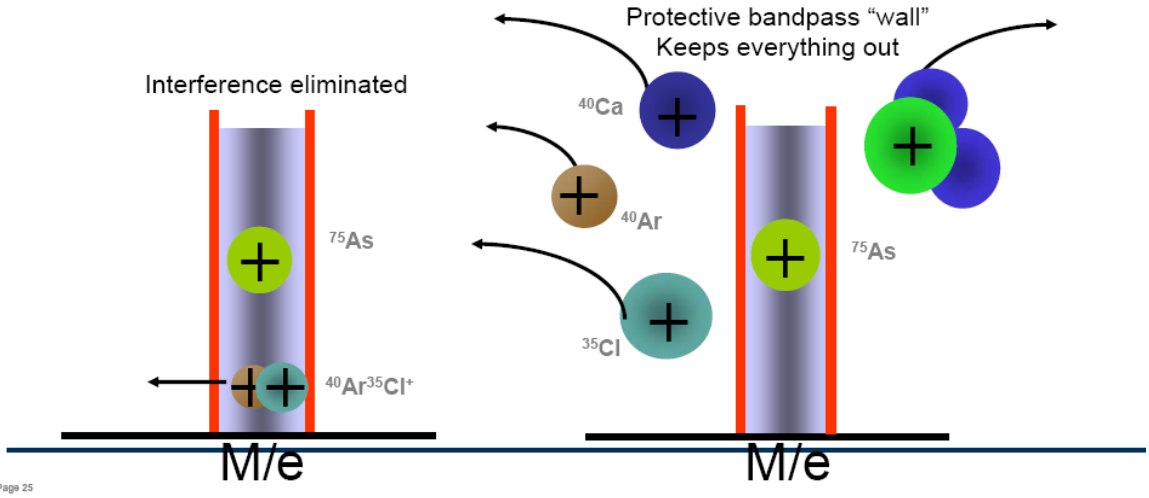
- But what are those extra peaks!!??

Page 24

Dynamic Reaction Cell

PerkInElmerSCIEX

- **Establish mass stability window inside cell**
  - **Rejects products of interference removal reactions**
  - **Rejects unwanted reaction products**
  - **Protects chemistry inside cell**
  - **Controls chemistry inside cell**



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ICP-MS Conditions: Br Speciation (DRC)

PerkInElmerSCIEX

Instrument	ELAN DRC II
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Analytes	BrO^{+} (m/z 95, 97)
Reaction Gas	N_2O = 0.5 mL/min
RPq	0.5
Dwell Time	250 ms (per analyte)

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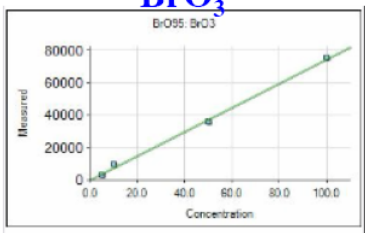
Calibration – 5, 10, 50, 100 ppb

PerkInElmerSCIEX™

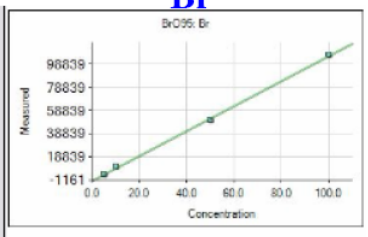
BrO 95

BrO_3^-



y = 745.4706x + 473.6835
R-Squared: 0.998850

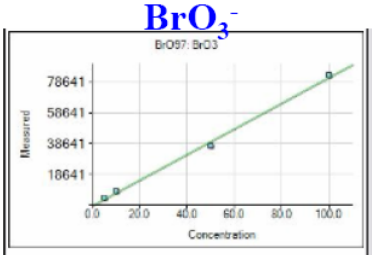
Br^-



y = 1076.1710x + -1160.6228
R-Squared: 0.999676

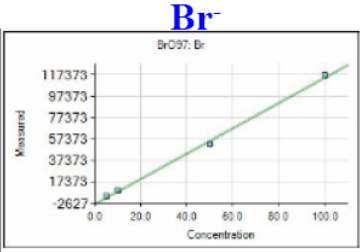
BrO 97

BrO_3^-



y = 830.7061x + -1359.0128
R-Squared: 0.998479

Br^-



y = 1181.1056x + -2626.6373
R-Squared: 0.999107

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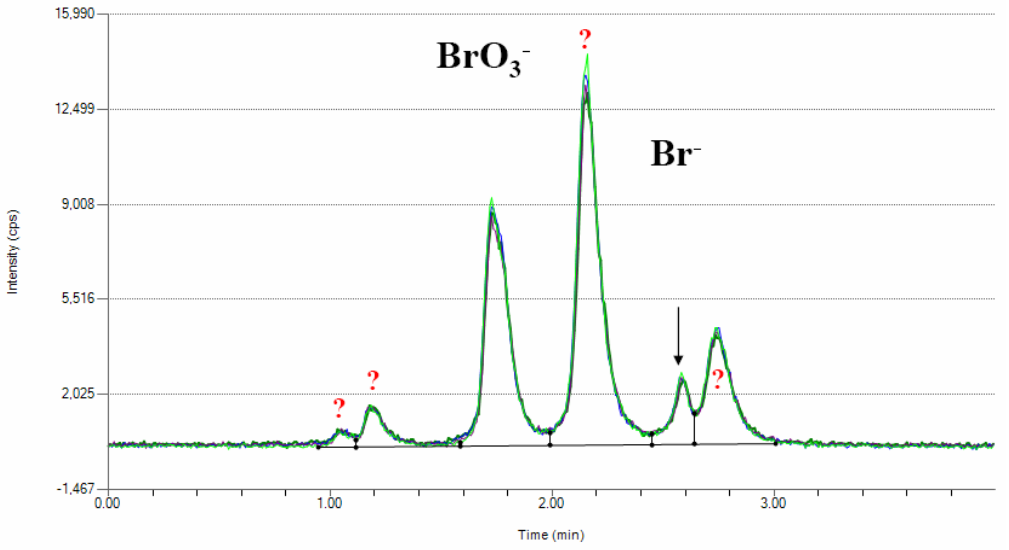
China – Waterman – 2 Injections

PerkInElmerSCIEX™



BrO 95 = Green **BrO 97 = Blue**

Confirms peaks all contain bromine

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Gradient Method to Enhance Separation

PerkInElmerSCIEX™

- Isocratic method faster
- But gradient may provide additional separation of more complex mixtures

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HPLC Conditions: Br Speciation Gradient

PerkInElmerSCIEX™

HPLC System	PerkinElmer Model 200 Quaternary Pump, Column Oven, and Autosampler
Column	3μm x 10 cm ZirChrom - SAX
Mobile Phase	Solvent A: 14mM NH_4OH + 6mM HNO_3; pH 7.3 Solvent B: 18mM NH_4OH + 3mM HNO_3; pH 10.2
Gradient Program	Equilibrate = 5 min Solvent A = 2 min Step to Solvent B Solvent B = 4 min
Flow Rate	1.5 mL/min
Injection Volume	50 μL
Total Time between Injections	11 min.

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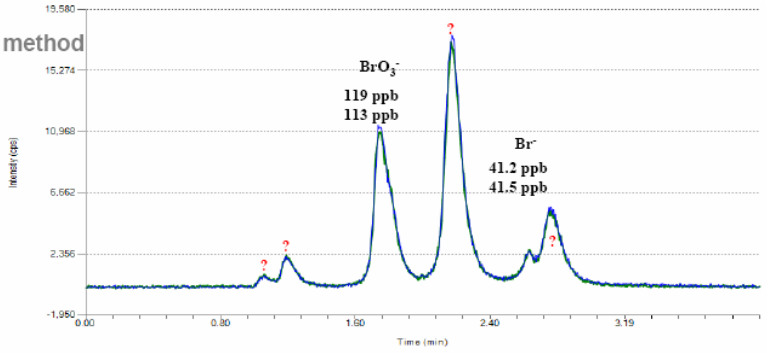
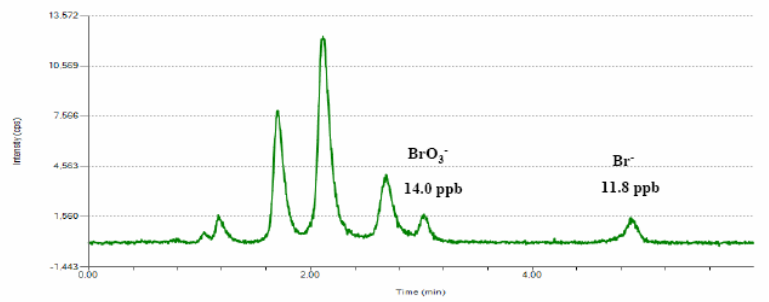
China – Waterman

PerkInElmerSCIEX™

Isocratic method



Gradient method uncovers another peak



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Summary

PerkInElmerSCIEX™

- Unusual peaks observed in several samples
- Confirmed that peaks include bromine using DRC by shifting mass of interest
- Unknown peaks require additional work for identification

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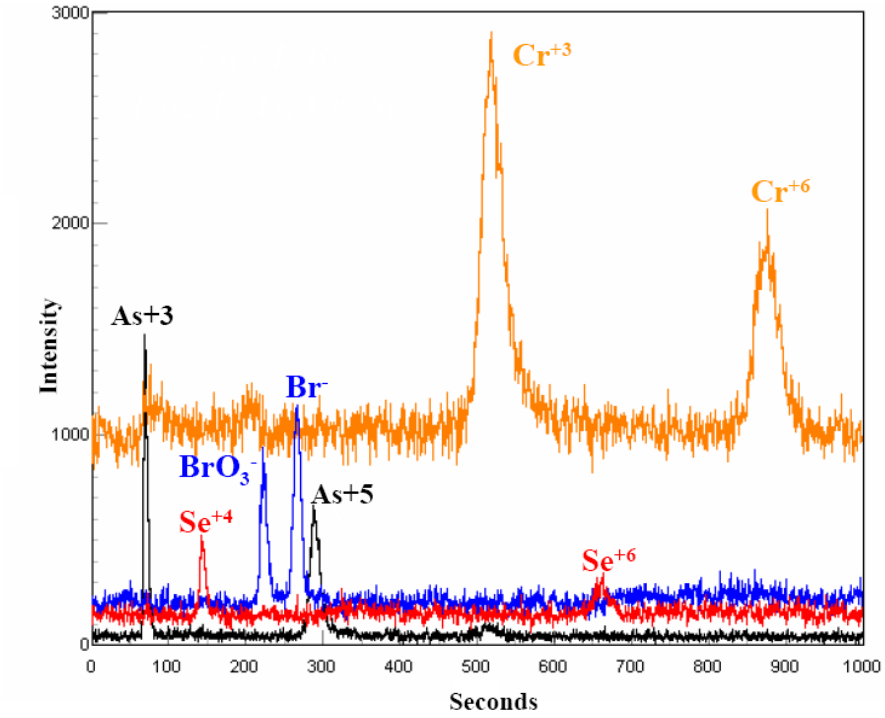
Simultaneous As-Br-Cr-Se Speciation Possible



Analytes: Cr 52, Se 80, AsO 91, BrO 97

Conclusions

- Summarized some of the challenges of speciation method development
- A improved stable method for Bromide/Bromate speciation is demonstrated in drinking waters
  - Separations are accomplished in 3 minutes
- Simultaneous As-Br-Cr-Se speciation is possible
  - May serve as a drinking water speciation method
  - More closely matches the capability of the detector

WEDNESDAY A.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Inorganic Methods

IMPLEMENTATION OF THE METHODS INNOVATION RULE AS A MAJOR FACTOR IN THE RCRA PERFORMANCE-BASED MEASUREMENT (PBMS) PROGRAM

Lesnik, Barry; U.S. EPA Office of Solid Waste-EMRAD

This talk will give a brief overview of the performance-based measurement approach to project planning and analytical methods selection and how it applies to the RCRA Program. It will also cover the basic changes to the RCRA regulations as a result of the promulgation of the Methods Innovation Rule (MIR) on June 14, 2005 and its effect on the regulatory and regulated communities, particularly enforcement and compliance. It will also cover the changes in how analytical methods will be added to SW-846.

IMPLEMENTATION OF THE METHODS INNOVATION RULE (MIR) AS A MAJOR FACTOR IN THE RCRA PERFORMANCE BASED MEASUREMENT (PBMS) PROGRAM

Barry Lesnik

U.S. Environmental Protection Agency
Office of Solid Waste – Methods Team

Major Topics to Be Covered

- What is the Methods Innovation Rule (MIR)?
- What will the MIR do and not do?
- How will it affect the existing RCRA Program?
- What are the responsibilities of Regulators and the Regulated Community under the Performance Approach?
- What are “appropriate methods”?

Some IUPAC Definitions (Ref. 1)

- Rational Method - a method that determines one or more identifiable chemicals or analytes for which there may be several equivalent methods of analysis availablle
- Empirical Method – a method that determines a value that can be arrived at only in terms of the method *per se* and serves, by definition, as the only method for establishing the measurand. (used to measure "method-defined parameters" or MDPs)

What is the MIR?

- The Methods Innovation Rule, or MIR, was designed to remove the unnecessary requirements to use only SW-846 methods for RCRA applications that did not require the use of empirical methods.
- The MIR allows more flexibility in RCRA-related sampling and analysis using rational methods, which is one of the Agency's steps towards implementing the Performance Approach (formerly PBMS).
- The MIR was published in the *Federal Register* as a Proposed Rule on October 30, 2002 (67 *FR* 66251).
- The MIR was published in the *Federal Register* as a Final Rule on June 14, 2005 (70 *FR* 34537).

What Will the Final MIR Do?

- Removes unnecessary required uses of SW-846 methods in the RCRA regulations and returns SW-846 to its originally intended purpose, as a guidance document
- Finalizes SW-846 Update IIIB
- Allows the Agency to fully implement the Performance Approach in the Federal RCRA Program
- Allows the Agency to publish rational SW-846 methods as guidance rather than through the formal Rulemaking process

Why is EPA Removing Unnecessary Required Uses of SW-846?

- EPA wants to allow more flexibility in RCRA-related sampling and analysis, and concentrate on measurement objectives rather than measurement technologies, i.e., the Performance Approach.
- Some regulated entities told EPA that they would like to use other reliable methods during RCRA compliance.
- Therefore, EPA has finalized the MIR to remove unnecessary requirements to use SW-846 methods in the RCRA regulations, and allow the use of other appropriate methods.

What Required Uses of SW-846 Methods Are Necessary and Have Not Been Removed?

- The MIR did not remove requirements to use a method if it is the only method capable of measuring the regulated property – i.e., empirical methods used to measure method-defined parameters (MDPs). Regulated entities will still have to use those methods.
  - For example, 261.24 (a) requires the use of SW-846 Method 1311, TCLP, for toxicity characteristic analysis
  - The required use of the TCLP is necessary and thus has not been removed by the MIR
- We identified 29 SW-846 methods that may be required to analyze RCRA-required MDPs.

What Required Uses of SW-846 Methods Are Not Necessary and Have Been Removed?

- Other required uses of SW-846 methods do not involve the analysis of required MDPs.
  - For example, § 260.22(d)(1)(i), part of the delisting regulations, requires the use of SW-846 methods to delist a waste listed with code "T".
- For these regulations other methods can be used without affecting the regulatory decision, provided the project data quality objectives (DQOs) are met.
- The required use of only SW-846 methods is not necessary, and the use of other appropriate methods is allowed.

What Might be the Impact of Removing Required Uses of SW-846?

- Regulated entities will be able to use other methods besides the SW-846 methods, when appropriate. They might choose these other methods to save costs and time.
- This greater flexibility will also stimulate the development and timely use of innovative and more cost-effective monitoring technologies and approaches in the RCRA Program.

Now That We Have Adopted the Performance Approach, What Are the Responsibilities of the Affected Entities?

- Regulatory Agency Responsibilities
  - Regulators and Permit Writers
  - Enforcement
- Regulated Community

Regulator Responsibilities Under the Performance Approach

- Regulators must establish clearly delineated DQOs appropriate for regulatory activities. Examples include:
  - Permits will need to include regulatory limits for target analytes with tolerable error rather than a general reference to use a particular method
  - Specific DQOs including tolerable error for demonstration of compliance to regulatory criteria need to be written directly into regulations.

Regulator Responsibilities Under the Performance Approach

- Enforcement approach would be to determine if the quality of the data generated and documentation provided met DQO/MQO requirements, rather than whether a particular method was followed exactly
- EPA-published methodology is guidance

Responsibilities of Regulated Community Under the Performance Approach

- Generator is responsible for demonstrating regulatory compliance
  - Selection of appropriate methods to demonstrate ability to meet project-specific DQOs/MQOs
  - Must maintain appropriate documentation for this demonstration, e.g., SAP, SOPs, QC data, etc.

Responsibilities of Regulated Community Under the Performance Approach (Contd.)

Allowable Flexibility

- Any method that yields acceptable data quality for a particular application may be used (See "Appropriate Method" slides)
- Published methods may be modified, as necessary, to generate acceptable data quality without pre-approval by EPA

Responsibilities of Regulated Community Under the Performance Approach (Contd.)

Allowable Flexibility (Contd.)

- New technology may be used as soon as it is developed and validated, provided that it can be demonstrated to be appropriate for generating acceptable data quality for a particular application
- The facility is responsible for meeting DQOs/MQOs and documenting that they were met for a particular application

How Will the Performance Approach Change the Current Way of Doing Business?

- The data review focus would shift from whether a method was exactly followed to whether the methods used were appropriate to meet the required DQOs/MQOs.
- It will require the generator to provide more substantial documentation than is currently being generated in most programs whether EPA-published methods are used or not.

What Is An "Appropriate Method"?

The MIR replaces unnecessary required uses of SW-846 by allowing the use of other "appropriate methods such as those found in SW-846 or other reliable sources."

1. Appropriate methods are reliable and accepted as such in the scientific community.
2. Appropriate methods generate effective data -- data of sufficiently known and of adequate quality for supporting the project-specific decisions.

What Is An "Appropriate Method"? (Contd.)

- Simply stated, an "appropriate method" is one that can be demonstrated to be able to see the analytes of concern at the level of concern in the matrix of concern and generate data of appropriate quality to be used for its intended application, i.e., effective data.

Who Chooses the Appropriate Method?

- Choosing an appropriate method begins during project planning and involves all key participants.
- The regulated entity is ultimately responsible for compliance with the subject regulation.
- We recommend consultation with the regulating authority during method selection, if necessary, and with the laboratory that is ultimately doing the work.

What Are the Key Steps in Choosing an Appropriate Method?

- Identify regulatory requirements (e.g., the analyte, matrix, and regulatory action level), the decision to be made, and the data quality needed to support that decision.
- Identify analytical goals (including for example performance requirements related to the matrix and analyte detection, e.g., recovery and precision).
- Select a method believed to be capable of meeting the performance requirements and other goals.

What Are the Key Steps in Choosing an Appropriate Method? (Cont.)

- Seek guidance as needed during method selection, e.g., from your laboratory, your regulating authority and SW-846 Chapter Two.
- Identify the data quality objectives, the method to be used, and the quality control indicators and make sure to put them into the planning document (e.g., QAPP, WAP, SAP).

What Are the Key Steps in Choosing an Appropriate Method? (Cont.)

- Use the data generated during the implementation phase to demonstrate that the method is appropriate – to show that the criteria were met.
- The performance data in SW-846 methods are just examples and not requirements – the actual performance acceptance criteria should be project-specific.
- As part of a dynamic approach, method selection and optimization may be revisited during the implementation phase.

Why We Selected the "Appropriate Method" Approach

1. The appropriate method approach is universally applicable to the affected regulations and requires minimal regulatory revisions.

2. The appropriate method approach is not new to RCRA regulations.

3. Also, regulated entities already should be using a similar approach to determine if a method is appropriate to a particular waste and analytical purpose.

Does the MIR Add New Requirements to the RCRA Regulations?

No new requirements are added!

- The use of other appropriate methods will be an option, not a requirement.
- Regulated entities can still use the SW-846 methods, if they are appropriate for the intended application.
- EPA is not adding new testing or information collection and reporting requirements beyond what should already be done now.

Adoption by Authorized State Programs

- Authorized States do not have to adopt the removal of unnecessary required uses of SW-846 methods, although we strongly encourage them to do so.
- Adoption may not cause significant impacts because States should already review method selection and quality control data to determine regulatory compliance; and most entities will probably continue to use SW-846.

EPA to Offer Training and Guidance

- EPA plans to offer training to the States and other entities on the MIR concepts and practices via training modules, workshops, and fact sheets.
- We hope that training will help ensure consistent implementation of the MIR and limit any costs.
- Please provide us with feedback as to what major topics we need to cover and which audiences we need to address

The MIR Also Finalizes SW-846 Updates IIIB

- Update IIIB includes a revised Chapter Seven, removing the reactivity test guidance.
- Update IIIB includes empirical methods used in the analysis of MDPs, and most were revised to remove the unnecessary required use of SW-846 Chapter Nine.

Status of the RCRA Waste Sampling Draft Technical Guidance

- The RCRA Waste Sampling Draft Technical Guidance was noticed as part of the proposed MIR.
- We have currently addressed all comments and are working with OGC to determine whether there is sufficient change in content to warrant our putting it out again for public comment.

New Sampling Guidance Features

- Summary of RCRA regulatory drivers for waste sampling and testing
- Emphasis on systematic planning using the Data Quality Objectives (DQO) Process
- Sampling theory and practical methods for managing sampling error
- Sampling tools
- New sampling designs and guidance on composite sampling and "hot spot" detection

New Sampling Guidance Features (Cont.)

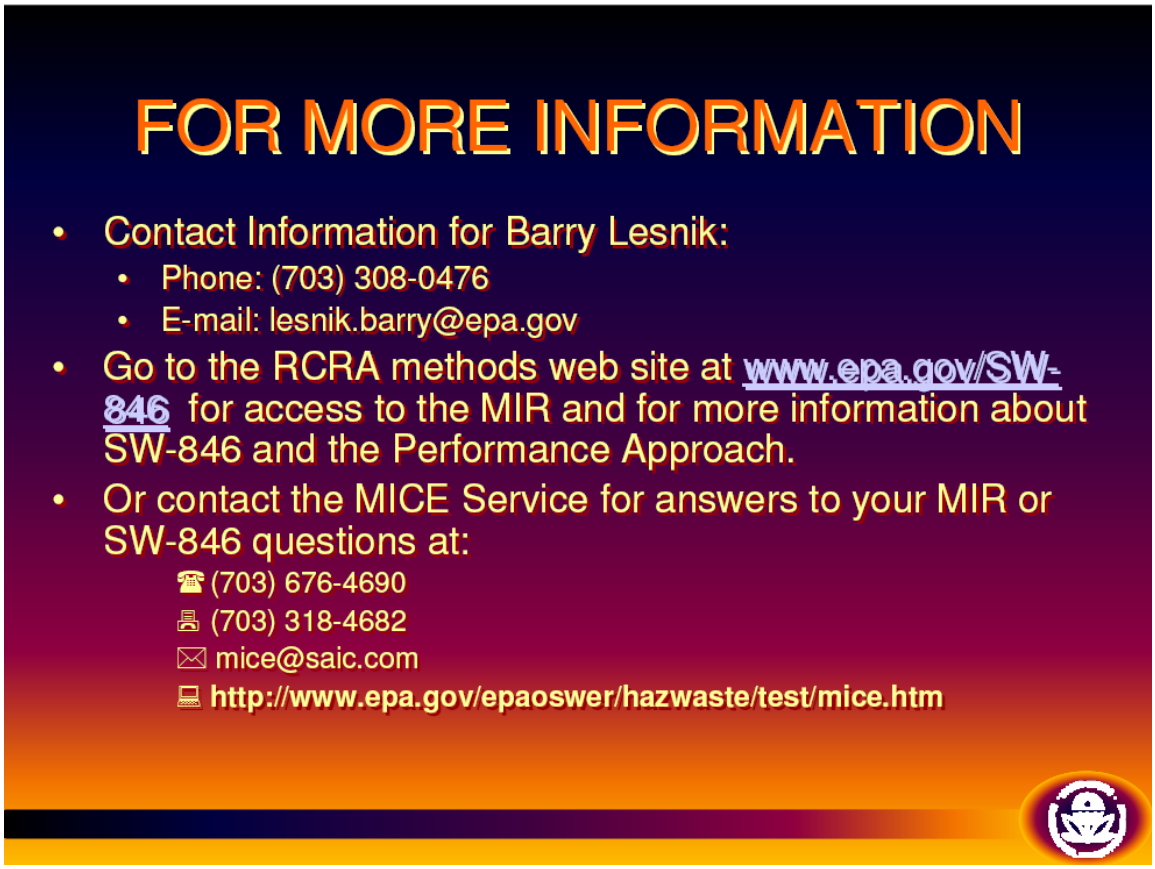
- Subsampling techniques
- Statistical methods and statistical tables
- Strategies for sampling heterogeneous waste
- Comprehensive examples that integrate use of the DQO Process, sampling theory, PBMS, and data quality assessment

Reference

1. *Thompson et. al., IUPAC Technical Report Pure & Applied Chemistry, Vol. 71, No. 2, pp. 337-348, 1999.*

Acknowledgement

- Thanks to Kim Kirkland of the Methods Team who completed the MIR project.


FOR MORE INFORMATION
• Contact Information for Barry Lesnik:
• Phone: (703) 308-0476
• E-mail: lesnik.barry@epa.gov
• Go to the RCRA methods web site at www.epa.gov/SW-846 for access to the MIR and for more information about SW-846 and the Performance Approach.
• Or contact the MICE Service for answers to your MIR or SW-846 questions at:
(703) 676-4690
(703) 318-4682
mice@saic.com
http://www.epa.gov/epaoswer/hazwaste/test/mice.htm

Current Status: RCRA Inorganic Methods Development Program

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22nd Annual NEMC
August 30, 2006

Westin Arlington Gateway
Arlington, VA

Topics for Discussion

- Promulgation of the Methods Innovation Rule
- Revisions to SW-846
  - Updates IIIB and IV to Third Edition
  - Fourth Edition
- New Methods
- Methods Development Projects
  - Current
  - Future

2

Promulgation of the Methods Innovation Rule (MIR)

- Regulation development initiated to remove mandatory requirements to use SW-846 methods for analyses that are not method-defined parameters (empirical methods) in RCRA regulations.
- MIR proposed on October 30, 2002 (67 *FR* 66251).
- MIR promulgated on June 14, 2005 (70 *FR* 34537).

3

Promulgation of the MIR (contd.)

- Promulgation of the MIR eliminates the need to publish SW-846 Updates as regulations.
- SW-846 functions as originally intended, as a "guidance document."
- Updates will be put out for public comment in the *Federal Register* as Notice of Data Availability (NODA).
- Updates will be added to SW-846 through Federal Register notices modifying a guidance document.
- No change to method-defined regulations.

4

Promulgation of the MIR (contd.)

- RCRA is now a performance-based program.
- Any reliable method can be used for RCRA applications, excluding regulatory requirements to use empirical methods.
- Approximately 25 to 30 empirical methods remain incorporated by reference in the RCRA regulations (40 CFR 260.11).

5

Promulgation of the MIR (contd.)

- A reliable method is one that can be demonstrated to be able to determine the analytes of concern in the matrix of concern at the level of concern to meet project-specific DQOs.
- Any method used for a RCRA application must be demonstrated to perform appropriately for that application, including methods published in SW-846.
- Prior approval of methods by EPA for certain applications is encouraging, but not required.

6

Update IIIB of Third Edition

- Update IIIB was issued to remove references which required the use of Chapter Nine in existing method-defined parameters.
- Promulgated as part of MIR.
- These 11 methods will remain "incorporated by reference" in the RCRA regulations.
- No other changes were made to these methods, except for correcting a typo in the method number of Method 9070A.

7

Update IIIB of Third Edition

- Method 1010A: Pensky-Martens Closed-Cup Method for Determining Ignitability.
- Method 1020B: Small Scale Closed Cup Method for Determining Ignitability.
- Method 1110A: Corrosivity Toward Steel.
- Method 1310B: Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test.
- Method 9010C: Total and Amenable Cyanide: Distillation.
- Method 9012B: Total and Amenable Cyanide: Automated Colorimetric, with Off-line distillation.
- Method 9040C: pH Electrometric Measurement.
- Method 9045D: Soil and Waste pH.
- Method 9060A: Total Organic Carbon.
- Method 9070A: Hexane Extractables from Aqueous Matrices (Method Number Correction)
- Method 9095B: Paint filter Liquids Test.

8

Update IV of Third Edition

- Will be finalized as a NODA next 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, one for FLAA and one for GFAA).
- All methods in Fourth Edition format (Style Guide on Methods Team Homepage).

9

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.
- 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.

10

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.

11

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.

12

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.

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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.

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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 are looking to have the Fourth Edition ready to go out for public comment in 2007.

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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.

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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 inter-lab method validation studies were completed. Paper published: "Inter-laboratory Validation of EPA Method 3200 for Mercury Speciation Analysis using Prepared Soil Reference Materials," Rahman et al., Appl. Organomet Chem., 2005, 19-301-307;
- The method was posted July 2005 on the OSW Methods website for public use and comments.

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Method 9013A

- All CN species are soluble under alkaline conditions
  - **Simple CN salts:** $ACN \xrightarrow{pH \geq 11} A^+ + CN^-$
  - **Metal CN complex salts:** $A_a[M(CN)_x] \xrightarrow{pH \geq 11} aA^+ + [M(CN)_x]^{y-}$

    $T_t[M(CN)_x]_b \xrightarrow{pH \geq 11} tT^+ + b[M(CN)_x]^{y-}$

    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 9013A evaluated during Method 9015 inter-lab study
  - **Real-world solids spiked with $Fe_4[Fe(CN)_6]_3$ ("Prussian Blue")**
  - **Solid extracts analyzed for total CN - Good recoveries obtained**

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 9013A) for solids
- Developed and drafted by Sharon Drop of ALOCA, 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
- The study reports and method were reviewed by the Workgroup and revised based on their comments
- Methods 9013A/9015 were posted November 2004 on the OSW Methods website for public use and comments

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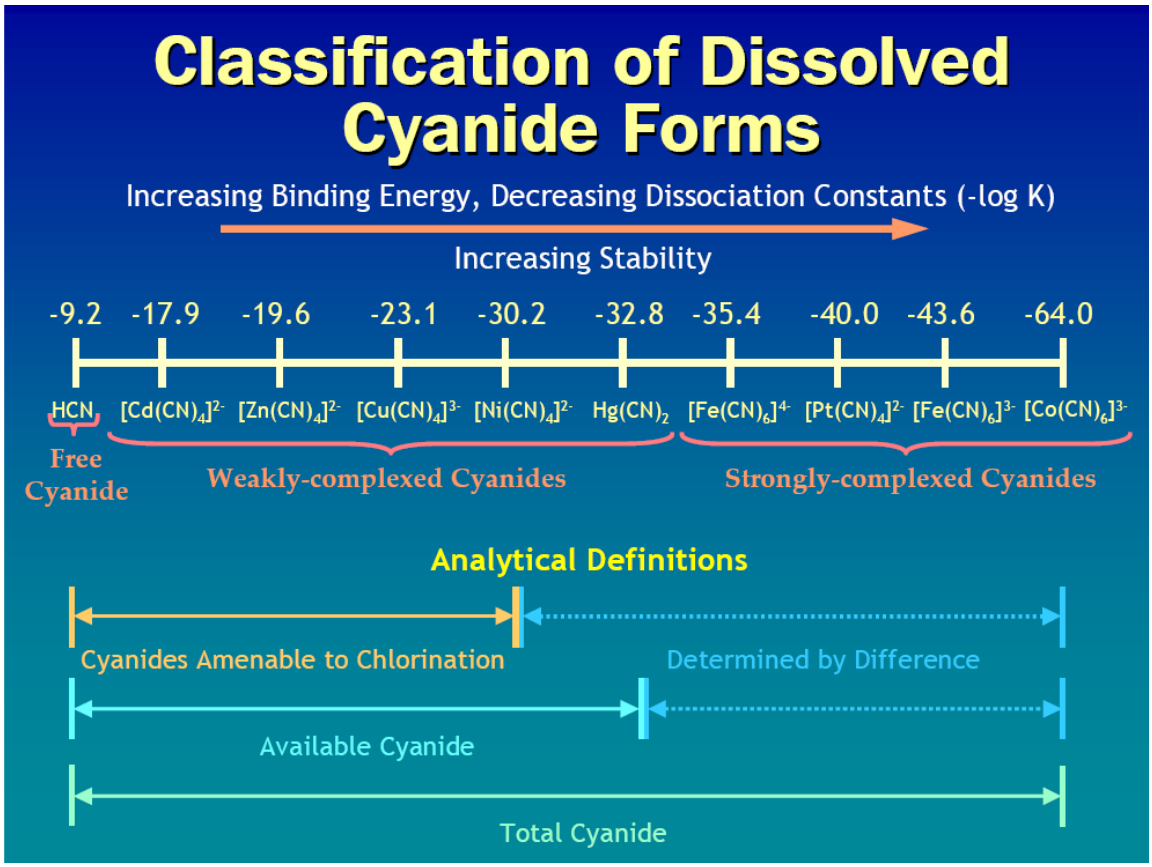
Classification of Dissolved Cyanide Forms



Current Methods Development Projects for Perchlorate

- Method 9058 (by IC)
- Method 6850 (by LC/MS or LC/MS/MS)
- Method 6860 (by IC/MS or IC/MS/MS)

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Method 9058 (IC)

- Proposed in November 2000.
- Current method scope and applicability:
  - 4 µg/L for spiked reagent water samples.
  - Performs adequately on water samples with conductivities up to 1000 µS/cm.
  - Water samples with conductivities >1000 µS/cm have not been tested.
  - Potential for false positive and false negative results due to sample matrix interferences attributed to co-eluants and high total dissolved solids.
  - No written procedure for extracting perchlorate in solids.

22

Methods 6850 / 6860

- (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 may allow flexibility in detection pending outcome of validation study:
  - 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

23

Future Methods and Reference Materials Development Projects

- Development of Non-Aqueous Cr (VI) SRM
- XRF (Method 6300)
- XRD (Method 6250)
- As Speciation
- Free cyanide

24


Relevant Contact Addresses and Phone Numbers
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25

SAMPLE PREPARATION OF ELECTRONIC COMPONENTS TO ENSURE COMPLINACE WITH THE NEW ROHS/WEEE REGULATIONS

Bath, Frank and Batzke, Matthias; Retsch, Inc.

While there is some ongoing debate as to the full impact of the new RoHS/WEEE regulations, one of the major challenges is how to prepare samples of sufficient fineness for subsequent analysis and particularly if elemental species are to be accurately analyzed. Electronic boards and components present difficulties in that they are composed of a number of materials including ceramic, metal and plastics. Generally, each one of these materials requires its own different technique for size reduction, and the combination of materials onto a "PC board" presents a unique challenge for standard laboratory mills and crushers.

A technique will be presented which has been proven to be successful in reducing the size of such components to analytical fineness. The technique requires the use of a heavy duty cutting mill which utilizes a slow speed high torque motor and a specially designed cutting rotor with hardened cutting tips that can cope with the demands of the material. The cutting mill is used for initial size reduction and a second mill is used to reduce the size to analytical fineness. This mill is a vibratory disk mill or "ring and puck" mill that is commonly used in cement and mineral industries. The second process is carried out in specially designed grinding sets made of tungsten carbide which ensures that the required fineness is achieved in less than 5 minutes. For plastic only parts, a third mill may be required and depending on the required fineness, the material may need pre-chilling with liquid nitrogen or dry ice.

Data will be presented showing this process being performed on electronic boards precut to approximately 60 x 150 mm together with cell phones "as is" with only the battery removed.

Sample Preparation of Electronic Components to ensure Compliance with RoHS/WEE regulations.

NEMC 22nd Annual Conference
30 August 2006
Frank Bath

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OBJECTIVES

WEEE – the environmentally safe disposal of electrical and electronic devices.

RoHS – restriction in use of certain hazardous substances in these devices.

Manufacturers, sellers, recyclers and disposers of electrical and electronic devices are required to demonstrate **through analytical determinations** that the directives are being observed.

Analysis methods – XRF or ICP or ???

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Affected items include:

- Large & small household appliances
- Electrical and electronic items
- Lamps and lights
- Entertainment electronics
- Communication equipment – cell phones
- Electronic toys
- Electric power tools

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RoHS – Requirements

Places limitations on toxic substances

Regulations for heavy metals

Cadmium (Cd)

Lead (Pb)

Mercury (Hg)

Hexavalent Chromium (Cr VI)

Regulations for 2 types brominated flame retardants

Polybrominated Biphenyl (PBB)

Polybrominated Diphenyl-Ether (PBDE)

* 0.1% for lead, mercury, hexavalent chromium, PBB and PBDE
0.01% for Cadmium

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Current situation regarding compliance.

Confusion as to how companies should comply. Official regulations require creating homogenous sample materials from item or components where practical.

Some advocate a "bottom up" approach where the onus is on the raw material suppliers to prove compliance and have this pass up the line to the finished product.

BUT

There can be a high price for non-compliance. Example – Sony PlayStations.

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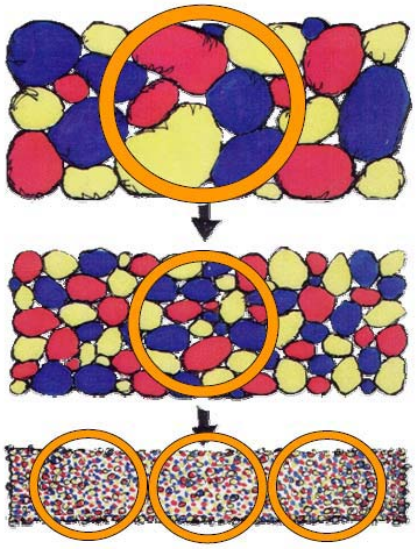
Milling/Grinding

Retsch understands milling as size reduction of solids within the context of sample preparation and homogenization as required for **representative analyses.**



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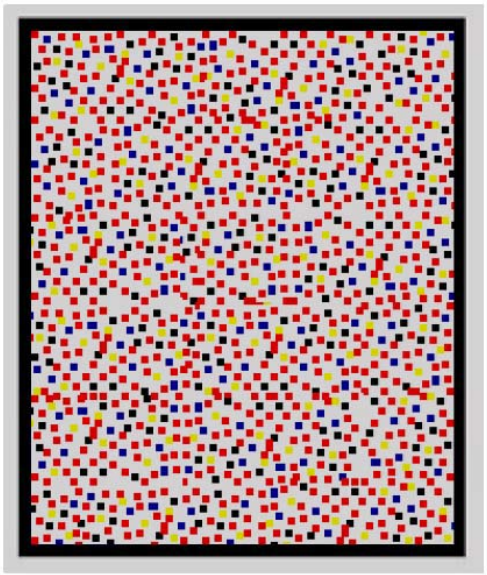
The Art of Milling



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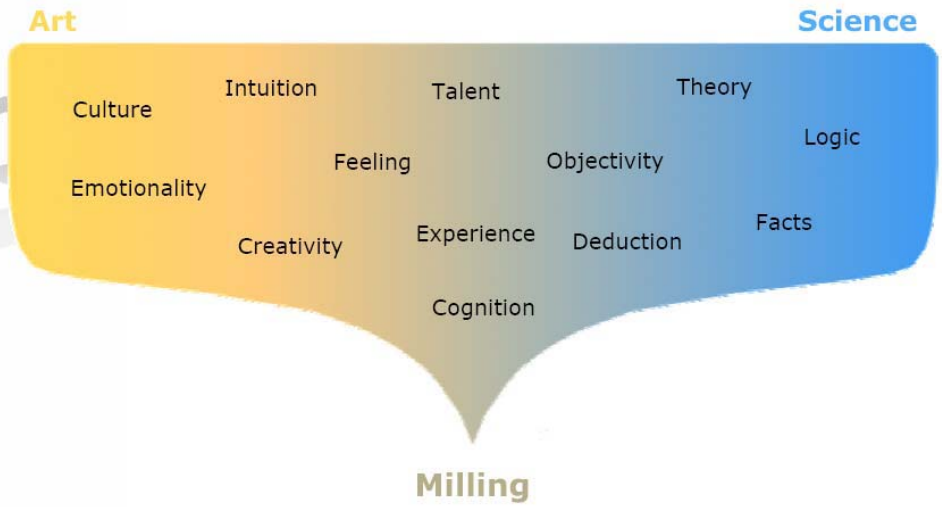
Art – Science – Milling



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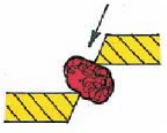
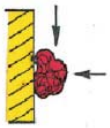
Principles



Cutting

Impact



Impact & friction

Shearing

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Challenge – how to homogenize electronic & other components.

Contents can include hard brittle abrasive materials, soft ductile materials and everything in between.

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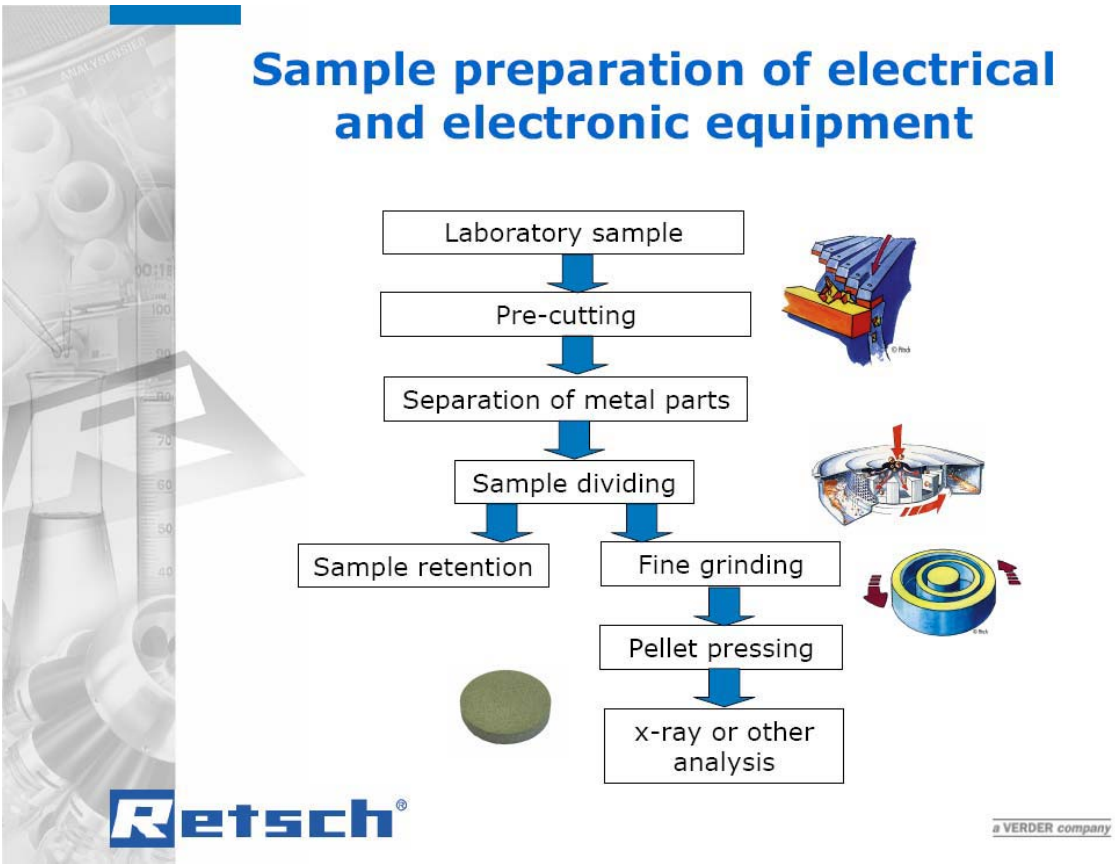
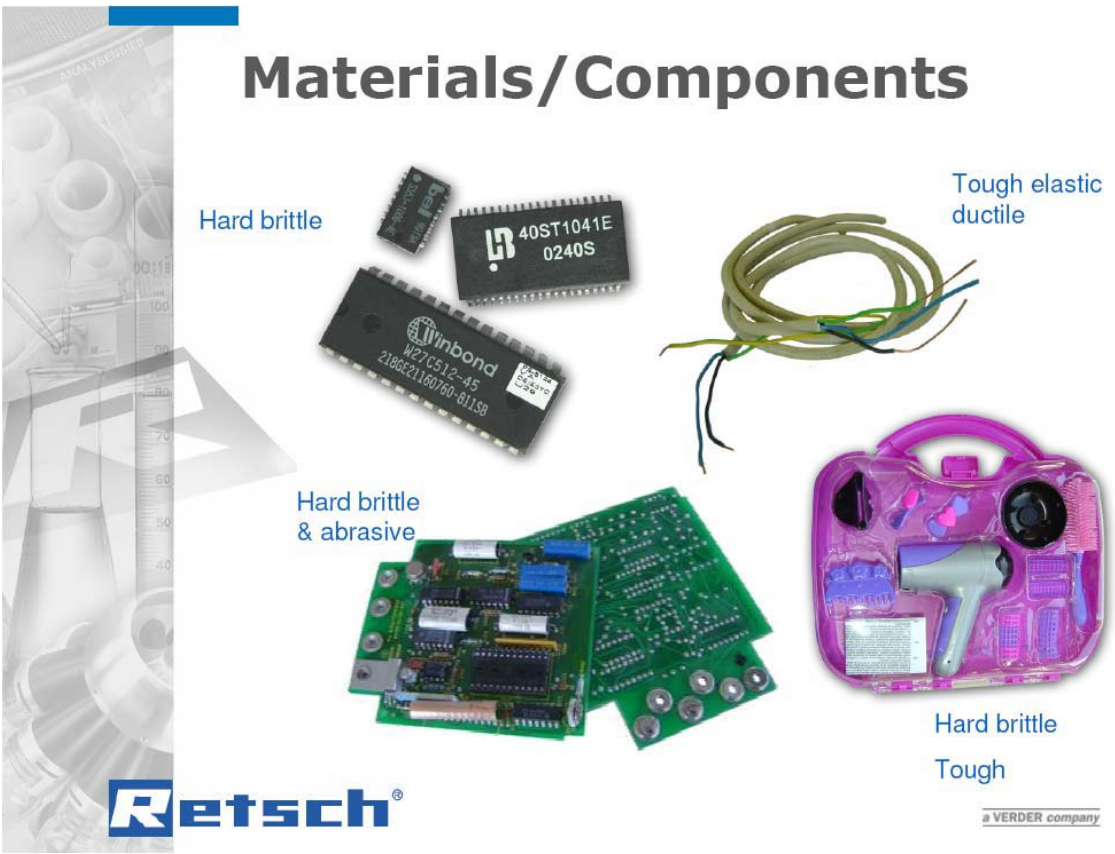
Sample preparation of electrical and electronic equipment



Materials/Components



SM 2000

SM 2000 heavy duty cutting mill

large feed size – up to 60 x 80 mm
Fineness to < 1mm
Used for pre-grinding of PC boards, cell phones, line cords using 4 mm bottom sieve.

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SM 2000

Options SM 2000

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Heavy Duty Cutting Mill SM 2000

Initial grinding of electronic boards and power cords using the low speed version, bottom sieve 4 mm

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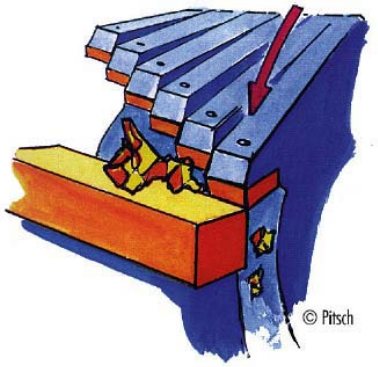
Heavy Duty Cutting Mill SM 2000

Cutting effect between sharp edges, tangential cut



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Heavy Duty Cutting Mill SM 2000

... a short overview

- powerful disintegration of even thick-walled samples and heterogeneous mixtures
- defined ultimate fineness with exchangeable bottom screens
- sample subjected to low thermal stress
- hinged housing with central lock
- filter system sealed dust-tight
- rotors for parallel cut and tangential cut
- 3 hopper versions for different samples (lumpiness)
- simple and safe operation

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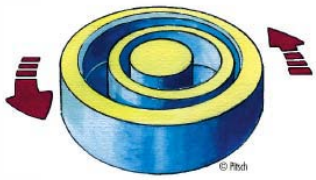
Vibratory Disk Mill RS 100

Analytical fineness in a few seconds



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Vibratory Disk Mill RS 100

... a short overview

- extremely short grinding time for high ultimate fineness
- digital timer setting, quartz accuracy to the second
- grinding sets made of 5 different materials
- two motor speeds
- speed reduction by automatic agate recognition
- quick-clamping device for grinding jars
- grinding chamber sealed and noise-insulated

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Grinding of electronic products.

RoHS/WEEE requirements.

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Grinding of electronic products

RoHS/WEEE requirements – SM 2000 cutting mill.

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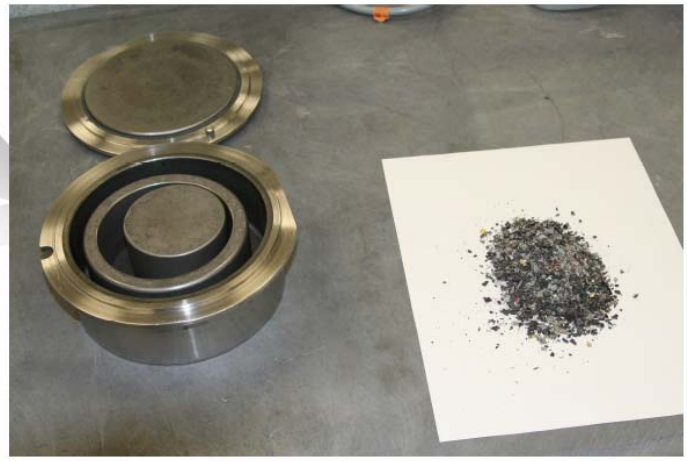
Grinding of electronic products

RoHS/WEEE requirements – WC grinding tools from RS 100.



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Grinding of electronic products

RoHS/WEEE requirements – resultant grind from RS 100.

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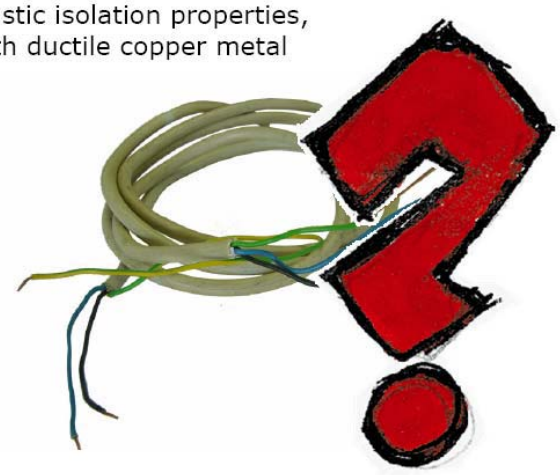
Preparation of a line cord

Elastic isolation properties,
with ductile copper metal



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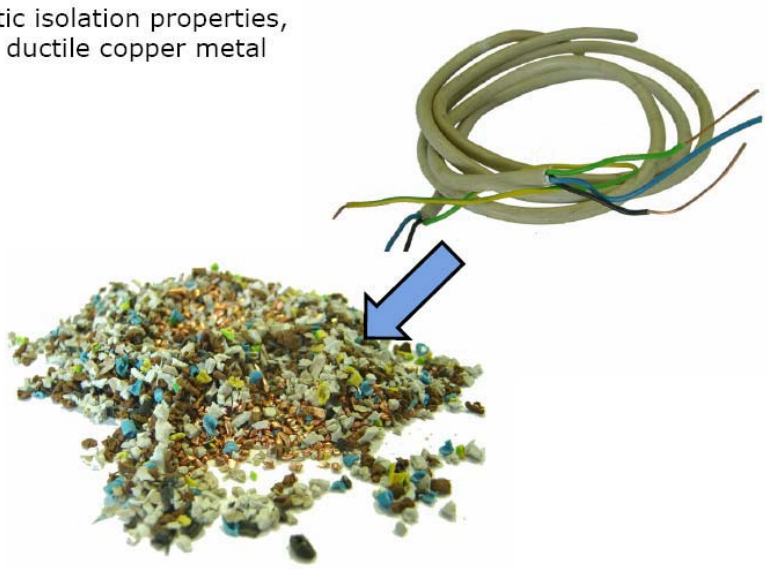
Pre-cutting of a line cord

Elastic isolation properties,
with ductile copper metal



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Separation of PVC and copper by flotation in a water flow

250 cc Beaker

Test sieve 250 µm

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Separation of PVC and copper

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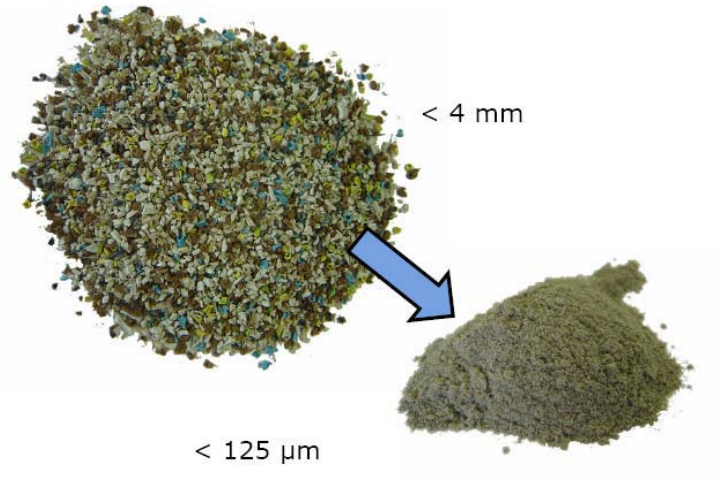
Fine grinding of pure PVC with the Ultra Centrifugal Mill ZM 200



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Ultra Centrifugal Mill ZM 200

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Cassette Design

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Solutions in Milling & Sieving

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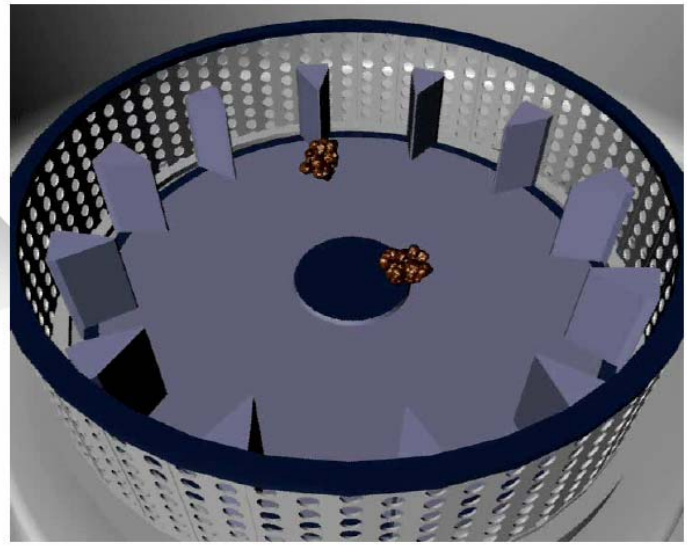
ZM 200

Operation principle ZM 200



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ZM 200

Fine grinding of PVC granulate

pre-cooling with
liquid nitrogen

after grinding using a ring sieve 0.25 mm: approx. 80 % < 125 µm

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Rotors and Ring Sieves ...

... in different versions allow optimal adaptation of the ZM 200 to meet a wide range of size reduction applications.

Stainless steel
Wear resistant coating
Titanium

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Eeproms

Grinding of IC's

Mill
MM 301 – bead/ball mill

Parameter
Jar: 25 ml tungsten carbide
Grinding balls: 2 x 12 mm
Grinding time: 3 Minutes

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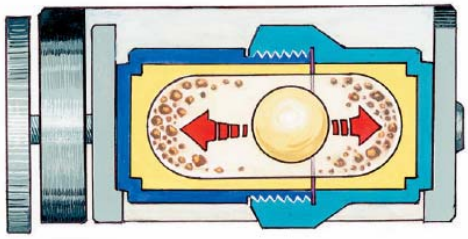
Mixer Mill MM 301

For individual adaptation to a wide variety of grinding tasks



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Mixer Mill MM 301

Screw-top grinding jars

- stainless steel
- special steel
- tungsten carbide
- zirconium oxide
- agate
- PTFE

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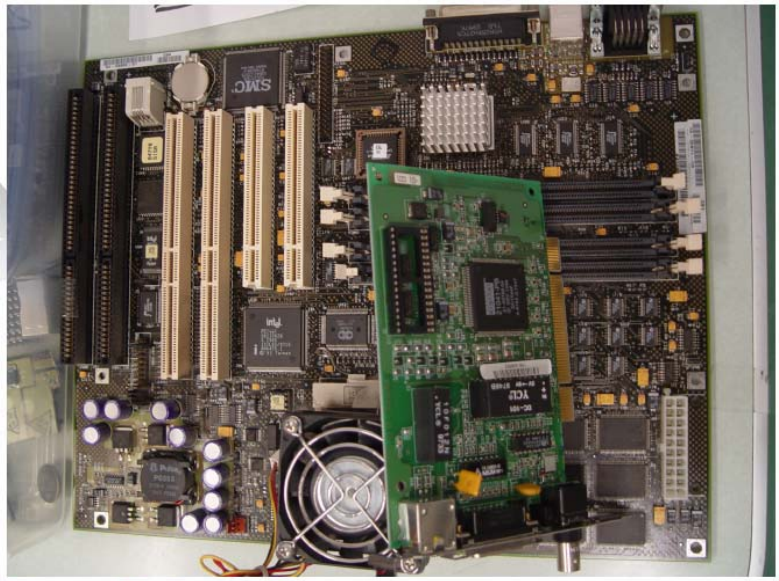
Lab Test – "microway board" slide 1.



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Lab Test – "microway board" slide 2.

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Microway board analysis results.

Digestion method EPA Method 3052

2 combinations of acids were used. One with conc. HNO3 and HF and the other with conc. HNO3 & fluoroboric acid.

Details of digestion method available from H.M. "Skip" Kingston & others – Duquesne University.

Element	9 mL HNO_3 + 3 mL HF (µg/g)[a]	9 mL HNO_3 + 3 mL FBA* (µg/g)
Cr	29.6405 ± 5.7080	17.7085 ± 1.8503
Cd	1.9195 ± 0.1468	3.2352 ± 0.0770
Hg	1.3807 ± 0.1070	3.2557 ± 0.1560
Pb	19,220 ± 727	22,355 ± 440

•FBA – Fluoroboric acid.

•Uncertainties are at 95% CL, n = 15.

•a Precipitation occurs after storing in cold room at 4 °C.

From this study, it is found that the MICROWAY circuit board passed the ROHS regulation for Cr, Cd and Hg but failed for Pb.

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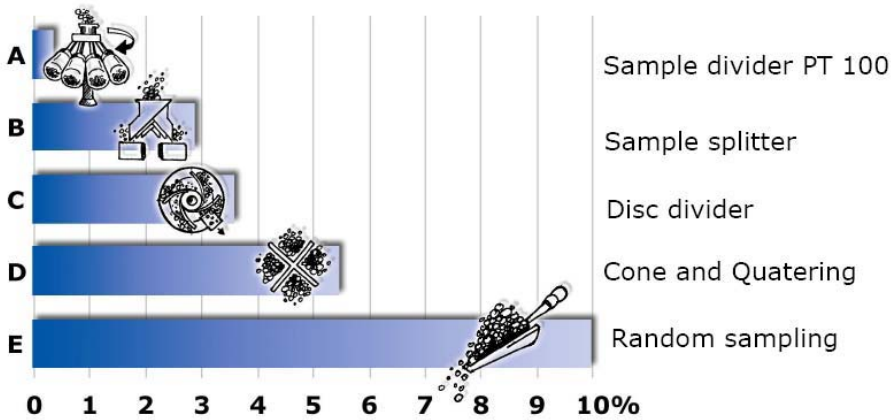
Standard Deviations of various sample divisions methods



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Laboratory Sample Divider PT 100

for 6 / 8 or 10 single samples

All bulk materials, for example:

Minerals, fertilizers, food granulates, carbon and coke, chemicals, soil and grains, metal powders.

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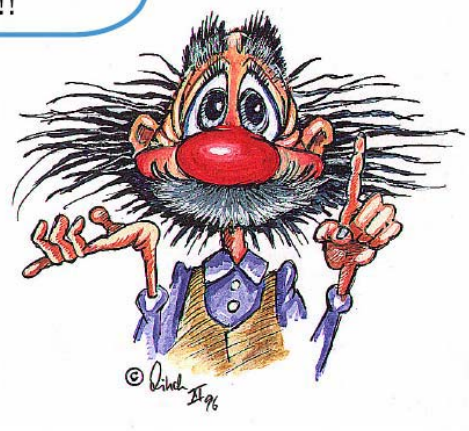
Conclusion

Only a representative sample is a guarantee for reliable and trustworthy analytical results !!!!



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Inorganic Analysis for Environmental RoHS Compliance

Zoe Grosser and Laura Thompson
PerkinElmer Analytical Sciences

ABSTRACT

The recent European directives for recycling of waste electronic products (WEEE) and reduction of hazardous materials (RoHS) that may result in environmental contamination are affecting the manufacture of electronic products on a worldwide basis. Four metals must be measured in materials complying with this regulation, including cadmium, lead, mercury, and hexavalent chromium. Additional countries are considering similar legislation and may add additional analytes of interest.

The preparation of the sample is a key component to successful measurement of the metal content and the requirements will be briefly outlined. As the RoHS rule is implemented, questions have arisen about the sampling, compositing, and analysis of materials that must comply with the rule. Total digestion versus a hot-acid leach is important for complete characterization of a waste sample, such as a battery, cable, or circuit board. The challenges of analyzing samples that are inhomogeneous will be considered.

The measurement of the elements of interest using AA, ICP or ICP-MS will be discussed. Differences in analytical capability, workload, and cost of ownership will be contrasted in a variety of scenarios as guidance on technique choice.

INTRODUCTION

The European Union has put a set of directives into place to further protect the environment. The first directive regulates recycling of waste electronic and electrical equipment (WEEE). The second directive requires reduction of hazardous materials (RoHS) through the restriction of products containing $\geq$ 0.1% Cr VI, Hg, Pb and $\geq$ 0.01% Cd in homogeneous materials. The RoHS directive also regulates two brominated flame retardants.

Although these directives are only enforceable in Europe they are affecting manufacturing around the world. Most global companies ship to many places in the world and it would be expensive and time-intensive to segregate the merchandise manufactured for European consumption. Therefore, this regulation has far reaching effects on all manufacturing firms.

Analyses to ensure compliance with this regulation requires the digestion of a wide variety of materials. An example of the types of materials that may be observed is shown in Figure 1.

Figure 1: Examples of Electrical Components and Raw Plastic Materials to be Measured for RoHS Compliance

This paper will discuss sample preparation challenges and solutions. The analysis of the materials after digestion will be discussed and the choice of inorganic analysis technique explored.

EXPERIMENTAL

Samples of old electronic components were obtained from various sources. One wire cover and clip sheath were reported to be undergoing a manufacturing change because of RoHS non compliance and was included in the sampling. Raw plastics were obtained from a manufacturer in China.

Samples were digested using the Multiwave™ 3000 (Anton Paar). Electronic components were cut into small pieces and the pieces mixed thoroughly before weighing approximately 0.1 gram into a quartz or PTFE digestion vessel. Electronic components were digested with 6 mL HNO_3/2 mL H_2O_2/1 mL HF. Raw plastics were digested with 9 mL HNO_3. Samples were digested following a 45 min power program:

- Ramp from 0-600 W for 5 min, hold for 15 min
- Ramp from 600-1400 W for 5 min, hold for 20 min

Digestates were transferred and diluted to 50 mL with ASTM Type I water.

Analysis was performed using inductively coupled plasma optical emission (ICP-OES) and Flame Atomic Absorption (FAAS). Default conditions were used for the analysis of Pb and Cd using the AAnalyst™ 400.

The Optima™ 5300 ICP-OES was used for a full, suite of elements, including mercury.

- Axial mode used for elements where increased sensitivity was required, such as Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Se, etc.
- Radial mode used for elements expected at higher concentrations, such as Ba, Mg, Mn, etc.
- Low-flow GemCone Nebulizer

- Cyclonic spray chamber
- On-line addition of internal standard

Total analysis time was approximately 3 minutes per sample.

RESULTS AND DISCUSSION

Digestion of samples can be a challenge due to the homogeneity of the sample. The regulations are unclear on whether each component or subassembly should be sampled or whether a composite more clearly represents the product for regulation. Many companies are taking their best guess at how to interpret the regulation and comply with testing.

Some of the samples tested here were clearly homogeneous, such as the raw plastic material and yellow plastic sleeves. Some were not homogeneous, such as the circuit board and ribbon cable. With more sophisticated grinding tools the homogeneity of the sample for replicate digestions could have been improved.

Microwave digestion proved satisfactory for the wide range of materials digested. Increased temperature and pressure ensure that resistant components are solubalized and the closed system retains the mercury in solution. The acid ratio was adjusted on the least homogeneous sample until a clear digest was obtained. This program was used for the rest of the electronic component samples.

Inorganic analysis using FAAS, ICP-OES, and inductively coupled plasma mass spectrometry (ICP-MS) techniques were evaluated for possible analysis of samples. AA requires the lowest initial investment and is simple to use. However, it measures a single element at a time which can be slow if a large number of elements need to be measured. It also requires a separate analysis for mercury using the cold vapor technique. ICP-OES requires a moderate initial investment and is a fast multielement technique. Mercury can be included in the multielement list of analytes and determined at the same time. Since additional elements increase the analysis time by a negligible amount, elements that may be of interest in the future can be monitored. ICP-MS requires a higher initial investment and also provides a fast multielement technique. It provides lower detection limits for the use of a smaller sample size or compliance with lower limits. Like ICP-OES, mercury can be included in the suite of analytes and additional elements can be included for screening.

The concentration in solution after digestion may be several ppm, indicating that ICP-OES may be the best choice. Axial configuration ICP-OES will be evaluated and compared with flame AA, with similar concentration range strengths. Table 1 shows a recent draft ISO standard listing guidelines for sample preparation, both mechanical and digestion, and analysis. It seems logical to measure total chromium first and only measure chromium VI if the limit is exceeded with the total amount.

Table 1: Draft ISO Standard Analysis Guidelines

Steps	Substances	Polymer Materials	Metal Materials	Electronics(PWBs/ Components)
Mechanical sample preparation		Direct Measurement Grinding	Direct Measurement Grinding	Grinding
Chemical sample preparation		Microwave digestion Acid digestion Dry ashing Solvent extraction	Acid digestion	Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (incl. typical margins of errors)	PBB/PBDE	GC/MS HPLC/UV	NA	GC/MS HPLC/UV
	Cr VI	Alkaline digestion/colorimetric method	Spot-test procedure/boiling-water extraction procedure	Alkaline digestion/colorimetric method
	Hg	ICP-AES, ICP-MS, CVAAS, AFS		
	Pb/Cd	ICP-AES, ICP-MS, AAS		

The results of ICP-OES analysis of the raw plastic matrices are shown in Table 2. None of the limits specified in the guidelines are exceeded. High levels of antimony are observed in the colored plastics and may be of concern in the future.

Table 2: Plastic Results (mg/kg in the solid)

	#1 Plastic (white)	#3 Plastic (white)	#4 Plastic (white)	#5 Plastic (green)	#6 Plastic (black)	#7 Plastic (black)
Cadmium	ND	ND	ND	ND	ND	ND
Chromium	1.39	1.37	0.96	13.4	5.18	10.0
Lead	1.53	1.90	1.12	14.1	16.4	14.6
Mercury	ND	ND	ND	ND	ND	ND
Aluminum	ND	ND	ND	11140	87475	11378
Antimony	6.61	5.78	4.39	4685	9.54	6744
Arsenic	ND	ND	ND	10.4	9.55	13.2
Barium	ND	ND	ND	2.43	21.6	1.84
Beryllium	ND	ND	ND	ND	ND	ND
Calcium	25.2	64.8	34.0	86690	108600	90290
Copper	21.0	17.0	14.2	50.6	14.9	16.5
Iron	ND	ND	ND	175	48.4	172
Magnesium	3.96	3.51	2.04	2249	1149	2298
Manganese	ND	ND	ND	22.8	26.1	20.6
Nickel	2.03	2.57	1.38	0.42	1.93	ND
Selenium	12.8	13.1	9.91	ND	ND	ND
Silver	ND	ND	ND	ND	ND	ND
Thallium	ND	ND	ND	ND	ND	ND
Vanadium	ND	ND	ND	8.85	ND	8.12
Zinc	82.9	78.1	45.1	325	1024	317

ND: Not Detected

Table 3 shows the results from the various electrical components measured. Lead and cadmium levels are exceeded for several of the products. Several other elements are also present and may be of concern.

Table 3: Electrical Components (mg/kg in the solid)

	#7 Circuit Board	#6 Wire Insulation	#4 Red Connector Sheath	#3 Ribbon Cable	#2 Yellow Sleeve
Cadmium	ND	297	ND	ND	ND
Chromium	25.7	44.9	4.36	72.9	ND
Mercury	ND	ND	ND	ND	ND
Lead	1610	14.4	0.95	4920	1.67
Aluminum	5009	20885	59.2	65.5	40.1
Antimony	2225	6.46	ND	1549	ND
Arsenic	38.1	10.0	ND	ND	ND
Barium	1985	495	2.60	2650	3872
Beryllium	ND	1.22	ND	ND	0.66
Calcium	33642	90011	101	13367	ND
Copper	192470	70.2	17.1	329995	89.9
Iron	634	1255	1027	27.1	5.0
Magnesium	1123	2214	ND	37.4	ND
Manganese	22.8	29.1	5.08	7.53	ND
Nickel	61.5	33.5	3.39	ND	1.53
Selenium	ND	10.9	10.4	5.9	11.9
Silver	10.7	ND	ND	16.1	ND
Thallium	ND	ND	ND	ND	ND
Vanadium	11.2	39.6	ND	ND	ND
Zinc	1122	68.1	9.70	166	9.16

Table 4 shows the precision between two digested aliquots of the same material. Most of the elements agree well, however the selenium concentration differs by approximately 156%. This is most likely due to measurement near the detection limit which increases variability.

Table 4: Precision – Relative Percent Difference

	#6 Wire Insulation	#5 Wire Insulation	%Diff
Aluminum	20885	20416	2.3
Antimony	6.46	7.08	9.2
Arsenic	10.0	11.3	13
Barium	495	360	31
Beryllium	1.22	1.27	3.7
Cadmium	297	210	34
Calcium	90011	88347	1.9
Chromium	44.9	48.4	7.4
Copper	70.2	64.9	7.9
Mercury	ND	ND	
Iron	1255	1508	18
Lead	14.4	11.8	20
Magnesium	2214	2544	14
Manganese	29.1	28.2	3.2
Nickel	33.5	38.4	14
Selenium	10.9	1.35	156
Silver	ND	ND	
Thallium	ND	ND	
Vanadium	39.6	40.8	2.9
Zinc	68.1	64.1	6.0

To further confirm performance of the digestion/analytical technique combination a predigestion spike was measured on a homogeneous matrix (Table 5). Recoveries were excellent.

Table 5: Pre-digestion Spike Recovery

	#1 Plastic (white)	#1 Plastic SPIKE	%Recovery
Antimony	0.01	0.88	87
Arsenic	ND	0.88	88
Beryllium	ND	0.94	94
Cadmium	ND	0.96	96
Calcium	0.05	1.11	106
Chromium	ND	1.00	100
Copper	0.04	1.03	99
Iron	0.01	1.04	103
Lead	ND	0.97	97
Magnesium	0.01	1.03	102
Manganese	ND	1.03	103
Nickel	ND	1.03	102
Selenium	0.03	0.82	80
Thallium	ND	0.86	88
Vanadium	ND	0.97	97
Zinc	0.17	1.08	91

Spike was 1 ppm in solution

Lead and cadmium determination by ICP-OES and flame AA were compared. Table 6 compares the analytical results on a variety of matrices.

Table 6: AA and ICP-OES Analysis Compared (mg/kg in the solid)

	Pb AA	Pb ICP-OES	Cd AA	Cd ICP-OES
#1 Yellow Sleeve	ND	1.7	ND	0.6
#2 Yellow Sleeve Dup	ND	1.7	ND	0.6
#3 Ribbon Cable	4710	4917	ND	ND
#4 Red Connector	20	0.95	ND	ND
#5 Wire Insulation	45	11.8	248	210
#6 Wire Insulation DUP	43	14.4	330	297
#7 Circuit Board	1590	1612	ND	ND
#1 Plastic (white)	ND	1.5	ND	ND
#3 Plastic (white)	ND	1.9	ND	ND
#4 Plastic (white)	ND	1.1	ND	ND
#5 Plastic (green)	30	14.1	ND	ND
#6 Plastic (black)	37	16.4	ND	ND
#7 Plastic (black)	31	14.6	ND	ND

ND: not detected

The results obtained with the two techniques compared favorably. ICP-OES took approx 3 minutes for the analysis of 18 elements AA took about 15 seconds for the analysis of 1 sample for 1 element, after calibration. ICP-OES can include Hg in a multielement analysis if the sample preparation preserves Hg. If more than 8 elements are being determined, ICP-OES is the faster technique. Many laboratories will find ICP-OES to be the more suitable technique for this analysis because of the considerations mentioned and the versatility of the technique for other projects that may require metals analysis.

CONCLUSION

Microwave digestion is an excellent sample digestion technique for RoHS compliance because of sample variability tolerance and the ability to retain volatile elements. Digestion time is predictable and reduced below hot plate digestion time due to high temperature/pressure.

ICP-OES provides several benefits for the analyses of RoHS matrices including multielement capabilities to provide rapid information on a variety of elements, suitable detection limits, and wide dynamic range to meet the needs of potentially diverse samples. Analysis of a variety of samples demonstrates repeatability, spike recovery, and good precision for materials containing different levels of analytes of interest and other elements that may be needed for informational purposes.

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Inorganic Analysis for Environmental RoHS Compliance

Zoe Grosser Ph.D., and Laura Thompson
NEMC 2006

European Union (EU) Regulations

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- Waste Electrical and Electronic Equipment (WEEE) directive
  - In effect in the EU since August 2004
  - Requires manufacturers to take back and recycle electrical products

- Restriction of Hazardous Substances (RoHS) Legislation
  - Applies to the entire EU from July 2006
  - Bans products containing ≥ 0.1% Cr VI, Hg, Pb and ≥ 0.01% Cd in homogeneous materials and regulates two brominated flame retardants

Appropriate sample preparation and analysis techniques must be performed to demonstrate compliance

Who will need to perform these analyses?

- Large manufacturers with laboratories
- Contract laboratories
  - Environmental
  - Materials testing

Anyone who plans to sell their product in the European Union

Page 3

Compliance with RoHS

- As of July 1, 2006 electrical equipment sold in the EU must comply with these regulations
  - Producers will need to be confident their products comply, but the directive does not provide guidance
  - Analysis of every component would be expensive
  - But analysis of assemblies or finished materials might give false confidence if compared to a limit determined on a component basis (homogeneity is also a challenge)
  - Large manufacturers have exhaustively considered their products and suppliers and developed implementation plans with the limited information available

Page 4

Specifications of Metals Contents of EU & Major Companies(2004/03/01) (ppm)

Company/ Specifications	Cd	Pb	Hg	Cr^{+6}	Packing Material	Ni	Reference
Sony	5	100	5	-	100	-	SS-00259
Microsoft	25	100	5	100	100	-	H00594
Dell	50(250)	100(400)	5	100	100	-	6T-198
Panasonic	75	100	100	100	100	-	Ver.2.1
Motorola	100	100	100	100	100	100	GS2257

Page 5

Objectives of this Paper

- Evaluate inorganic analysis techniques for a variety of materials and business situations
  - Digested and analyzed a range of electrical components, assemblies and raw materials
  - Raw materials that will be used to produce cable coverings and other electrical components
  - Assemblies and components that represent a variety of colors and materials

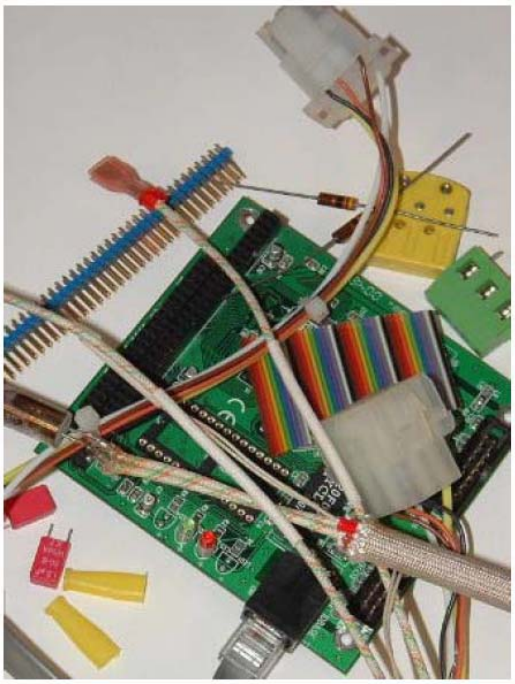
Page 6

Objectives of this Paper

- Develop a sample preparation technique to meet requirements of RoHS regulations
  - Diverse sample matrices
  - Total dissolution necessary
  - Limit contamination
  - Prevent volatile element loss (Hg, Cd, Pb)

Page 7

Sample Variety



Page 8

Microwave versus Conventional Digestion

1. Fast, about 30 - 40 minutes
2. Digestion Temp. up to 300 °C
3. Minimized contamination
4. Can use HF, H_2SO_4, & H_2PO_4
5. No losses of volatile elements such as Hg, As, Sb & Se etc.
6. Pressures range up to 80 bar
7. Suitable for organic as well as inorganic materials
8. Fully automatic, user supervision not required

1. Larger Sample quantity
2. Longer digestion time: 30 min. to 2 hours
3. Total Digestion can be difficult
4. Digestion temperature limited to ~130 °C
5. Serious corrosive acidic fumes, contamination & operators' health issues
6. Corrosive to lab. environment and instruments
7. Loss of volatiles possible
8. Close supervision is normally required, to prevent charring of samples

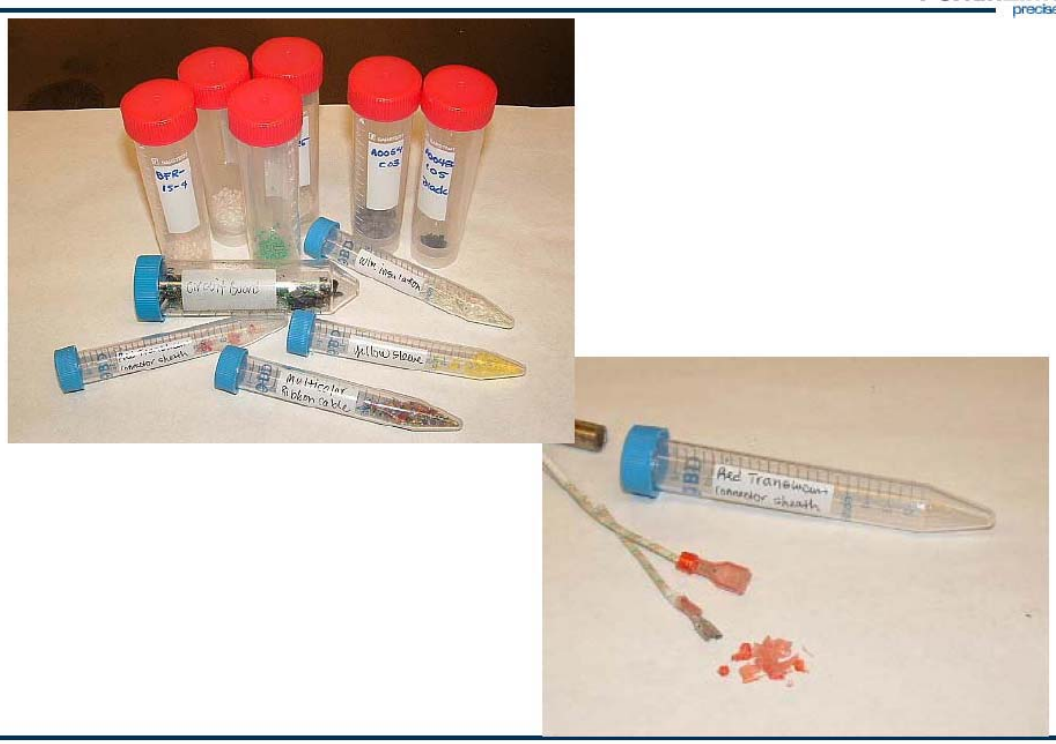
Page 9

Microwave Digestion

- Microwave digestion chosen
  - Multiwave 3000 digestion system
  - 50 mL ceramic-jacketed Teflon vessels
  - 8-position Rotor with full pressure control at each position
  - 1400 W maximum power program

Page 10

Sample Preparation



Page 11

Microwave Digestion

- Approximately 0.1 g of each sample was weighed and transferred to the digestion vessel
- Reagents were added to the vessels
  - Plastics: 9 mL HNO_3
  - Components and assemblies: 6 mL HNO_3/2 mL H_2O_2/1 mL HF
  - Samples were digested following a 45 min power program
    - Ramp from 0-600 W for 5 min, hold for 15 min
    - Ramp from 600-1400 W for 5 min, hold for 20 min
  - Digestates transferred and diluted to 50 mL with DI H_2O

Page 12

Inorganic Techniques

- Atomic Absorption (AA)
  - Low initial investment
  - Simple to use
  - One element at a time can be slow
  - Separate analysis for mercury
- ICP-OES
  - Moderate initial investment
  - Fast multielement technique
  - Can include mercury in the analysis
  - Can screen for other elements that may be of interest in the future
- ICP-MS
  - Higher initial investment
  - Fast multielement technique
  - Lower detection limits for use of smaller sample size or compliance with lower limits
  - Can include mercury in the analysis
  - Can screen for other elements that may be of interest in the future

Page 13

Choice of Technique

- Concentrations in the solid may range up to 1000 ppm, yielding up to several ppm in solution
- ICP-MS can measure the elements of interest at once, but dilutions may be required to avoid contaminating the instrument
- Flame AA or axial ICP-OES will provide a sufficient detection limit and good linear range
- Axial ICP-OES can measure all the elements of interest in one run: Pb, Cr (total), Cd, and Hg

Axial ICP-OES will be evaluated with comparison to flame AA

Page 14

ICP-OES Analysis

- Optima 5300 DV
- Axial mode used for elements where increased sensitivity used, such as Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Se, etc..
- Radial mode used for elements expected at higher concentrations, such as Ba, Mg, Mn, etc..
- Low-flow GemCone Nebulizer
- Cyclonic spray chamber
- On-line addition of internal standard
- Total analysis time approximately 3 minutes per sample

Page 15

Instrumental Analysis

- Draft Standard

111/24/CD

COMMITTEE DRAFT (CD)

IEC/TC or SC: 111	Project number IEC 62321, Ed.1	
Title of TC/SC: Environmental standardization for electrical and electronic products and systems	Date of circulation 2005-06-24	Closing date for comments 2005-09-23
Also of interest to the following committees IEC/TC3, SC17B, SC62A, TC 108	Supersedes document 111/2/NP & 111/9/RVN and 111/25/INF	
Functions concerned: ☐ Safety ☐ EMC	☒ Environment	☐ Quality assurance
Secretary: Andrea Legnani (Italy) E-mail: andrea.legnani@anie.it	THIS DOCUMENT IS STILL UNDER STUDY AND SUBJECT TO CHANGE. IT SHOULD NOT BE USED FOR REFERENCE PURPOSES. RECIPIENTS OF THIS DOCUMENT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.	

Title:
IEC 62321, Ed.1: Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products

Page 16

Draft Standard Summary

Steps	Substances	Polymer Materials	Metal Materials	Electronics(PWBs/ Components)
Mechanical sample preparation		Direct Measurement Grinding	Direct Measurement Grinding	Grinding
Chemical sample preparation		Microwave digestion Acid digestion Dry ashing Solvent extraction	Acid digestion	Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (incl. typical margins of errors)	PBB/PBDE	GC/MS HPLC/UV	NA	GC/MS HPLC/UV
	Cr VI	Alkaline digestion/colorimetric method	Spot-test procedure/boiling-water extraction procedure	Alkaline digestion/colorimetric method
	Hg	ICP-AES, ICP-MS, CVAAS, AFS		
	Pb/Cd	ICP-AES, ICP-MS, AAS		

But it might also make sense to measure the total amount of chromium first, thereby allowing all the elements to be measured simultaneously. If the amount exceeds the limit, the determination of Cr VI would further define compliance.

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Plastic Matrices (mg/kg in the solid)

	#1 Plastic (white)	#3 Plastic (white)	#4 Plastic (white)	#5 Plastic (green)	#6 Plastic (black)	#7 Plastic (black)
Cadmium	ND	ND	ND	ND	ND	ND
Chromium	1.39	1.37	0.96	13.4	5.18	10.0
Lead	1.53	1.90	1.12	14.1	16.4	14.6
Mercury	ND	ND	ND	ND	ND	ND
Aluminum	ND	ND	ND	11140	87475	11378
Antimony	6.61	5.78	4.39	4685	9.54	6744
Arsenic	ND	ND	ND	10.4	9.55	13.2
Barium	ND	ND	ND	2.43	21.6	1.84
Beryllium	ND	ND	ND	ND	ND	ND
Calcium	25.2	64.8	34.0	86690	108600	90290
Copper	21.0	17.0	14.2	50.6	14.9	16.5
Iron	ND	ND	ND	175	48.4	172
Magnesium	3.96	3.51	2.04	2249	1149	2298
Manganese	ND	ND	ND	22.8	26.1	20.6
Nickel	2.03	2.57	1.38	0.42	1.93	ND
Selenium	12.8	13.1	9.91	ND	ND	ND
Silver	ND	ND	ND	ND	ND	ND
Thallium	ND	ND	ND	ND	ND	ND
Vanadium	ND	ND	ND	8.85	ND	8.12
Zinc	82.9	78.1	45.1	325	1024	317

ND: not detectable, below the estimated detection limit

Page 18

Results and Discussion

- Plastic raw materials and components do not exceed the specified limits and are in general quite low.
- Other elements show high levels of antimony in two colored plastics. This element may be of concern in the future.

Page 19

Electrical Components (mg/kg in solid)

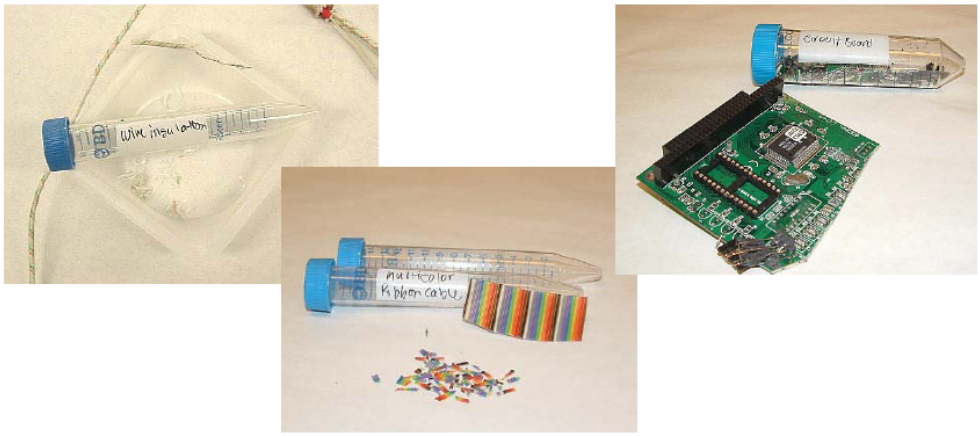
	#7 Circuit Board	#6 Wire Insulation	#4 Red Connector Sheath	#3 Ribbon Cable	#2 Yellow Sleeve
Cadmium	ND	297	ND	ND	ND
Chromium	25.7	44.9	4.36	72.9	ND
Mercury	ND	ND	ND	ND	ND
Lead	1610	14.4	0.95	4920	1.67
Aluminum	5009	20885	59.2	65.5	40.1
Antimony	2225	6.46	ND	1549	ND
Arsenic	38.1	10.0	ND	ND	ND
Barium	1985	495	2.60	2650	3872
Beryllium	ND	1.22	ND	ND	0.66
Calcium	33642	90011	101	13367	ND
Copper	192470	70.2	17.1	329995	89.9
Iron	634	1255	1027	27.1	5.0
Magnesium	1123	2214	ND	37.4	ND
Manganese	22.8	29.1	5.08	7.53	ND
Nickel	61.5	33.5	3.39	ND	1.53
Selenium	ND	10.9	10.4	5.9	11.9
Silver	10.7	ND	ND	16.1	ND
Thallium	ND	ND	ND	ND	ND
Vanadium	11.2	39.6	ND	ND	ND
Zinc	1122	68.1	9.70	166	9.16

Page 20

ND: not detectable, below the estimated detection limit

Results and Discussion

- Materials contain a wide variety of elements
- Several of the elements of concern exceed the regulated limits (highlighted in pink)



Page 21

Precision – Relative Percent Difference of Duplicates

Samples not washed first, is the inhomogeneity a result of surface contamination?

	#2 Yellow Sleeve	#1 Yellow Sleeve	%Diff
Aluminum	40.1	60.8	41
Antimony	ND	ND	
Arsenic	ND	ND	
Barium	3872	3950	2.0
Beryllium	0.66	0.35	60
Cadmium	ND	ND	
Calcium	ND	ND	
Chromium	ND	ND	
Copper	89.9	225	86
Mercury	ND	ND	
Iron	5.0	4.2	17
Lead	1.67	1.72	3.1
Magnesium	ND	ND	
Manganese	ND	ND	
Nickel	1.53	1.85	19
Selenium	11.88	11.35	4.6
Silver	ND	ND	
Thallium	ND	ND	
Vanadium	ND	ND	
Zinc	9.16	9.11	0.6

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Precision – Relative Percent Difference of Duplicates

	#6 Wire Insulation	#5 Wire Insulation	%Diff
Aluminum	20885	20416	2.3
Antimony	6.46	7.08	9.2
Arsenic	10.0	11.3	13
Barium	495	360	31
Beryllium	1.22	1.27	3.7
Cadmium	297	210	34
Calcium	90011	88347	1.9
Chromium	44.9	48.4	7.4
Copper	70.2	64.9	7.9
Mercury	ND	ND	
Iron	1255	1508	18
Lead	14.4	11.8	20
Magnesium	2214	2544	14
Manganese	29.1	28.2	3.2
Nickel	33.5	38.4	14
Selenium	10.9	1.35	156
Silver	ND	ND	
Thallium	ND	ND	
Vanadium	39.6	40.8	2.9
Zinc	68.1	64.1	6.0

Duplicate Digestion Analysis

- Duplicates of samples appearing to be reasonably homogeneous were performed to assess reproducibility
- Surface contamination was not eliminated by washing and may contribute to inhomogeneity
- Duplicates are with 20% RSD in most cases, showing adequate reproducibility

Pre-digestion Spike Recovery

	#1 Plastic (white)	#1 Plastic SPIKE	%Recovery
Antimony	0.01	0.88	87
Arsenic	ND	0.88	88
Beryllium	ND	0.94	94
Cadmium	ND	0.96	96
Calcium	0.05	1.11	106
Chromium	ND	1.00	100
Copper	0.04	1.03	99
Iron	0.01	1.04	103
Lead	ND	0.97	97
Magnesium	0.01	1.03	102
Manganese	ND	1.03	103
Nickel	ND	1.03	102
Selenium	0.03	0.82	80
Thallium	ND	0.86	88
Vanadium	ND	0.97	97
Zinc	0.17	1.08	91

1 ppm spike in solution

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Predigestion Spike

- A predigestion spike on a raw material was performed to demonstrate recovery of the microwave digestion sample preparation technique
- Recoveries were excellent, confirming that microwave digestion does not add additional uncertainty to the analysis

Page 26

AA and ICP-OES Compared (mg/kg in solid)

	Pb AA	Pb ICP-OES	Cd AA	Cd ICP-OES
#1 Yellow Sleeve	ND	1.7	ND	0.6
#2 Yellow Sleeve Dup	ND	1.7	ND	0.6
#3 Ribbon Cable	4710	4917	ND	ND
#4 Red Connector	20	0.95	ND	ND
#5 Wire Insulation	45	11.8	248	210
#6 Wire Insulation DUP	43	14.4	330	297
#7 Circuit Board	1590	1612	ND	ND
#1 Plastic (white)	ND	1.5	ND	ND
#3 Plastic (white)	ND	1.9	ND	ND
#4 Plastic (white)	ND	1.1	ND	ND
#5 Plastic (green)	30	14.1	ND	ND
#6 Plastic (black)	37	16.4	ND	ND
#7 Plastic (black)	31	14.6	ND	ND

ND: not detectable, below the estimated detection limit

Page 27

Comparison with Flame AA

- Analysis compared with flame AA for Pb and Cd
- ICP-OES took approx 3 minutes for the analysis of 18 elements AA took about 15 seconds for the analysis of 1 sample for 1 element, after calibration
- ICP-OES can include Hg in a multielement analysis if the sample preparation preserves Hg
- If more than 8 elements are being determined, ICP-OES is the faster technique

Page 28

Conclusions

- Microwave digestion is an excellent sample digestion technique for RoHS compliance
  - Sample variability tolerance
  - Volatile element retention
  - Reduced digestion time due to high temperature/pressure
- ICP-OES provides several benefits for the analyses of RoHS matrices
  - Multielement to provide rapid information on a variety of elements
  - Suitable detection limits and wide dynamic range to meet the needs of a potentially diverse sample variety
- Analysis of a variety of samples demonstrates repeatability, spike recovery, and good precision for materials containing different levels of analytes of interest and other elements that may be needed for informational purposes

MODERN INTERFERENCE CORRECTION INCLUDING CELL-BASED TECHNOLOGY FOR ICP-MS ENVIRONMENTAL ANALYSES

Foglio, Lorraine and Neubauer, Kenneth; PerkinElmer Analytical Sciences

ICP-MS has become increasingly popular for environmental analyses because of the low detection limits and ability to measure a large number of elements very quickly. In addition, the ICP-MS offers the ability for isotope ratio measurements and is an excellent detector for speciated inorganic analyses.

Interferences are problematic in most instrumental analytical techniques. Depending on the matrix, interference effects may be mild or severe. In most cases, some type of compensation is available to minimize the effect of interferences. The nature of interferences problematic in ICP-MS will be discussed. The historical forms of interference compensation will be described.

The development of cell-based technology to correct interference problems in this technique will be outlined and the corresponding benefits described.

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Modern Interference Correction Including Cell-based Technology for ICP-MS Environmental Analyses

Lorraine Foglio
Kenneth Neubauer, Ph. D.

Introduction

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- Most analytical techniques have interferences
- Usually can be understood, minimized and controlled

- Talk will discuss the interferences found in the use of ICP-MS for environmental analysis
- Mechanisms of interferences and methods of correction will be discussed
- Update on cell usage for US environmental methods

Interferences in ICP-MS

- Caused by something in the sample not present in the Calibration Blank and Standards….. leads to incorrect results.

- Physical, Bulk Property of Sample
  - Viscosity
  - Matrix
  - Space Charge

- Spectral, Atomic or Molecular Content of Sample
  - Atomic Isotope
  - Molecular Polyatomic Ion

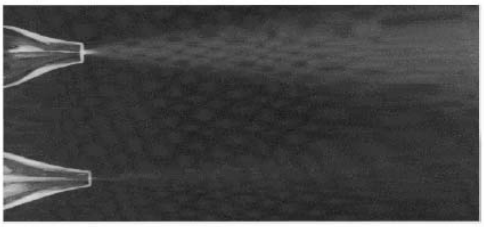
Page 3

Physical Interference Viscosity

- **Common in ICP emission and ICP-MS**

  - **Sample Different from Calibration Solutions**
    - **Surface tension**
    - **Viscosity**
  - **Aerosol transport effects**
    - **droplet formation by nebulizer**
    - **droplet size selection in spray chamber**

- **Internal Standardization**
  - **Can compensate for Physical Interferences**



Page 4

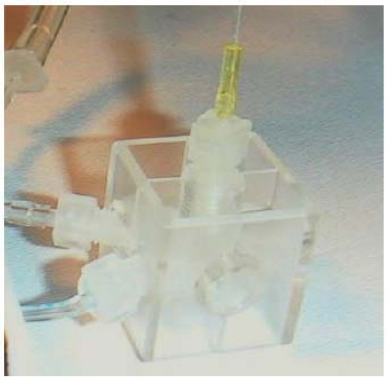
Internal Standardardization

PerkinElmer precisely.

Analytes are Ratioed to Internal Standard recovery

Frequently Employed as Internal Standards

Element	Mass
Li	6
Sc	45
Ge	72
Y	89
Rh	103
In	115
Tm	169
Lu	175



EPA Methods Require at Least 5 Internal Standards

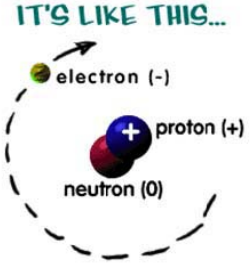
Page 5

Physical Interference *Matrix*

PerkinElmer precisely.

- Energy reduced in plasma sometimes called "Plasma Loading"
- Readings are generally suppressed
- Can be minimized
  - Keep dissolved solids below 0.1%
  - Robust plasma conditions

- Use internal standards matched by ionization potentials as well as mass.
  - Se = 9.75
  - Zn = 9.34
  - Ge = 7.90
  - In = 5.79



Page 6

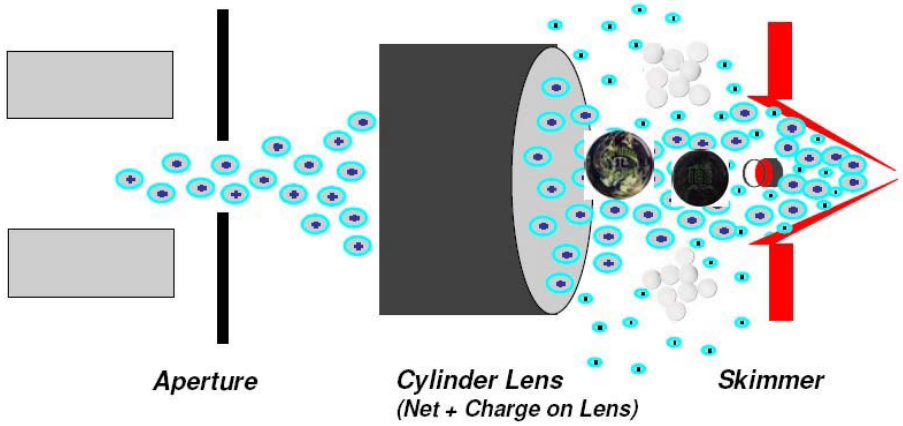
Spike Recovery vs. Internal Standard Element

Element	Internal Standard	Spike Recovery
Zn	In	76.2
	Ge	103.1
As	In	84.5
	Ge	96.3
Se	In	79.3
	Ge	83.2

Page 7

Physical Interference Space Charge Effect

- High mass matrix elements can suppress low mass analyte signals
- Like Bowling Balls and Ping Pong Balls
- EPA Methods require the use of at least 5 internal standard spread across the mass range to correct for Space Charge Effects.



Page 8

Detection of Physical Interferences

- Spiked samples
- Check Reference materials
- Non-linear response after dilution indicates probable interference
- Poor "Recovery" of Internal Standard Elements

- Or, just assume they are always present

Page 9

Spectral Interference Atomic and Polyatomic Mass Overlaps

Samples containing particular elements may have atomic isotope overlaps or form polyatomic molecular ions.

The most common are:

- Samples with High Metallic content
- Argon-forming or ArX where X=O, Cl, P, S, etc.
- Oxides: MoO, TiO, CaO
- Dimers: Ar_2, N_2, O_2, S_2, P_2
- Hydrides: ArH, BrH
- Hydroxides: CaOH, ArOH

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ICP-MS Spectral Interferences

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Some spectral interferences found in common matrices

Interference	Analyte
^{40}Ar	^{40}Ca
$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	^{56}Fe
$^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$	^{52}Cr
$^{40}Ar^{13}C$, $^{40}Ar^{12}C\ ^{1}H$	^{53}Cr
$^{35}Cl^{40}Ar$	^{75}As
$^{44}Ca^{16}O$	^{60}Ni
$^{40}Ar\ ^{23}Na$	^{63}Cu
$^{35}Cl^{16}O$	^{51}V
^{81}BrH	^{82}Se

Page 11

Spectral Interference Correction Options

PerkinElmer precisely.

- **Isobaric Correction Equations**
- **Cold Plasma:** Reduces argon-based interferences in Simple Matrices
- **High Resolution MS:** Can resolve some interferences nicely
- **Collision Cell**
  - Uses passive fixed potential rods (multi-poles)
  - Dependent on Kinetic Energy Reduction by Passive Collisions with Inert Gas
- **Dynamic Reaction Cell**
  - Uses second Active Quadrupole
  - Uses Reactive Gas to “Chemically Remove” Interferences

Page 12

Spectral Interference Atomic Isobaric Overlap

- Isobaric Overlaps
  - Be aware of what is in your samples when selecting isotopes

Percent Abundance

Element	46	47	48	49	50
Ca	0.004		0.187		
Ti	8.0	7.3	73.8	5.5	5.4

Page 13

Handling the Interference Isobaric Correction Equations

- Built into the software to automatically correct for atomic isobaric overlaps
- Similar to IECs in ICP emission spectroscopy
- Except isotope ratios don't change, they are fixed in nature

Quantitative Analysis Method - d:\elandata\Method\200_8\EPA200-modif.mth

Timing | Processing | Equation | Calibration | Sampling

Isotope Information

Isotope	Mass	Abundance	Interferences
Be 9	9.0122	100.000000	

	Int Std	Analyte (*)	Mass (amu)	Corrections	Potential Interferences
8		V	50.944	-3.127*(ClO 53-(0.113*Cr 52))	HSO, ClO
9		Cr	51.9405	-0.03*C 13	SO, ArO, ArC, ArN, ClO, HClO
10		Fe	53.9396	- 0.028226 * Cr 52	Cr, HClO, ArO, ArN
11		Mn	54.9381		HClO, ArN, ClO
12		Co	58.9332		CaO
13		Ni	59.9332	-0.004* Ca 43	CaO
14		Cu	64.9278		TiO, PO2, SO2, Ba++
15		Zn	65.926		TiO, VO, SO2, Ba++
16		Zn	67.9249		VO, ClO2, SO2, TiO, ArS, Ba++, C
17	▶	Ge	71.9217		ArS, Nd++, Nd++, Sm++
18		As	74.9216	-3.127*(ArCl 77-(0.815*Se 82))	ArCl, Sm++, Eu++, Nd++
19		Se	77.9173		Kr, Ar2, Gd++, Gd++, Dy++
20		Se	81.9167	-0.002*Br 81	Kr, Ar2H, BrH, Ho++, Er++, Dy++
21		Kr	82.9141		Er++, Er++
22		Mo	97.9055	- 0.110588 * Ru 101	Ru
23		Ag	106.905		ZrO, YO
24		Cd	110.904	-1.073*(MoO 108 - (0.712*Pd 106	MoO
25		Cd	113.904	- 0.026826 * Sn 118	Sn, MoO
26	▶	In	114.904	- 0.014032 * Sn 118	Sn, MoO

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What's going on at Mass 51? Polyatomic Interference

PerkinElmer precisely

Example: $^{35}Cl^{16}O$ interference on ^{51}V at mass 51

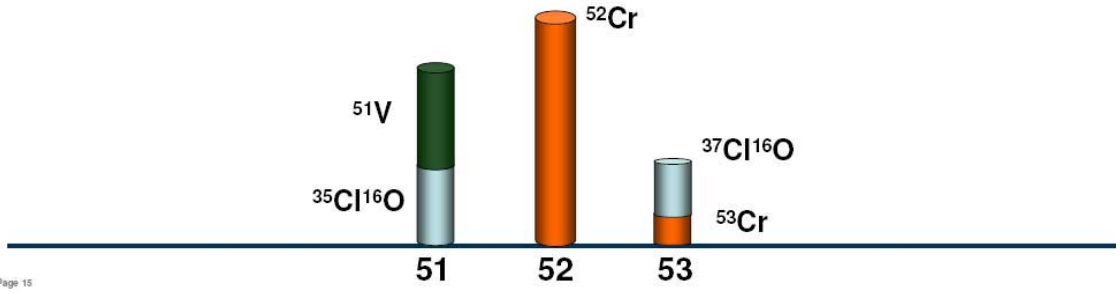
But: $^{37}Cl^{16}O$ forms proportionally at mass 53

$$^{51}V = mass51 - a^{35}Cl/a^{37}Cl^{*} \; mass53$$

$$^{51}V = mass51 - 3.127^{*}ClO53$$

But, Cr is also at mass 53, so must correct for Cr on ClO53!

$$^{51}V = mass51 - 3.127^{*}(ClO53 - (0.113^{*}Cr52))$$



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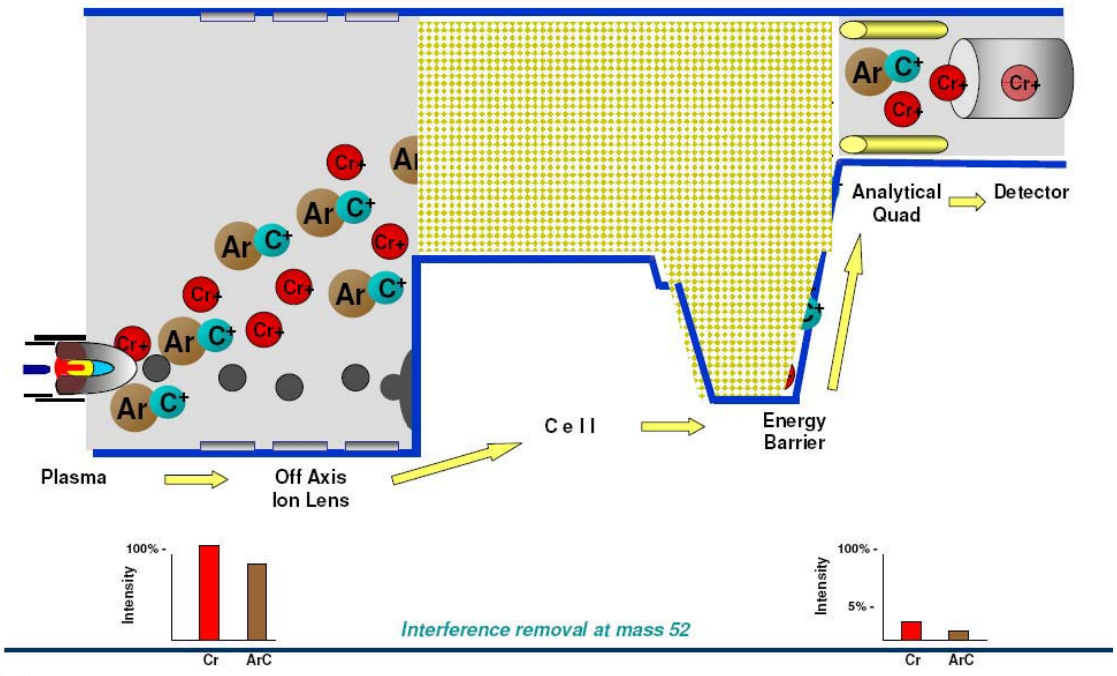
Collision Cells Trap and Retain Interfering Species

PerkinElmer precisely



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Collision Cell Limitations

- **Relies on Probability of Collisions with Inert Gas and Kinetic Energy Discrimination (KED)**
  - Analyte Signal Loss Severe With KED
  - All ions lose energy, including analytes of interest
  - Analyte loss of greater than 95% not uncommon
  - All Collision Cells require the use of a shielded torch
  - Cannot make analytical use of polyatomic ions created in the cell (AsO^+)
  - Mass Dependant: Analytes with energy less than the KED set point will be lost
- **Ions are not removed - All ions are free to recombine, forming new and unpredictable molecular interferences**
  - Reactive gases can generate new interferences that cannot be removed from the cell (passive guide only-non scanning) so they cannot use reactive gases in multi-element determinations.
- **Cannot make analytical use of polyatomic ions created in the cell (AsO^+)**

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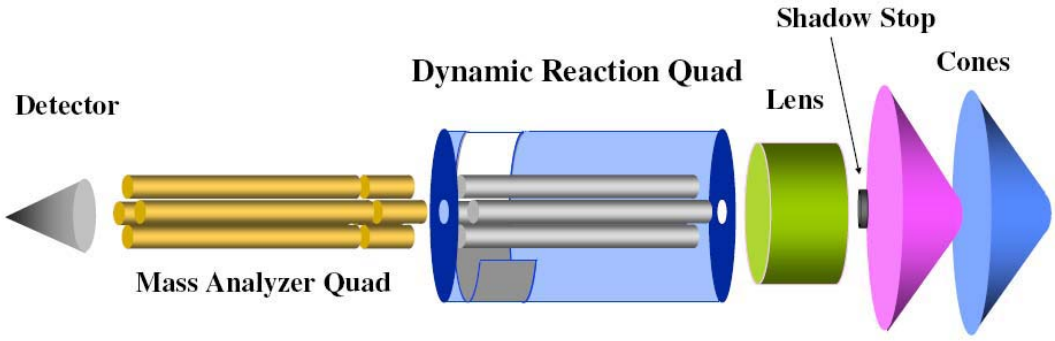
Handling the Interference — Dynamic Reaction Cell



Two means of Interference Reduction

1. Achieved through Chemical and Charge Transfer Reactions
2. Achieved through Dynamic Bandpass Tuning of the DRC QUAD

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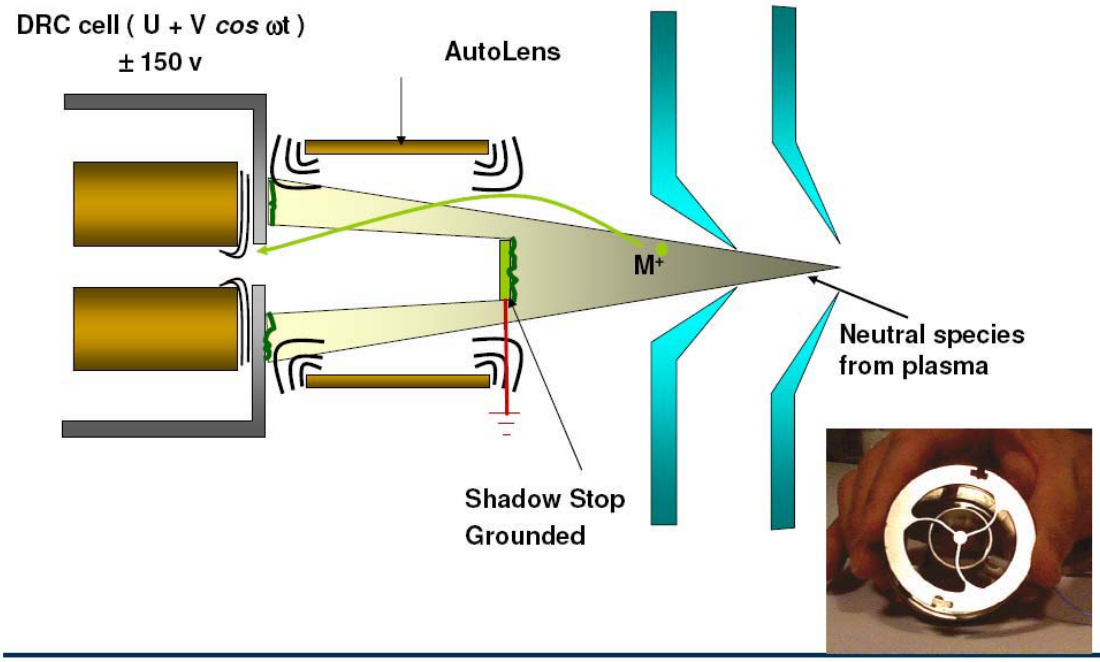
Robust Ion Lens System of ELAN DRC



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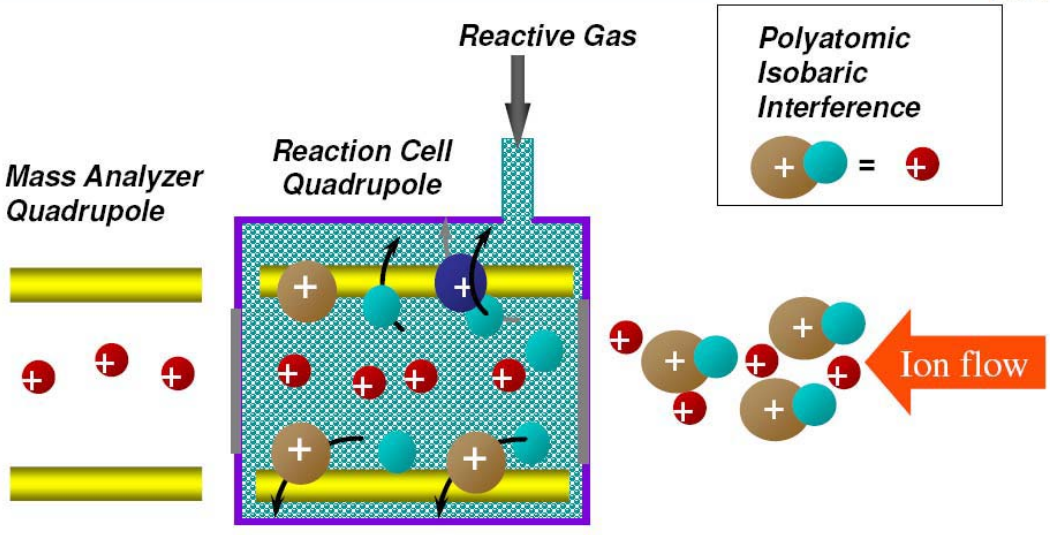
Example of a Reaction Inside the DRC



$CaO^+ + CH_4 \rightarrow CH_4^+ + Ca + O$

(Exothermic reaction)

$Ni^+ + CH_4 \rightarrow$ little or no reaction

(Endothermic reaction)

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Handling the Interference — Dynamic Reaction Cell

- The DRC is pressurized by a reaction gas. Any gas can be used based on its ability to:
  - React with the analyte
    - Dissociate polyatomic species
    - Electron or proton transfer
  - React with the analyte
- Dynamic bandpass tuning of the quadrupole ejects all unwanted reaction products and removes them from the cell
- Only analyte ions are focused through both the reaction cell and the analytical quadrupole

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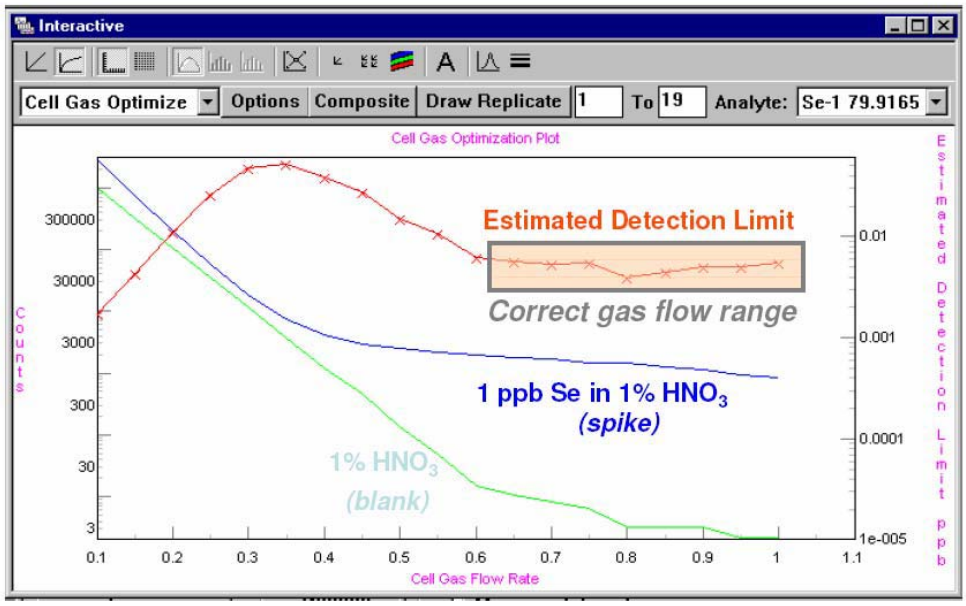
DRC Mode Optimization for Selenium

Typical Cell Gas Optimization Curve



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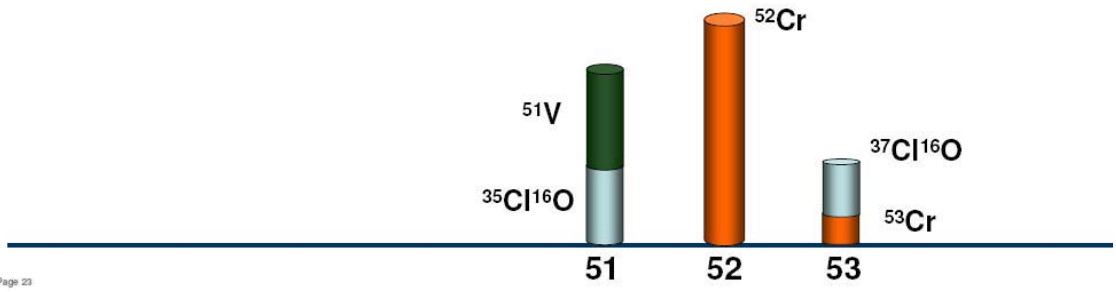
Vanadium in a Chloride Matrix

- Problem: $^{35}Cl^{16}O^+$ occurs at the same m/z as the major V isotope
- Goal: Eliminate ClO^+ interference
- How
  - Use a Dynamic Reaction Cell
  - Reaction Gas = NH_3
  - Matrix = 5% HCl
  - Spike = 1 µg/L V in 5% HCl



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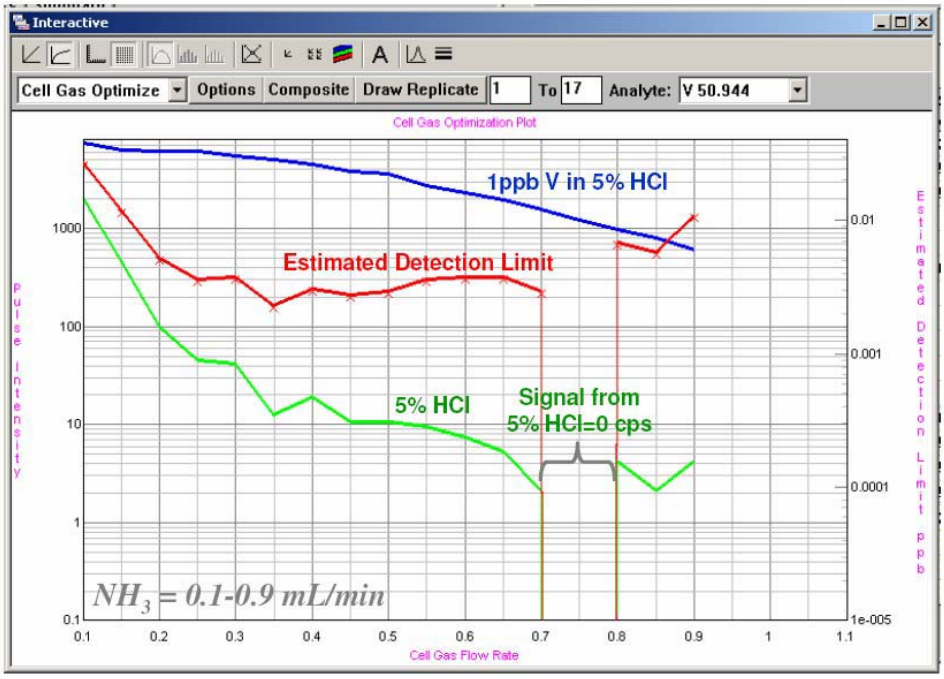
Cell Gas Optimization



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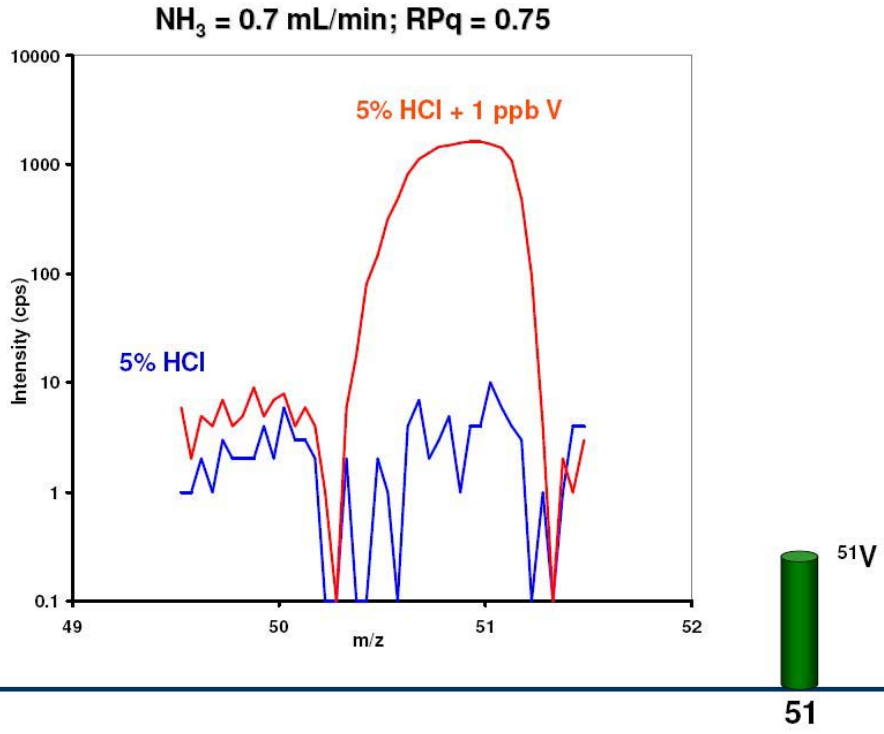
Complete Elimination of ClO^+



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Moving the Analyte *Creating Species in the Cell*

- Move analyte away from the interference
  - Lower backgrounds
  - Possible because of controlled chemistry
- Many times this can be accomplished using O_2 as reaction gas
  - ^{75}As into ^{91}AsO

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What Interferes with Arsenic Analysis?

- **Chlorides**
  - $ArCl^+$
  - $CaCl^+$

- **Examples of chloride or calcium containing matrices**
  - **Environmental**
    - **Wastewater, seawater, brines, soil digests**
  - **Clinical**
    - **Urine**
  - **Semiconductor**
    - **High purity HCl**

- **Isobaric Correction Equation for Standard ICP-MS**
  As = As75 - 3.127*{ArCl77 – (0.815*Se82)}

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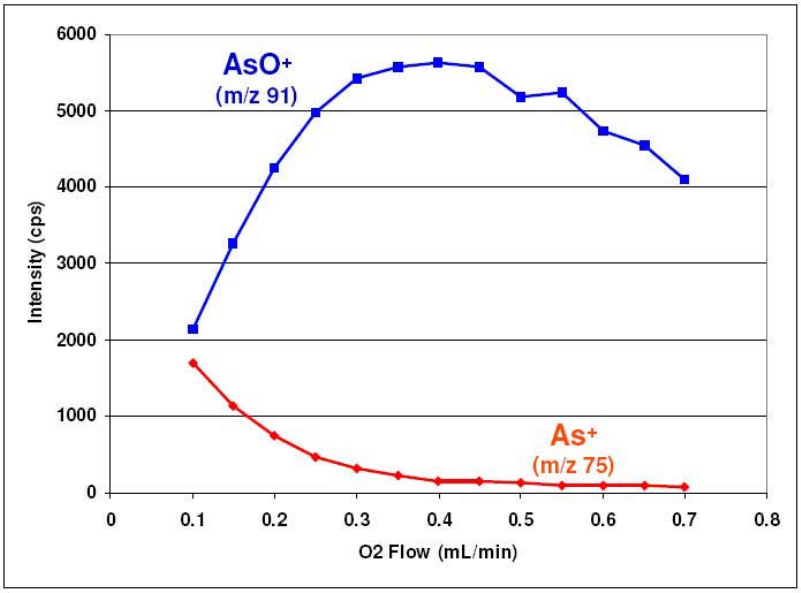
Moving the Analyte — Reaction of As^+ with O_2



AsO^+ forms while As^+ disappears

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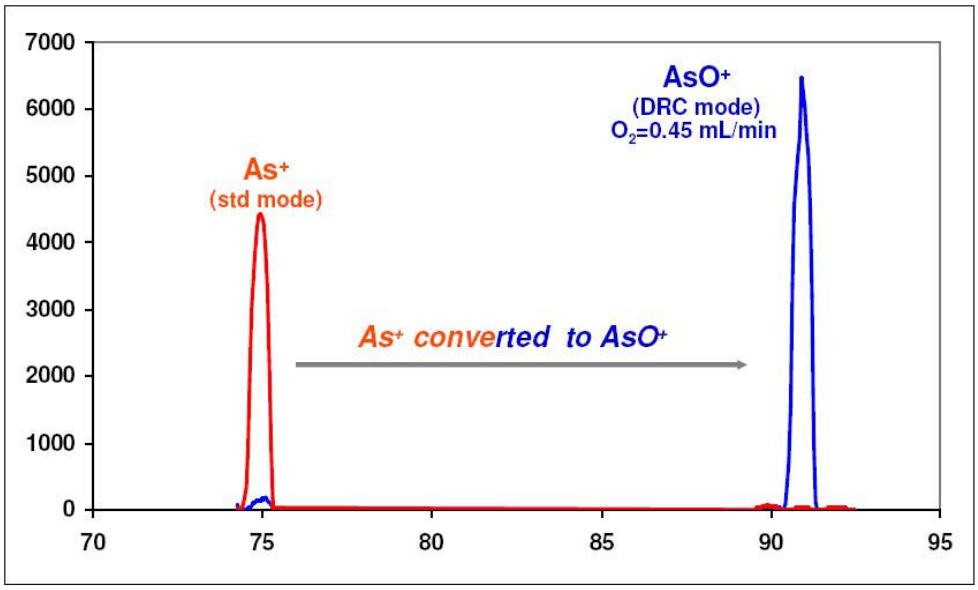
Conversion of As^+ to AsO^+



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DRC Advantages

- **Minimal Sensitivity Loss**
  - Collisions are not the primary interference removal pathway
  - DRC promotes analyte movement through the cell with AFT
  - No kinetic energy barriers are set
- **Reactions are predictable**
  - Interference removal follows predictable chemistry
  - Not dependant on interference concentration
- **Interference ejected**
  - Dynamic bandpass tuning ejects interferences and does not allow them to reach the analytical quadrupole

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DRC Modes of Operation

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- **Dynamic Reaction Cell Mode**
  - Cell is pressurized with continuous flow of reaction gas
  - Bandpass is optimized for elimination of interfering species
- **Standard Mode**
  - Cell is vented (no reaction gas)
  - Operates as a standard ELAN with the advantage of lower noise
- **Mixed Mode Method**
  - DRC and standard mode elements are grouped by the software and automatically run in the same method
  - 30 second delay switching modes

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Method 200.8 Overview

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- **Version 5.4, May 1994**
  - Available EPA/600/R-94/111
- **Applicable Elements**
  - Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Tl, Th, U, V, and Zn
- **Applicable Matrices**
  - Ground waters, surface waters, drinking waters
  - Wastewaters, sludges, soils
    - With sample prep contained in method

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Method 200.8 for SDWA

- Approved for all 12 primary contaminants from Safe Drinking Water Act
  - As, Ba, Be, Cd, Cr, Hg, Pb, Ni, Cu, Sb, Se, and Tl
  - Must meet <1 NTU rule to avoid sample prep
- First time a *single* method may be used to determine all 12 primary contaminants
  - Allows reduction in monitoring costs
    - Reduced analysis and prep costs
- Although not primary contaminants, Ca, Fe, Na, K, and Mg may be monitored by ICP-MS
- Not Approved for "Cell" use. Can use a DRC or DRC-e version in Standard mode.

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EPA Method 200.8 Correction Equations

Aluminum	27	
Antimony	121, 123	Sb 123 = Sb 123 – 0.127189 * Te 125
Arsenic	75	As 75 = As 75 – 3.127 * [Se 77 – (0.815*Se 82)]
Barium	135, 137	
Beryllium	9	
Cadmium	106, 108 111, 114	Cd 111 = Cd 111 – 1.073 * Pd 108 – (0.712*Pd 106) Cd 114 = Cd 114 – 0.026826 * Sn 118
Chromium	52, 53	
Cobalt	59	
Copper	63, 65	
Lead	206, 207, 208	Pb 208 = Pb 208 + 1* Pb 206 + 1* Pb 207
Manganese	55	
Mercury	202	
Molybdenum	95, 97, 98	Mo 98 = Mo 98 – 0.110588 * Ru 101
Nickel	60, 62	
Selenium	77, 82	Se 82 = Se 82 – 1.008696 * Kr 83
Silver	107, 109	
Thallium	203, 205	
Thorium	232	
Uranium	238	
Vanadium	51	V 51 = V51 – 3.127*[Cr 53 – (0.113*Cr 52)]
Zinc	66, 67, 68	

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EPA 200.8 Potential Interferences

Aluminum	27	
Antimony	121, 123	
Arsenic	75	$^{40}Ar^{35}Cl+$, $^{40}Ca^{35}Cl+$,
Barium	135, 137	
Beryllium	9	
Cadmium	106, 108 111, 114	
Chromium	52, 53	$^{40}Ar^{12}C+$, $^{37}Cl^{16}O^{+}$, $^{40}Ar^{13}C+$
Cobalt	59	
Copper	63, 65	$^{40}Ar\ ^{23}Na+$
Lead	206, 207, 208	
Manganese	55	
Mercury	202	
Molybdenum	95, 97, 98	
Nickel	60, 62	$^{44}Ca^{16}O+$
Selenium	77, 82	$^{81}BrH+$, $^{40}Ar^{37}Cl+$, $^{40}Ca^{37}Cl+$
Silver	107, 109	
Thallium	203, 205	
Thorium	232	
Uranium	238	
Vanadium	51	$^{35}Cl^{16}O+$
Zinc	66, 67, 68	

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Instrumental Conditions

Instrument	**ELAN DRC II**
RF Power	**1500 w**
Sample Uptake	**0.5 mL/min**
Nebulizer	**Concentric**
Spray Chamber	**Cyclonic**
Calibration	**External, aqueous**
Internal Standards	**Li 6, Ga 71, Rh 103, Ir 193 at 10 ppb**

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Method 200.8 DRC Results (ng/L)

PerkinElmer precisely

Element	Mass	Matrix	Matrix + 1 ppb	Matrix + 5 ppb
Aluminum	27	0.05	1.23	5.08
Antimony	121, 123	0.02	1.1	5.46
Arsenic	75	0.57	1.59	6.21
Arsenic DRC (O_2, 0.5)	91	0.06	1.09	5.81
Barium	135, 137	ND	ND	3.72
Beryllium	9	0	1.02	5.57
Cadmium	114	0.17	1.18	5.49
Cadmium DRC (O_2, 2)	114	0.03	1.03	5.31
Chromium	52	0.06	1.06	5.12
Chromium DRC (CH_4, 0.6)	52	0.05	1.06	5.12
Cobalt	59	0.08	1.02	5.03
Copper	65	0.06	1.07	5.04

Matrix:
Ca 50 ppm
C: 100 ppm (from HAc)
Cl: 500 ppm (from HCl)
Mo: 2 ppm
Br: 50 ppm

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Method 200.8 DRC Results (ng/L)

PerkinElmer precisely

Element	Mass	Matrix	Matrix + 1 ppb	Matrix + 5 ppb
Lead	206, 207, 208	0.02	0.97	4.86
Manganese	55	0	0.97	4.93
Molybdenum	95, 97, 98	>Calibration curve	>Calibration curve	>Calibration curve
Nickel	60	0.85	1.91	5.96
Nickel DRC (O_2, 2)	60	0.71	1.76	6
Selenium	82	63	65	69
Selenium DRC (O_2, 2)	80	0.14	1.13	6.18
Silver	107, 109	0	0.95	2.37
Thallium	203, 205	0	0.94	4.83
Thorium	232	0.01	0.99	5.01
Uranium	238	0	0.96	4.98
Vanadium	51	0.65	1.63	5.81
Zinc	66, 67, 68	0.43	1.16	5.57

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Method 200.8 DRC Results

PerkinElmer precisely

Element	Mass	Orlando Public	Orlando Public + Matrix	CT Well Water	CT Well Water + Matrix
Arsenic	75	0.15	0.82	0.1	0.84
Arsenic DRC (O_2, 0.5)	91	0.02	0.08	0	0.07
Cadmium	114	0.01	0.17	0.03	0.21
Cadmium DRC (O_2, 2)	114	0.01	0.02	0.03	0.04
Chromium	52	ND	0	ND	0.04
Chromium DRC (CH_4, 0.6)	52	0.04	0.08	0.12	0.16
Nickel	60	0.45	1.07	0.69	1.21
Nickel DRC (O_2, 2)	60	0.54	1.45	0.85	1.57
Selenium	82	0.22	66	0.26	0.78
Selenium DRC (O_2, 2)	80	0.22	0.33	1.09	1.12

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More Complicated Matrices - Seawater SRM: NASS-5

PerkinElmer precisely

Goal: < 1 µg/L

Analyte	Reaction Gas	Measured (µg/L)	Certified (µg/L)	Estimated MDL	Recovery (%)
Cr 52	CH_4	0.26	0.011	0.03	93%
Fe 56	CH_4	0.14	0.027	0.01	85%
Ni 60	CH_4	0.33	0.025	0.03	85%
Cu 65	CH_4	0.61	0.030	0.1	91%
Se 78	O_2	0.22	(0.002)*	0.1	92%
AsO 91	O_2	0.18	0.127	0.03	101%

* = not certified

Spike = 10 µg/L

Work done in a "normal" laboratory environment

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Method Approvals for NPDES

- EPA Method 200.8 - NPDES Monitoring
  - General approval pending (September????)
  - Approval as Alternate Test Procedure
  - US EPA Region 8:
    - Approved as ATP Feb 23, 1999
    - Ref: 8TMS-QA
      - Tony Medrano (303) 312-6336

- EPA Method 200.8 - NPDES Rule for Incinerators
  - January 27,2000 (FR 65 (18) p. 4360)
  - Approves use of 200.8 for NPDES for this industrial category
    - Does NOT approve Method 200.8 for other monitoring purposes
  - Also approves use of ASTM Method D 5673-96 for this category

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SW-846 Method 6020A Overview

- SW-846 Method 6020A (RCRA Programs)
  - Update IVA of Third Edition of SW-846
  - Method 6020A (January 1998)
- 23 elements Total
  - Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, Zn, Ca, Fe, Mg, Hg, K, Se, Na, and V
  - Can be used to analyze Se in TCLPs
- Applicable Matrices
  - Ground water, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes
  - Requires digestion by referenced methods
    - SW-846 Methods 3005-3051
    - But only method 3051 approved for Sb and Ag in soils
- EPA states DRC may be used as a form of interference correction because of complex matrices

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Method 6020 QC Requirements

- Initial Performance Demonstration
  - IDLs (3-day IDL on blank)
  - MDL according to Chapter One
  - No Stated Linear Range definition or requirements
- Calibrate (minimum blank and one standard)
- Verify calibration with ICV 90-110% limits
- Internal Standard monitoring required
  - 80-120% for calibration blank and instrument check
  - 30-120% for samples
- Run Interference Check Solutions A and B
  - NOTE: There are NO STATED CONTROL LIMITS
  - Purity of these solutions is critical
    - can see impurities from 0.02 - 5 ppb with ICP-MS

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6020A Interference Check Samples A and B

Component	Solution A (mg/L)	Solution B (mg/L)
Al	100	100
Ca	300	300
Fe	250	250
Mg	100	100
Na	250	250
P	100	100
K	100	100
S	100	100
C	200	200
Cl	2000	2000
Mo	2	2
Ti	2	2
As	0	0.100
Cd	0	0.100
Cr	0	0.200
Co	0	0.200
Cu	0	0.200
Mn	0	0.200
Hg	0	0.020
Ni	0	0.200
Se	0	0.100
Ag	0	0.050
V	0	0.200
Zn	0	0.100

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Standard ICP-MS - 6020A ICSA - No Correction Equations!

Analyte	Mass	Mean (ug/L)
V	51	6.604
Cr	52	3.253
Mn	55	5.898
Co	59	0.541
Ni	60	5.531
Cu	63	4.869
Cu	65	3.387
Zn	66	6.301
Zn	67	15.656
Zn	68	2.567
As	75	15.067
Se	82	1.107
Cd	111	6.745
Cd	114	4.772

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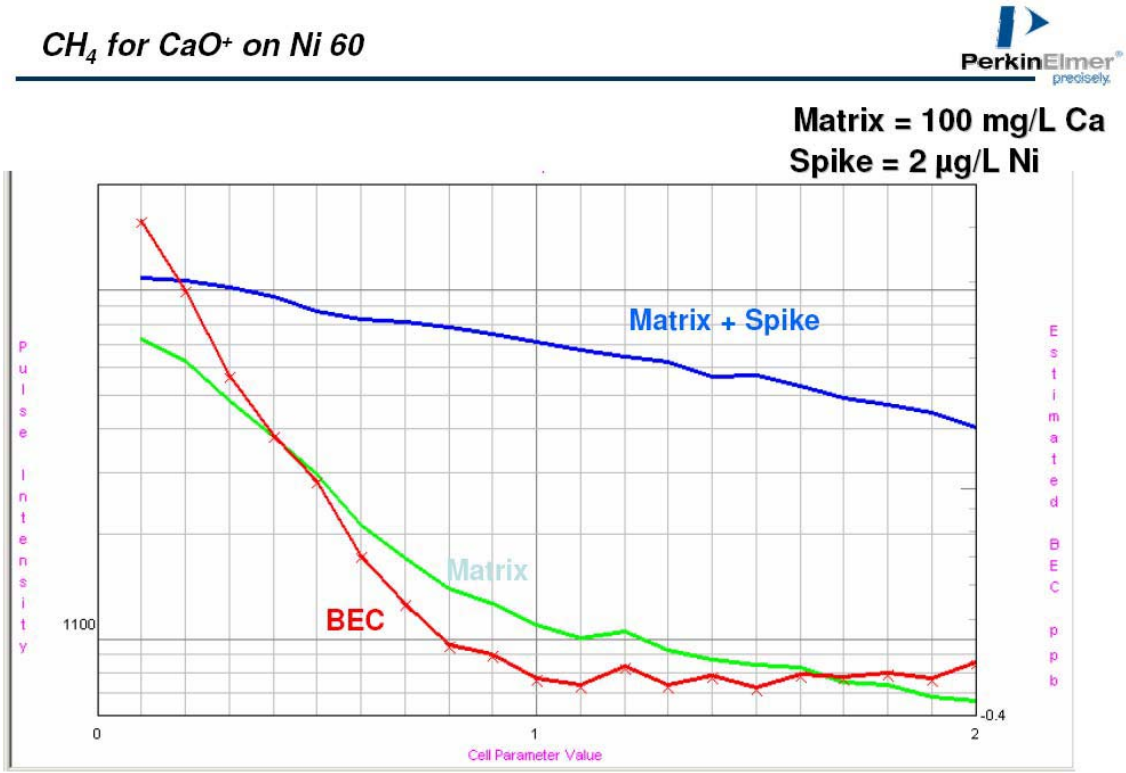
CH_4 for CaO^+ on Ni 60



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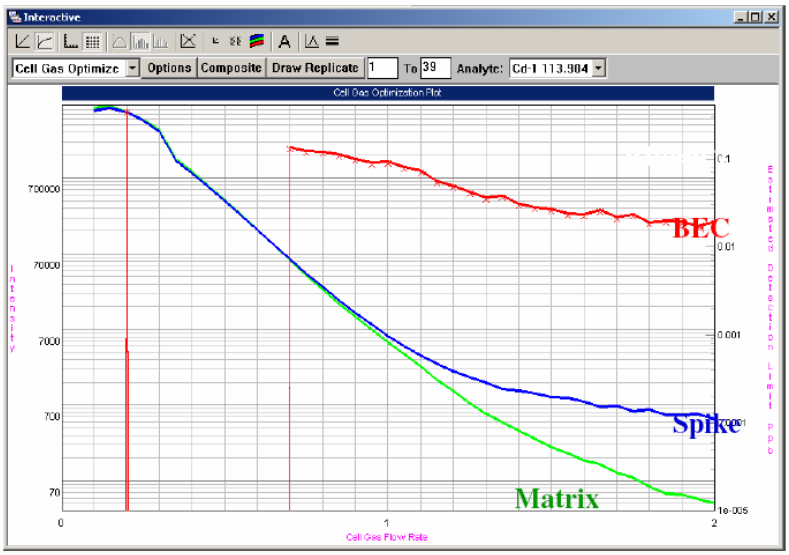
MoO^+ on Cd 114

- Use O_2 to form MoO_2^+
  - Cd^+ does not react with O_2



0.5 µg/L Cd in 28 mg/L Mo

Interference Check Standard A

- Goal: Run ICSA and read common DRC elements at < 1 µg/L

Analyte	Reaction Gas	Measured (µg/L)	10 µg/L Spike Recovery (%)
Cr 52	CH_4	0.41	119
Ni 60	CH_4	0.42	112
Cu 65	CH_4	0.47	111
Se 80	CH_4	0.10	113
Se 78	O_2	0.15	109
AsO 91	O_2	0.12	101

Summary

- Cell not necessary for routine drinking water analysis, but can help avoid unexpected levels of interferences
- Cell may be useful for complex wastewater, soil, or waste samples
  - Depending on detection limit required
  - Depending on matrix (potential interferences)
- Cell provides
  - A tool for Interference removal
  - Cell use and standard mode can be used in same run
  - Two gases can be used
  - DRC provides controlled chemistry
  - DRC provides opportunity to use reaction products such as AsO to gain enhanced sensitivity
  - DRC easy to set up, reproducible day-to-day
  - DRC does not need to be cleaned

Determination of Total Cyanide without Distillation

William Lipps
Product Line Specialist, ACA Products, OI Analytical

ABSTRACT

Determination of total cyanide by existing EPA methodology requires either manual or on-line distillation from a sample acidified with a strong acid. Serious problems have been recognized with these traditional methods. This paper presents interferences associated with EPA approved methods and describes a non-distillation method based on segmented flow on-line UV digestion-gas diffusion with amperometric detection. This technique eliminates the need for time-consuming distillations, has a throughput of up to 30 samples per hour, and is virtually interference free.

INTRODUCTION

The EPA has defined "total cyanide" as the amount of cyanide ion liberated by distillation with a sulfuric acid – magnesium chloride solution followed by either colorimetric, titrimetric, or ion selective electrode measurement. The high heat and low pH of the distillation process have been demonstrated as causing low reproducibility and questionable accuracy, as well as being known to produce both false positive and false negative results depending upon the sample matrix. Table 1 lists current EPA approved methods for the determination of total cyanide in wastewater analysis along with their known interferences.

Table 1: EPA Approved Methods for Total Cyanide 40CFR Part 136

Methodology	Reference	Sample Processing	Determinative Step	Listed Interferences
Manual Distillation with Magnesium Chloride and Sulfuric Acid	EPA 335.2	The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution.	The cyanide ion in the absorbing solution is then determined by volumetric titration using silver nitrate or colorimetrically using pyridine-barbituric acid procedure.	1. Oxidizing agents can destroy cyanides during storage. Sulfide can complex with cyanide in sample or distillate. Fatty acids cause interference during distillation. Carbonate causes interference during distillation. Aldehydes cause interference during distillation. Glucose/Sugars cause interference during distillation. Sulfur-containing compound causes interference during distillation by forming free sulfide that is captured in distillate.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	SM 4500 CN E	The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means	Cyanide in the alkaline distillate from preliminary treatment is converted to CNCl by reaction with	Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars,

Methodology	Reference	Sample Processing	Determinative Step	Listed Interferences
		of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution.	chloramine-T at pH<8 without hydrolyzing to CNO^-. After reaction, CNCl forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color absorbance in aqueous solution is between 575 and 582 nm.	high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	SM 4500-CN D	The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution.	Cyanide in the alkaline distillate from the preliminary treatment procedure (4500-CN-B) is titrated with standard silver nitrate ($AgNO_3$) to form the soluble cyanide complex, $Ag(CN)^{2-}$. As soon as all CN^- has been complexed and a small excess of Ag^+ has been added, the excess Ag^+ is detected by the silver-sensitive indicator, p-dimethylaminobenzalrhodanine, which immediately turns from a yellow to a salmon color. The distillation has provided a 2:1 concentration. The indicator is sensitive to about 0.1 mg Ag/L.	Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	ASTM D2036	Test Method A, Total Cyanides, is based on the decomposition of nearly all cyanides in the presence of strong acid, magnesium chloride catalyst, and heat during a 1-h reflux distillation.	Either the titration, colorimetric or selective ion electrode procedure can be used to quantify the cyanide concentration.	Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	USGS I-3300-85	The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The	This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide

Methodology	Reference	Sample Processing	Determinative Step	Listed Interferences
		distillation also removes certain interferences from water samples.	form a stable complex dye.	greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.
Cyanide by Automated Colorimetry	USGS I-4302-85	This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.	This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.
Cyanide by Automated Colorimetry	EPA 335.3	Cyanide, as HCN, is released from cyanide complexes by means of UV digestion and distillation.	Cyanides are converted to cyanogen chloride by reactions with chloramine-T, which subsequently reacts with pyridine and barbituric acid to give a red-colored complex that is measured with an on-line colorimeter.	Thiocyanates are positive interferences. Sulfides can adversely affect the color procedure. Remove sulfide by precipitating with cadmium carbonate, and remove precipitate by filtration.

Table 2: Interferences with the Determinative Step

Technique	Interferences*
Titration with Silver Ion	Sulfide, phosphate, and arsenate. Chloride if in excess.
Ion Selective Electrode	Sulfide, silver, bromide, copper, mercury, lead, thallium. Chloride if in excess.
Colorimetric	Thiocyanate, sulfide, cyanogen chloride, reducing agents, color, dissolved solids, and turbidity.

*These interferences must be eliminated prior to analysis.

Distillation

In the absence of interference, simple cyanides such as HCN, KCN, and NaCN are determined readily by each of the determinative steps, however, to determine "total" cyanide metal cyanide bonds must be broken and cyanide separated to produce simple cyanide. In all the approved EPA methodology this is accomplished by distillation from acid solution. Although distillation is assumed to eliminate, or at least minimize, most interferences the high temperature and strong acid solutions can potentially introduce significant positive or negative bias.

Table 3: Interferences Introduced by Distillation

Compound	Description of Interference
Oxidizers	React with CN during distillation causing negative bias.
Sulfide	Distills over and reacts with CN is the alkaline absorber solution to form thiocyanate, causing a negative bias
Oxidized Sulfur Compounds	React with CN in absorber solution to form thiocyanate, causing negative bias.
Thiocyanate	Decomposes to oxidized sulfur compounds, which react with cyanide in the absorber solution to form thiocyanate causing a negative bias.
Thiocyanate + Nitrate	Thiocyanate decomposes forming cyanide, causing a positive bias.
Sulfur Dioxide	Sulfur dioxide in the absorber solution can react with chloramine T during the colorimetric step, resulting in a negative bias.
Nitrate or Nitrite + Organics	Can react to form cyanide causing a positive bias.

Thiocyanate and sulfide are commonly occurring compounds in industrial waters and wastewaters and are the most common and significant interferences in distillation-based cyanide methods. While there are ways to remove sulfide, there are no adequate solutions for the removal of thiocyanate prior to analysis. The assumption that thiocyanate interference can be compensated for by the analysis of "Total Cyanide including Thiocyanate" and subtracting thiocyanate determined by a separate analysis depends on the accuracy of the cyanide measurement made in the presence of thiocyanate. Because thiocyanate can produce both positive and negative interferences, without an accurate analysis of each matrix, one can never be sure whether to add or subtract.

Development of a Distillation-Free Method for the Determination of Total Cyanide

Recognizing that most interferences in accepted total cyanide determination methods stemmed from the distillation step that was supposed to eliminate interferences, researchers developed a distillation-free total cyanide method based on segmented flow, on-line UV digestion, and gas diffusion with amperometric detection.[1] This novel method quantitatively liberates most strong metal cyanide complexes and accurately measures total cyanide from 0.002 to 5.00 mg/L at a rate of two minutes per sample. The method is available from OI Analytical as Total Cyanide by UV-Digestion Amperometric Detection.

Description of Instrumentation and Procedures

A Flow Solution FS 3100 Analyzer (OI Analytical, College Station, TX, USA) is configured for total cyanide according to the diagram in Figure 1.

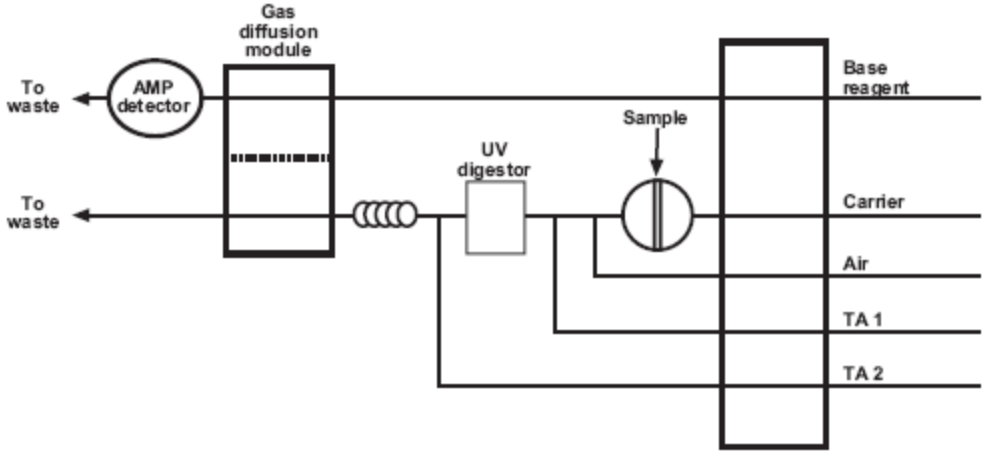


Figure 1: Flow Diagram of Total Cyanide Analysis

Two hundred micro-liters of sample is introduced by the carrier solution into an acid stream (Total Acid Reagent 1 or TA 1) and segmented with air to prevent excessive dispersion. After a mixing coil the sample is irradiated at 350 nm dissociating cyanide complexes but preventing the decomposition of thiocyanate and other side reactions. After exiting the UV digester, the sample is mixed with another reagent (Total Acid Reagent 2 or TA 2) that contains a complexing agent that can remove up to 50 mg/L sulfide. The stream then passes under a gas diffusion membrane where the HCN formed passes through into an absorber solution of dilute sodium hydroxide. The amperometric detector quantitatively determines cyanide in the absorber solution. Figures 2 through 5 illustrate the performance of the method.

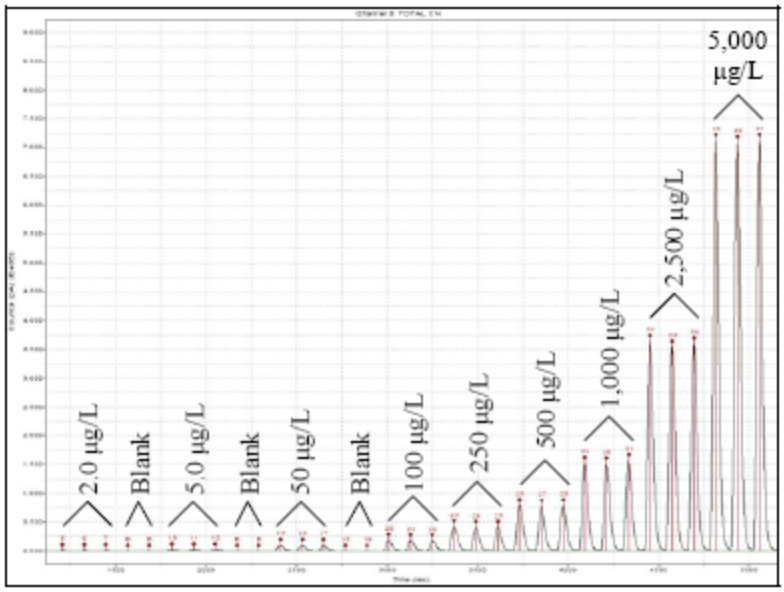


Figure 2: Total Cyanide Calibration Standards (2.0–5,000 µg/L)

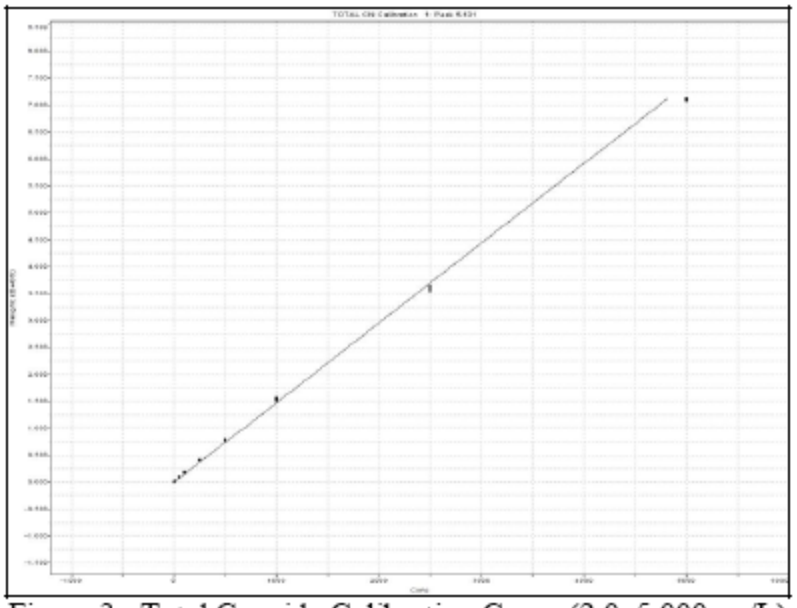


Figure 3: Total Cyanide Calibration Curve (2.0–5,000 µg/L)

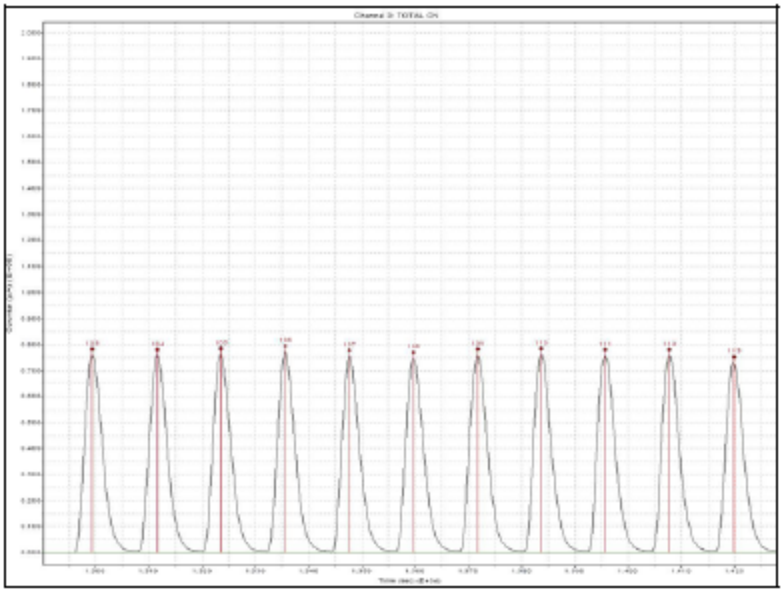


Figure 4: Total Cyanide Precision at 500 µg/L

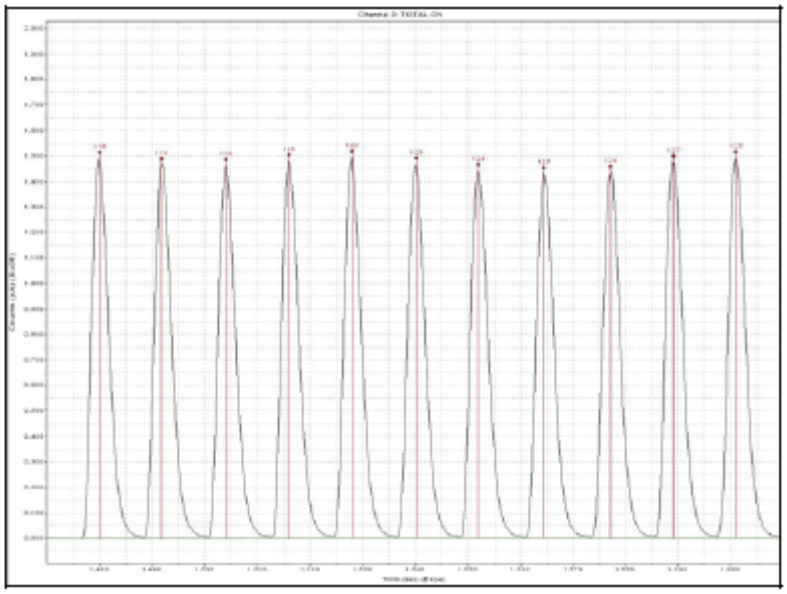


Figure 5: Total Cyanide Precision at 1,000 µg/L

Table 4: Cyanide Recoveries from Distillation (EPA Method 335.2) Compared to OI In-house Diffusion Method (0.2 mg/L CN added)

Species	Distillation (% Recovery)	OI Method (% Recovery)
$[Zn(CN)_4]^{2-}$	99.5	97.2
$[Cd(CN)_4]^{2-}$	104	104
$[Cu(CN)_4]^{3-}$	97.7	100
$[Ag(CN)_2]^{-}$	97.8	104
$[Ni(CN)_4]^{2-}$	104	98.3
$[Hg(CN)_4]^{2-}$	95.8	96.7
$Hg(CN)_2$	98.0	96.1
$[Fe(CN)_6]^{4+}$	101	102
$[Fe(CN)_6]^{3-}$ *	104	95.4
$[Pd(CN)_4]^{2-}$	69.1	17.7
$[Pt(CN)_4]^{2-}$	0.0	0.54
$[Pt(CN)_6]^{2-}$	0.0	0.0
$[Ru(CN)_6]^{4+}$	50.1	50.1
$[Au(CN)_2]^{-}$	56.6	49.5
$[Co(CN)_6]^{3-}$	0.0	13.8

* Ferric cyanide complexes are used in most water pollution (WP) check samples for the evaluation of Total Cyanide Methods.

Table 5: Cyanide Interference during Distillation Compared to OI Method

Interfering Species Added at 20 ppm	Untreated Samples EPA Method (CN found mg/L)	Untreated Samples OI Method (CN found mg/L)	Treated Samples EPA Method (CN found mg/L)	Treated Samples OI Method (CN found mg/L)
Nitrite	0.155	0.199	0.203	0.198
Sulfite	0.080	0.199	No treatment	No treatment
Chlorine	Not Detected	Not Detected	0.120	0.118
Thiosulfate	0.124	0.196	No treatment	No treatment
Thiocyanate	0.174	0.208	No treatment	No treatment
Sulfide	Not tested	0.198	0.120	0.189

There are no known spot tests to detect thiocyanate, sulfite or thiosulfate accurately at 20 mg/L so no treatment was applied to these samples. All samples were spiked at the Drinking Water Maximum Contaminant Level of 0.2 mg/L Cyanide. Data indicates that cyanide can co-exist in solution with oxidizers such as sulfite and thiosulfate. Data also indicates a potential issue that could arise from not detecting cyanide when it is actually present.

Table 6: Distillation Interferences That Cause False Positives[2]

	Thiocyanate (mg/L)	Nitrate (mg/L)	Cyanide Found (mg/L; sulfamic acid not added)	Cyanide Found (mg/L; sulfamic acid added)
Sample 1	50	100	12.0	3.4
Sample 2	6	127	2.00	0.26
Sample 3	9	40	2.80	0.16

Even though sulfamic acid is recommended in the methods to eliminate nitrate interference, cyanide was still detected in samples that did not contain cyanide.

Table 7: Other Interferences that Cause False Positives by Distillation[3]

Compounds Added	Cyanide Found
Ammonia, Bleach, Ascorbic Acid	Detected
10 g Sodium Nitrite + 10 mmol i-propanol	112 mg/L
10 g Sodium Nitrate + 10 mmol i-propanol	14.2 mg/L

Nitrogen compounds, common in most wastewaters, can react with organic matter during the distillation process and create cyanide.

CONCLUSIONS

Approved total cyanide methods requiring a preliminary distillation step often produce unreliable data in complex real world samples. A method developed by OI Analytical, "Total Cyanide by On-Line UV Digestion Amperometric Detection", solves most interference problems and produces reliable data in the presence of known interferences.

Although the method has not been approved by EPA, it is still advantageous to analyze cyanide by a method known to produce correct results. Analyzing strictly for compliance purposes can result in serious errors including potential under-reporting when cyanide is actually present or in over-reporting when cyanide is not even there.

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1. Ljiljana Solujic, Emil B. Milosavljevic, and Michael R. Straka, 1999. *Analyst* (124, 1255-1260).

2. Adapted from N.J. Csikai and A.J. Barnard, Jr., 1983. *Determination of Total Cyanide in Thiocyanate-Containing Wastewaters*, *Anal. Chem.* (55, 1677-1682).

3. Ljiljana Solujic, Emil B. Milosavljevic, 2005. *How to Analyze for Cyanide*. Presented to ASTM Committee D19.06, Reno, Nevada.

Total Cyanide Without Distillation

William Lipps
OI Analytical
August 2006

O·I·Analytical
A World of Solutions

Cyanide Chemistry

- Cyanide is CN^- .
- The pKa of Hydrogen Cyanide is 9.36.
- At pH = 7 about 99% CN^- exists as HCN.
- CN^- forms complexes with most metals.
- Methods for the determination of Cyanide are defined by the relative strength of the metal complexes.

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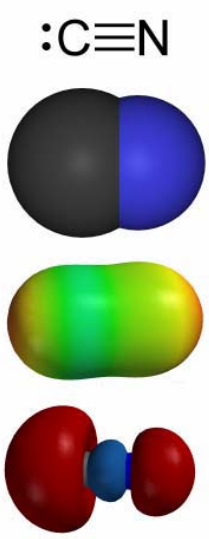
The Cyanide Ion

- Strong Covalent Bonds between Carbon and Nitrogen.
- Transition metals form strong bonds with the carbon.
- Alkali metals form ionic bonds with the CN molecule.



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Sources and Uses of Cyanide

- Cyanide is produced in nature by certain bacteria, and found in numerous foods and plants.
- Organic Cyanide compounds are called Nitriles. (these are not very hazardous)
- Hydrogen Cyanide is a product of Combustion and is found in:
  - Automobile exhaust (single largest source of HCN pollution)
  - Cigarette smoke
  - Burning of plastic (house fires, etc.)

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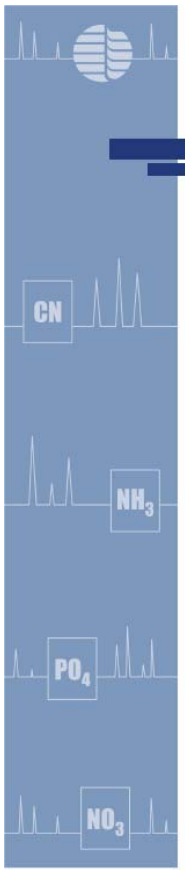

Industrial Uses of Cyanide

- Electroplating
- Pharmaceuticals
- Metallurgy
- Jewelry
- Photography
- Precious Metal Extraction

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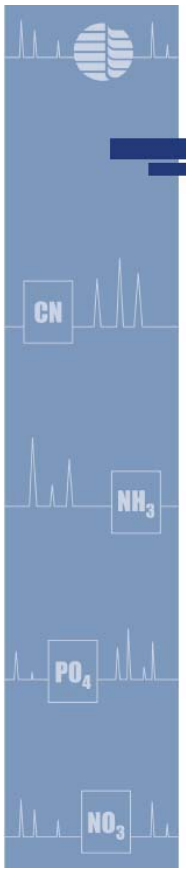

Industries with Cyanide Bearing Waste Streams

- Petroleum Refineries
- Coal fired Power production
- Precious Metals
- Wastewater Treatment

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Cyanide Speciation

- The "species" of Cyanide present in a water sample is determined by:
  - pH
  - Presence of Oxidizers
  - Presence of Transition metals (and which ones)
  - Presence of sulfur and sulfur compounds

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Cyanide Species

- Free cyanide
  - CN^-, HCN
- Simple cyanide
  - Readily soluble: NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$
  - Relatively insoluble: $Zn(CN)_2$, CuCN, $Ni(CN)_2$, AgCN
- Weak metal-cyanide complexes
  - $Zn(CN)_4^{2-}$, $Cd(CN)^{3-}$, $Cd(CN)_4^{2-}$
- Moderately strong metal-cyanide complexes
  - $Cu(CN)^{2-}$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)^{2-}$
- Strong metal-cyanide complexes
  - $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$, $Au(CN)^{2-}$

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Analysis of Cyanide Species

- The methods for the determination of Cyanide are defined by an attempt to measure the various cyanide species.
  - Free Cyanide
    - HCN + CN^- + (NaCN, KCN)
  - Weak Acid Dissociable (WAD)
    - Free Cyanide + Cu, Ni, Ni, Zn, Ag
  - Total Cyanide
    - Free Cyanide + WAD Cyanide + Fe, Co, Au, Pt

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Free Cyanide

- Free Cyanide is defined as the amount of HCN liberated from a buffer solution adjusted to the pH of the receiving stream.
- The ASTM validation of Free Cyanide determined CN in a pH 6 solution.

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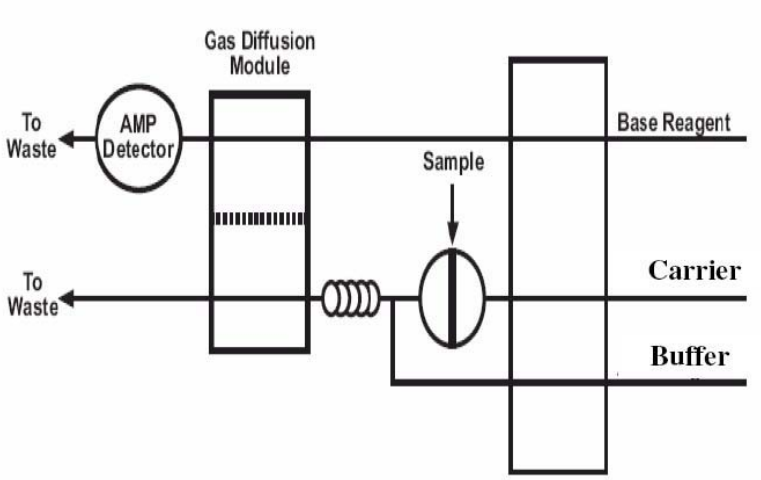
Free Cyanide Method



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WAD Cyanide

- Defined as the amount of HCN released by distillation at pH 4.5
- The HCN released is absorbed into a solution of Sodium Hydroxide and determined colorimetrically.

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Cyanide Amenable to Chlorination (CATC)

- Similar Cyanide species recovery as the WAD method.
- This method requires samples be split into two portions.
- One half is chlorinated and the other is not.
- Both are distilled according to the "total" cyanide method, and the difference is Amenable Cyanide.

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Available Cyanide

- Flow Injection – Gas Diffusion with amperometric detection. (no distillation)
- "Same" result as CATC or WAD
- Measures Free Cyanide and Weak Acid Dissociable Cyanide
- Does not measure strong metal cyanide complexes (iron cyanides)
- Ligands are added for complete recovery of Ni and Hg Cyanide.
- EPA Method OIA 1677 and ASTM D6888.

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"Total" Cyanide

- "Total" Cyanide is operationally defined as the amount of HCN liberated by distillation from a MgCl2/Sulfuric Acid Solution (>100° C, pH < 1).
- The HCN is absorbed into a sodium Hydroxide solution and measured, usually Colorimetrically.
- By Definition, Total Cyanide does NOT Include Thiocyanate, or Cyanate

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WAD, CATC and Total CN Distillation

Macro Distillation

MIDI Distillations

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Disadvantages with Distillation Methods

- Time Consuming
  - One hour long distillation (does not take into account setup, and teardown)
  - CATC requires two distillations.
- Bulky and Relatively Expensive Glassware
- Operator dependent results (technique)
- Multiple Interferences

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Interferences in Current Cyanide Methods

- Determinative Step
  - Titration
  - ISE
  - Colorimetric
  - Amperometric

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Interferences – Determinative Steps

- Titration
  - Titration of Cyanide with Silver Ion
  - Many references consider this to adequately measure free cyanide.
  - Interferences
    - Sulfide
    - Phosphate
    - Arsenate
    - Excess Chloride

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Interferences – Determinative Steps

- Ion Selective Electrode (ISE)
  - Found in many test kits
  - Interferences are:
    - Sulfide
    - Silver
    - Bromide
    - Copper
    - Mercury
    - Lead
    - Thallium
    - Excess Chloride

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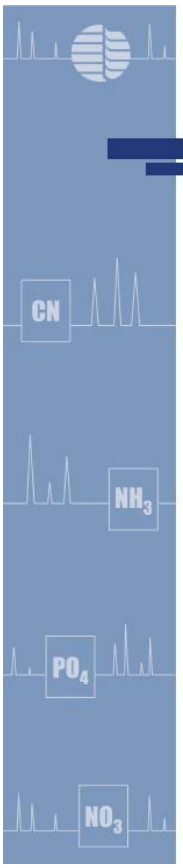

Interferences – Determinative Steps

- Colorimetric Methods
  - Usually Pyridine-Barbituric Acid
  - Interferences are:
    - Thiocyanate
    - Sulfide
    - Cyanogen Chloride
    - Reducing Agents
    - Color, Turbidity, and high salinity

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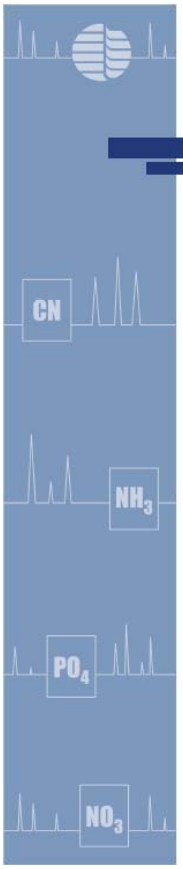

Interferences – Determinative Steps

- Amperometric Detection
  - Sulfide, and mercaptans

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Interferences - Distillation

- The Distillation Step was designed to separate the cyanide ion from the previously listed interferences.
- In samples of well known and/or simple matrices distillation is adequate.
- In complex samples, the combination of heat, and high acid strength with other constituents in the sample can either destroy cyanide or create it.

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Interferences - Thiocyanate

- Thiocyanate is present in almost all wastewaters (10 – 50mg/l normal)
- The amount of thiocyanate present is enough to interfere with the distillation.
- Interferences can be both positive (CN created) or negative (CN destroyed).
- There are no “spot” tests to determine thiocyanate.

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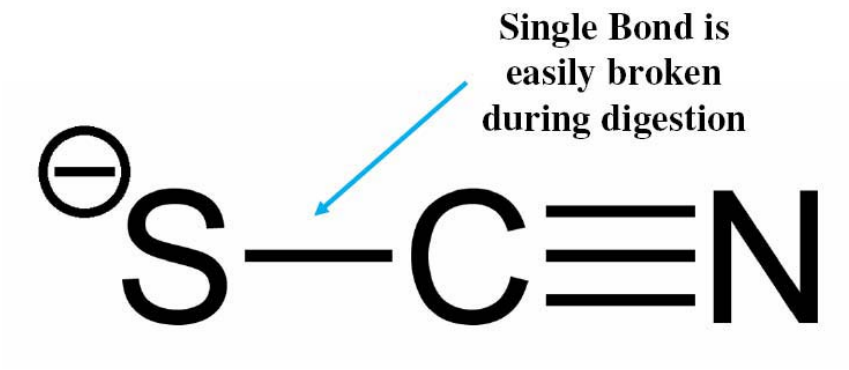
Interferences - Thiocyanate



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Interferences - Thiocyanate

- Thiocyanic acid, or HSCN, does not distill, however, the distillation process in the absence of oxidizers can form elemental sulfur, sulfur (IV) oxide, and carbonyl sulfide which are converted to sulfide in the absorber solution.
- Sulfide in the absorber solution reacts with any cyanide to form thiocyanate and a negative bias.

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Interferences - Thiocyanate

- 0.200 mg/l CN^- + 20 mg/l SCN^- :
  - Cyanide Found = 0.174 mg/l
  - Recovery = 87%
- 0.200 mg/l CN^- + 200 mg/l SCN^- :
  - Cyanide Found = 0.054 mg/l
  - Recovery = 27%

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Interferences - Thiocyanate

- In the presence of Nitrate, thiocyanate decomposes to form CN^- resulting in a positive bias. (actual interference is from Nitrite)
- The addition of Sulfamic acid does not sufficiently reduce this interference.
  - A real POTW sample with 0.1 mg/l SCN^- and 63.5 mg/l $NO3^-$ detected total CN^- at 0.10 mg/l even after the addition of Sulfamic Acid.(1)

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Interferences - Thiocyanate

SCN^- (mg/l)	$NO3^-$ (mg/l)	CN^- (mg/l)
0.100	1.00	ND
0.100	10.0	0.01
0.100	25.0	0.017
0.100	50.0	0.060
0.100	100	0.086
1.00	10.0	0.009
1.00	50.0	0.038

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Interferences – Sulfur Compounds

- Elemental Sulfur
  - $8CN^- + S_8 \rightarrow SCN^-$
- Metal Sulfides (distilling with solids present, or if sulfide complexing metals are added to distillation flask)
  - Cu_2S, FeS, PbS, $CuFeS_2$, CdS, ZnS, etc
  - S reacts with CN^- to form SCN^-
- Thiosulfate
  - $CN^- + S_2O_3^{-2} \rightarrow SCN^- + SO_3^{-2}$
- Sulfite
  - $Na_2SO_3 + 0_2 + CN^- \rightarrow OCN^- + Na_2SO_4$

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Interferences – Sulfur Compounds

- Thiosulfate
  - 0.200 mg/l CN^- + 20 mg/l $S_2O_3^{-2}$
    - Cyanide Found = 0.124 mg/l
    - Recovery = 62%
  - 0.200 mg/l CN^- + 200 mg/l $S_2O_3^{-2}$
    - Cyanide Found = 0.040 mg/l
    - Recovery = 20%

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Interferences – Sulfur Compounds

- Sulfite
  - 0.200 mg/l CN^- + 20 mg/l SO_3^{-2}
    - Cyanide Found = 0.080 mg/l
    - Recovery = 40%
  - 0.200 mg/l CN^- + 200 mg/l SO_3^{-2}
    - Cyanide Found = 0.000 mg/l
    - Recovery = 0%

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Interferences – Sulfur Compounds

- There are no "spot" tests that adequately detect the sulfur compounds that significantly interfere with total cyanide distillations.

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Interferences - Oxidizers

- Hypochlorite
  - $CN^- + OCl^- \rightarrow CNO^- + Cl^-$
- Peroxide
  - $CN^- + H_2O_2 \rightarrow CNO^- + H_2O$
- Caro's Acid
  - $CN^- + H_2SO_5 \rightarrow CNO^- + H_2SO_4$

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Distillation Free Total Cyanide

- Based on OIA Method 1677 and ASTM D6888 Ligand Exchange Flow Injection-Gas Diffusion Amperometric methods for determination of Available Cyanide.
- Instead of ligands, metal cyanide complexes are 'broken up' by UV irradiation.
- The method determines the same cyanide species as "total" cyanide by distillation.
- Results are obtained in minutes instead of hours.

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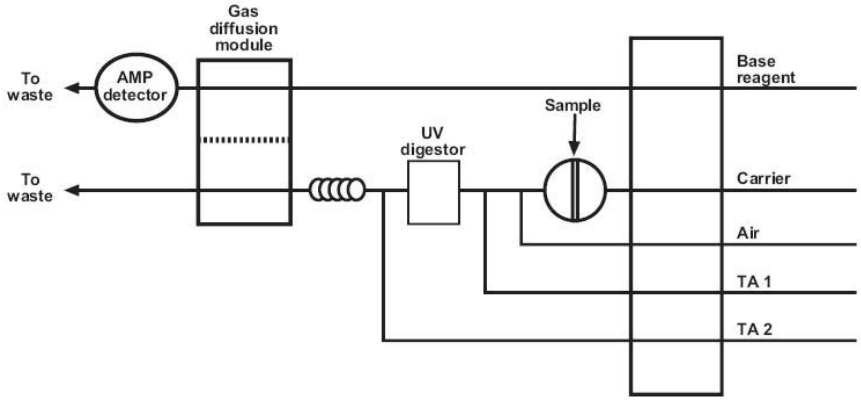
Total Cyanide without Distillation



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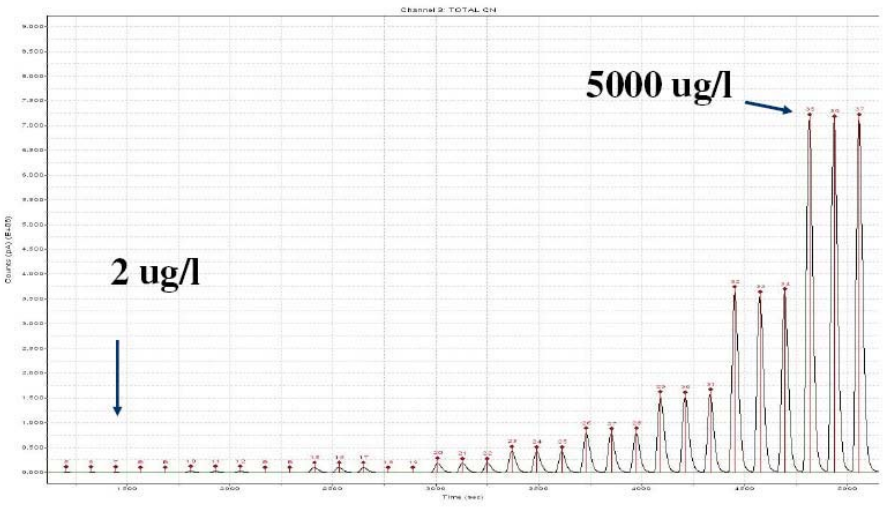
Total Cyanide without Distillation

- Simplified method that does not suffer from interferences introduced by distillation.
- Cyanide complexes release cyanide after UV irradiation.
- The Hydrogen Cyanide formed diffuses into a dilute NaOH stream.
- Cyanide is determined amperometrically.

O·I·Analytical

Total Cyanide without Distillation



O·I·Analytical

Total Cyanide without Distillation

Species	Distillation Method 335.2 (% Recovery)	UV-Irradiation (% Recovery)
$[Zn(CN)_4]^{2-}$	99.5	97.2
$[Cd(CN)_4]^{2-}$	104	104
$[Cu(CN)_4]^{3-}$	97.7	100
$[Ag(CN)_2]^{-}$	97.8	104
$[Ni(CN)_4]^{2-}$	104	98.3
$[Hg(CN)_4]^{2-}$	95.8	96.7
$Hg(CN)_2$	98.0	96.1
$[Fe(CN)_6]^{4-}$	101	102
$[Fe(CN)_6]^{3-}$	104	95.4
$[Pd(CN)_4]^{2-}$	69.1	17.7
$[Pt(CN)_4]^{2-}$	0.0	0.54
$[Pt(CN)_6]^{2-}$	0.0	0.0
$[Ru(CN)_6]^{4-}$	50.1	50.1
$[Au(CN)_2]^{-}$	56.6	49.5
$[Co(CN)_6]^{3-}$	0.0	13.8

O·I·Analytical

Eliminating Interferences

Interfering Species Added at 20 mg/l	Untreated Samples Method 335.2	Untreated Samples UV Irradiation	Treated Samples Method 335.2	Treated Samples UV Irradiation
Nitrite	0.155	0.199	0.203	0.198
Sulfite	0.080	0.199	No treatment	No treatment
Chlorine	Not Detected	Not Detected	0.120	0.118
Thiosulfate	0.124	0.196	No treatment	No treatment
Thiocyanate	0.174	0.208	No treatment	No treatment
Sulfide	Not tested	0.198	0.120	0.189

Cyanide added at 0.200 mg/l (EPA MCL SDWA)

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Interferences – UV Irradiation Method

- Thiocyanate can photo decompose to form CN^- and S^{-2} which are positive interferences.
- S^{-2} can be complexed after formation eliminating its interference.
- Thiocyanate interference is minimized by UV irradiation > 312 nm.
- High amounts of surfactants can "poison" the gas diffusion membrane.

O·I·Analytical

Total Cyanide without Distillation

- A simplified method that does not suffer from as many interferences as currently approved methods.
- Less than one milliliter of sample is required.
- Very little hazardous waste is generated.
- No pyridine containing reagents.
- Amperometric detection is simple, very sensitive, selective, and has a large linear range.

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References

- Zheng A., Dzombak D.A., Luthy R.G. *Effects of Thiocyanate on the Formation of Free Cyanide during Chlorination and Ultraviolet Disinfection of Publicly Owned Treatment Works Secondary Effluent*, Water Environment Research. Volume 76, Number 3, pp 205 - 212
- Berman R., Christmann D., Renn C, A*utomated determination of Weak Acid Dissociable and Total Cyanide without Thiocyanate Interference* American Environmental Laboratory, June 1993
- OIA Draft Method 1678
- OIA Method 1677

O·I·Analytical

Total Cyanide Without Distillation

William Lipps
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College Station TX 77845

O·I·Analytical
A World of Solutions

WEDNESDAY A.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Homeland Security

Building Environmental Laboratory Capability in Support of Emergency Response

NEMC Presentation

August 29, 2006

By Allan Antley

Brief History of the Integrated Consortium of Laboratory Networks

- **Discussions in Spring of 2004 between EPA and CDC triggered the genesis of the current Integrated Consortium of Laboratory Networks (ICLN)**
- **White House Homeland Security Council involvement began in November 2004**
  - **Gathered agencies involved, endorsed independent network involvement, and recognized the benefits gained from creating a collaborative alliance**
- **Vision: A U.S. homeland security infrastructure with a coordinated and operational system of laboratory networks that provide timely, high quality, and interpretable results for early detection and effective consequence management of acts of terrorism and other events requiring an integrated laboratory response**

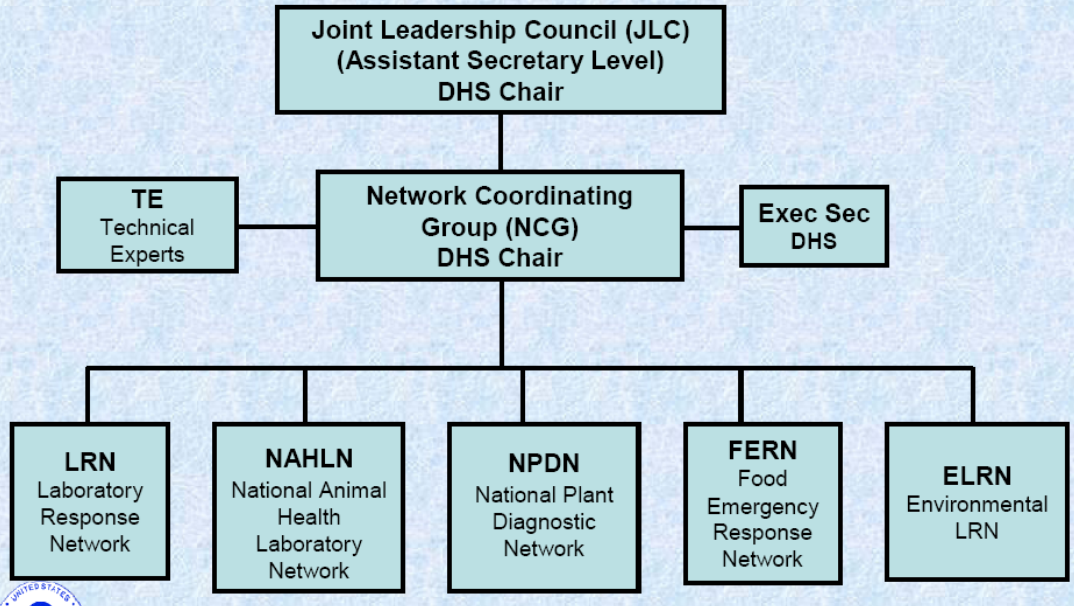
Memorandum of Agreement

- MOA establishing roles and responsibilities of the signatories April 2005
- Signatories include EPA, DOA, DOD, DHS, DOI, DHHS, DOS, DOC, DOJ, and DOE
- Some have networks, some do not
- MOA establishes specific roles of Responsible Federal Agency

Responsible Federal Agency

- Responsible to assure the operational capacity of the individual Networks to meet testing requirements for surveillance, incident response, forensic analysis, and incident remediation and recovery
- Includes functional requirements for research, methods, quality assurance, performance testing, training, communications, etc.
- "High quality, timely, and interpretable data for its intended use"

ICLN Organizational Structure



Building Environmental Laboratory Capability in Support of Emergency Response 4

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 Water	EPA	EPA	EPA	FBI	**Drinking Water**	EPA	EPA	EPA	FBI

*JLC agreed to RFAs identified for each phase of response

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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
- Filling a cell on this chart does NOT mean the capability really needs to exist under current prevailing threat conditions
- *MOAs/MOUs will be required to clarify supporting agency roles and commitments to RFAs*

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Status

- **NCG has met monthly since March of 2005**
  - **-Formed operational relationships and assignments**
  - **-Established 6 Technical Expert Panels**
  - **-Identified gaps in capacity and budgetary needs**
  - **-On-going review of 9 Scenarios to test lab capacity**
- **JLC met September 2005**
  - **-Affirmed RFA assignments**
  - **-Supported unified approach to address CWA and Rad gaps**
  - **-Supported unified budget proposals for all network needs**

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Building CWA Capacity

- DHS has FY 06 funding to establish two prototype fixed labs
- Priority locations are Northeast and Mid-Atlantic
- Survey/Solicitation has been issued
- Costs for one year (infrastructure, instruments, maybe 1FTE, training, all other costs)
- PHILIS units under redesign to fit EPA response template

Priorities for CWA and Analytical Enhancements for eLRN

- Form and operate an environmental laboratory response network and build increased CWA capabilities/capacities for environmental samples

Enhance Lab Analytical Capabilities

-Develop additional CWA environmental state laboratory capabilities through grants/cooperative agreements

OR

-Purchase and operate PHILIS – portable high-throughput mobile unit(s)

- Align eLRN with other networks through proficiency testing, data management, and other analytical resources

EPA's Environmental Laboratory Response Program

- **The Environmental Laboratory Response Program**
  - Virtual Center/Program Office now operational
  - Focus of 06 to model Toxic Industrial Chemical (TIC) network as template
  - Engaged Federal and State Partners and will need continued interaction
  - Engaged APHL to provide State access
  - Evaluated HSPD 10 Scenarios
  - BOAs/IAG in place to partially address CWA needs
  - Resolved Ultra-dilute CWA program w/ DOD
  - All Hazard Receipt Facility prototypes Summer 2006*
  - WaterSentinel proceeding on own track
  - PHILIS Units role redefined and retrofit/redesign proposed

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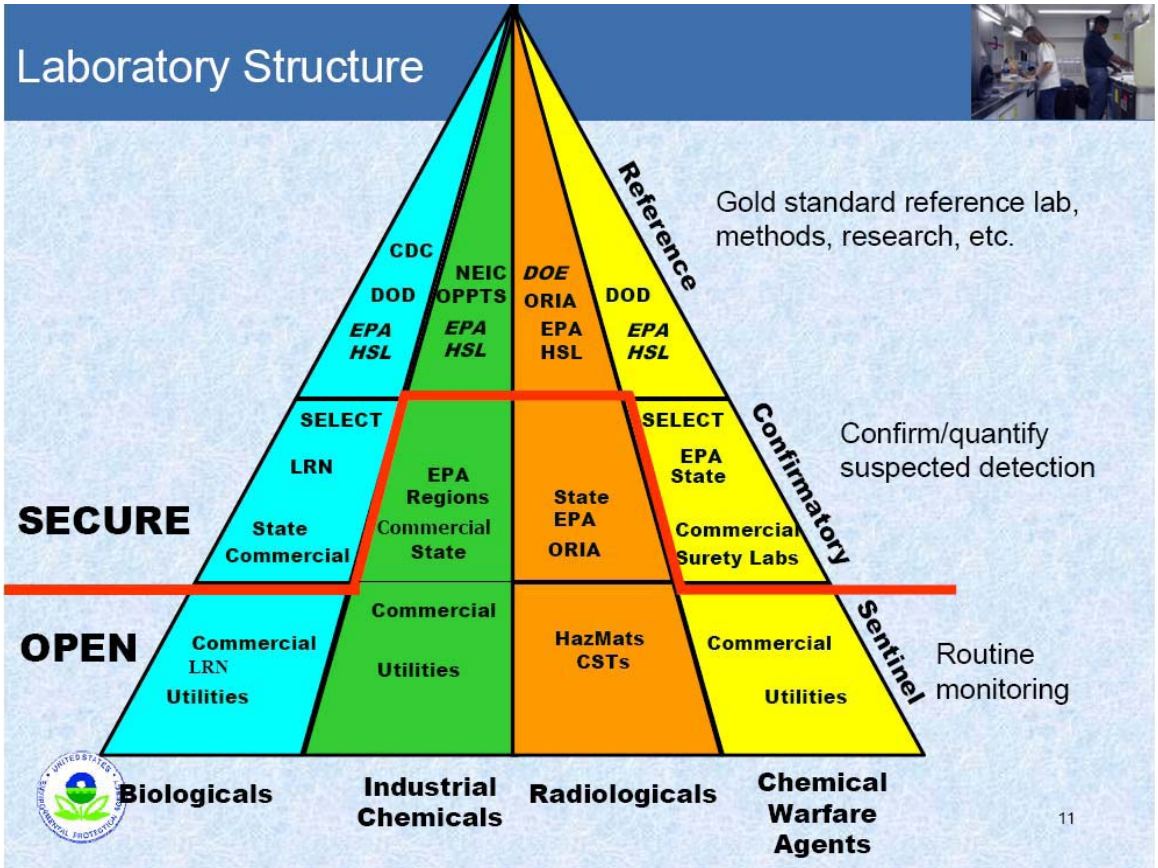
Laboratory Structure



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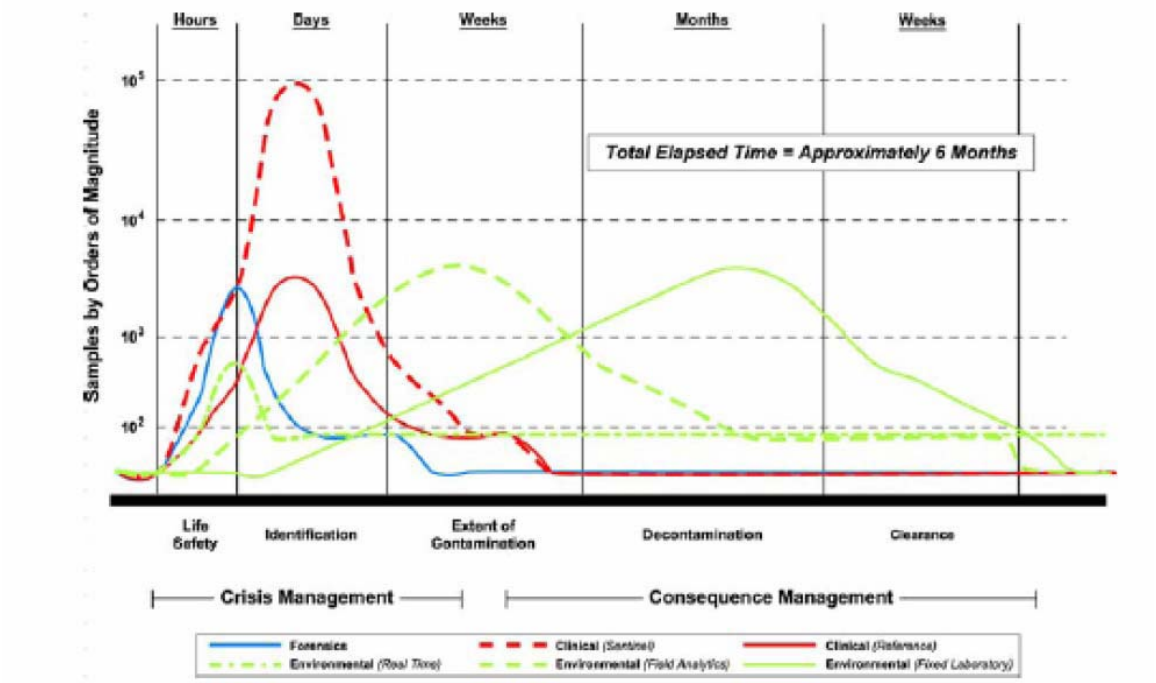
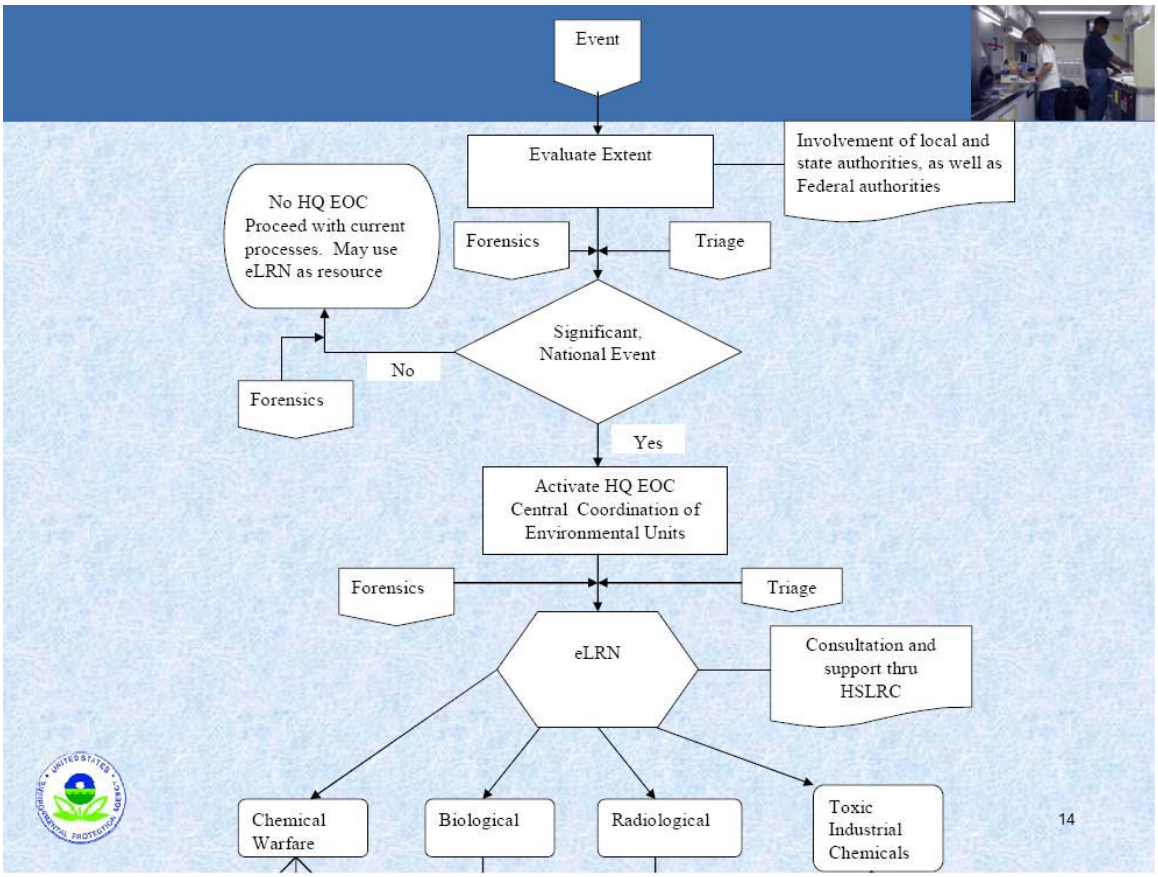
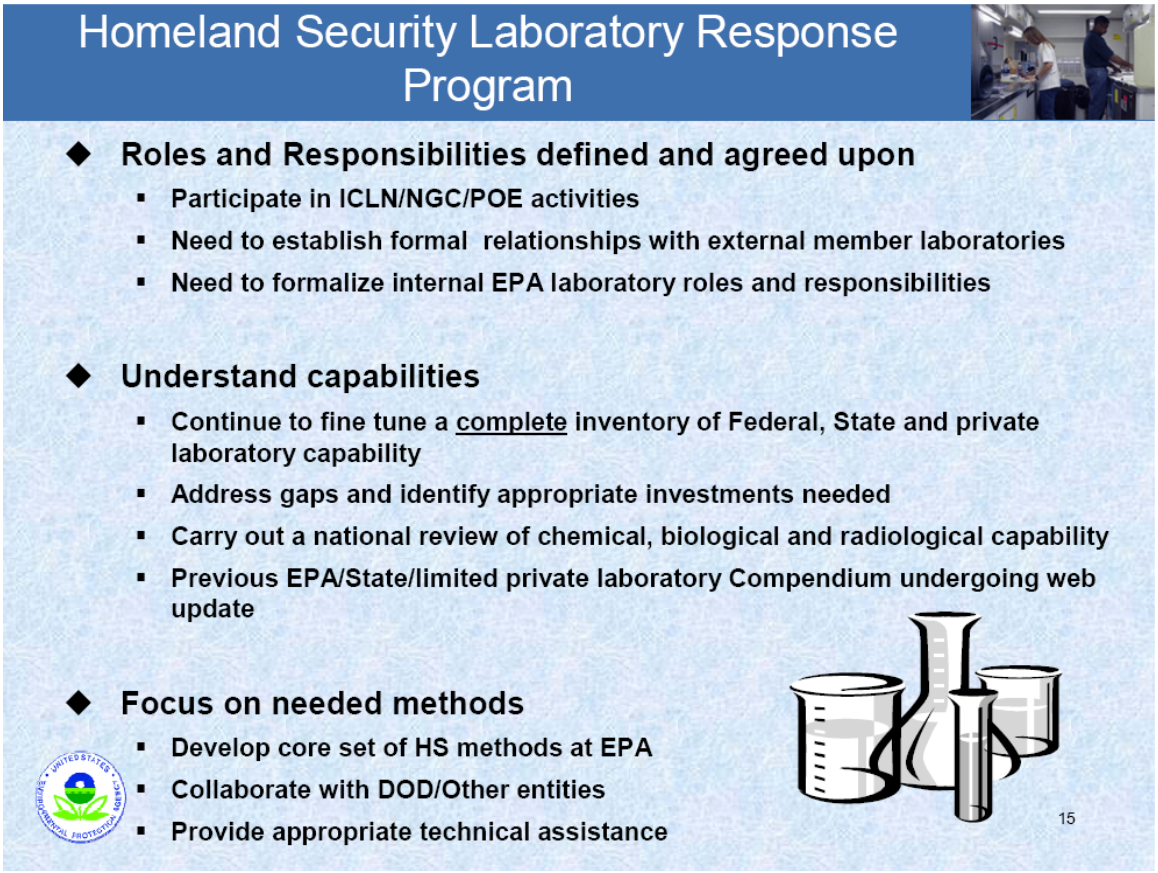
Anatomy of a Response



Response Matrix

			TIC (Toxic Industrial Chemicals)		Biological		Chemical Warfare Agents		Radiological	
Mode	Phase	Analysis	Lab Type	Preferred	Lab Type	Preferred	Lab Type	Preferred	Lab Type	Preferred
Surveillance	Routine Monitor	Presumptive	Contract EPA State Utility	Contract Utility	Contract Local Federal State Utility	State Utility	Federal	N/A	EPA Federal State Utility	EPA Utility
Response	Life Safety	Safety Screen	EPA Federal Local State Utility	N/A	EPA Federal Local State Utility	N/A	EPA Federal Local State Utility	N/A	EPA Federal Local State Utility	N/A
	ID of agent or threat	Confirmatory	Contract EPA Federal State	Contract EPA State	Federal State	State	Contract Federal	Federal	Contract EPA Federal State	Contract Federal
	Extent of threat	Presumptive/ Confirmatory	Contract EPA Federal State	Contract EPA State	Contract Federal Local State	Federal State	Contract Federal	Federal	Contract EPA Federal State	Contract Federal State
Remediate and Recover	Clean-up	Presumptive/ Confirmatory	Contract EPA State	Contract	Contract Federal State	Contract Federal	Contract EPA Federal State	Contract	Contract EPA Federal State	Contract
	Clear for Reuse	Confirmatory	Contract EPA State	Contract	Contract Federal State	Federal State	Contract EPA Federal State	Federal	Contract EPA Federal State	Contract EPA State


Event
Evaluate Extent
Involvement of local and state authorities, as well as Federal authorities
No HQ EOC Proceed with current processes. May use eLRN as resource
Forensics
Triage
Significant, National Event
No
Forensics
Yes
Activate HQ EOC Central Coordination of Environmental Units
Forensics
Triage
eLRN
Consultation and support thru HSLRC
Chemical Warfare
Biological
Radiological
Toxic Industrial Chemicals
14


Homeland Security Laboratory Response Program
Roles and Responsibilities defined and agreed upon
Participate in ICLN/NGC/POE activities
Need to establish formal relationships with external member laboratories
Need to formalize internal EPA laboratory roles and responsibilities
Understand capabilities
Continue to fine tune a complete inventory of Federal, State and private laboratory capability
Address gaps and identify appropriate investments needed
Carry out a national review of chemical, biological and radiological capability
Previous EPA/State/limited private laboratory Compendium undergoing web update
Focus on needed methods
Develop core set of HS methods at EPA
Collaborate with DOD/Other entities
Provide appropriate technical assistance
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Homeland Security Laboratory Response Workgroup

- Homeland Security Lab Response Workgroup, created in August of 2002 has continued operations
- The HSLR Workgroup has made substantial progress on several key laboratory preparedness issues for the Agency including:
  - Standardized Analytical Methods (SAM I & II)
  - EPA's Lab Response Compendium
  - Estimating Lab Capability and Capacity Gaps (in response to HSPD 10 Tasking)
  - All Hazard Receipt Facility Protocols

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HSLRWG

- <u>Standardized Analytical Methods for Use During Homeland Security Events</u> (SAM)
  - List of methods for use in identifying chemical and biological agents that could be used as weapons of mass destruction.
  - Version I published and distributed in September 2004.
  - Version II is now complete and has undergone SAB review (www.epa.gov.nhsrc)
- Recent ORD activities:
  - National Homeland Security Research Center (NHSRC) currently determining prioritization of FY 06 methods development & validation
  - NEMC-Las Vegas will serve as Agency chemical reference lab

Building Environmental Laboratory Capability in Support of Emergency Response

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Other Activities

- **EPA's Lab Response Compendium (www.epa.gov/compendium)**
  - EPA's Compendium is a web-based system designed to identify laboratory capabilities to analyze full range of chemical, radiochemical, and biological analytes
  - Data has been received from over 280 State, Commercial, and EPA laboratories (need data from non-EPA Federal Labs)
- **HSPD 10 Tasking**
  - 5 of the Whitehouse Homeland Security Council threat scenarios reviewed to determine the number of analyses required for large scale releases
  - Current capacity was estimated using the EPA Compendium, CDC and its LRN laboratories, US Army Medical Information Research Institute of Infectious Diseases, and DOE

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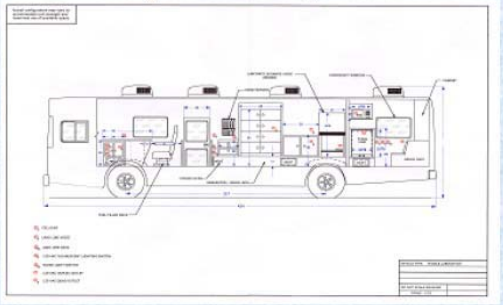
All Hazard Receipt Facilities

- **Design & Develop Modular All Hazard Receipt Facility for Unknowns**
  - Combined Effort of EPA, DHS, DOD and other Agencies, to develop and test prototype designs
  - EPA is funding development & testing of protocols and procedures
  - DHS is funding design and assembly of Units by DOD
  - Draft Protocols out
  - Two field prototypes to be delivered Summer 06?



Building Environmental Laboratory Capability in Support of Emergency Response

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Portable High-Throughput Integrated Laboratory Identification System (PHILIS)

- Originally a high-throughput screening system designed to identify and quantify TICs and CWAs above PEL
- Field Testing of 3 Prototype Designs completed July 2005
- Redesign of system, niche, and integration with EPA response needs underway with merged contract teams (DHS lead w/EPA input)
- Discussions include deployment of 2 existing units and re-design of 3rd

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Next Steps

- **External**
  - Develop national strategy with DHS to address gaps in environmental analyses
  - Expand the national capacity for Chemical, Biological and Radiological analysis in environmental samples
  - Participate with ICLN Networks
  - Outreach to States, other stakeholders

- **Internal**
  - Continue formation of eLRP
  - Continue work on WaterSentinel
  - Develop and deploy All Hazard Receipt Facilities
  - Develop 08 Budget approaches
  - Continue HSRC/NEMC activities

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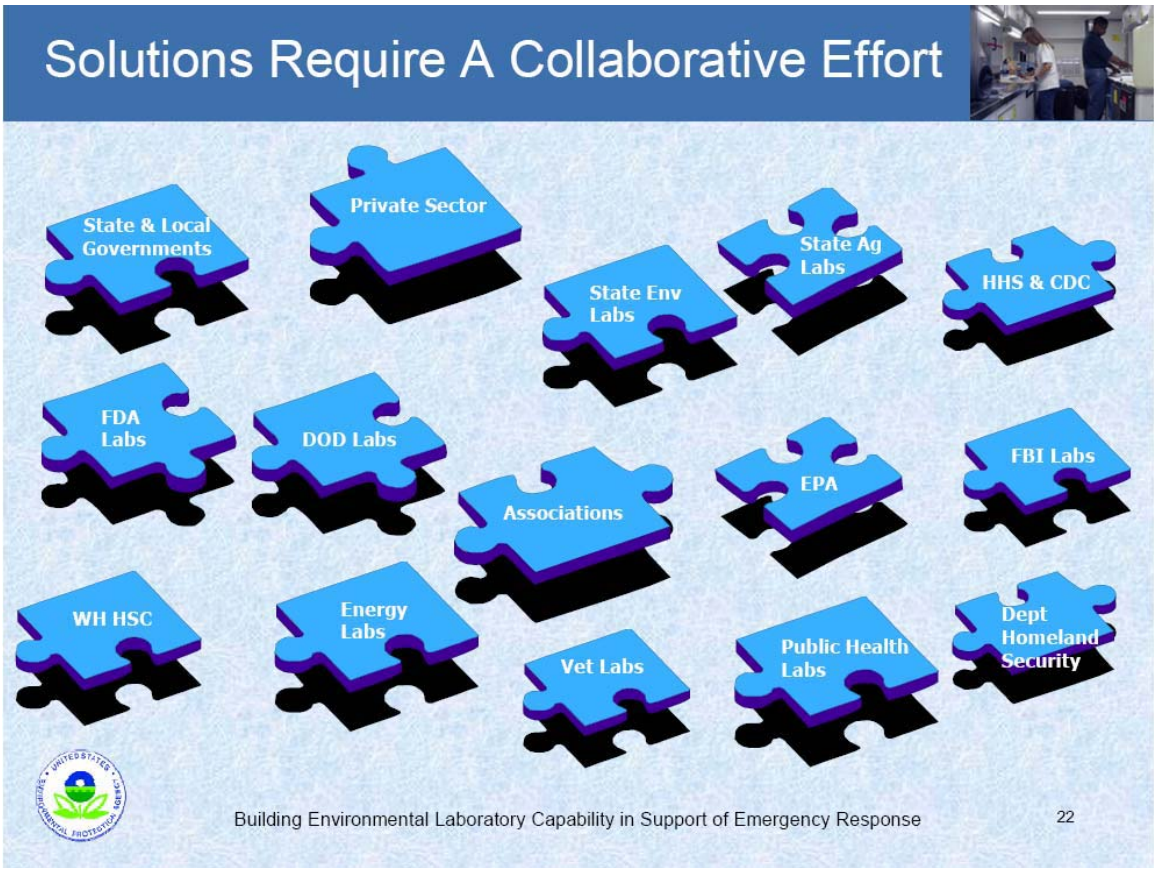
Solutions Require A Collaborative Effort
State & Local Governments
Private Sector
State Env Labs
State Ag Labs
HHS & CDC
FDA Labs
DOD Labs
Associations
EPA
FBI Labs
WH HSC
Energy Labs
Vet Labs
Public Health Labs
Dept Homeland Security
Building Environmental Laboratory Capability in Support of Emergency Response
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ENVIRONMENTAL LABORATORY RESPONSE NETWORK

Rothman, R.; USEPA

Following the 9/11/2001 attack and the subsequent anthrax events, it became apparent that EPA would have to be better prepared to respond to the possibility of future chemical, biological and radiological attacks. One key area of concern is laboratory capability/capacity. Historically, EPA has focused on toxic industrial chemicals. New high risk threats such as chemical warfare agents (cwas), toxins, biological agents and radionuclides visa vi "dirty booms", all pose catastrophic risk that would require a massive timely laboratory response.

When responding to an event, lab results would need to be of high quality, fast and consistent. To accomplish this, EPA must first establish reliable and validated analytical methods for each agent on concern. For many of these agents, proven methods simply do not exist and are complicated by various environmental media/conditions. At the same time methods are being developed, laboratory capacity is needed to receive potentially 10s of thousands of samples per week. This kind of capacity for the more than 100 high risk threat agents is daunting, particularly given the cost for method development, specialized equipment, training requirements and the need for regional representation.

This presentation will discuss some of the National Homeland Security Research Center's (NHSRC) initiatives to support laboratory capacity and capabilities. This includes the latest publication of the Standard Analytical Methods (SAM) that highlights agents of concerns and preferred analytical methods. In many cases, indicated methods are considered "best fit" but are not validated. Other initiatives addressed in this presentation include cwa and biological method development, expansion of lab capacity through the DHS philis, and establishment of the network reference lab in Las Vegas Nevada.

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EPA's National Homeland Security Research Center

Response Capability Enhancement

Rob Rothman

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RESPONSE CAPABILITY ENHANCEMENT TEAM

SUPPORT ELRN

METHODS DEVELOPMENT

METHOD VALIDATION

SAMPLE COLLECTION VALIDATION

ACCESS TO CWAs

EMERGENCY RESPONSE SUPPORT

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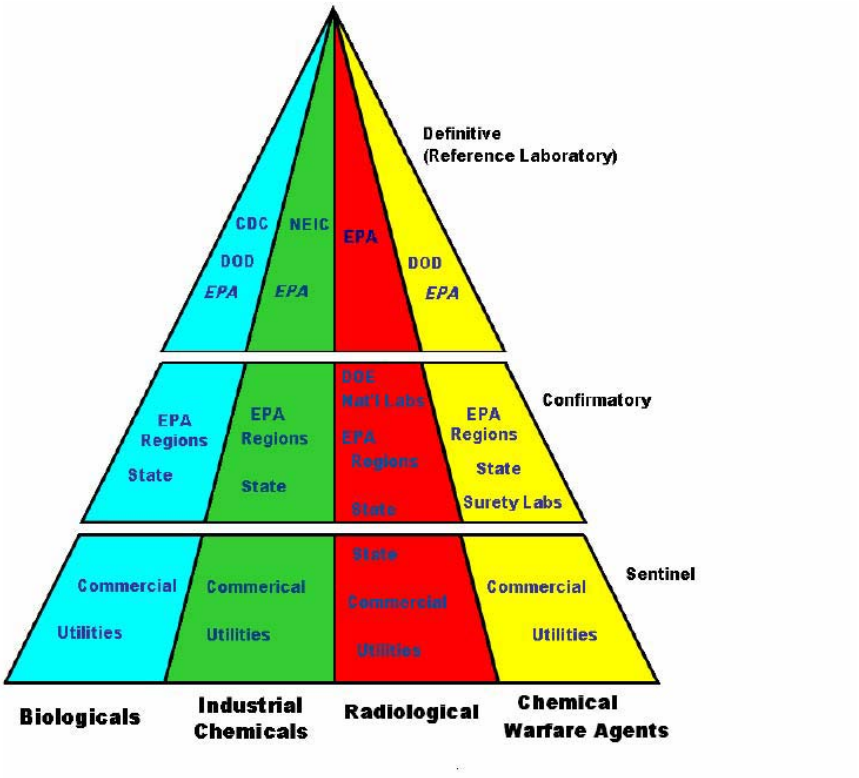
LABORATORY RESPONSE NETWORK



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National Exposure Measurement Center

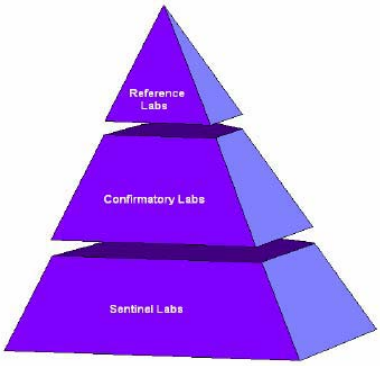
NEMC Headquartered in Las Vegas

- Chemical – Las Vegas

EPA's Reference Laboratory

Charged with :

- Methods Development
- Method validation
- Surge Capacity
- Quality Assurance
- Training
- PT Samples



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Triage/All Hazard Receipt Facilities (AHRF)

- DHS requested to address State Lab vulnerability in relation to analyzing unknowns, "white powders"
- EPA, DHS, DOD, FBI, APHL collaborate to develop and test screening protocol and AHRF design
- EPA will conduct assessment to determine its efficacy development & testing of protocols and procedure
- Two field prototypes to be delivered 06
  - Albany, NY
  - Region 1

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AHRF

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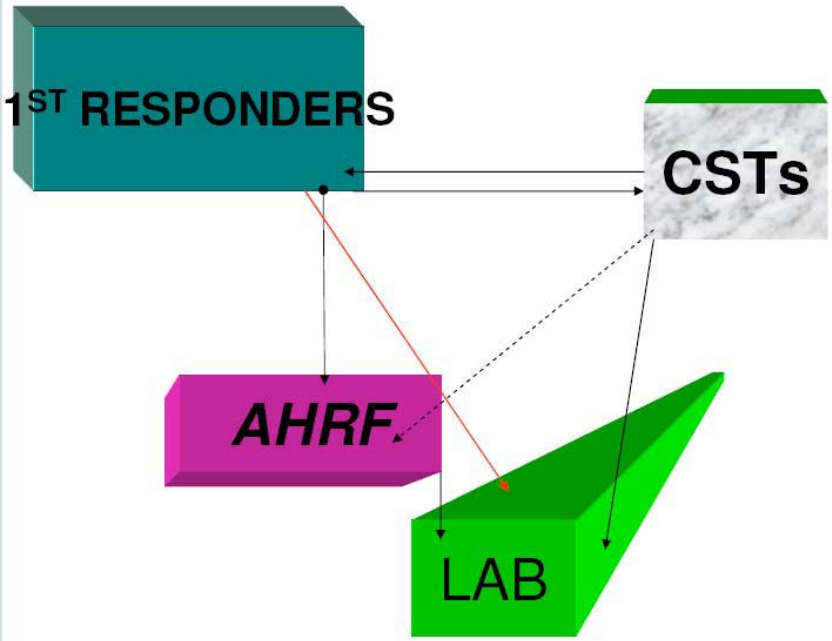

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Portable High-Throughput Integrated Laboratory Identification System (PHILIS)

- Designed to identify and quantify TICs and CWAs
- Designed to analyze and report on at least 1,000 (vapor, liquid, solid, mixed state) samples per 24 hour period
- Field Testing of 3 Prototype Designs completed July 2005
- Rapidly field-deployable lab analysis system
- Redesign of system with EPA response needs underway

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System Summary

Contractor	Analytical Technology	Number of Vehicles
Hamilton Sundstrand	6 – GC/MS/FPDs, 4 -ICs	2 Tractor Trailers
Battelle	3 – GC/MS/TOF	1 – Bus, 2 Trailers
EAI	10 – GC/MS Also XRF	4- Trailers, 2 Tow vehicles

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Hamilton Sundstrand

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Battelle

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EAI

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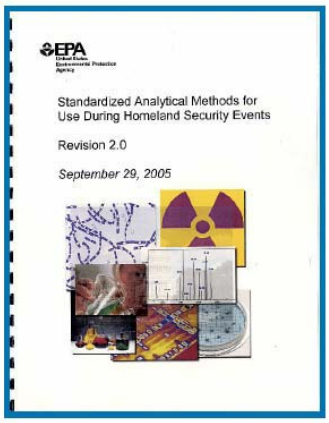
SAM Document

- Compilation of Chemicals, Biologicals and Radionuclides
- Specific method for analyte and media
- Selection based on detection level, equipment availability and scope of method
- SAM Version II released September 29, 2005



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SAM/SAP Process and Schedule

- Draft method gap analysis available
- Standard Analytical Protocols (SAPs)
  - 5 drafted to date
  - 6 more will be written by September 2006
- SAP Method validation
  - Semi-Volatile Organics Method validated during 2006
  - Degradation product validation using Method 8270 ongoing

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CWA Concentration

AGENT	*Dilute Per AR 50-6*		*Ultra Dilute per EPA*	
	Maximum Total Quantity / agent	**Maximum Concentration**	**Maximum Total Quantity / agent**	**Maximum Concentration**
Tabun (GA), Sarin (GB), Soman (GD), Cyclosoman (GF)	20 mg	2.0 mg/mL (2000 ppm)	100ug (in 10, 1 ml vials)	10ug/ml (10 ppm)
VX	10 mg	1.0 mg/mL (1000 ppm)	100ug (in 10, 1 ml vials)	10ug/ml, (10ppm)
Mustards (H, HD, HQ, HT, Q, T)	100 mg	10.0 mg/mL (10,000ppm)	100ug (in 10, 1 ml vials)	10ug/ml, (10ppm)
Lewisite (L, HL)	50 mg	5.0mg/ml (5000 ppm)	100ug (in 10, 1 ml vials)	10ug/ml, (10ppm)

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DHS CWA Lab Prototypes

DHS to sponsor two laboratories to analyze environmental samples containing ultradilute concentrations of CWA in 2006

- Region 1 and WV PHL
- Possibly, two more labs to be established 2007

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Red Team

Emergency advisory team to offer scientific guidance to senior management

- Volunteers from throughout EPA
- Expertise in 12 different areas
- Secondary support role to NHSRC

<u>Three divisions:</u>
Washington, DC,
Research Triangle Park, NC
Cincinnati, OH

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Red Team Approach

- Monthly conference calls and newsletter
- Team members on-call 24/7
  - Equipped with Blackberry, cell phone, laptop and GETS card
- Activated by EOC or NHSRC
  - Does not necessarily deploy to incident site
- Red Team Quickplace
  - Intranet website with Red Team resources; acts as central hub for activities and information

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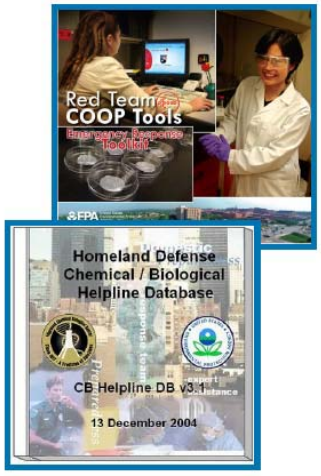
Response Tools

COOP Tools DVD

- Reference database with EPA, ECBC, DHS, military and medical resources
- FOUO and external versions



CB Helpline

- New web-based version
- Detailed chemical and biological agent profiles including exposure, detection, decon, protection
- MSDS, organizational contacts

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Response Tools

Homeland Security Experts

- Over 300 experts from EPA on-call for advice
- Working to include Regional volunteers

ECBC Reachback

- 24/7 technical support line for a nationally significant event

EPA Models and Databases

- Available on EPA website

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Trainings & Exercises

- Semi-annual training sessions and tabletop exercises for Red Team
- Red Team and NHSRC Participation in exercises with local responders
  - July 20: Post Office/Norfolk Southern tabletop with chemical release scenario
  - Sept. 30: Hamilton Co. Emergency Mgmt. Office full-scale exercise with chemical release and IED scenario

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Future Activities

- Support AHRF testing
- Validate sample collection methods
- Validate chem/bio SAPs
- Conduct ER Exercises w/ Red Team
- Support DHS – PHILIS/CWA labs
- Method Development
- Support ELRN--CWA

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Questions?

Sampling and Analytical Planning For Re-Entry and Recovery Following a Chemical Release Incident – Thinking Ahead

Hewett, Paul L.; Kimmell, Todd A.
Argonne National Laboratory

Chemical warfare agents have been released in a major metropolitan area. The initial response, which included evacuation of a portion of the population, has been completed and several days have elapsed. Pressure for allowing the evacuated public to return to their homes is mounting, but decision makers want a high degree of certainty that risks are acceptable before return is allowed. Sampling and analysis of various media are needed over a wide area as input to the determination of acceptable risk. A high degree of certainty translates to hundreds, perhaps thousands of samples.

- How can we be prepared with all the resources needed to support the sampling effort, including sample handling and transport?
- Given laboratory capacity limitations, how can we make sure that we are not taking more samples than our laboratories can handle?
- Given the number of samples and laboratories and the need for some level of data quality review, when will data be available to support decision making?
- What effect would bringing on additional sampling teams or laboratories have?
- How much will the sampling and analytical effort cost?

While decision makers may agree on the number of samples to support an agreed-upon level of certainty, they must be aware of the level of resources and amount of time it will take to obtain results. The purpose of this presentation is to review concepts for thinking ahead in determining the magnitude of the sampling and analytical effort required to support re-entry and recovery following a chemical release incident.

Argonne NATIONAL LABORATORY

Sampling and Analytical Planning for Re-Entry Following a Chemical Release Incident: Thinking Ahead

22nd Annual National Environmental Monitoring Conference

Todd A. Kimmell and Paul L. Hewett, Jr.

THE UNIVERSITY OF CHICAGO

Office of Science U.S. DEPARTMENT OF ENERGY

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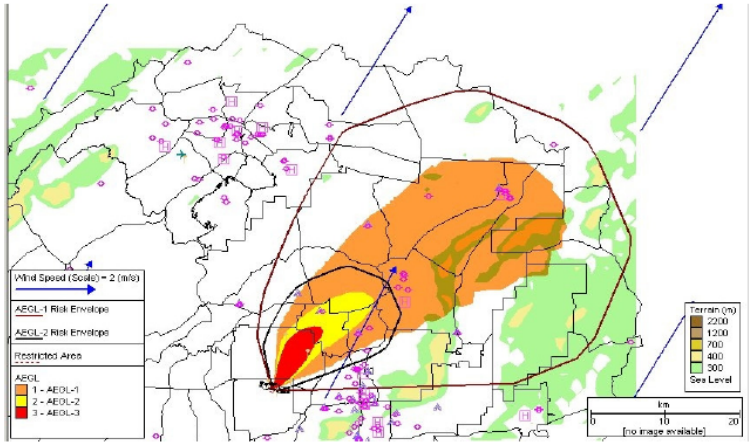
Hypothetical Scenario

- Chemical warfare agents released in a major urban area
- Vapor cloud forming a plume with subsequent deposition
- Population evacuation



Hypothetical Scenario

- Several days have elapsed and Subject Matter Experts are suggesting that agent has degraded or dispersed to acceptable levels
- Pressure is mounting for allowing population re-entry
- Decision makers want a high degree of certainty that risks are acceptable before return is allowed
- Sampling and analysis of various media are needed over a wide area – to support a risk determination

We recently attended an emergency response exercise that had a similar scenario. Without considering resources and timing, decision-makers selected a certainty of 95% for data in support of a re-entry decision.

Major Considerations for Re-Entry

- Meeting a high level of certainty can translate to a need for thousands of samples and multiple analyses per sample
- Many issues will require a quick but well-reasoned resolution
- The logistics of the sampling and analytical operation can be very complex
- The resources needed to support the operation can be extensive and a constant supply of consumables is needed
- The sampling and analytical effort can take many days to complete

During the exercise, to meet 95% certainty, a sampling and analytical plan was developed that called for approximately 3,000 samples. When asked about sample through-put, the response was: We have two laboratories that can each process 500 samples per day – 3 days.

But Let's Get Real

- How many sampling teams, and of what makeup, would it take to collect 500 samples per day (not including QC samples), considering:
  - Travel from sampling site to sampling site (some indoors)
  - Sample documentation
  - Safety concerns and personal protective equipment (PPE)
  - Sample screening and decontamination
- How many laboratories, running two or three methods per sample, would it take to process 500 samples per day, considering:
  - Laboratory documentation
  - QA/QC and procedures
  - Common laboratory issues

You can throw more sampling teams and laboratories at the problem, but what affect will this have on the logistics, resources and timing?

And What of Other Issues?

- Many issues may be faced in developing a sampling and analytical plan in support of emergency response and re-entry
  - Overarching Programmatic Issues
  - Logistical Issues
  - Technical Issues
- Many of these issues have tremendous implications in terms of public acceptability, resources considerations, timing, and liability
- Should decision-makers be involved in resolution of these issues?

Absolutely. But were decision-makers involved in issue resolution during the exercise? Were these issues even addressed during the exercise? Is it wise to address these issues during a real emergency response?

Lets take a quick look at some of the issues…

Programmatic "Overarching" Issues

- Technical approach to sampling (Statistical vs. Judgmental, Direction relative to Plume)
- Level of Certainty or Degree of Confidence
  - How sure do you want to be that you have not missed a hot spot?
  - How sure do you want to be that you have not misidentified a chemical?
- Decision Criteria
  - What levels (concentrations) are acceptable (safe)?
  - Will these levels be acceptable to the public?
  - Will any level be acceptable to the public?
  - What about degradation products?
- The Decision-Making Process
  - Who decides? On what basis? When? Is it a phased re-entry?
  - Adoption of National Incident Management System (NIMS) Incident Command System (ICS) – Incident Command Structure

Logistical Issues

- Timing and Coordination
  - Sampling and analysis (sample collection, screening, packaging, security, transport, analysis)
  - After analysis (reporting, quality reviews, databasing, evaluation, presentation, decision making)
- Accessibility of sampling locations
  - Grid points may translate to inaccessible locations
  - Private property issues and need for escort
- Resources
  - Consumables and non-consumables
  - Purchasing agreements
- PPE and decontamination requirements
- The weather!

Technical Issues

- Site Conceptual Model (SCM) and Data Quality
  - Even though its an emergency response you still need a SCM!
  - Pre-definition of desired level of data quality
- Analytical Methods
  - Laboratory Methods (Traditional Approach)
  - Field Methods (EPA's Triad Approach)
- Positive Results
  - False positives (or negatives)
  - Decision process
- Data Quality Evaluation
  - Screening assessment
  - Verification or Validation?
- Data Management (database selection and management of multiple formats)

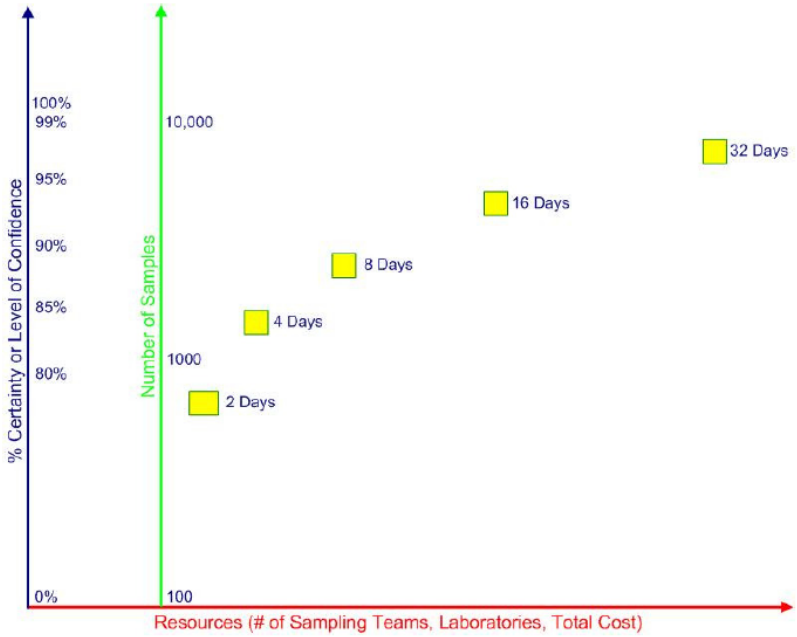
So, How Can We Get Prepared?

- Site- or situation-specific policy and guidance PREPARED BEFOREHAND
  - Resolves or at least explores the issues in different scenarios
  - Agreed to by decision-makers likely to be included in an incident command structure, perhaps with public input
- Training and emergency response exercises
  - Specific to the re-entry phase
  - Modeled on the National Incident Management System (NIMS) and Incident Command System (ICS)

Pre-Evaluation of Decision Criteria

Decision-makers need to be able to select a level of certainty or a level of confidence WHILE UNDERSTANDING the number and types of samples that need to be collected, the types of analyses that need to be performed, the issues and their implications, the amount of resources needed (personnel, equipment, consumables, funding), and the time that will be needed to complete sampling and analysis and related activities, and come to an informed decision.

Consider the following diagram…



Argonne's Synchronization Matrix (Sync Matrix©) Software

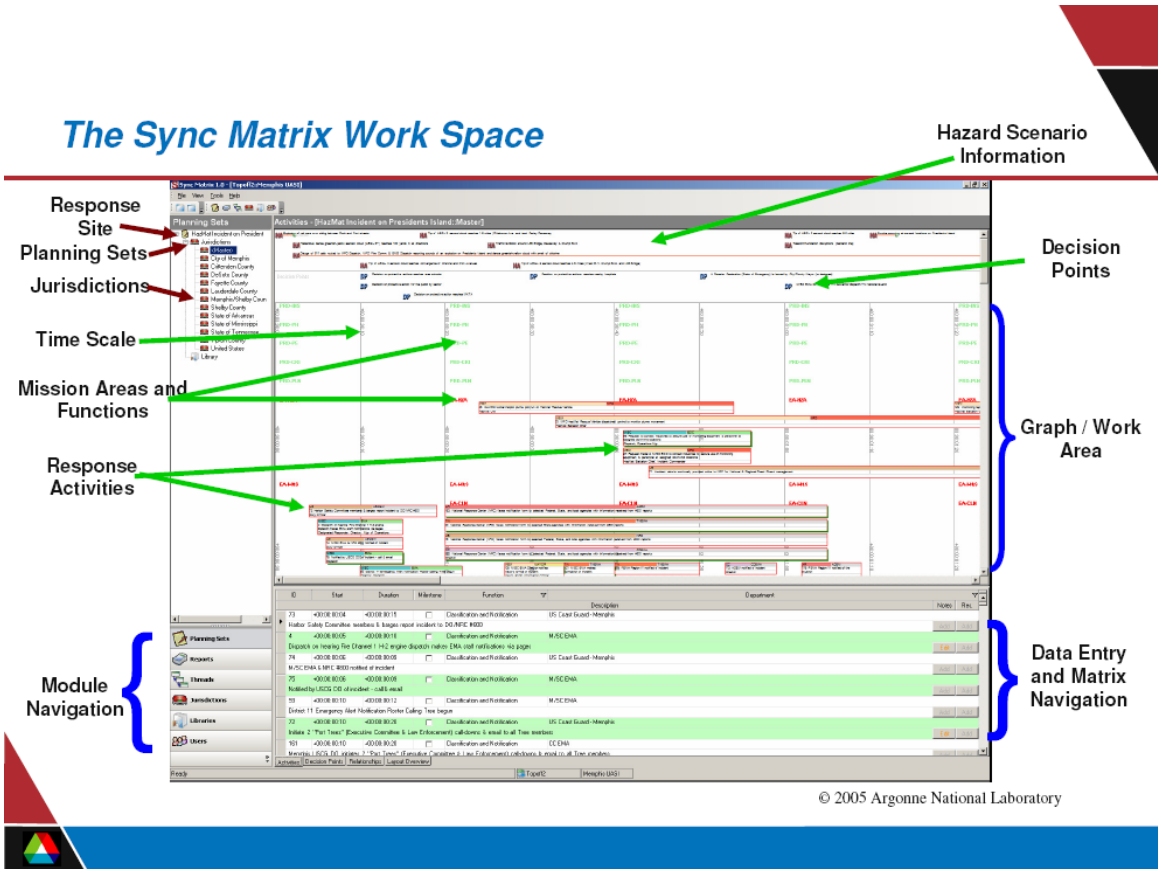
- What is Sync Matrix?
  - A planning software package intended to facilitate development, integration, coordination and synchronization of emergency response planning
  - A graphic depiction of a community's intended response, synchronized across time, space, and purpose in relation to a specific hazard scenario
  - Scenarios are limitless (hurricane, tornado, train derailment, chemical release, improvised explosive device, evacuation, event planning)

A "Sync Matrix" plan provides the framework from which you adapt a response, not a script to be followed to the letter.

Sync Matrix Planning

- Views emergency response as a set of human activity systems
- Uses a problem solving approach to planning
- Emphasizes relationships between the actions and capabilities of the various jurisdictions and departments within jurisdictions involved in a response
- Organizes activities over time by mission areas and functions, which are groupings of related response activities (e.g., monitoring and sampling)
- Identifies activities and relationships between activities over time in relation to the hazard scenario (e.g., hurricane landfall) and decision points (e.g., disaster declaration)

So we developed a Sync Matrix to plan-out sampling and analysis activities for re-entry, based on the exercise. Lets take a look, but first a quick primer on Sync.


The Sync Matrix Work Space
Hazard Scenario Information
Response Site
Planning Sets
Jurisdictions
Time Scale
Mission Areas and Functions
Response Activities
Decision Points
Graph / Work Area
Module Navigation
Data Entry and Matrix Navigation
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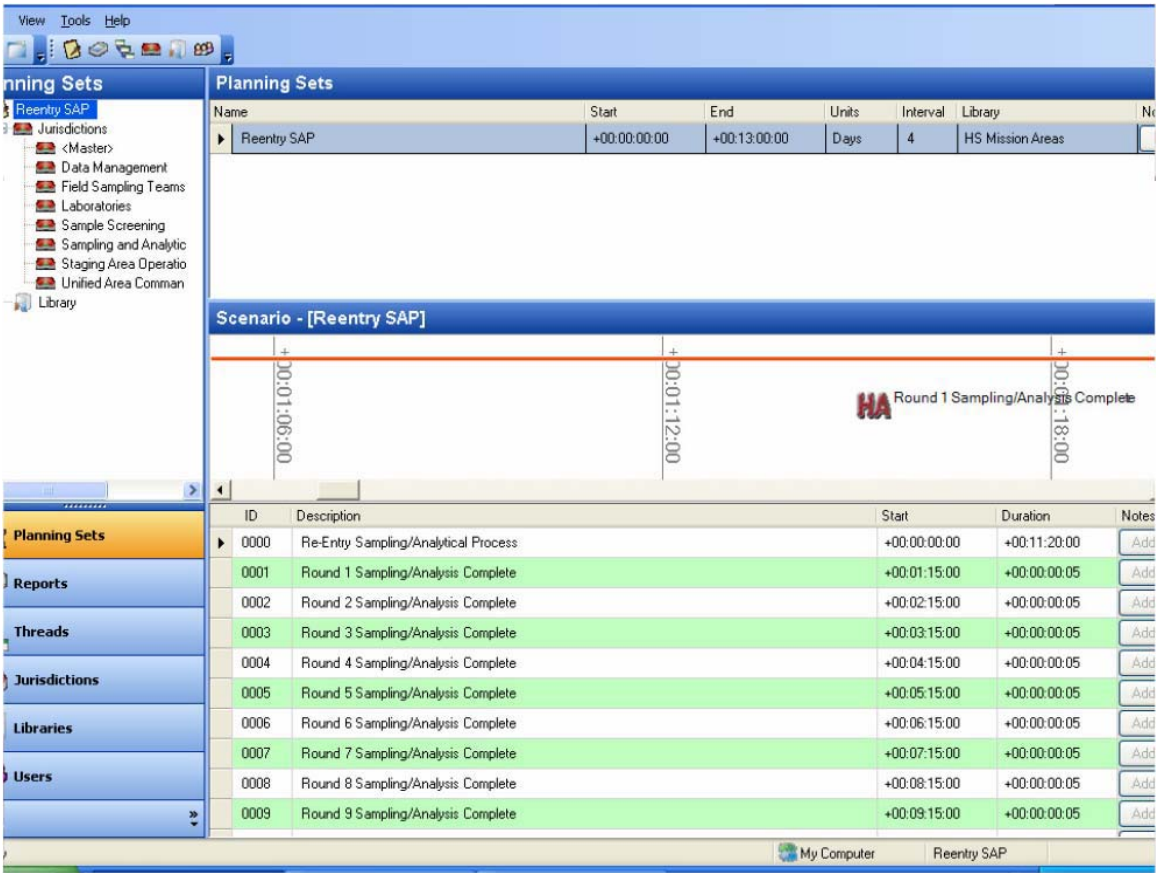
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Scenario - [Reentry SAP]
+00:01:06:00
+00:01:12:00
+00:01:18:00
HA Round 1 Sampling/Analysis Complete
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ID Description Start Duration Notes
0000 Re-Entry Sampling/Analytical Process +00:00:00:00 +00:11:20:00
0001 Round 1 Sampling/Analysis Complete +00:01:15:00 +00:00:00:05
0002 Round 2 Sampling/Analysis Complete +00:02:15:00 +00:00:00:05
0003 Round 3 Sampling/Analysis Complete +00:03:15:00 +00:00:00:05
0004 Round 4 Sampling/Analysis Complete +00:04:15:00 +00:00:00:05
0005 Round 5 Sampling/Analysis Complete +00:05:15:00 +00:00:00:05
0006 Round 6 Sampling/Analysis Complete +00:06:15:00 +00:00:00:05
0007 Round 7 Sampling/Analysis Complete +00:07:15:00 +00:00:00:05
0008 Round 8 Sampling/Analysis Complete +00:08:15:00 +00:00:00:05
0009 Round 9 Sampling/Analysis Complete +00:09:15:00 +00:00:00:05
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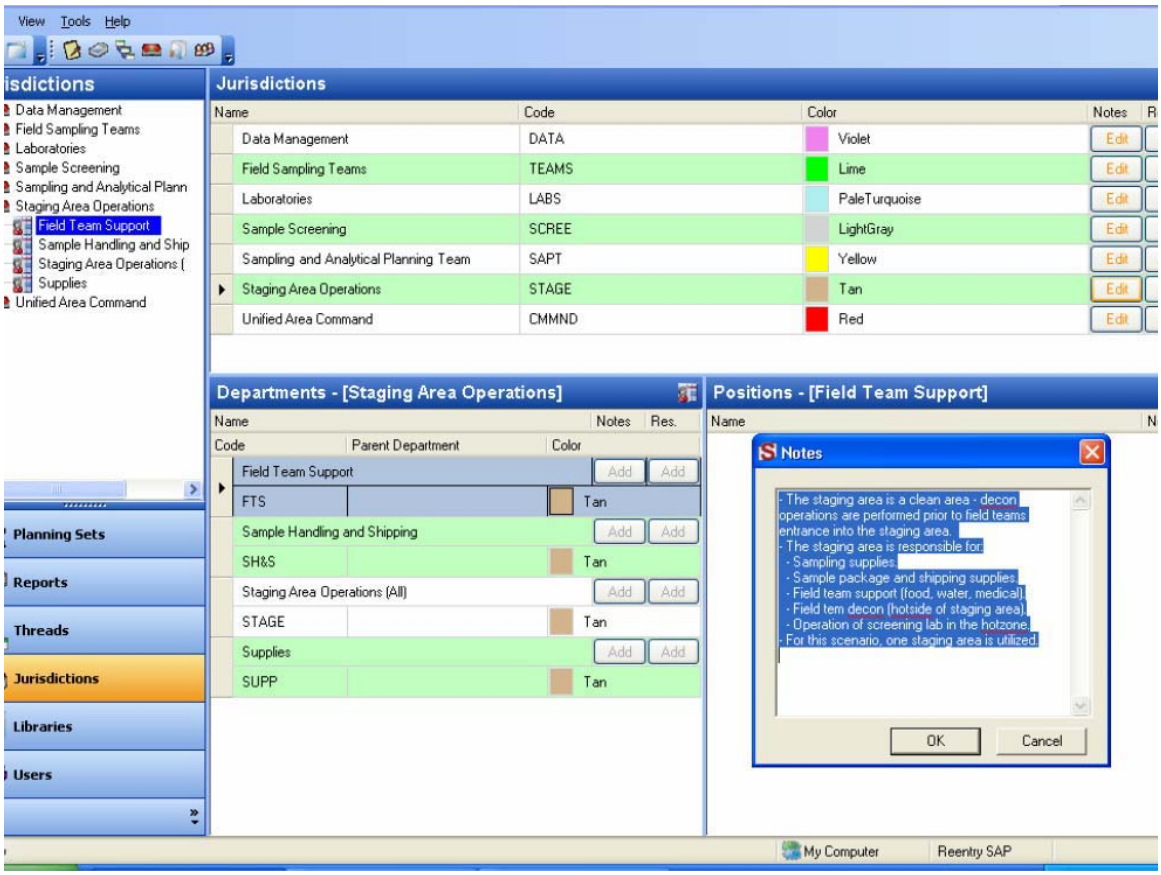
Reentry SAP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Field Team Support
Sample Handling and Ship
Staging Area Operations (
Supplies
Unified Area Command
Name Code Color Notes
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Field Sampling Teams TEAMS Lime Edit
Laboratories LABS PaleTurquoise Edit
Sample Screening SCREE LightGray Edit
Sampling and Analytical Planning Team SAPT Yellow Edit
Staging Area Operations STAGE Tan Edit
Unified Area Command CMMND Red Edit
Departments - [Staging Area Operations]
Name Notes Res.
Code Parent Department Color
Field Team Support Add Add
FTS Tan
Sample Handling and Shipping Add Add
SH&S Tan
Staging Area Operations (All) Add Add
STAGE Tan
Supplies Add Add
SUPP Tan
Positions - [Field Team Support]
Name
Notes
- The staging area is a clean area - decon operations are performed prior to field teams entrance into the staging area.
- The staging area is responsible for:
- Sampling supplies
- Sample package and shipping supplies
- Field team support (food, water, medical)
- Field tem decon (hotside of staging area)
- Operation of screening lab in the hotzone.
- For this scenario, one staging area is utilized.
OK Cancel
Planning Sets
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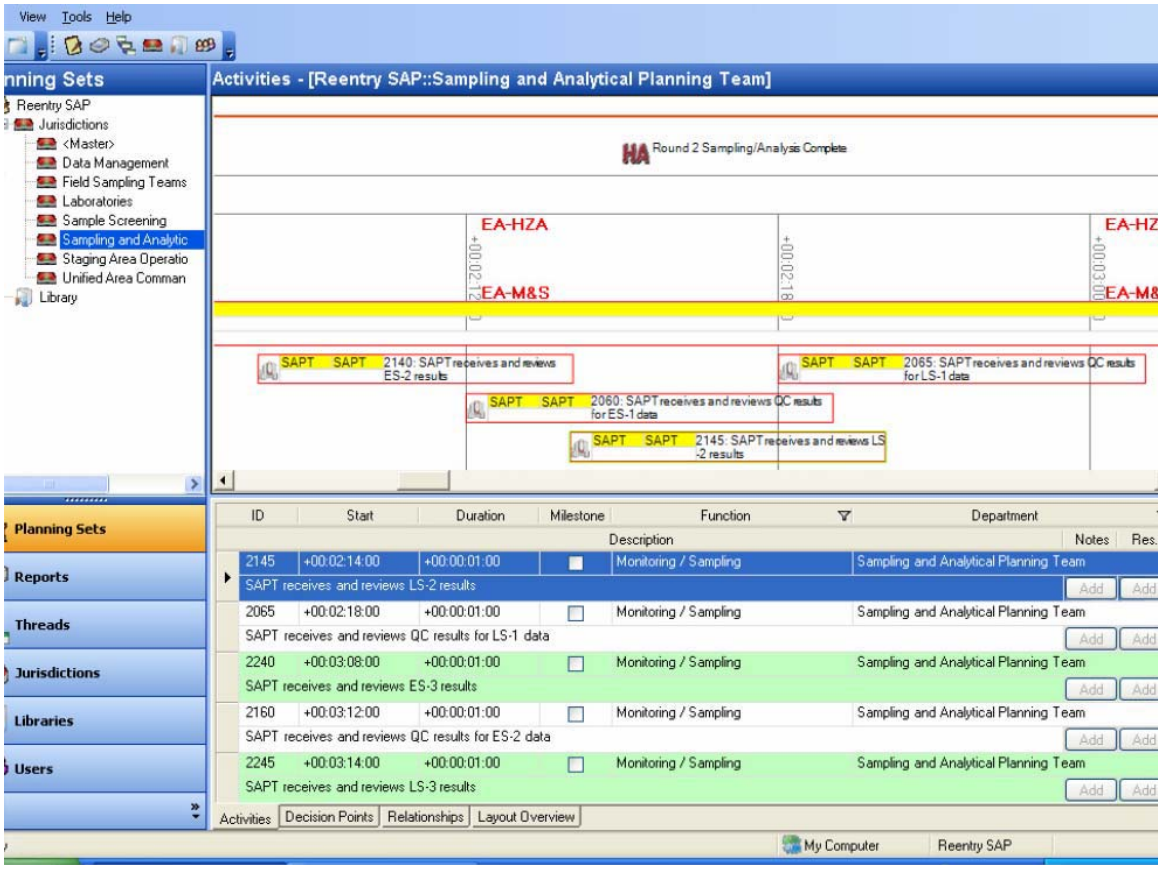
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Activities - [Reentry SAP::Sampling and Analytical Planning Team]
HA Round 2 Sampling/Analysis Complete
EA-HZA
EA-M&S
SAPT SAPT 2140: SAPT receives and reviews ES-2 results
SAPT SAPT 2065: SAPT receives and reviews QC results for LS-1 data
SAPT SAPT 2060: SAPT receives and reviews QC results for ES-1 data
SAPT SAPT 2145: SAPT receives and reviews LS -2 results
ID Start Duration Milestone Function Department
Description Notes Res.
2145 +00:02:14:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews LS-2 results
2065 +00:02:18:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews QC results for LS-1 data
2240 +00:03:08:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews ES-3 results
2160 +00:03:12:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews QC results for ES-2 data
2245 +00:03:14:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews LS-3 results
Add
Activities Decision Points Relationships Layout Overview
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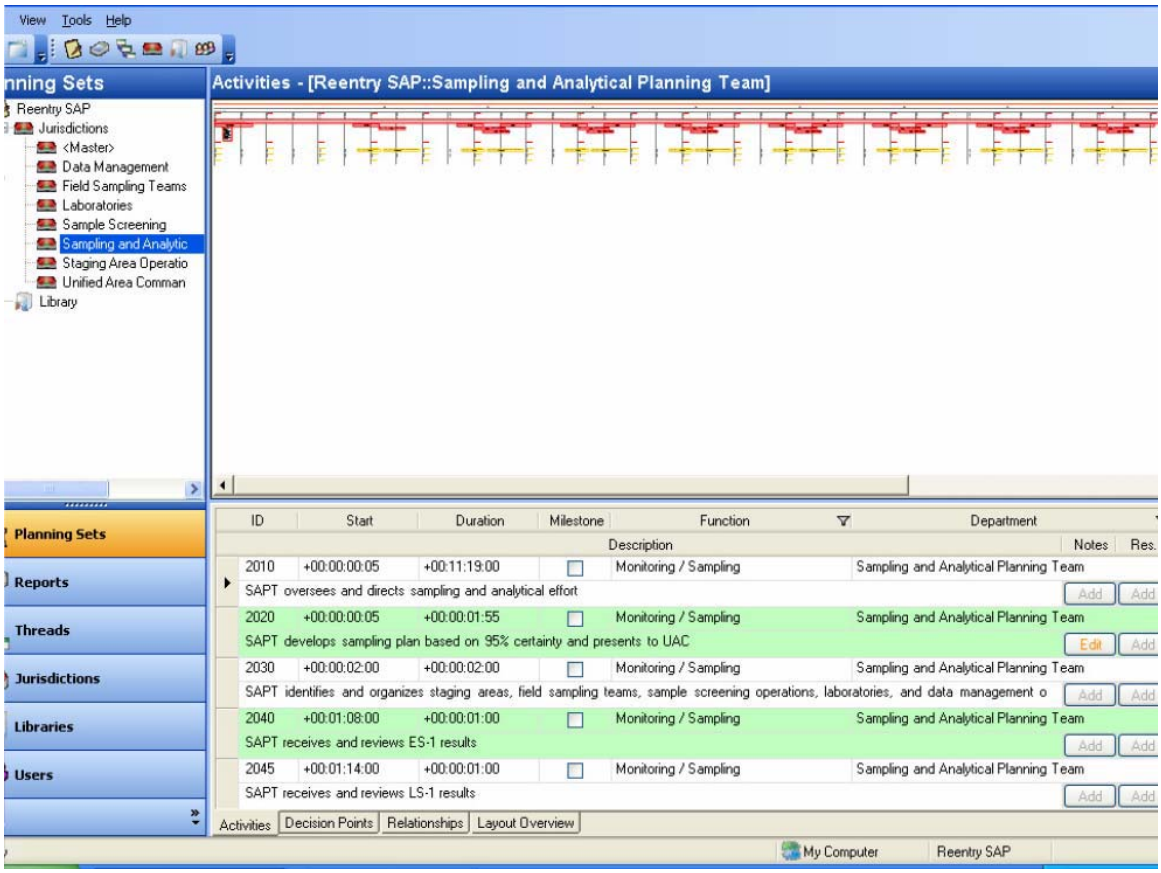
Reentry SAP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ID Start Duration Milestone Function Department
Description Notes Res.
2010 +00:00:00:05 +00:11:19:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT oversees and directs sampling and analytical effort
2020 +00:00:00:05 +00:00:01:55 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT develops sampling plan based on 95% certainty and presents to UAC
2030 +00:00:02:00 +00:00:02:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT identifies and organizes staging areas, field sampling teams, sample screening operations, laboratories, and data management o
2040 +00:01:08:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews ES-1 results
2045 +00:01:14:00 +00:00:01:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT receives and reviews LS-1 results
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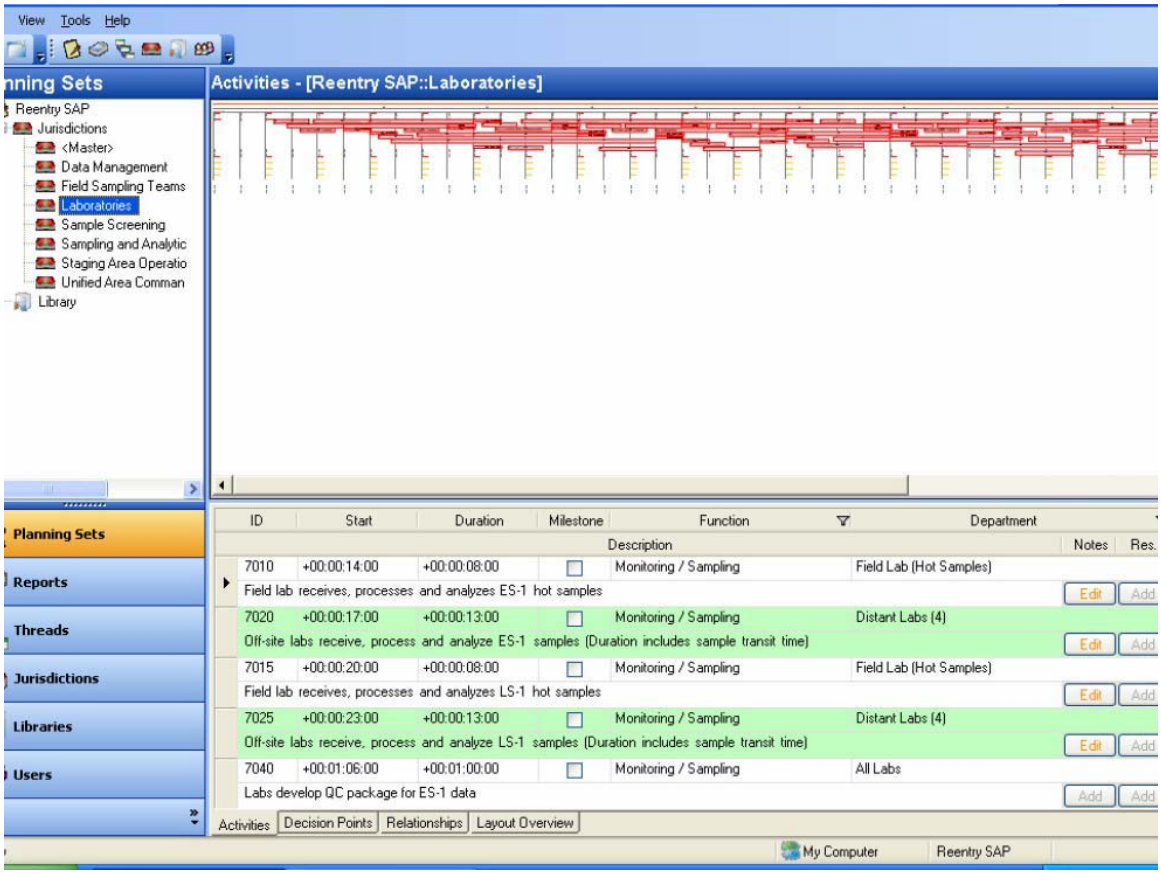
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ID Start Duration Milestone Function Department
Description Notes Res.
7010 +00:00:14:00 +00:00:08:00 Monitoring / Sampling Field Lab (Hot Samples)
Field lab receives, processes and analyzes ES-1 hot samples
7020 +00:00:17:00 +00:00:13:00 Monitoring / Sampling Distant Labs (4)
Off-site labs receive, process and analyze ES-1 samples (Duration includes sample transit time)
7015 +00:00:20:00 +00:00:08:00 Monitoring / Sampling Field Lab (Hot Samples)
Field lab receives, processes and analyzes LS-1 hot samples
7025 +00:00:23:00 +00:00:13:00 Monitoring / Sampling Distant Labs (4)
Off-site labs receive, process and analyze LS-1 samples (Duration includes sample transit time)
7040 +00:01:06:00 +00:01:00:00 Monitoring / Sampling All Labs
Labs develop QC package for ES-1 data
Add
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Activities Decision Points Relationships Layout Overview
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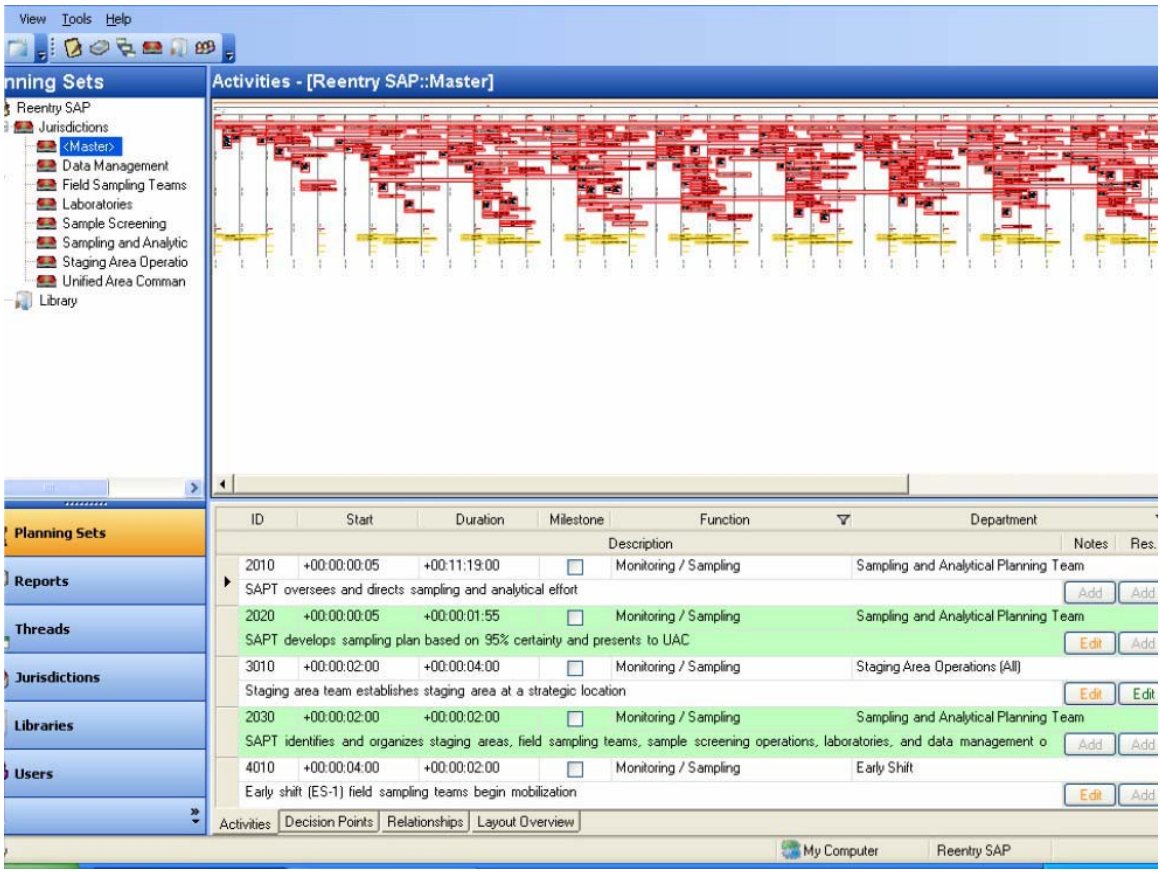
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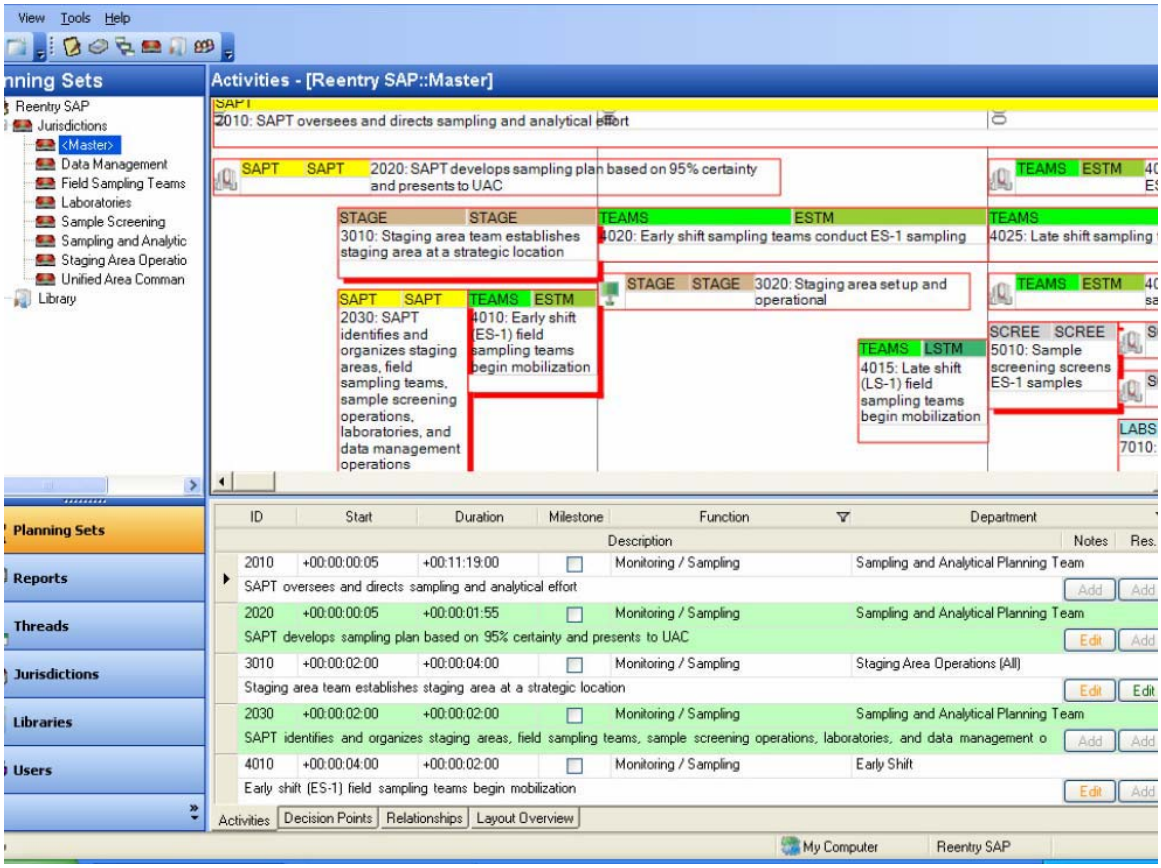
2010 +00:00:00:05 +00:11:19:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT oversees and directs sampling and analytical effort
2020 +00:00:00:05 +00:00:01:55 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT develops sampling plan based on 95% certainty and presents to UAC
3010 +00:00:02:00 +00:00:04:00 Monitoring / Sampling Staging Area Operations (All)
Staging area team establishes staging area at a strategic location
2030 +00:00:02:00 +00:00:02:00 Monitoring / Sampling Sampling and Analytical Planning Team
SAPT identifies and organizes staging areas, field sampling teams, sample screening operations, laboratories, and data management o
4010 +00:00:04:00 +00:00:02:00 Monitoring / Sampling Early Shift
Early shift (ES-1) field sampling teams begin mobilization
Activities Decision Points Relationships Layout Overview
My Computer Reentry SAP


View Tools Help
Activities - [Reentry SAP::Master]
2010: SAPT oversees and directs sampling and analytical effort
SAPT SAPT 2020: SAPT develops sampling plan based on 95% certainty and presents to UAC
STAGE STAGE 3010: Staging area team establishes staging area at a strategic location
TEAMS ESTM 4020: Early shift sampling teams conduct ES-1 sampling
TEAMS 4025: Late shift sampling
STAGE STAGE 3020: Staging area set up and operational
SAPT SAPT 2030: SAPT identifies and organizes staging areas, field sampling teams, sample screening operations, laboratories, and data management operations
TEAMS ESTM 4010: Early shift (ES-1) field sampling teams begin mobilization
TEAMS LSTM 4015: Late shift (LS-1) field sampling teams begin mobilization
SCREE SCREE 5010: Sample screening screens ES-1 samples
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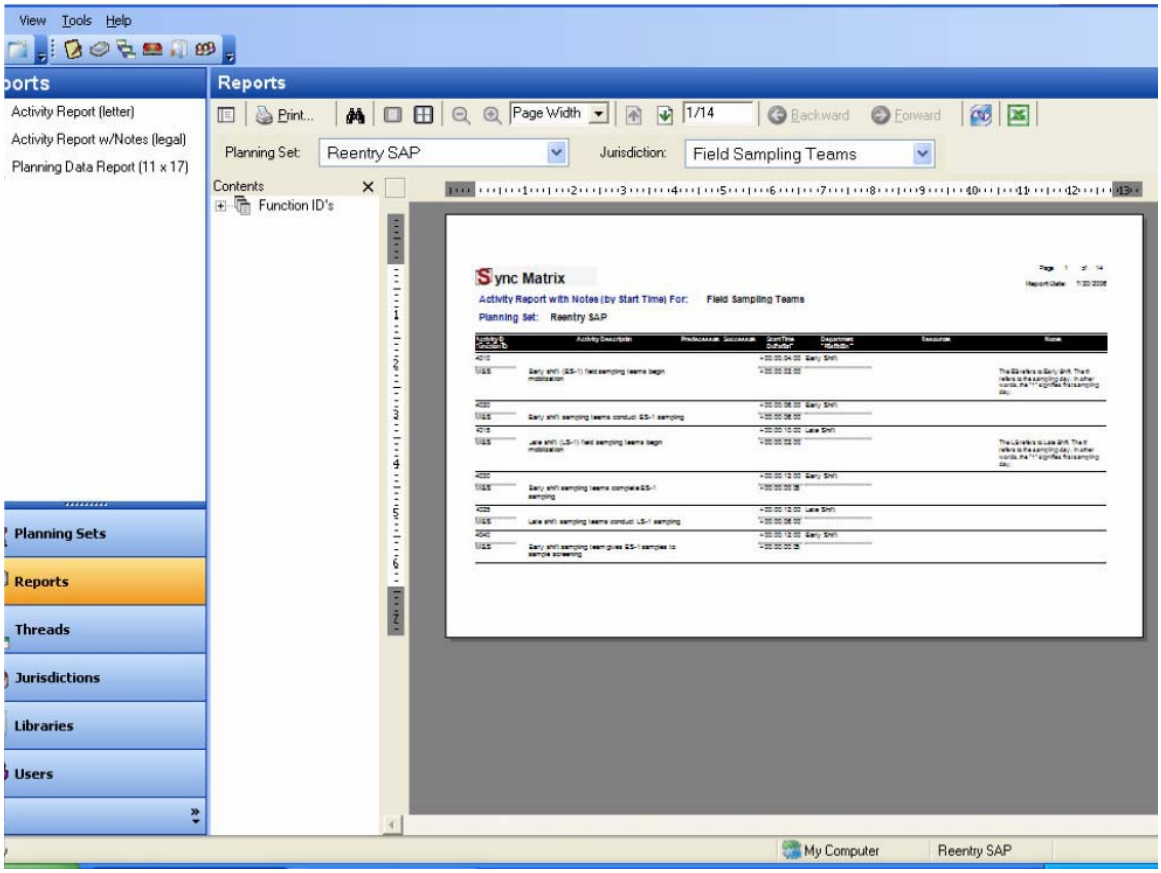
4010 +00:00:04:00 +00:00:02:00 Monitoring / Sampling Early Shift
Early shift (ES-1) field sampling teams begin mobilization
Activities Decision Points Relationships Layout Overview
My Computer Reentry SAP



By developing a Sync Matrix for the Exercise SAP we were able to show…

- The complexity of the sampling and analytical operations and support functions
- The time involved for the various steps of the process, by function and by jurisdiction
- The relationships between each of the jurisdictions
- The overall time required for each sampling/analysis phase
- The overall time for the entire operation

Using two sampling shifts per day, with two teams per shift, one on-site laboratory (for hot samples), one laboratory within driving distance, and three off-site laboratories, and considering data management and reporting, it was almost 12 days before an informed decision, based on 95% certainty, could be made.

Questions

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ETV and Real World Deployment Testing of an On-line, Learning Based System for Drinking Water Security Monitoring

Dan Kroll, Karl King and Greg Klein
Hach Homeland Security Technologies, Loveland, Colorado

ABSTRACT

The drinking water distribution system is vulnerable to deliberate or accidental back flow events. The large number of agents that could be potential threats and the innumerable access points make this a difficult scenario to defend against. This was clearly stated in a GAO report to Congress that listed the vulnerability of the distribution system to attack as the largest security risk to water supplies. A system designed to address the problem of distribution system monitoring is described here. The developed system employs an array of common analytical instrumentation, such as pH and chlorine monitors, coupled with advanced interpretive algorithms housed in an event monitor to provide detection/identification-response networks that are capable of enhancing system security. A variety testing protocols were used to verify the efficacy of the system. Data obtained from a Battelle/EPA ETV study and a cooperative research and development agreement (CRADA) between Hach HST the EPA Office of Research and Development addresses issues such as long-term deployment and ability to detect and characterize contaminants. Information obtained from test loop studies carried out by Hach HST, the US Army Corp of Engineers Research Lab, and the Edgewood Biological and Chemical Command as the result of a 3-way CRADA demonstrate data collected when the system is exposed to actual warfare agents. Real world deployment data is used to demonstrate recognition and classification of actual events. The system is shown to be a practical measure to help detect and characterize backflow events.

INTRODUCTION

The recognition that our water supplies are vulnerable to sabotage is not a recent discovery made after the attacks of 9/11. As early as 1941, just after the surprise attack on Pearl Harbor, FBI Director J. Edgar Hoover wrote, "Among public utilities, water supply facilities offer a particularly vulnerable point of attack to the foreign agent, due to the strategic position they occupy in keeping the wheels of industry turning and in preserving the health and morale of the American populace. Obviously, it is essential that our water supplies be afforded the utmost protection."[1] The US Military also recognized the threat prior to 9/11. The historic department of defense policy that requires domestic military base reliance on local utility infrastructure whenever possible was explored and recognized as a threat by Major D. C. Hickman in his seminal report issued in September of 1999 entitled "*A Chemical and Biological Warfare Threat; USAF Water Systems at Risk.*[2] There is a long history of water being vulnerable to such attacks.

That the water supplies are a target is also reinforced by the fact that domestic terrorist and fringe groups have shown continued interest in using a Chemical, Biological, or Radiological (CBR) agent in their attacks and Islamic terrorist groups have also exhibited interest in water supply

systems. While these attempts were thwarted, as history shows, al Qaeda has a unique ability to diligently perfect and refine attack strategies. This threat is particularly important for U.S. military bases, as it is for private and government "icon" facilities. Researchers from the U.S. Air Force and Hach Homeland Security Technologies (HST) have calculated that an attack on drinking water distribution systems can be mounted for between $0.05 and $5.00 per death, using rudimentary techniques, and amass casualties in the thousands over a period of hours.[3,4]

While the threat from Islamic terrorists is dire, it is not the only threat. Domestic terrorists and disgruntled employees may represent a scenario just as serious and possibly more likely. Even though threat of deliberate attack gets a lot of attention, the greatest vulnerability to water quality in the distribution system is not from intentional contamination but accidental contamination due to mistakes made in systems operation or failure of aging infrastructure. Many components of the ageing U.S. drinking water distribution system are verging on collapse. These failures in the system can be of a catastrophic nature, such as a burst pipe, or, as is more often the case, the slow degradation of the system that can lead to infiltration of contaminants from ground water or other sources. Do to the meager monitoring that is currently being done in the distribution system many of these types of problems remain undetectable until they result in a catastrophic failure or a disease outbreak.

When observing a typical municipal water supply system (Figure 1) it is natural to assume that the main point of vulnerability to a CBR attack would be the introduction of an agent into the system at the source water (reservoir) or treatment plant. However; in order to create widespread casualties from an attack on the source water, the amount of contaminant required would, after taking dilution into account, be either too large to handle easily or be more expensive than other readily available terrorist weapons. Within the water industry, this concept is summarized by the phrase *dilution is the solution to pollution.* Blind acceptance and reliance upon this strategy for protecting water has delayed the recognition of the true danger, as it exists, little own the timely adoption of possible ways to mitigate the problem. It is only gradually that the industry has come to recognize that the dilution of pollutants is not a viable means to deal with the vulnerability, as not all components of the system would dilute a toxin to non-hazardous levels.

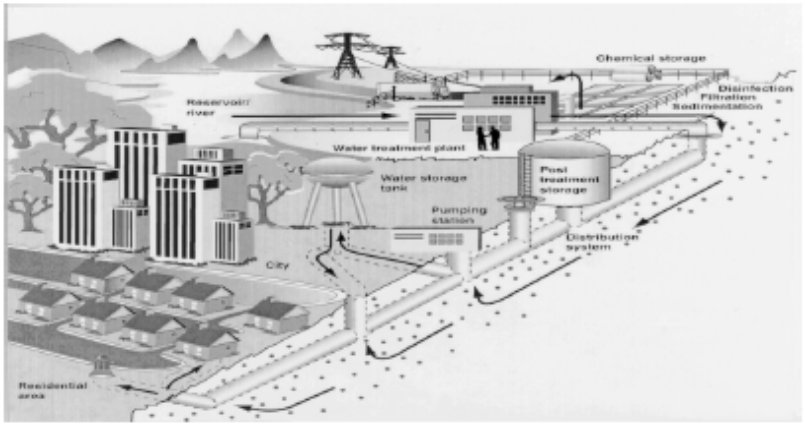


Figure 1: A Representative Municipal Water Supply System

Initially after the attacks of 9/11, government experts declared that, due to this dilution factor, our water supply systems were fairly secure. Ronald Dick, FBI Deputy Assistant Director for

Counter Terrorism Division, stated in testimony before congress that "In reality, targeting the water supply may prove difficult. In order to be successful, a terrorist would have to have large amounts of agent."[5] EPA administrator Christie Whitman stated on 10/18/2001, "People are worried that a small amount of some chemical or biological agent – a few drops for instance – could result in significant threats to the health of large numbers of people. I want to assure people – that scenario can't happen. It would take large amounts to threaten the safety of a city water system. We believe it would be very difficult for anyone to introduce the quantities needed to contaminate an entire system."[6]

The concept of dilution providing security for the system was short lived. It wasn't long before government officials and industry experts realized that the crucial vulnerability to contamination was is the distribution system. By October 2003, a GAO report to the Senate stated that the distribution system was the area most vulnerable to attack.[7] Conceding that an attack with CBR agents would most likely take place somewhere in the distribution system, several misconceptions about this type of attack still persist. Historic (and incorrect) dogma holds that such attacks require the assistance of several technicians, are expensive to carry out, and require complicated and expensive pumping equipment to inject contaminants into a pressurized system. More recent studies by the Army Corps of Engineers and Hach HST, among others, show that CBR attacks could in fact be carried out for 5 cents or less per lethal dose, that a single individual can obtain or produce effective contaminants in quantity, and that contaminants can be introduced into the distribution system with the aid of inexpensive and easy to obtain pumping equipment via a method called backflow attack.[8]

A backflow attack occurs when a pump is used to overcome the pressure gradient that is present in the distribution system's pipes. This is usually around 80 lbs/in^2 and can be easily achieved by using pumps available for rent or purchase at most home improvement stores. After the pressure has been overcome and a contaminant introduced, Bernoulli effects pull the contaminant into the flowing system and the normal movement of water in the system acts to disseminate the contaminant throughout the network effecting areas surrounding the introduction point. The introduction point can be anywhere in the system such as a fire hydrant, commercial building or residence. See Figure 2. Studies conducted by the US Air Force and Colorado State University have shown this to be a very effective means of contaminating a system.[8] A few gallons of highly toxic material was enough, if injected at a strategic location via continuous feed, to contaminate an entire system supplying a population of 150,000 people in a matter of a few hours. A terrorist could launch such an attack and be on a plane out of the country before the first casualties begin to show up.

Figure 2: All distribution systems are vulnerable to a backflow attack. The attack point can be anywhere in the system.

Currently, monitoring of drinking water supplies in the distribution system is limited. Previous to the terrorist threat, it was not a priority. The ability to detect an event in the distribution system and then identify it would be of incomparable value in responding to an incident in a timely and proper manner. Such an ability would also serve the purpose of mapping a system for clean up, and after words, it could be used as a forensic tool to identify the source of an event. Prior to this, there has not been a device capable of detecting such an event and alerting the system's managers so that the effects of an attack or accidental event can be contained. The general scientific consensus is that no practical, available, or cost-effective real-time technology exists to detect and mitigate intentional attacks or accidental incursions in drinking water distribution systems. The development of such a monitoring system was listed as by a panel of experts and industry leaders as a top priority in enhancing water security.[9]

Security monitoring in the distribution system is a difficult proposition. The shear number and diversity of potential threat agents that could be utilized in an attack against the system makes monitoring for them on an individual basis an effort that is doomed to failure from the start. What is needed is a broad-spectrum analyzer that can respond to any possible threat and even unknown or unanticipated events.

This need to detect such a large number of diverse contaminants requires a realignment of thinking from the traditional development of a sensor for a given compound or agent. Sensor arrays on a chip or the use of analytical instrumentation capable of detecting this variety is a definite challenge. Another approach is to use chemometrics to detect and characterize changes in basic water quality parameters and correlates them with threat agent introduction. This is the approach chosen by Hach HST and detailed in the remainder of this paper.

THE HACH HST APPROACH

Rather than attempting to develop individual sensors to detect contaminants or classes of contaminants, the Hach HST approach is to utilize a sensor suite of commonly available off-the-shelf water quality monitors such as pH, electrolytic conductivity, turbidity, chlorine residual and total organic carbon (TOC) linked together in an intelligent network. The logic behind this is that these are tried and true technologies that have been extensively deployed in the water supply industry for a number of years and have proven to be stable in such situations. One of the difficulties encountered when designing such a device is that the normal fluctuations in these parameters found within the water can be quite pronounced.

The problem then becomes, can we differentiate between the changes that are seen as a result of the introduction of a contaminant and those that are a result of everyday system perturbation? The secret to success, in a situation such as this, is to have a robust and workable baseline estimator. Extracting the deviation signals in the presence of noise is absolutely necessary for good sensitivity. Several methods of baseline estimation were investigated. Finally, a proprietary, patented, non-classical method was derived and found to be effective.

In the system as it is designed, signals from 5 separate orthogonal measurements of water quality (pH, Conductivity, Turbidity, Chlorine Residual, TOC) are processed from a 5-paramater measure into a single scalar trigger signal in an event monitor computer system that contains the algorithms. The signal then goes through the crucial proprietary baseline estimator. A deviation of the signal from the established baseline is then derived. Then a gain matrix is applied that weights the various parameters based on experimental data for a wide variety of possible threat agents. The magnitude of the deviation signal is then compared to a preset threshold level. If the signal exceeds the threshold, the trigger is activated.

The deviation vector that is derived from the trigger algorithm is then used for further classification of the cause of the trigger. The direction of the deviation vector relates to the agents characteristics. Seeing that this is the case, laboratory agent data can be used to build a threat agent library of deviation vectors. A deviation vector from the monitor can be compared to agent vectors in the threat agent library to see if there is a match within a tolerance. This system can be used to classify what caused the trigger event. This system can also be very useful in developing a heuristic system for classifying normal operational events that may be significant enough in magnitude to activate the trigger. When such an event occurs the profile for the vector causing it is stored in a plant library that is named and categorized by the system operator. When the event trigger is set off the library search begins.

The agent library is given priority and is searched first. If a match is made, the agent is classified. If no match is found, the plant library is then searched and, the event is identified if it matches one of the vectors in the plant library. If no match is found, the event is classified as an unknown and can be named if an investigation determines its cause. This is very significant because no profile for a given event need be present in the libraries for the system to trigger. This gives the system the unique ability to trigger on unknown threats. Also, the existence of the plant library with its heuristic ability to learn plant events results in a substantial and rapid decrease in unknown alarms over time. The developed system has been subjected to strenuous testing in both

laboratory and field scenarios as detailed in the remainder of this paper and has been found to be an effective tool for surveillance of the distribution system.

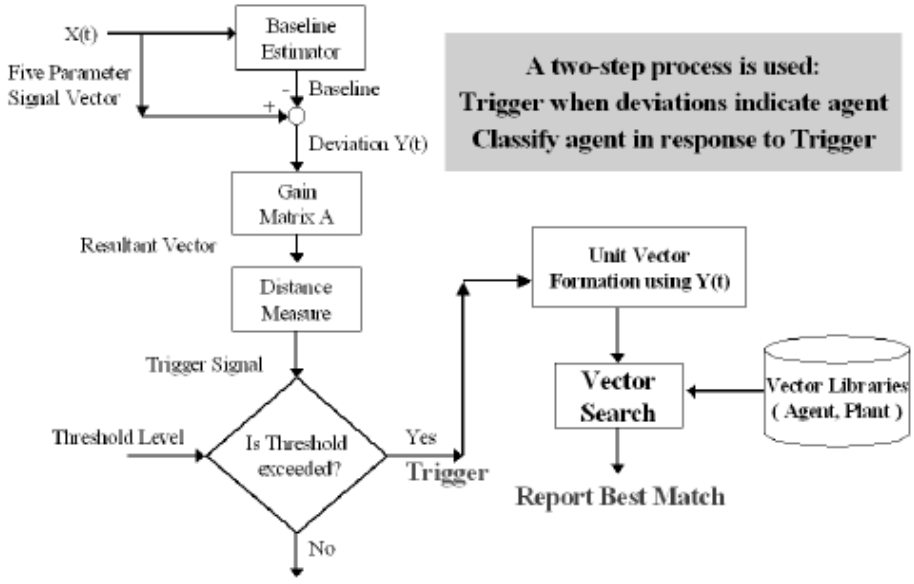


Figure 3: The use of intelligent algorithms with standard bulk parameter monitoring equipment allows for a robust system that is capable of triggering on and classifying a wide diversity of threat agents including.

BATTELLE EPA ETV VERIFICATION TESTING

In the fall of 2004, the developed technology was submitted for testing to the EPA Environmental Technology Verification (ETV) testing program run by Battelle. The ETV Program develops testing protocols and verifies the performance of innovative technologies that have the potential to improve protection of human health and the environment. ETV was created to accelerate the entrance of new environmental technologies into the domestic and international marketplace. The category being tested was Multi-parameter Water Monitors for Distribution. The technologies verified needed to function on line and be capable of monitoring chlorine and at least one other parameter. The tested technologies were evaluated for accuracy of instrument readings versus reference methods, ability to maintain integrity during long term deployment, system to system variability, ability to respond to contaminants, and classification of unknown contaminants (The Hach system was the only one evaluated for ability to classify contaminants). The complete ETV report and an explanation of the report can be down loaded at: [http://www.hach.com/fmmimghach?/CODE:ETV_EMTS-WDMP9266|1//true] and [http://www.hach.com/fmmimghach?/CODE:ETVEXP-HACHHST9203|1//true].

Accuracy

The on-line instruments were evaluated on an individual basis versus standard laboratory methods for the given parameters. See Table 2.

Table 2: Accuracy

Evaluation Parameter		Cl	Turb	Cond.	pH	TOC
Stage 1 Accuracy	Units 1 & 2, range of %D (median)	-47.4 to 4.5 (-3.9)	-53.9 to – 1.3 (-34.1)	-15.5 to 8.1 (2.2)	-6.6 to 3.1 (0.9)	-64.7 to 147.5 (-14.8)

Overall accuracy of all of the parameters measured was very good and correlation to laboratory methods was strong. Small absolute values in turbidity and TOC lead to large %D. Due to sampling errors in some cases on-line instrument readings may be more reliable than the reference method e.g. chlorine.

Inter-Unit Reproducibility

Two separate but identical sets of instrumentation were deployed for the duration of the study. Measurements versus reference instruments were compared through out the course of the study.

Table 3: Reproducibility

Parameter		Cl	Turb.	Cond.	pH	TOC
Inter-unit Reproducibility	Slope (intercept)	0.98 (0.03)	0.97 (0.005)	0.92 (4.19)	1.06 (-0.40)	0.97 (0.31)
	r^2	0.994	0.881	0.961	0.919	0.991
	p-value	0.779	0.884	0.006	0.517	0.374

With the exception of conductivity both units generated similar results. See Table 3.

Contaminant Injection

During this phase of the test the instruments were installed in a recirculating pipe loop. Various contaminants were injected to determine if they altered the baseline response pattern of the instruments. Similar injections were preformed after the long-term deployment test to ascertain if there had been any degradation of instrument response.

Total chlorine and TOC were dramatically affected by injections of nicotine, *E. coli,* and Aldicarb; and turbidity, pH, and conductivity were affected by some or all of the injections, but not as consistently as total chlorine and TOC. Aldicarb altered pH during testing after extended deployment but not before. See Table 4. Agreement in both cases with reference readings indicates that the instruments were functioning properly and, the difference was in the injection preparation.

Table 4: Response to Contaminant Injection

Parameter			Cl	Turb	Cond	pH	TOC
Initial response to injected contaminants	Nicotine	Ref	-	(a)	NC	NC	+
		Hach	-	+	NC	NC	+
	Arsenic Trioxide	Ref	-	(a)	+	+	NC
		Hach	-	+	+	+	NC
	Aldicarb	Ref	-	(a)	NC	NC	+
		Hach	-	+	NC	NC	+
Response after extended deployment	E. coli	Ref	-	+(b)	+	-	+
		Hach	-	+	+	-	+
	Aldicarb	Ref	-	+(b)	NC	-	+
		Hach	-	+	NC	-	+

(a)Relatively large uncertainty in the reference measurements mad it difficult to detect a significant change; (b)Magnitude of change different between duplicate injections; +/- Parameter measurement increased/decreased upon injection; NC No change in response to contaminant injection

Long-term Deployment

During this phase of the testing, the systems were operated continuously for 52 days with only normal maintenance, such as reagent replenishment, being performed. During the course of the test, instruments were regularly compared to reference instruments. See Table 5. At the end of the 52 days a second response to contaminant injection procedure was performed. See Table 4. The results of the extended deployment study indicate that the system can be effectively deployed for long periods of time with only routine maintenance. Relative large %D in turbidity and TOC measurements are artifacts of the low total values for these parameters encountered during the testing procedure and do not indicate a problem with these sensors.

Table 5: Post-extended Deployment Results

		Unit 1		Unit 2	
Parameter	Reference Average (SD)	Average (SD)	%D	Average (SD)	%D
Free chlorine	1.03 (0.03)	0.98 (0.02)	-4.9	0.98 (0.02)	-4.9
Turbidity	0.17 (0.02)	0.16 (0.03)	-5.9	0.15 (0.04)	-11.8
Temperature	22.66 (0.16)	22.61 (0.03)	-0.2	23.70 (0.06)	4.6
Conductivity	356 (1)	380 (1)	6.7	357 (1)	0.3
pH	8.59 (0.01)	8.40 (0.01)	-2.2	8.61 (0.00)	0.2
TOC	0.88 (0.01)	0.70 (0.01)	-20.5	0.91 (0.01)	3.4

Inter-Unit Reproduceablity

Two Hach units were compared, using data collected from reference samples throughout the verification test to determine whether similar results were generated. See table 6.

For free chlorine, pH, TOC, and turbidity, the linear regression had coefficients of determination greater than 0.91 and slopes within 6% of unity, indicating similar and repeatable results. The t-

test p-values confirmed the sensors were generating statistically similar results. The conductivity meters had a linear regression coefficient of determination of 0.961 and a slope of 0.92, indicating that the data were highly correlated with one another. The t-test generated p-values significantly less than 0.05, which indicated that the results from the two conductivity sensors were significantly different. This difference was driven by the small amount of variability in the conductivity measurements; therefore, the small difference between the means of the two units was statistically significant. It is important to note that the offsets in the measured parameters do not affect the performance of the algorithm because the baseline is removed and the classification is performed based only on deviations from baseline.

Table 6: Inter-unit Reproducibility Evaluation

Parameter	Slope	Intercept	r^2	t-test p-value
Free chlorine	0.98	0.03	0.994	0.779
Turbidity (outlier removed)	0.97	0.005	0.881	0.884
Temperature	0.72	7.68	0.758	5.5 × 10-6
Conductivity	0.92	4.19	0.961	0.006
pH	1.06	-0.40	0.919	0.517
TOC	0.97	0.31	0.991	0.374

Shading indicates a significant difference between the two units.

Contaminant Classification

During the final stage of the verification test thirteen contaminants (See Table 7) were injected at a concentration of approximately 15 mg/L, in duplicate, into a 1500 foot straight line pipe and allowed to flow past the monitoring sensors. Every contaminant injection resulted in the system exceeding the trigger threshold and producing a corresponding agent alarm. Each minute-by-minute search of the agent library can result in more than one agent being identified. For both Hach Units, the agent alarms occurred as few as eight times and as many as 79 times during the 20-minute injection periods. No agent alarms occurred outside of the 20-minute injection periods. If the system recognized deviations from the baseline, the agent library identified and recorded these deviations as "unknown" event. Due to the dynamic nature of the leading and trailing edges of the injected contaminant, it is possible that an injection event generated alarms other than the known injected contaminant. Table 7 shows all contaminant injections classified according to the fraction of agent alarms attributable to the correctly classified injected contaminant. The data is depicted concisely by classification rates divided into five levels: Level 5 – greater than 70%, Level 4 – between 31% and 69%, Level 3 – between 1% and 30%, Level 2 – injected contaminant not identified but other contaminants were identified, and Level 1 – no injections detected.

From the tests conducted on Hach Version 1 System, weak results were obtained for Methanol and Dichlorvos, while poor results were obtained for Glyphosate, Nicotine, Arsenic Trioxide and *E. coli*. The data from the tests on VERSION 1 of the HHST technology at the EPA center were recorded at the time of the tests. The Event Monitor Trigger System also acts as a data logger and provides a copy of the sensor signals recorded during the tests. This situation afforded us the ability to analyze failures detected in the VERSION 1 tests, improve and upgrade software, and

then replay new versions of the technology to test for efficacy. A variety of causes were found to affect the test results of VERSION 1.

Because of a misunderstanding, the original Version 1 threat agent library included Round-UP Herbicide (a form of glyphosate), while the ETV protocol used pure glyphosate. When pure Glyphosate was added to the agent library in Version 3, the system correctly classified the agent.

HHST had previously tested nicotine (in house, and at ECBC) with good results. However, the data from the ETV test facility revealed that the excessive mixing method employed prior to injection had caused the nicotine base to react with the carbon dioxide in the air, changing the chemical nature of the contaminant. The Agent Library was improved by adding a signature for reacted nicotine, and Version 3 shows the positive test results. These two examples demonstrate the sensitivity of the system, and how the comprehensive data structure of its Agent Library derives its classification accuracy.

In addition while first developing the Agent Library, HHST employed bench-scale chlorine analyzers that contained EDTA (a metal sequestering agent) as a reagent component, whereas the EMTS sensor panel includes chlorine analyzers that do not use this substance. The EPA/ETV tests revealed this flaw, and VERSION 3 includes upgraded library signatures. Signatures for some other agents were examined for tabular errors and those were corrected as needed. This second set of test results could not be included in the ETV report, as any re-testing was not a part of the original test protocols. Following analysis and upgrades, two succeeding algorithm versions were produced; the test results from VERSION 3 is summarized in Table 8.

Table 7: Contaminant Classification Results

	Injection 1		Injection 2	
Contaminant	**Unit 1**	**Unit 2**	**Unit 1**	**Unit 2**
Aldicarb	4	4	4	4
Arsenic trioxide	2	2	2	2
Colchicine	4	4	4	4
Dicamba	4	5	5	5
Dichlorvos	4	3	3	2
E. coli	3	2	4	2
Ferricyanide	5	5	5	5
Fluoroacetate	5	5	4	4
Glyphosate	4	3	2	2
Lead nitrate	5	5	5	5
Mercuric chloride	4	4	4	4
Methanol	4	4	4	3
Nicotine	2	2	2	2

Table 8: Classification Results from Algorithm Version 3

	Injection 1		Injection 2	
Contaminant	**Unit 1**	**Unit 2**	**Unit 1**	**Unit 2**
Aldicarb	4	4	4	4
Arsenic trioxide	4	5	4	5
Colchicine	4	4	4	4
Dicamba	4	3	5	5
Dichlorvos	2	2	3	3
E. coli	4	3	4	3
Ferricyanide	5	5	5	5
Fluoroacetate	5	5	5	5
Glyphosate	4	4	4	4
Lead nitrate	5	5	5	5
Mercuric chloride	5	5	5	5
Methanol	4	4	4	3
Nicotine	4	4	4	4

BEAKER TESTING AND FLOW LOOP TESTING AT EDGEWOOD CHEMICAL AND BIOLOGICAL COMAND (ECBC)

The purpose of this effort was to challenge water distribution systems and sensors, with agent simulants and real threat agents, in order to characterize the response of the distribution system and Early Warning System to agents. Agent concentrations and water solutions were varied to allow for the development and demonstration of distribution methodologies and performance data acquisition. In addition, this work evaluates the effectiveness of Hach Homeland Security Technologies real-time detection technology and provides important information necessary for the U.S. Army to perfect its theories of operation and response mechanisms. The scope of the work performed during these tests was two fold. The first part of the test was to perform beaker studies on agents that are not available for use in the Hach Laboratories in Colorado such as VX, Sarin, Soman, Ricin and Anthrax etc. The second part of the testing protocol called for verification of signatures in a flowing loop to validate the transfer of the beaker signature data to real world scenarios. See Figure 4.

It is known that in a real attack on a water distribution system the concentrations of the agents would vary throughout the distribution system. The concentrations tested were to either infectious amounts, $ID_{50,}$ for replicating agents, or LD_{50} amounts for chemical agents. Each agent was tested at three dose values, as defined in a test plan matrix. Two types of disinfectant are commonly used in water distribution systems: free chlorine, and monochloramine. It is necessary to test agents in both types of media to have information representative of each type. It is also clear that variable amounts of chlorine would be in the distribution system water, so tests used different solutions: 0.2 ppm Free Available Chlorine (FAC), 1 ppm FAC, and 2 ppm Monochloramine, as these are the limits of typical system concentration. Monochloramine is usually less variable in concentration and can be tested at typical values. Real-time loop tests were run on nicotine, ricin, BA, and methanol.

Figure 4: Hach HST constructed a special variable volume flow loop inside of an ECBC surety chamber.

All fingerprints were successfully developed and ROC curves were generated for all agents tested. It was also found that the fingerprints developed from the lab work could be successfully transferred to a flowing system by successfully triggering and classifying agents in the flow loops. Because of security concerns and confidentiality, only selected nicotine test data is provided in Figures 5 and 6.

The test concentration of nicotine was 19.7 mg/L. In a single test run, nicotine was recognized by the system, with detection angles ranging from 0.94 degrees (essentially a perfect match) to 9.84 degrees (a weak match). The fluctuating trigger signal is due to the mixing dynamics of a recirculating loop.

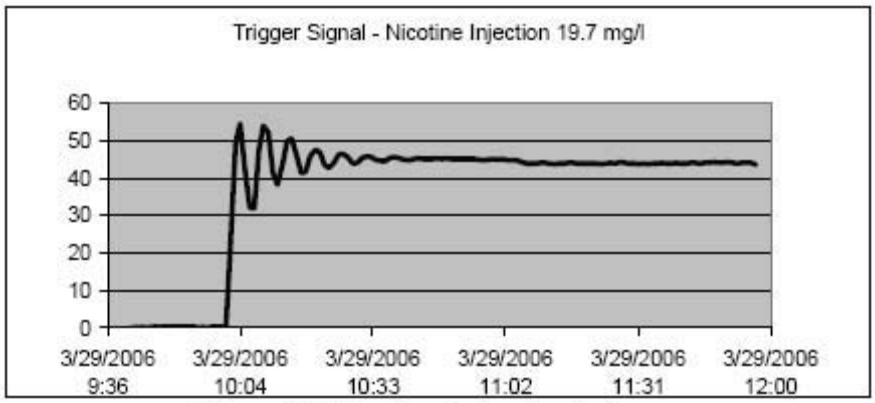


Figure 5: Nicotine Injection in Loop

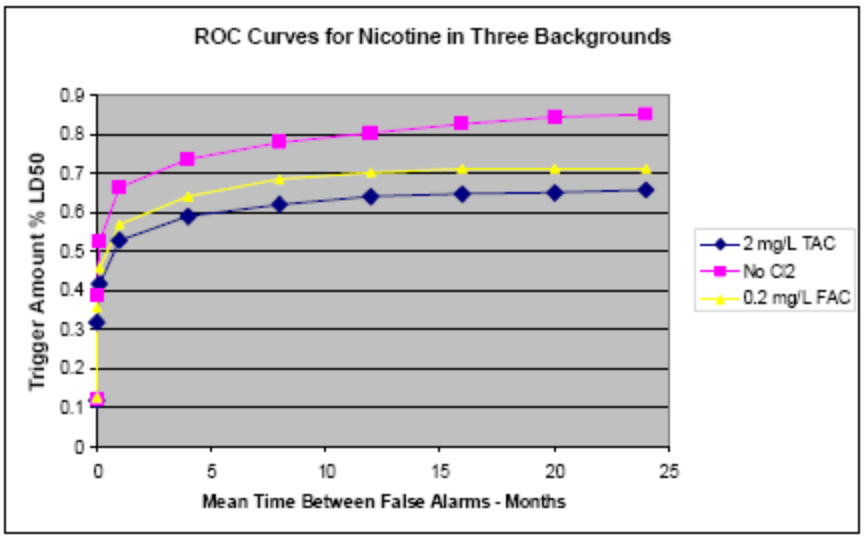


Figure 6: ROC Curves for Nicotine in Three Backgrounds

Threshold trigger levels range from 0.36 to 1.26 for all curves

FIELD TESTING OF THE DEVELOPED SYSTEM

Figure 7: A Real World Deployment Site Showing the System in Operation

Prior to the onset of this project, there was a definite lack of data concerning conditions in the distribution system. Very few utilities carried out data collection in the distribution system othe than periodic grab samples. Those that did have some on-line continuous data were usually limited to only one or two parameters. Since the out set of this program over, 120,000 hour of real time data has been collected across a wide variety of different distribution systems exhibiting different water matrix profiles revealing many interesting attributes of the distributio systems. These systems represent a wide diversity of water quality conditions and operational

situations. The site locations need to remain anonymous due to security considerations and non-disclosure agreements but, they represent a wide diversity of system sizes and geographic locations throughout the United States. The deployments are at both civilian and military sites. The following are a few examples of incidents that have been recorded during these real world deployments. These incidents help to demonstrate the systems ability to learn and to become a useful tool not just for security but also for every day operational improvements.

A Chlorine Upset Event

A water panel distribution monitor and an event monitor were installed at a location in a major east coast city just down stream from a water storage tank. The event monitor recorded a regular alarm. See Figure 8.

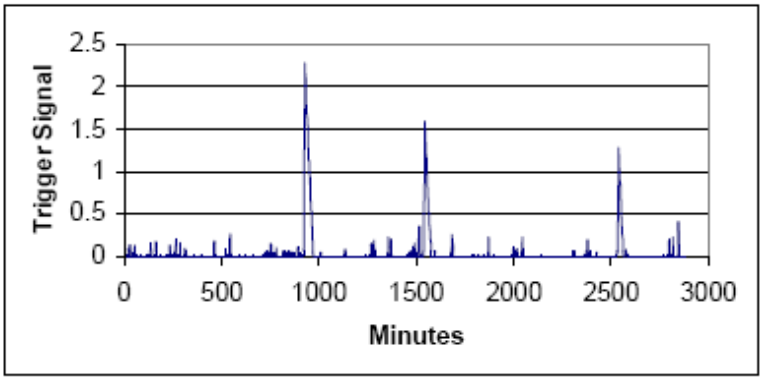


Figure 8: East Coast Location Showing Regular Alarm Events

Careful evaluation of the baseline parameter data showed that the alarms were being triggered by a chlorine upset. The chorine levels would gradually rise over time and then suddenly drop. It was this sudden drop that was triggering the alarm. See Figure 9.

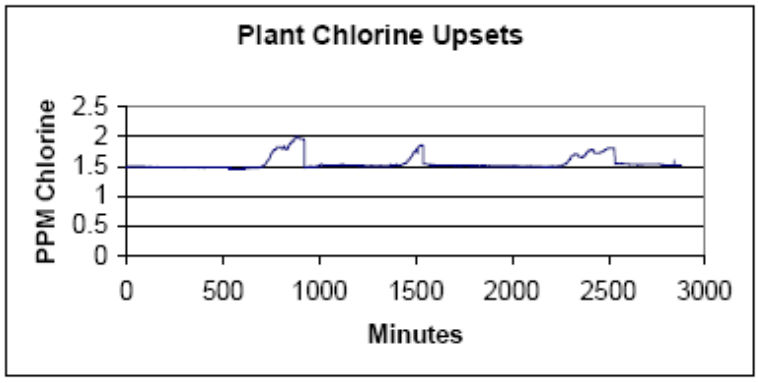


Figure 9: Chlorine Readings Caused the Trigger

Further investigation revealed that these upsets were due to the fact that the storage tank was normally filled from water source A, but at times of peak demand both source A and source B were turned on to fill the tanks. Source B has a higher chlorine residual than source A, therefore,

when it is used to fill the tank the chlorine level slowly creeps up. When source B is turned off, due to hydrodynamic short-circuiting, the chlorine level drops rapidly to the concentration of source A. This rapid drop to the level of A was adequate to cause an alarm trigger. After this was determined the learning capability of the algorithm was used to name and classify this event as benign, so, when it occurred again the alarm was recognized. The screen would report the event as Name: Pump Shut Off, Type: NORMAL.

The Strange Case of the Chlorine Spikes

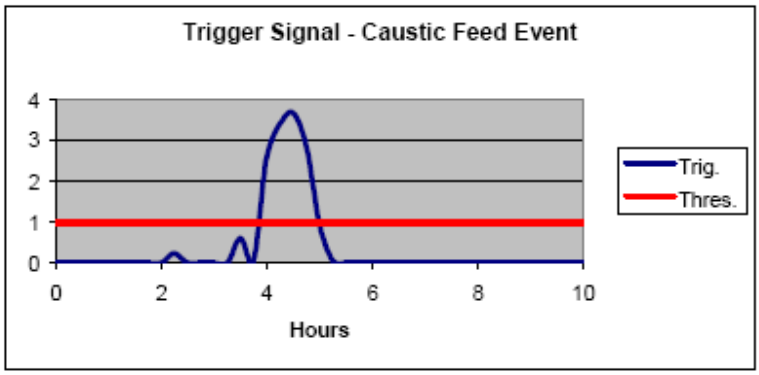
In one field deployment scenario, the system was very quiescent and rarely came anywhere close to causing a trigger alarm to go off. Except, that every night at around midnight, the chlorine level would spike dramatically and cause an alarm. This was deemed very strange and extensive trouble shooting of the instruments and power supply revealed no abnormal conditions that could be causing the problem.

After a thorough investigation, the night operator for the treatment plant was queried about the strange chlorine response. His reply was that of course the system's chlorine level spikes every night at midnight that is when he super chlorinates the system just like he had been told to do. It appears that several years ago, when there was a pipe rupture in the system that may have allowed contamination to seep in, the night operator had been told to super chlorinate the system. Unfortunately, the operator was new at the time and the instructions were not explicit that the super chlorination should take place that night only. The operator had continued to perform the operation every night for years resulting in a huge unnecessary cost in chlorine. This situation was remedied and should result in substantial chemical cost savings in the future.

Caustic Overfeed Event

In this deployment scenario, the plant uses caustic feed to control water pH. The system experienced a trigger alarm that when investigated was identified as an operational problem that resulted in the feed of excess caustic. The result was that the overfeed affected the pH and the conductivity of the water, causing the Event Monitor to alarm. See Figure 10.

Figure 10: Caustic Event



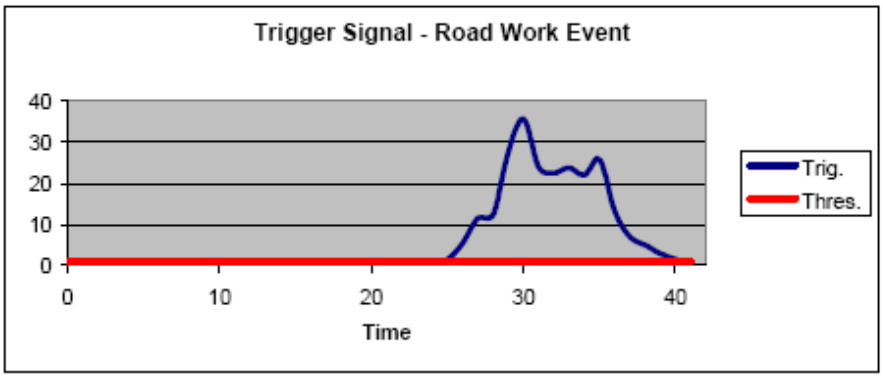
The reason behind this was that the vendor from which the casuistic was being purchased had delivered the wrong concentration of the solution. No one had checked to see if the concentration was correct before feeding in the material. New procedures were put in place to

verify the identity and strength of chemical additives before addition to the treatment process. The Event Monitor learned this Plant Event and can identify a recurrence of the event in the future if there is another failure in the system and it is repeated.

Road Work Event

In this event, roadwork (jackhammers) near a distribution line dislodged biomass and other particulate matter from the lining of the pipe. There was a massive increase in turbidity, which not only showed up on the turbidimeter, but also showed up as an interference in the chlorine measurement (optical). As expected, the conductivity and pH also showed minor changes. The increase in biomass in the water was indicated by the TOC analyzer. See Figure 11. This event illustrates the ability of the Event Monitor to detect and alarm on unanticipated events. This event also provides a signature for the materials adhering to the walls of the pipes in this location and should recognize any future excursions of this type.

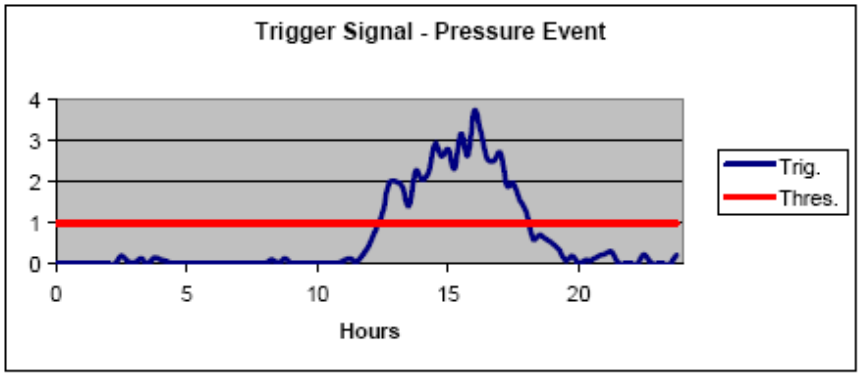
Figure 11: Roadwork Event



Pressure Event

In this scenario, the system was located in a building, which experiences a daily variation in water pressure. The sample variation is associated with a turbidity increase that causes a Trigger. See graph 5. There is also a small pH decrease at that time, possibly because of increased solubility of CO2 in the water, dropping the pH slightly. After recognition of the cause and proper naming of this pattern, it is recognized by the Event Monitor as a "Normal" event, rather than an alarm condition, and appropriately classified and named as such.

Figure 12: Pressure Event

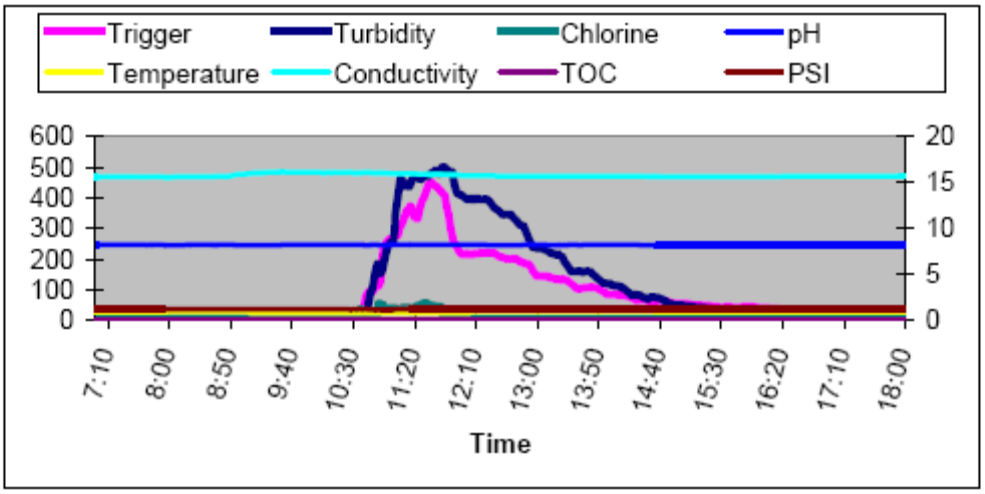


Main Break Event

In this situation the system had only just been installed a few days previously. Hach HST personnel were informed that the instruments were behaving abnormally and were giving strange readings. An investigation of the sensors found no problems. A short time later a major main ruptured in a catastrophic mode. See Figures 13 and 14. The system was able to detect the perturbation in water quality parameters that were precursors to the main break and trigger upon them. Unfortunately, the system was newly installed and the event was not recognized until it was too late. The system has memorized this pattern and hopefully if a similar situation arises it may be able to alert before the problem is out of control and a catastrophic failure occurs.

Figure 13: The system was able to detect water quality perturbations that were forerunners to this catastrophic main break.

Figure 14: Main Break Event



Learning Ability

As has been previously indicated, the system is equipped with a learning algorithm, so that as unknown alarm events occur over time the system has the ability to store the signature that is generated during the event. The operator can then go into the program and identify that function and associate it with a known cause such as the turning on of a pump or the switching of water sources, etc. Then the next time that event occurs it will be recognized and identified appropriately. Over time, as the system learns, the probability of an unknown alarm that has not been previously encountered and classified will continue to decrease and will eventually approach zero. One point however that should be noted, is that as soon as the system is turned on, it will be actively working and will have the ability to trigger and classify immediately if the signature of a known threat agent is encountered. The probability of an unknown alarm due to a given event depends upon the frequency of the occurrence of such an event and the time that the algorithm has had to learn that event. Events that occur frequently will be quickly learned while rare or singular events will take longer to be learned and stored.

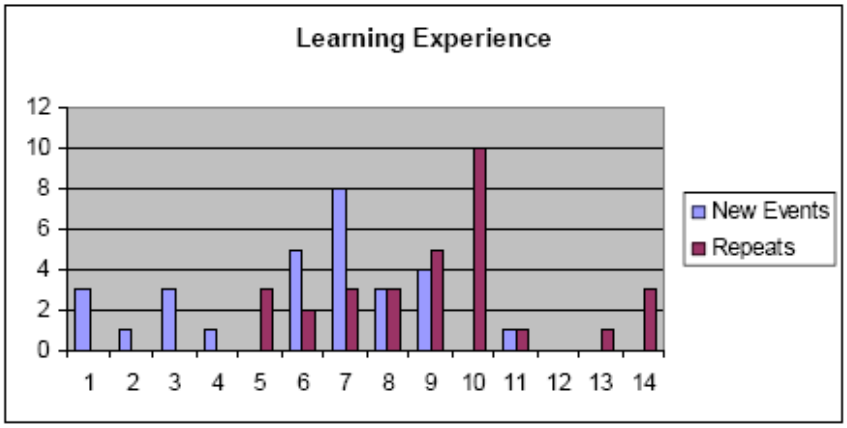


Figure 15: Learning Speed Demonstrated

The data in this case represent a real world deployment situation that had very noisy water quality. In this scenario, there were 26 unique trigger events in the first 11 days of operations. All were fingerprinted and learned by the system. 11 of the events were repeated. This demonstrates that common events are rapidly learned by the system resulting in a rapid decrease in unknown alarms. See Figure 15.

CONCLUSION

Extensive laboratory and pipe loop testing that is detailed in a separate paper indicate that these systems appear to be a good choice for detecting water quality excursions that could be linked to water security events. There are a number of advantages to using such systems. The chief advantage is that these instruments are not new. They are based on common everyday parameters that the average industry worker is quite familiar with, thus, adding a degree of comfort in operations not afforded by other new technology. As existing technologies, these instruments have been proven to be robust and dependable in prior field deployments. They represent measurements that would be of interest and use to water utility personnel above and beyond their role as water security devices. The testing detailed in this paper confirms this and also demonstrates the applicability of utilizing these everyday parameters by linking them with

advanced algorithms. The field deployment studies not only demonstrate robustness in the field and the ability to recognize a wide variety of events, but these studies also demonstrate such system's ability to learn. It is foreseeable that these devices will become much more than a system that is capable of detecting terrorist events. They could easily become a critical tool for improving everyday operations.

For example, through many years of experience, the best old hands at treatment plant operations have developed "a sense" for knowing something in the treatment system is amiss. It can be a smell, color, clarity (or lack there of), sound or just tingling in the nape of the neck. One gains this sense only by extensive experience in a particular facility. These senses do not exist in distribution systems because there has typically been little measurement done upon which to gain these "senses" and, therefore; "Bulk Parameter Monitoring in the Distribution System with Interpretive Algorithms" has the potential to become the artificial "sense" able to quickly "learn" the quirks of the distribution system and have those quirks labeled by those with extensive experience so that less experienced employees have the benefit of that knowledge without having to wait 5, 10 or more years. A good phrase to describe this knowledge base would be "institutional intuition." (Kroll 2006) With the aging of the work force and rapid employee turnover "institutional intuition" has the chance of quickly dying out. Above and beyond their obvious security benefits, algorithms could be a way to circumvent this loss of knowledge and to build a knowledge base where none has previously existed. This in turn could allow improvements is system operation that may result in cost savings and definitely will result in a higher quality product being delivered to the consumer

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4) US Army Corps of Engineers Calculations on threat agents and requirements and logistics for mounting a successful backflow attack.

5) Dick, R.L. 2001. Statement for the Record of Ronald L. Dick, Deputy Assistant Director, Counter Terrorism Division, and Director, National Infrastructure Protection Center, Federal Bureau of investigation Before the House Committee on Transportation and Infrastructure Subcommittee on Water Resources and Environment October 10, 2001.

6) Whitman, Christie, 2001. EPA Press Release Thursday, Oct 18. Environmental News Whitman Allays Fears for Water Security; Possibility of Successful Contamination is Small.

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8) Allman, T.P. 2003. "Drinking Water Distribution System Modeling for Predicting the Impact and Detection of Intentional Contamination. Masters Thesis. Summer. Dept. of Civil Engineering. Colorado State University. Fort Collins, Colorado

9) OSTP, 2003.The White House, "The National Strategy for the Physical Protection of Critical Infrastructures and Assets," February.

Operational and Laboratory Verification Testing of a Heuristic Online Water Monitoring System for Security

By Dan Kroll, Karl King and Greg Klein

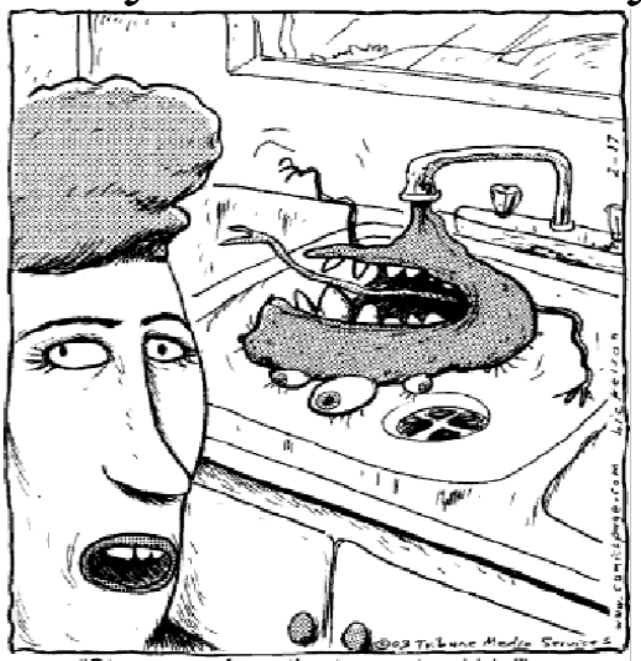
National Environmental Monitoring Conference

August 27th-31st

Arlington, Virginia

1

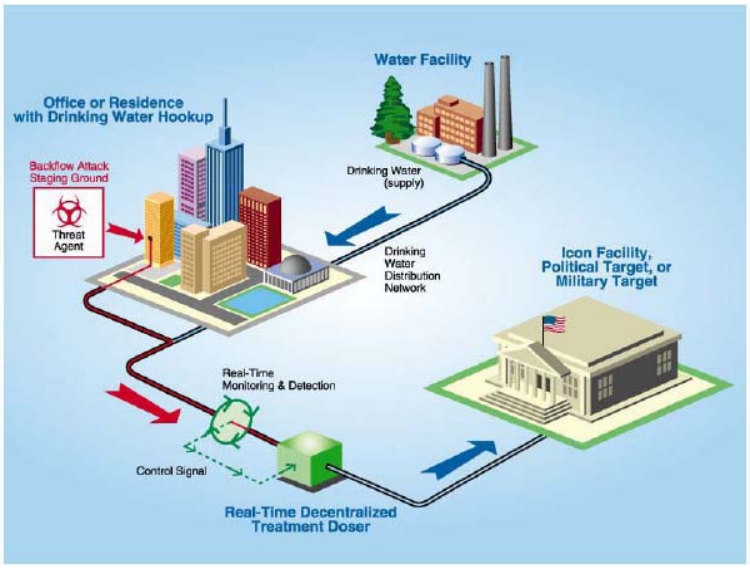
If only it were this easy.



"Stay away from the tap water, kids!"

2

Distribution Systems are Vulnerable to Backflow Attacks



3

Statement of the Problem

Can we use basic water quality sensors to spot deviations from normal in a distribution system, and then mathematically analyze the deviation signals to:

- TRIGGER when something harmful is present
- DETECT what agent is present, and
- QUANTIFY the amount in the water?

The conventional wisdom is that this cannot be done.

4

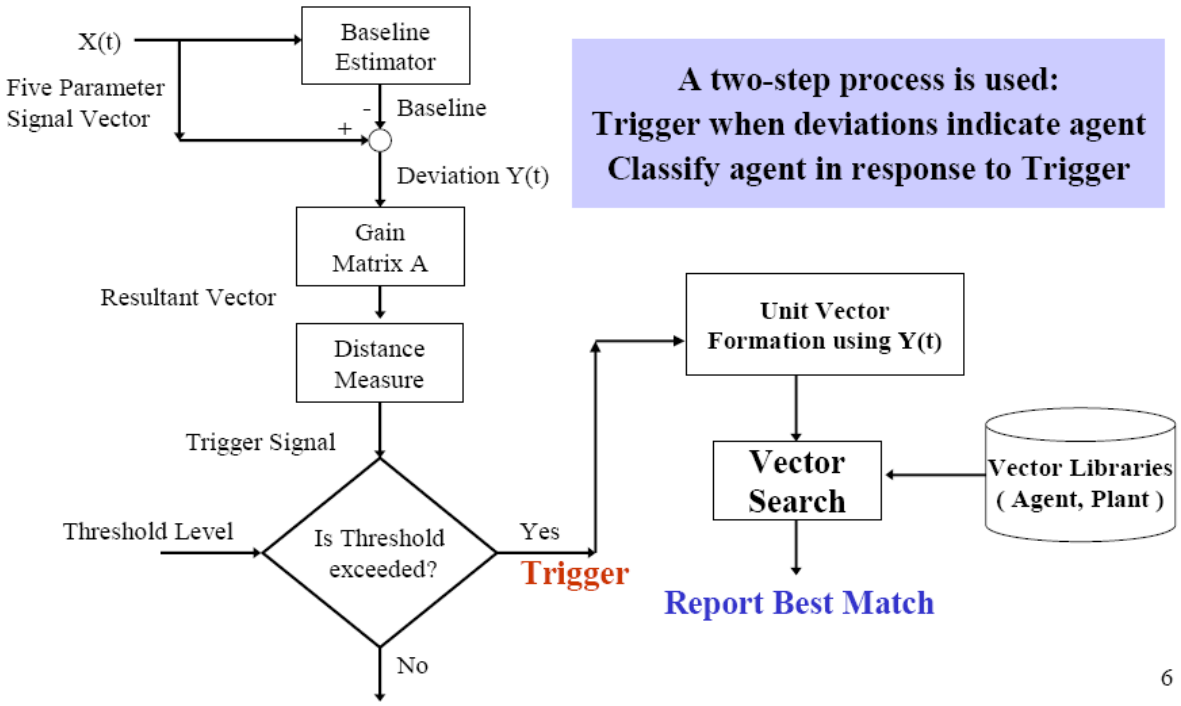
Sensor set selected

- pH - acid/base relationships
- Electrolytic Conductivity – ionic concentrations
- Chorine – disinfectant levels, oxidant reduction
- Turbidity – particles in water (bio agents)
- Total Organic Carbon – carbon content of organic molecules

ORP – NOT SELECTED because it is unstable and prone to poisoning in long-term installations

Sensors were selected for reliability and ability to measure fundamentally different characteristics of threat agent substances.

Detection Algorithm added to Trigger

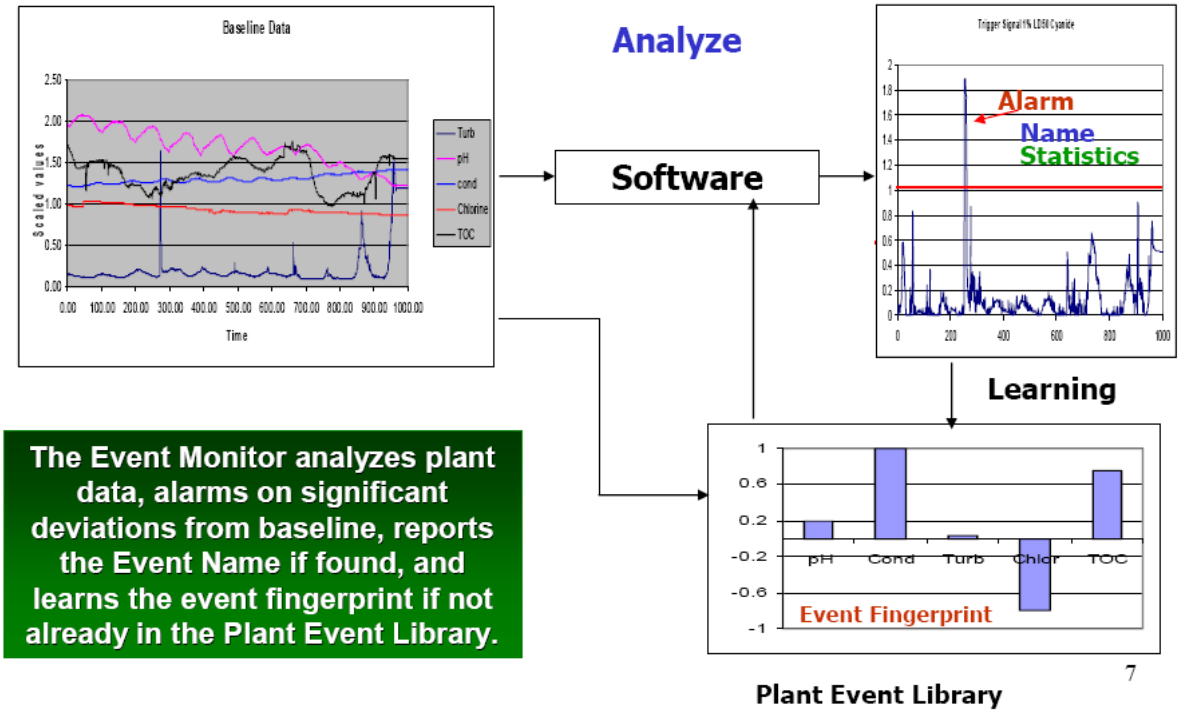


A two-step process is used:
Trigger when deviations indicate agent
Classify agent in response to Trigger

6

What is our vision?

Input Five Parameter Signals **Output Single Signal**



The Event Monitor analyzes plant data, alarms on significant deviations from baseline, reports the Event Name if found, and learns the event fingerprint if not already in the Plant Event Library.

7

Beaker Testing What Can We See?

Testing at the Hach Loveland, Colorado facility on a variety of agents: Over 80 Agents Characterized so far.

Pesticides and Herbicides Including Organophosphates and Carbamates, Biotoxins, Bacterial Cultures, Heavy Metals, Cyanides, Street Drugs, Treatment Chemicals Such as Fluoride, Exotic Agents, Toxic Industrial Chemicals, Common Accidental Agents Such as Diesel Fuel and Antifreeze.

Edgewood Biological and Chemical Command

Anthrax, Ricin, VX, Soman, sarin, nicotine

8

ETV Study (EPA/Battelle Conducted by Ryan James)

- Accuracy verification of instrument readings vs. reference methods at various pH ant Temps. (Loop)
- Long term deployment (Loop)
- System to system variability (Loop)
- Response to contaminants (Loop)
- Classification of unknowns (Straight pipe)

9

Accuracy Chlorine

Conditions	Reference Average (SD)	Unit 1 Average (SD)	Unit 1 %D	Unit 2 Average (SD)	Unit 2 %D
Amb. pH Amb Temp	0.97 (0.07)	0.96 (0.01)	-1.20	0.99 (0.00)	1.71
Dec pH Amb Temp	0.86 (0.02)	0.82 (0.01)	-4.64	0.84 (0.02)	-2.09
Dec pH Amb Temp	0.73 (0.01)	0.49 (0.09)	-32.97	0.49 (0.09)	-32.70
Dec pH Amb temp	0.38 (0.03)	0.20 (0.06)	-48.42	0.32 (0.01)	-16.32
Amb pH Dec temp	0.51 (0.08)	0.50 (0.01)	-1.98	0.50 (0.01)	-1.98
Dec pH Dec Temp	1.56 (0.05)	1.63 (0.07)	4.10	1.64 (0.07)	4.74
Amb pH Inc temp	0.69 (0.01)	0.64 (0.01)	-7.51	0.65 (0.01)	-6.36
Dec pH Inc Temp	0.65 (0. 07)	0.60 (0.05)	-7.43	06.0(0.05)	-6.50
Amb pH Amb temp	0.98 (0.02)	0.95 (0.03)	-3.05	0.96(0.03)	-2.44

10

Accuracy Turbidity

Cond.	Reference Average (SD)	Unit 1 Average (SD)	Unit 1 %D	Unit 2 Average (SD)	Unit 2 %D
Amb. pH Amb Temp	1.27 (0.95)	0.59 (0.04)	-53.75	0.63 (0.04)	-50.41
Dec pH Amb Temp	1.14 (0.40)	0.98 (0.48)	-13.66	0.79 (0.07)	-30.56
Dec pH Amb Temp	0.97 (0.33)	0.69 (0.11)	-29.49	0.68 (0.09)	-30.29
Dec pH Amb temp	1.54 (0.20)	1.37 (0.11)	-11.9	1.52(0.52)	-1.00
Amb pH Dec temp	1.89(2.50)	0.45 (0.02)	-76.42	0.41 (0.03)	-78.27
Dec pH Dec Temp	0.99(0.21)	0.48(0.09)	-51.94	0.68 (0.01)	-31.45
Amb pH Inc temp	0.92 (0.16)	0.44 (0.03)	-51.74	0.58 (0.01)	-37.19
Dec pH Inc Temp	1.00 (0.35)	0.69 (0.00)	-30.38	0.74 (0.00)	-26.29
Amb pH Amb temp	0.46 (0.11)	0.27 (0.02)	-41.55	0.29 (0.02)	-38.45

11

Accuracy Conductivity

Conditions	Reference Average (SD)	Unit 1 Average (SD)	Unit 1 %D	Unit 2 Average (SD)	Unit 2 %D
Amb. pH Amb Temp	451 (1)	474 (3)	5.20	43 9(5)	-2.73
Dec pH Amb Temp	484 (10)	51 1(12)	5.44	409 (5)	-15.53
Dec pH Amb Temp	503 (6)	540 (8)	7.28	540 (8)	7.30
Dec pH Amb temp	694 (12)	742 (13)	6.91	693 (11)	-0.15
Amb pH Dec temp	412 (1)	421 (2)	2.16	383 (3)	-7.03
Dec pH Dec Temp	501 (10)	512 (10)	2.31	461 (9)	-7.94
Amb pH Inc temp	447 (1)	483 (3)	8.09	454 (5)	1.57
Dec pH Inc Temp	529 (2)	571 (6)	7.81	538 (8)	1.67
Amb pH Amb temp	442 (1)	469 (1)	6.18	438 (3)	-0.82

12

Accuracy pH

Conditions	Reference Average (SD)	Unit 1 Average (SD)	Unit 1 %D	Unit 2 Average (SD)	Unit 2 %D
Amb. pH Amb Temp	8.76 (0.02)	8.85 (0.10)	1.02	9.03 (0.03)	3.08
Dec pH Amb Temp	7.88 (0.09)	7.87 (0.16)	-0.23	7.37 (0.70)	-6.5
Dec pH Amb Temp	7.52 (0.04)	7.33 (0.04)	-2.5	7.34 (0.05)	-2.4
Dec pH Amb temp	6.77 (0.09)	6.37 (0.06)	-5.9	6.42 (0.07)	-5.2
Amb pH Dec temp	8.48 (6.02)	8.55 (0.02)	0.8	8.57 (0.01)	1.06
Dec pH Dec Temp	7.43 (0.27)	7.15 (0.08)	-3.8	7.18 (0.08)	-3.4
Amb pH Inc temp	8.37 (0.55)	8.25 (0.02)	-1.4	8.32 (0.02)	-0.60
Dec pH Inc Temp	7.6 (0.06)	7.25 (0.03)	-4.6	7.29 (0.02)	-4.1
Amb pH Amb temp	8.74 (0.01)	8.60 (0.01)	-1.6	8.63 (0.01)	-1.3

13

Accuracy TOC

Conditions	Reference Average (SD)	Unit 1 Average (SD)	Unit 1 %D	Unit 2 Average (SD)	Unit 2 %D
Amb. pH Amb Temp	0.59 (0.030	0.87 (0.29)	47.19	1.46 (0.05)	147.44
Dec pH Amb Temp	0.56 (0.05)	0.36 (0.04)	-35.45	0.34 (0.06)	-39.70
Dec pH Amb Temp	0.43 (0.25)	0.22 (0.03)	-48.76	0.51 (0.04)	17.57
Dec pH Amb temp	0.51 (0.02)	0.18 (0.11)	-63.74	0.44 (0.04)	-12.92
Amb pH Dec temp	1.20 (0.40)	1.24 (0.09)	3.44	1.20 (0.44)	-0.19
Dec pH Dec Temp	0.48 (0.2)	0.18 (0.08)	-61.72	0.70 (0.41)	46.75
Amb pH Inc temp	0.57 (0.02)	0.23 (0.08)	-59.44	0.48 (0.06)	-15.65
Dec pH Inc Temp	0.54 (0.01)	0.25 (0.09)	-53.53	0.51 (0.06)	-6.06
Amb pH Amb temp	0.55 (0.12)	ND	ND	0.53 (0.01)	3.29

14

Accuracy

- Good correlation with instruments to reference
- Small values in Turbidity and TOC led to large %D
- In some cases instrument may be more reliable than reference. e.g. Chlorine

15

Inter-unit Reproducibility

Parameter	Slope	Intercept	R^2	t-test p-value
Chlorine	0.98	0.03	0.994	0.779
pH	1.06	-0.40	0.919	0.517
TOC	0.97	0.31	0.991	0.374
Conductivity	0.92	4.19	0.961	0.006
Turbidity (outlier removed)	0.97	0.005	0.881	0.884

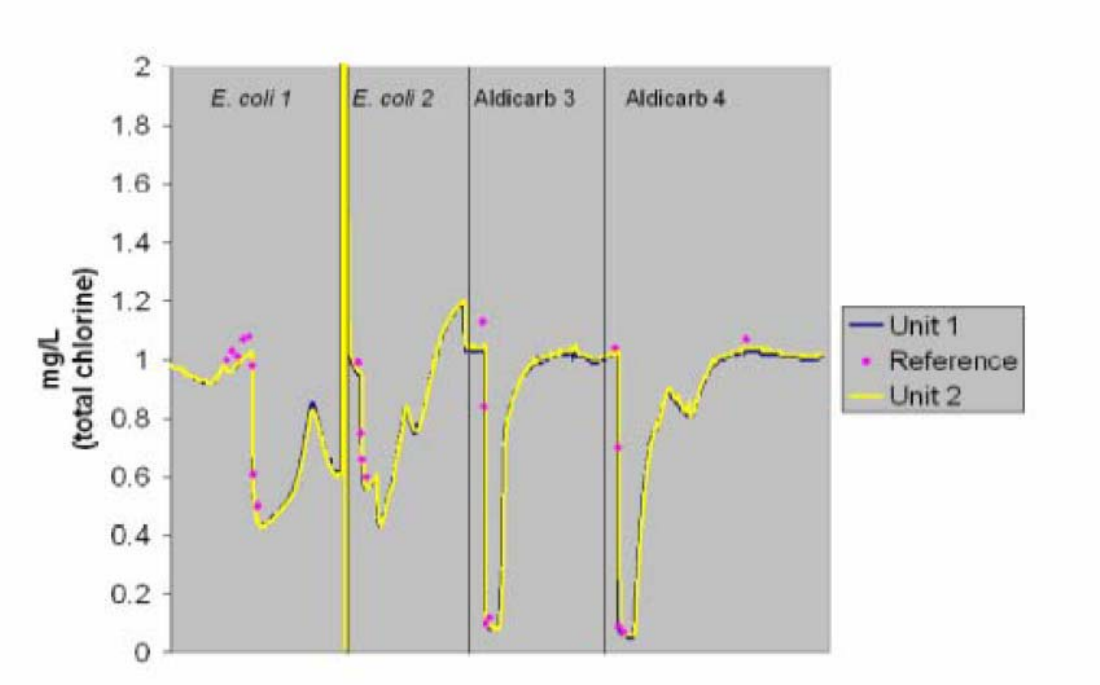
16

Reproducibility

- All correlated
- All except Conductivity statistically the same
- Small variability in Conductivity lead to a small real differences in measurement resulting in the 2 instruments being statistically different

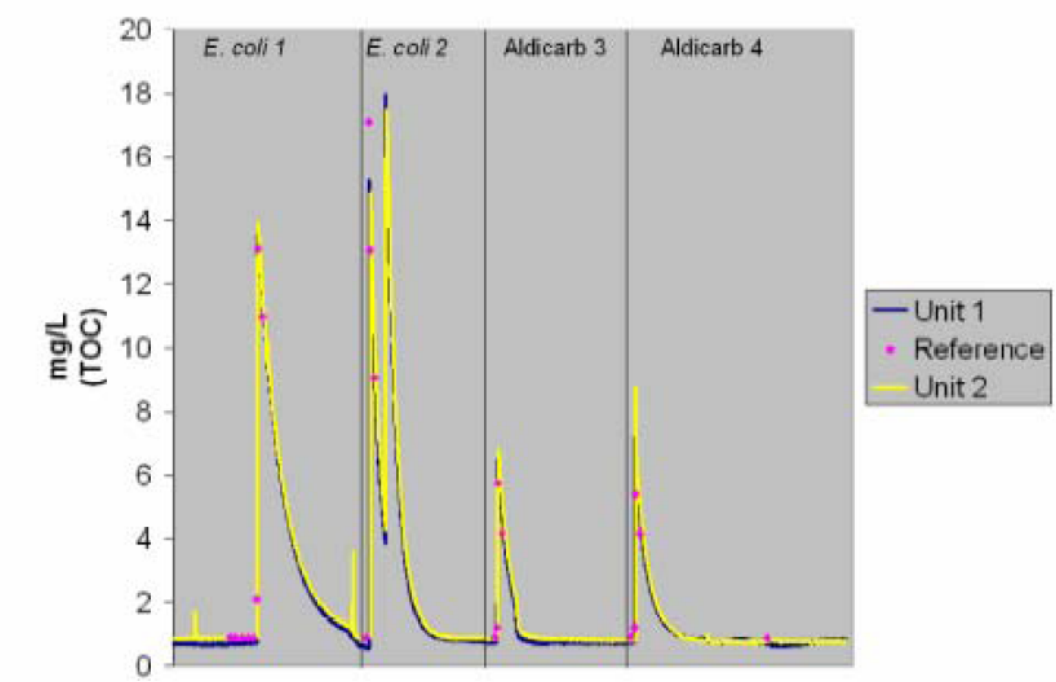
17

Contaminant Injection Chlorine



18

Contaminant Injection TOC



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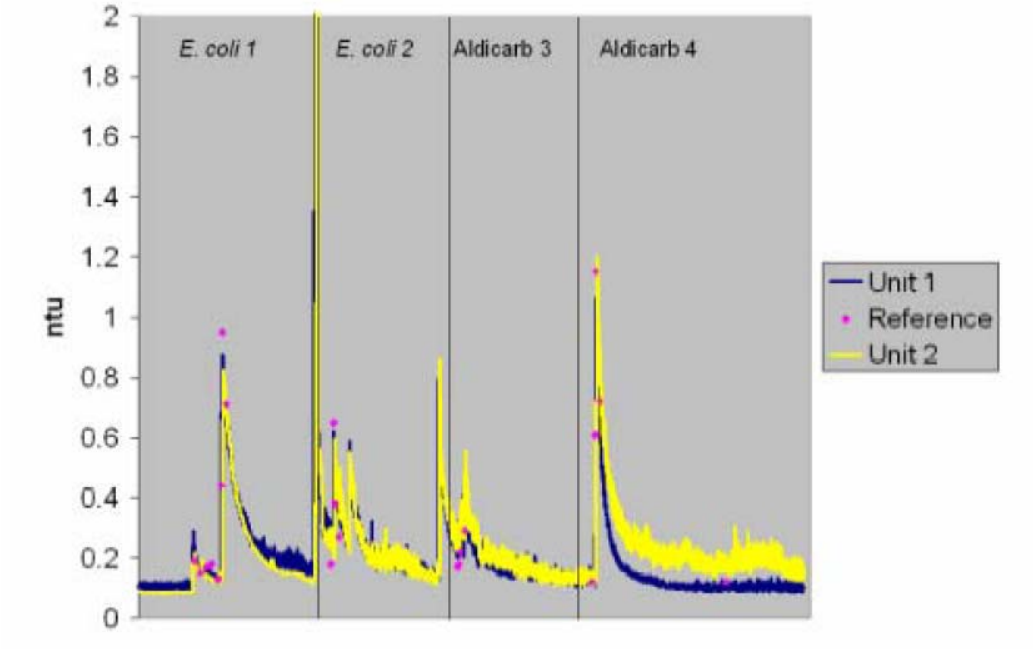
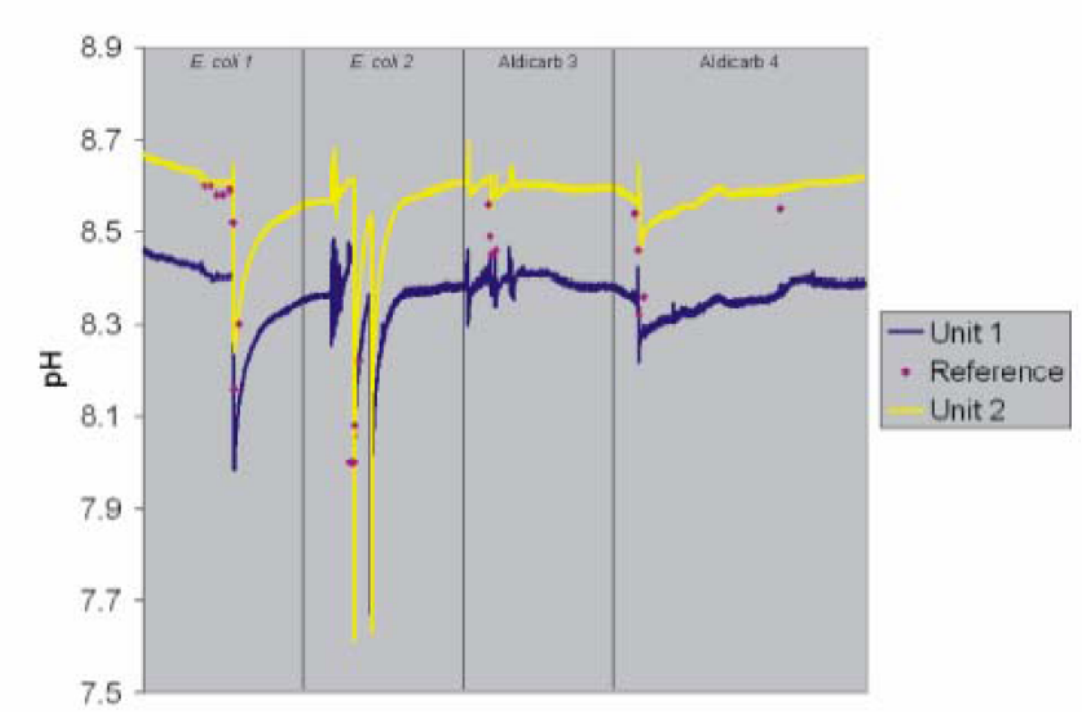
Contaminant Injection Turbidity



20

Contaminant Injection pH



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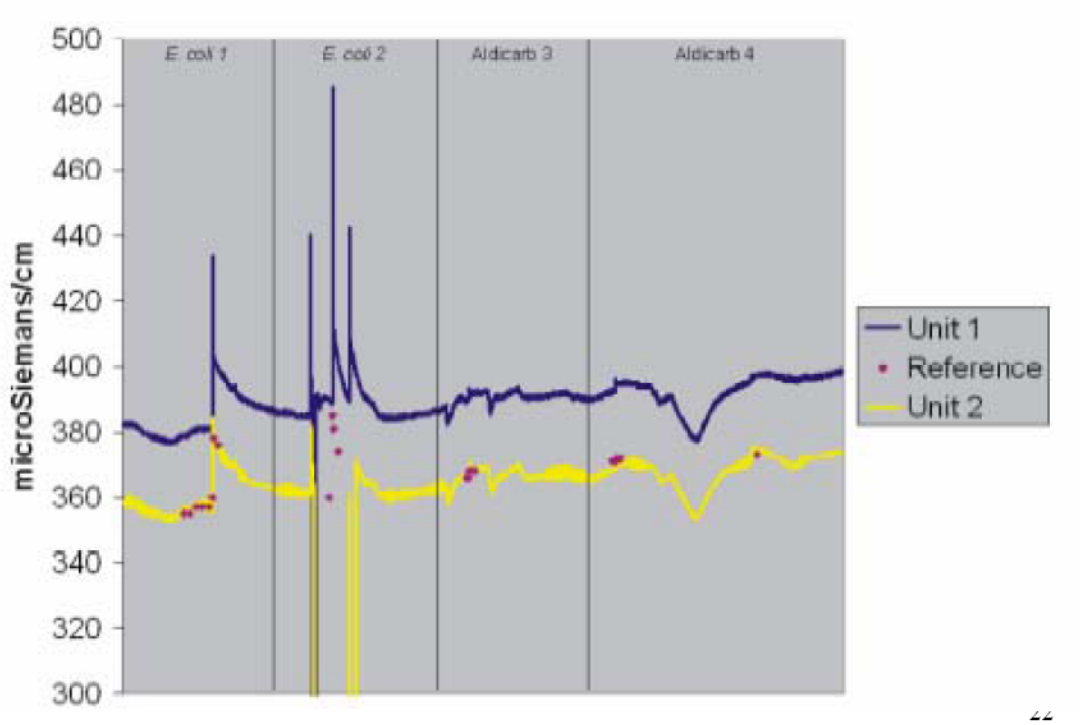
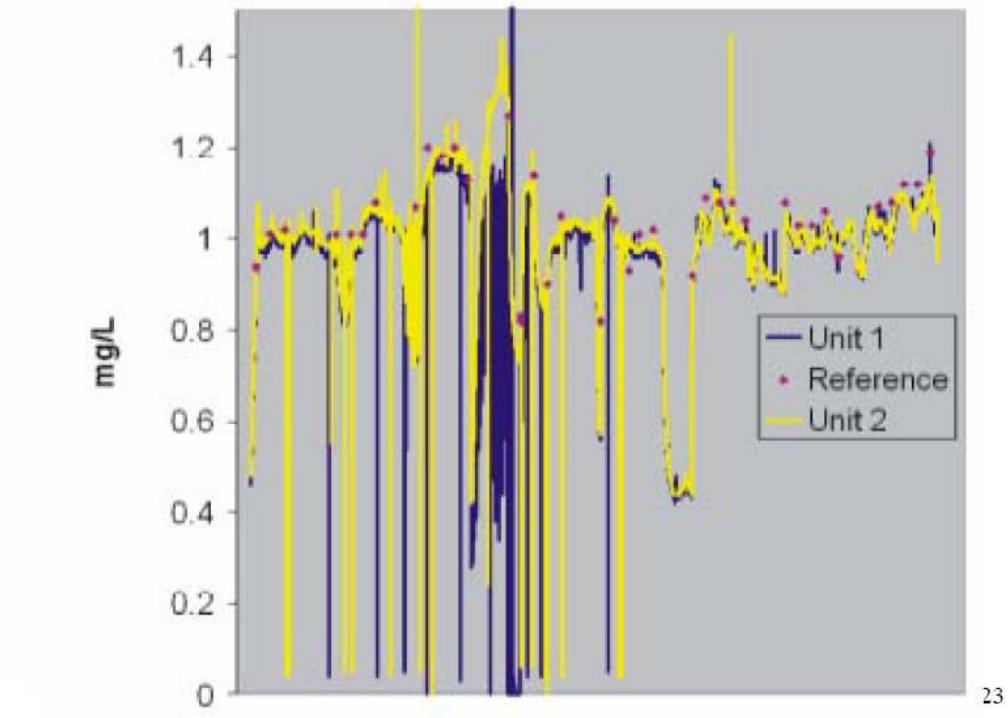
Contaminant Injection Cond.



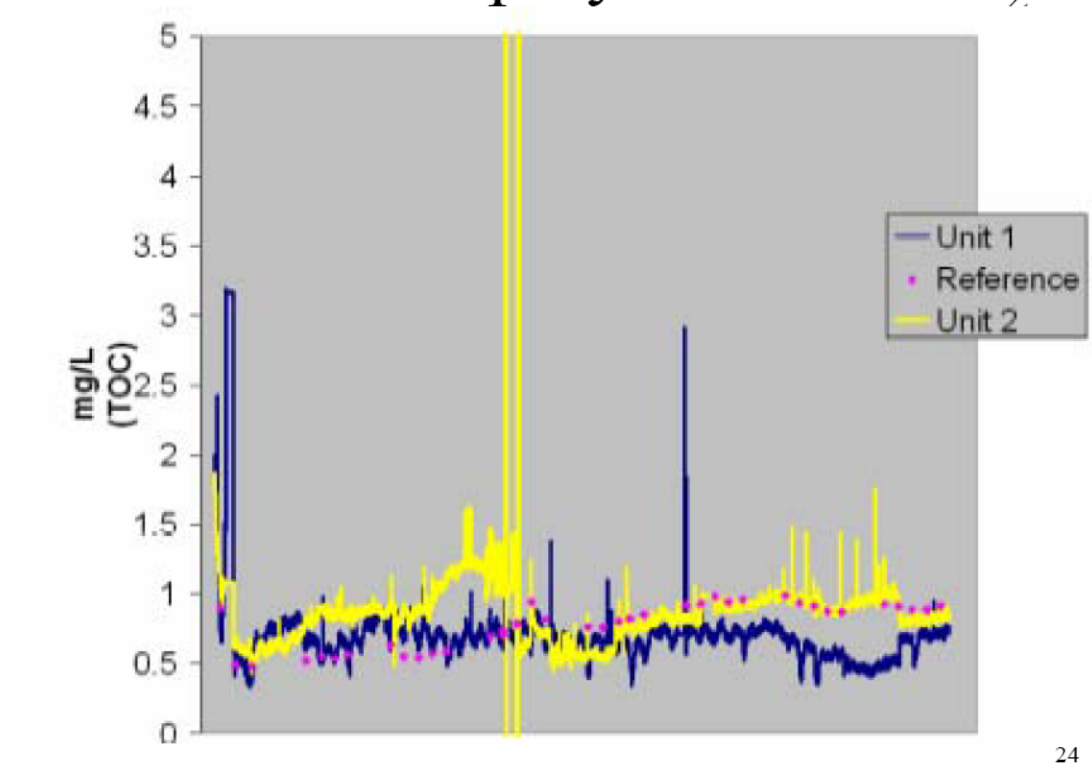
22

Extended Deployment (52 day) Cl_2



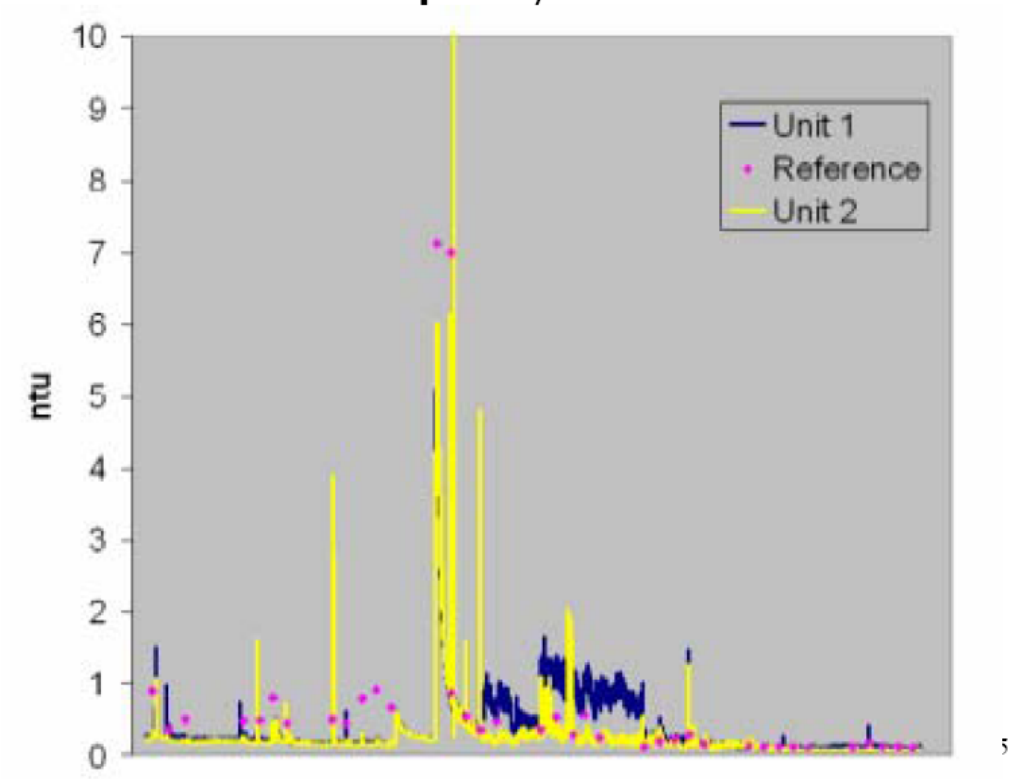
23

Extended Deployment (52 day) Cl_2



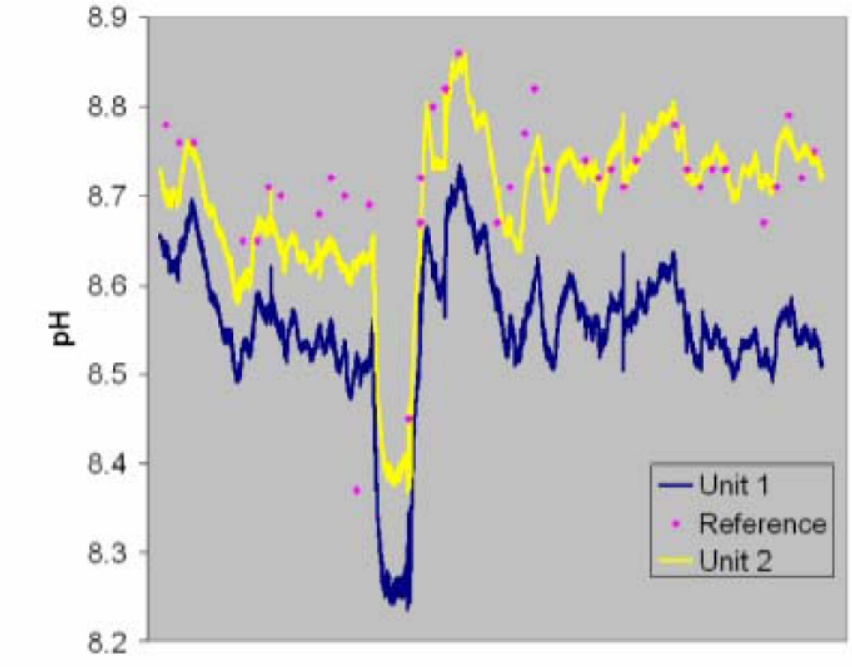
24

Extended Deployment Turb.



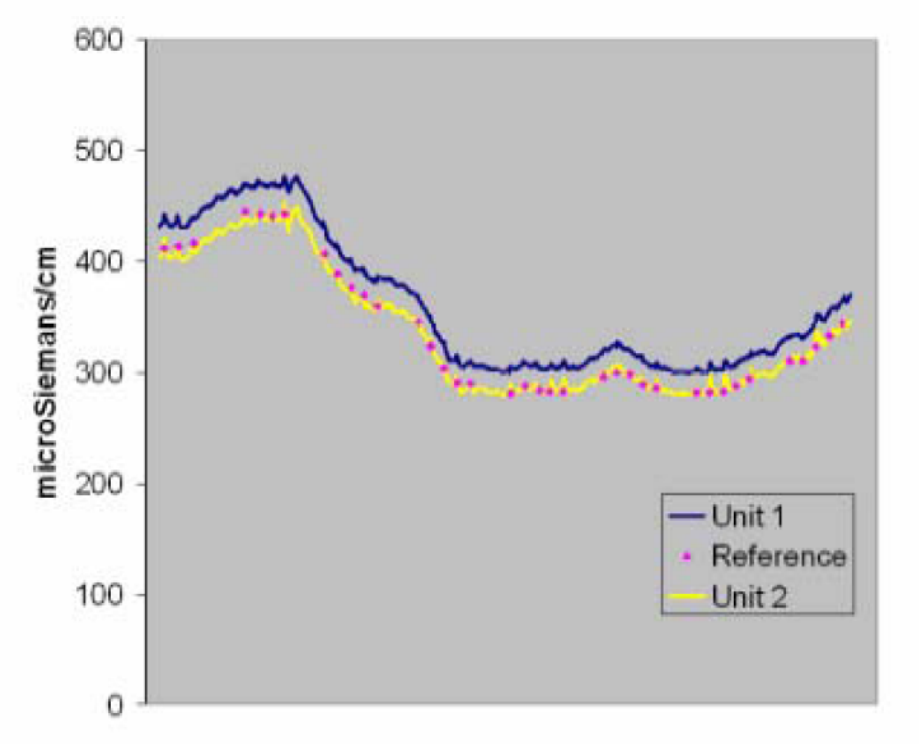
5

Extended Deployment pH



26

Extended Deployment Cond.



27

Extended deployment

- All parameters tracked very well for entire length of test
- Only routine maintenance and calibrations
- Results of contaminant injection the same before and after extended deployment

28

Large Volume Single Pass Flow Testing for Agent Classification

- 1500 foot straight line one pass pipe
- An unknown contaminant is injected over a short period to verify trigger response and ability to classify.
- Only technology evaluated for this function

29

Classification Results

5 = >70% ID; 4= 31-70% ID 3 = 1-30% ID 2 = Incorrect ID 1= No ID

Contaminant	Unit 1 Test 1	Unit 2 Test 1	Unit 1 Test 2	Unit 2 Test 2	Average
Aldicarb	4	4	4	4	4
AsO_3	2	2	2	2	2
Colchicine	4	4	4	4	4
Dicamba	4	5	5	5	4.75
Dichlorvos	4	3	3	2	3
E coli	3	2	4	2	2.75
Ferricyanide	5	5	5	5	5
Fluoroacetate	5	5	4	4	4.5
Glyphosate	4	3	2	2	2.75
Lead Nitrate	5	5	5	5	5
Mercuric chloride	4	4	4	4	4
Methanol	4	4	4	3	3.75
Nicotine	2	2	2	2	2

31

Classification interpretation

- All substances triggered
- Some problems with classification
  - Glyphosate vs Round-up
  - Different forms of nicotine
  - Problem with flow to Cl unit 2
  - Problem with signature for chlorine on metals
  - Updated library data and replayed data

32

Updated Software

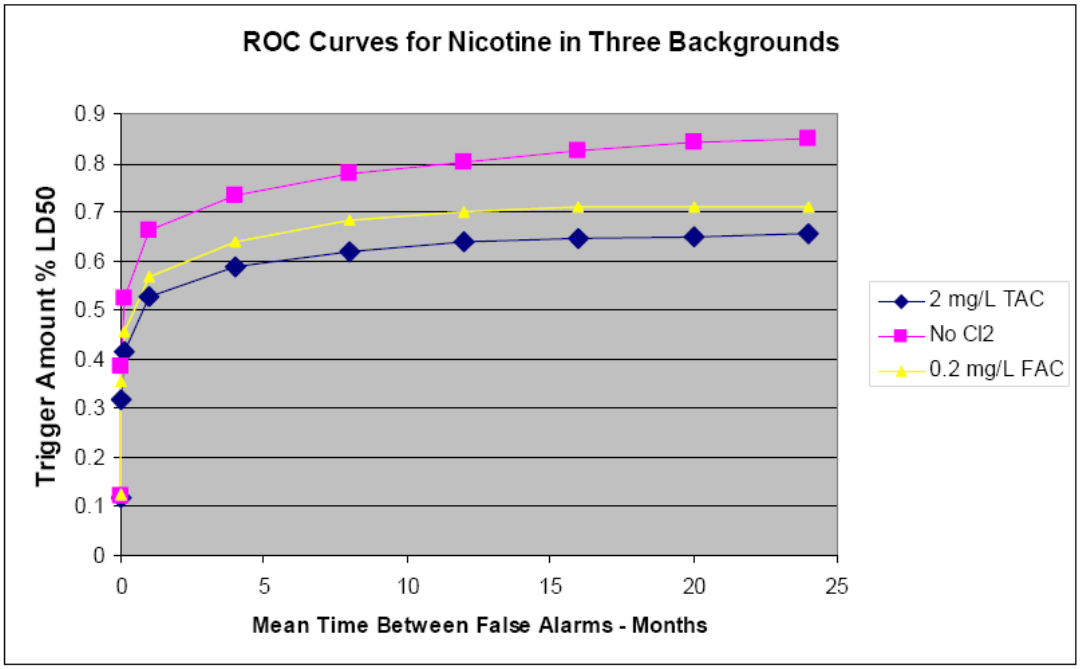
Glyphosate	4	4	4	4	
Nicotine	4	4	4	4	Test with altered nicotine
Arsenic Trioxide	4	5	4	5	
E. Coli	4	3	4	3	U2 showed smaller chlorine change than U1
Dichlorvos	4	4	4	4	Fingerprint corrected
Mercuric chloride	5	5	5	5	
Dicamba	4	3	5	5	5 trigger unique ID
Methanol	4	4	4	3	4 trigger strong ID
Aldicarb	4	4	4	4	3 trigger tenative ID
Colchicine	4	4	4	4	2 trigger ID others
Fluoroacetate	5	5	5	5	1 trigger no
Lead nitrate	5	5	5	5	0 no trigger on ID
Ferricyanide	5	5	5	5	
All Agents	56	55	57	56	
Test Average	55.5		56.5		
Test Score	4.27		4.35		
Total Average	56				
Score	4.31				

33

Beaker Testing at ECBC

- Fingerprints for all agents developed in a variety of matricies
- ROC curves prepared
- Transfer to real world scenario verified by selected loop testing.

34



- Trigger level varied form 0.36 to 1.36

35

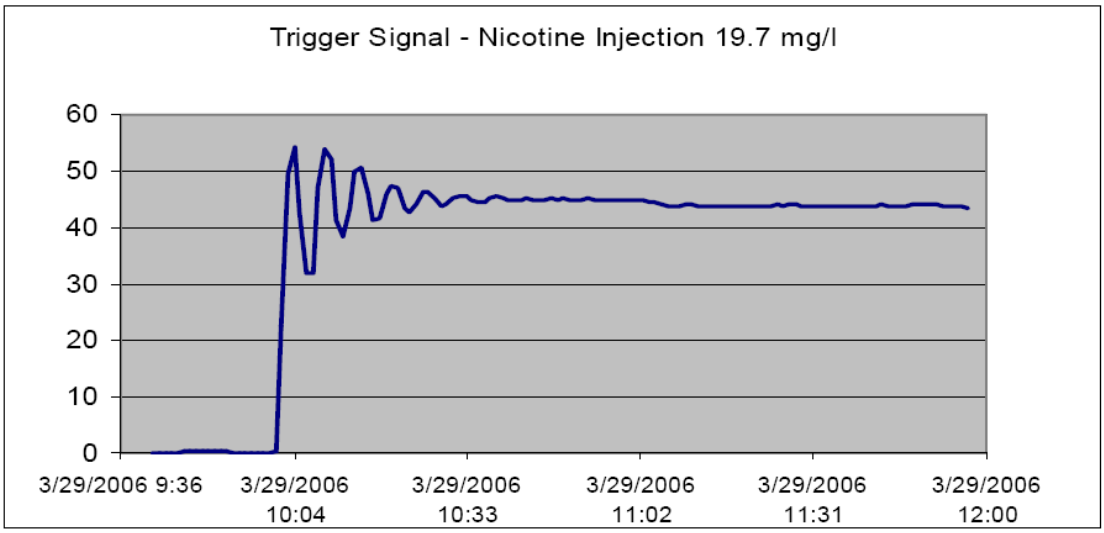
Loop Testing at ECBC

- Warfare and threat agents with disposal and handling problems such as Nerve agents and biotoxins are tested on a closed loop system to prevent loss of the agent to the environment.

36

ECBC Loop

37



- The test concentration of nicotine was 19.7 mg/L. In a single test run, nicotine was recognized by the system, with detection angles ranging from 0.94 degrees (essentially a perfect match) to 9.84 degrees (a weak match). The fluctuating trigger signal is due to the mixing dynamics of a recirculating loop.

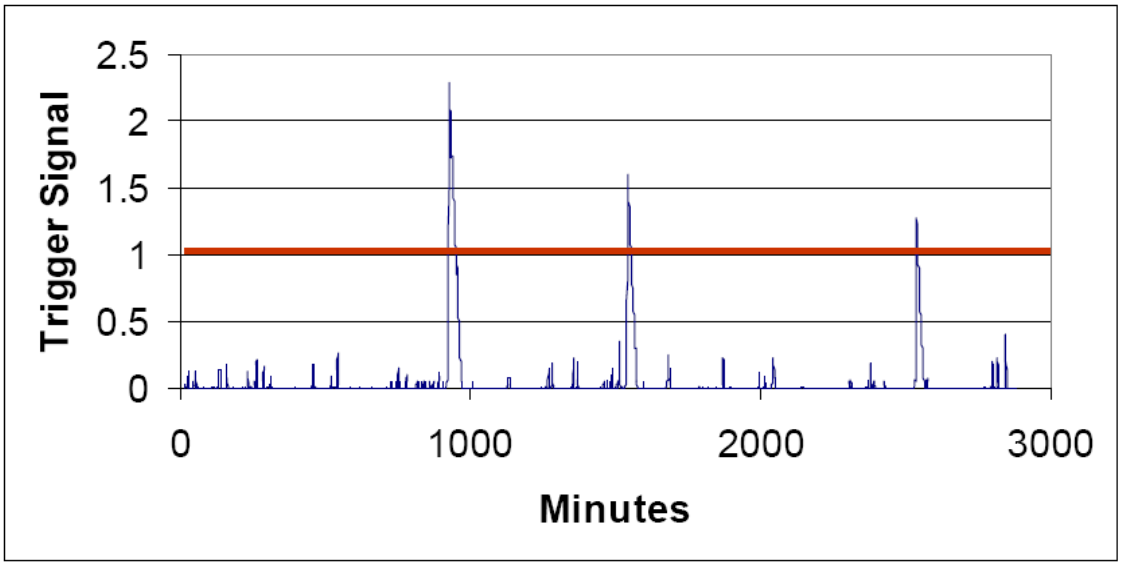
38

Real World Deployment

- Over 120, 000 hours of real world data generated and analyzed so far.
- Various sites throughout the United States
- Demonstrates ability to learn common events and respond to abnormal activities.

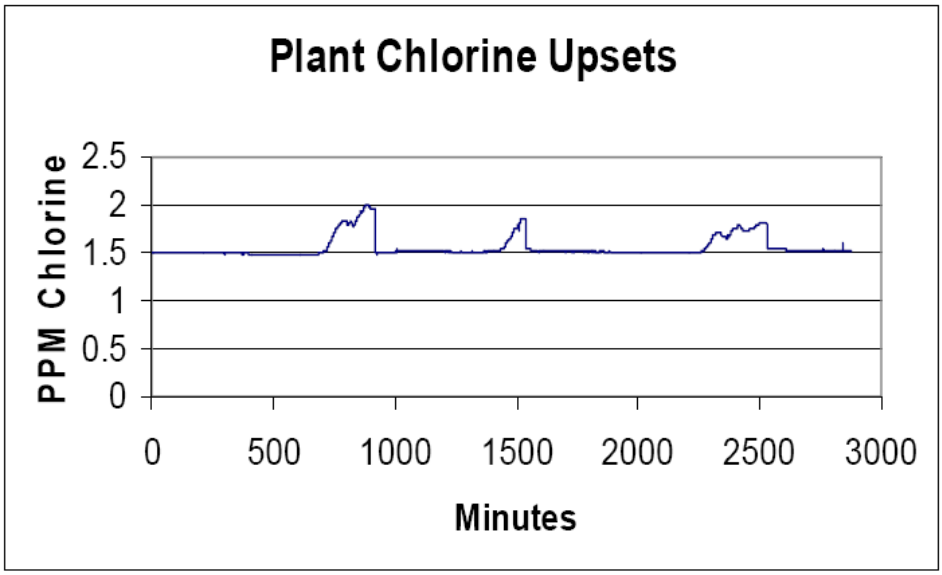
39

East Coast Location Near Water Storage Tank– alarm triggered .



40

Plant Event Defined
Name: Pump Shut Off, Type: NORMAL



41

Learning Method for Plant Events

Without learning, the system sees a False Alarm each time a benign event occurs.

With learning, the probability of a false alarm is reduced.

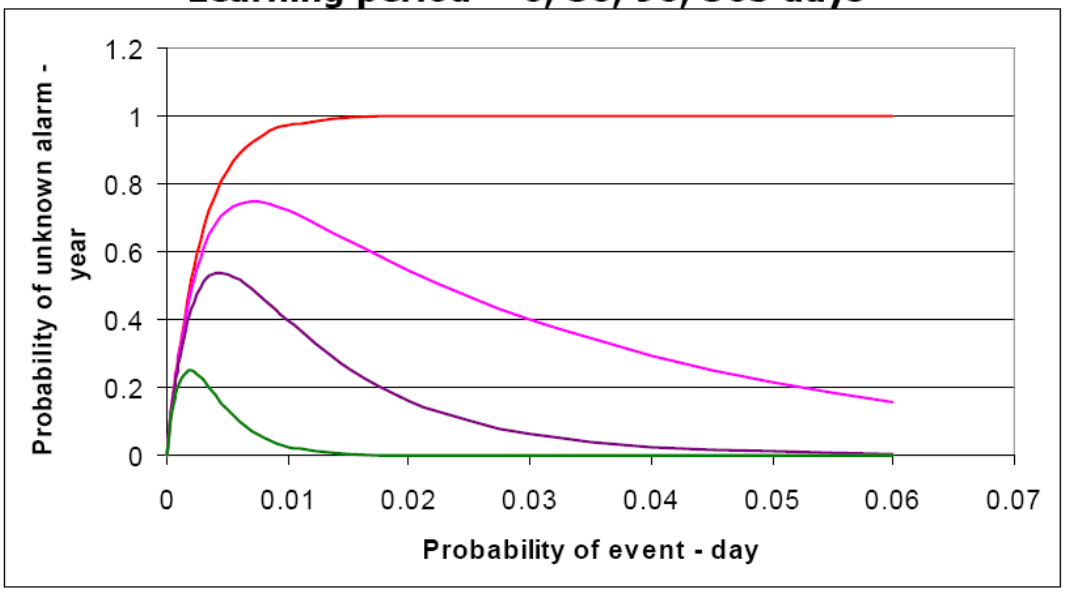
P(false alarm) = P(not learned)*P(event)

Over time, P(not learned) goes from 1 to zero.

Learning recurring events reduces the False Alarm Rate

42

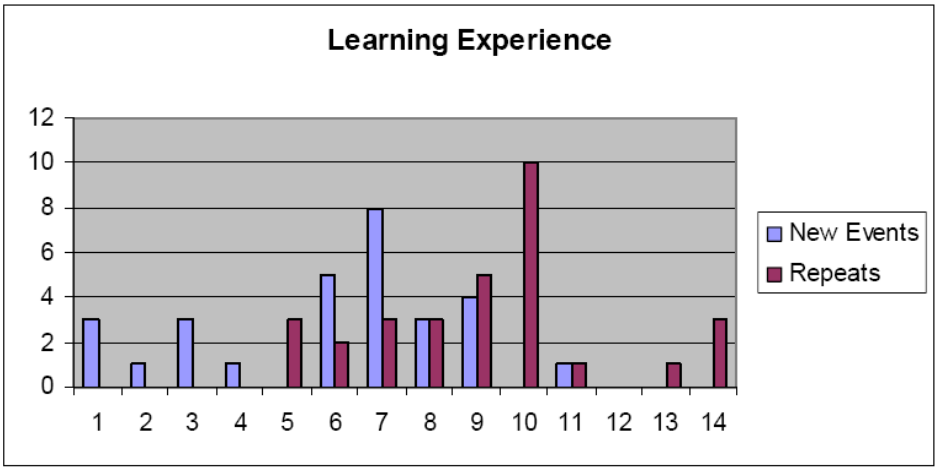
Reduction of Unknown Alarms via Hach Learning Algorithm
Learning period = 0, 30, 90, 365 days



Longer learning times reduce UAR from Plant Events.

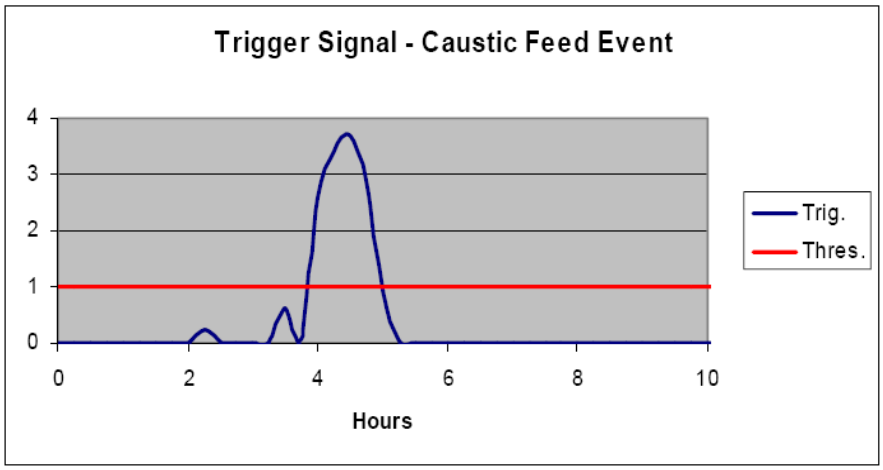
43

Results of Learning at a Very Noisy Location



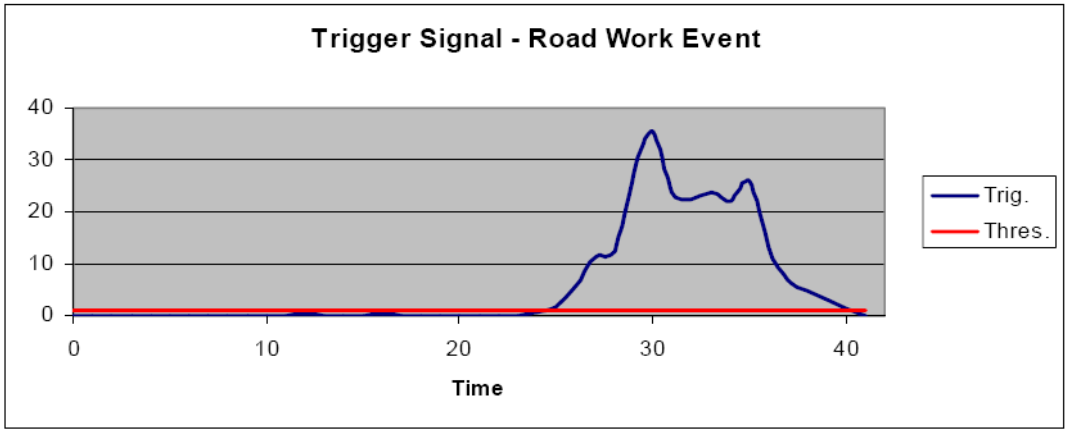
There were 26 unique events over 11 days of operation.
All were learned, 16 of them were repeated.

44



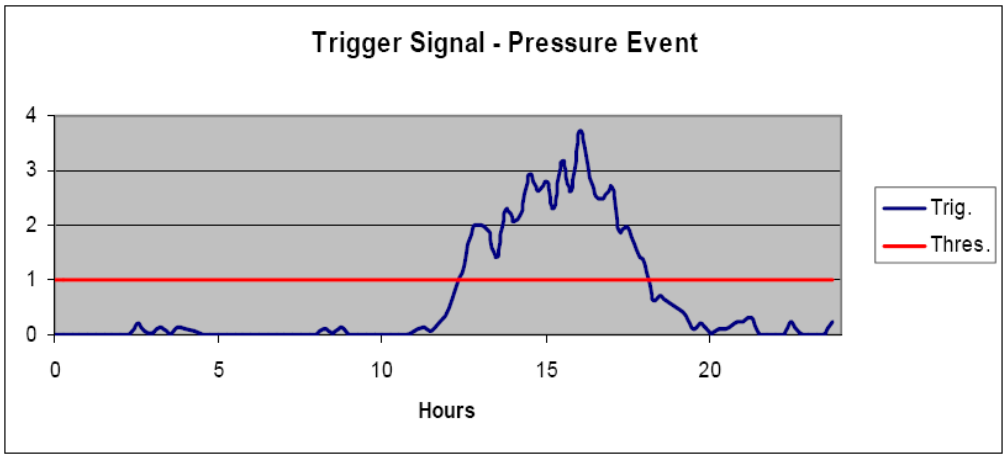
The plant uses caustic feed to control water pH and experienced an operational problem that resulted in the feed of excess caustic. That affected the pH and the conductivity of the water, causing the Event Monitor to alarm.
The Event Monitor learned this Plant Event and can identify a recurrence of the event.

45



Road work near a distribution line dislodged biomass and other particulate matter from the lining of the pipe. There was a massive increase in turbidity, which not only showed up on the turbidimeter, but also showed up as an interference in the chlorine measurement (optical). As expected, the conductivity and pH also showed minor changes. The increase in biomass in the water was indicated by the TOC analyzer. This event illustrates the ability of the Event Monitor to detect and alarm on unanticipated events. This event also provides a signature for the materials adhering to the walls of the pipes in this location.

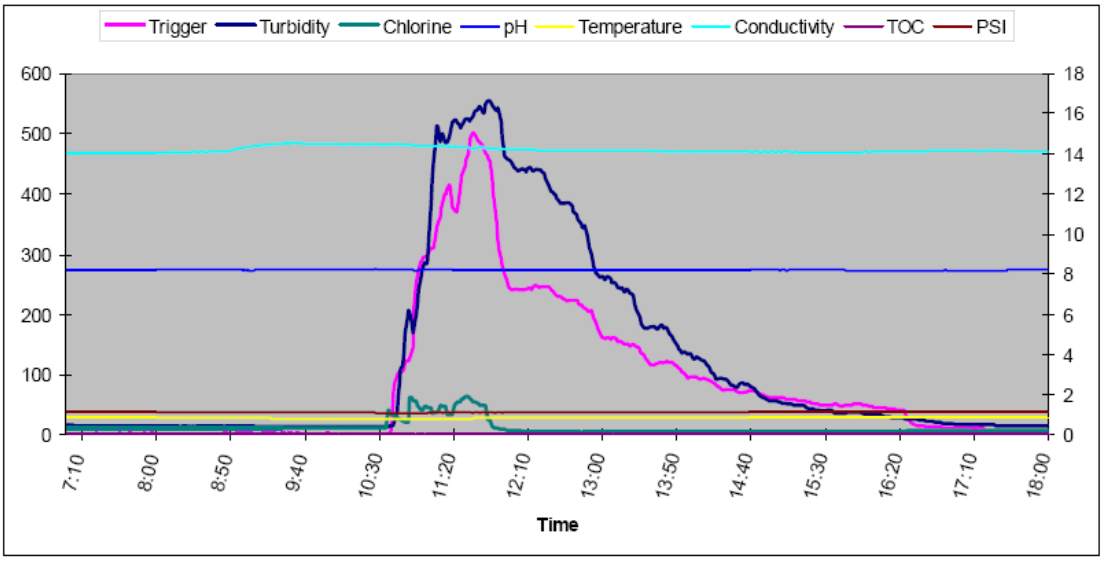
46



The Event Monitor is located in a building which experiences a daily variation in water pressure. The sample variation is associated with a turbidity increase that causes a Trigger. There is also a small pH decrease at that time, possible because of increased solubility of CO2 in the water, dropping the pH slightly. This pattern is recognized by the Event Monitor as a "Normal" event, rather than an alarm condition.

47

Pennsylvania Event



48

Pittsburgh 36 Inch Main Break

• A geyser caused by a severed 36-inch water line erupts from Fort Duquesne Boulevard at about 10:30 a.m., August 17th. One of the largest water main breaks in the city's modern history.

A driver who was able to rescue a vehicle follows a man on foot out of a flooded Gateway Center parking garage, following a water main break on Fort Duquesne Boulevard.

50

More than 20 million gallons of water poured out of Fort Duquesne Boulevard and into nearby parking garages and other low-lying areas Downtown yesterday morning.

51

- Workmen do preliminary work before the 36 inch main could be repaired on Fort Duquesne Boulevard

52

Workers move a section of new pipe into position as the broken 36-inch water main can be seen in the background.

53

Water Distribution Monitoring
An Enhanced System

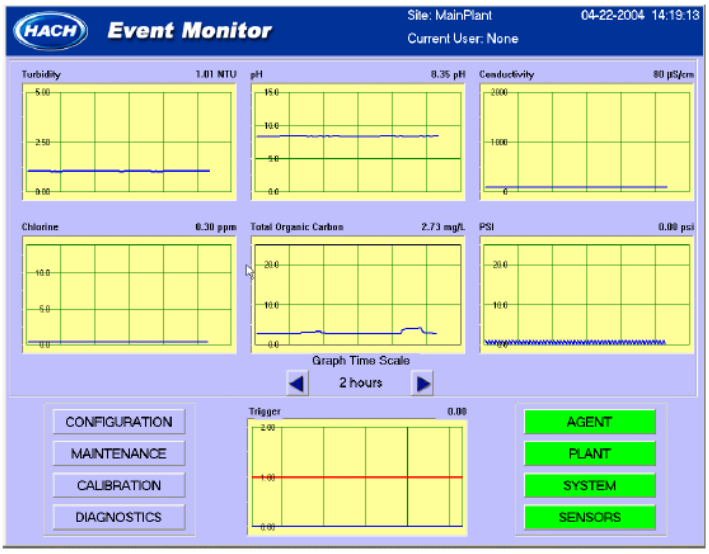
- Add
  - TOC
  - Auto sampler
    - Configure w/24-1L sample bottles
  - ToxTrak
  - Eclox
  - Emergency Response Toolbox
  - Other - depending on water source and quality

54

55

HACH

Event Monitor Main Screen



View all measurements and trigger signal from the main screen.

6

56

Conclusions and Summary

HACH
Homeland Security Technologies

- Effective distribution system monitoring provides significant benefit to operational management
- Taken in aggregate, with interpretive software, an appropriate group of on-line sensors can identify deviations from normal water quality in the distribution system
- Data analysis does require advanced interpretive algorithms to help separate the normal from the abnormal
- Creating a multi-dimensional monitoring network provides a robust system allowing managers to be on top of issues and changing conditions before customers experience them
- We are continuing our development efforts to extend the application of the Event Monitor Trigger System to also include a real-time security monitoring solution

The earlier you have systems installed, the more Plant Events you will observe for the algorithm to learn from … the larger the data set, the fewer unknown events you will see.

Hach HST Proprietary 36

Questions?

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HAND-PORTABLE TOROIDAL ION TRAP DETECTOR FOR HOMELAND SECURITY

Contreras, Jesse A. – Brigham Young University; Lammert, Stephen A. – Brigham Young University; Lee, Edgar D. – Palmar Technologies; Lee, Milton L. – Brigham Young University; Murray, Jacolin A. – Brigham Young University; Oliphant, James R. – Palmar Technologies; Tolley, H. Dennis – Brigham Young University; Tolley, Samuel E. – Palmar Technologies

There is an increasing demand for hand-portable instrumentation for detection of target chemicals in defense and homeland security operations. The requirements of such instrumentation include robustness, and small size and weight, in addition to the universally sought virtues of sensitivity, selectivity, and speed. A hand-portable gas chromatograph-mass spectrometer (GC-MS) system is attractive for this application because of its unmatched selectivity and sensitivity for a variety of target compounds. The MS reported in this paper is a novel, miniature toroidal RF ion trap that can be operated at RF voltages significantly lower than required for conventional traps. The large trapping volume characteristic of the toroidal geometry allows miniaturization while still preserving high sensitivity. The miniaturized ion trap provides unit mass resolution. A low thermal mass GC with 5 m x 0.10 mm i.d. capillary column provides rapid analysis with low power consumption. Helium mobile phase is supplied by a small pressurized gas cartridge. Sample introduction is based on solid phase micro extraction (SPME), which can be applied to a variety of sample matrices. A new SPME syringe with identification chip was developed for one-hand operation. The complete system weighs approximately 8.2 kg (including batteries) and has a volume of 0.014 m^3. A typical analysis for chemical agents and simulants can be completed within 3 minutes.

Hand-Portable GC-MS for CBA Detection

The 22nd Annual National Environmental Monitoring Conference
Arlington, Virginia
August 28—31, 2006

Douglas W. Later, Milton L. Lee,
Stephen A. Lammert, and Edgar D. Lee

Rationale for Approach

- Use proven technologies
- Reduce size of technologies
- Combine in multidimensional arrangement
- Use smart information–sorting algorithms
- Provide easy operation

Proven Technologies

- Solid Phase Microextraction (SPME)
- Gas Chromatography (GC)
- Ion Trap Mass Spectrometry (ITMS)

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Confidential

CB007 Hand-portable GC-MS

- **Dimensions: 13 x 10 x 6 inches**
- **Weight: < 20 lbs (including batteries)**
- **Power:**
  - **Battery operated (12/24 VDC)**
  - **AC Power Adaptable**
- **Easy to operate**

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Hand-Portable GC-MS Solid Model

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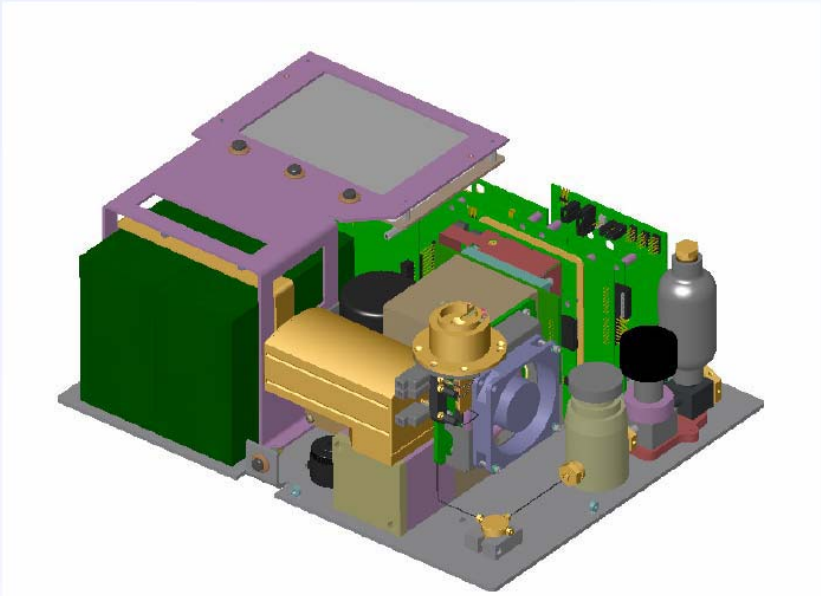
Hand-Portable GC-MS Solid Model



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Why Mass Spectrometry?

- GC/MS is the legal and laboratory standard for chemical identification
- High sensitivity and high selectivity (especially using GC inlet)
  - High Sensitivity ⇨ Low false negative rates
  - High Selectivity ⇨ Low false positive rates

    Much higher selectivity than spectroscopic techniques or ion mobility spectrometry (i.e., molecular weight, fragment ions, relative intensities vs. one ion mobility value)

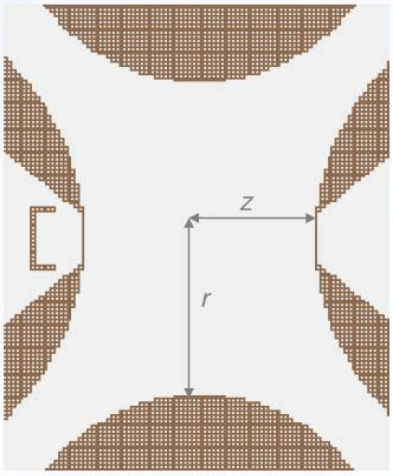
Why Ion Trap Mass Spectrometry?

- Simple, rugged design (no critical alignment ion optics)
- Tolerant of low vacuum conditions (requires 1 mtorr operating pressure ⇨ less stringent vacuum requirements
- MS/MS and MS^n capability in one mass analyzer
- High duty cycle ⇨ high sensitivity
- Low power (especially with small ion trap mass analyzers)

Ion Trap Constraints

- 3-D ion trap is an "ion bottle" with somewhat fixed relative dimensions (r_0 vs. z_0)
- Ion-ion repulsion (space charge)
- Commercial traps optimized at r_0 = 1 cm, ~16 kV_{p-p}
- Further increase in r_0 not practical due to arcing of rf high voltage
- Decrease of r_0 yields lower rf power, but will lead to earlier onset of space charge

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



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Approaches to Address Space Charge in Small Ion Traps

(1) Arrayed, reduced r_0 cylindrical ion traps

Simple to machine, but ion capacity must be recovered by increasing the number of trapping cells in an array

(2) Alternative Geometries

Increased ion storage using different IT geometries

- Linear IT
- Toroidal IT

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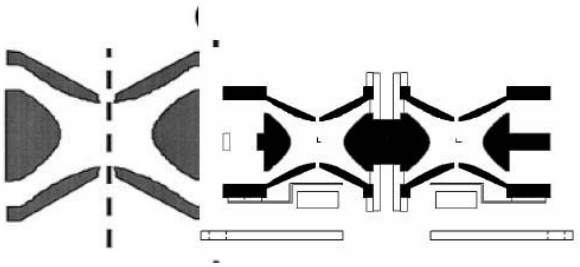
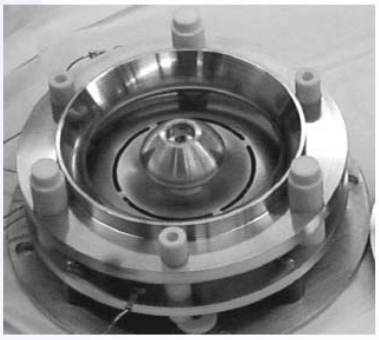
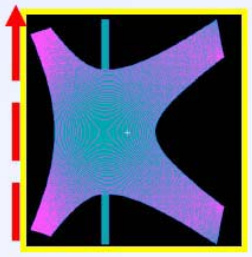
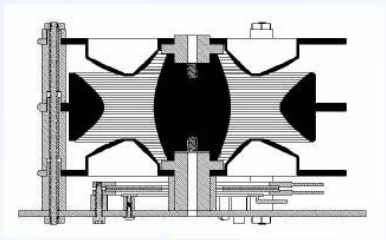
Rotations of IT Cross-Section

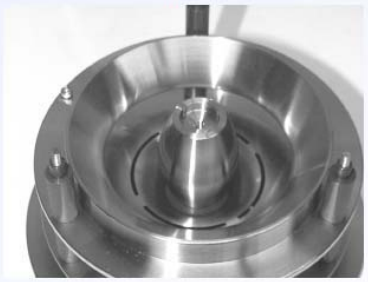


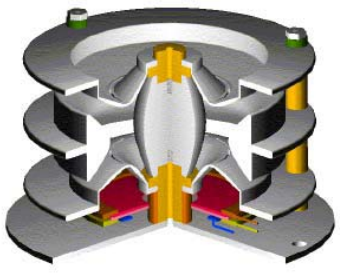


Toroidal RF IT (Asymmetric Corrections)









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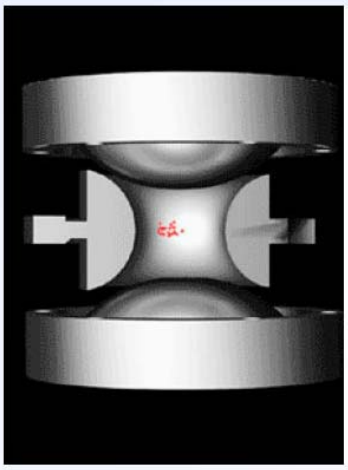
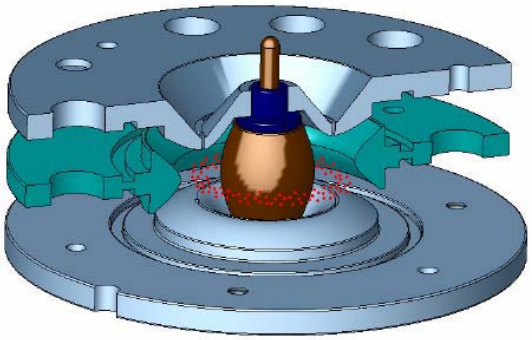
Ion Storage Volume





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Why Toroidal RF Ion Trap Mass Spectrometry?

- Single mass analysis volume (compared to arrayed miniature cylindrical ion traps)
  - All ions experience the same trapping/mass analysis field
  - Easier coupling to ionization and detection optics
- Compact geometry (compared to linear ion traps of similar storage capacity)
- Homogenous field (compared to linear ion traps)
  - No end effects. All spatial positions within mass analyzer are equivalent

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Mini-Toroidal RF IT Design

- Small toroidal geometry
  - r_0 = 2 mm; R = 6 mm (R/r_0 = 3)
  - Voltage requirement reduces by ~ r_0^2
- Custom electron gun designed to provide a gated e^- beam through a small portion of the entrance endcap slit
- Custom electron multiplier (DeTech)
  - Operation with >10^5 gain at pressures as high as 10^{-2} mbar

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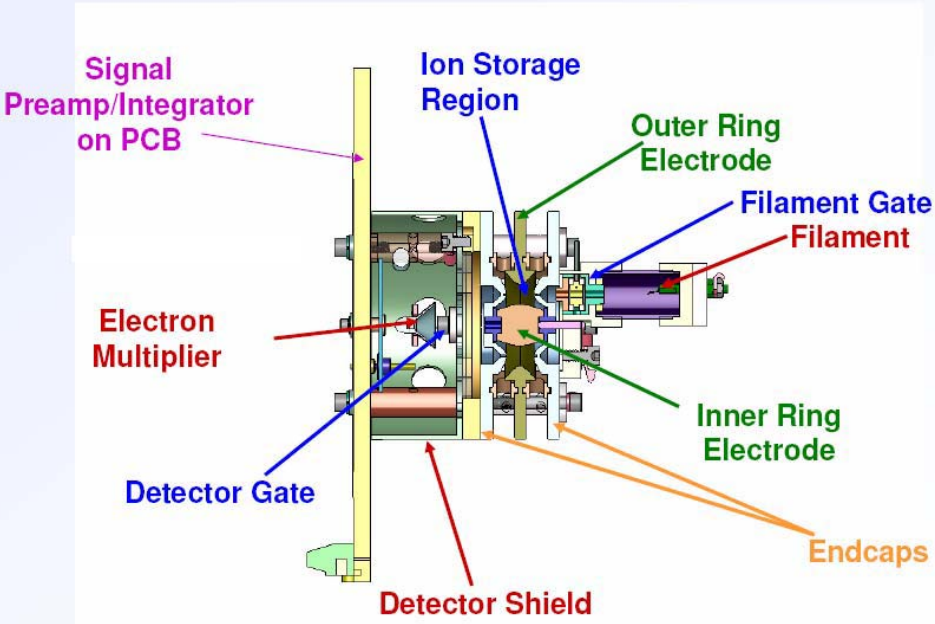
Cross-Section Drawing of Mini-Toroidal RF IT



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Electrodes and Analyzer Assembly

Entrance/Exit Slits = 0.011”

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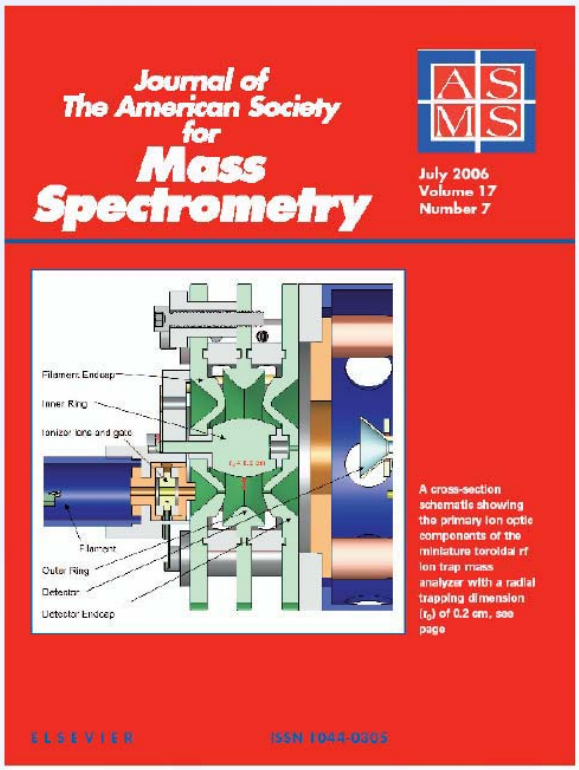

S.A. Lammert, A.L. Rockwood, M. Wang, M.L. Lee, E.D. Lee, S.E. Tolley, J.R. Oliphant, J.L. Jones, R.W. Waite, J Am Soc Mass Spectrom 2006, 17, 916-922

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Mini-Toroidal RF ITMS

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Prototype CB007 GC-ITMS Systems

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Operating Parameters

- **RF trapping field:**
  - **1.9 MHz, ~200-1200(max) V_{p-p}**
  - **Amplitude scan (linear), 200 ms scan**
- **Resonance ejection frequency:**
  - **~900 KHz, approx. 4 V amplitude**
- **Ionization:**
  - **Typically 10-100 ms**
  - **Gated focusing lens assembly on electron gun and detector**
- **Pressures:**
  - **Sample: typically between 1 x 10^{-6} and 4 x 10^{-5} mbar (uncorrected)**
  - **Helium buffer gas: typically 2-4 x 10^{-4} mbar (uncorrected)**

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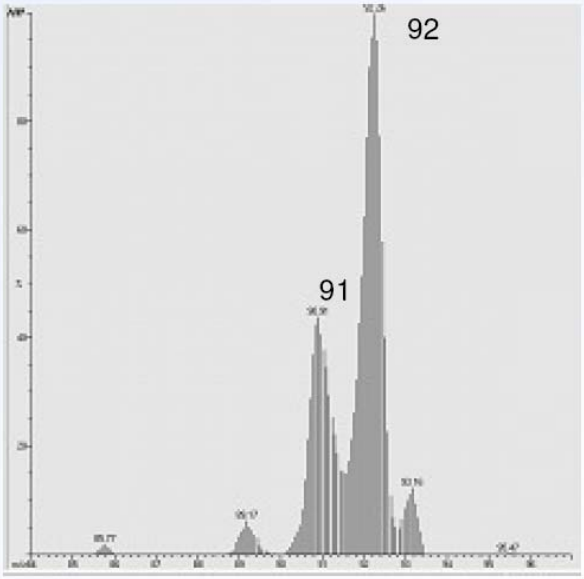
Toluene Mass Spectrum of Molecular Ion Region



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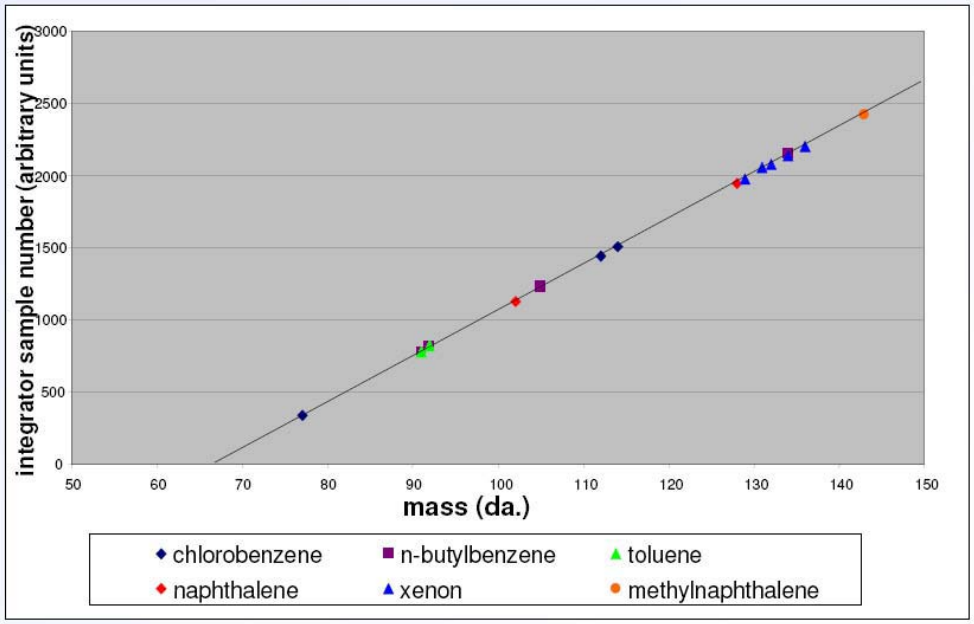
Mass Calibration



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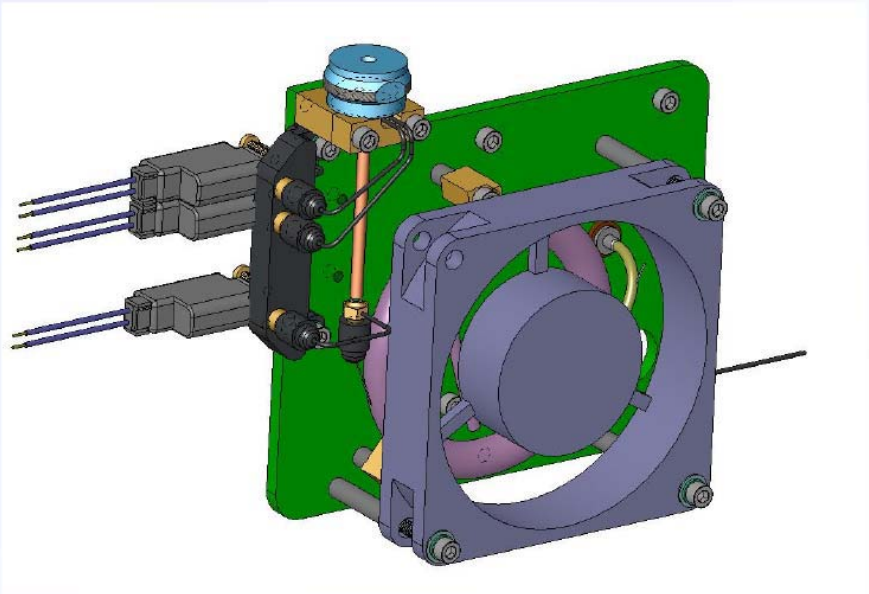
LTM GC Module



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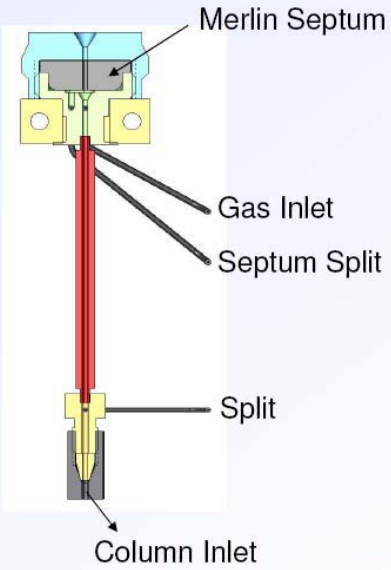
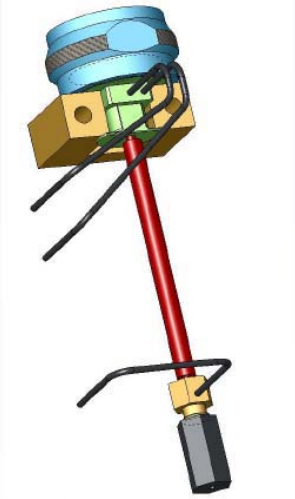
Low Thermal Mass SPME Injector





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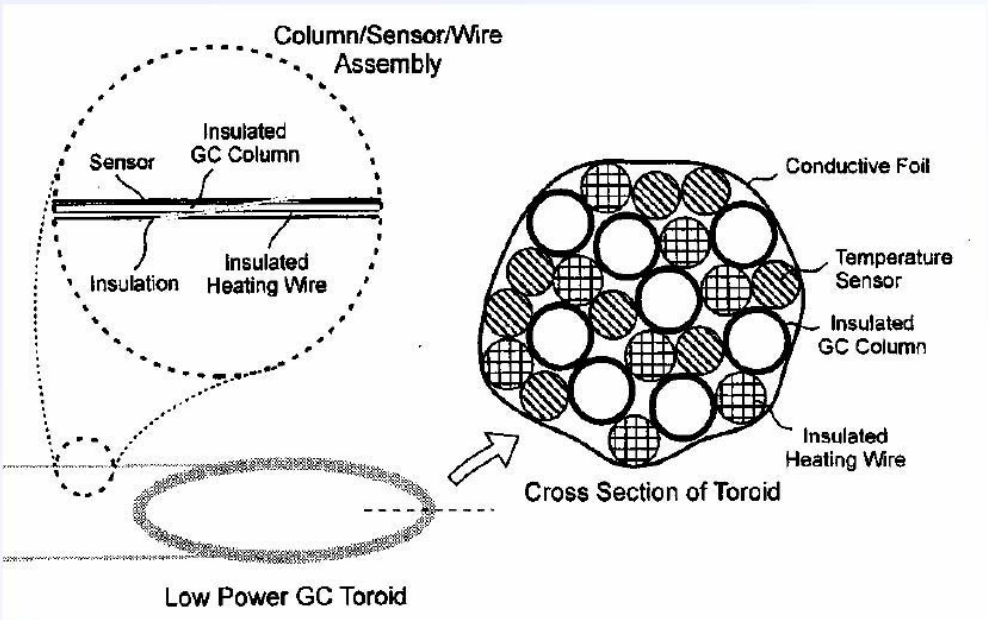
Low Thermal Mass (LTM) GC Assembly



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Courtesy RVM Scientific

LTM GC Features

- Most efficient GC technology for temperature programming
- Compatible with wide range of temperature programs
- Any capillary column in any length
- Fast cool down rate
- Any laboratory temperature programming method can be run with only 1% of the power compared to laboratory instrument

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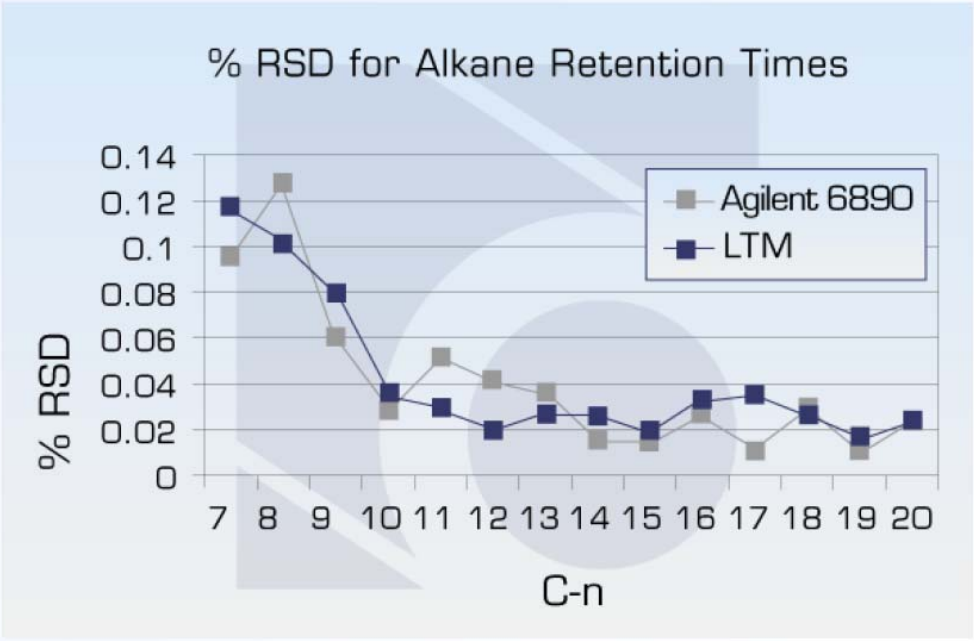
LTM GC Retention Time Reproducibility



Sloan, K.M., et al., Field Anal. Chem. Technol. 5, 288-301 (2001)

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Courtesy RVM Scientific

SPME Syringe Design

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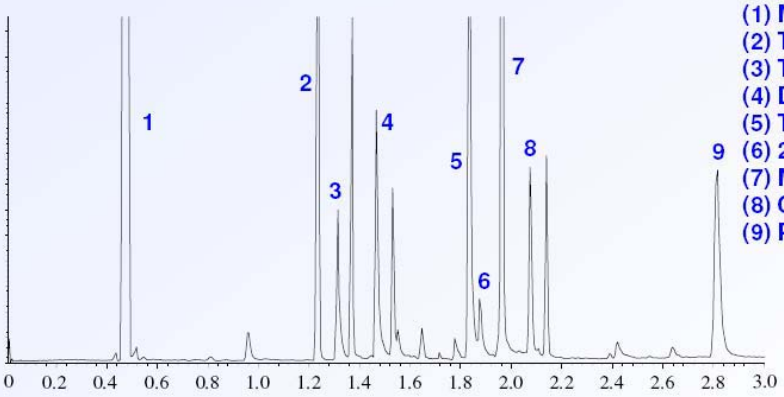
LTM GC-MS TIC Chromatogram



(1) Methanol
(2) Toluene
(3) Trimethylphosphite
(4) DMMP
(5) Triethyl phosphate
(6) 2-Chloroethylmethyl sulfide
(7) Methyl salicylate
(8) Chloroacetophenone
(9) Parathion

PDMS/DVB SPME fiber
1 min sampling from MeOH solution
Thermal desorption @ 250°C for 3 s

5 m x 0.1 mm i.d. DB-5 column (0.4 μm d_f)
40°C (hold 30 s) to 280°C (hold 30 s) @ 120°C/min
25 psig helium
Split injection (20:1)

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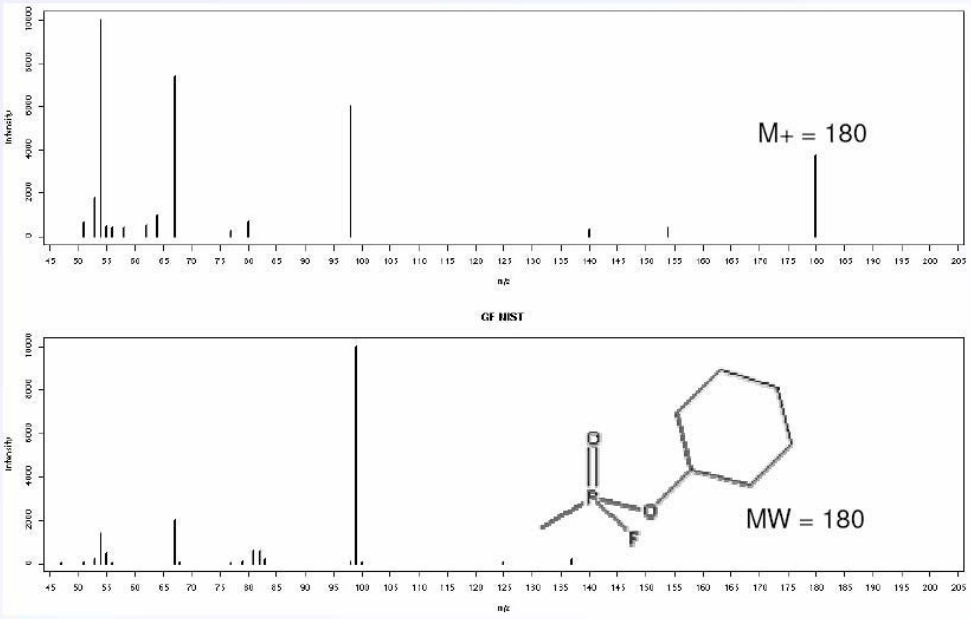
Mass Spectrum of Cyclosarin (GF)



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Spectral Factorization Algorithm

- Extract relevant spectra from data matrix
- Calculate correlations to target library
- Identify matches
- Fast
- Mathematically sound
- Numerically stable
- Chemically sensible

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Palmar Approach to Bacterial Threat Detection

- Catalytic generation of volatile/semi-volatile biomarkers
  - Better control of conditions and reactions
  - Preservation of biomarker structures
  - Lower temperature than pyrolysis
- Multidimensional chemical analysis
  - GC-MS
- Multiple biomarker classes
  - Dipicolinic acid
  - Fatty acids
  - Aromatic amines
  - Carbohydrates
- Powerful deconvolution/classification algorithms

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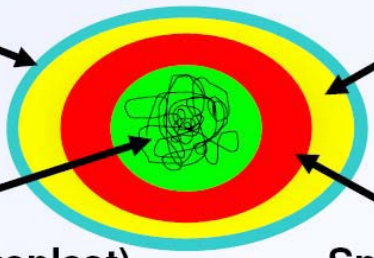
Anthrax Spore

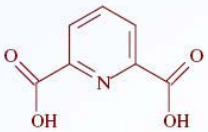
Exosporium
50% protein, 20% carbohydrate, 20% lipid

Spore Coats
crosslinked protein



Spore Core (protoplast)
DNA, cytoplasm, high amounts of dipicolinic acid, (DPA - ~10% dry weight of spore), pX01 and pX02 plasmids

Spore Cortex
crosslinked peptidoglycan



Dipicolinic Acid

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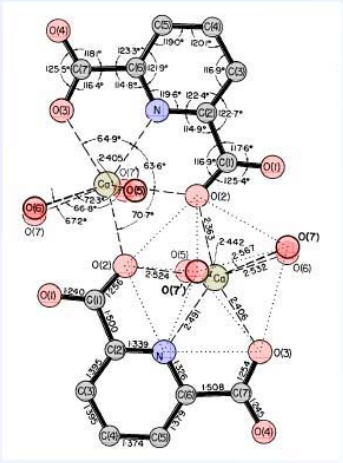
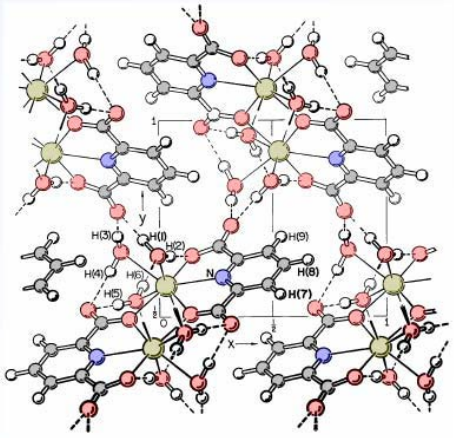
Form of DPA in Endopores



Molecular arrangement of crystalline CaDPA·3H_2O

(Strahs and Dickerson, 1968)

- DPA complexed with Ca^{2+} in endospores
- H_2O also present in endospore complex (ratio may vary)



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Endospore Sample Preparation

- Mix 100-µL endospore suspension with 50 µL 1.0 vol% H_2SO_4 in MeOH (20-150°C)
- Add 40 µL 0.5 M TMAH
- Sample with whisk
- Withdraw whisk into SPME syringe and insert into GC injection port at 290°C

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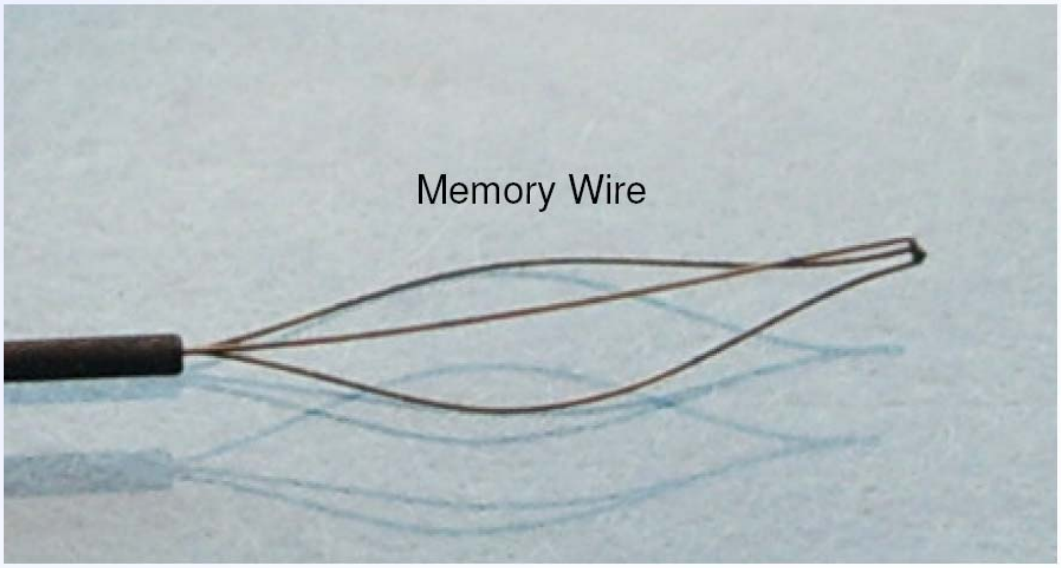
Biological Agent Sampling Whisk



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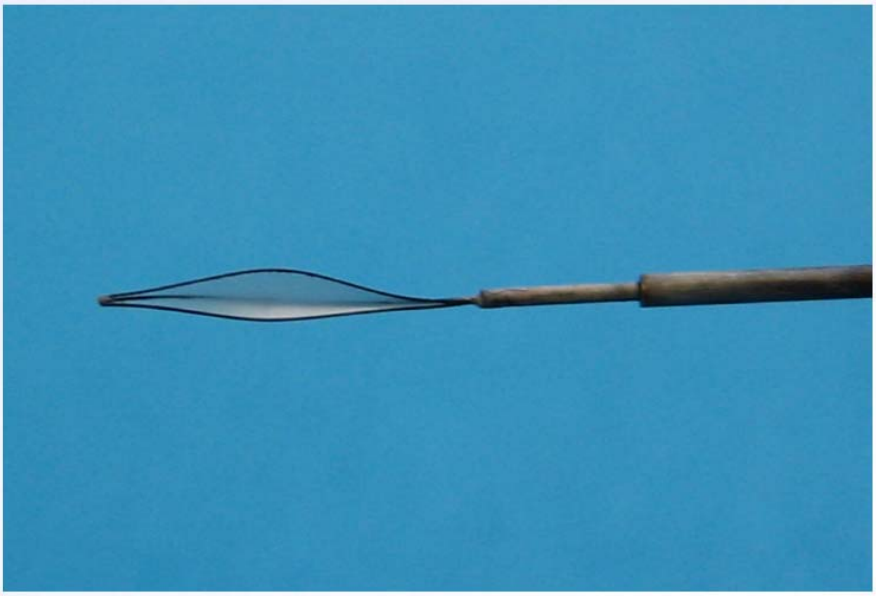
Sampling Whisk Containing Sample



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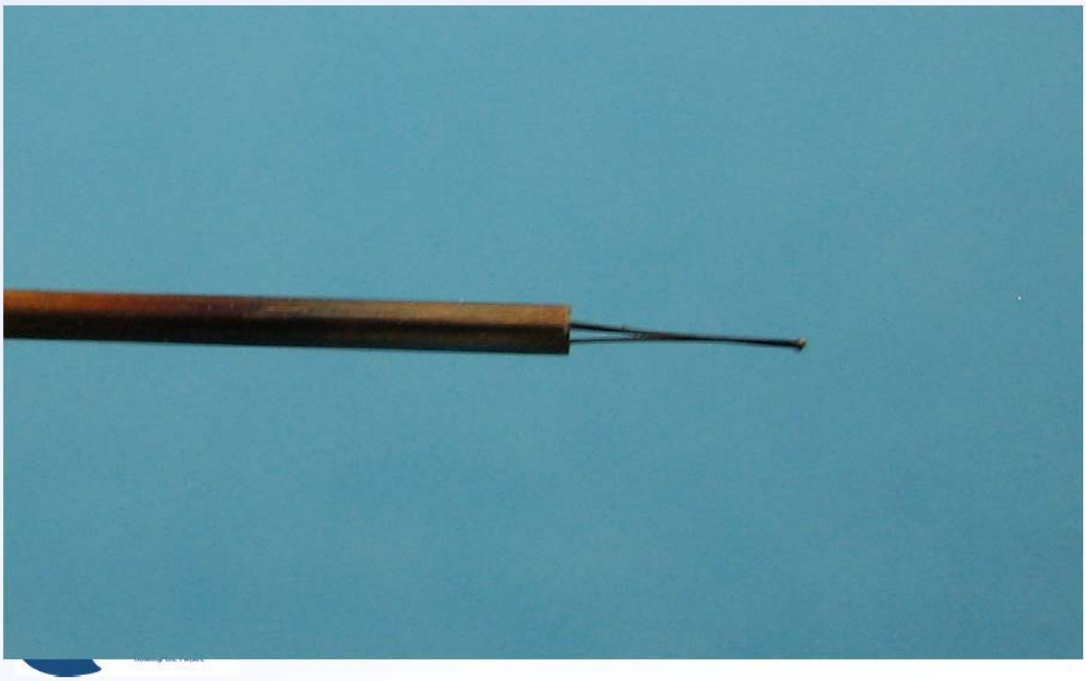
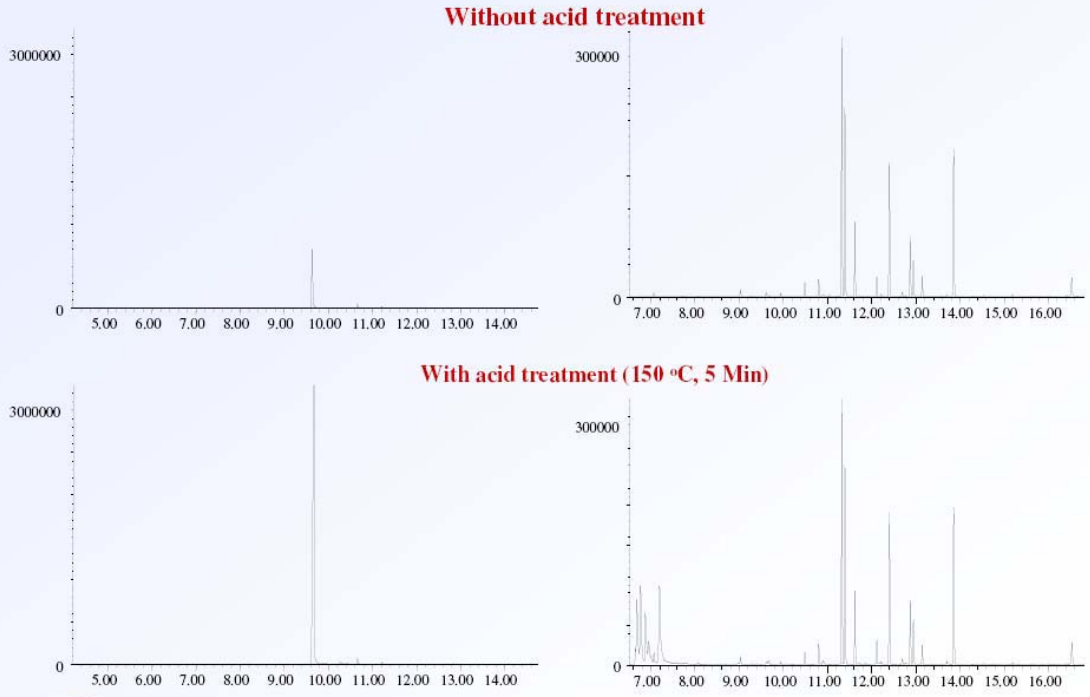
Sampling Whisk Partially Retracted into Needle



DPAME and FAME Profiles With and Without Acid Treatment



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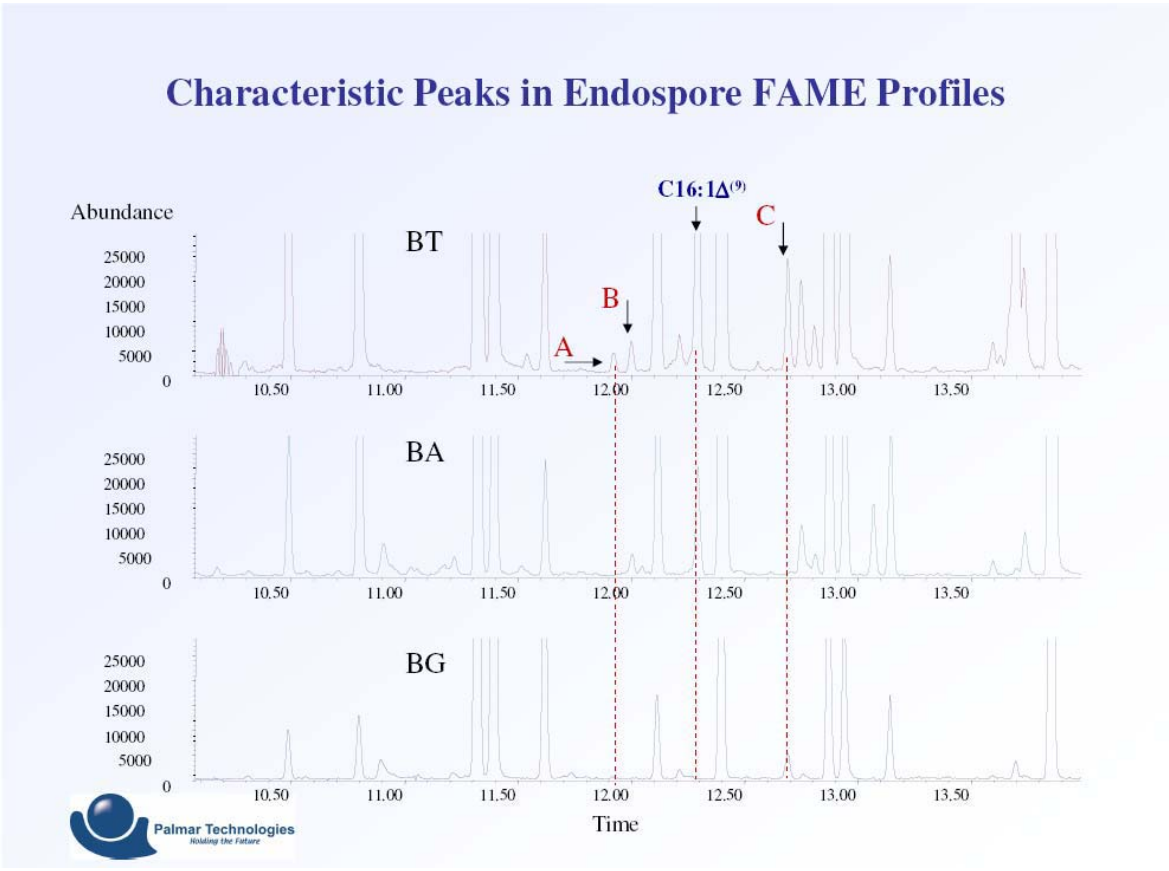
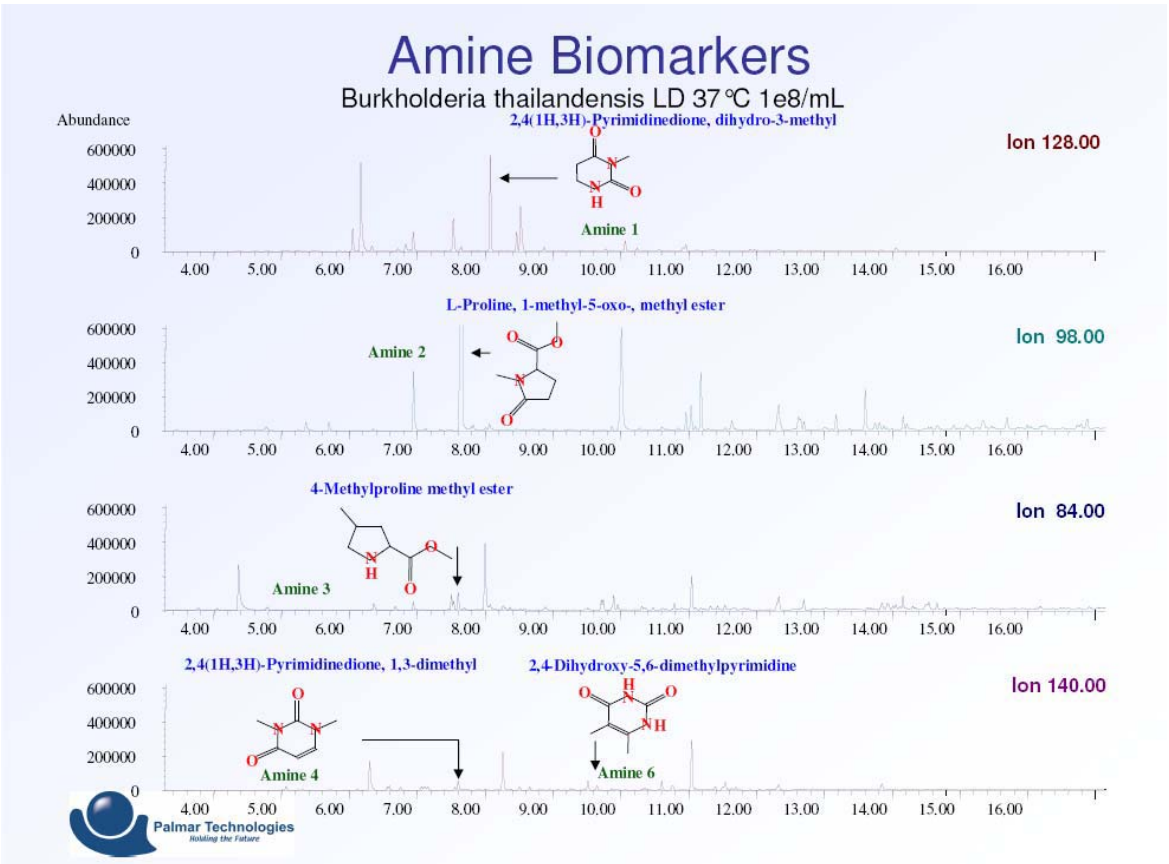

Characteristic Peaks in Endospore FAME Profiles
Abundance
C16:1Δ(9)
C
B
A
BT
BA
BG
25000
20000
15000
10000
5000
0
10.50
11.00
11.50
12.00
12.50
13.00
13.50
Time
Palmar Technologies


Amine Biomarkers
Burkholderia thailandensis LD 37 °C 1e8/mL
Abundance
2,4(1H,3H)-Pyrimidinedione, dihydro-3-methyl
Ion 128.00
Amine 1
L-Proline, 1-methyl-5-oxo-, methyl ester
Amine 2
Ion 98.00
4-Methylproline methyl ester
Amine 3
Ion 84.00
2,4(1H,3H)-Pyrimidinedione, 1,3-dimethyl
Amine 4
2,4-Dihydroxy-5,6-dimethylpyrimidine
Amine 6
Ion 140.00
600000
400000
200000
0
4.00
5.00
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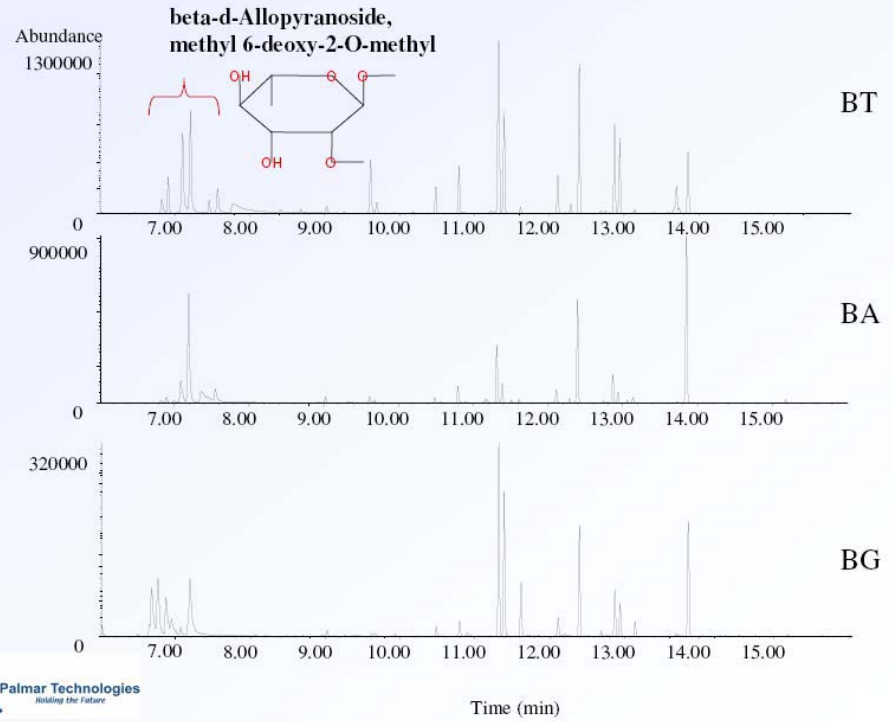
Carbohydrate Biomarkers



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Development Timeline

- Oct 03 Funding for CB007 started
- Jul 04 Solid phase microextraction syringe started
- Sep 04 Miniature toroidal IT started
- Dec 04 Ion trapping with miniature toroidal IT demonstrated
- Apr 05 Low thermal mass resistively heated GC started
- Sep 05 Brassboard CB007 completed
- Oct 05 Brassboard CB007 tested at Dugway
- Mar 06 Prototype CB007 operated with NI computer interface
- Jul 06 Library for prototype CB007 started
- Jul 06 9 Prototype CB007 systems operated with firmware
- Aug 06 Preparation for DTRA CV started
- Jan 07 Development of GOTS and COTS systems started

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BYU/Palmar Research/Development Team

Gas Chromatograph (GC)

Milton Lee	PhD Chemist
Jesse Contreras	Graduate Student
Jacolin Murray	Graduate Student

Ion Trap Mass Spectrometer (ITMS)

Ed Lee	PhD Chemist
Steve Lammert	PhD Chemist
Samuel Tolley	PhD Bioengineer
Alan Rockwood	PhD Chemist

Biological Agent Detection

Cal Bartholomew	PhD Chemical Engineer
Rich Robison	PhD Microbiologist
Tai van Truong	Graduate Student
Aaron Nackos	Graduate Student
John Kimball	Undergraduate Student

Instrument Control & Data Processing

Ken Nemelka	Software Engineer
Dennis Tolley	PhD Statistician
James Oliphant	MS Statistician/Programmer

Engineering

Jeff Jones	Mechanical Engineer
Randy Waite	Electrical Engineer
Gary Collins	Electrical Engineer
Scott Losee	Electrical Engineer
Greg Henry	Manufacturing Engineer

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LABORATORY CAPABILITY IN SUPPORT OF EMERGENCY RESPONSE

Fitz-James, Schatzi; U.S. Environmental Protection Agency

Last year, Agency representatives presented a session regarding plans to address laboratory needs in the event of a terrorist incident. In the event of an actual or suspected terrorist incident, comprehensive laboratory resources will need to be called upon to allow the nation to deal with any situation. Over the past year, the federal Integrated Consortium of Laboratory Networks (ICLN) has formed and begun to address national analytical capabilities for chemical, biological and radiological contaminants of concern in clinical, food, plant and environmental media.

The President's National Homeland Security Strategy calls upon EPA to be the primary agency responsible for environmental sampling and analyses in response to a terrorist incident. In response to this strategy, and in concert with the Agency's role in the ICLN, an environmental laboratory response network program (eLRN) is in the formative stages in the Office of Emergency Management, Office of Solid Waste and Emergency Response at EPA Headquarters.

EPA possesses limited capabilities and capacities to analyze environmental samples for chemical, biological and nuclear materials associated with Weapons of Mass Destruction (WMD). The eLRN is exploring approaches to address this limitation. The Agency's primary analytical capability is oriented toward routine analysis of industrial chemicals, pesticides, and conventional pollutants. The first phase of the eLRN will be to formalize network relationships using these pollutants as the model. Later phases will integrate biological and radiological materials into the eLRN. EPA also intends to fully integrate state public health/environmental laboratory counterparts into the eLRN similar to the integration utilized in the other networks.

A brief history of the ICLN and the associated networks will be discussed, as well as a summary of the past year's activity. The structure, approach and status of the eLRN will also be presented.

The eLRN approach will continue to follow the precepts below:

- to the extent possible, make use of the nation's current laboratory resources
- address the problem in the most cost-effective manner
- develop a solution as quickly as possible

WEDNESDAY P.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Organic Methods

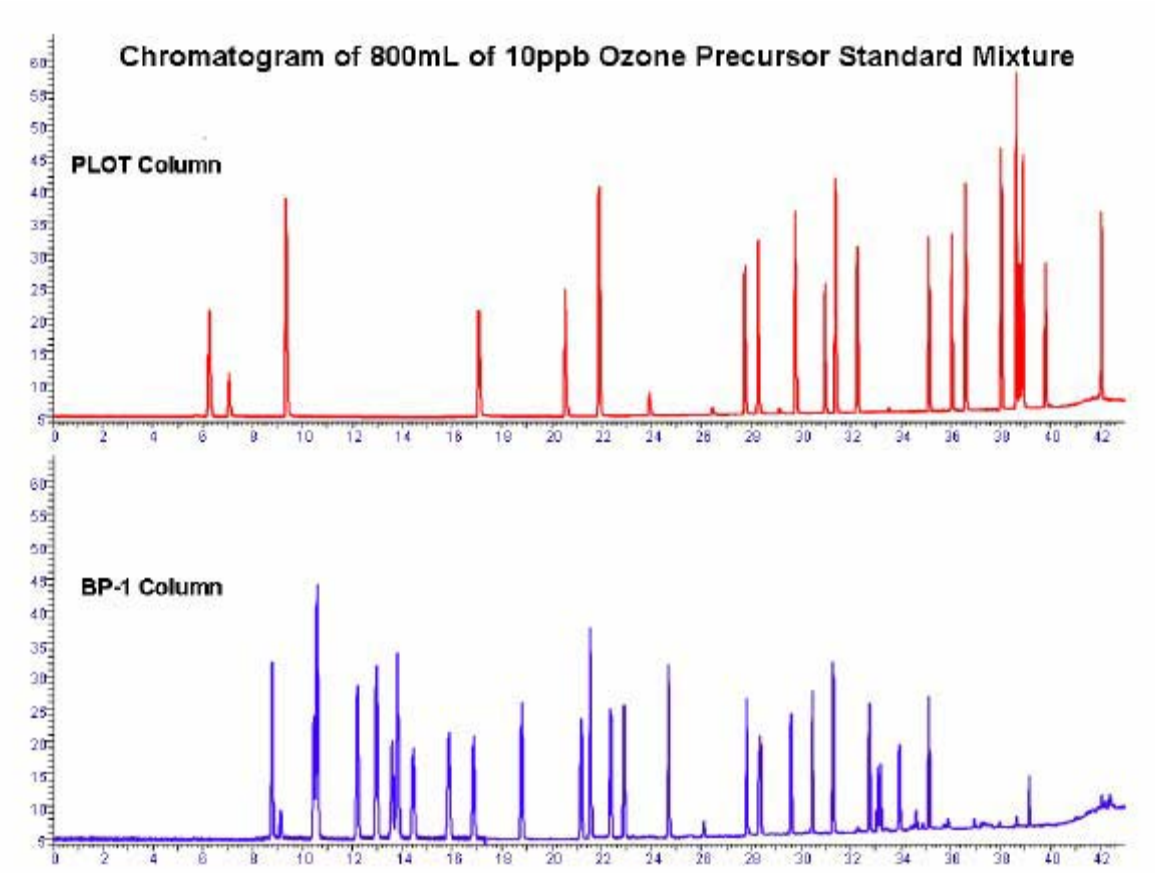
RECENT ADVANCES IN THERMAL DESORPTION

Grosser, Zoe; PerkinElmer Analytical Sciences
Tipler, Andrew; PerkinElmer Analytical Sciences

Environmental air analyzers require rugged and precise performance. Some of these systems must be run unsupervised in remote locations and so full access is needed to the operational aspects of the system.

In this paper we describe the development of a fully automated air analyzer based on thermal desorption (TD) and gas chromatographic (GC) instrumentation. A critical requirement for this system was the provision of electronically programmable pneumatic controls (PPC) throughout. Such controllers are less susceptible to drift than manual pneumatics and are ideal for long term unattended operation.

This analysis involves the sub-ppb determination of volatile organic compounds (VOCs) known to promote the formation of ozone in atmospheric air. These VOCs are essentially alkyl hydrocarbons and aromatics that cover the carbon range C2 to C11. Air to be analyzed is drawn at a controlled flow rate and for a metered time through a cooled adsorbent trap. A Nafion drier is used to remove moisture from the sample before it enters the trap. The trapped analytes are thermally desorbed and carried by carrier gas supplied by a PPC device into a GC. The GC uses a Dean's switched heartcut device to separate analytes by volatility between two columns of differing retention to effect a parallel chromatographic separation. By using a PPC controller to supply carrier gas to the heartcut device, setup of the necessary pressure-balanced conditions is very straightforward and, once set, the conditions do not need further adjustment during normal use. Programmable pneumatic controllers are also used to supply the two flame ionization detectors on the GC system. The figure shows example chromatography from this system. Further data will be presented to demonstrate the ruggedness and precision of the instrumentation.


Chromatogram of 800mL of 10ppb Ozone Precursor Standard Mixture
PLOT Column
BP-1 Column

Recent Technical Advances in Thermal Desorption – Gas Chromatographic Instrumentation for Fully Automated Ozone Precursor Analysis

Andrew Tipler, and Zoe Grosser
PerkinElmer LAS

ABSTRACT

Environmental air analyzers require rugged and precise performance. Some of these systems must be run unsupervised in remote locations and so full access is needed to the operational aspects of the system.

We describe the development of a fully automated air analyzer based on thermal desorption (TD) and gas chromatographic (GC) instrumentation. A critical requirement for this system was the provision of electronically programmable pneumatic controls (PPC) throughout. Such controllers are less susceptible to drift than manual pneumatics and are ideal for long term unattended operation.

This analysis involves the sub-ppb determination of volatile organic compounds (VOCs) known to promote the formation of ozone in atmospheric air. These VOCs are essentially alkyl hydrocarbons and aromatics that cover the carbon range C_2 to C_{11}. Air to be analyzed, is drawn at a controlled flow rate and for a metered time, through a cooled adsorbent trap. A Nafion™ drier is used to remove moisture from the sample before it enters the trap. The trapped analytes are thermally desorbed and carried by carrier gas supplied by a PPC device into a GC. The GC uses a Deans' switched heart-cut device to separate analytes by volatility between two columns of differing retention to effect a parallel chromatographic separation. By using a PPC controller to supply carrier gas to the heartcut device, setup of the necessary pressure-balanced conditions is very straightforward and, once set, the conditions do not need further adjustment during normal use. Programmable pneumatic controllers are also used to supply the two flame ionization detectors on the GC system. Data is presented that demonstrates the performance of the instrumentation.

INTRODUCTION

Hydrocarbon vapors (known as ozone precursors) in the troposphere react in the presence of nitrogen oxides (NO_X), carbonyls, etc. and in the presence of UV from sunlight, to create ozone. Such reactions become apparent as haze above urban areas during hot sunny weather.

Ozone is poisonous and will also readily react with other organic vapors to produce other toxic vapor species with long half-lives. The persistent presence of these vapors in the air that we breathe has become a major concern in many parts of the world and there is now a strong need to measure and ultimately *control* the emissions of these compounds.

In the United States, the Clean Air Act of 1973 mandated the monitoring and control of NO_x, SO_x, CO, PM, Pb and O_3 in the atmosphere. To this end, the US-EPA introduced a method of analysis [1] to monitor levels of over 50 organic compounds in ambient air known to promote the formation of ozone as listed in Table 1.

Table 1: Analytes Listed in US-EPA Technical Assistance Document

Ethane	2-Methylpentane	Ethylbenzene
Ethylene	3-Methylpentane	m/p-Xylene
Acetylene	n-Hexane	Styrene
Propylene	Methylcyclopentane	o-Xylene
Propane	2,4-Dimethylpentane	n-Nonane
Isobutane	Benzene	Isopropylbenzene
1-Butene	Cyclohexane	n-Propylbenzene
n-Butane	2-Methylhexane	m-Ethyltoluene
trans-2-Butene	2,3-Dimethylpentane	p-Ethyltoluene
cis-2-Butene	3-Methylhexane	1,3,5-Trimethylbenzene
Isopentane	2,2,4-Trimethylpentane	o-Ethyltoluene
n-Pentane	n-Heptane	1,2,4-Trimethylbenzene
Isoprene	Methylcyclohexane	n-Decane
trans-2-Pentene	2,3,4-Trimethylpentane	1,2,3-Trimethylbenzene
cis-2-Pentene	Toluene	m-Diethylbenzene
2,2-Dimethylbutane	2-Methylheptane	p-Diethylbenzene
Cyclopentane	3-Methylheptane	n-Undecane
2,3-Dimethylbutane	n-Octane	

The work presented here describes a system that fully automates this analysis to enable continuous results to be collected at field locations.

Several key requirements for the analytical system have been requested by the US-EPA* and these are listed in Table 2.

Table 2: Key Requirements for an Ozone Precursor Analysis System

No use of liquid cryogen
Unattended Operation
Chromatography of all analytes in single run
Hourly sampling
Simultaneous sampling and chromatography
Automatic system calibration
Full data processing
Full remote control of system
Automatic data archival

* Cooperative Research and Development Agreement between US-EPA and PerkinElmer, 1991

SYSTEM DESCRIPTION

The system described here that fulfils the analytical requirements comprises three primary components:

- A thermal desorption system that collects and concentrates the vapors from the atmosphere being monitored and injects them into the gas chromatograph. It also manages the timing of the sampling and analytical processes.
- A gas chromatograph that performs the separation and detection of the collected vapor compounds.
- A data processing system that generates the results and provides access to the system from a remote location.

Thermal Desorption System

The function of the thermal desorption system is illustrated in Figure 1. The analytical system is placed close to the sampling location. Ambient air is drawn through a tube connected to the thermal desorption system. A vacuum pump is connected to an outlet on the thermal desorption system. During sampling, the vacuum pump will draw ambient air through a Peltier-cooled adsorbent trap at -30°C which will retain all analytes listed in Table 1. Modern adsorbents that are cooled to this temperature are very capable of retaining the C_2 analytes without recourse to liquid cryogen. An electronic mass flow controller, which is connected between the trap and the vacuum pump, regulates the rate of air flow through the trap to a user-entered value which is typically 15mL/min. A Nafion™ dryer (DuPont) is used to remove moisture from the air stream before it reaches the cold trap. The system will continue to sample the air for a period of time entered by the user - typically 40 minutes. Once sampling is complete, the trap is rapidly heated to an elevated temperature to desorb the analytes which are then carried by helium carrier gas, via a fused silica transfer line to the gas chromatographic column. To ensure optimum peak shape of the early eluting compounds, a small split (typically 3 to 5mL/min) is applied between the trap and the GC column.

An electronic programmable pneumatic controller is used to regulate the carrier gas pressure into the GC column. Besides facilitating easier setup, the carrier pressure is less likely to drift than conventional manual pneumatic systems over the long periods of time over which this analysis is performed.

The system is designed so that the sampling plumbing is independent of the carrier gas flowing into the GC column. This enables sampling of the next sample to commence during the chromatography of the current sample. In this manner, samples may be collected and analyzed every chronological hour.

The thermal desorption control functions manage the timing of the sampling and analysis.

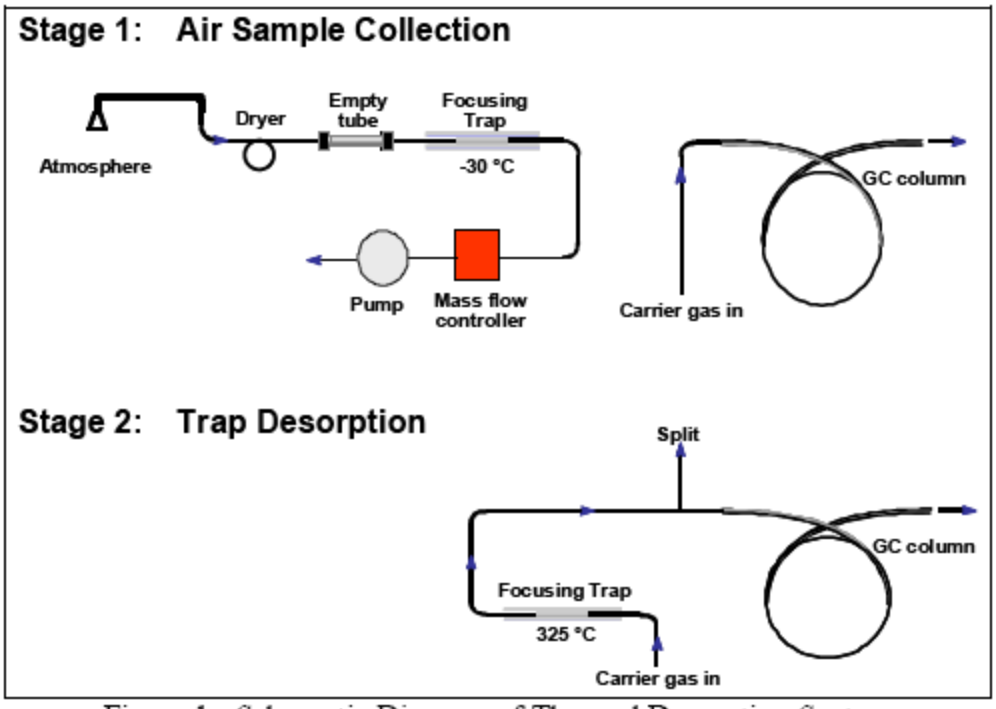


Figure 1: Schematic Diagram of Thermal Desorption System

A new feature developed for this system is the ability to monitor the impedance to flow through the adsorbent trap. Technology has been developed to measure the pressure drop across the trap during operation so that the physical integrity of the trap can be ensured. If the pressure drop suddenly changes as a result, for instance, of movement of the packing, the system can be made to automatically stop. Figure 2 shows measurements made on a single trap over an extended run of samples.

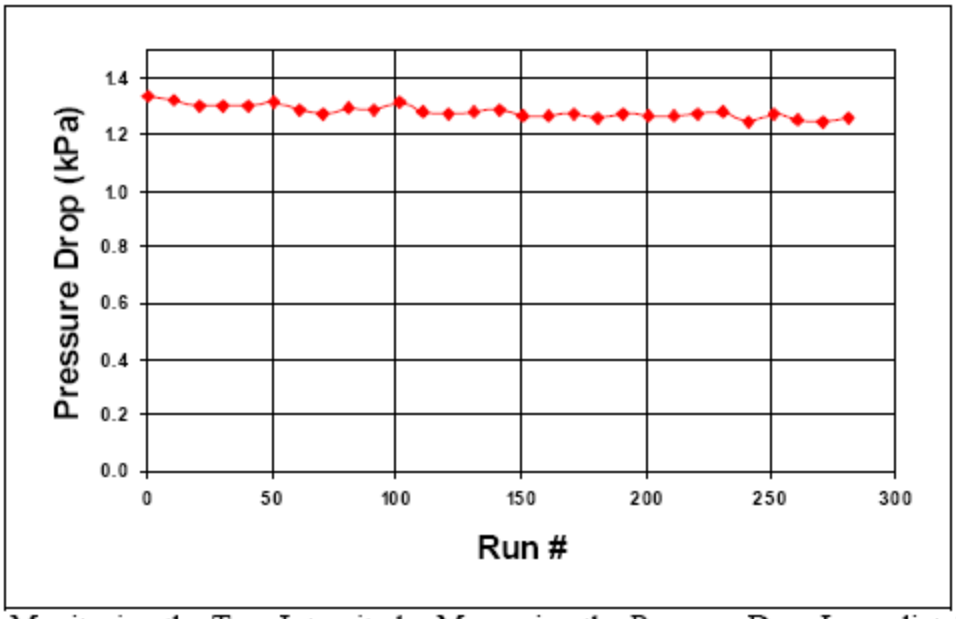


Figure 3: Monitoring the Trap Integrity by Measuring the Pressure Drop Immediately Before each Analysis

Gas Chromatograph

While the Peltier cooled trap on the thermal desorption system effectively eliminates the need for liquid cryogen in the sample collection process, attention must be given to ensure that the need for liquid cryogen is eliminated from the chromatography.

The gas chromatography of the analytes listed in Table 1 is particularly demanding and it would be difficult to perform a separation on a single column without resorting to sub-ambient operation.

To obviate this need, two columns of dissimilar retentiveness are deployed in a Deans' switched heart-cut configuration [2] as shown in Figure 4.

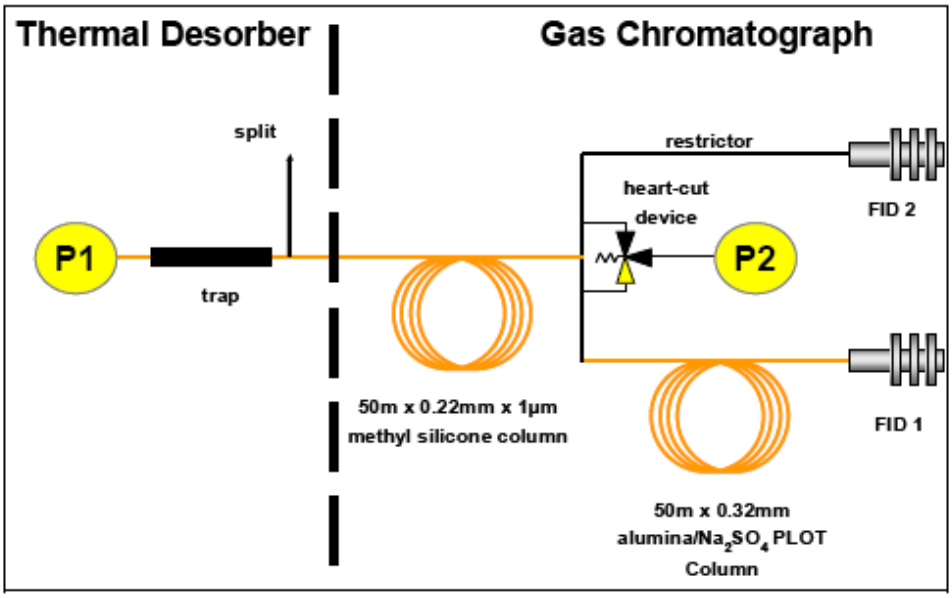


Figure 4: Schematic Diagram of 2-column Configuration with Deans' Switched Heart-cut Device

Initially, as the vaporized analytes are carried from the thermal desorption system to the gas chromatograph, they are passed into a methyl silicone column. The heart-cut device directs the effluent of this first column to a second, more retentive, PLOT column. The PLOT column will separate the C_2 to C_6 analytes at a temperature above ambient and these will be detected on a flame ionization detector. Once these analytes have passed into the PLOT column, the heart-cut device directs the effluent from the methyl silicone column to a second flame ionization detector and the remaining analytes up to C_{11} are detected. In this manner, the sample is effectively split into two fractions of differing volatility that are chromatographed in parallel on the two detectors. Figure 5 shows an example of the typical chromatography produced by this system. A full separation of C_2 to C_{12} (C_{12} is added as a marker) is obtained in about 45 minutes with an initial programmed temperature of 45°C and so totally eliminates the need for liquid cryogen to cool the GC oven.

A programmable pneumatic controller regulates the carrier gas pressure within the heart-cut device – again to simplify setup and minimize long term pressure drift.

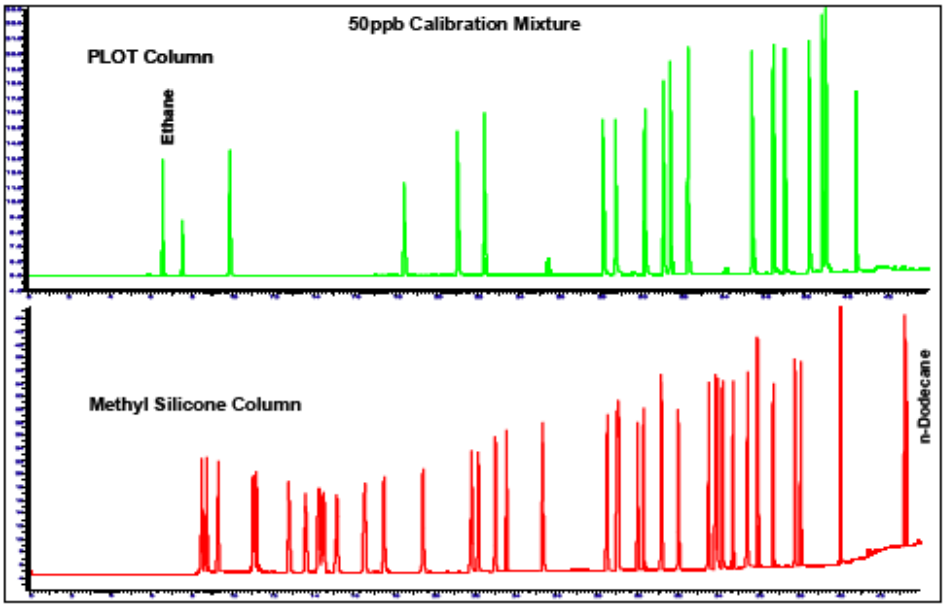


Figure 5: Parallel Chromatography of Analytes from Table 1 on a 2-column Heart Cut System Programmed from 45°C

Data Handling

The third key system component is the data handling system. This not only identifies and quantifies the chromatographic data but it also provides the control of the gas chromatograph and the thermal desorption system. This approach gives the user a single interface to the system control and status and to the analytical data. Because this software is PC based, third party tools may be used to access these function by telephone or internet. This allows users to collect data and check status remotely and eliminate unnecessary field site visits.

RESULTS

Table 3 gives some example analyte peak retention time and area precision and linearity from the system described previously. The conditions given in Table 4 were used to perform this analysis.

Table 3: Precision and Linearity Data for Typical Analytes

Compound Name	Column	Retention Time, RSD%	50ppb Peak Area, RSD%	1 to 50ppb Linearity
Ethane	PLOT	0.042	2.33	0.9998
Ethylene	PLOT	0.125	3.53	0.9998
n-Butane	PLOT	0.155	2.70	1.0000
Acetylene	PLOT	0.263	3.09	0.9996
Cyclopentane	PLOT	0.094	2.79	1.0000
Isoprene	PLOT	0.113	3.69	0.9977
n-Hexane	Me-Si	0.280	2.69	1.0000
Benzene	Me-Si	0.308	2.75	0.9999
Toulene	Me-Si	0.128	2.72	1.0000
Styrene	Me-Si	0.044	2.73	1.0000
1,2,3- Trimethylbenzene	Me-Si	0.015	2.86	0.9997
n-Dodecane	Me-Si	0.009	2.65	0.9990

Table 4: System Conditions for Ozone Precursor Analysis

Chromatograph	PerkinElmer Clarus 500 with Heartcut Device and Internal LINK
Column	Ozone Precursor Column Set: • 50m x 0.22mm x 1µm methyl silicone column and • 50m x 0.32mm alumina/$NaSO_4$ PLOT column
Oven	45°C for 15 minutes, then 5°C/minute to 170°C, then 15°C/minute to 200°C and hold for 6 minutes (48-minute chromatogram)
Detector	Dual Flame Ionization Detectors at 250°C
Carrier gas	48psig helium at the precolumn inlet 17psig helium at the heartcut device
Thermal Desorber	PerkinElmer TurboMatrix 650 with Online Sampling Accessory
Trap	Air Toxics Trap packed with carboneous sorbents
Trap Low	–30°C
Trap High	400°C
Transfer Line	200°C
Operating Mode	On Line
Inlet split	Off
Outlet split	5mL/min (~2:1 split ratio)
Data Handling System	TotalChrom and TurboMatrix Remote Control Software
Air Sampling	15mL/min for 40 min (600mL total)

CONCLUSIONS

Ground level ozone has become an increasingly important issue in developed nations, as the health effects of smog are more clearly understood. The monitoring of VOC ozone precursor compounds will continue to play a role in defining and reducing air pollution in developed and developing nations in the next decade.

The PerkinElmer Ozone Precursor Analyzer has a proven record of several hundred thousand hours reliable field operation. With quantification limits below 1 ppb and the capability of sampling for 40 minutes of every hour, the system meets the requirements of this exacting method.

The new systems described here are based on these established technologies and bring the additional benefits of electronically programmed pneumatic controls for ease of use and stability and trap integrity testing for increased confidence in the analysis.

REFERENCES

1. U.S. Environmental Protection Agency, 1998, Ozone Precursor Technical Assistance Document for Sampling and Analysis of Ozone Precursors, EPA/600-R-98/161.

2. Deans, D.R., Chromatographia 1 (1968) 18.

EPA Quantification of Low Molecular Weight Alcohols, Ketones and Ethers using Headspace Trap - GCMS

William Goodman, Heidi Grecsek
PerkinElmer LAS

ABSTRACT

Low molecular weight alcohols, ketones, and ethers are of increasing interest to environmental monitoring programs nationwide. In environmental samples, these compounds provide unique analytical challenges as a result of their high miscibility and solubility in water. Utilizing headspace trap as a sample introduction technique for GCMS analysis provides the laboratory with many advantages over traditional techniques. The headspace trap uses heat to extract (partition) the compounds from the sample into the headspace, this headspace is focused onto an adsorbent trap and rapidly transferred to the GC column.

Headspace trap technology provides laboratories the benefits of static headspace sampling, (no carry-over, no cross-contamination, no foaming, and ease of sample preparation) along with the detection limit improvement of a trap allowing a 80x to 100x improvement in sensitivity. This technology is capable of sampling the entire headspace, utilizing a pulsed pressure headspace extraction process followed by refocusing on an adsorbent trap. Additionally, headspace trap has the ability to extract analytes, while interferences remain in the sample matrix.

Presented will be quantitative results and detection limits for a list of low molecular weight alcohols, ketones, and ethers. Results including linearity, precision, and detection levels will be discussed.

INTRODUCTION

Low molecular weight alcohols, ketones, and ethers are of increasing interest to environmental monitoring programs nationwide. In environmental laboratories, it is with increasing frequency that these compounds are included in standard volatile organic analysis, under EPA method 8260. In environmental samples these compounds provide unique set of analytical challenges as a result of their high miscibility and/or solubility in water. Utilizing headspace trap as a sample introduction technique for GCMS analysis of fuel oxygenates provides the laboratory with many advantages over traditional techniques.

The Clean Air Act amendments of 1990 require that oxygenated compounds be added to gasoline to produce fuel with increased oxygen content. A number of different compounds can be used to oxygenate fuel, a list of the most common are: methyl-tert–butyl-ether, tert-amyl-methyl-ether, ethyl-tert-butyl-ether, tert-butyl alcohol, and ethanol. Oxygenated fuel is desirable because it burns more completely, thereby reducing tailpipe emissions. Currently, the most commonly used fuel oxygenate additive is methyl-tert-butyl-ether (MTBE). MTBE receives much scrutiny as a result of its widespread use as a fuel oxygenate and as a result of environmental concerns surrounding it. As a result of this some states are phasing out MTBE as a gasoline oxygenate.

The transportation, transfer, and storage of oxygenated fuel in underground tanks present an environmental a risk. Leaks and spillage can contaminate ground, surface, and waste waters; creating a significant opportunity for releases into the environment. The polar nature of fuel oxygenates creates contamination plumes that spread quickly and are difficult to control and remediate. Ground and surface water polluted with MTBE and other fuel oxygenates is widespread and poses a potential threat to human health.

The regulation of MTBE and the monitoring of other fuel oxygenates has created a need for a simple, robust, and reliable method to analyze low molecular weight alcohols, ketones, and ethers, in environmental samples. These compounds pose a series of challenges to traditional organic volatile analysis techniques, including poor purging efficiencies, cross contamination, and foaming. The headspace trap technique uses heat to extract (partition) the compounds from the sample into the headspace improving recoveries for many compounds that traditionally do not purge well. Additionally, the risk of contamination is dramatically reduced as the sample never contacts the instrumentation.

EXPERIMENTAL

Headspace Trap Theory and Technology

Headspace is a very well established sample introduction technique for GC analysis of volatile organic compounds. The use of headspace in environmental laboratories is limited by the need for lower detection limits. The combination of headspace with another very well established technique, thermal desorbtion, has allowed it to become applicable to the low level analysis demanded by the environmental industry today. To completely understand Headspace - Trap we must first look at classical (static) headspace. Within a headspace vial exists a partitioned system in which equilibrium must be met, equilibrium depends on the temperature of the system, the volume of the gas phase, and the volume of the sample phase. If the temperature, sample volume, and vial volume are constant you will have a number (K) that will directly describe the ratio a compound between the gas (headspace) and sample phase (equation 1).

Equation 1: Partition Coefficient

$$\mathbf{K = C^l/C^g}$$

K = Partition coefficient of a volatile

C^l = Concentration in the liquid phase

C^g = Concentration in the gas phase

Headspace analysis works best for compounds with low partition coefficient. A low partition coefficient represents a compound with a high concentration in the gaseous phase relative to its concentration in the liquid phase. If the temperature of the system is increased the partition coefficient of a compound will decrease, again a decrease in the partition coefficient represents an increase in its headspace (gas phase) concentration. In headspace the samples are heated and allowed to thermally equilibrate before sampling, to reach the maximum concentration of analytes in the gaseous phase.

The partition coefficient (K) can also be affected by the addition of salt to water samples. The salt is added directly to the headspace vial; the oven of the HS-trap can be fitted with an optional

shaker that will aid in diffusion of the salt in the sample matrix. The salt will act to decrease the partition coefficient of more polar compounds, further improving the quantitation limits. In this analysis many of the compounds are polar, and salting is a viable technique to improve recovery, however the data presented here does not utilize salting.

In classical headspace a small portion of the headspace is injected into the analytical column; the GC column has a limited flow rate, too long a sampling time will cause peak broadening and poor resolution. As a result, only a small percentage of the headspace volume can be sampled, in 8260 this is further limited by the gas flow into the mass spectrometer. Since a small percentage of the sample is injected a large dilution is unavoidable. The headspace trap technique eliminates this dilution; the entire headspace is passed across a cool thermal desorbtion trap. Allowing the collection of the entire sample; the maximum amount of the analytes of interest are collected and transferred to the column without overloading the carrier gas.

The elimination of the dilution effect can be pushed one step further with multiple headspace extractions. The vial can be repressurized, allowed to equilibrate, and the headspace collected, up to three more times. This acts as a concentration step improving detection limits one step further. The multiple headspace extraction technique was not necessary in the analysis presented here.

Once the headspace is collected on the adsorbent trap, the trap goes through dry purge with carrier gas to remove any residual moisture. Following sample collection and dry purge the trap is ballistically heated to desorb the analytes through the heated transfer line and into a tight band on the head of the analytical column. During the sample collection process, a column isolation flow keeps a constant flow down the column and into the mass spectrometer. The column isolation flow can also be utilized to keep the GCMS system free from air while maintenance procedures are performed on the headspace system.

Instrument Conditions

The instrumentation used in the technique was a PerkinElmer Clarus™ 500 GC/MS system is configured with a PerkinElmer TurboMatrix™ Headspace 110 Trap. The instrumental conditions are summarized in Table 1.

Table 1: Instrument Conditions Used for (Volatile) 8260 Analysis Presented in the Paper

HS-Trap Conditions	
Needle	90 °C
Transfer Line	120 °C
Vial Oven	80 °C
Trap Low	40 °C
Trap High	280 °C
Dry Purge	5 min
Trap Hold	5 min
Thermostat Time	10 min
Pressurization Time	1 min
Decay Time	2 min
Outlet Split	15 ml/min
Column Pressure	25 psig
Vial Pressure	35 psig
Desorb Pressure	10 psig

GCMS Conditions	
GC	PerkinElmer Clarus® 500
Oven Program	Initial Temperature: 40 °C
	Hold 0.0 minutes
	Ramp 1: at 10 °C/min to 100 °C
	Hold for 0.0 minutes
	Ramp 2: 30 °C/min to 240 °C
	Hold for 4 minutes
Column	Elite Volatiles - 30m x 250u x 1.4um
Mass Spectrometer	PerkinElmer Clarus® 500 MS
Mass Range	35-300 amu (full scan)
Transfer line Temperature	200 °C
Source Temperature	200 °C
Transfer Line Column	20m x 320µm

QA/QC Protocol

The analysis presented here was carried out following the QA/QC protocol of 8260. Method 8260 mandates that QA samples be analyzed on a GCMS system every 12 hours (called a "clock"). When the data presented here was collected each clock was initiated with a blank and BFB (Bromoflurorbenzene) injection, to verify the system integrity and mass spectrometer tuning. The BFB check is a background subtracted average of the three scans across the apex of the peak which is compared to EPA-specified ion ratio.

Method 8260 calls for a minimum of five calibration levels in the initial calibration. The calibration used in this application uses 6 – 8 points across a wider than average calibration range. A wide calibration range was chosen to allow laboratories to reach lower quantitation (reporting) limits, while still bracketing higher level samples, without dilution. Most compounds were calibrated from 0.5 µg/L to 200 µg/L, with TBA and 1,4 Dioxane at a decreased range (see Table 2).

To prepare analytical standards an intermediate stock solution was created in methanol; this was diluted in water to the final concentration of each curve point. The standards were added to 22mL headspace vials, with surrogates, and internal standards. In the case of the curves presented in table 1, no special techniques were employed, such as salting or multiple headspace extractions, to aid in recovery.

Table 2: Concentration Range and Percent Relative Standard Deviation for an Example List of Fuel Oxygenates via 8260

Calibration Compound	Low Standard Concentration	High Standard Concentration	%RSD
MTBE	0.5 µg/L	200 µg /L	10.80
TBA	10 µg/L	1000 µg /L	8.97
Diisopropyl Ether	0.5 µg/L	200 µg /L	7.67
ETBE	0.5 µg/L	200 µg /L	4.88
1,4-Dioxane	10 µg/L	150 µg /L	10.27
TAME	0.5 µg /L	200 µg /L	6.12

After calibration, the precision of the system was tested 5 duplicate standards were prepared, each was sampled twice to give 10 replicate analytical runs. The precision test standards were prepared in a similar fashion to the initial calibration standards. Internal standards and surrogates were added with a gas tight syringe by hand to each vial. The average concentration of the 10 duplicate injections was calculated and the percent relative standard deviation calculated. The percent relative standard deviation for all of the fuel oxygenates in this analysis was well below 10% (see table 3). This data shows that the sample introduction is very precise and reproducible.

Table 3: The Percent RSD of Relative Concentration over 10 Injections

Compound	% RSD (over 10 injections)
methyl tert butyl ether	5.03%
tert butyl alcohol	4.01%
Isopropyl ether	4.60%
ethyl tert butyl ether	4.01%
1,4-dioxane	6.66%
tert amyl methyl ether	4.49%

DISCUSSION

The combination of two commonly used analytical techniques, static headspace and thermal desorbtion, has provided an analytical method well suited for low level analysis of low molecular weight alcohols, ketones, ethers in environmental matrices. The increasing interest surrounding the environmental analysis of fuel oxygenates has created a need for the analysis of this class of compounds. Without modifying instrumental parameters optimized for a full 8260 analysis, we have shown it possibly to include a full list of fuel oxygenates using the technique presented here.

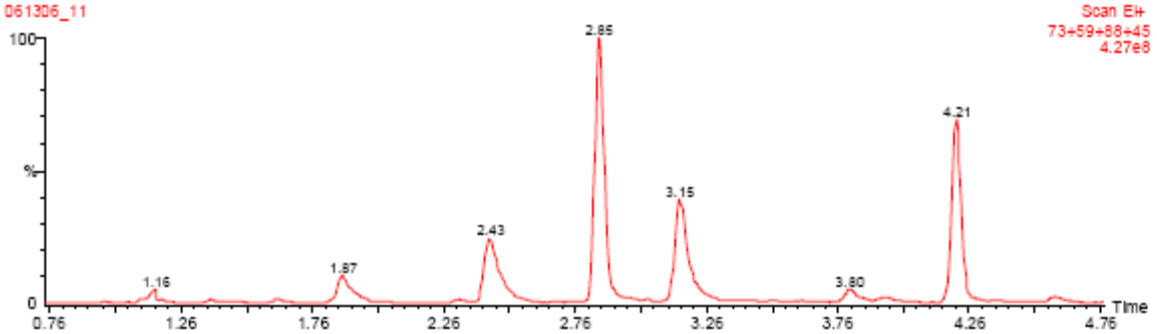


Figure 1: Composite Extracted Ion Chromatogram of Selected Fuel Oxygenates

The scale of chromatogram is skewed by the strong responding DIPE and 1,4-difluorobenzene an internal standard (4.21 min.). MTBE (2.43 min), DIPE (2.85 min), (ETBE 3.15 min).

The QA/QC criteria of 8260 have been adhered to, the integrated HS-Trap, GSMS system continuously meets the ion ratio criteria for BFB mandated by 8260. An initial calibration curve with 5 points or more shows excellent percent relative standard deviations across a wider than average calibration range.

CONCLUSION

Many states are requiring that laboratories include additional compounds in their 8260 list; very often these compounds are low molecular weight alcohols, ketones, and ethers. Typically laboratories are challenged to meet detection limits and QA/QC requirements on this extended list. Presented here is a simple method to provide an option for laboratories. The technology of the HS-Trap allows it to excel in the analysis of this class of compounds, as a result of a heated

headspace and the ability to sample the entire headspace on an adsorbent trap. Thus meeting the low detection limits imposed by many states and the QA/QC criteria mandated by 8260.

This technique provides the simplicity of headspace sample preparation, with an extremely low risk of cross contamination and sample matrix interference. Additionally, salting and multiple headspace extraction may provide the laboratory options for improved sensitivity if need be.

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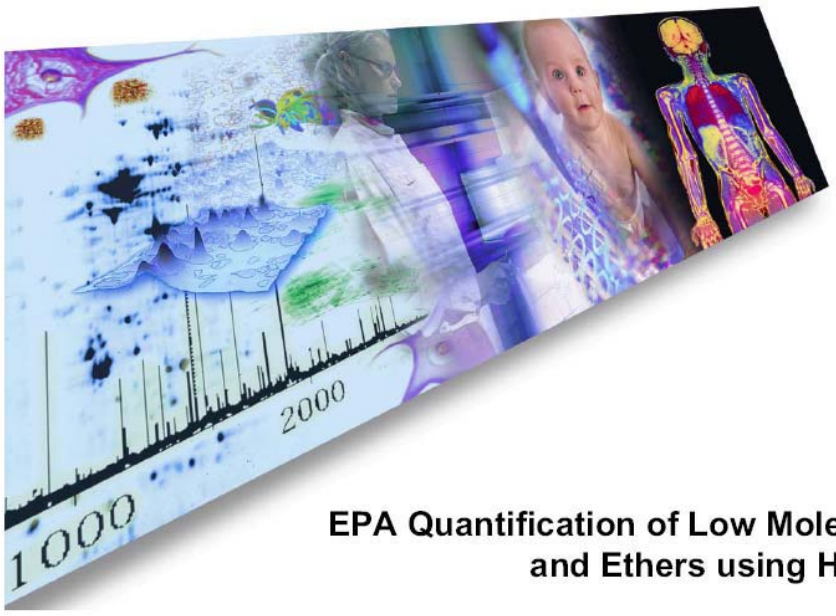
1. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)" U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 Method 8260B, revision 2, December 1996.

2. "Determinative Chromatographic Separations" U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 Method 8260B, revision 2, December 1996.

3. L. S. Ettre and B. Kolb "Static Headspace-Gas Chromatography", Wiley New York, 1997.



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EPA Quantification of Low Molecular Weight Alcohols and Ethers using Headspace Trap GC/MS

William Goodman
Applications Specialist

Heidi Grecsek
Product Manager GC/MS, Headspace

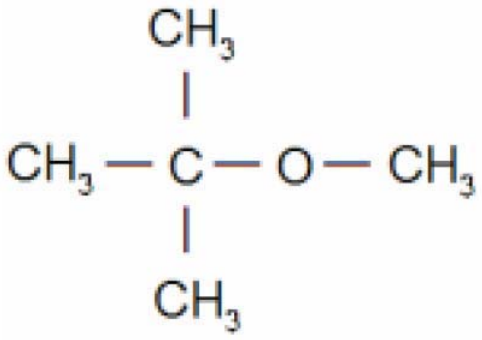
Summary

PerkinElmer® precisely.

- Why a simple, reliable, and quick method for quantification of these compounds is necessary?
- Headspace Theory and Trap Technology
- Quantification of low molecular weight alcohols, ketones, ethers, and other volatile organic compounds

Use of Low Molecular Weight Alcohols, Ketones, and Ethers

- A major use of this class of compound is Fuel Oxygenates
- The oxygenated fuel burns more completely in automobile engines, reducing tailpipe emissions
- The Clean Air Act of 1990 required the addition of oxygenated compounds to gasoline.
- The most commonly used fuel oxygenate additive is methyl tertiary butyl ether (MTBE).
- Other oxygenates include:
  - Tert-Amyl-Methyl Ether
  - Ethyl-Tert-Butyl Ether
  - Tert-Butyl Alcohol
  - Ethanol



Environmental Risks Associated with Fuel Oxygenates

- The transportation, transfer, and storage of oxygenated fuel in underground tanks presents a opportunity for release into the environment.
- A result of their more polar nature, fuel oxygenates are easily miscible and/or soluble in water.
- Thus leaks and spillage will contaminate ground, surface, and waste waters. The polarity will create waste plumes which spread rapidly and are difficult to control and remediate.
- Additionally many are believed to pose a potential threat to human health.

Regulatory Concerns

- Many states have regulations controlling acceptable levels of fuel oxygenates in ground, surface and waste water.
- MTBE is being phased out as a fuel oxygenate.
- Consequently, there is an increasing need for the analysis of fuel oxygenates in water.
- This technique describes the use of headspace with trap GC/MS for low level determination of fuel oxygenates by EPA Method 8260.
- This technique will provide a simple, robust, and reliable method to quantify a full list of VOCs, including an expanded list of ethers and alcohols.

Trap Theory and Technology Summary

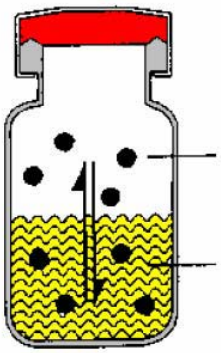
- Governed by the equilibrium headspace principle
- Headspace focused onto an adsorbent trap, allowing the collection of the 'whole' headspace
- Multiple cycle headspace extraction option
- Trap dry-purge to remove moisture

Equilibrium Headspace Principle

- Equilibration must be met.
- Must consider matrix (partition coefficient is matrix dependent)
- Sample must represent a partitioned system

$$K = C^l/C^g$$

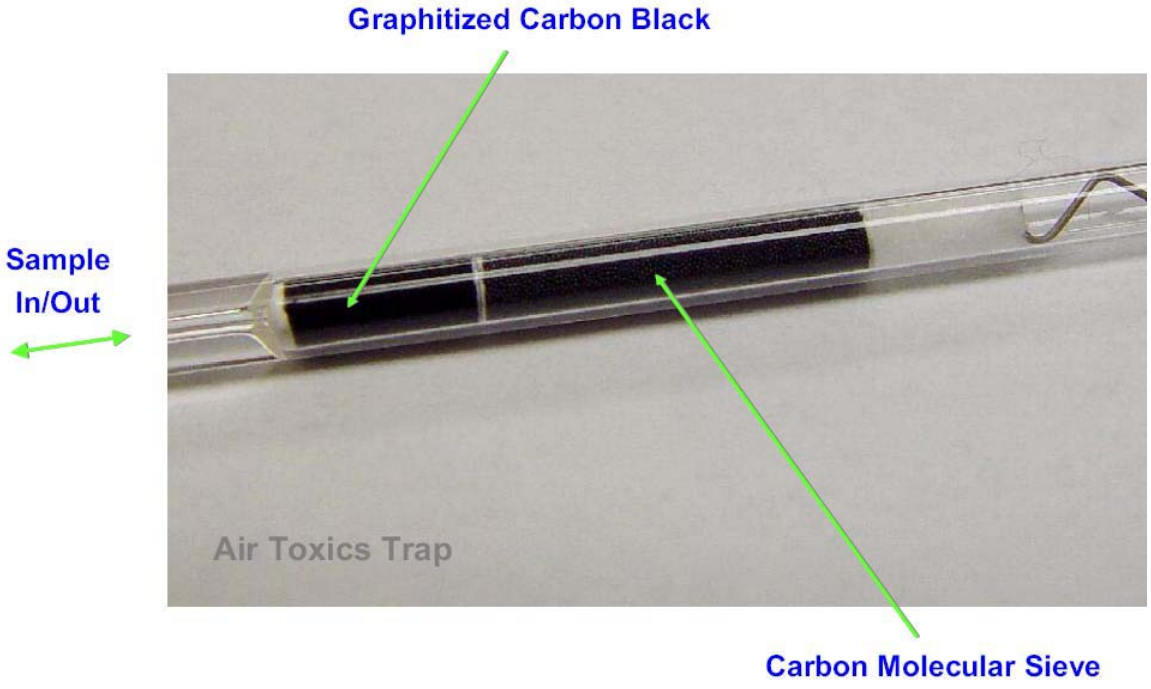
K = Partition coefficient of a volatile
Cl = Concentration in the liquid phase
Cg = Concentration in the gas phase



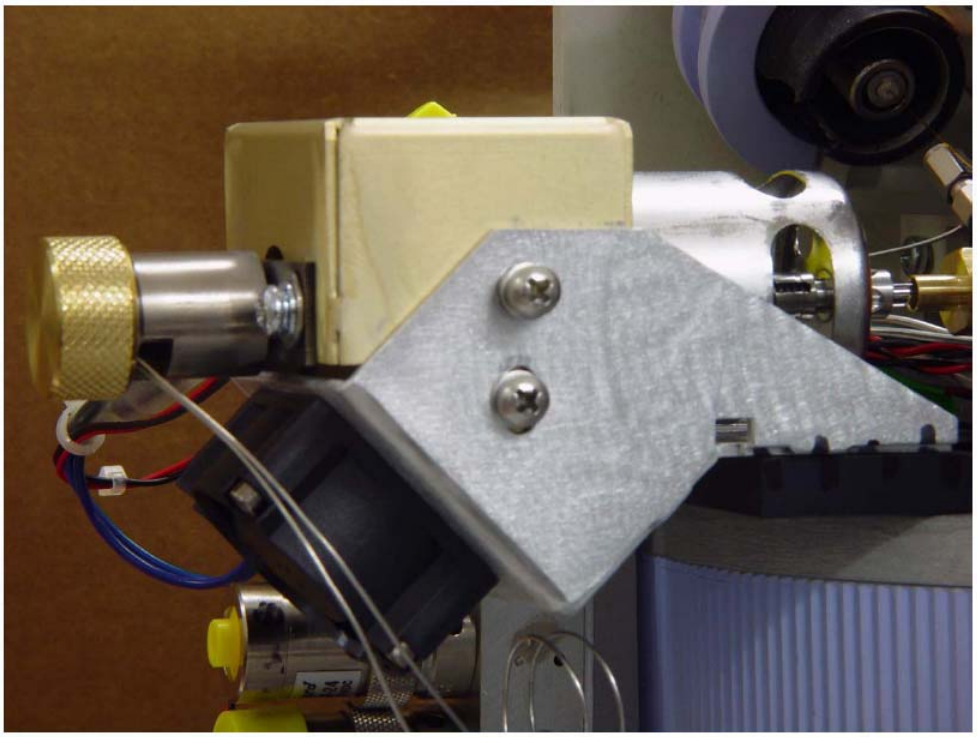
Partition Coefficients in Water

COMPOUND	50 °C	60 °C	80 °C
ETHANOL	1220	630	240
n-PROPANOL	520	350	150
IPA	445	250	120
t-BUTANOL	280	150	60
ACETONE	270	110	55
ETHYL ACETATE	42	30	18
BENZENE	1.2	0.4	0
TOLUENE	0.8	0	0
TRICHLOROETHYLENE	0.7	0	0

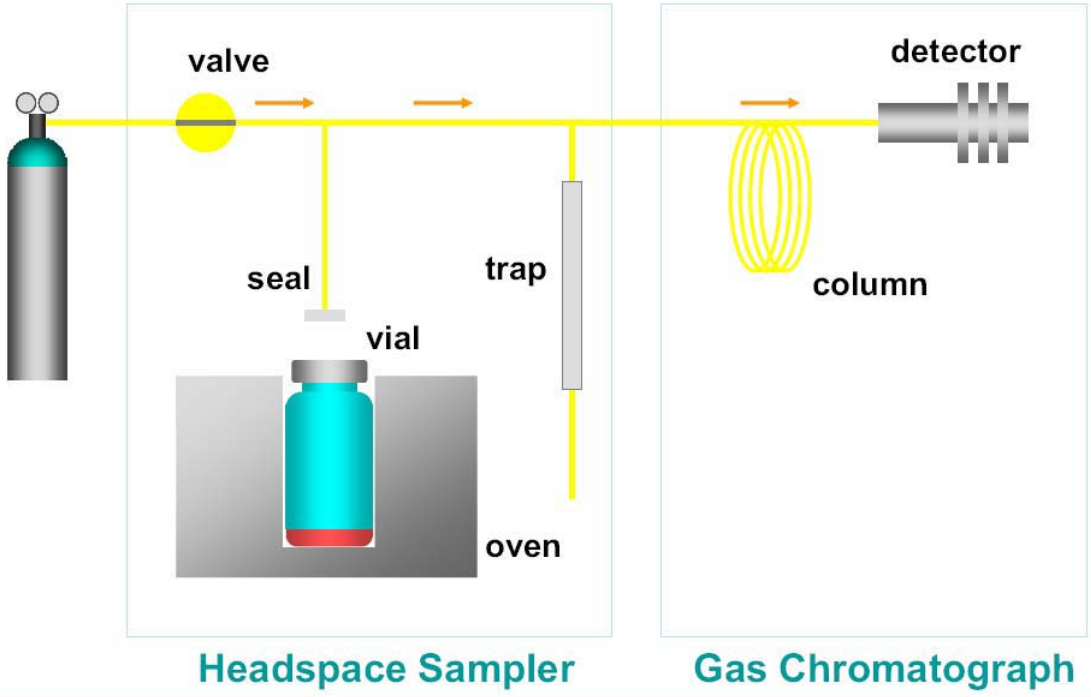
Air Toxics Trap



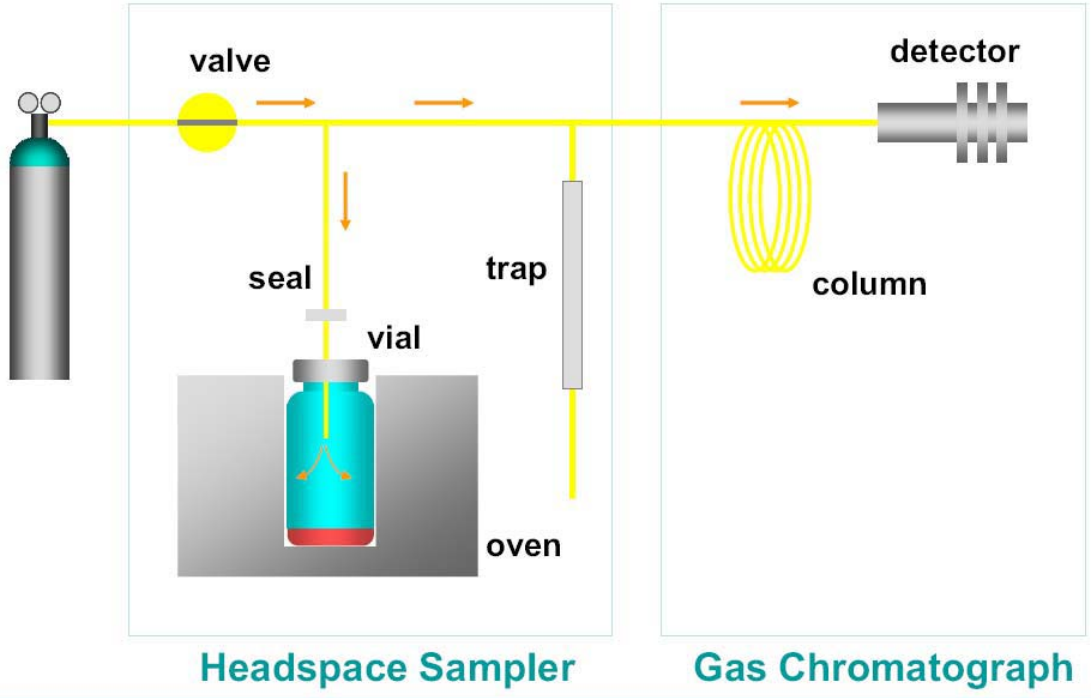
The Trap



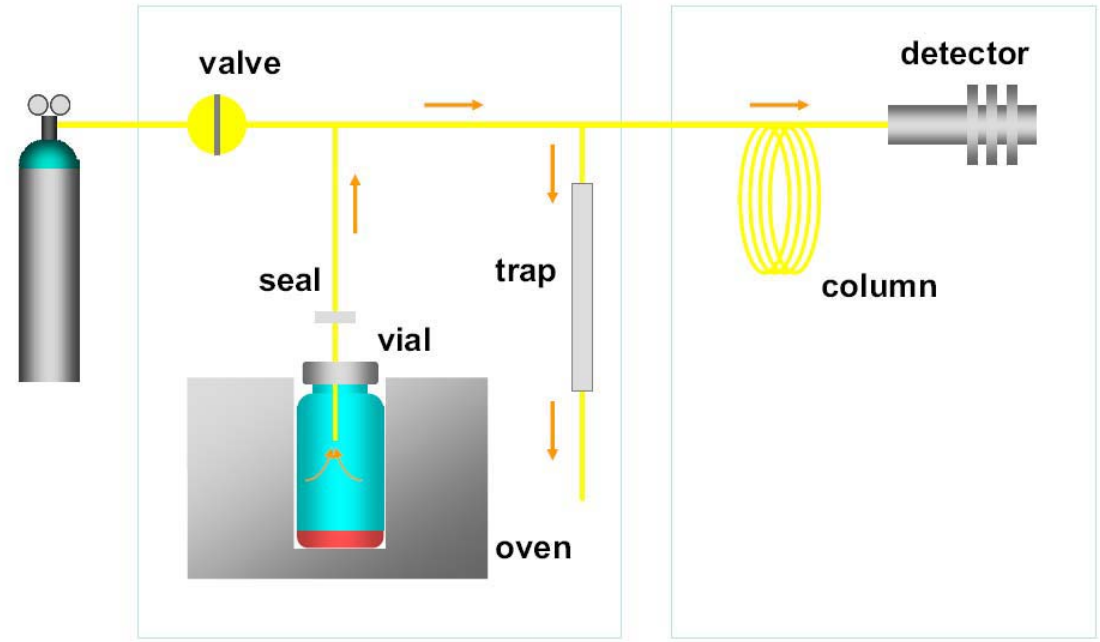
Sample Vial Thermal Equilibration



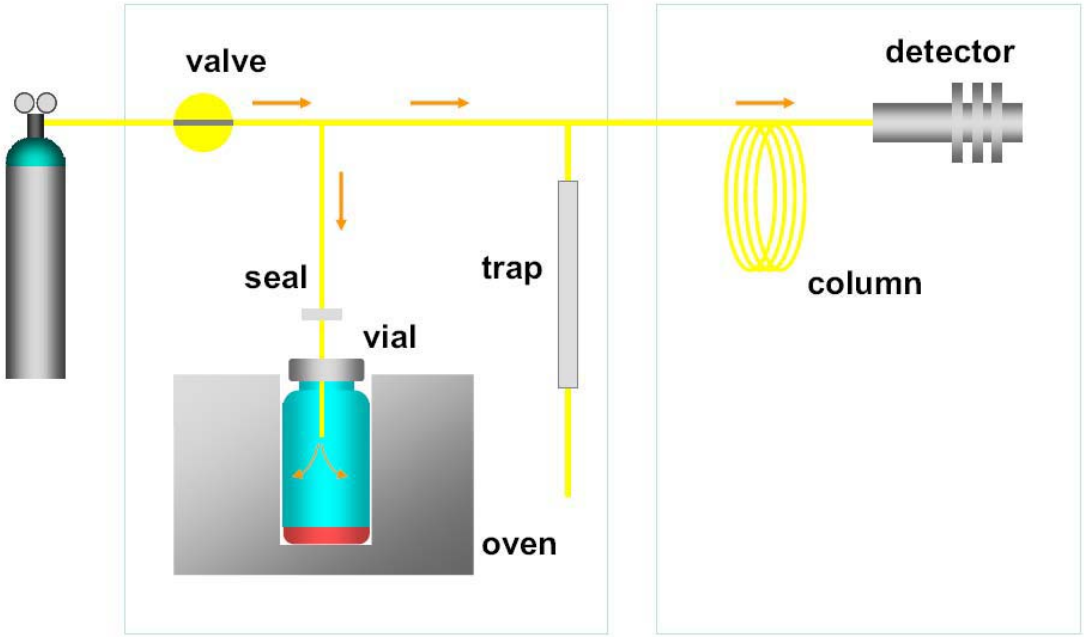
Vial Pressurization



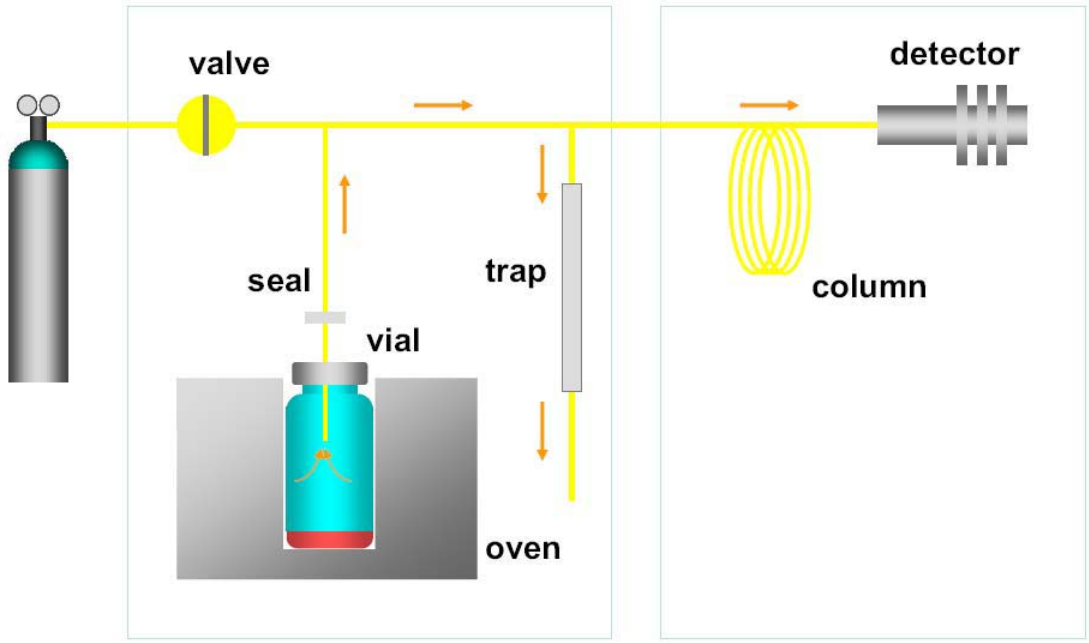
Trap Load



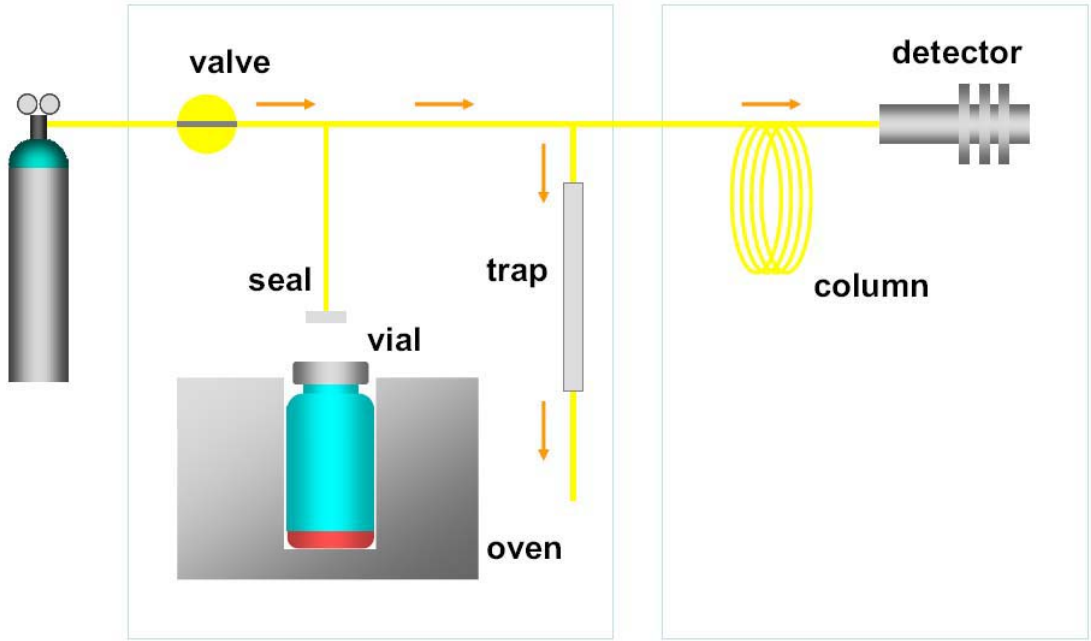
Vial Re-Pressurization



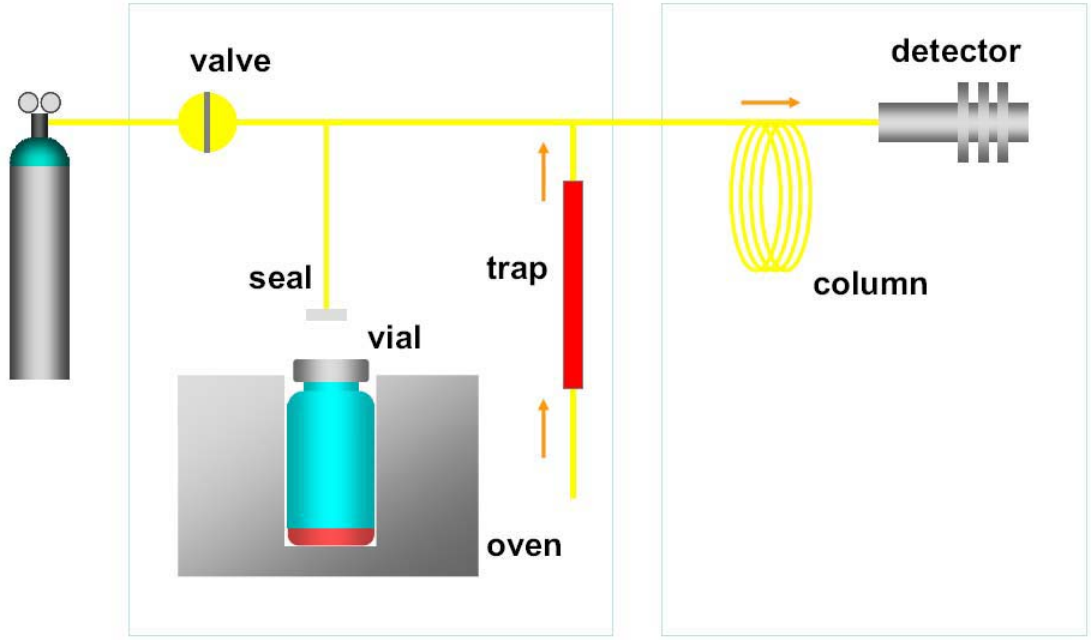
Trap Re-Load



Dry Purge



Trap Desorption



Advantages of Headspace with Trap

- The ease of Headspace sample prep with lower minimum detectable levels
- One instrument will extract and concentrate the headspace
- Dry purge removes moisture
- Recovers VOCs that have low purging efficiencies
- Water, waste, and soil analysis flexibility

Headspace Trap Parameters

Needle Temperature	90 °C
Transfer Line	120 °C
Oven	80 °C
Trap Low	40 °C
Trap High	280 °C
Dry Purge	5 min
Trap Hold	5 min
Thermostat Time	10 min

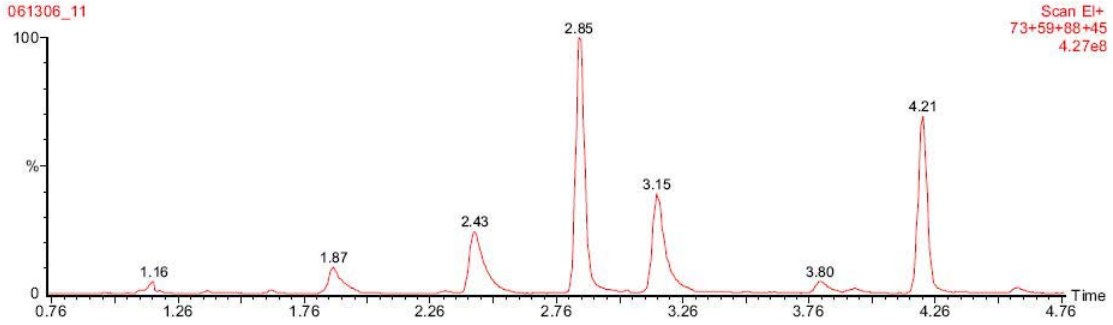
Pressurization Time	1 min
Decay Time	2 min
Outlet Split	15 ml/min
Column Pressure	25 psig
Vial Pressure	35 psig
Desorb Pressure	10 psig
Transfer Line Column	Deactivated Fused Silica 20m x 320um

GC/MS Parameters

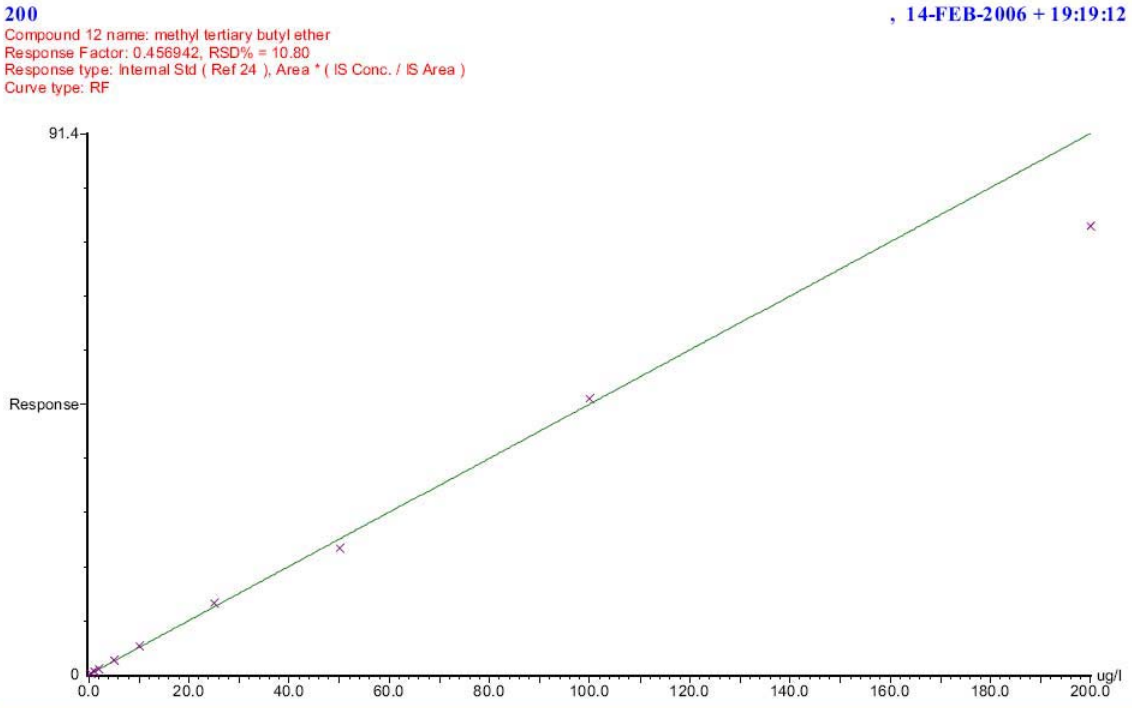
GC	**PerkinElmer Clarus® 500**
Oven Program	**Initial Temperature: 40 °C** **hold 0.0 minutes** **Ramp 1: at 10 °C/min to 100 °C** **hold for 0.0 minutes** **Ramp 2: 30 °C/min to 240 °C** **hold for 4minutes**
Column	**Elite Volatiles - 30m x 250u x 1.4um**
Mass Spectrometer	**PerkinElmer Clarus® 500 MS**
Mass Range	**35-300 amu (full scan)**
Transfer line Temperature	**200 °C**
Source Temperature	**200 °C**

Fuel Oxygenate Chromatogram

- Composite extracted ion chromatogram of selected fuel oxygenates
  - MTBE (2.43 min)
  - DIPE (2.85 min)
  - ETBE (3.15 min)

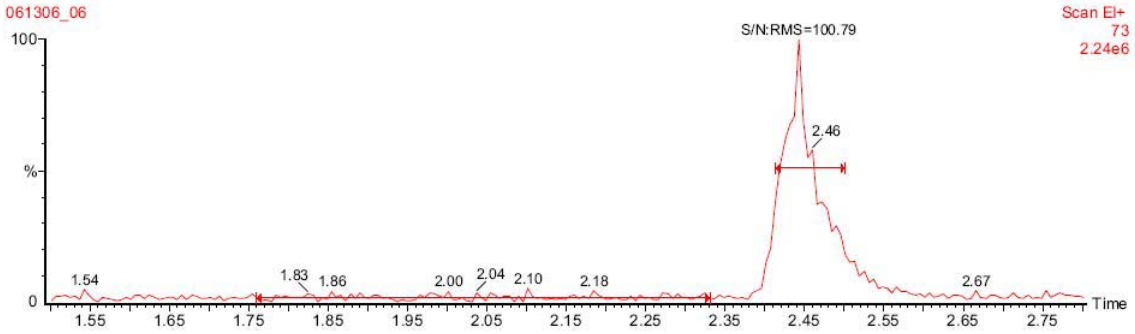


MTBE Calibration (0.5 – 200 ppb)

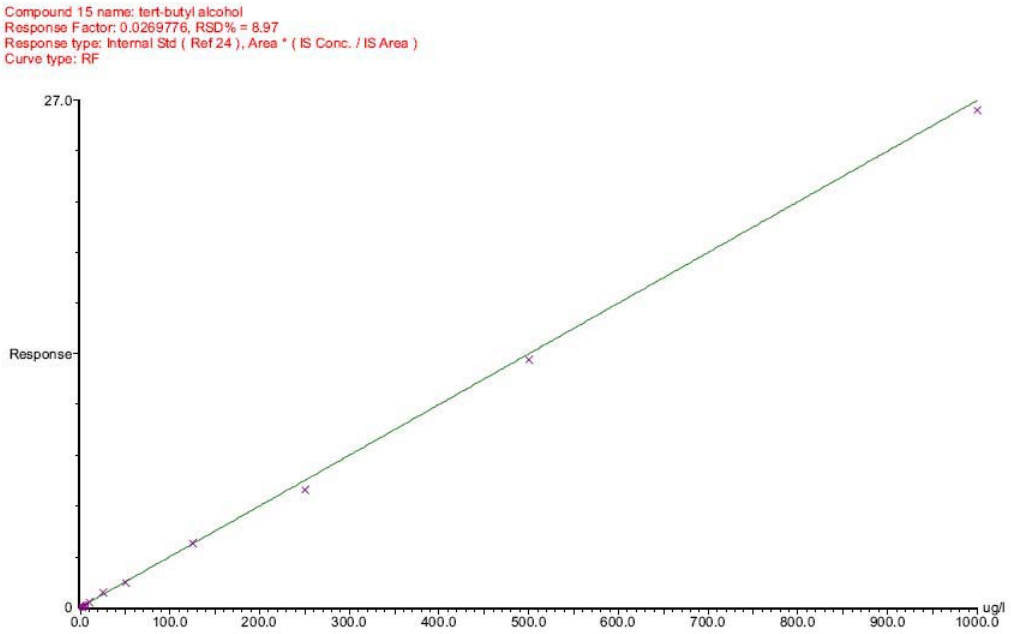


MTBE Chromatogram - 1 ppb

- RMS Signal to noise of 100:1
- Greater than 30 scans across the peak

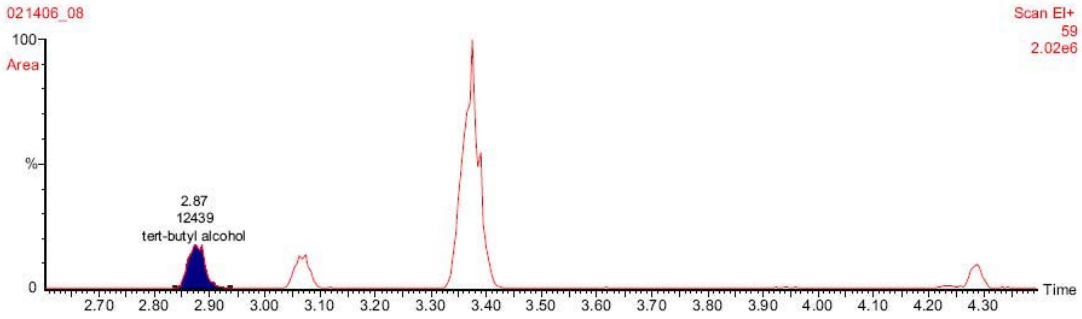


TBA Calibration (10 – 1000 ppb)

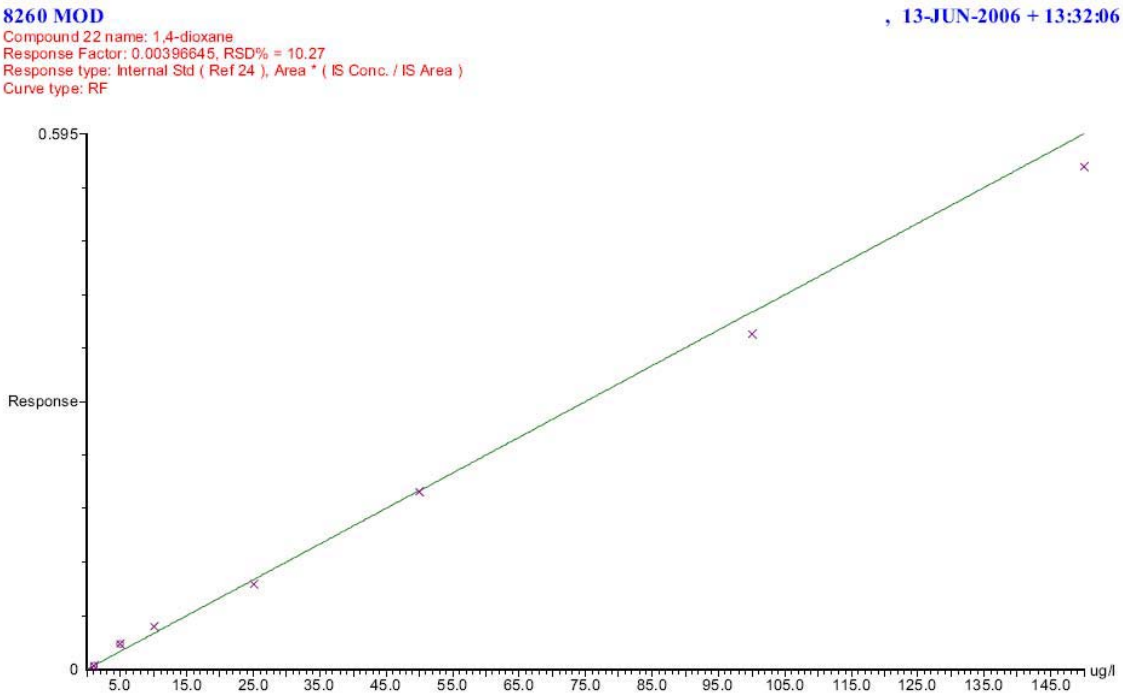


TBA Chromatogram - 10ppb

- **RMS signal to noise of 290:1**

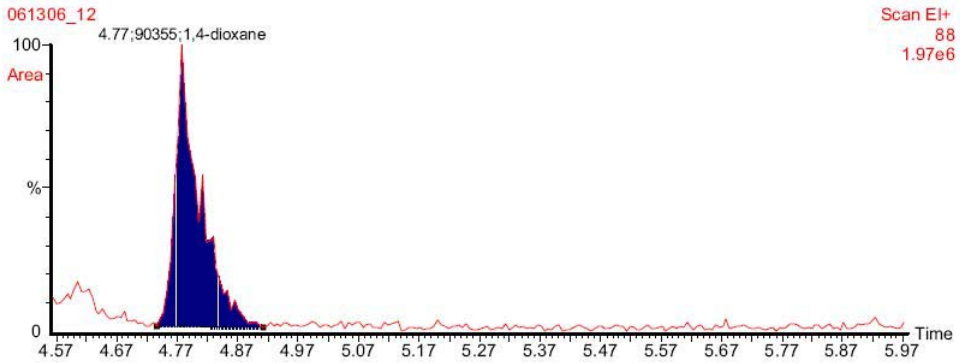


1,4 – Dioxane Calibration (10 - 150 ppb)

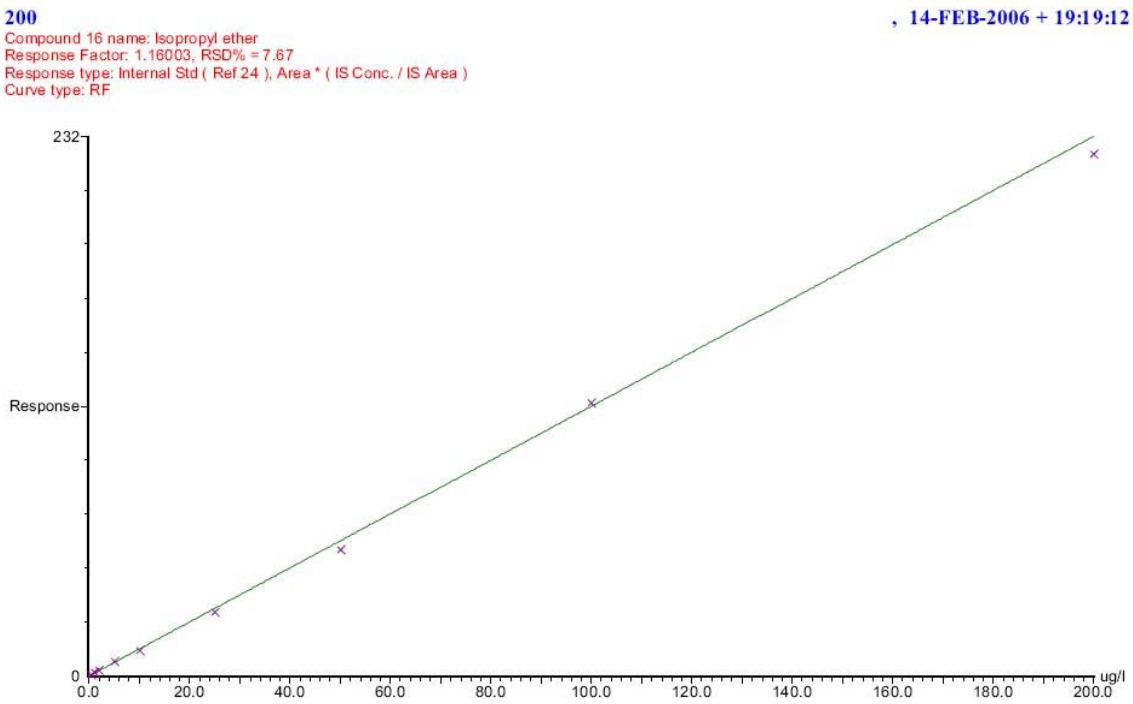


1,4-Dioxane Chromatogram - 100ppb

- RMS Signal to Noise of 150:1
- 25 scans across the peak

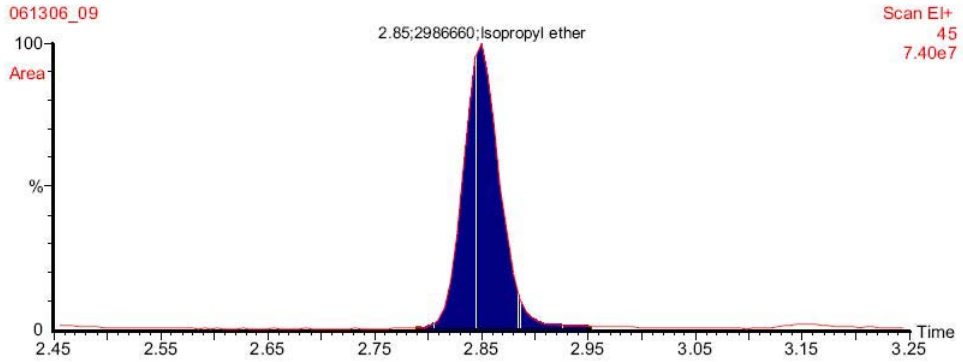


Diisopropyl Ether Calibration (0.5 – 200 ppb)

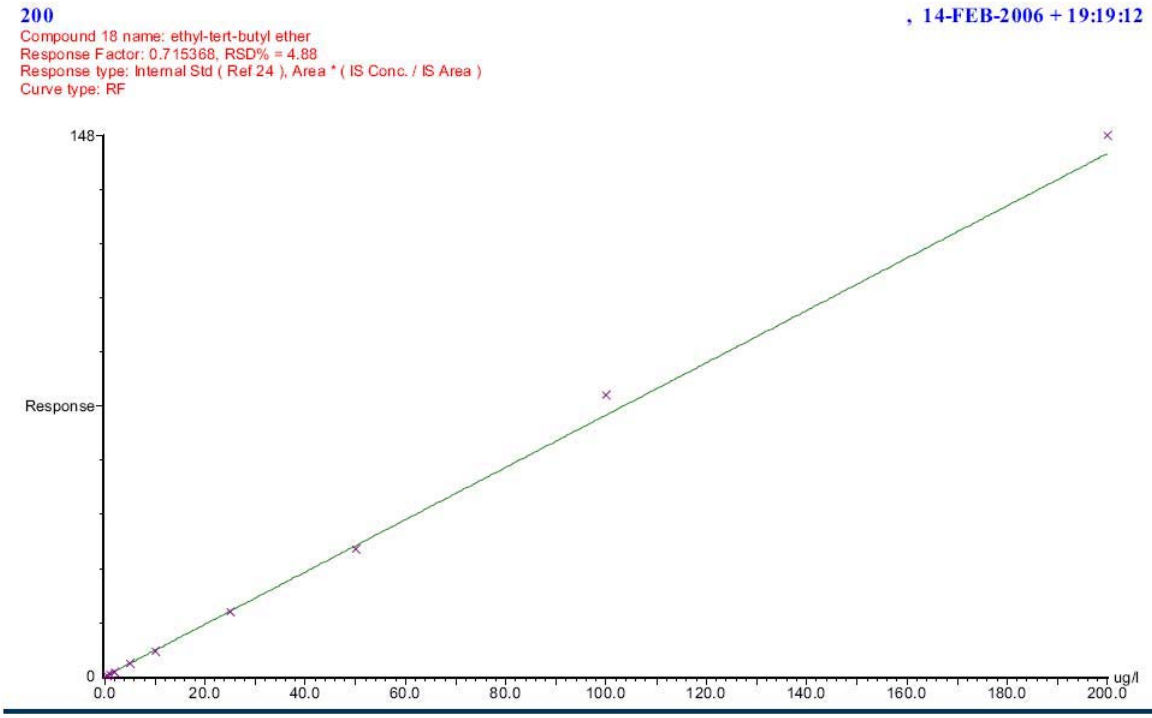


Diisopropyl Ether Chromatogram - 10ppb

- RMS Signal to noise of greater than 1200:1
- Greater than 20 scans across the peak

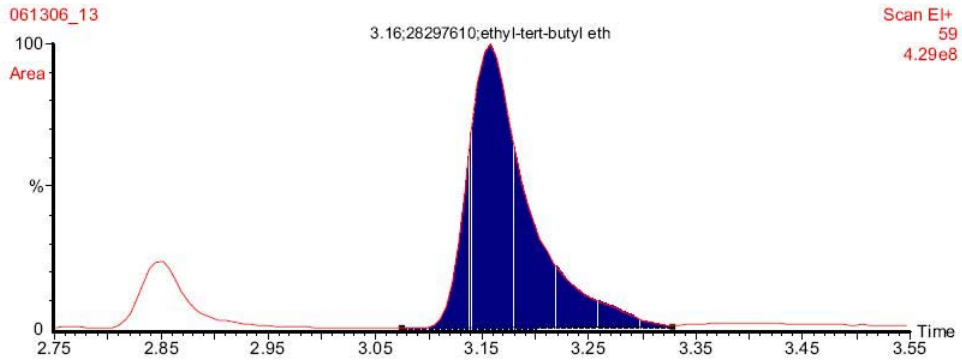


Ethyl Tert Butyl Ether Chromatogram (0.5 to 200 ppb)

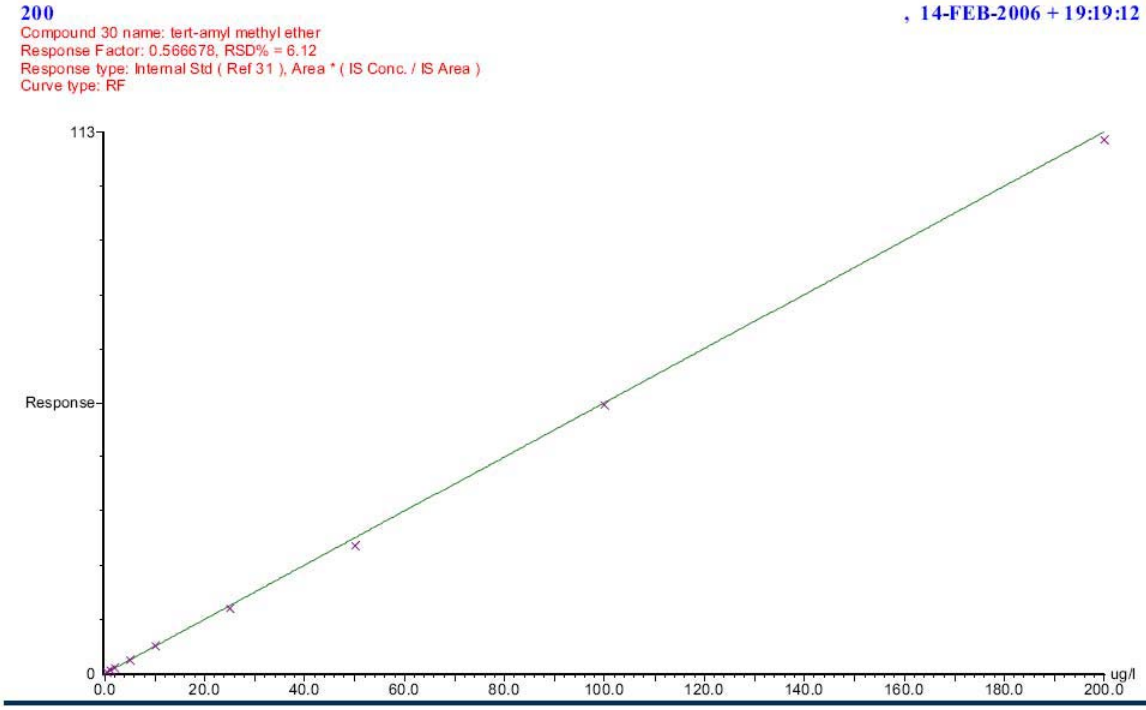


Ethyl Tert Butyl Ether Chromatogram - 150ppb

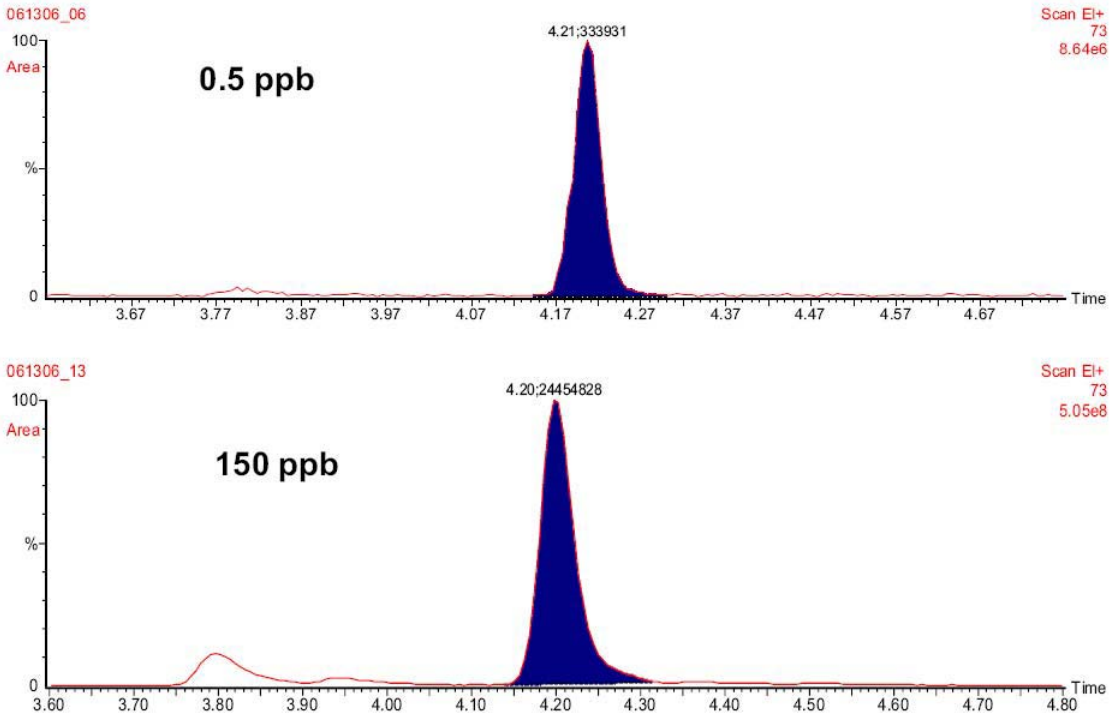
- At 150ppb, curve remains linear and peak shape does not show saturation



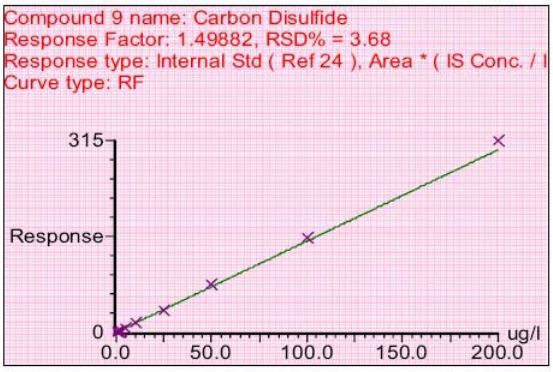
Tert Amyl Methyl Ether Calibration (0.5 to 200 ppb)

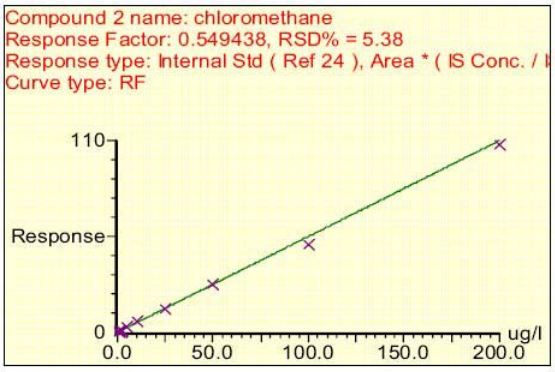


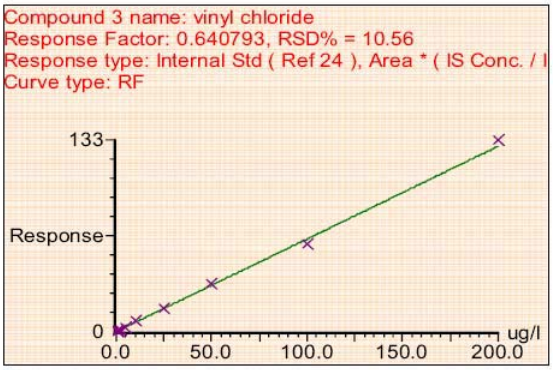
Tert Amyl Methyl Ether Chromatogram – 0.5 & 150ppb

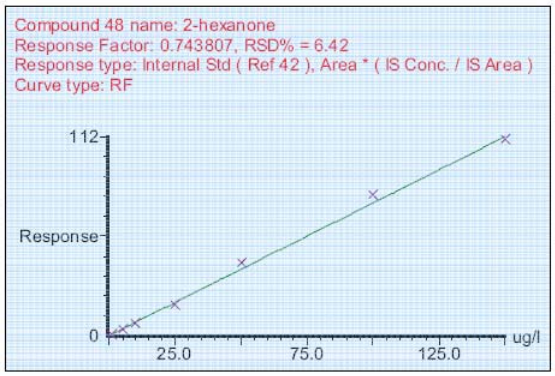


Calibration Curves





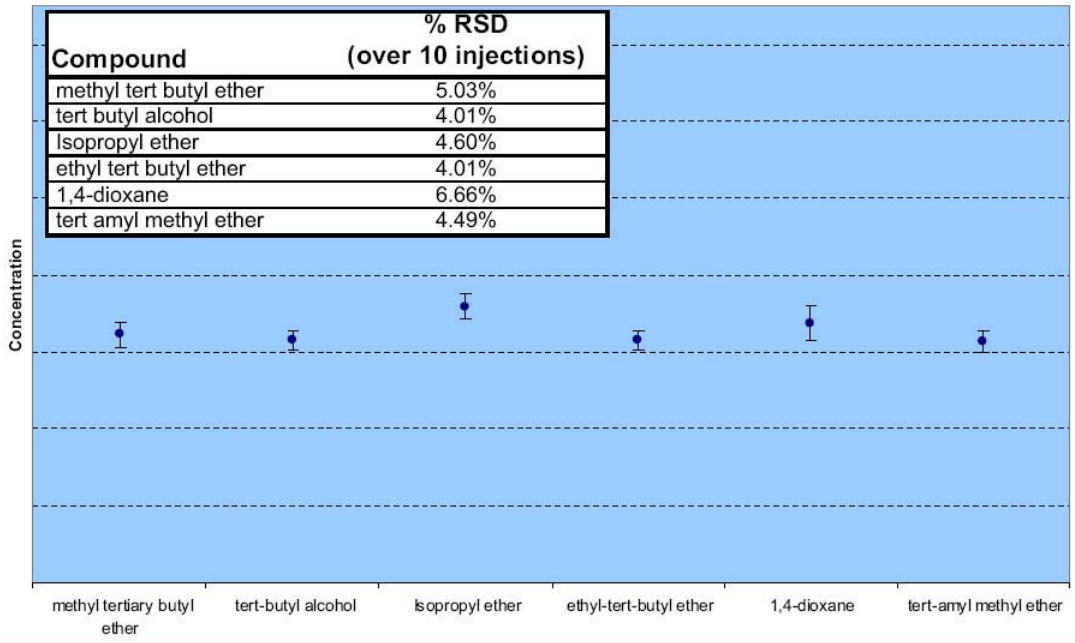




Precision Study

Average Concentration and Standard Deviation of 10 Injections (~70 ppb)
(Error Bars Represent 1 Standard Deviation)

Compound	% RSD (over 10 injections)
methyl tert butyl ether	5.03%
tert butyl alcohol	4.01%
Isopropyl ether	4.60%
ethyl tert butyl ether	4.01%
1,4-dioxane	6.66%
tert amyl methyl ether	4.49%



Conclusions

- **This technique for 8260 analysis passes QA/QC requirements**
  - **BFB - Instrument tuning**
  - **Initial calibration**
  - **Precision**
- **In addition the it offers other advantages:**
  - **Easy sample preparation**
  - **Simple robust analysis**
  - **Options for analyzing difficult components at low levels**

Variables in Lipids Analyses and Affect on Data Quality

Craig Hutchings and Ann K. Bailey
EcoChem, Inc.

ABSTRACT

The methodology for the determination of "percent lipids" in tissues is often not specified nor described in study protocols even though "percent lipids" results are commonly used to normalize contaminant data. Any errors or differences in the determination of percent lipids will be propagated throughout a study of biota-sediment accumulation factors (BSAF), undermining the quality or comparability of contaminant data. In many environmental laboratories "percent lipid" results are simply gravimetric determinations of the residue after solvent extraction of the tissue, and better labeled as total extractable organics (TEO). While laboratories evaluate the extraction efficiencies for contaminants, the extraction efficiency of lipids from tissue is many times not considered. However, lipids results can vary significantly depending on the method of extraction and the solvents used. Various methods for the determination of percent lipids (or TEO), and the use of reference materials (RM) to evaluate the uncertainty and comparability of lipids or TEO measurements will be discussed.

INTRODUCTION

The term lipid is used to describe a broad range of compounds that include fats, oils, waxes, sterols, and triglycerides and are used by organisms to store energy and in cell structures. Lipids exist within tissues in many forms, and the majority of organic contaminants are associated with two major forms referred to as the neutral pool and the membrane bound pool (*1*).

In environmental contaminant studies lipids are commonly used in assessing the bioaccumulation of organic compounds. The concentrations of contaminants in tissues are normalized to the percent lipids of the tissue and these normalized values are compared to sediment contaminant levels that have been normalized to total organic carbon (TOC) to develop biota/sediment accumulation factors (BSAF). These BSAF may be used in modeling the impact of contaminated sediments on organisms coming in contact with the sediment. One example is the use of BSAF in assessing the suitability of disposal of dredged sediments in deep water areas (*2, 3*). Lipid content is also frequently used in the food web modeling studies assessing the transfer of contaminants from one trophic level to another (*4*).

Many times little attention is paid to the analytical methodology used for determining lipids. Study protocols and academic papers frequently specify in detail the methods used for the determination of the contaminants, the technique used to determine percent lipids is rarely specified. Furthermore, no standard method for lipids, determination exists leaving laboratories with little guidance. Various studies (*5, 6*) have found that the use of different extraction solvents and methods will deliver different results for lipids and these differences can have significant affects on the comparability and usefulness of the data.

DISCUSSION

There are two common types of analytical errors that can apply to the analysis of lipids: 1) analytical bias, which can cause problems with comparability to other data sets; and 2) inconsistent application of methodology causing imprecise results. Analytical bias can be caused by the use of differing extraction solvents, extraction equipment, and/or methods which are inappropriate for the matrix. Inaccurate or imprecise lipids data can be caused by improper application of the extraction equipment or improper laboratory techniques.

Analytical Bias

The lipids pools described above each have different extraction requirements. The neutral pool is best extracted using non-polar or semi-polar solvents while the membrane bound pool requires a mixture of polar and non-polar solvents (*1*). Several factors influence with pool environmental contaminants are associated with including chemical structure, the species, the tissue type, such as muscle, viscera, skin, etc. The association to these pools can also vary by season and physical and chemical stresses on the organism can also affect the association (*5*).

Lipids concentrations are usually determined by extracting the tissue with one or more solvents and allowing this extract to evaporate at room temperature. The weight of any residue remaining after evaporation is divided by the weight of the tissue extracted and expressed as percent lipids. The value determined by this technique is better described as total extractable organics (TEO) as it is strictly gravimetric as no distinction is made between lipids or any other residue remaining after evaporation. This gravimetric determination is usually performed on a portion of the extract that is used for the contaminant analysis. And while laboratories can go to great lengths to optimize and validate their procedures for the recovery of contaminants through the use of spiked matrices and reference materials, it is not common, nor always practical, to do so for TEO.

In the absence of a standard method it is commonly suggested that whatever technique is used for the determination of lipids be compared to the Bligh Dyer method (*5, 7*) by performing separate analyses on a subset of the samples. However, due to limitations in sample size and additional costs this comparison is not often performed. The U.S. Environmental Protection Agency (*8*) recommends methylene chloride as extraction solvent for all lipid analyses, however under USEPA prescribed or performance based methods laboratories may use a wide variety of extraction techniques and solvents for the contaminant analysis. These extraction techniques and solvents are summarized in Table 1.

Not all of the listed extraction techniques and solvents in Table 1 are equally efficient at extracting all types of lipids Studies (*5, 9*) have found differences of up to three fold resulting from the use of different extraction solvents. As far as extraction techniques, studies (*6, 10*) have indicated that soxhlet does not always yield complete lipid extraction. Validation of a method focusing only on chemical pollutants may miss potential problems in extracting lipids.

Other factors affecting lipid results are sample size (*11*), the type of species and the tissue type being analyzed (*5, 8*). As mentioned above, Randall (*5*) has shown that at different times contaminants may be associated with one lipid pool at one time but this association can change based on where the organism is in its reproductive cycle, the time of year, and any stresses placed on the organism. These variations make it exceedingly difficult to adequately evaluate an

extraction method for what may have worked initially may not be applicable to other species or other seasons.

As an example of analytical bias, a data set of total DDT (defined as the sum of 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE. 2,4′-DDT and 4,4′-DDT) and total PCB homologues results from the analysis of a fish tissue of a single species is provided in Table 2, and the lipid corrected data is provided in Table 3. These tables provide example contaminant and lipid results for the same set of fish fillet samples from an initial analysis and subsequent re-analysis. The initial set of results was obtained after the laboratory's standard extraction methodology, based on EPA Method 8270C (*12*) and applied to DDTs and PCB congeners. The second data set was reported after refining the extraction procedures. While the results that have not been lipid corrected are relatively similar for the two data sets (Figures 1a and 1b), the lipid corrected results have much greater differences (Figures 1c and 1d). Figure 2 illustrates the differences between the lipid results (as TEO) before and after method refinement.

Imprecise Results

Because lipids analysis is simply a gravimetric technique, many times the importance of implementing careful and consistent techniques is not considered as critical as the more complex aspects of analytical methodologies. Thus, the more experienced analyst usually will be found performing the instrumental analysis involving, for example, mass spectrometry, while the "simple" measuring and weighing process for lipids is assigned to a less experienced analyst. However, this gravimetric measurement can involve as little as 100 microliters of solvent, and the weighing of residues as little as 1 milligram.

Care must be taken that the solvent measurement process is accurate and consistently performed. Potential sources of error can be:

- Syringe not calibrated,
- Inconsistent reading of sample volume,
- Inconsistent delivery of sample volume.

When measuring such small quantities consistent technique is critical. Even a change in humidity or minor drift of the balance can significantly affect the results.

For most analytical methods, quality control is assessed on a batch by batch basis by the analysis of a spike or blank spike for accuracy; and a duplicate or matrix spike duplicate for precision. Because lipids are a multi-component determination, the mixing and spiking of representative material is not readily performed. Thus matrix spikes (MS) are not usually performed for lipids. Also, the accuracy of lipids results in blank spikes or laboratory control samples (LCS) many times are not assessed, rather the focus of the quality control checks is for the contaminants of concern. So, unless a reference or control material with a known concentration of lipid is specified as a quality control check there may be no method for independent assessment of accuracy.

As far as an assessment for precision, duplicate analysis usually provides only a measure of precision for one sample every batch. If only a few samples or batches are analyzed, poor

precision may be documented, but from the analysis of only a few samples it is difficult to assess the significance of poor replication. Thus, standard quality control checks many times do not provide enough information to assess the accuracy and precision of lipid analysis. A reference or control material similar in matrix to samples being analyzed can be most useful in determining the quality of the lipid results (*13*).

Figure 3 is a summary of the lipid results for NIST SRM1946, Lake Superior Fish Tissue, which accompanied the analysis of 37 batches of fish fillet samples. The data used in the examples above are from this dataset. For these batches the LCS, MS, and laboratory duplicate data was generally very good indicating adequate accuracy and precision for the contaminant data. The contaminant data from the reference material was also generally very good. However, the results from the reference material lipids analysis were not as good. The initial analysis data was seemingly random, being both inaccurate and imprecise. Based on this observation the laboratory performed further method development and subsequently performed re-analysis.

CONCLUSION

While it is common for quality assurance project plans (QAPP) and other project set up documents to specify in great detail how samples are to be collected and analyzed for the primary target analytes, rarely is the method for the determination of lipids specified. However, there can be much variability in lipids values depending on how the value is determined. A 3 to 5 fold variation in lipids values can mask patterns that may be present in the contaminant data, or mis-identify correlations.

Because lipid results are used many times to normalize contaminant data from tissue analysis, it is important that quality control of the test method be more consistently performed. This can be improved by: 1) A standard method for lipids, or TEO, should be agreed upon and clearly specified during project planning that involves tissue analyses. Extraction procedures and solvents should be specified and methods clearly described in the laboratory Standard Operating Procedures (SOPs). As for any other performance-based methodology, the lipid analysis should be validated using a reference tissue similar in matrix to the tissue of interest. 2) An analysis of a control or reference materials for lipids should be incorporated into the quality control samples with each analytical batch. The analysis of a laboratory duplicate alone cannot provide enough information regarding overall precision and accuracy.

Table 1: A Sampling of Methods used for the Determination of Percent Lipids

Method	Primary Target Analytes	Extraction Technique	Solvent(s)
SW-846 8081/8082	Pesticides/PCBs	Soxhlet or Pressurized Fluid Extraction (PFE) or Sonication	Hexane/Acetone (1:1) or Methylene Chloride/Acetone (1:1)
SW-846 8290	Dioxins/Furans	Soxhlet	Methylene Chloride or Hexane/Methylene Chloride (1:1)
1668a	PCB Congeners	Soxhlet	Hexane/Methylene Chloride (1:1)
1613	Dioxins/Furans	Soxhlet or HCl Digestion	Hexane/Methylene Chloride (1:1)
Bligh-Dyer	Lipids	Tissuemizer	Chloroform/Methanol (1:2) then Chloroform then DI Water
Performance Based Methods	Pesticides/PCBs	PFE	Methylene Chloride
	Pesticides/PCBs	Shaker Table	Methylene Chloride/Acetone (1:1)

Table 2: Data from Initial and Re-Analyses

Sample	Initial Analyses			Re-analyses		
	%Lipids (TEO)	Total DDTs (ng/g)	Total PCB Homologues (ng/g)	%Lipids (TEO)	Total DDTs (ng/g)	Total PCB Homologues (ng/g)
1	0.19	701	110	0.39	657	89.3
2	0.09	120	44.8	0.21	154	25.5
3	0.10	324	105	0.30	456	63.7
4	0.06	457	65.6	0.21	617	74.3
5	0.08	115	48.4	0.29	171	31.3
6	0.08	110	51.6	0.31	191	35.6
7	0.02	66.7	31.7	0.09	62.3	17.4

Table 3: Lipid Corrected Data

Sample	Initial Analyses		Re-analyses	
	Total DDTs (ng/g lw)	Total Homologues (ng/g lw)	Total DDTs (ng/g lw)	Total Homologues (ng/g lw)
1	3690	579	1680	230
2	1330	498	733	121
3	3240	1050	1520	212
4	7620	1090	2940	354
5	1440	605	590	108
6	1380	645	616	115
7	3340	1580	692	193

Figure 1a: Comparison of Total DDT Results
Not Normalized to Lipids

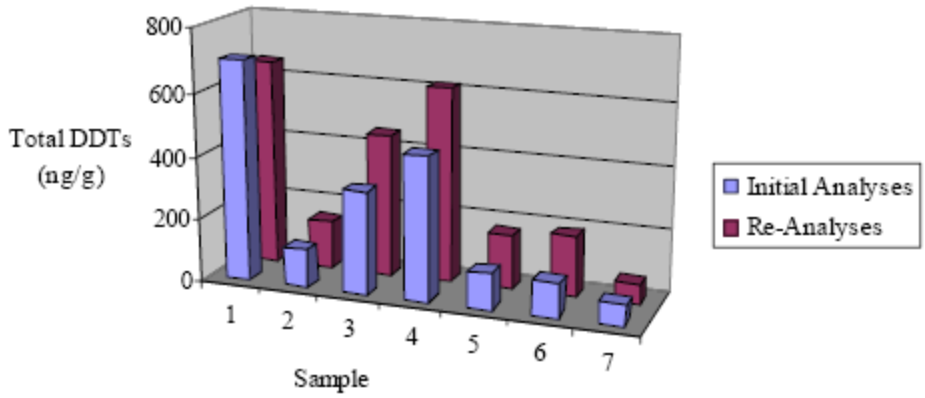


Figure 1b: Comparison of Total PCB Homologue Results
Not Normalized to Lipids

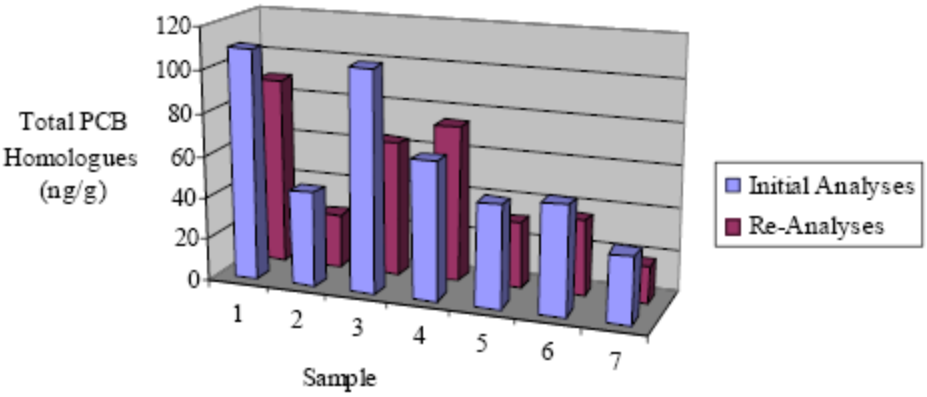


Figure 1c: Comparison of Total DDT Resuls
Lipid Normalized

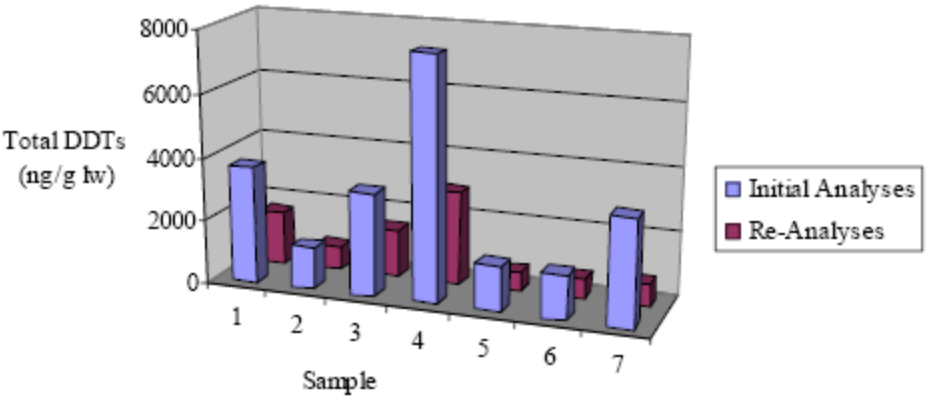


Figure 1d: Comparison of Total PCB Homologue Results
Lipid Normalized

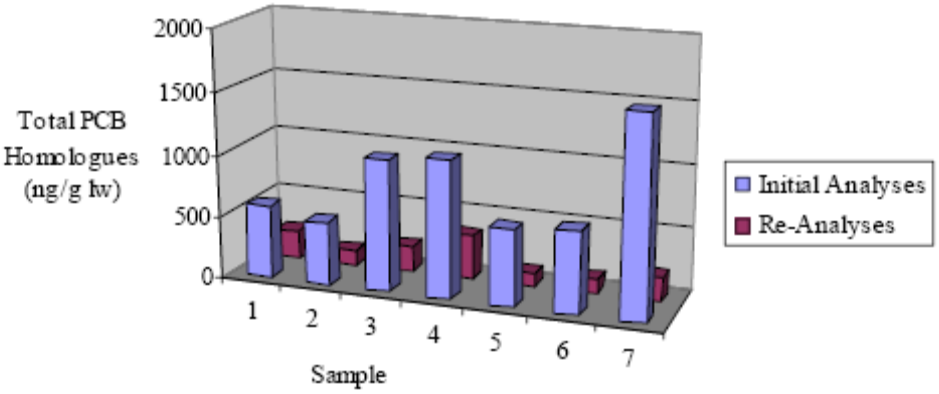


Figure 2: Comparison of Percent Lipids (TEO) Results

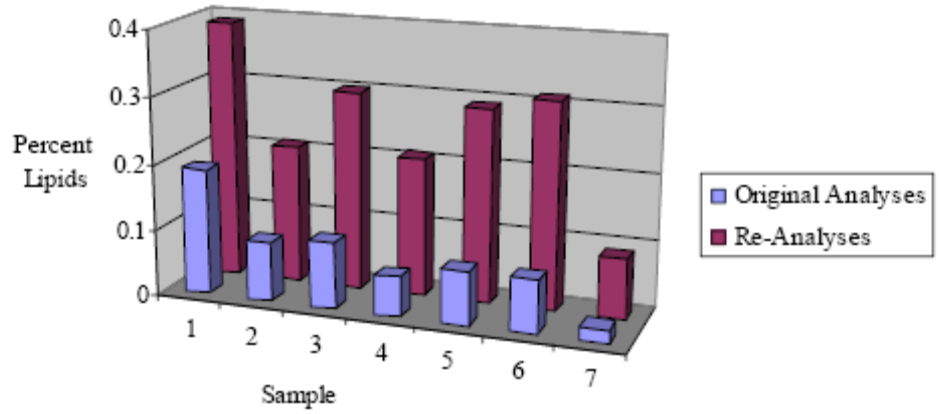
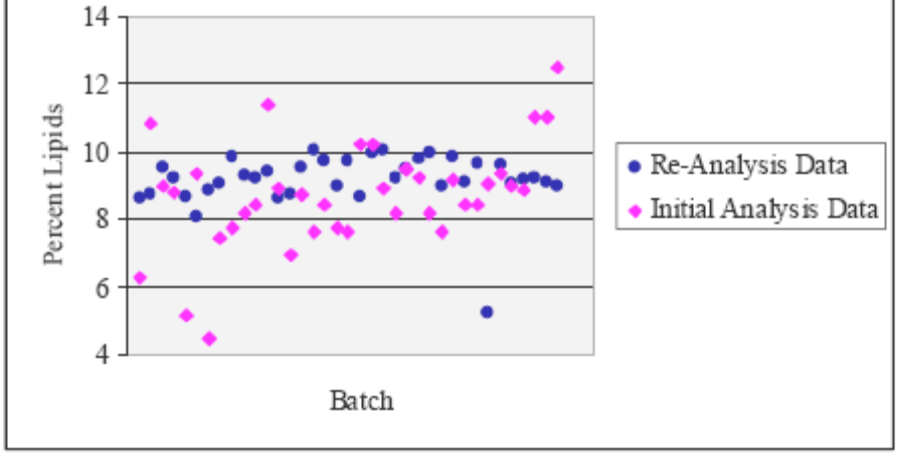


Figure 3: SRM1946 Percent Lipids Results
Certified Value = 10.17% +/- 0.48%



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Variables in Lipid Analyses and Affect on Data Quality

Craig Hutchings and Ann K. Bailey
EcoChem, Inc.

"Watch every detail that affects the accuracy of your work."

Arthur C. Nielsen

- Lipid Normalized Data is used for:
  - Food Web Modeling
  - Development of Biota/Sediment Accumulation Factors (BSAF)

- There is no standard method for the analysis of lipid content
- Lipid content determined gravimetrically and therefore more accurately referred to as Total Extractable Organics (TEO)

Lipid Pools

- Neutral
  - Extracted with non-polar solvents
- Membrane Bound
  - Extracted with mixture of polar and non-polar solvents
- Covalently Bound
  - Requires acid or base digestion prior to extraction with non-polar solvents

Methods and Solvents

- **SW-846 8081/8082** : Hexane/Acetone (1:1)or Methylene Chloride/Acetone (1:1)
- **SW-846 8290** : Methylene Chloride or Hexane/Methylene Chloride (1:1)
- **1613** : Hexane/Methylene Chloride (1:1)
- **Bligh-Dyer** : Chloroform/Methanol (1:2) then Chloroform then DI Water

Methods and Extraction Techniques

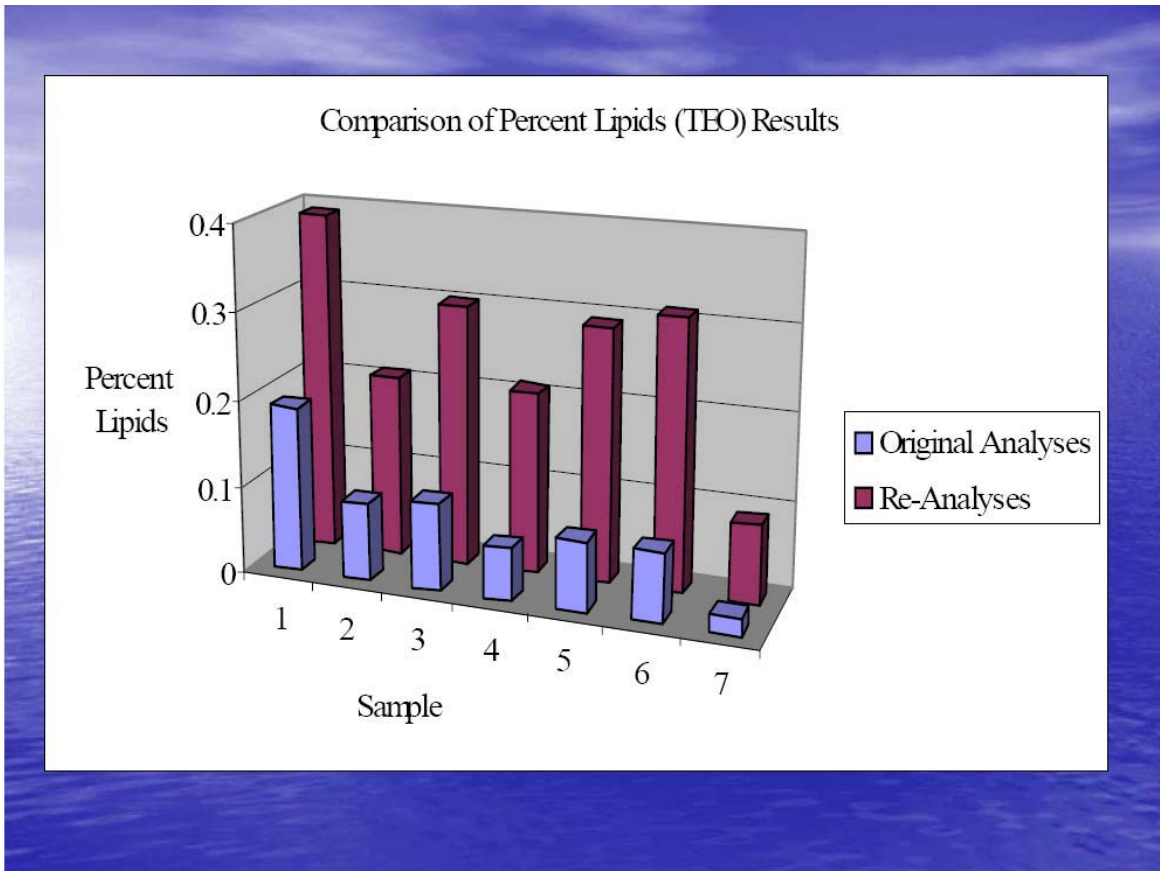
- **SW-846 8081/8082** :Soxhlet or Pressurized Fluid Extraction (PFE) or Sonication
- **SW-846 8290** : Soxhlet
- **1613** : Soxhlet or HCl Digestion
- **Bligh-Dyer** : Tissuemizer

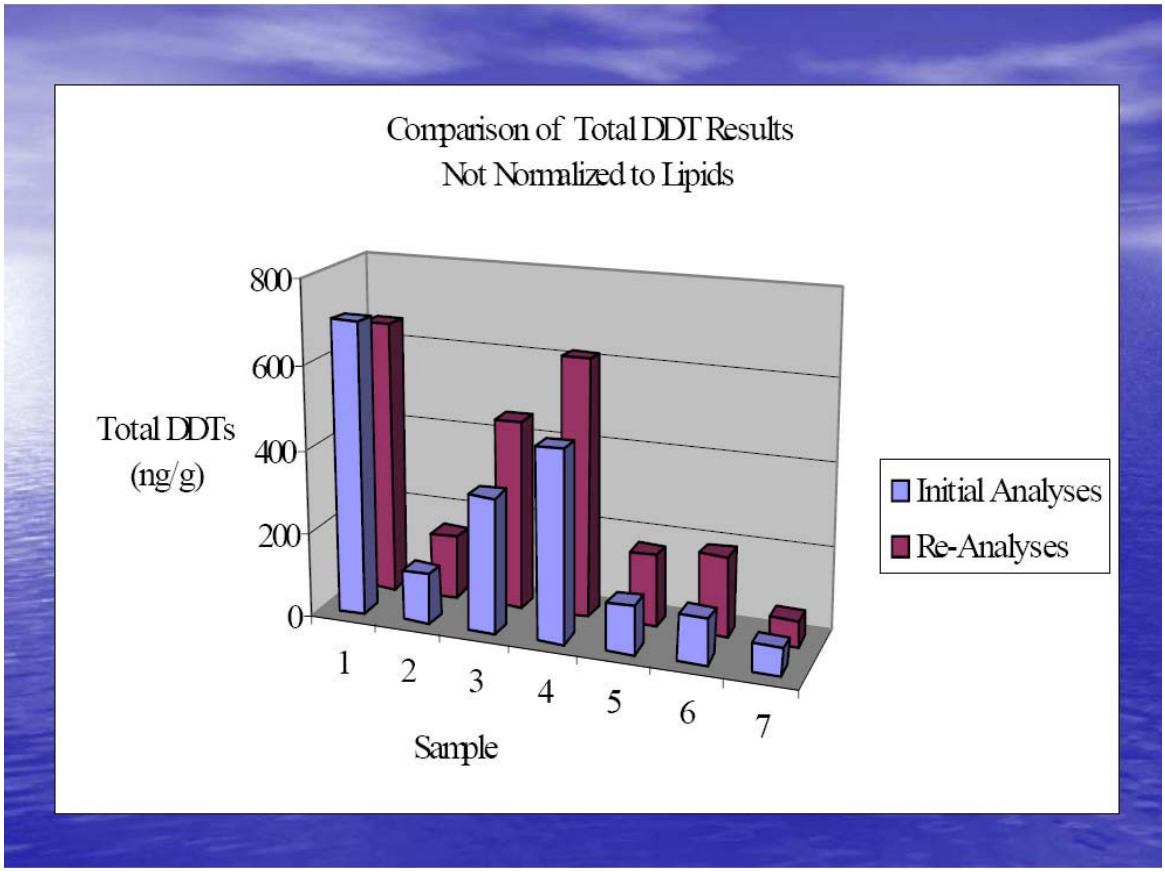
- Organic pollutants reside in the neutral lipid pool, the membrane-bound lipid pool, or both.
- The choice of solvent and extraction technique will affect the efficiency of extraction of these pools.
- The association of pollutants to the lipid pools is affected by a number of factors

Factors Affecting Pollutant Association to Lipid Pools

- Time of Year
- Chemical structure of pollutant
- Species
- Type of tissue (muscle, skin, etc.)
- Reproductive cycle
- Stress

- Routine USEPA Batch Quality Control
  - Method blank
  - Laboratory control sample (LCS)
  - Matrix spike (MS)
  - Laboratory duplicate (or MS duplicate)


Comparison of Percent Lipids (TEO) Results
Percent Lipids
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
Sample
Original Analyses
Re-Analyses


Comparison of Total DDT Results
Not Normalized to Lipids
Total DDTs (ng/g)
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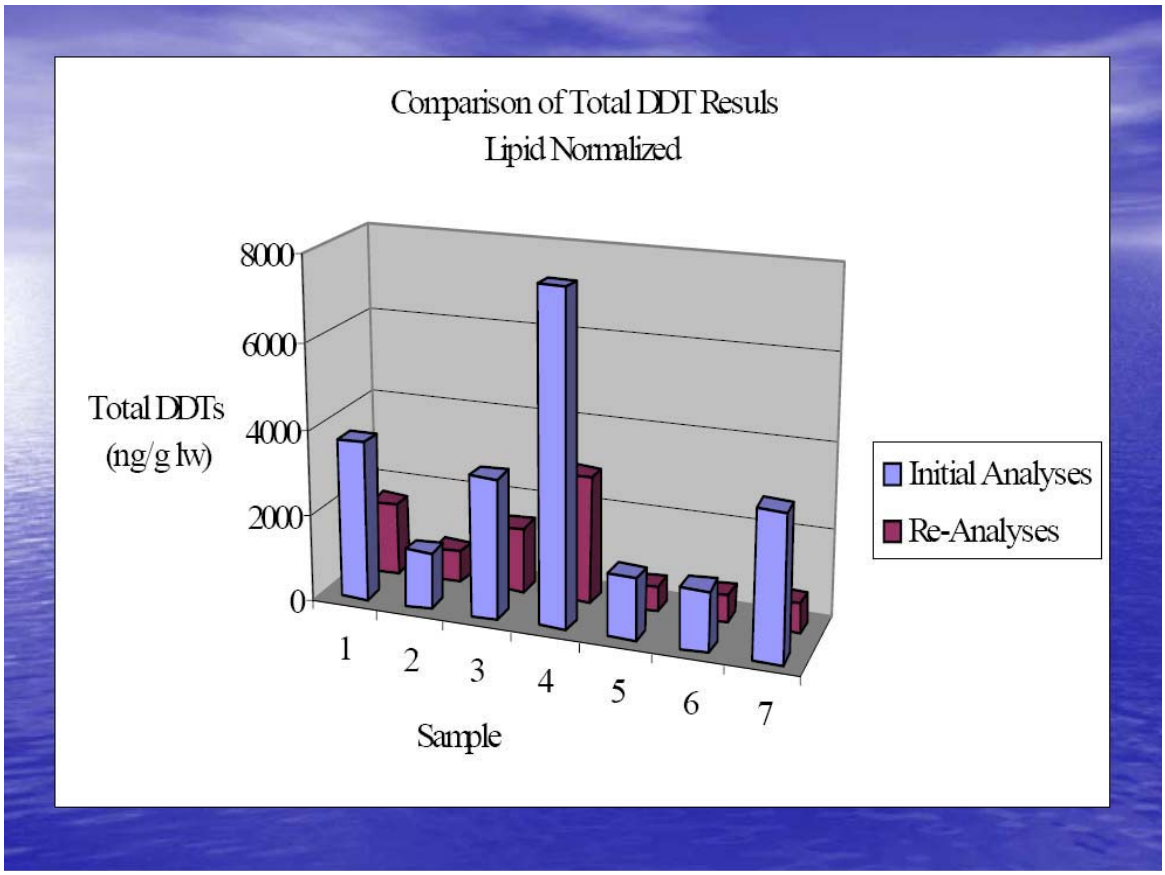
600
400
200
0
1
2
3
4
5
6
7
Sample
Initial Analyses
Re-Analyses


Comparison of Total DDT Resuls
Lipid Normalized
Total DDTs
(ng/g lw)
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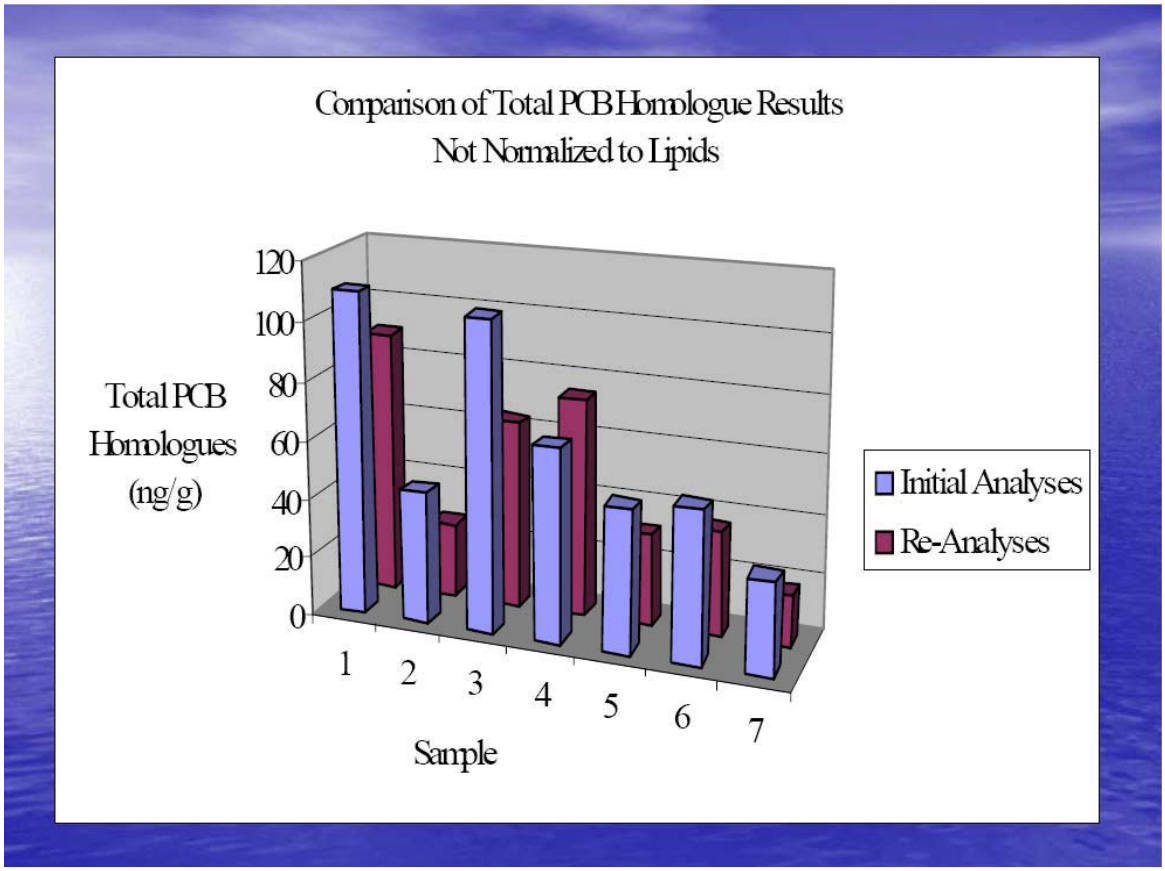
6000
4000
2000
0
1
2
3
4
5
6
7
Sample
Initial Analyses
Re-Analyses


Comparison of Total PCB Homologue Results
Not Normalized to Lipids
Total PCB
Homologues
(ng/g)
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100
80
60
40
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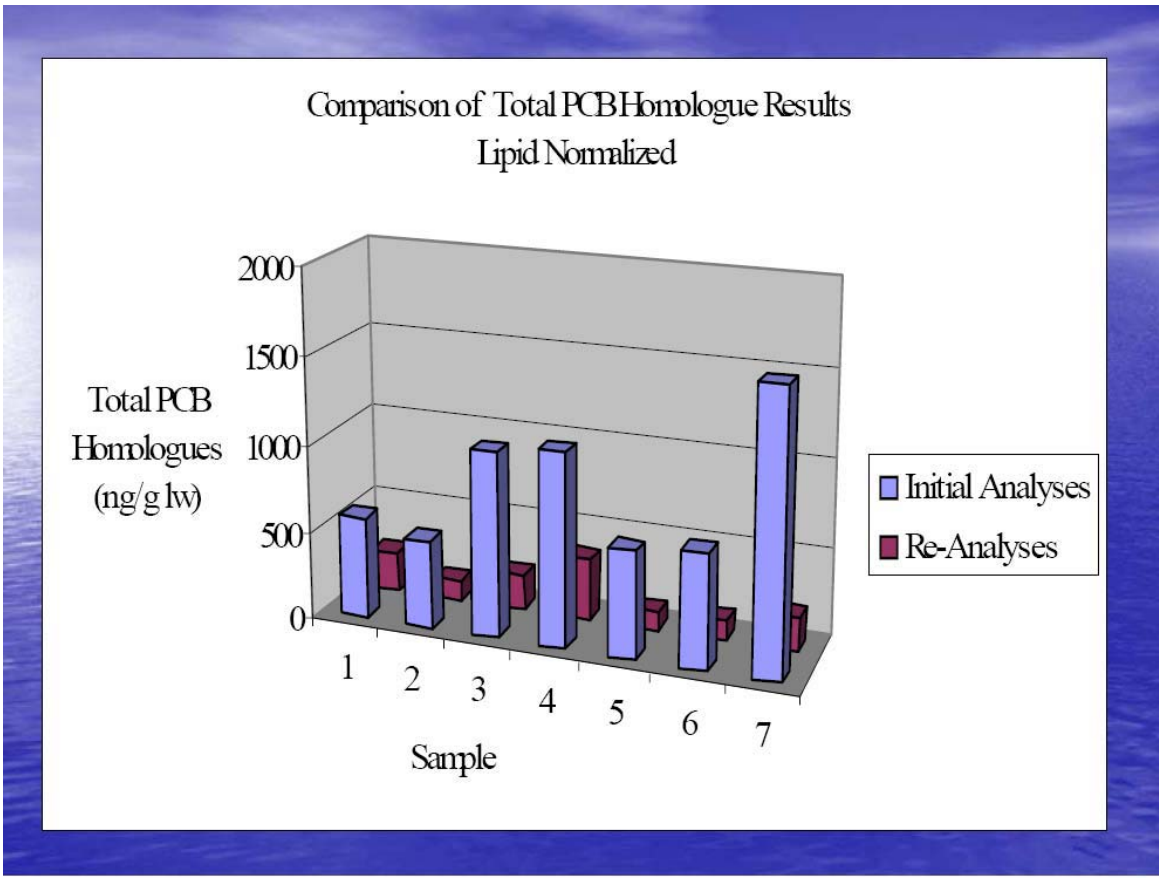
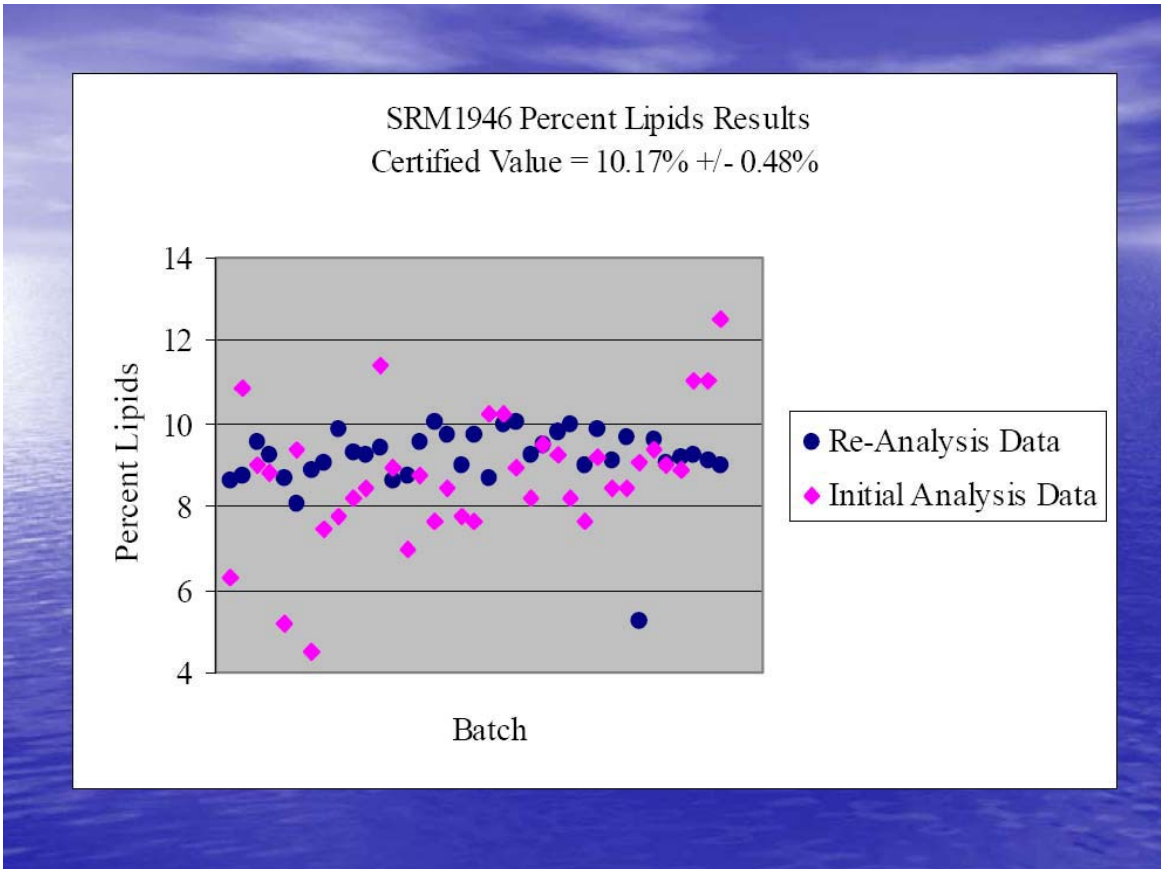
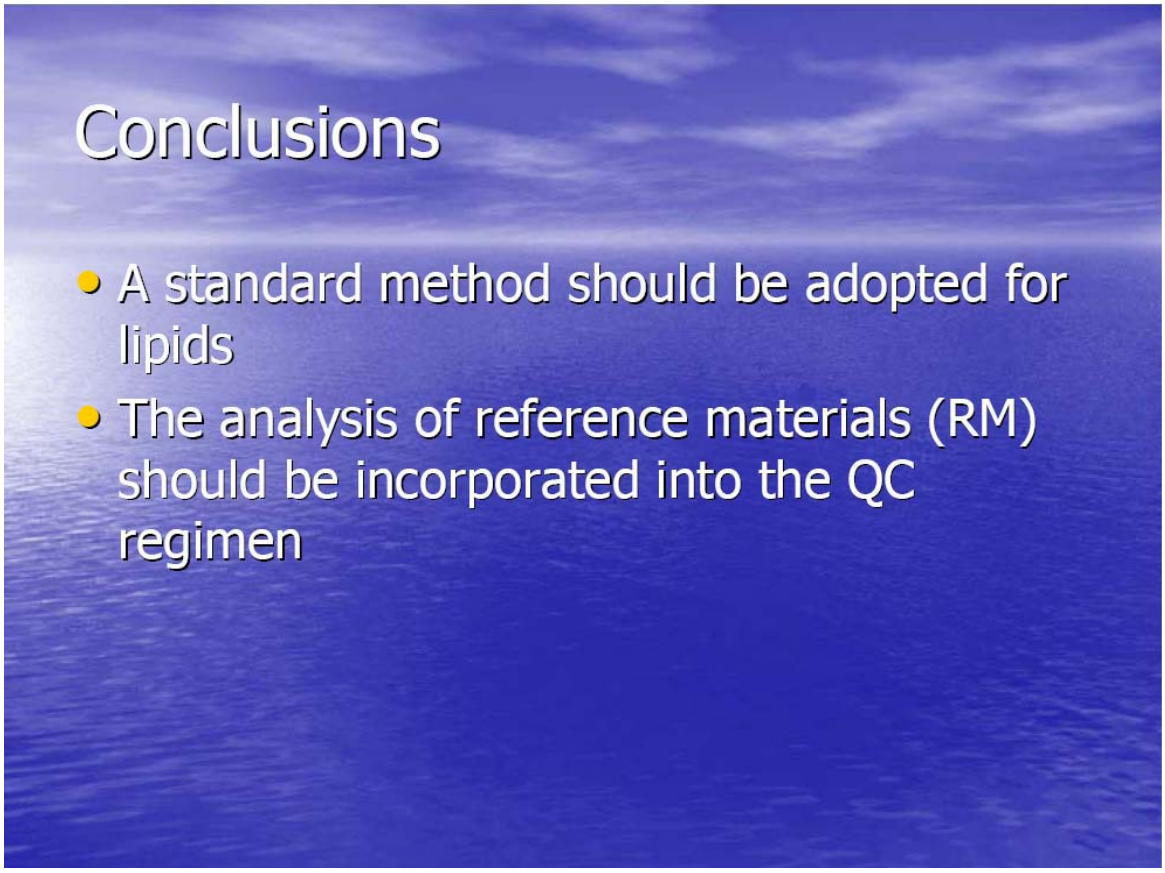
1
2
3
4
5
6
7
Sample
Initial Analyses
Re-Analyses


Comparison of Total PCB Homologue Results
Lipid Normalized
Total PCB Homologues (ng/g lw)
2000
1500
1000
500
0
1
2
3
4
5
6
7
Sample
Initial Analyses
Re-Analyses


SRM1946 Percent Lipids Results
Certified Value = 10.17% +/- 0.48%
Percent Lipids
14
12
10
8
6
4
Batch
Re-Analysis Data
Initial Analysis Data


Conclusions
A standard method should be adopted for lipids
The analysis of reference materials (RM) should be incorporated into the QC regimen

Quantitative Defense of Extract Dilution for Hydrocarbon Interferences in Semi-Volatile Organic Analysis by GC/MS

Mark Bruce Ph.D., Marcel Mol, Tom Hula
Severn Trent Laboratories, Inc., North Canton, OH

ABSTRACT

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 calibration standard at the quantitation limit. As the hydrocarbon content increased, a low bias was observed for analytes such as benzyl alcohol, benzidine and 2,4-dichlorophenol. Of greater concern were 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 ug/kg. Once the diesel fuel concentration reached 11.7 mg/kg, nitrobenzene was non-detect.

INTRODUCTION

Push for Lower Reporting Limits

Low concentration risk assessment goals such as the EPA Region 9 Preliminary Remediation Goals, are fueling the drive for analysis of environmental samples 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. Newer gas chromatography - mass spectrometry instrumentation has improved environmental monitoring sensitivity, however interference problems from hydrocarbons remain.

Elevated reporting limits (RLs) usually occur when the sample components necessitate dilution of the sample extract to maintain the integrity of the analytical process and instrumentation. Occasionally this produces non-detect results at RLs that are higher than the action limit or decision threshold. Thus, the environmental data user is not able to demonstrate that particular hazardous contaminants are below a predetermined action limit. This situation can lead to additional environmental cleanup or property usage restrictions that might not be necessary and are usually expensive.

Reasons to Dilute

There are several reasons that a laboratory might dilute a sample or sample extract prior to analysis. If an appropriate dilution is not performed, data quality can be compromised for the sample of interest. In some instances data quality of subsequent samples in the analytical process can also be compromised. The most common reasons for dilution of environmental water and soil samples or their extracts are to prevent calibration range exceedance, carryover of analyte or non-analyte components into subsequent analyses, damage to the analytical system and chromatographic or mass spectral interference or overload.

This last dilution cause is the focus of this paper. High concentrations of non-analyte components can overload either the chromatograph or mass spec detector. Non-analyte components can mask the presence of target analytes by adding to the chromatographic and spectral background, making it impossible to definitively identify analytes using standard chromatographic data systems commonly employed for US EPA methodologies. In extreme overload conditions, retention time shifts and distorted mass spectra occur. Unfortunately for multi-analyte methods covering many different types of functional groups such as US EPA Method 8270, there are no universal cleanup methods that remove hydrocarbon interferences without reducing analyte recovery as well.

EXPERIMENTAL DESIGN AND PROCESS

Focus on GC/MS Overload Scenario

This paper will focus on dilutions caused by moderate GC/MS (Method 8270 semivolatile organics) overload conditions produced by diesel fuel and motor oil. Identifying analytes becomes increasingly difficult as the concentration of hydrocarbons on-column increases. Interferences occur both in the selected ion chromatograms and mass spectra. Eventually the interfering component concentrations become too high to positively identify certain target analytes. Sample extract dilutions are then needed to reduce the background interference to a tolerable level in order to maintain defensibility of non-detect results. Inadequate dilutions will lead to false negative results because high concentrations of hydrocarbons in the sample extract obscure the presence of low concentration target analytes.

Design

Target analyte standards (0.25, 0.5 and 1.0 ng on-column) containing the most frequently requested semi-volatile organic analytes were prepared at concentrations corresponding to the normal reporting limits (RL) in soil samples (33, 67 and 133 ug/kg). Five different concentrations (22, 44, 88, 176 and 352 mg/L in the extract) of diesel fuel or motor oil were added to these RL standards. These hydrocarbon concentrations would correspond to 1.5, 2.9, 5.9, 11.7 and 23.5 mg/kg in a contaminated soil sample. All hydrocarbon spiked standards were analyzed sequentially. The GC/MS chromatograms were evaluated using a standard Target (Thermo) chromatography data system.

Analytical Sequence

The analytical sequence is summarized in Table 1. The spiked RL standards with the lowest hydrocarbon concentrations were analyzed first, followed by subsequent standards with increasing hydrocarbon concentration. A mid-level continuing calibration standard was analyzed

between each diesel fuel and motor oil spiked standard to assess the condition of the GC/MS system.

Table 1: Analysis Sequence

Diesel 1 - 2000x diesel fuel + 0.25 ng OC std
Cont. Cal. 1
Motor 1 - 2000x motor oil + 0.25 ng OC std
Cont. Cal. 2
Diesel 2 - 1000x diesel fuel + 0.25 ng OC std
Cont. Cal. 3
Motor 2 - 1000x motor oil + 0.25 ng OC std
Cont. Cal. 4
Diesel 3 - 500x diesel fuel + 0.25 ng OC std
Cont. Cal. 5
Motor 3 - 500x motor oil + 0.25 ng OC std
Cont. Cal. 6
Diesel 4 - 250x diesel fuel + 0.25 ng OC std
Cont. Cal. 7
Motor 4 - 250x motor oil + 0.25 ng OC std
Cont. Cal. 8
Diesel 5 - 125x diesel fuel + 0.25 ng OC std
Cont. Cal. 9
Motor 5 - 125x motor oil + 0.25 ng OC std
Cont. Cal. 10

Equipment and Method

Method 8270 analysis was performed using an Agilent 6890/5973 inert source GC/MS system equipped with Agilent injection port liner and column (DB-5.625 20m X 0.18 mm ID). The temperature program was: 60°C for 1 min., ramp at 35°C /min to 320°C and hold for 2 min.

GENERAL RESULTS

The analyte results fell into four different categories: no effect, high bias, low bias or false negative. The majority of the semivolatile organic analytes were not affected by the hydrocarbons within the concentration range studied. Several polyaromatic hydrocarbon analytes (PAHs) were in the diesel fuel and showed high biased results. This was not an indication of interference, but did eliminate these analytes from further study. Some analytes exhibited a decrease in response as the concentration of hydrocarbons was increased, thus producing a low biased result. Other analytes produced false negative results as the hydrocarbon concentration increased. These analytes were known to be present in the RL standard but could not be identified in the chromatogram because of interference from the hydrocarbon mixtures. These false negative responses would produce non-detect results that cannot be defended. Thus, extract dilution with corresponding elevation of the reporting limit would be necessary.

The repeatability of the continuing calibration standards (average 4% RSD) interspersed throughout the sequence demonstrate that the conditions of the GC system did not degrade

during the course of the experiment. The lack of permanent damage to the GC is not surprising since hydrocarbons are generally unreactive under the GC conditions of Method 8270.

DIESEL FUEL RESULTS

The chromatogram of the highest concentration diesel fuel analysis was overlaid with that of the RL standard to show the magnitude of the concentration differences between the target analytes and the interfering hydrocarbon mix (Figure 1).

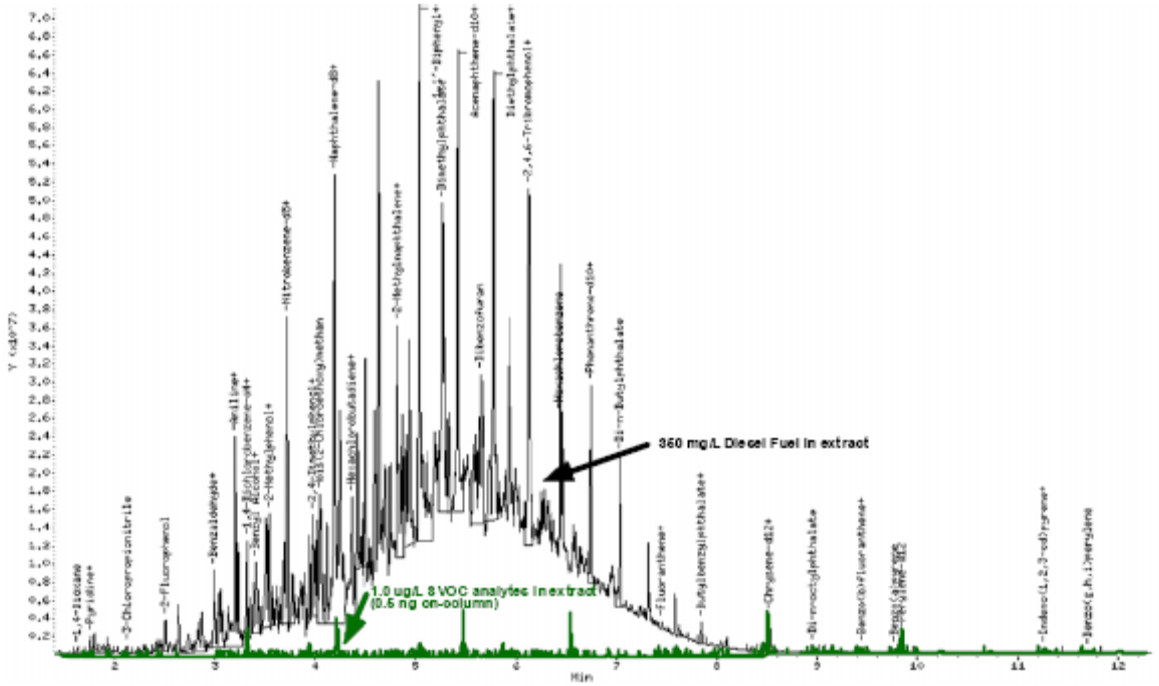


Figure 1: Diesel Fuel & Standard Chromatogram

Non-affected Analytes

Most of the analyte responses were not affected by the increasing diesel fuel concentration within the range studied. These are shown in Figure 2. Note the consistency of the analyte response despite the increasing hydrocarbon concentrations or sample extract dilution factors. This is a demonstration of the effectiveness of modern GC/MS systems to minimize the effects of potentially interfering hydrocarbon mixtures.

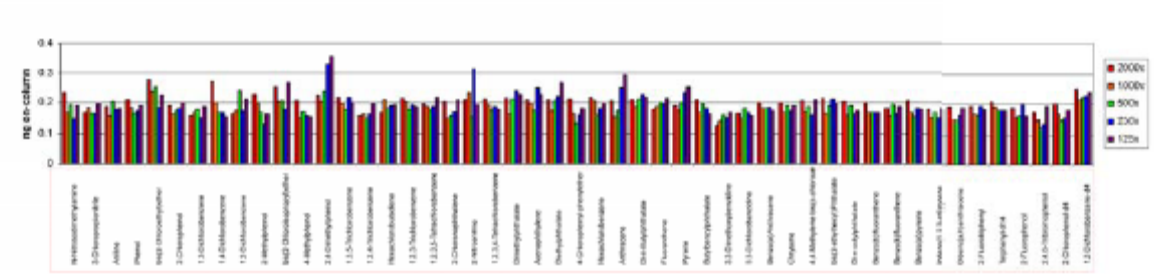


Figure 2: Analytes Not Affected by Diesel Fuel

Diesel Component Analytes

Several of the analytes were also components in the diesel fuel. Thus, the extract concentration and on-column amount of these PAHs and other semi-volatile organic analytes increased as the concentration of diesel fuel increased. This produced a high biased result for these analytes, but was not indicative of any method shortcomings. The effect of increasing diesel fuel concentration could not be studied for these analytes shown in Figure 3.

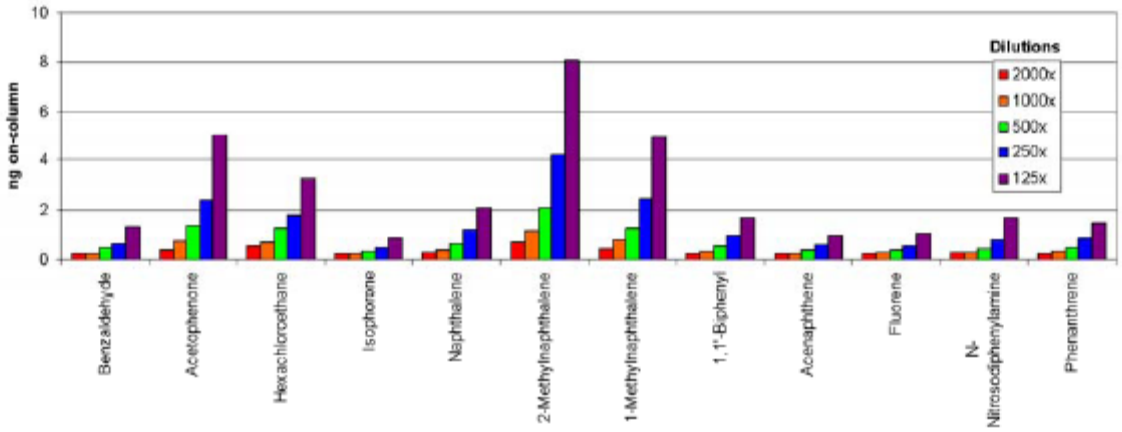


Figure 3: Diesel Fuel Component Analytes

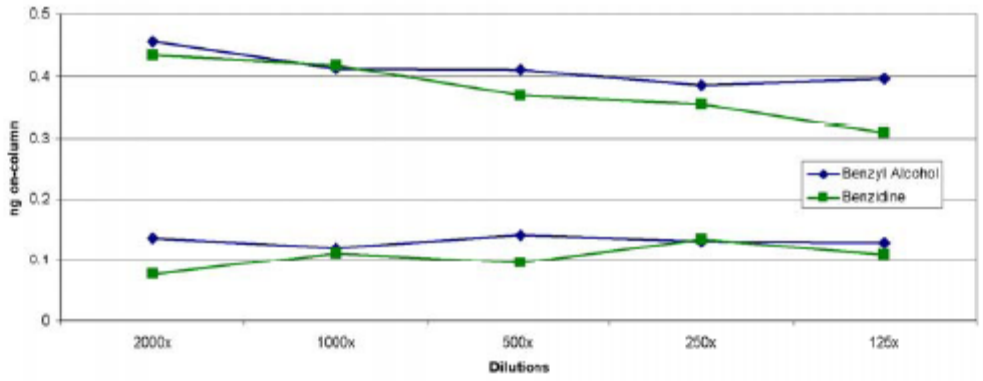


Figure 4: Analytes Biased Low by Diesel Fuel

Low Biased Analytes

A few analytes showed decreasing response (Figure 4) as the effective dilution was decreased, thereby increasing the final extract concentration of diesel fuel. In other words, increasing the diesel fuel concentration decreased the response from these analytes producing a low biased result.

False Negative Analytes

The false negative results were the most alarming response to increasing diesel fuel interference At high dilutions (low diesel fuel concentration) these analytes were detected and accurately quantified. However, as the diesel fuel concentration increased, these analytes were not detected even though they were known to be present. The hydrocarbon background had increased to the point of obscuring the chromatographic peaks and mass spectra of these analytes. This false

negative result (non-detect) at the associated reporting limit produced data that understated actual target analyte concentration. This could compromise the accuracy of a risk assessment or other decisions based on the result of this under-diluted sample. Figure 5 shows the increasing frequency of false negative responses for these analytes as dilution decreases and diesel concentration increases.

The increasing diesel fuel interference effect is shown in Figures 6 and 7 for nitrobenzene. As the hydrocarbon background increases in the ion chromatograms and mass spectra, interference precluded detection of the analyte. Figure 6 shows the disappearance of the three major ions amongst the co-eluting hydrocarbons. Figure 7 shows hydrocarbon spectra over running the nitrobenzene spectrum.

MOTOR OIL RESULTS

The chromatogram of the highest concentration motor oil analysis was overlaid with that of the RL standard to show the magnitude of the concentration differences between the target analytes and the interfering hydrocarbon mix. This is shown in Figure 8.

Non-affected Analytes

Most of the analyte responses were not affected by the increasing motor oil concentration within the range studied. These are shown in Figure 9. Note the consistency of the analyte response despite the increasing hydrocarbon concentrations or sample extract dilution factors. This is a demonstration of the effectiveness of modern GC/MS systems to minimize the effects of potentially interfering hydrocarbon mixtures.

Motor Oil Component Analytes

There were no analytes that appeared to be a component in the motor oil.

Low Biased Analytes

A few analytes showed decreasing response (Figure 10) as the effective dilution was decreased, thereby increasing the final extract concentration of motor oil. In other words, increasing the motor oil concentration decreased the response from these analytes producing a low biased result.

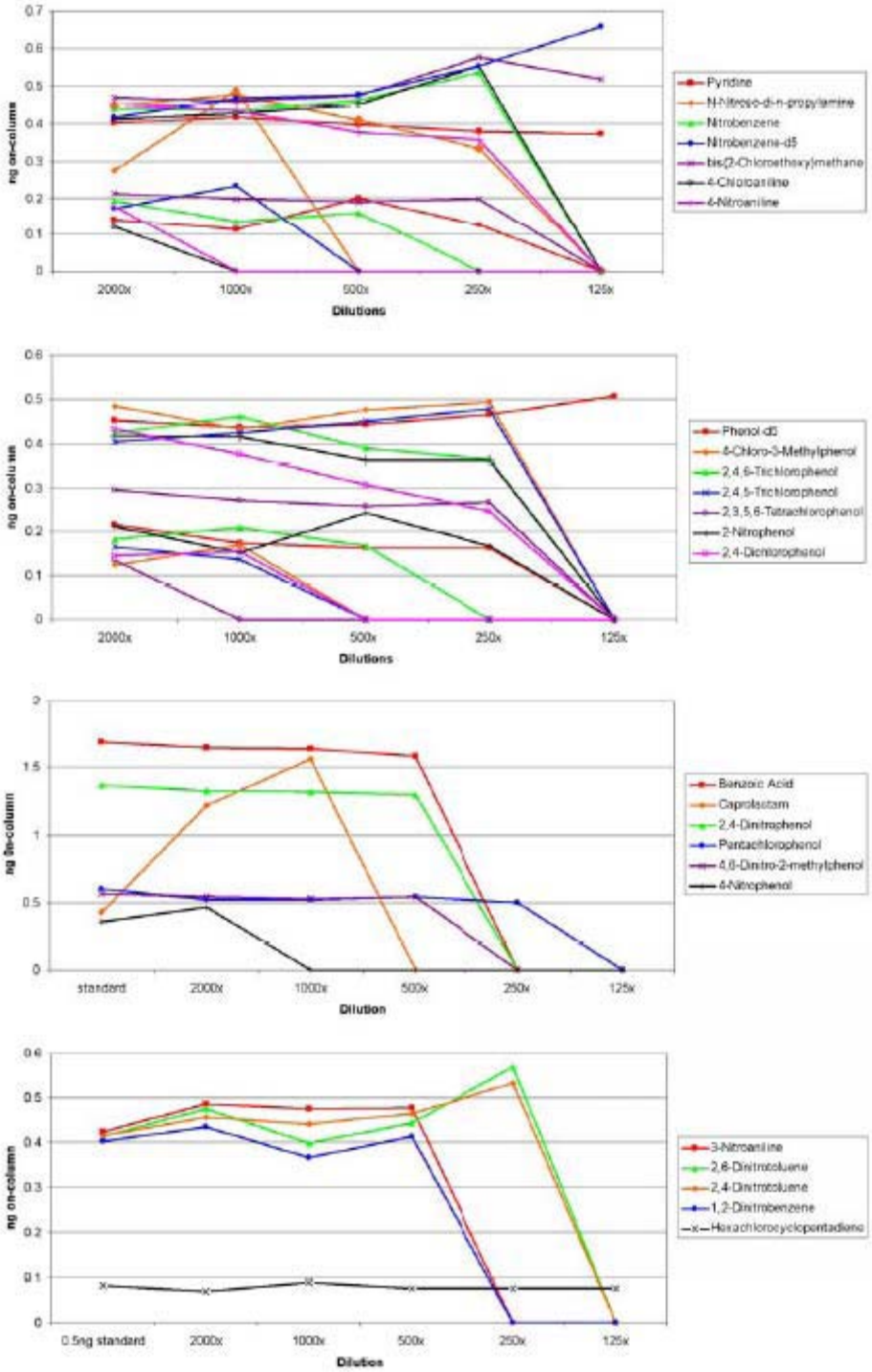


Figure 5: False Negatives Caused by Diesel Fuel

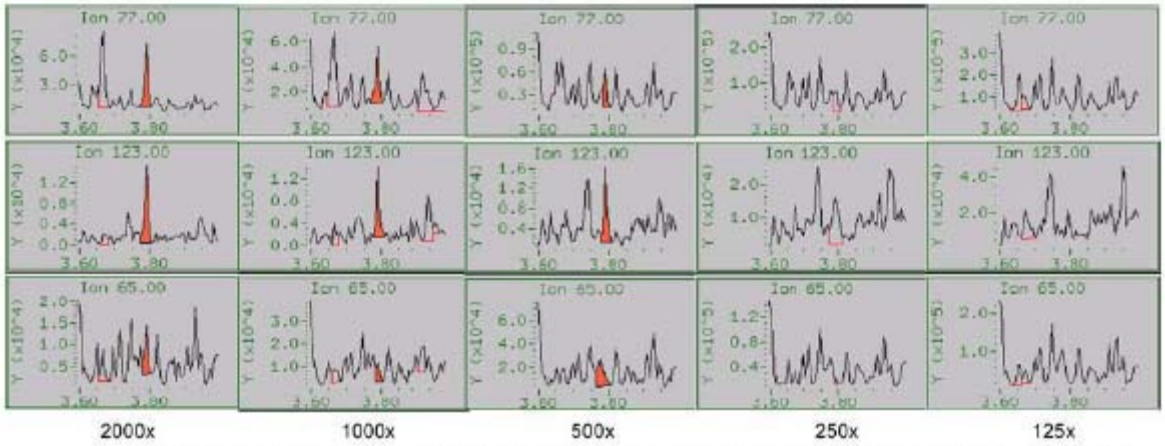


Figure 6: Nitrobenzene Ion Chromatograms at Various Diesel Fuel Dilutions

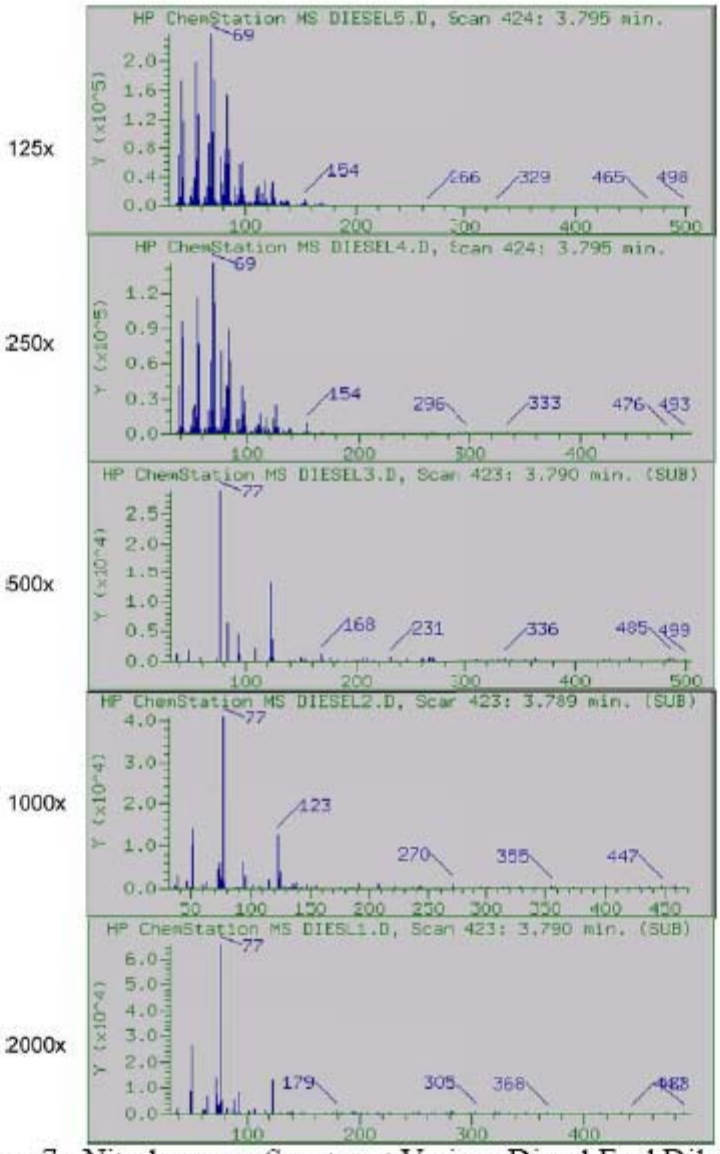


Figure 7: Nitrobenzene Spectra at Various Diesel Fuel Dilutions

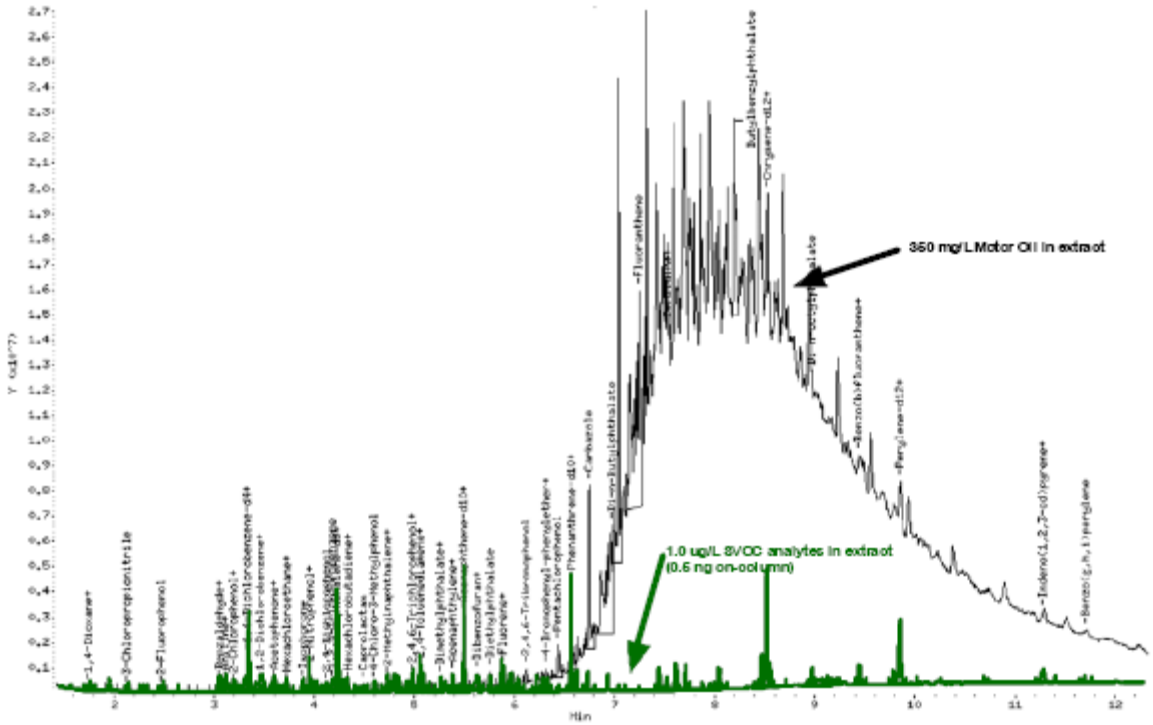


Figure 8: Motor Oil & Standard Chromatogram

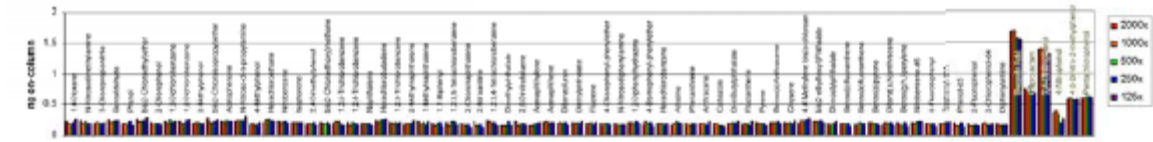


Figure 9: Analytes Not Affected by Motor Oil

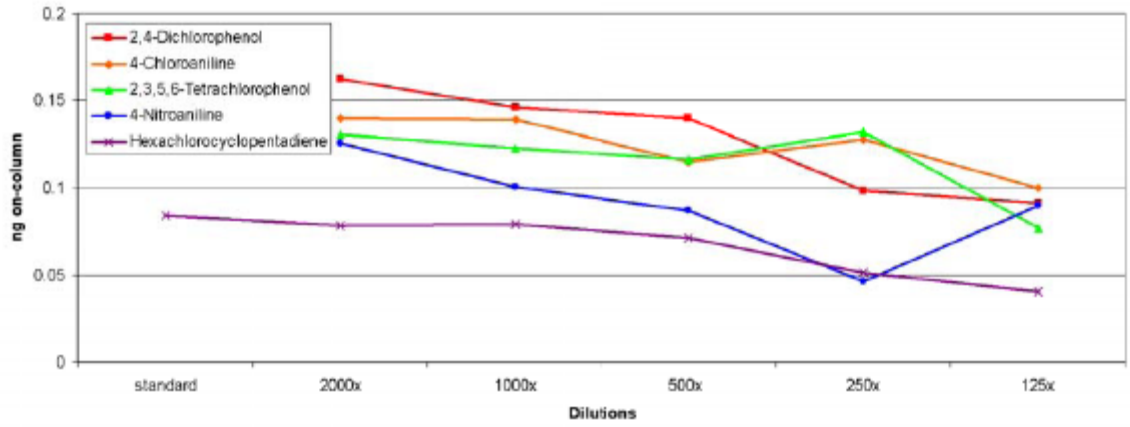


Figure 10: Analytes Biased Low by Motor Oil

False Negative Analytes

False negative responses were also found for high concentration motor oil samples. At high dilutions (low motor oil concentration) these analytes were detected and accurately quantified. However, as the motor oil concentration increased, these analytes were not detected, even though they were known to be present. The hydrocarbon background had increased to the point of obscuring the chromatographic peaks and mass spectra of these analytes. Similar to the diesel fuel results, this false negative result (non-detect) at the associated reporting limit produced data that understated actual target analyte concentration. This could compromise the accuracy of a risk assessment or other decisions based on the result of this under-diluted sample. Figure 11 shows the increasing frequency of false negative responses for two analytes as dilution decreases and diesel concentration increases.

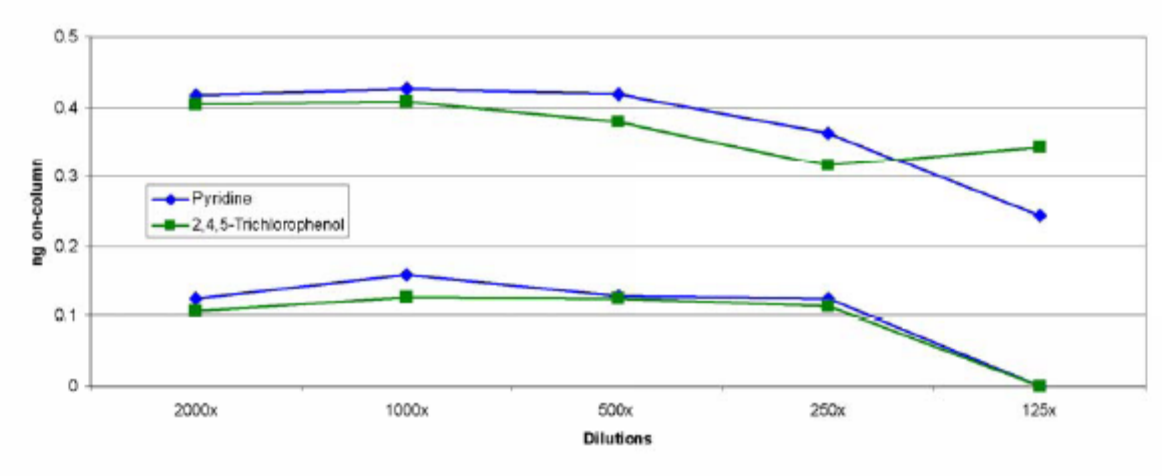


Figure 11: False Negatives Caused by Motor Oil

CONCLUSION

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.

Inadequate dilution to mitigate diesel fuel and motor oil interferences causes false negative and low bias results for 22 semivolatile organic analytes when analyzing by EPA Method 8270. In particular, the non-detect results for these analytes from under diluted sample extracts do not demonstrate the absence of the analyte at the normally calculated reporting limit. Dilution or other means of estimating an appropriate elevated reporting limit are necessary. The push to lower reporting limits in order to meet risk based criteria in hydrocarbon contaminated samples should not compromise the defensibility of those analyte reporting limits by potentially masking the presence of the analytes of interest.

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Quantitative Defense of Extract Dilution for Hydrocarbon Interferences in Semi-volatile Organic Analysis by GC/MS

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North Canton, OH

mbruce@stl-inc.com

NEMC 2006

Arlington, VA, August 30, 2006

Consultation with experts is recommended, do not rely solely on this presentation for guidance.

Abstract

- **Hydrocarbon interferences can cause false negative results**
  - Semivolatile Organic Compounds
  - Method 8270 – GC/MS
  - Usually soils or other contaminated solids
- **Example - Nitrobenzene: 33 ug/kg**
  - Diesel fuel
    - 5.9 mg/kg – dilution OK, analyte found
    - 11.7 mg/kg – not enough dilution, false non-detect

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Push for Lower Reporting Limits

- **Low concentration risk assessment goals**
  - EPA Region 9 Preliminary Remediation Goals
- **Hydrocarbon impacted sites**
- **GC/MS sensitivity improved**
- **Some interferences remain**

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Elevated reporting limits

- **Sample components >> dilution**
- **Avoid "damage" to analytical data or instrumentation**
- **Occasionally RLs > action limit**
- **Not able to prove < action limit**

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Reasons to Dilute

- Calibration range exceedance
- Carryover of analyte or non-analyte components into subsequent analyses
- Damage to the analytical system
- Chromatographic or mass spectral interference or overload

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High concentrations of non-analyte components

- Overload GC or MS
- Mask the presence of target analytes
  - Chromatographic and spectral background
- Extreme overload conditions
  - Retention time shifts
  - Distorted mass spectra occur
- No good cleanup methods that remove hydrocarbon interferences

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Focus on GC/MS Overload Scenario

- **Method 8270 semivolatile organics**
- **Diesel fuel & motor oil**
- **Interferences occur**
  - In selected ion chromatograms
  - In mass spectra
  - Too high to identify target analytes
- **Dilutions reduce interference**
  - Defensible non-detect result
- **Inadequate dilutions > false negatives**

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Experimental Design

- **Hydrocarbon mix (diesel or motor oil)**
  - Five concentrations
    - 1.5, 2.9, 5.9, 11.7 and 23.5 mg/kg
- **Analyte spiked at RL**
  - Three concentrations
    - 33, 67 and 133 ug/kg
- **Analyze with 8270 process**
  - Start with lowest concentration
  - CCals to assess GC/MS condition

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Analytical Sequence (Example)

1) Diesel 1 - 2000x diesel fuel + 0.25 ng OC std
2) Cont. Cal. 1
3) Motor 1 - 2000x motor oil + 0.25 ng OC std
4) Cont. Cal. 2
5) Diesel 2 - 1000x diesel fuel + 0.25 ng OC std
6) Cont. Cal. 3
7) Motor 2 - 1000x motor oil + 0.25 ng OC std
8) Cont. Cal. 4

....

19) Motor 5 - 125x motor oil + 0.25 ng OC std
20) Cont. Cal. 10

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General Results

- **No effect**
- **High bias**
- **Low bias**
- **False negative**

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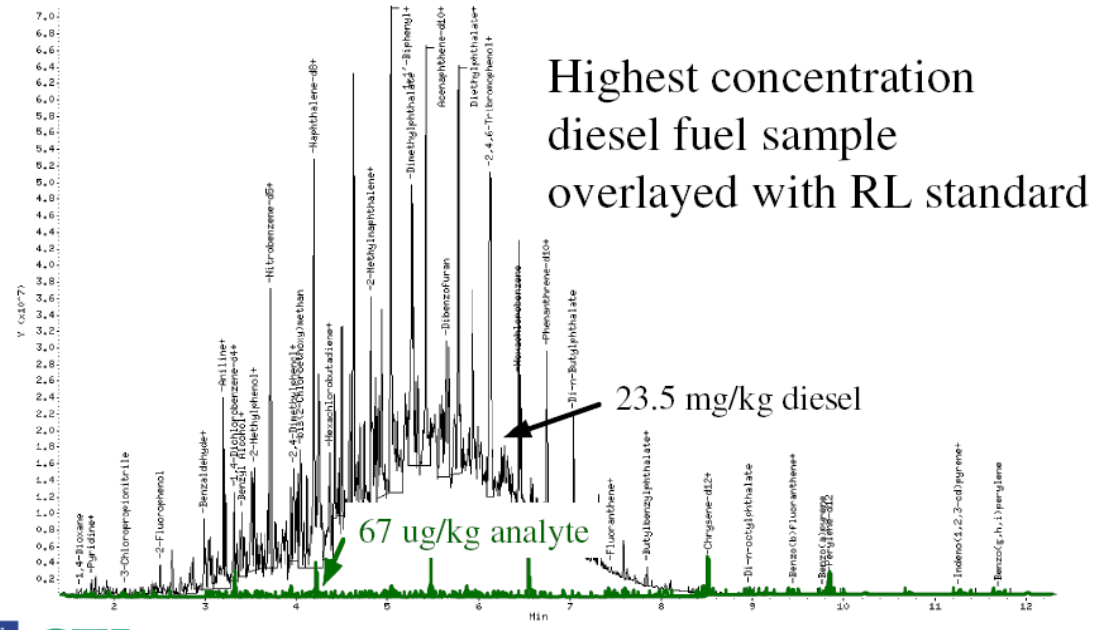
Diesel Fuel Results



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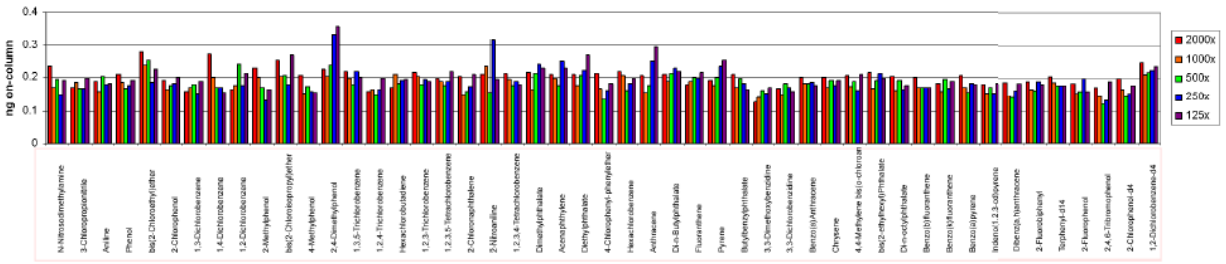
No Effect by Diesel

- **Consistent analyte response despite increasing diesel concentration**



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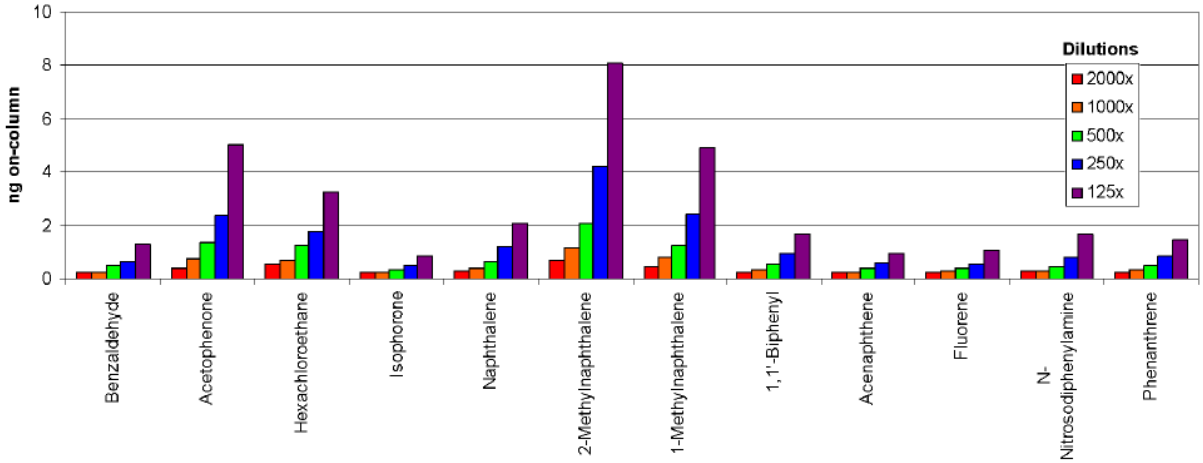
High Bias by Diesel

- Components in diesel increase



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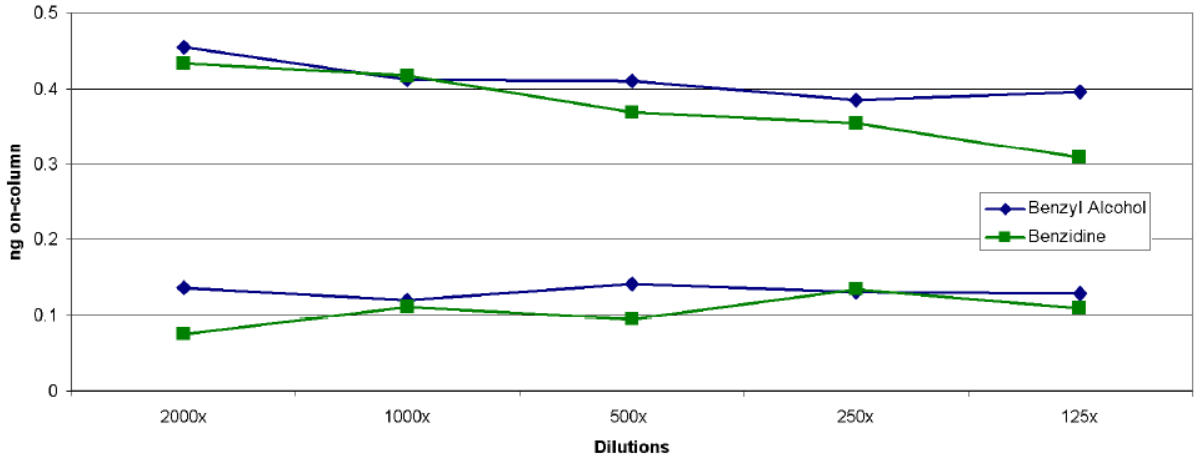
Low Bias by Diesel

- Measured concentration decreases



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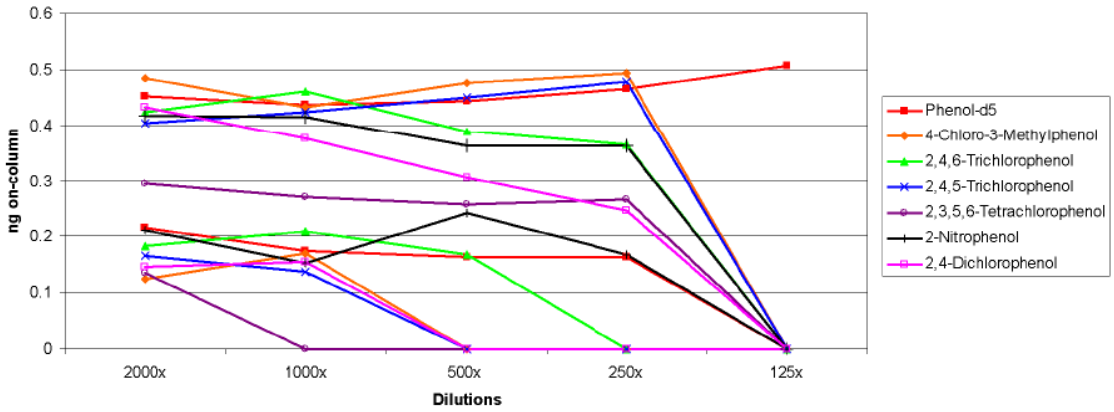
False Negatives by Diesel

- Analytes "disappear" with increasing diesel concentration



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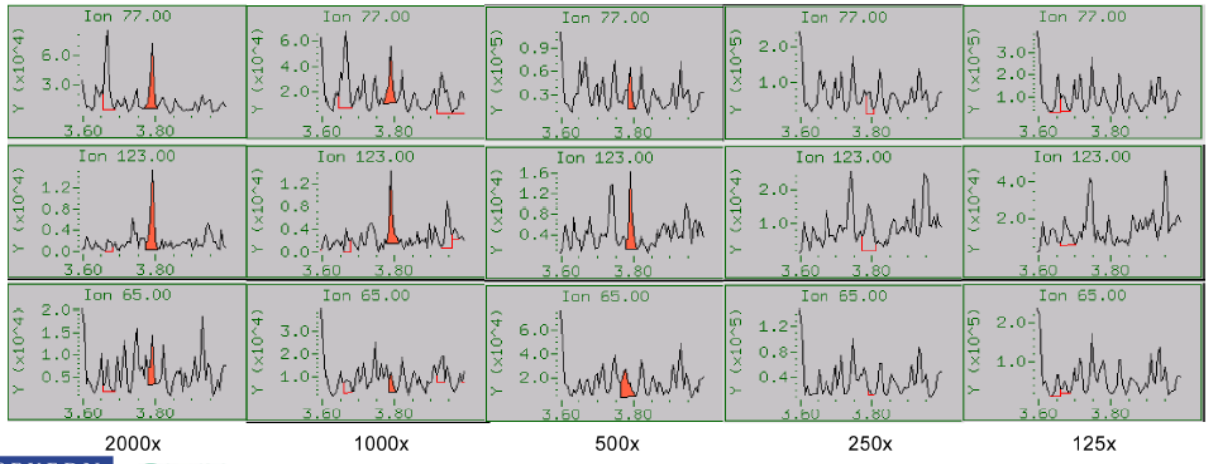
False Negatives by Diesel

- Nitrobenzene Ion Chromatograms at Various Diesel Fuel Dilutions



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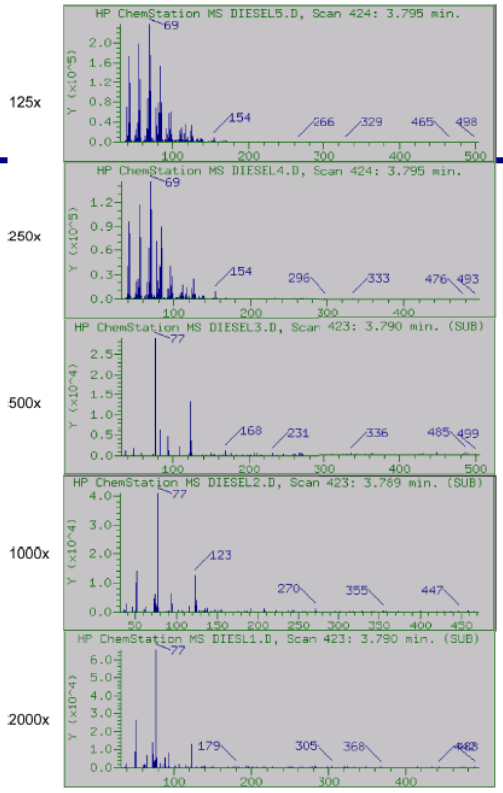
False Negatives by Diesel

- Nitrobenzene spectra at various diesel fuel dilutions



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False Negatives by Diesel

benzoic acid	3-nitroaniline
bis(2-chloroethoxy)methane	4-nitroaniline
caprolactam	nitrobenzene
4-chloroaniline	2-nitrophenol
4-chloro-3-methylphenol	4-nitrophenol
2,4-dichlorophenol	n-nitroso-di-n-propylamine
1,2-dinitrobenzene	pentachlorophenol
2,4-dinitrophenol	pyridine
2,4-dinitrotoluene	2,3,5,6-tetrachlorophenol
2,6-dinitrotoluene	2,4,5-trichlorophenol
4,6-dinitro-2-methylphenol	2,4,6-trichlorophenol

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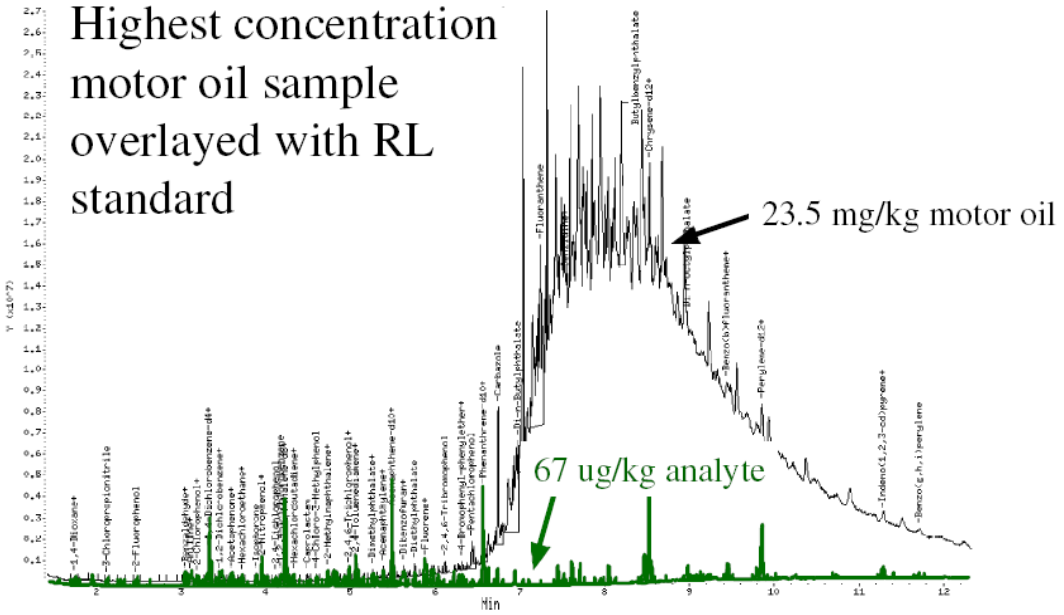
Motor Oil Results



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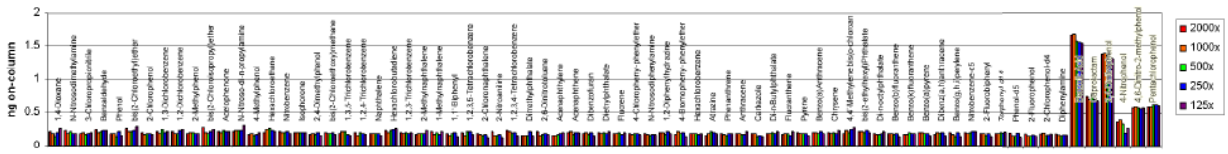
No Effect by Motor Oil

- **Consistent analyte response despite increasing motor oil concentration**



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High Bias by Motor Oil

- No SVOC analytes (from this study) in motor oil

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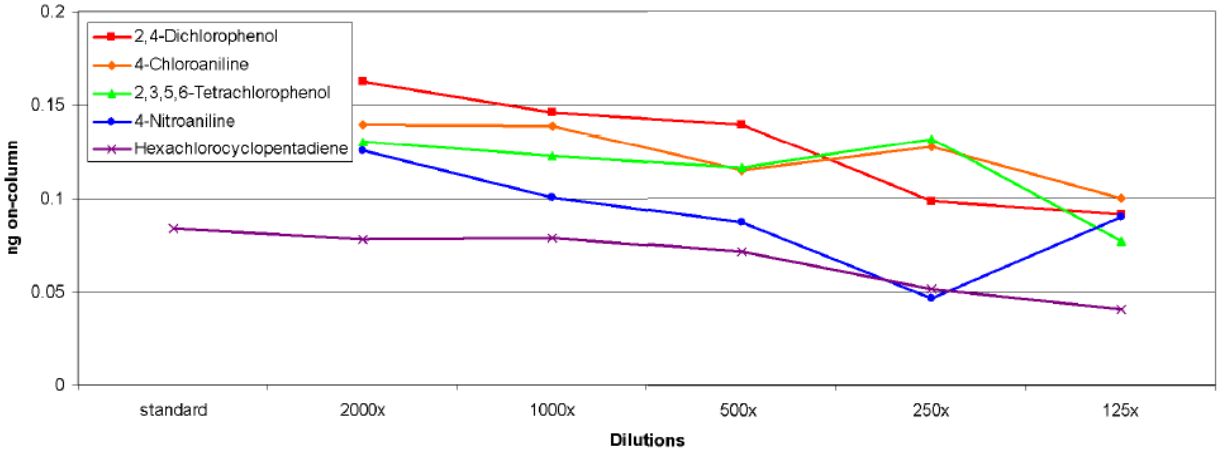
Low Bias by Motor Oil

- Measured concentration decreases



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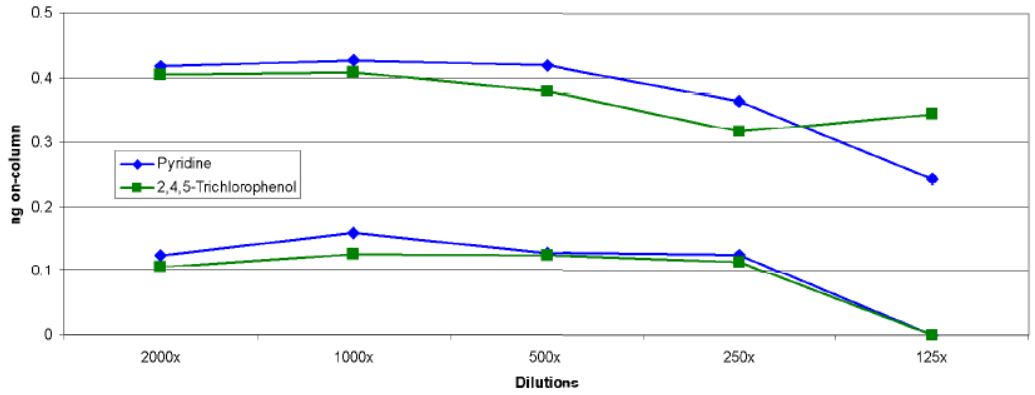
False Negatives by Motor Oil

- **Analytes "disappear" with increasing motor oil concentration**



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Summary – Dilution Defense

- **Diesel Fuel**
  - 22 analytes with false negative results
- **Motor Oil**
  - 2 analytes with false negative results

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Future Work

- **Develop "equation"**
  - estimate minimum dilution to avoid false negatives
- **Test**
  - spike real extracts at the reporting limit

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Conclusions – Dilution Defense

- **Appropriate dilution**
  - defensible reporting limits
- **Insufficient dilution**
  - indefensible non-detects

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WEDNESDAY P.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Chemical Speciation – Cr (VI) Species

A NEW TOOL TO ASSURE THE ACCURACY OF CR(VI) MEASUREMENTS

Buckley, Dr. Brian – Rutgers University Environmental Occupational Health Sciences Institute; Long, Dr. Stephen – United States Department of Commerce National Institute for Standards and Technology Analytical Chemistry Division; MacDonald, Bruce – NIST Measurement Services Division; Nagourney, Stuart J. – New Jersey Department of Environmental Protection Office of Quality Assurance; Werner, Rachel – NJDEP OQA; Yang, Shen-Yi – United States Environmental Protection Agency Office of Solid Waste

The accuracy of analysis of speciated metals in non-aqueous matrices has been a dilemma for the scientific and regulatory communities for many years. For example, most soil samples analyzed for Cr(VI) by EPA Methods 7196A (alkaline extraction) and 7196A (colorimetry) for the New Jersey Department of Environmental Protection 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 NJDEP, NIST, 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 chromium SRM from a natural source. A description of the sampling, sample preparation, stability testing and analysis plans will be presented.

A NEW TOOL TO ASSURE THE ACCURACY OF Cr(VI) ANALYSES

Stuart J. Nagourney, Research Scientist
NJ Department of Environmental Protection
Office of Quality Assurance

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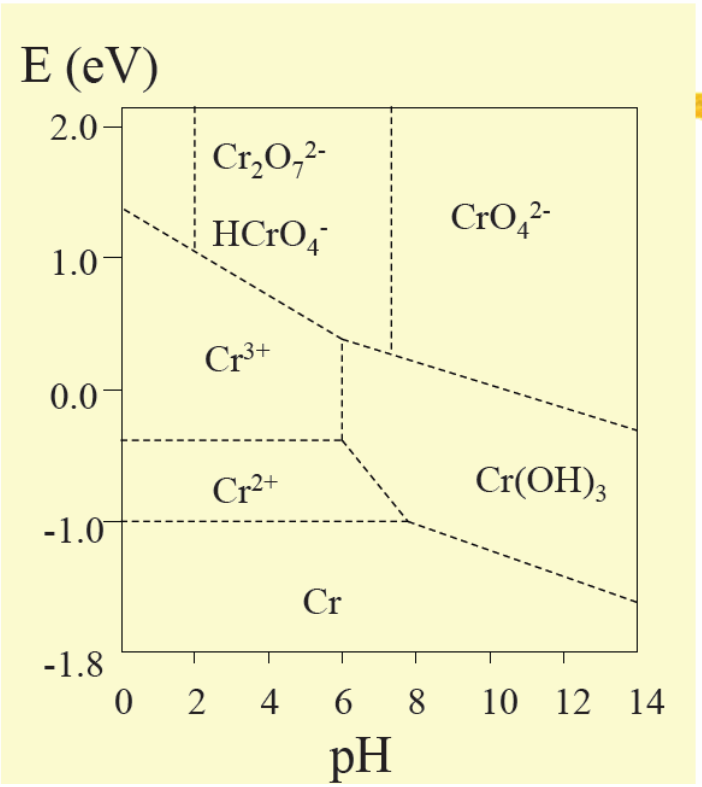
609-292-4945

Cr SPECIATION

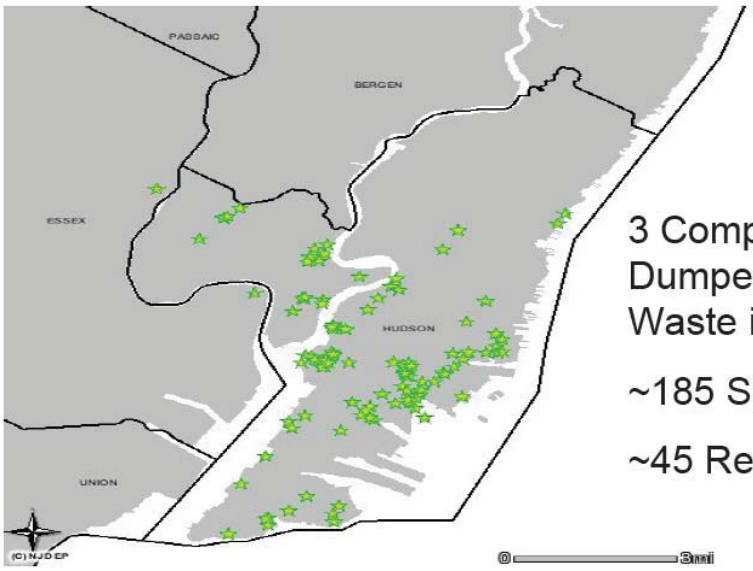
- Elemental: Crustal Abundance ~ 0.00001%
- Trivalent:
  - Micronutrient
  - Cr^{+3}, Cr_2O_3
- Hexavalent:
  - Toxic and much more mobile
  - $(CrO_4)^-$, $(Cr_2O_7)^{-2}$

Cr SPECIATION



- Cr(VI) is relatively stable at high pH and E
- Cr(III) is relatively stable at low pH and E
- Free ion of Cr(III) and freshly precipitated $Cr(OH)_3$ are kinetically easier to oxidize than Cr(III) complex or aged $Cr(OH)_3$

NJ Cr(VI) CONTAMINATED SITES



3 Companies Dumped Chromate Waste in 40s & 50s

~185 Sites ID'd

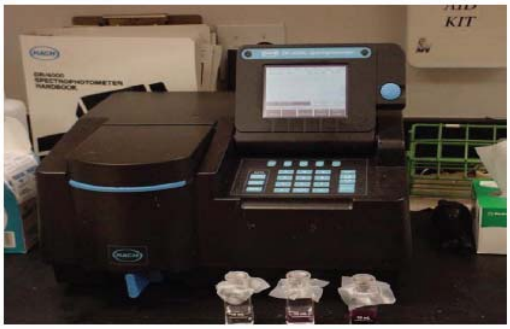
~45 Remediated

ANALYSIS OF Cr(VI)

- Air: sample collection issues
  - NIOSH 425
  - OSHA 215
- Waters: little or no sample preparation
  - Colorimetric: 3500
  - IC: 218.6
- Soils: Much more complicated

ANALYSIS OF Cr(VI) IN SOILS

- Two steps needed:
  - Extraction
  - Determination



EXTRACTION OF Cr(VI) IN SOILS: METHOD 3060A

- Take 2.5 g soil sample in 50 ml. of basic extraction solution (0.28 M Na_2CO_3/0.5 M NaOH)
- Cover, stir, and heat at 90-95°C for 60 min.
- Filter solution through 0.45 mm membrane filter
- Neutralize the extract by slowly adding HNO_3
- Adjust to pH of 7.5
- Transfer and dilute to 100 ml.
- Now you are ready for analysis

Cr(VI) IN SOIL: DETERMINATIVE OPTIONS

- Method 7196A - UV-Vis
- Method 7199 - IC w/UV-Vis
- Method 6800 - Speciated ICP-MS

Cr(VI) IN SOIL: NJ ANALYTICAL CHRONOLOGY

- 1980's" SW846 includes Method 3060 (hot alkaline digestion) and colorimetric determination (Method 7196A)
- 1992: Many problems (mostly low spike recoveries) cause EPA to withdraw Method 3060; **a 1st and only!!**
- Some states, including NJ, come up with their own alkaline extraction methods
- 1994: EPA approves Method 7199 (IC)
- 1995: Industry-sponsored research provides data for an alternate alkaline extraction method, brought to EPA
- 1996: EPA approves as 3060A, **but with additional QA**
- 1996 - 2005: NJ continues to use its own ext. method
- 1998: EPA approves Method 6800 (SIDMS)

METHOD 3060A CONCERNS

- Extraction must be quantitative and selective, without causing:
  - Oxidation of Cr(III) to Cr(VI) and/or
  - Reduction of Cr(VI) to Cr(III)
- Known problems include:
  - During extraction, some metals promote oxidation (Mn); others can cause reduction (Fe)
  - Organics, sulfides and others promote reduction
  - What about the method of detection??

DETERMINATIVE METHOD CONCERNS

- Does Method 7196A induce errors? Yes!
- Does Method 7199 induce errors? ????
- Are biases high or low? Yes! and Yes!
- Any reliable QA tools? Not Yet
- What about Method 6800??

SOME OF THE CHEMISTRY PROBLEMS

- Method 3060A does not automatically reject data that fails method QC
- >70% of soils tested in NJ fail Method 3060A QC; what to do w/data w/0% spike recoveries?
- How do you know that your sample behaves like the sample in the batch that was spiked?
- How do you develop a reliable QA program?

BIGGER PICTURE ISSUES w/CR(VI) IN NJ

- Lots of sites still to be cleaned up; clean-up costs in $billions; real-estate potential much greater
- Environmental justice concerns
- RPs have done almost all current Cr(VI) research
- Press and local political action committees are now heavily involved

WHAT'S GOING ON NOW IN NJ?

- Until late '03, all data by 3060/7196A: > 70% fails QA. Many sites issued NFAs based upon data that fails QA
- 12/03: Judge ruled NJDEP was not being protective enough; questioned analytical methods used to close sites
- 3/04: NJDEP Cr(VI) Workgroup formed
- 2/06: Workgroup Report finalized

NJDEP Cr WORKGROUP RECOMMENDATIONS I

- OQA will add USEPA Method 6800 to its list of certifiable analytical methods.
- Method 3060A will be used for digestion of all future soil samples for Cr(VI) analysis.
- A tiered approach to selection of determinative methods for Cr(VI) will be used
- Total chromium will be analyzed concurrently with Cr(VI) for all samples.

NJDEP Cr WORKGROUP RECOMMENDATIONS II

- Method 6800 could be used when spike recoveries by other methods are < 75% or > 125%.
- The Department will develop a data usability policy for Cr(VI). Spike recoveries that do not meet method QA requirements will not be used for unconditional "No Further Action" decisions.
- Measurements of the oxidative/reductive (eH and pH) properties of the soil matrix will be made for all samples from sites with oxidizing or reducing conditions.

NJDEP Cr WORKGROUP RECOMMENDATIONS III

- Spike recoveries must meet the requirements stated in the analytical measurements for the Cr(VI) results to be acceptable without qualification.
- A Sample Delivery Group will consist only of samples of a similar matrix type.
- NJDEP will not re-visit old data
- The Department will arrange and participate in the development of speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices.

NJDEP Cr WORKGROUP RECOMMENDATIONS V

- To see the NJDEP Cr Workgroup Report:
- www.njdep.gov/dsrt

CR(VI) SRM PROJECT SUMMARY

- Project Team: NJDEP, NIST, EPA & Rutgers U.
- Source material collected at LSP
- Homogenization by USGS
- Stability of Cr(VI) in processed material to be studied 1st
- Interlaboratory comparison: 7196A, 7199 and 6800
- Evaluation of results

Cr(VI) SAMPLE COLLECTION at LIBERTY STATE PARK

Cr(VI) SAMPLE COLLECTION at LIBERTY STATE PARK

SOURCE MATERIAL HOMOGENIZATION BY USGS

- 80 kg dried at RT for 3 days
- 1 kg. disaggregated to < 2 mm mesh size
- 50 kg. aliquots ball-milled for 16 hrs.
- Blending in $10ft^3$ V-blender for 16 hrs.
- UV-Irradiated using 2.5MRad Co-60 source
- Blended material (6.5 kg. batches) then spilt using custom 80 in. spinning riffler
- Bottled samples (80-100 g.) evaluated for correct mass range
- 1/100 selected for chemical analysis

Steve Wilson, USGS

STABILTY TESTING

- There is justifiable concern about the long-term stability of the processed material; this is a requirement for a SRM
- A selection across the lot of ~2500 bottles will be sent to labs. to be analyzed in triplicate over several months by:
  - 3060A/7196A
  - 3060A/7199
  - 3060A/6800
- Data will be reviewed by the Project Team before proceeding

INTERLABORATORY TESTING

- Once the stability of the processed material is assured, samples will be sent to ~35 laboratories worldwide that have volunteered to participate in an interlaboratory study
- Each laboratory will extract using 3060A, but analyze by their determinative method(s) of choice
- All data will be returned to the NJDEP who will organize and sort; results then sent to NIST for statistical analysis

AND THEN?

- If the data meets NIST's criteria for SRM issue, then the material will be commercially available sometime in 2007.

- NJDEP may require analysis of this SRM with all Sample Delivery groups for future Cr(VI) in soil measurements

- With commercial availability of Method 6800 and a reliable SRM, we will FINALLY be able to evaluate the efficacy of measurements of Cr(VI) in soils.

RECOVERY OF CHROMIUM SPECIES FROM SOILS; WHAT FACTORS ARE MOST IMPORTANT?

Buckley, Brian – Rutgers University Environmental and Occupational Health Sciences Institute; Lippincott, Lee – NJ Department of Environmental Protection; Murphy, Eileen – NJ Department of Environmental Protection; Nagourney, Stu – NJ Department of Environmental Protection; Johnson, Willie - Rutgers University Environmental and Occupational Health Sciences Institute; and Stiles, Robert - Rutgers University Environmental and Occupational Health Sciences Institute

Speciation of chromium is important because the chemical form of the metal means it is either a lung carcinogen or a micronutrient. At first glance, chromium speciation should be a relatively easy process. Both of the key species are stable under a wide variety of pH conditions. So why is this such a difficult assay? The answer lies in the extraction of the chromium from its matrices. Once the species are solublized, the redox chemistry of the chromium is governed by: the extracting solution, the concomitant elements in the matrix, and the pH. This process will affect the species of chromium extracted but not the amount and can generally be compensated for using stable isotope spikes. Method 6800 is beginning to receive more attention as analysts try to compensate for interconversion of the species but do not address the recovery issue of many soil matrices. We have found liquid to solid ratio makes a difference in recovery of each species from the soil. Concomitant ions and age of soil are two key factors in predicting the efficacy of the extraction technique. Total chromium measurements should be used as a check for overall extraction efficiency. This presentation will focus on the variables associated with a good recovery of both chromium species from soil and how we use the total chromium value as a measurement of extraction efficiency.

Recovery of Chromium Species from Soils: What Factors Are Most Important

Brian Buckley[1], Robert Stiles[1] and Willie Johnson[1], Stuart Nagourney[2], Lee Lippincott[2] and Eileen Murphy[2]

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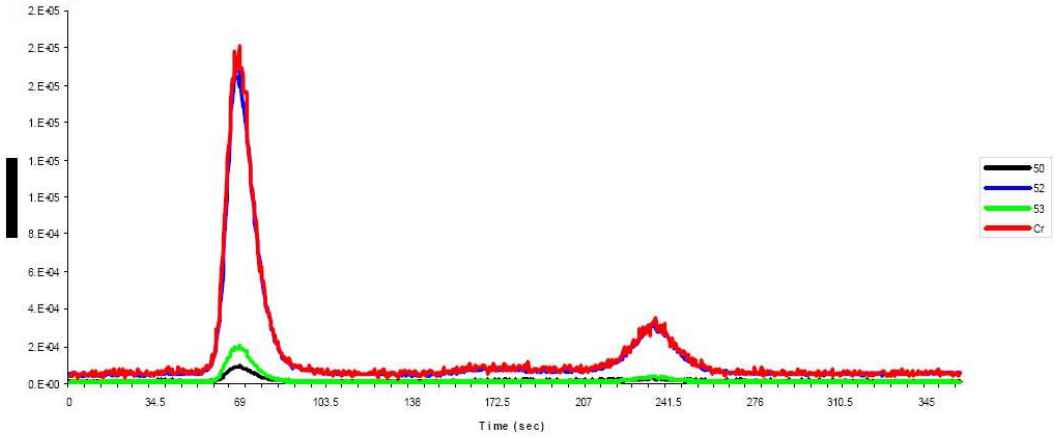
2. NJ Department of Environmental Protection, Division of Science, Research and Technology

Environmental and Occupational Health Sciences Institute

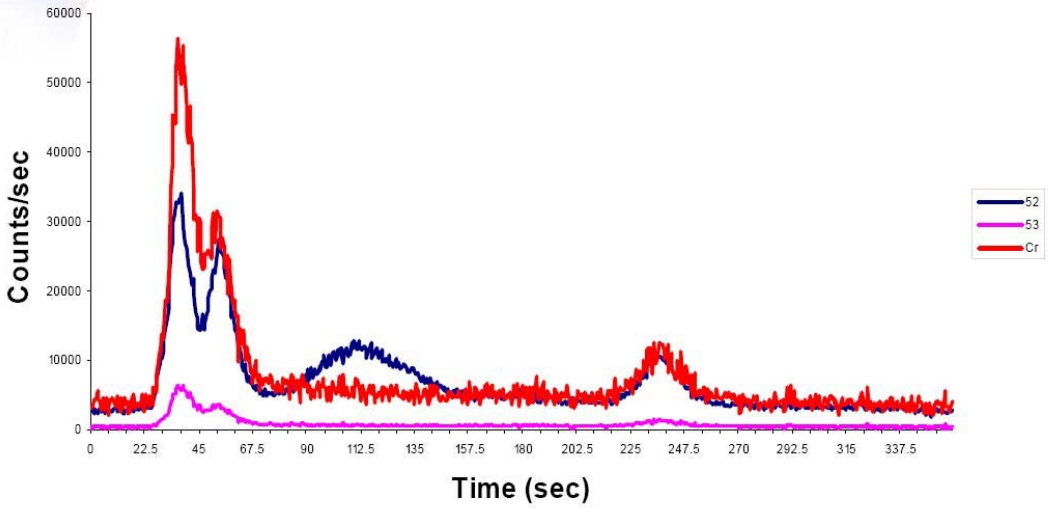
Dionex DX 600

Inductively Coupled Plasma Mass Spectrometer

Chromium from soil
Isotopic ratio comparisons



Chromium (VI) and (III) in gastric juice
Eliminating interferences with ratios



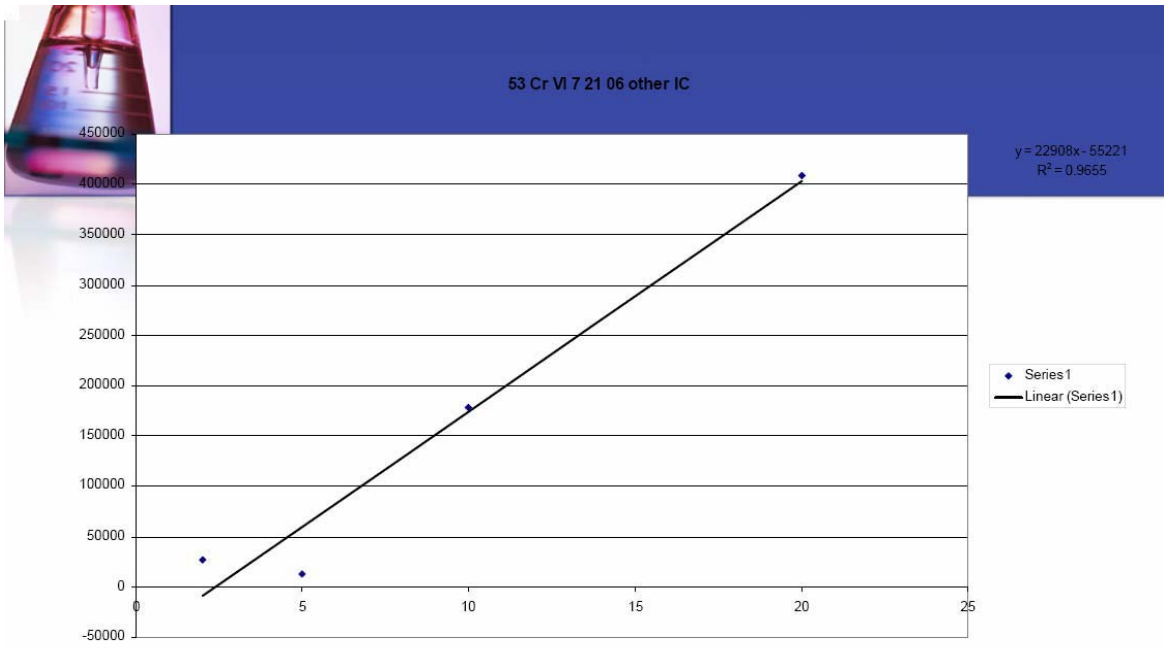


Figure 1: Four Point Calibration Curve for the Direction Injection of 53CrVI standard into IC-ICP/MS.

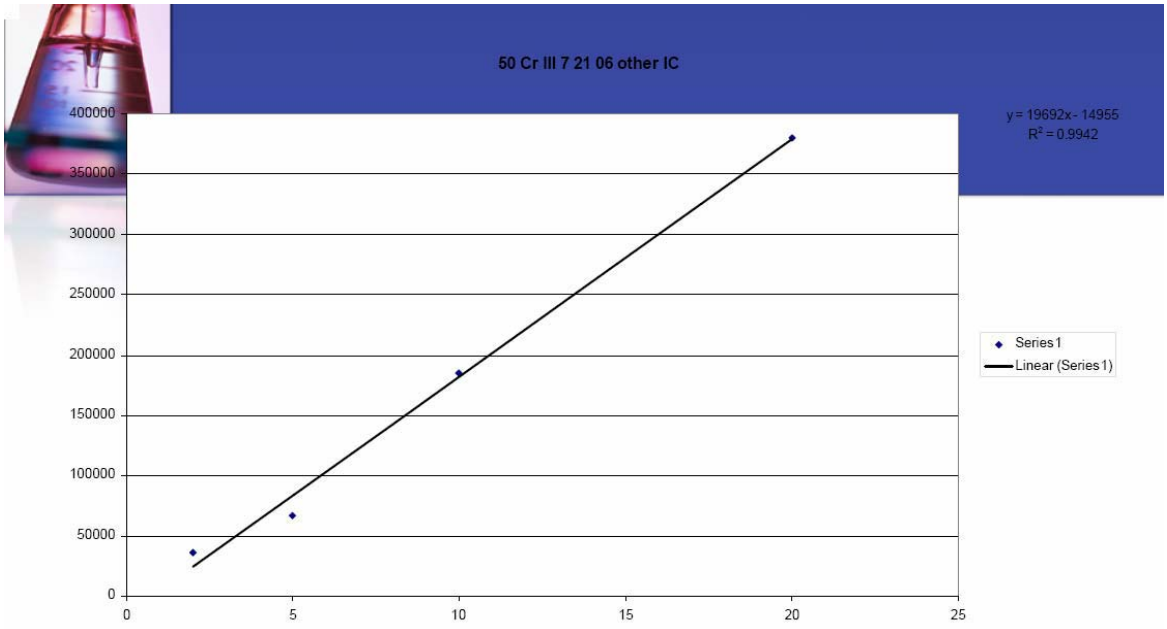


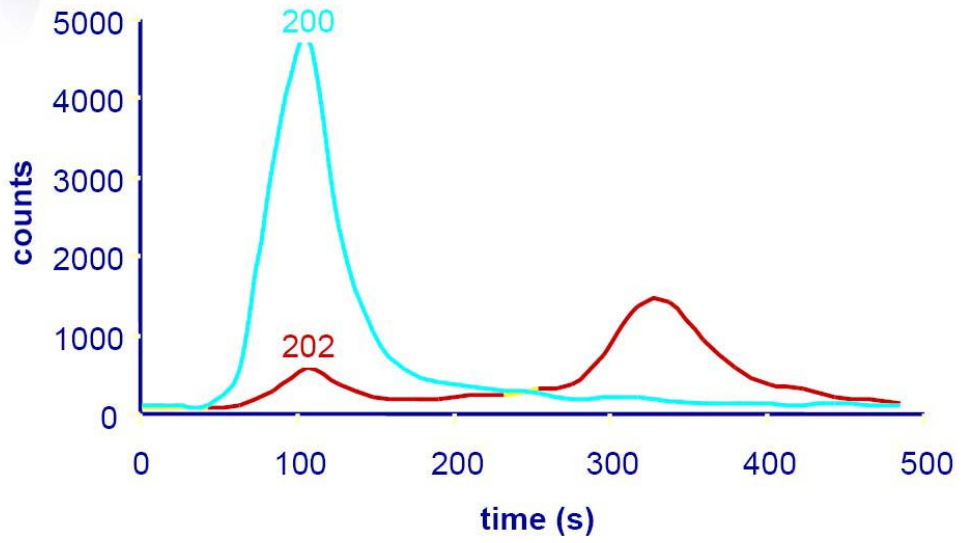
Figure 2: Four Point Calibration Curve for the Direct Injection of 50CrIII standard into IC-ICP/MS.

Specie intact extraction

Microwave advantage

- Higher pressure and temperature
- Better infiltration of extratant into material
- “mobilization” of all material that absorb microwaves

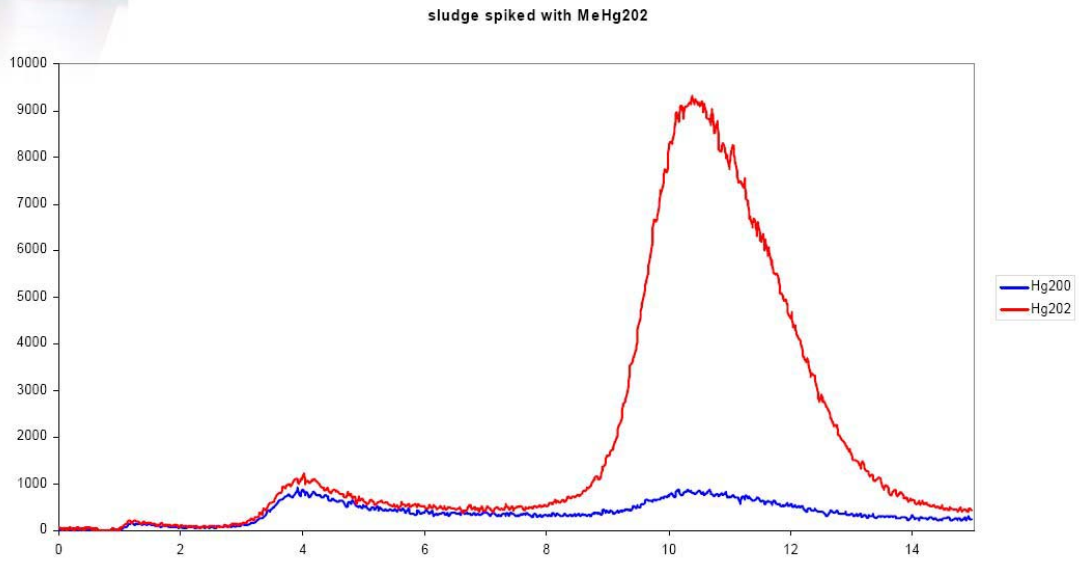
Chromatograms of mercury species spiked soil sample 1 ppm $^{200}Hg^{2+}$ and 1 ppm $Me^{202}Hg^{+}$



Percent recoveries of mercury species from spiked soils

Sample	IC-ICP-MS		IC-CV-ICP-MS	
	Hg^{2+}	CH_3Hg^{+}	Hg^{2+}	CH_3Hg^{+}
Soil 1 (Bayonne, NJ)	94 ± 3	106 ± 5	103 ± 8	95 ± 6
Soil 2 (Aiken, SC)	107 ± 8	93 ± 6	105 ± 7	92 ± 8

Stable isotope of mercury spike



Mercury recoveries from sludge spike experiment

Sample	Hg2+ conc (ppb)	MeHg2+ conc (ppb)	Recovery of MeHg202
0203 ANDR	503.12	54.84	0.93
0203 CAND	N/D	26.90	1.06
0203 GRDR	106.78	155.32	0.89
0203 GRLI	N/D	48.92	0.99

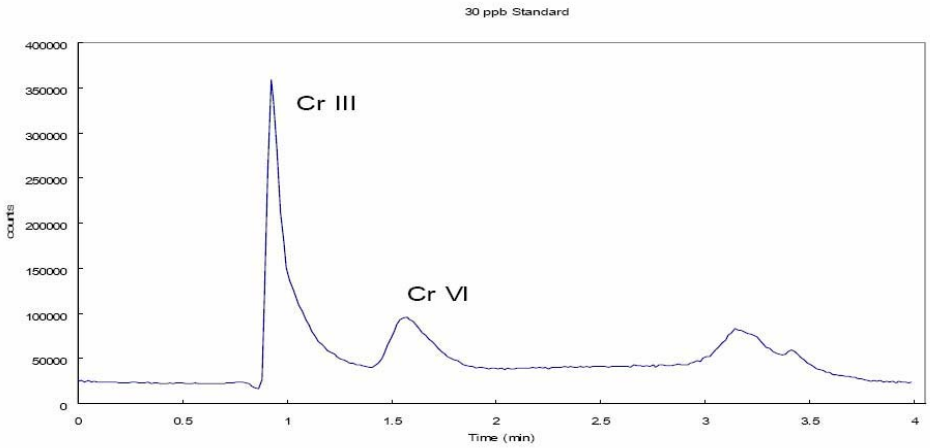
Total chromium determination by microwave extraction

- 0.08 and 0.10 g of soil
- digested with 10 mL of 100% HNO3.
- 1200 W power
- 350 psi pressure
- 180°C temperature
- 10 minute ramp time
- 15 minute hold time

Method validation

- Need to account for both extraction loss and species changes during extraction
- Compare total chromium recovery to sum of individual species
- Look for interconversion with method 6800

Chromatography



Modified 3060a Method Summary

- $NaOH/NaCO_3$ extraction
- Extraction in microwave*
- “Soil” samples mixed with sand for dilution*
- Solution made neutral to acid**
- Extrantant solution diluted**
- Injected into IC**
- Separated on an anion exchange column**
- Redox monitored by stable isotopes

* Modification to EPA method

* * Our method

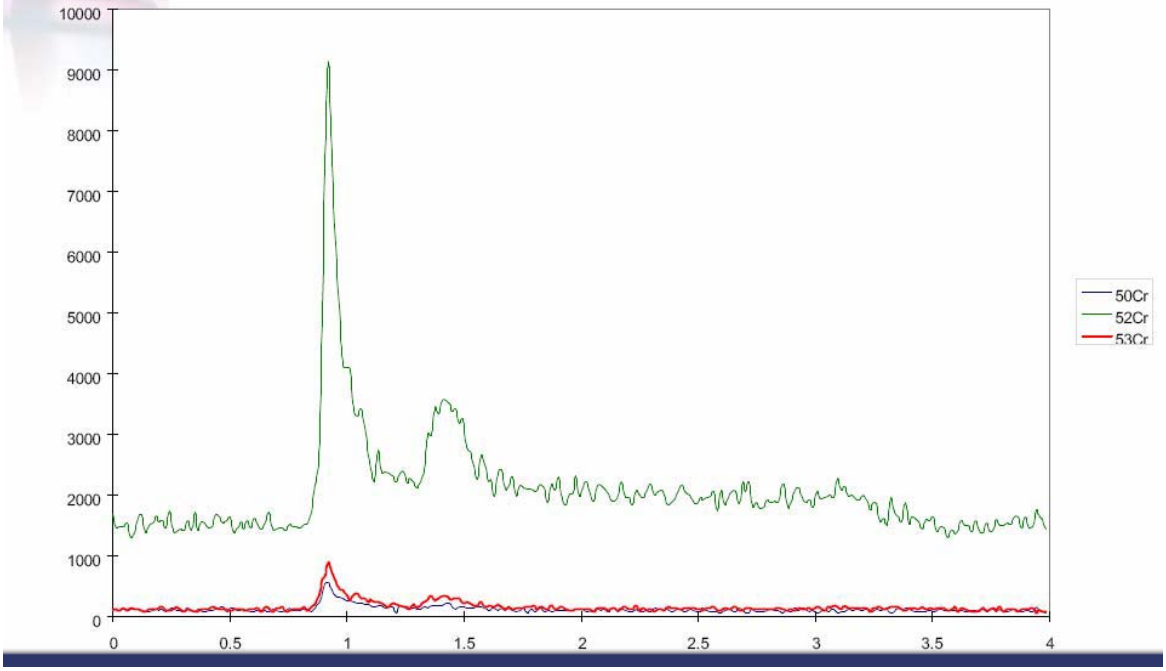
Problems to overcome

- Largely basic extractant designed to stabilize Cr VI
- Does not extract Cr III well
- Can cause Cr III to precipitate (postulated)
- Extraction efficiency determined by sample matrix

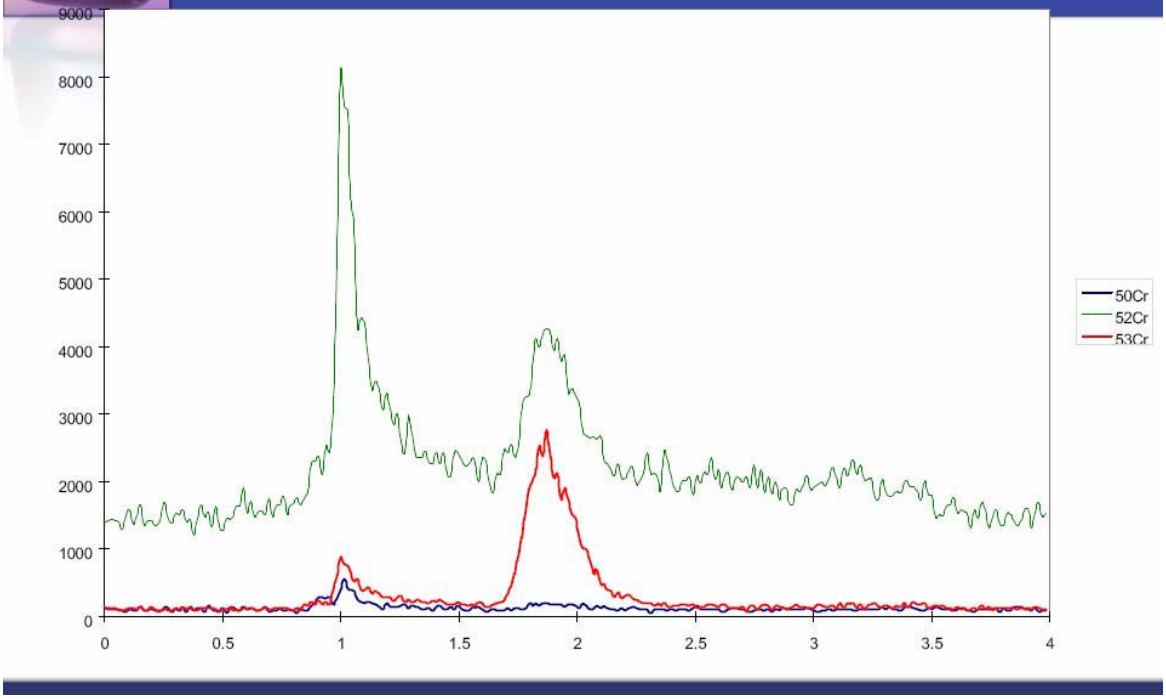
Early spike recoveries from sand

	Acid	Base
Cr III	114%	25%
Cr VI	114%	142%

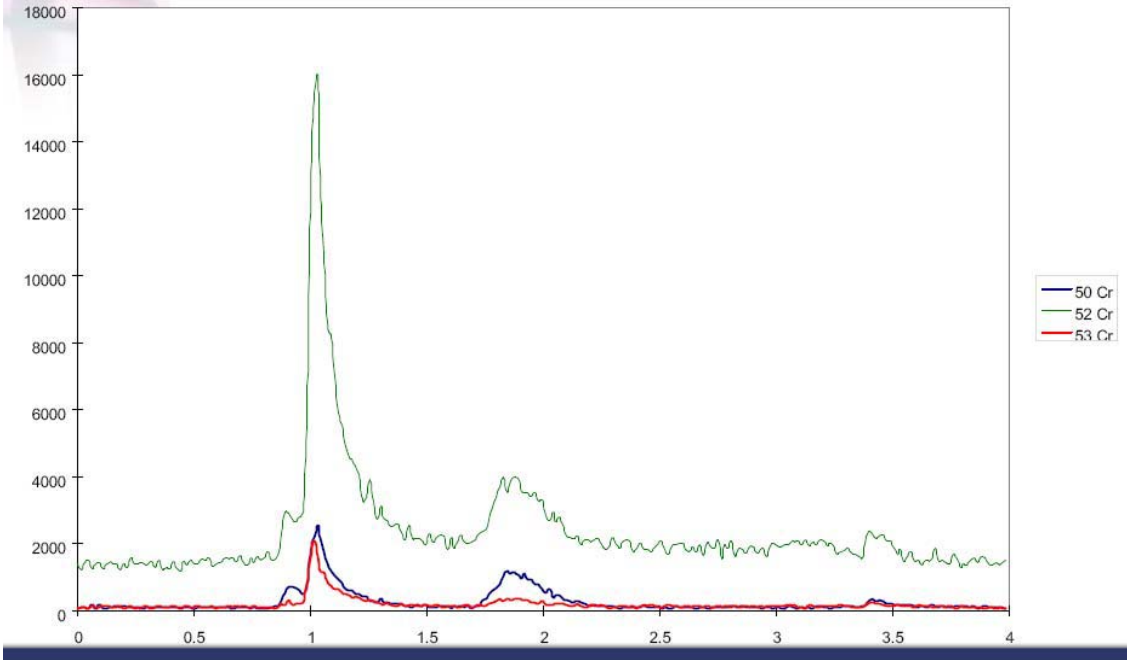
Chromatogram of 3060a of an Unspiked Liberty State Park Soil Sample.



Chromatogram of 3060a 266 ppb Spike of ^{53}CrVI onto 0.2 g Liberty State Park Soil and 1.8 g Silica.



Chromatogram of 3060a with 266 ppb Spike of ^{50}CrIII onto 0.2 g Liberty State Park Soil and 1.8 g Silica.



Recoveries for L/S ratio studies

Sample Mass	Extract Vol	Dilution Factor	Cr III	%CV	Cr VI	%CV	Total	Recovery
0.1g	25 mL	1:100	107.9	17%	100.1	4%	208	41%
0.1g	36.25 mL	1:100	83.1	28%	170	17%	253.2	50%
0.1g	36.25 mL	1:125	103.7	26%	199.5	9%	303.2	60%
0.1g	42.5 mL	1:100	179.3	83%	194.8	5%	374.1	74%
0.1g	42.5 mL	1:125	191.9	72%	211	9%	403	80%

Optimized LSP soil extraction and analysis

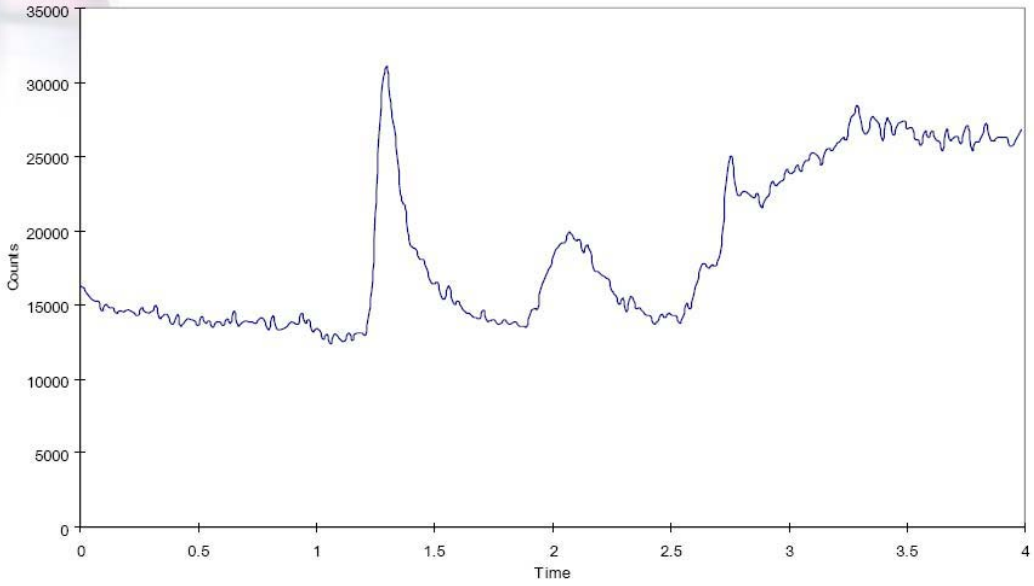
- 0.08 g soil
- 0.74 g Sodium Bicarb
- 7.5 mL 2.5 M NaOH
- 35 mL dI H20
- 300 W power, 95°C for 60 minutes
- AS11 Analytical Column
- 1.5 mL/min flow rate
- 100 mL injection loop
- 0 – 1.5 min 30%:70% 1M HNO3:H20
- 1.5 -4.0 min 100% 1M HNO3

Optimum Conditions

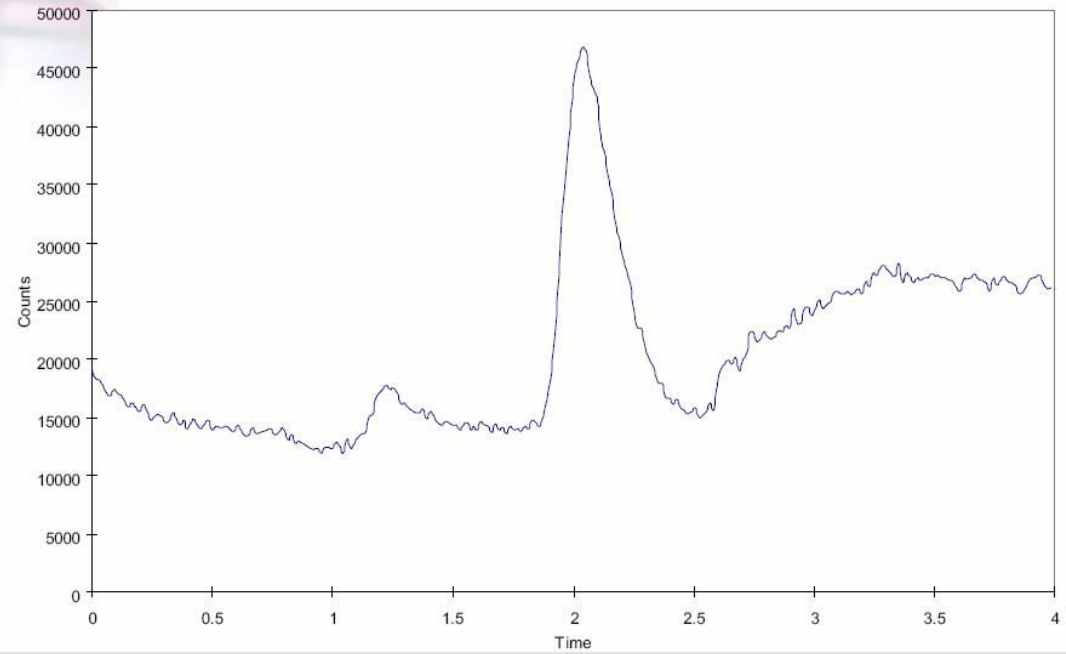
68 mL
0.16 g
1:125

	Cr III	Cr VI	Total Cr	Recovery
1	296.5	218.2	514.7	102.3
2	237.3	176.6	413.9	82.3
3	269.9	175.4	445.3	88.5
Average	267.9	190.1	458.0	91.0
ST Dev	29.7	24.4	51.6	10.3
% CV	11.1	12.8	11.3	11.3

Chromatogram of 3060a Extraction of Liberty SP Soil.



Chromatogram of 3060a of 0.2 g Liberty Soil with 0.8 g Al NO_3



Recoveries with $AlNO_3$ added

Liberty	Cr VI	Cr III	Total	Recov
Extract 1	439.1	24.7	463.8	92.2%
Extract 2	61.4	725.4	786.8	156.4%
Extract 3	85.1	155.5	240.6	47.8%
Average	195.2	301.9	497.1	98.8%

Some additional findings with sand surrogate

- Cr VI 80.6% vs CrIII 40.0%.
- Clean soil Cr III spike 103.6% ± 6.7% before addition of base.
- After basic extractant soluiton, recovery of Cr III is poor even with a high concentration of acid
- Pb and Ba do not have an effect on the recovery of trivalent chromium
- < half Cr VI recovered surrogate soil spike with Ba and Pb

New soils new methods

	3060a L/S high		20 psi Pressure		Increased Bicarb *	
	Recovery	CV	Recovery	CV	Recovery	CV
Liberty SP	85.1	2.3	88.3	3.7	137	11
Society Hill	7.7	15	9	4	13.6	8
Garfield Ave	26	3.6	33.2	2	64.2	15
Gateway	8.6	9.5	9.3	14	10.9	2.4

* 2.2 g bicarb vs. 0.74 no increase in psi

Borate Extraction

	Cr VI (ppm)	Cr VI (CV)	Cr III (ppm)	Cr III (CV)	Total	Recovery
Garfield Ave	32.7	21.8%	12.8	21.2%	45.5	1.5%
Society Hill	40.6	8.8%	13.6	17.6%	54.2	1.0%
Gateway	106.7	8.1%	8.4	28.2%	115.1	1.8%

Future work

- Test extraction method ruggedness using concomitant ions
- Test interconversion interference of current extraction protocol
- Use optimized method on multiple chromium contaminated samples
- Measure each species in new SRM

Acknowledgement

Acknowledgements

- NJDEP SR05-048
- NIEHS Center ES05022
- EOHSI

SPECIES ANALYSIS DURING MEASUREMENTS PROCESS

Bath, Frank; Retsch, Inc.
Batzke, Matthias; Retsch, Inc.
Fahrenholz, Timothy; Retsch, Inc.
Kern, John; Duquesne University
Kingston, K.M. 'Skip'; Duquesne University
Pamuku, Matt; Retsch, Inc.
Rahman, Mizanur; Duquesne University

Elemental speciation is unique in that the species of interest or the analyte being evaluated may change and become another analyte during the analysis process. This phenomenon and related parameters make species measurement one of the most challenging fields of metrology, especially when the goal is to achieve accuracy. Significant areas contributing to the lack of accuracy are the lack of certified standard materials and the lack of proven, reliable diagnostic tools. Many elemental species undergo conversion or degradation of the species of interest during measurement processes and even sometimes during sampling, storage and transport. Until recently, there have not been any effective diagnostic tool to trace the fate of species; conventional speciation methods measure the species' concentrations in the final solutions at the time of measurement but provide no information on species transformations. Knowing the transformation of the species is critical in the preparation and certification of standard reference materials and for accurate speciated measurements. Newly approved EPA RCRA Method 6800, known as Speciated Isotope Dilution Mass Spectrometry (SIDMS), facilitates to identify and enable correction for such degradations or conversions. SIDMS may also be directly applied to validate a variety of other speciated protocols to accurately measure species like methylmercury, ethylmercury and other alkylmercury species in tissues and other materials (1, 2, 7, 15). SIDMS has been demonstrated to determine the species concentrations at the time of spiking, as well as during sampling and measurement processes. The method also provides the ability to perform diagnostic analysis by isolating procedural protocol steps in specific matrices and reveal species-shifting potential. By spiking the sample at multiple steps with enriched stable isotopes of the same species, SIDMS can identify the steps at which the species are altered (3-7).

As examples, SIDMS has been applied to monitoring the fate of methylmercury and Hg(II) and other alkylmercury species as well as Cr(III) and Cr(VI), during the sample processing and analysis steps. The results of recent studies showed that classical methods may not be able to detect alteration of the species from difficult matrix samples and sample preparation steps that cause transformation of species (3, 5, 8, 10). Recently, known pollutant-species have been found to be even more toxic, prompting lowering of the acceptable limits of these species in the workplace by OSHA.

After July 1, 2006, electronic products exported to European Union countries require that hexavalent chromium accurately measured and the allowable species limits be met before they are allowed to be sold in the EU. This new regulation is referred to as "Restriction of Hazardous Substances" or (RoHS) and is required before sales of products are allowed (14). China, Korea and many other countries have already indicated that they will impose similar species-specific limits for electronic products sold in their countries. RoHS and all other derivative regulations also require measurement of Hg, Cd and Pb. Discussion and examples of sample preparation for

these regulations will be discussed, limitation of surface techniques such as x-ray fluorescence techniques examined with respect to speciation measurement and certification.

Mercury has been demonstrated to undergo transformations between methylmercury and inorganic mercury during the measurement process (5, 8, 10). SIDMS is a method that can be generalized for most poly-isotopic species that have the potential to be transformed from species to species during the evaluation process. SIDMS has been successfully applied to measure species of poly-isotopic elements such as Cr, Hg, Se and Sn. Standards may also be produced with isotopically enriched species and used if the processes alter the species forms (9, 10).

Coal-fired power plants around the world are a dominant source of electric energy, particularly in developing nations. As much as 20% of the chromium contained in coal may be converted to Cr(VI) during power plant production of energy. Field environmental examples are presented, demonstrating the effectiveness of applying the SIDMS measurement for Cr in the coal-fired power industry (13). As a measurement and diagnostic tool, SIDMS has been standardized and approved as EPA method 6800, and as part of the new Method 3200 (10, 11, 15).

These new EPA stable isotopically-based methods provide new tools and assist with some of the uncertainty in speciated environmental measurements. The general method is described and applications to both Cr species and Hg species are demonstrated in the latest draft of the method. In applying Method 6800, commercially available species-specific reagent and standard kits simplifies the entire SIDMS protocol and make it possible to implement Method 6800 in a routine fashion. Software in these kits, with equations keyed to enriched stable isotopes of each kit improve, simplify and accelerate quality assurance, data acquisition and final calculation steps. A tutorial SIDMS-software is now available from the EPA and Duquesne University to assist in understanding the equations associated with Method 6800. This past year analyst proficiency testing was made available to commercial analytical laboratories in order to enable high volume speciation analyses in a routine and automated fashion. The efforts of proficiency-certified laboratories described and some of the data of their speciation analysis work are presented.

Some COPR or chromium ore processing residue wastes that are concentrated or that have been mixed with other soils are unstable even after treatment. Recent unpublished work by Kingston, co-workers and collaborators, demonstrated that some well-known treatment process do not keep Cr species stable and transformations from Cr(III) to Cr(VI) occur in time frames from several years to several weeks time.

New Jersey is in the midst of many large remediation projects that involve several competing technologies that attempt to contain the Cr(VI) in various inert forms. EPA Method 6800 is being used to analyze these samples and forms. New Cr(VI) contaminants in major western states are emerging in roads that are paved with Cr(VI) leaching materials which contaminate soil in the surrounding communities serviced by these roads (13). Interferences and contributions from the soil chemistry in samples frequently skew the result of several analytical methods, making decisions difficult. Advanced species measurement methods will be demonstrated and application to critical environmental measurement needs will be described.

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Rahman, G. M. Mizanur; Kingston, H. M. ‚Skip'; Towns, Theodore G.; Vitale, Rock J.; Clay, Kyle R. "Determination of Hexavalent Chromium using Speciated Isotope Dilution Mass Spectrometry on Microwave Speciated Extraction of Environmental and Other Solid Materials." Anal. Bioanal. Chem. Vol. 382. 1111-1120, 2005

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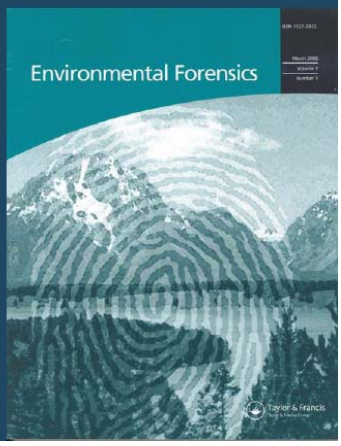
Rahman, G. M. M.; Kingston, H. M. S.; Kern, J.C.; Hartwell, S. W.; Anderson, R. F.; Yang, S.Y. "Inter-Laboratory Validation of EPA Method 3200 for Mercury Speciation Analysis using Prepared Soil Reference Materials." Appl. Organomet. Chem. 19, 301-307,2

Achieving Quantitative Species Analysis When Analytes Turn Into Other Analytes During the Measurement Process

H. M. Skip Kingston, and Mizanur Rahman, Timothy Fahrenholz, Gonzalo Manchego, Matt Pamuku, John Kern, Dengwei Huo
Duquesne University, Pittsburgh PA

NEMC 2006
Washington DC - August 30 , 2006



Extending Species Analysis Applications: Method 6800

- Tissue
- Food
- Environmental Forensics
- Homeland Security
- Human Samples
- Environmental Industrial Materials
- Validation - of other speciation applications
- Hi Volume Laboratories Performance Qualified

Tissues and Food - Tuna Fish CRM

3

Tissue and Food - Tuna Fish CRM

irm
Institute for Reference Materials and Measurements

ERM
European Reference Materials

CERTIFICATE OF ANALYSIS

ERM®- CE464

TUNA FISH		
Parameter	Mass fraction	
	Certified value [1] mg/kg	Uncertainty [2] mg/kg
Total Hg	5.24	0.10
CH_3Hg^+	5.50	0.17

1) Unweighted mean value of the means of 8 (total Hg) and 12 (methyl Hg) accepted sets of data, each set being obtained in a different laboratory and / or with a different method of determination. The certified value is traceable to SI.

2) The certified uncertainty is the half-width of the 95 % confidence interval of the mean defined in 1). k-factors were chosen according to the t-distribution depending of the number of accepted sets of results.

4

Results from Tuna Fish CRM Analyses

(Samples Prepared Using EPA Method 3200 unless otherwise indicated)

	Total mercury (µg/g)	Methyl-mercury (µg/g)	Methyl-mercury (as mercury µg/g)	Hg^{2+} to $MeHg^{+}$ (%)	$MeHg^{+}$ to Hg^{2+} (%)
Certified value	5.24 ± 0.10	5.50 ± 0.17	5.12 ± 0.16	NA	NA
ICP-MS	4.41 ±0.15 (5.44 ± 0.06 using EPA 3052)	NA	NA	NA	NA
LC-ICP-MS	NA	4.35 ±0.19	4.05 ±0.18	NA	NA
SCF-LC-ICP-MS	NA	4.24 ±0.16	3.94 ± 0.15	NA	NA
SIDMS	5.708 ± 0.422	6.02 ±0.359	5.599 ± 0.334	18.07 ± 4.14	0.84 ± 0.62

5

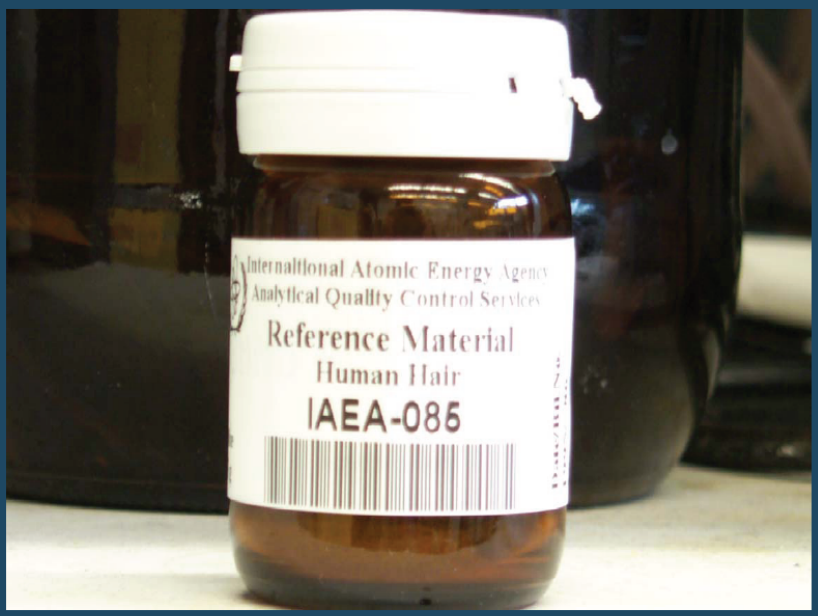
Sample calculation: conversion of µg/g $MeHg^{+}$ as $MeHg^{+}$ to µg/g $MeHg^{+}$ as Hg

- Given 5.50 µg/g $MeHg^{+}$ as $MeHg^{+}$, find µg/g $MeHg^{+}$ as Hg:

- 5.50 µg $MeHg^{+}$ as $MeHg^{+}$/g tissue = 5.50 x 10^{-6} g $MeHg^{+}$ as $MeHg^{+}$/g tissue
- 5.50 x 10^{-6} g $MeHg^{+}$ as $MeHg^{+}$/g tissue ÷ FW $MeHg^{+}$ =
- 5.50 x 10^{-6} g $MeHg^{+}$ as $MeHg^{+}$/g tissue ÷ 215.6247 g $MeHg^{+}$/mol=
- 2.551 (carry one extra sig fig) x 10^{-8} mol $MeHg^{+}$ as $MeHg^{+}$/g tissue
- 2.551 x 10^{-8} mol $MeHg^{+}$ as $MeHg^{+}$/g tissue =
- 2.551 x 10^{-8} mol $MeHg^{+}$ as Hg/g tissue
- Molar mass of Hg = 200.59 g/mol
- 2.551 x 10^{-8} mol $MeHg^{+}$ as Hg/g tissue x 200.59 g/mol
- 5.12 x 10^{-6} g $MeHg^{+}$ as Hg/g tissue =
- 5.12 µg/ g $MeHg^{+}$ as Hg/g tissue

6

Human Tissue - Hair CRM
Environmental Forensic Analysis



7

Human Hair CRM

REFERENCE MATERIAL

IAEA-085

METHYLMERCURY, TOTAL MERCURY AND OTHER TRACE ELEMENTS IN HUMAN HAIR (METHYLMERCURY SPIKED)

Date of issue: May 2000⊕

Recommended Values
(Based on dry weight)

Element	Recommended Value mg/kg	95% Confidence Interval mg/kg	N*
Hg	23.2	22.4 – 24.0	67
Fe	79.3	71.0 – 87.8	16
Zn	163	156 – 170	24
MeHg§	22.9	21.9 – 23.9	5

8

METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

- Sample preparation
  - 100 mg hair sample in microwave vessel
  - Add 10 mL of concentrated HNO_3
  - Seal the microwave vessel
  - Heat at 180 ± 5 °C 10 min
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis

Sample	Certified value (µg/g)	This study (µg/g)
IAEA-085	23.2 ± 0.8	23.19 ± 0.73

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METHOD 3200

MERCURY SPECIES FRACTIONATION AND QUANTIFICATION BY MICROWAVE ASSISTED EXTRACTION, SELECTIVE SOLVENT EXTRACTION AND/OR SOLID PHASE EXTRACTION

ARTICLE

JAAS www.rsc.org/jaas

Development of a microwave-assisted extraction method and isotopic validation of mercury species in soils and sediments†

G. M. Mizanur Rahman and H. M. 'Skip' Kingston*

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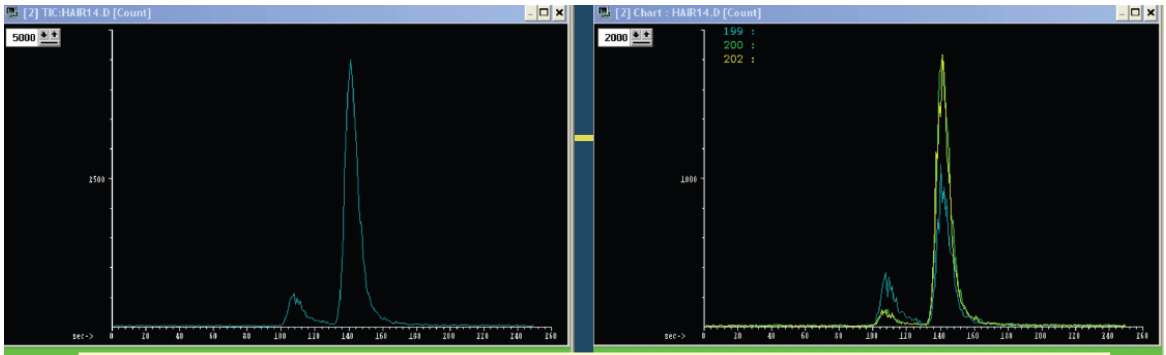
Received 26th March 2004, Accepted 7th January 2005
First published as an Advance Article on the web 4th February 2005

- Sample preparation
  - 100 mg of hair sample in microwave vessel
  - Double spike with known amount of isotope enriched mercury species ($^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^{+}$)
  - 10 mL of 4M HNO_3
  - Extract at 100 °C for 10 min.
  - Filter through 0.22 µm glass fiber filter
  - Store at 4 °C until analysis
- Validated using EPA 6800 isotopically

10



	Inorganic mercury (µg/g)	Methyl-mercury (µg/g)	Hg^{2+} to $MeHg^{+}$ (%)	$MeHg^{+}$ to Hg^{2+} (%)
Certified value	0.3	22.9 ± 1.4	NA	NA
LC-ICP-MS	1.80 ± 0.61	22.67 ± 1.54	NA	NA
SCF-LC-ICP-MS	2.28 ± 0.20	22.69 ± 0.91	NA	NA
SIDMS	0.59 ± 0.22	23.65 ± 1.42	4 ± 2	6 ± 1

IAEA-085 by 6800, Reference Dr. Rahman, NEMC 2006

11

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

Lu Yang* Elena Ciceri[1], Zoltán Mester and Ralph E. Sturgeon

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

5% of Cr in Yeast is Cr(VI)

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"

Pharmaceutical Brewer's Yeast used for Production of Dietary Supplements

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

Lu Yang, Zoltan Mester and Ralph E. Sturgeon – Nat. Research Council of Canada, by permission, accepted for publication in Analytical and Bioanalytical Chemistry

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Method 6800 – Independent Validation Comments

- "SSDIDMS [Method 6800] provides an elegant approach to attaining this information [quantitation of Cr(III) and Cr(VI)] and may be considered as the current state-of-the-art, with the exception of more esoteric approaches such as XFAFS, for which a synchrotron source is needed to probe redox states directly in solids."
- "Kingston group solved the problem [inaccurate speciation] by using species specific isotope dilution mass spectrometry for the highly accurate determination of Cr(VI) in environmental samples that cannot otherwise be determined using conventional instrumental analytical methods."

Lu Yang, Zoltan Mester and Ralph E. Sturgeon – Nat. Research Council of Canada, by permission, accepted for publication in Analytical and Bioanalytical Chemistry (2006)

14

Autism: An Epidemic

"Autism has risen over 1000% in the last 20 years which is not possible if genetic mutation is the only cause. There must be an environmental component that is inducing these susceptible children to become autistic."

- Dr. Bryan Jepson, MD, 2003

Diagnoses

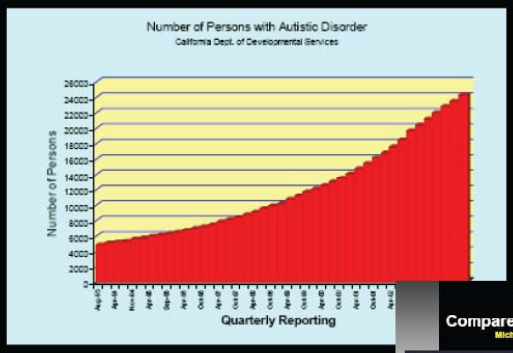
Dr. Scott Faber, MD

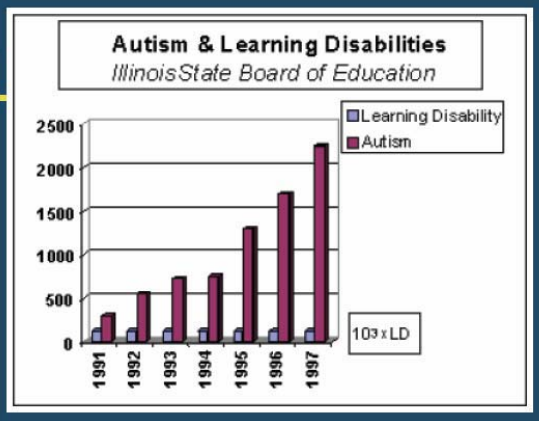
"one of my kids"

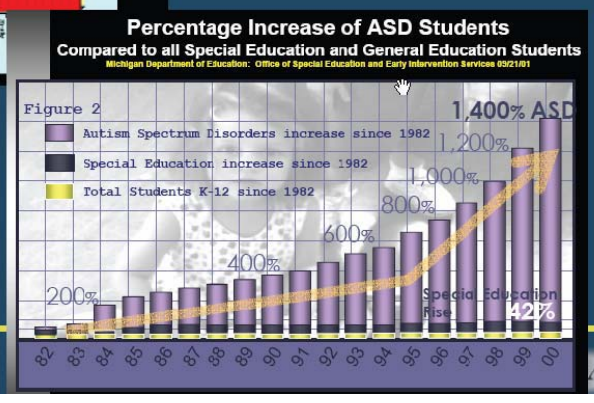
Children's Institutes, Pittsburgh

Duquesne University

Number of Persons with Autistic Disorder
California Department of Developmental Services
Quarterly Reporting: April 1993 - April 2004







Duquesne University

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Have Commercial Laboratories Implemented High Throughput Speciated Analysis – 6800?

- What are their proficiencies?
- How were they evaluated/assisted?
- Are they ready?

AIT - Analyst Proficiency Evaluated

Definitive Method

Legally Defensible Data

IDMS/SIDMS

DEP Recognitions

Client Confidence

Regulatory Update

Quality

Leads, Referrals

License

Free Software Upgrades

AIT Confirms Skills and Knowledge of Analyst

Certifying Analysts in Commercial Testing Laboratories for Methods 6800 and 3060A

- Training and Tech Support
- NIST-Traceable Standards
- Unique 6800-Software
- Proficiency Materials
- SOP drafting assistance
- Complete Kits, Protocols
- Hyphenation, Automation, LC Method and Integration Assistance

Laboratory Proficiency:
Severn-Trent Labs, Pittsburgh, PA
Applied Speciation and Consulting

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Cr Species Analyst Proficiency Evaluation Kit (CAPTK™) - Complete and Comprehensive

TM - CAPTK and ESIS are trademarks of Applied Isotope Technologies, Inc.

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Chromium Analyst Proficiency Testing Kit (CAPTK)

Part No. 20540 – Complete Kit: Chromium Analyst-Proficiency Testing Kit (CAPTK)

		Part No	Description	Qty/Kit
1		20541	CAPTK-A: Combo for Total Chromium, Soil Extracts	
	1A	20542	Cr Soil Extract for Total Chromium, 25g	1
	1B	20543	Cr Soil Extract Reagent Blank, 25g	1
2		20544	CAPTK-B: Combo for Cr(VI), Soil Extracts	
	2A	20545	Cr(VI) Soil Extract, 25g	1
	2B	20546	Cr(VI) Soil Extract Reagent Blank, 25g	1
3		20547	CAPTK-C: Soil Matrix Combo, Cr-Species Matrix	
	3A	20548	Cr Soil Matrix, Cr(VI) only, 10g	1
	3B	20549	Cr Soil Matrix, Cr(VI) and Cr(III), 10g	1
	3C	20550	Cr Soil Matrix Blank, 10g	1
4		20551	CAPTK-D: Analytical Standard Combo for Cr-Species	
		20552	^{50}Cr-Enriched Cr(III) Standard, 100ug/10g	1
		20553	^{53}Cr-Enriched Cr(VI) Standard, 100ug/10g	1
5		20554	CAPTK-E: ICP-MS Combo, for Mass-bias and Deadtime Correction Standards	
	5A	20556	Naturally Abundant Cr(III), 100ug/10g	1
	5B	20556	Naturally Abundant Cr(VI), 100ug/10g	1

(***) *Kits 4 and 5 constitute AIT's SIDMS Analytical kit and are shipped with a CD containing AIT's special SIDMS software that is used for final calculations of concentration of and percent (%) conversion between Cr(III) and Cr(VI).*

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AIT – Training and Analyst Proficiency for Methods 6800 and 3060A

- Training and Technical Support
- Unique 6800-Software, Free Upgrades, License
- Comprehensive Proficiency Materials – One Source
- SOP Drafting Assistance
- Assistance in Pricing and Cost Analysis (commercial Labs)
- Application Assistance (Automation and LC separation)
- Complete Kits, Protocols
- Others to Follow: 6800-3200 for Mercury Next

22

"RoHS"

111/24/CD

COMMITTEE DRAFT (CD)

IEC/TC or SC: 111	Project number IEC 62321, Ed.1	
Title of TC/SC: Environmental standardization for electrical and electronic products and systems	Date of circulation **2005-06-24**	Closing date for comments **2005-09-23**
Also of interest to the following committees IEC/TC3, SC17B, SC62A, TC 108	Supersedes document 111/2/NP & 111/9/RVN and 111/25/INF	
Functions concerned: ☐ Safety ☐ EMC	☒ Environment ☐ Quality assurance	
Secretary: Andrea Legnani (Italy) E-mail: andrea.legnani@anie.it	THIS DOCUMENT IS STILL UNDER STUDY AND SUBJECT TO CHANGE. IT SHOULD NOT BE USED FOR REFERENCE PURPOSES. RECIPIENTS OF THIS DOCUMENT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.	

Title:
IEC 62321, Ed.1: Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products

(Titre) :

Introductory note

Global legislation dealing with hazardous substances, most notably the Directive on "Restriction of Hazardous Substances" (RoHS) in Europe, is forcing the electrotechnical industry to develop methods for analytical testing of its components and products for regulated substances. Recognizing the electrotechnical industry's need to develop global, standardized test methods for regulated substances in electrical, electronic and electrotechnical products, ACEA (IEC's Advisory Committee on Environmental Aspects) decided in March 2004 to form an *ad hoc* working group to develop test procedures that will allow the electrotechnical industry to determine the levels of six regulated substances (Pb, Hg, Cd, Cr VI, PBB, PBDE) in electrotechnical products on a consistent global basis.

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RoHS Screening Limits

Table 2: Screening limits in mg/kg for regulated elements in various matrices.

Element	Polymer Materials	Metallic Materials	*Electronics*
Cd	P ≤(70-3σ)< X <(130+3σ)≤ F	P ≤(70-3σ)< X <(130+3σ)≤ F	LOD< X <(250+3σ)≤ F
Pb	P ≤(700-3σ)< X <(1300+3σ)≤ F	P ≤(700-3σ)< X <(1300+3σ)≤ F	P ≤*(500*-3σ)< *X <(1500*+3σ ≤ F
Hg	P ≤(700-3σ)< X <(1300+3σ)≤ F	P ≤(700-3σ)< X <(1300+3σ)≤ F	P ≤*(500*-3σ)< *X <(1500*+3σ ≤ F
Br	P ≤ (300-3σ)< X		P ≤ *(250*-3σ)< *X*
Cr	P ≤ (700-3σ)< X	P ≤ (700-3σ)< X	P ≤ *(500*-3σ)< *X*

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RoHS Sample Preparation

Courtesy of Duquesne University and Retsch RoHS Collaboration

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Method 3052 of ROHS-2811 (Microway circuit board)

Element	9 mL HNO_3 + 3 mL HF (µg/g)[a]	9 mL HNO_3 + 3 mL FBA* (µg/g)
Cr	29.6 ± 5.7	17.7 ± 1.8
Cd	1.91 ± 0.14	3.2 ± 0.08
Hg	1.4 ± 0.1	3.3 ± 0.16
Pb	19,220 ± 727	22,355 ± 440

Note: 6800 removes matrix effects

*FBA – Fluoroboric acid.
Uncertainties are at 95% CL, n = 15.
[a] Precipitation occured after storing in cold room at 4 °C.

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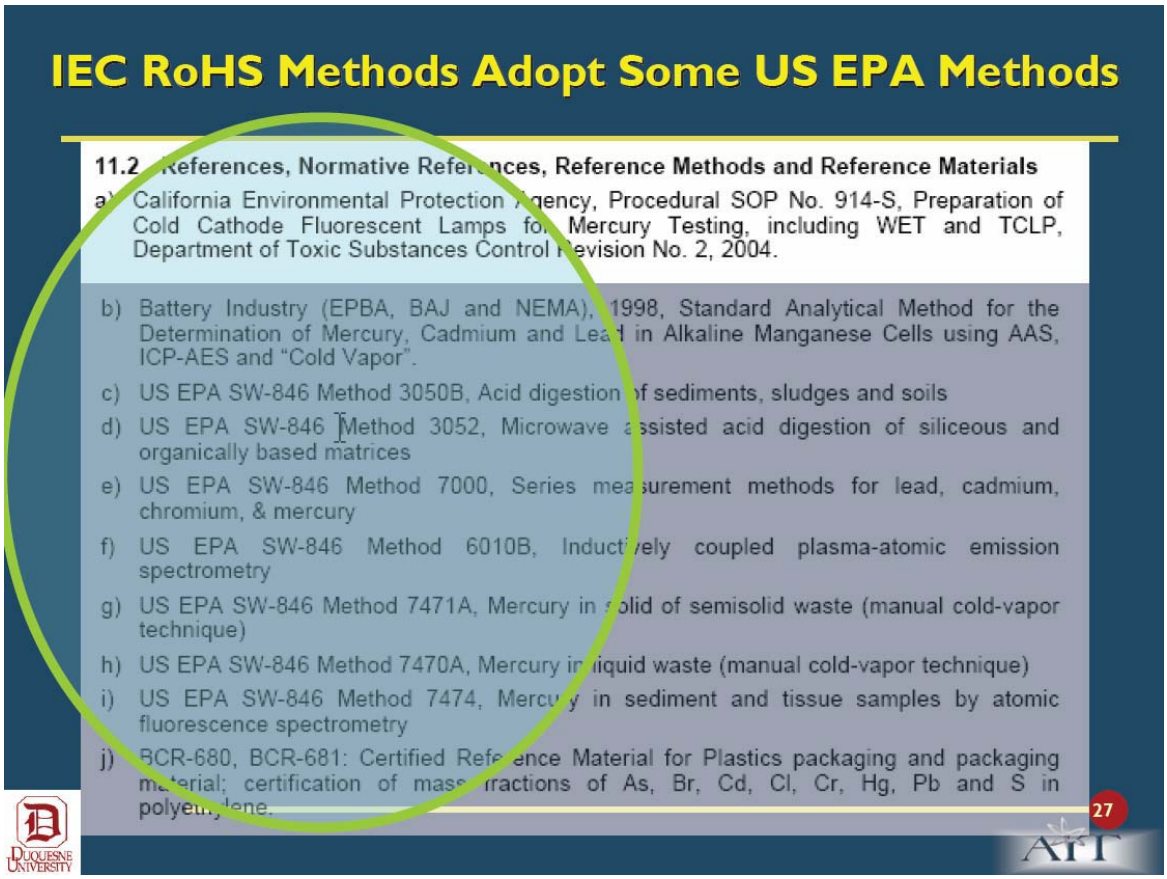
IEC RoHS Methods Adopt Some US EPA Methods
11.2 References, Normative References, Reference Methods and Reference Materials
a) California Environmental Protection Agency, Procedural SOP No. 914-S, Preparation of Cold Cathode Fluorescent Lamps for Mercury Testing, including WET and TCLP, Department of Toxic Substances Control Revision No. 2, 2004.
b) Battery Industry (EPBA, BAJ and NEMA), 1998, Standard Analytical Method for the Determination of Mercury, Cadmium and Lead in Alkaline Manganese Cells using AAS, ICP-AES and "Cold Vapor".
c) US EPA SW-846 Method 3050B, Acid digestion of sediments, sludges and soils
d) US EPA SW-846 Method 3052, Microwave assisted acid digestion of siliceous and organically based matrices
e) US EPA SW-846 Method 7000, Series measurement methods for lead, cadmium, chromium, & mercury
f) US EPA SW-846 Method 6010B, Inductively coupled plasma-atomic emission spectrometry
g) US EPA SW-846 Method 7471A, Mercury in solid of semisolid waste (manual cold-vapor technique)
h) US EPA SW-846 Method 7470A, Mercury in liquid waste (manual cold-vapor technique)
i) US EPA SW-846 Method 7474, Mercury in sediment and tissue samples by atomic fluorescence spectrometry
j) BCR-680, BCR-681: Certified Reference Material for Plastics packaging and packaging material; certification of mass fractions of As, Br, Cd, Cl, Cr, Hg, Pb and S in polyethylene.
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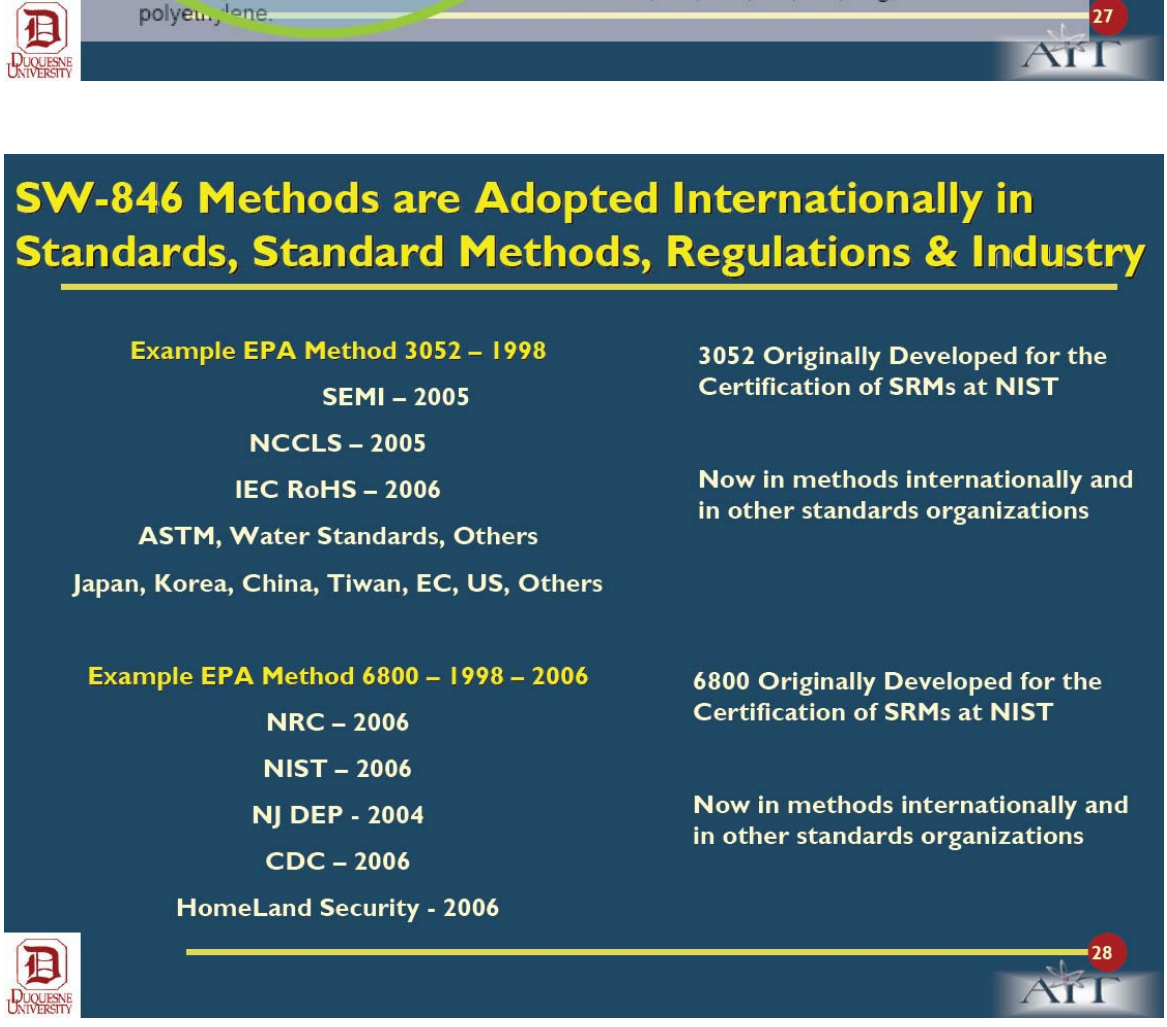
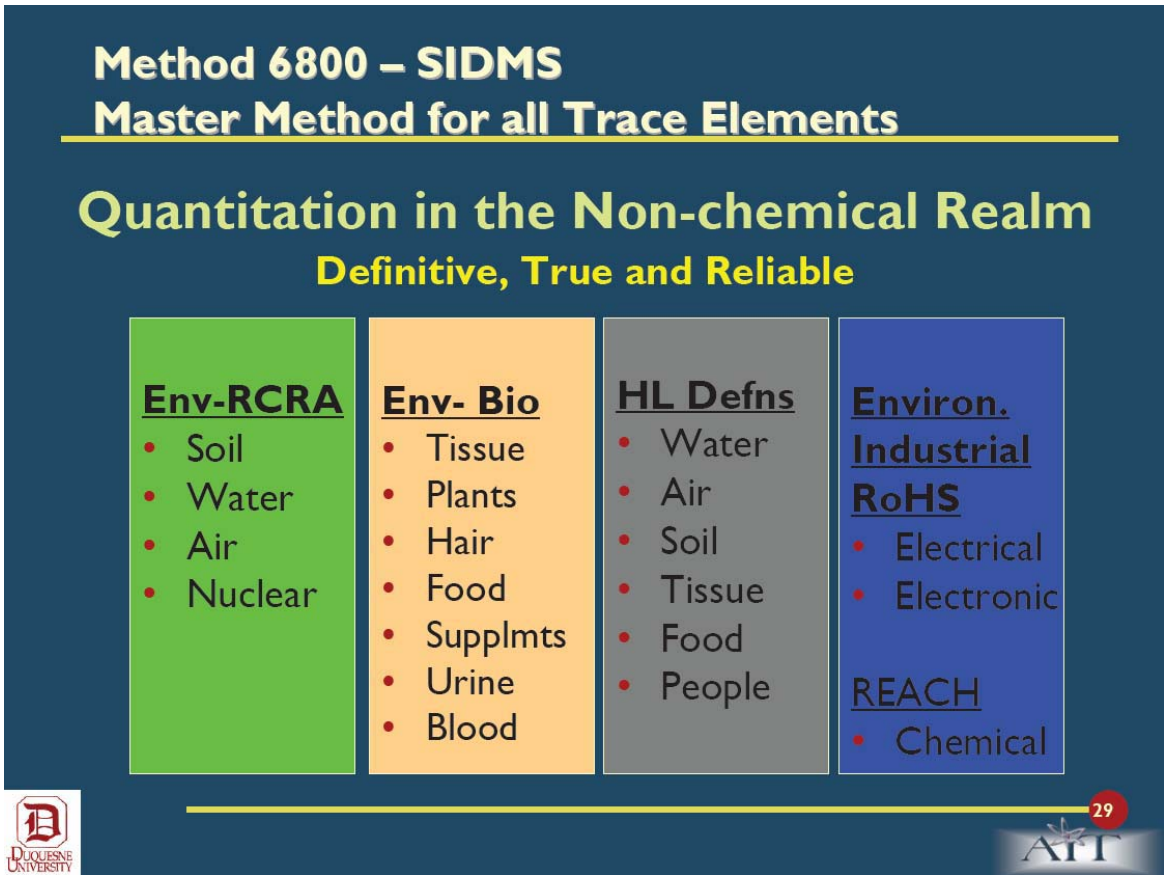
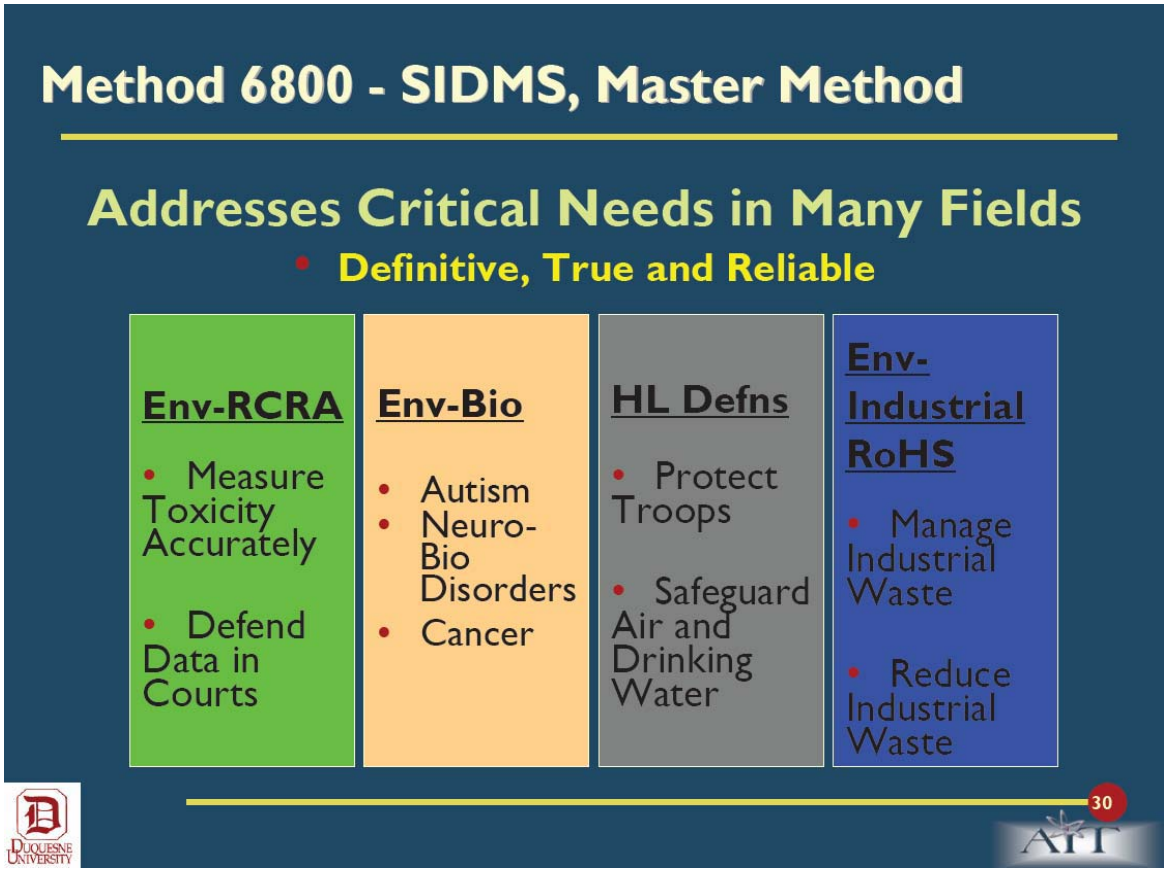

SW-846 Methods are Adopted Internationally in Standards, Standard Methods, Regulations & Industry
Example EPA Method 3052 – 1998
SEMI – 2005
NCCLS – 2005
IEC RoHS – 2006
ASTM, Water Standards, Others
Japan, Korea, China, Tiwan, EC, US, Others
3052 Originally Developed for the Certification of SRMs at NIST
Now in methods internationally and in other standards organizations
Example EPA Method 6800 – 1998 – 2006
NRC – 2006
NIST – 2006
NJ DEP - 2004
CDC – 2006
HomeLand Security - 2006
6800 Originally Developed for the Certification of SRMs at NIST
Now in methods internationally and in other standards organizations
28


Method 6800 – SIDMS
Master Method for all Trace Elements
Quantitation in the Non-chemical Realm
Definitive, True and Reliable
Env-RCRA
• Soil
• Water
• Air
• Nuclear
Env- Bio
• Tissue
• Plants
• Hair
• Food
• Supplmts
• Urine
• Blood
HL Defns
• Water
• Air
• Soil
• Tissue
• Food
• People
Environ. Industrial RoHS
• Electrical
• Electronic
REACH
• Chemical
29


Method 6800 - SIDMS, Master Method
Addresses Critical Needs in Many Fields
• Definitive, True and Reliable
Env-RCRA
• Measure Toxicity Accurately
• Defend Data in Courts
Env-Bio
• Autism
• Neuro-Bio Disorders
• Cancer
HL Defns
• Protect Troops
• Safeguard Air and Drinking Water
Env-Industrial RoHS
• Manage Industrial Waste
• Reduce Industrial Waste
30

Method 6800 - SIDMS, Master Method

Directions for the Next 10 years

Env-RCRA

- On-site measurement
- Portable MS Systems

Env - Bio

- Dedicated, Field Bench-top Analyzers
- Portable Therapy Management

HL Security

- Deployable Chem/Bio Agent Detectors
- Drinking Water Network Detection Grid

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Acknowledgements

Current and Former Research Group Contributors

Dr. Mizanur Rahman
Mr. Matt Pamuku
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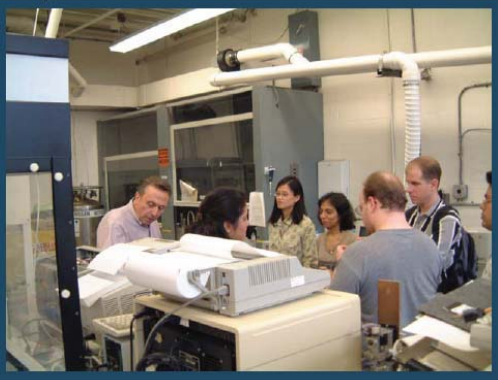
Dr. Peter Walter
Dr. Dirk Link
Dr. Stuart Chalk
Dr. Robert Richter
Dr. Dan Taylor
Ms. Yesheng Lu



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National Science Foundation (NSF)
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Applied Isotope Technologies (AIT)
US Air Force
Agilent Technologies
EPA
Allegheny Energy Supply Co.
Milestone Inc.
Duquesne University

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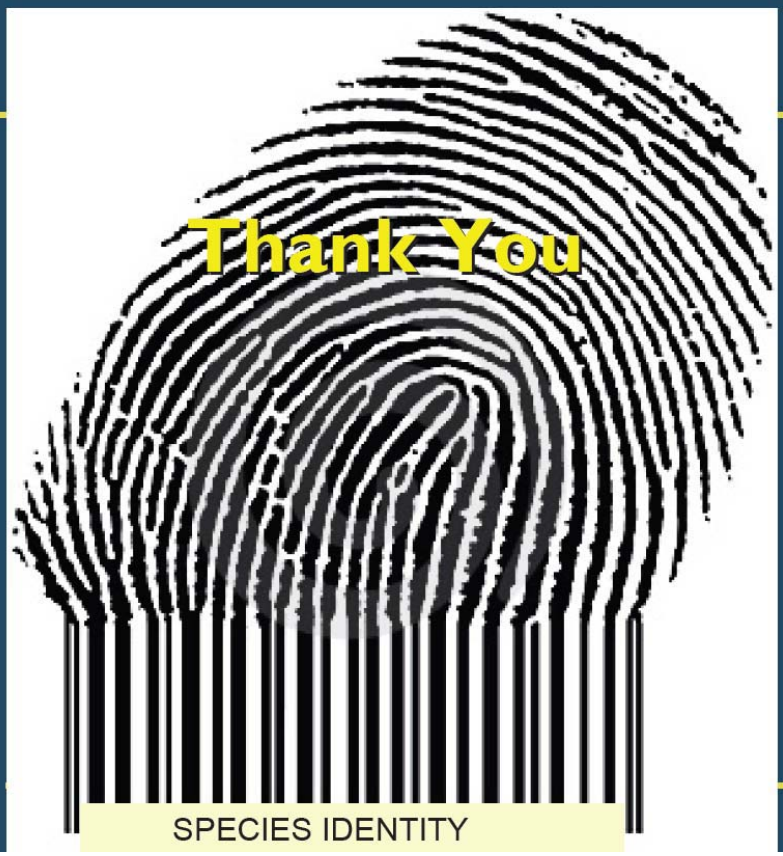
Thank You



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SW-846 Methods are Adopted Internationally in Standards, Standard Methods, Regulations & Industry

Example EPA Method 3052 – 1998

SEMI – 2005

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NRC – 2006

NIST – 2006

NJ DEP - 2004

CDC – 2006

HomeLand Security - 2006

6800 Originally Developed for the Certification of SRMs at NIST

Now in methods internationally and in other standards organizations

TABLE 2(B)

OXIDATION OF Cr(III) TO Cr(VI) DURING EXTRACTION WITH METHOD 3060A FROM THREE COPR SAMPLES AND DETERMINED WITH METHOD 7196 AND SIDMS (SPIKED BEFORE EXTRACTION)
(Reference 3,12)

	Total Cr	Cr(VI) ($\mu g\ g^{-1}$)		*RE*[e]
	($mg\ g^{-1}$)	SIDMS Corrected for Cr(III) to Cr(VI) conversion	Method 7196 Uncorrected for Cr(III) to Cr(VI) conversion	(%)
COPR 1	10.4[a]	2573 ± 35[d]	2671 ± 17	3.8
COPR 3	1.97[a]	161 ± 6	351 ± 8	118
COPR 4	4.60[a]	614 ± 13	877 ± 21	43
Fresh Fly Ash	0.0475[b]	8.3 ± 0.3	10.0 ± 0.4	21
Fly Ash (at 41 ft.)	0.0582[b]	3.3 ± 0.3	4.1 ± 0.1	24
SRM 1645 (River sediment)	29.6[c]	1045 ± 46	2753 ± 31	163

[a] provided by Environmental Standards, Inc.

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Speciated Analysis by HPLC-ICP-MS
(Class 1000-100 Clean Laboratory Duquesne University)

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USING METHOD 6800 FOR CHROMIUM (VI) ANALYSIS

Bruce Ph.D., Mark; Severn Trent Laboratories
Reinheimer, Bill; Severn Trent Laboratories
Vicini, Rusty; Severn Trent Laboratories

The Kingston research group at Duquesne University developed Method 6800 several years ago. Several research laboratories have used this speciated isotope dilution mass spec method to determine chromium (VI) in soil and water samples. Application by commercial environmental laboratories has been very limited. Complete commercial implementation includes the following areas: acquisition of ion chromatograph and ICP/MS, hardware and software interface of instrumentation and data systems from different instrument providers, acquisition of isotopically label standards, sample preparation, instrumental analysis, raw data collection, quantitative isotope ratio calculations and final data reporting.

This paper will describe STL's experience of bringing what appears to be complex methodology and instrumentation into a production laboratory setting where accuracy, sensitivity and productivity goals must be met.

The Commercialization of Method 6800- Speciated Isotope Dilution Mass Spectrometry for the Determination of Hexavalent Chromium

Albert F. Vicinie III,* Mark Bruce, PhD. ** William Reinheimer*
*Severn Trent Laboratories, Inc., Pittsburgh, PA; **Severn Trent Laboratories, Inc., North Canton, OH

ABSTRACT
Method 6800 has recently been approved for the determination of the various species of metals such as Chromium III and Chromium VI. It is a hyphenated technique that couples ion chromatography (IC) with Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). To date use of this method has been primarily in academia and limited project support. The method offers two primary challenges. It utilizes a mathematical approach to deconvolute the species that is unique to other traditional methods utilized in commercial environmental methods. Also the method does not specify in detail quality control practices and deliverables to be performed and provided to allow the data user to effectively evaluate the data set. This paper identifies the primary differences in this method from traditional as well as proposed QA/QC practices along with a deliverable to allow effective data validation and assessment.

INTRODUCTION
Method 6800 may be utilized to determine the total metal content for various elements using isotope dilution mass spectrometry (IDMS) and determining the elemental species for numerous metals using speciated isotope dilution mass spectrometry (SIDMS). We are focusing our discussions on the analysis of soils, leachates and waters for hexavalent chromium (Cr VI) using the SIDMS approach of 6800.

This method is providing investigators much new and valuable additional information to allow the assessment of hexavalent chromium in soil matrices that are not suitable to provide data of known and acceptable quality with other analysis methods in order to support environmental decisions. Method 6800 provides solutions to the analytical challenges and refers to the base technology methods and Chapters One and Two of SW-846 as well as individual project plans for the development and incorporation of appropriate quality control procedures. We discuss in the following paragraphs suggested practices and procedures that will provide additional information to the investigators and regulating community to assist in assessing the data generated by this method.

Specified Quality Control Measures
Method 6800 SIDMS specifies the following quality control measures explicitly.

Dead Time Determination- This determines the interval during which the detector and its associated counting electronics are unable to resolve successive pulses. The measured counts are lower than the true counts if no correction occurs. Current instrument operating software allows this to be set and controlled for each instrument. Alternatively method 6800 provides guidance on determining the dead time. This should be performed/evaluated daily.

Mass Bias- This is the deviation of the measured isotope ratio from the true value caused by the differential sensitivity of the instrument to mass. This effect may occur in the ionization process or from differential transition/detection by the mass spectrometer. The resultant mass bias factor is the number used to correct for the mass bias of the measured isotope ratios and is determined by performing 4 replicate measurements of an isotopically certified standard. We are proposing that this be performed at the beginning of each analytical sequence and at the end of each analytical sequence or every 4 hours whichever is more frequent.

Background Blank- This is the background associated the solutions used for sample dilution (eluent) and with the chromatographic baseline.

Preparation (Reagent) Blank- This is blank laboratory grade water that is carried through the complete preparation procedure and contains the same volumes of reagents as the sample solutions. We propose that this be performed at a minimum of 1 per sample batch with batch size not to exceed 20 samples that is consistent with normal quality control practices.

These are QC measures that are not routinely included in the base ICP/MS methods such as SW-846 6020 but are inherent to the performance of this method. There are no existing criteria to assess their performance, nor any precedent in presenting them as part of a deliverable. The dead time determination ensures that the measurements are made within the appropriate range and the mass bias factor becomes part of the solution to solving the equation to determine the actual isotope ratios used for the calculation.

Non-Specified Quality Control Measures

These measures are not directly specified as part of method 6800 for Cr VI or other elements. We are proposing the following measures that are either normally included in laboratory/project quality plans, part of the base methods such as method 6020 for the use of ICP/MS in the determination of metals in waters and soils or other related hexavalent chromium methods.

1. ***Holding Times***
   a. For soils we default to existing published guidance in method 3060A of 30 days for soils stored cool at 4 deg C. Once extracted the alkaline digestion has been demonstrated to be stable for 7 days by this same method. Method 3060A is the alkaline digestion sample preparation method used to prepare soil/sediment samples for analysis using method 6800 for Cr VI.

   b. For waters being analyzed by the routine method of 7196A these are typically collected unpreserved and submitted for analysis within a 24 hour holding time. Due to the more complex nature of method 6800 this may be impractical in routine use. USEPA method 1636 provides that aqueous samples preserved by pH adjustment to > 9 may be stored for up to 30 days at 4 deg. C. We recommend this preservation technique for any project associated field QC samples such as equipment blanks to be analyzed by method 6800 for Cr VI.

2. ***Instrument Performance***
   a. Cross Calibration of Mass Spectrometer Detector- this determines levels at which the detector switches from pulse to analog measurements and is related to the dead time of the instrument. We are proposing that this be performed each day of instrument operation for this method. There are no performance limits associated with this action.

   b. Tune Check- (Performance Report) this tunes the mass spectrometer to a known material. We are proposing that the tuning criteria for the mass spectrometer be the same as that published in USEPA method 6020.

   c. Dynamic Range Determination- for screening samples using the Time Resolved Analysis (TRA) mode we propose analyzing 4 aqueous standards of Cr VI at concentration of 10, 50, 100 and 200 ug/L to provide quantitation of the screened samples that have not been spiked with the enriched isotopes. Data will be acquired using the 50, 52 and 53 amu masses with quantitative analysis performed using the 52 amu mass. There are no criteria set to evaluate this calibration and as it is only used to provide screening level data to allow appropriate spiking of enriched isotopes no criteria is proposed. We are however proposing to bracket the analytical sequence with a 50 ug/L solution that will be analyzed and quantitated against the instrument calibration and evaluated using method 6020 criteria. Samples should be diluted if necessary and analyzed within the range identified.

   d. Instrument Sensitivity- While not specified we recommend that instrument sensitivity be evaluated using aqueous standards of either Cr III or Cr VI by performing 7 replicate analyses and evaluating the data for the mean and standard deviation. No criteria is provided but we recommend utilizing the same criteria as provided for evaluating MDL studies in 40 CFR 136 to ensure the analysis is able to reliably be differentiated versus a blank. We recommend this be performed on a quarterly basis. Example data is provided in Table 1.

3. ***Method Performance***
   a. Accuracy- We are proposing the analysis of a soil sample of known concentration such as an NIST SRM or a material provided by a NELAC approved PE vendor such as ERA or equivalent. These samples should be analyzed at a minimum of 1 for every batch of samples prepared through the alkaline digestion with batch size not to exceed 20 samples. Manufacturer provided criteria should be used to evaluate performance.

   b. Detection Limits- Due to the unique nature of this method as it applies mathematics to the direct measurement of the isotopic ratios which are spiked into each sample at known quantity the traditional method detection study as described in 40 CFR 136 does not directly apply to this method as there will by the nature of the method always be detectable levels of isotope. However we conducted and are proposing that a traditional MDL study be conducted through the alkaline digestion of a Cr VI spiked sample that is not spiked with the enriched isotope to provide an idea of the level at which the naturally occurring chromium isotopic abundance can be expected to be detected. We have provided an example of this data in Table 2.

c. Matrix Effect- As each sample is spiked with both a Cr III and Cr VI species the matrix of each sample is able to be evaluated and addressed by the method. As such there is no reason to include additional MS/MSD samples that are typically included in analytical batches.

d. Interference Checks- ICSA/ ICSB interference checks that are commonly included in the ICP-AES and ICP/MS are not included in this method and not required as there is chromatographic separation, confirmation of retention time and mass spectral evaluation of isotope ratios at 50, 52 and 53.

CONCLUSIONS

Method 6800 is a much needed and useful tool in providing a more definitive evaluation of hexavalent chromium in soil samples that due to their matrix may not be able to be accurately characterized by other traditional methods. As this method provides a novel solution to these challenges it also presents challenges to the analytical community as well. These challenges are primarily involve the training and understanding of the analysts and data users to ensure the highest quality of data is generated and that the data can be assessed appropriately. We have proposed appropriate measures to allow for the evaluation of data using this method and that will allow it to be reproduced and evaluated.

ACKNOWLEGEMENTS

The authors would like to acknowledge Dr. H.M. "Skip" Kingston and Dr. G. M. Mizanur Rahman of Duquesne University, Department of Chemistry and Biochemistry, Pittsburgh, PA 15282 for all of their training and assistance in transitioning this analytical method into a commercial environmental laboratory.

Table 1: Cr VI Instrument Detection Limit

Concentration ug/L	
actual	measured
5	6.80
5	4.78
5	5.00
5	5.60
5	5.63
5	6.45
5	5.55
avg	5.69
%RSD	13%
IDL	2.28

Table 2: Cr VI Method Detection Limit

Concentration ug/L	
spike	measured
10	7.79
10	8.63
10	7.05
10	7.00
10	5.46
10	8.37
10	6.39
avg	7.24
%RSD	15%
MDL	3.52

REFERENCES

1 U.S. Environmental Protection Agency, Jan. 1998. *Method 6800, Elemental and Speciated Isotope Dilution Mass Spectrometry*. Office of Solid Waste.

2 U.S. Environmental Protection Agency, 1992. *SW-846 Chapters One & Two*. Office of Solid Waste.

3 U.S. Environmental Protection Agency, Dec. 1996. *Method 3060A, Alkaline Digestion for Hexavalent Chromium,* Office of Solid Waste.

4 U.S. Environmental Protection Agency, Jul. 1992. *Method 7196A, Chromium, Hexavalent (Colorimetric),* Office of Solid Waste.

5 U.S. Environmental Protection Agency, Jan. 1996. *Method 1636, Determination of Hexavalent Chromium by Ion Chromatography,* Office of Water.

Welcome to STL

Leaders in Environmental Testing

The Commercialization Of Hexavalent Chromium Determination Using Method 6800 With Speciated Isotope Dilution Mass Spectrometry (SIDMS)

NEMC- August 2006

Albert "Rusty" Vicinie
William Reinheimer
Mark Bruce Ph.D.
Nasreen DeRubeis

Common Commercial Hexavalent Chromium Methods

Water

Colorimetric
- SW 846-7196A
- SM 3500 B

Ion Chromatographic
- SW 846-7199
- SM 3500 C
- EPA (OW) 1636

Soil

Colorimetric
- SW 846-3060A/7196A

Ion Chromatographic
- SW 846-3060A/7199

What is Method 6800?

- USEPA SW 846 Method
- Isotope Dilution and Speciated Isotope Dilution Mass Spectrometry
- Utilizes Chromatographic Separation and MS Detection
- Utilizes isotopically enriched spikes
- Monitors interconversions of species

Why Method 6800?

- Addresses matrix related effects
- Corrects for interconversion of species during sample preparation and analysis
- Diagnostic tool for the evaluation of species altering procedures
- Permits evaluation and validation of traditional speciation data

Why is this Method Unique?

Allows species interconversions to occur as part of extraction & analytical process and corrects mathematically

Aspects of Method Implementation

Sample preparation technique
- Extraction efficiency/stability

Instrumental analysis
- Interferences
- Sensitivity
- Linearity
- Dynamic range
- Carryover/contamination
- Stability/drift
- Reproducibility

Data reduction and evaluation

Method 6800 QA/QC Differences

Introduces unique QA/QC

Limited method specified QA/QC

Traditional measures not applicable

- ICAL
- CCAL/CCV
- Interference checks (ICSA/ICSAB)
- Reporting limit verification
- 40 CFR 136 MDL process

Specified QA/QC Measures

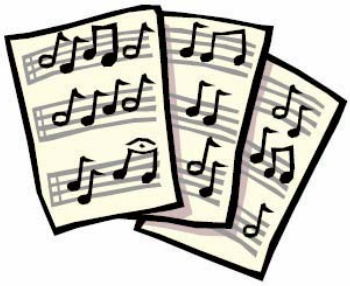
Measures Specified in Method 6800

- Dead time determination
- Mass bias correction
- Isotope ratio evaluation
- Background blank
- Preparation blank
- Rinse blank
- Duplicate analysis
- Reference material (LCS)

Additional QA/QC

Non-Specified Measures

- Holding time (1636/3060A)
- Instrument performance
  - Tune check (6020)
  - Dynamic range (6020)
  - Sensitivity (SOP)
  - Retention time window (SOP)
- Method Performance
  - Replicate determination
  - Reporting/ Detection limits (SOP)



Method 6800 Deliverables

- Cross Calibration Report (Dead Time Verification)
- Mass Calibration Verification
- Isotope Certificate
- Reference Material Certificate
- Sample Data
- Digestion Log
- Chromatograms
- Calculation Worksheets
- EDD results only

SEVERN TRENT STL

Discussion Topics

Interconversion from sampling to preparation
- Field Spiking of water samples

Complete conversion of species

Elevated concentration (>500 mg/kg)

Sample homogeneity/ sub-sampling

SEVERN TRENT STL

Challenges

✓Instrumentation
- Ion chromatograph
- ICP/MS

✓Training
- Novel method principles

✓Data Reduction
- Complex mathematical deconvolution

✓Certification

❑Market Acceptance

Conclusion

- Another tool in the toolbox
- Provides improved precision and accuracy
- Addresses matrix related concerns

Acknowledgements

Dr. Skip Kingston
Dr. Mizanur Rahman

WEDNESDAY P.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Accreditation

THE HISTORY OF NELAC

Lara P. Autry
US EPA
August 30, 2006

OVERVIEW

- Background/History
- Structure
- Program Goals
  - Self-Sufficiency
  - Performance Approach
  - Growth/Outreach
- Contact information

BACKGOUND/HISTORY

- Why was NELAC/NELAP created?
  - Inconsistent/nonexistent inspections;
  - No reciprocity among states;
  - Loss of accreditation in one state does not affect status in another;
  - Accreditation in all areas is not available;
  - Customers have no access to information;
  - Accreditation not recognized in foreign markets; and
  - Programs generally viewed as inadequate.

NATIONAL ACCREDITATION TIMELINE

- Report to Congress 1986
- Committee on National Accreditation of Environmental Laboratories (CNAEL)
  - July 1991 – July 1992
- State – EPA Focus Group
  - January 1993 – September 1994
- NELAC/NELAP February 1994 - present
  - 1994 – 1997 Development Only
  - 1997 – June 5, 2003 Standard Development/Adoption
  - June 6, 2003 - present Adoption Only
- Environmental Laboratory Advisory Board (ELAB)
  - 1995 - present

PROGRAM COMPONENTS

- Standards Adoption (NELAC)
  - Proficiency Testing Board
  - Standards Review Committee
  - Membership & Outreach Committee
  - Nominating Committee
  - Special Task Groups or Committees (Varies)
- Standard Development Organizations
- Program Oversight (NELAP)
  - Accrediting Authority Committee
  - Accrediting Authority Review Board
  - Regional Assessors
- Advisory Group (ELAB)
  - Environmental Laboratory Advisory Board

STABILITY FOR NELAC STANDARD

- July 1, 2005 – June 30, 2009
  - August 2004 Version
    - C&B
  - 2003 Version
    - Chapter 1
    - Chapter 2
    - Chapter 3
    - Chapter 4
    - Chapter 5
    - Chapter 6
  - 2002 Version
    - Chapter 7 (only version)

PROGRAM GOALS

- Self-sufficiency of the program.
- Performance approach (i.e., method flexibility) to assure that standards foster the production of data of known and documented quality.
- Growth to provide consistency.

SELF-SUFFICIENCY

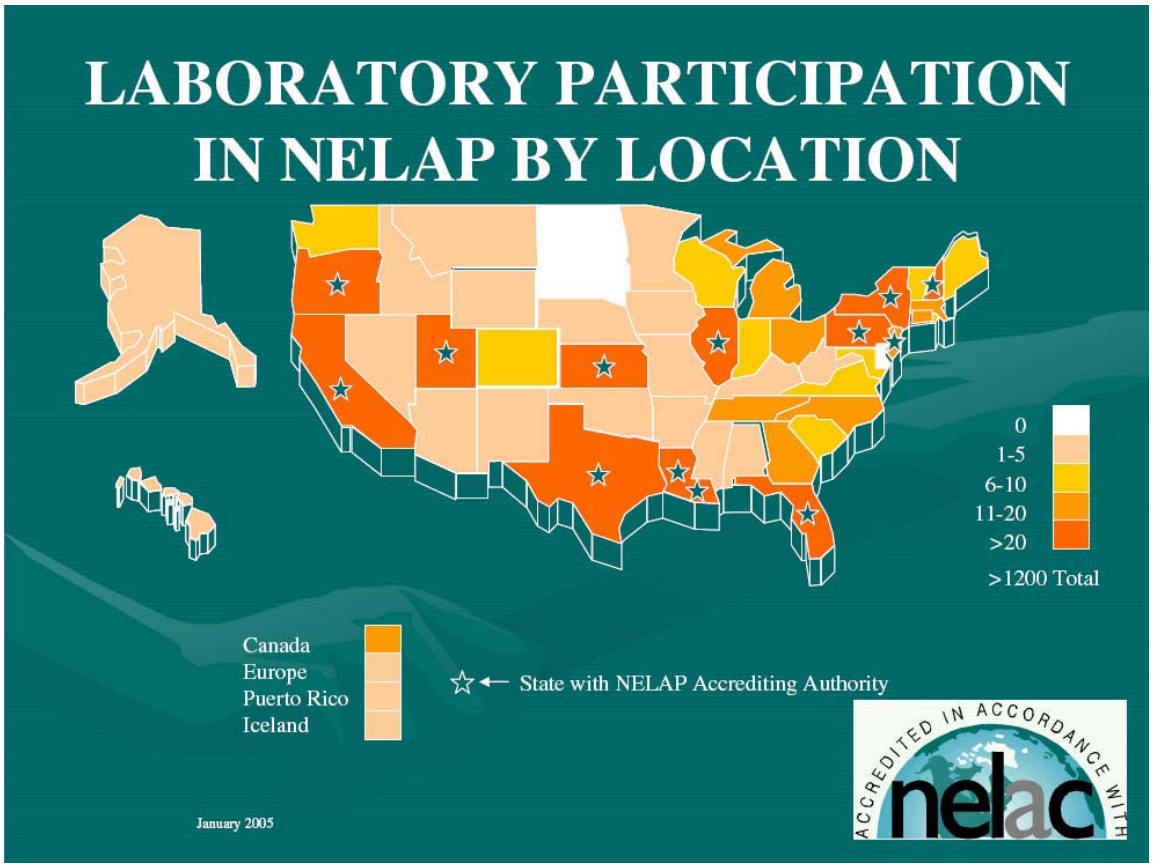
- Separation of Administrative Functions
- Cooperative Agreements
  - Standards Development and Technical Support Agreements
    - NSF International
    - Institute for National Environmental Laboratory Accreditation (INELA)
  - Program Administrator
    - National Forensic Science and Technology Center (NFSTC)

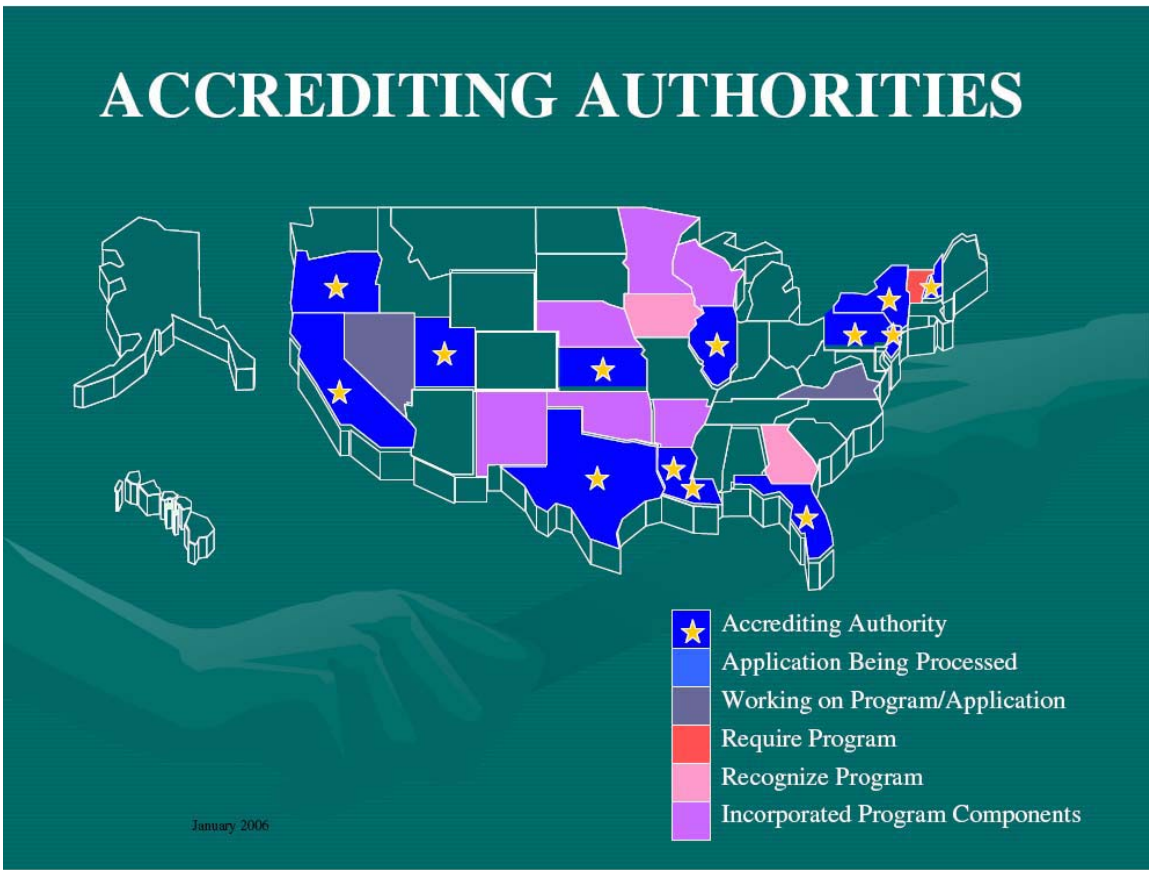
PERFORMANCE APPROACH

- Assures the Production of Data of Known and Documented Quality
- Agency Moving Forward Again
- Pilot Programs Being Established
- Incorporated into NELAC Standard
- Training is Available

TRAINING COOPERATIVE AGREEMENT

- Awarded to Independent Laboratories Institute (ILI)
- Focus is on Special and Practical Knowledge for Laboratory Accreditation
- Teaching Methods:
  - Classroom Style Training
  - Workshops/Conferences/Roundtables
  - Computer-Based Training


LABORATORY PARTICIPATION
IN NELAP BY LOCATION
0
1-5
6-10
11-20
>20
>1200 Total
Canada
Europe
Puerto Rico
Iceland
State with NELAP Accrediting Authority
ACCREDITED IN ACCORDANCE WITH
nelac
January 2005


ACCREDITING AUTHORITIES
Accrediting Authority
Application Being Processed
Working on Program/Application
Require Program
Recognize Program
Incorporated Program Components
January 2006


AGENCY RECOGNITION OF NELAC PROGRAM
• Regional laboratories being accredited.
• Program Office laboratories responding to laboratory competency requirements.
• Working on mechanisms to recognize and reward those with accreditation, certification, and/or quality programs.
• Working with all Program Offices to integrate individual programs into one National network.


INFORMATION
NELAC Website:
- http://www.epa.gov/nelac
ELAB Website:
- http://www.epa.gov/elab
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THE FUTURE OF NELAC PROGRESS UPDATE

NEMC
Arlington, VA
August 2006
Aurora Shields

2005

- The NELAC BoDs appointed the Self-Sufficiency Task Group to evaluate options for self-sufficiency.

2006

- The NELAC BoDs appointed the special committee on National Accreditation to evaluate why the goal for National Accreditation had not been accomplished and outline strategy to succeed

UPDATES

- Special Committee on National Accreditation
- Self-Sufficiency Task Group (SSTG)

NELAC Board
Special Committee on National Accreditation

Committee Members and Representation

- Gary Ward – commercial laboratory community (ACIL)
- Kenneth Jackson – NELAP State
- Marlene Moore – third party assessor/contractor
- Paul Kimsey – state primary laboratories (APHL)
- Susan Wyatt – non-NELAP State
- James Jordan – ELAB
- Kevin Coats – DOD
- Mark Carter – PT Vendor
- Lara Autry - EPA

Special Committee Task

- Evaluate the Committee for National Accreditation of Environmental Laboratories (CNAEL) recommendations; and
- Determine why the goal for National Accreditation had not been accomplished and outline strategy to succeed

Has NELAC achieved CNAEL goal as a national accreditation program ?

- CNAEL Recommends – establish program that has federal oversight and is implemented by states and/or third parties
- Key elements evaluated – CNAEL Report conclusions summary (next slide)

CNAEL Report Elements Evaluated

- Reciprocity and leveling of differences between the various state programs
- Uniform standard for all aspects of laboratory performance
- Consistent laboratory audits
- Uniform national PT program
- Minimize negative effects on the operation of existing state lab accreditation programs
- Minimize outlay of federal/state funds and operation through self-supporting mechanism

Position Paper Conclusion/ Action Item

- Key Conclusion – need buy-in by EPA Program Offices
- Action Item – Report (Committee) and letter to EPA Program Offices (Board)
- Report - "A Proposed Partnership to Achieve Data Quality Assurance through a National Laboratory Accreditation Program" (May 25 2006)

Report Key Elements

- Purpose
- History
- NELAC/NELAP Accomplishments
- Areas for Improvement
- Common Goals
- "A Place to Start"
- Benefits to EPA Program Offices
- Conclusion

Special Committee Report

- Purpose – "We suggest that EPA and the states can most effectively and efficiently meet their data quality assurance mandates through the existence of a national laboratory accreditation program and requiring that all environmental compliance monitoring data be generated by laboratories accredited by this program."
- Common Goals – "To be successful, NELAC needs EPA program offices to participate as truly engaged partners with a commitment to harmonize all Agency and NELAC requirements and programs designed to ensure the quality of all compliance data submitted to and used by EPA."

Special Committee Report Benefits to EPA Program Offices

- Harmonization all current EPA and State accreditation programs
- Recognition and coordination of state and federal accreditation programs
- Management all aspects PT programs
- Training lab assessors, management and technical personnel
- Mentoring state and federal accreditation programs
- Mentoring commercial, industrial, municipal, state and EPA laboratories
- Forum to promote nationally consistent lab evaluations
- National database of accredited labs and PT information

Special Committee Report Conclusion

- "As EPA and the states are mandated to ensure the quality of data that are used to assess and ensure regulatory compliance, it is essential that the national laboratory accreditation program be directed solely by state and federal personnel in an open process with appropriate consultation and input from all affected stakeholders."
- "The NELAC Board wishes to explore with EPA its vision as to how the EPA can best participate to help ensure the success of the national environmental laboratory accreditation effort."

SSTG

- Aurora Shields
- Judy Duncan
- Alfredo Sotomayor
- Ann Marie Allen
- Silky Labie
- Art Clark
- Barbara Finazzo
- Marcia Davies
- Patricia Hurr
- Lara Autry

Advise the NELAC Board of Directors regarding the development of a plan for NELAC/NELAP self-sufficiency.

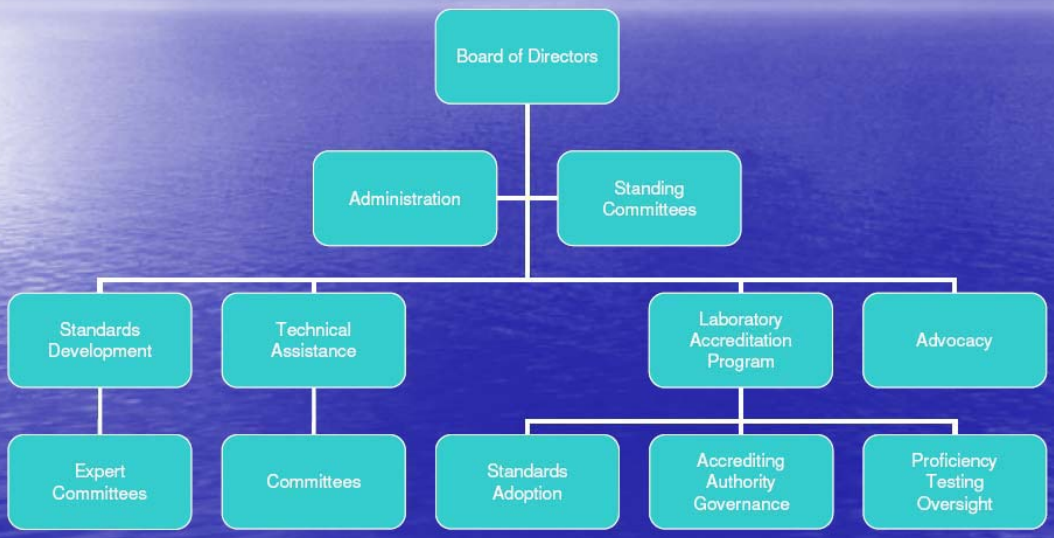
Draft Vision, Mission, and Purpose

- Provide a true national accreditation system.
- Foster the generation of environmental data of known and documented quality to assist efforts towards protecting and improving human health and the environment.
- Promote professionalism in the field of environmental analysis through quality, leadership, and training.

CHARACTERISTICS

- Incorporated, Not-for-Profit
- Contains Consensus Based International Standards
- Promotion of Professionalism
  - Quality
  - Leadership
  - Training and Education
- Products
- Services

PROPOSED ORGANIZATIONAL STRUCTURE



Interim Timeline Transition

- **Proposal for NELAP Director:**
  - AARB to assume the programmatic duties.
  - NELAC Board assume oversight.
  - Administrative assistance provided by NFSTC.
- **Proposal for NELAC Director:**
  - PT Board oversees PTOB/PTPA.
  - NELAC Board continues oversight.
  - Administrative assistance provided by NFSTC.

Solicit Stakeholders

- NFSTC solicited interest from organizations.
- Informed community the SSTG was open to offers of assistance.

Responses

- INELA
- ERA
- AEX
- ACIL
- APHL
- Basis for evaluation:
  - Common goals/mission,
  - Similar constituencies,
  - Experience with the program,
  - Fiscal independence, and
  - Value of assets.

INELA

- Similar/Compatible:
  - Purpose/Mission/Vision,
  - Characteristics,
  - Products, services, activities,
  - Infrastructure, and
  - Constituency.

Recommendations

- NELAC and INELA approved MOU.
  - Non-binding agreement to explore a partnership between NELAC and INELA.
  - Duration 6 months.
- Appoint a Partnership Planning Team
  - Team will submit a report and recommendations

National Accreditation for Environmental Testing

The Changing Role of INELA in Standards Development

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Agenda

- About INELA
- The INELA Process for Standards Development
- INELA's other activities
- How things will change

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INELA History

- Need for a non-profit identified in June 2000
- identified No organization came forward
- Small group saw the need and decided to form a non-profit
- INELA formed in May 2001

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Institute for National Environmental Laboratory Accreditation (INELA)

- Non-profit voluntary consensus organization
- Members can be anyone interested in laboratory accreditation
- Primary goal is the development of laboratory accreditation standards
- Secondary goal is to provide support to help implement a national program

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The Role of Consensus Standards

National Technology Transfer & Advancement Act
OMB Circular A-119
Consensus Standards Organizations
American National Standards Institute

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NTTAA & OMB Circular A-119

- Federal law and policy on use of voluntary consensus standards
- *Federal Agencies must use voluntary consensus standards except where inconsistent with law or otherwise impractical*
- Policy applies to all Federal government, including test procedures

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Consensus Standards Organization

- Must meet requirements of OMB A-119
  - Openness
  - Balance of interest
  - Due process
  - Consensus
  - Appeals process
- May become accredited by ANSI

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Basis of INELA Policy

- ANSI requirements for accreditation of voluntary consensus standards organizations
- Policies of ASTM
- Policies of the National Fire Protection Association, an organization comparable to INELA

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General Principles

- INELA expert committees write the standard, based on input from multiple sources
- Six Expert Committees
- Two-tier voting process
  - Expert Committee
  - General membership

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Openness

ANSI Requirements

- Anyone interested in the activities of the organization may participate
- Not required to become a member of the organization
- No undue financial barrier

INELA Policy

- Anyone can participate on any committee
  - Committee Members
    - 5-15 per committee, must meet balance criteria
    - Must vote at Tier 1, vote is counted towards determining passage or failure
  - Associate Committee Members
    - Unlimited number, no criteria for balance
    - May vote at Tier 1, negative vote must be considered
- Committee minutes published on the website

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Balance of Interest

ANSI Requirements

- Participants from diverse interest categories
  - No single interest category constitutes a majority of the membership of the consensus body
- Standards development process shall not be dominated by any single interest category, individual or organization

INELA Policy

- Committee Members selected to provide balance
  - Serve on only one committee
  - Represent stakeholder group
    - State accrediting authorities/regulators
    - Federal accrediting authorities/regulators
    - Laboratories
    - Other interests
  - No stakeholder group can be a majority

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Due Process & Appeals

INELA Policy

- Anyone can appeal any action of INELA
- Appeal process uses ANSI guidance
- All comments and their disposition are public information

Requirements

- Any person with a direct and material interest has a right to participate by:
  - Expressing a position and its basis
  - Having that position considered
  - Having the right to appeal
- Identifiable, realistic, and readily available appeals mechanism for the impartial handling of procedural complaints regarding any action or inaction

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Consensus

Requirement

- General agreement, but not necessarily unanimity.
- Process for attempting to resolve objections by interested parties
- Fair consideration of all comments/objections
- Disposition & reasons provided to commenter
- Consensus body members are given an opportunity to change their votes after reviewing comments.

INELA Policy

- All negative comments must be addressed at Tier 1
  - Can be ruled persuasive, non-persuasive, or hold for next revision cycle
- Any member can appeal
- Majority vote of all INELA members required for approval of Standard

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Approach for Standards Development

- Flexible format simplifies use, modification & new sector addition
- Sufficient time for development, review and adoption
- Full stakeholder involvement at every step
- ISO Standards 17011 and 17025 are the foundation

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Cycle for Standard Development

- Committee develops draft language
- Language provided to membership for review and comment (Working Draft Standard)
- Committee redrafts Standard, and publishes Draft Interim Standard
- Membership vote
- Consideration of comments
- Membership votes on Interim Standard
- Appeals considered
- Standard approved

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The 2006 INELA Draft Interim Standards

- Environmental Sector
  - Volume 1: Laboratory Requirements
  - Volume 2: Accreditation Body
  - Volume 3: Proficiency Testing
  - Volume 4: Proficiency Testing Oversight
- Field Sampling and Measurement Sector
  - Volume 1: Requirements for FSMO
  - Volume 2: Accreditation of FSMO

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Modules in Volume 1

- Accreditation Process
- Proficiency Testing
- On-site Assessment
- Quality System: General Requirements
- Asbestos Testing
- Chemical Testing
- Microbiological
- Radiochemical
- Toxicology

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Where are we in this process?

- Draft Interim Standard published in July
- >130 votes and >1000 comments received
- Comments discussed in INELA meeting in Kansas on August 17 and 18

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Nature of Comments

- Editorial
- Specific technical comments
- Fundamental issues to be resolved
  - Use of ISO language
  - Generic vs “NELAC” standard
  - Improvement over 2003 NELAC

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Probable Outcomes from Kansas

Environmental

- Volume 1 (Lab)
  - Modules 1 and 2 will become guidance
  - Modules 3 through 9 back to Draft Interim Standard
- Volume 2 (Accreditation Body)
  - Moving to Interim Standard
- Volume 3 (PT)
  - Back to Draft Interim Standard
- Volume 4 (PT Oversight)
  - Become guidance

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Probable Outcomes from Kansas

Field Activities

- Volume 1 and 2
  - Moving to Interim Standard

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Observations from this Process

- It takes time
- Everyone gets heard
- The end product is much better

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Next Steps for the INELA Standards

- New Ballot on December 4
- Comments considered in meeting in Denver on February 1 and 2
- Final standard approved in 2007

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Impact of NELAC Effort on INELA

- Standards development may become part of a much larger effort
- One primary internal customer
- Minimal changes to policy and committee structure
- May speed up implementation
- Bring consensus process into NELAC

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Key issues for INELA

- Use of ISO language
- General vs specific standard
- Process for implementation

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Ways to Participate

- Send a comment to the committee chair
- Come to a meeting and actively participate
- Join a committee and actively participate
- Vote negative with comment
- Vote positive with comment

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INELA's Other Activities

To support the implementation of a national accreditation program

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Implementation Support

- **More Than a CSDO**: INELA's Involvement Does Not End with Standards Passage
  - Training
  - Seminars
  - Small Organization Assistance
  - National Database
  - Mentor Program
  - Website

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Impact of NELAC Effort

- Reorganization of INELA committee structure for technical assistance
- Migration/reorganization of website
- Increased focus on advocacy
- More assistance for small labs and states
- Better communication and operation

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More Information

- http://www.inela.org

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NATIONAL FORENSIC SCIENCE TECHNOLOGY CENTER

NFSTC
Science Serving Justice

NELAC Self Sufficiency

NEMC

August 30, 2006

Proposal Priority & Focus

Solicitation No. EPA-ORD 25357:

"Development and implementation of a strategy and implementation plan for the long-term operation and sustainability of the NELAC National Environmental Laboratory Accreditation System"

CFDA No. 66.510

Proposal Priority & Focus

This Includes, but is not limited to:

- Marketing & Outreach to existing and future members for continued consistency and growth;
- Assessments of Accrediting Authorities per the NELAC Standards; and
- Assessments of Proficiency Testing Oversight Bodies/Proficiency Testing Provider Accreditors (PTOB/PTPA) in conjunction with the Proficiency Testing (PT) Board

Proposal Priority & Focus

"Data management to assure the production of data that is of known and documented quality"

- Includes Quality Assurance Project Plan (QAPP) that outlines the steps that will be taken to adequately address data management issues within the program.

History of the NFSTC

- The American Society of Crime Laboratory Directors (ASCLD) established the NFSTC as a private not-for-profit corporation in 1995.
- NFSTC's mission is to help all of forensic science achieve the highest quality of operations through:
  - Training
  - Education
  - Quality Systems Support

Corporation Members

- American Society of Crime Laboratory Directors
- American Society of Crime Laboratory Directors/ Laboratory Accreditation Board
- Bureau of Alcohol Tobacco and Firearms
- Drug Enforcement Administration
- International Association for Identification
- American Academy of Forensic Sciences
- American Board of Criminalistics
- University of South Florida
- University of Central Florida
- Saint Petersburg College
- Florida International University/International Forensic Research Institute

NFSTC

- Established by ASCLD in October 1995
- Purpose defined in Articles of Incorporation is:

In furtherance of the aforementioned purposes, the Corporation's purposes shall include the training, education and certification of persons engaged in providing forensic analysis in support of law enforcement and the accreditation of governmental and private laboratories.

NFSTC Development

- 1996 – 2000
  - Funded solely by cost recovery
- 2000 – 2004
  - Mix of Federal funds (NIJ Cooperative Agreement) and cost recovery
- Problems with mix
  - Complexity of operations to ensure no co-mingling
  - Annual burden to cost recovery services of the order of $100,000 per year
  - Perception in some places that cost recovery services were being subsidized from Federal funds
    - Despite annual external financial and compliance audits

Separation of activities

- Separate accounts for Federal and cost-recovery services
- Board decided in 2003 that organizational separation was needed to
  - Relieve cost recovery side of the overhead imposition
  - Clarify the separation of activities to the outside world
- Forensic Quality Services incorporated as non-profit in 2003

NFSTC and Accreditation

- In keeping with defined purpose, NFSTC offered from the outset:
  - Support to public crime labs seeking ASCDL/LAB accreditation, including over $250,000 from the NIJ Cooperative Agreement
  - Support to DNA sections and private labs that did not meet the ASCLD/LAB requirements in 1996
    - Sections of lab
    - Private
  - Support was in form of Certificate of Compliance with DNA Advisory Board standards

NFSTC and ISO accreditation

- Approached by EPA's NEIC to develop and accredit laboratory to ISO Guide 25
- Attained in 1999
- Part of deal was that NFSTC would seek and obtain external verification of the operation of its accreditation program
- Florida Racing Laboratory followed a year later

NFSTC and ISO

- Chose to respond to these requests by offering ISO accreditation supported by ILAC Guide 7 (Racing lab) and ILAC Guide 19 (NEIC)
- Private laboratories then came on board, mostly DNA testing
- NFSTC was offering complementary service to ASCLD/LAB's non-ISO service to public crime laboratories

NFSTC, ISO and Crime Labs

- Next development came through request from GBI
  - ISO 9001 certified
  - Introduction of ISO/IEC 17025 as replacement for Guide 25 meant that they could dispense with ISO 9001 certification and deal with the quality system management aspects through NFSTC ISO accreditation

NFSTC, FQS and FQS-I

- NFSTC separated its cost recovery services by creating a class in its accounts titled “FQS” (Forensic Quality Services)
- FQS operated the accreditations for NFSTC from 2001
- FQS applied for recognition by NACLA in 2002, granted in 2004
- Condition of NACLA recognition was separation of FQS consultancies and ISO accreditations

FQS and FQS-I

- When FQS was established as separate company it preserved the name “FQS-I” for its accreditation services

About FQS

- Provides training and quality systems consultancies
- Board is Ben Perillo (Chairman), Manuel Valadez, Kathy Lee, Art Eisenberg, Sudhir Sinha
- Membership is open to all laboratories accredited through FQS-I and to 2 representatives of the Crime Laboratory community
- Is recognized by NACLA for ISO 17025 accreditation with the scope of forensic science
- The only NACLA-recognized AB with a scope of forensic science
- Has an MoU with SCC

Recognition

- From the very beginning we have been committed to the concept of recognition
- Outside review of conformance to appropriate standards is an integral part of the value of accreditation, and the same applies to the Accreditation Bodies
- We chose recognition through NACLA as the way to provide independent confirmation of the quality of our ISO accreditations
- FQS is also recognized by NIJ and the NDIS board in terms of the Justice for All Act

Key Points

- The Standards
  - ISO 17025
  - ILAC G19
  - National QA Standards for DNA Testing
  - The laboratory's own Quality System requirements
  - Any other agreed standards
- The Process
  - FQS operates a process that complies with NACLA requirements and ILAC guidelines

Senior Staff

Over 60 years of forensic testing experience and over 30 years of forensic laboratory management experience

- **Kevin Lothridge,** Executive Director
- **Dr. Bill Tilstone,** Deputy Executive Director
- **David Epstein,** Chief Scientist

Staff

A full range of administrative and scientific resources:

- PhD Academic Program Manager
- 25 employees
- Group of more than 70 contractor consultants

Facilities

- 22,000 square foot building is leased at the Young-Rainey Star Center in Largo, FL.
  - Includes a training laboratory

Program Funding

Programs funded through Cooperative Agreements with the National Institute of Justice (NIJ) and the Environmental Protection Agency

Program Highlights

Fire Debris Validation Kit

- Partnered with Technical Working Group for Fire and Explosions (TWGFEX) and the National Center for Forensic Science (NCFS) in Orlando, FL to produce a set of instructions and flammable liquids for use by a laboratory in the validation of fire debris analysis
- Referee testing in progress (September – December 2005); shipped in Spring 2006

Program Highlights (cont.)

Quality Documents

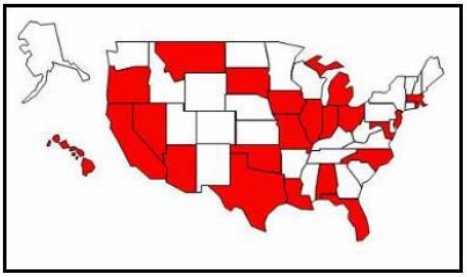
- Created by the NFSTC and a group of quality managers
- Easy-to-use Quality Manual Template and over 90 document samples designed as a guideline for crime laboratories in the creation of customized quality documents
- Developed to meet the laboratory's needs to ensure a comprehensive quality system

Posted to http://www.NFSTC.org/qualDocs.htm

Program Highlights (cont.)

DNA Audit Program

- Provides no-cost, biannual external DNA Laboratory Audits to public crime laboratories performing DNA analysis
- Conducted 149 audits since program inception (total of 166 by end of 2004)



Labs in states that have received or are scheduled to receive audits in 2004 are marked in red.

NFSTC Website

For Additional Information

- Visit the NFSTC Website:
  www.NFSTC.org

National Forensic Science Technology Center

NFSTC Science Serving Justice

NIJ

The NFSTC is a not-for-profit corporation funded by a Cooperative Agreement with the National Institute of Justice (NIJ) and provides programs that build individual competency and quality systems to the forensic science community in the United States.

Preliminary Report of the NELAC/INELA Partnership Planning Team

Originally presented at
NELAC 12 - Kansas
August 14, 2006

NELAC/INELA MOU

- Signed by NELAC and INELA chairs on June 15
- Formation of PPT and a commitment of up to 6 months of good faith negotiations toward a combined organization
- Representation to include:
  - 5 members selected by NELAC Board
  - 5 members selected by INELA Board

PPT Members

NELAC	INELA
– Marcia Davies (F)	– Steve Arms (S) #
– Judy Duncan (S)*	– Dave Speis (C) #
– Richard Sheibley (S)*	– Sharon Mertens (M) #
– Aurora Shields (S)*	– Jerry Parr (C)
– Karen Varnado (S)*	– Alfredo Sotomayor (S)#

(F) – Federal
(S) – State
(C) – Corporate
(M) – Municipal

* NELAC Board
# INELA Board

PPT Charter

- Explore options and develop recommendations on:
  - Timeline
  - Mission and vision
  - Bylaws
  - Board of directors
  - Executive leadership
  - Budget
  - Organization name
  - Corporate structure
  - Programs
  - Publicity and outreach
  - Implementation issues

Underlying Assumptions

- Combining the operations of NELAC and INELA will result in a stronger organization
- Combining operations will allow NELAC to achieve self-sufficiency quicker
- Combining operations is less disruptive to the stakeholder community

NELAC Assets

- Vision for a national accreditation program
- Established infrastructure for recognition of accrediting authorities and accrediting laboratories
- PT Program
- Dedicated volunteer group of state and federal officials
- Cooperative agreement funding through NFSTC to provide support for NELAC/NELAP

INELA Assets

- Vision for a national accreditation program
- Recognized by the IRS as a 501c3
- Infrastructure for consensus standards development, including accreditation from ANSI
- License agreements with ANSI and ASTM for use of ISO standards
- Dedicated volunteers representing all stakeholders
- Cooperative agreement funding from EPA for standards development and technical assistance
- Established business structure

Activities of PPT

- Preliminary proposal presented today for discussion and comment
- Addresses 11 key elements

Key Elements Addressed

- Values
- Mission
- Vision
- Programs
- Membership
- Board
- Name
- Personnel
- Timeline
- Transition
- Communication

7 Core Values

- **1. Inclusive**
- **2. Integrity/honesty**
  - No conflict of interest
- **3. Quality**
  - Belief that the program is worthwhile
  - Quality is an underlying value for everything we do
- **4. Responsive**
  - Visionary
  - Proactive
  - Progressive
  - Respect for diversity/balance
  - Flexible
  - Multi-faceted

7 Core Values

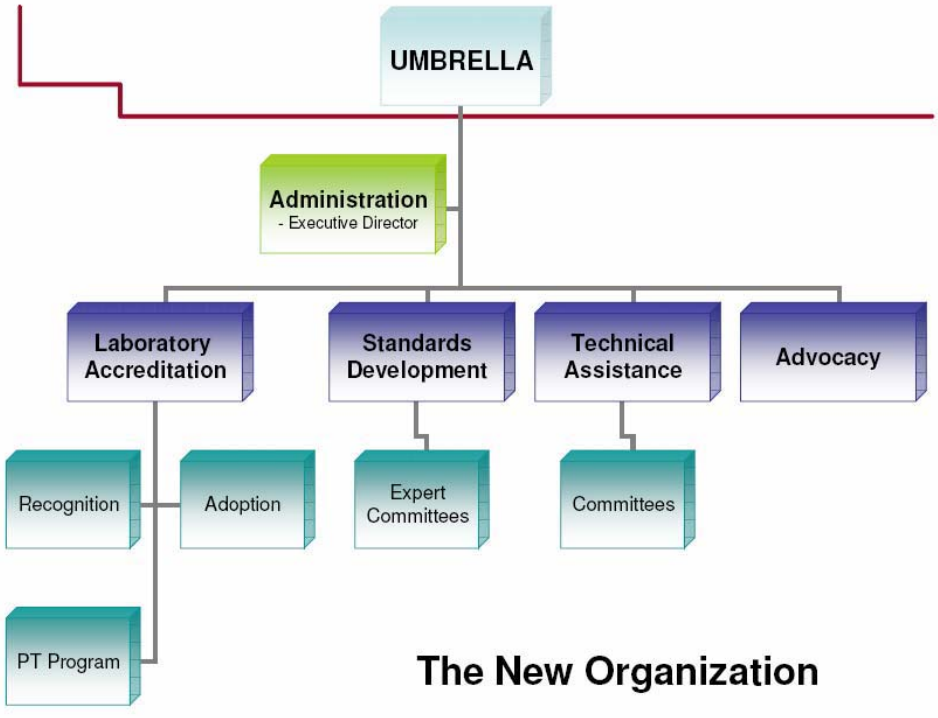
- **5. Open/transparent**
  - Information is available
  - The process is visible
- **6. Self-sustaining**
  - Partnership
  - Independence
- **7. Legally defensible**
  - Legitimate
  - Credible
- **Additional thoughts**
  - True national program
  - Professionalism
  - Program
    - Flexibility
    - Quality
    - Strive for consistency

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.

Vision

- All entities generating environmental data in the United States will be accredited to a national standard.



The New Organization

Key Programs

- Accreditation of Testing Laboratories
- Development of consensus standards
- Technical Assistance
- Advocacy
- Administration

Accreditation Program

- Standards Adoption
- Credible Recognition of AAs
- Recognition and oversight of PT providers
- Implementation and decision-making limited to government
- Additional input needed on structure and functions of this group

Standards Development

- Consensus process with inclusion of all
- Use INELA model and policies

Technical Assistance

- Outreach
  - Newsletter
  - Presentations
  - Participation at conferences
- Training
  - Laboratories
  - Assessors
  - Evaluators (of AAs)
- Mentoring
- Templates and tools
- Website
- Forum
  - Annual meeting
  - Other mechanisms to foster discussion and information exchange

Administration

- Member services
- Fiscal responsibilities and self-sustainability
- Voting processes
- Record maintenance and retention
- Operational administrative functions
- National database

Advocacy

- EPA program office acceptance/participation
- Laboratory participation
- State participation
- Other Federal (non-EPA) participation
- Users of laboratory data
- Generating documents to support advocacy

Corporate Structure

- Incorporated 501(c)3, not-for-profit
- Member organization
- Managed by a Board of Directors

Members

- Individual members
  - may vote
  - may serve on committees and the board
  - entitled to member discounts
  - access to members area of website
- Organizational members
  - may appoint individual members
  - are recognized
  - may not vote

Restricted Membership

- Additional membership requirements may be needed for specific programs, e.g. Accreditation Program

Board of Directors (Transition)

- Transition board will be combination of existing boards of NELAC and INELA, 9 members from each board
- New board elected as soon as possible

Board of Directors

- 12 members
  - 3 AA's
  - 3 Labs
  - 3 Other (to include regulators both state and federal, consultants, vendors, trainers)
  - 3 At large
- Staggered 3 year terms
- Need comments on structure and composition of Board

Personnel

- Executive Director to manage administrative activities of organization under direction of the Board
- Program Directors to manage each key program
  - May be hired staff, contractor, or volunteer
- Support staff for other functions
  - Web site, clerical, meetings, etc.

Name of New Organization?

- **ANELA** – Association for National Environmental Laboratory Accreditation
- **ASELA** – American Society for Environmental Laboratory Accreditation
- **NELAA** – National Environmental Laboratory Accreditation Association

Continuation of Key Programs

Essential for Success

- Accrediting Authorities must be able to have mutual recognition
- Accrediting Authorities must continue to accredit laboratories to a national standard
- A2LA must continue to serve as a PTOB/PTPA
- The INELA standards development process must continue
- Work on the EPA cooperative agreements must continue
- INELA must continue its essential business operations

Continuation of NELAC/NELAP Functions

- NELAC Board will continue to deal with NELAP issues in the interim
- NELAC Board will help AARB and PT Board until new organization formed
- The NELAC Standard is a public record and it will not go away
- Program to recognize AA's needed before migration

Continuation of INELA Functions

- INELA Board, staff and committees will continue current functions until the new organization begins operation
- Plans to migrate essential assets into the new organization will occur in late Fall 2006, after a decision is reached

Timeline: Fall 2006

- PPT continues work based on comments received at Kansas meeting
- PPT to present recommendations to Boards of NELAC and INELA in early November
- Each Board must independently decide to move forward
- If either Board votes "NO", the SSTG will return to a "go it alone" process

Timeline: 2007

- January 2007
  - Organization will have defined members
  - Organization will be operational
  - Transition board will be functional
  - Plan for election of new board announced in Denver

Communication

- Summary from breakout sessions presented at NELAC close on Tuesday, August 15
- Written comments may be sent to johns.susan@insightbb.com by August 25
- All attendees and INELA members will receive periodic updates
- Forum for posting comments and questions will be on the INELA web site
- Outreach efforts to others will continue

Breakout Sessions

- Your opportunity to review and comment on preliminary proposal
- Discussion topics focused on:
  - Organization and membership
  - Governance and structure
- Additional comments may be submitted up to August 25

Topics Discussed

- Organization
  - Key Programs
    - Accreditation
    - Standards Development
    - Technical Assistance
    - Advocacy
  - Duties
  - Participation
- Governance
  - Corporate Structure
  - Membership
  - Personnel
- Transition
  - Essential functions
  - Transition Plan
  - Name
  - Communication

Breakout Feedback

- Accreditation
  - ISO
  - Stability
  - Consistency
  - Mutual recognition
  - Dispute resolution
  - Regulatory issues
  - Develop programs to meet a wider customer base (e.g., for non-water)

Breakout Feedback

- Standards Development
  - Is standards adoption necessary or can standards development stand alone?
- Technical Assistance
  - Standardized training for assessors
- Advocacy
  - Need to educate what accreditation means
  - Outreach to EPA Programs and States

Breakout Feedback

- Broad participation vs. State acceptance
- Conflict of interest
- Identify limitations (if any) for government personnel
- Ensure balance
- Tap into unused resources

Breakout Feedback

- Legal advice needed for corporate issues
- NCCLS model
  - Organizations are members
  - Each organization has one vote
- Baseball commissioner model
  - Umbrella board will give the Director real power

Breakout Feedback

- Board composition
- The interest groups need to be well defined
- Adequate representation by non-governmental entities

Breakout Feedback

- Paid staff needed for at least 2 programs:
  - Standards development
  - Accreditation
- Roles, responsibilities and authority need to be defined
  - Executive Director
  - Program Directors
- Define use of consultants and 3rd parties

Breakout Feedback Transition Issues

- Ensure continuation of NELAP programs during transition
  - Laboratory accreditations by AAs
  - Recognition of AAs and related activities
- Change policies relating to the executive director
- Access historical NELAC and NELAP records
- Advocacy
- Name
- Time is needed to address the issues related to a name change

Bottom Line

- The overall sense of the comments received is that there are many issues to be addressed in detail but that the process of self-sufficiency should proceed.
- The PPT will take all the input given at NELAC 12 and deliberate how to incorporate the material into recommendations to the NELAC and INELA Boards

Addition to Transition Plan

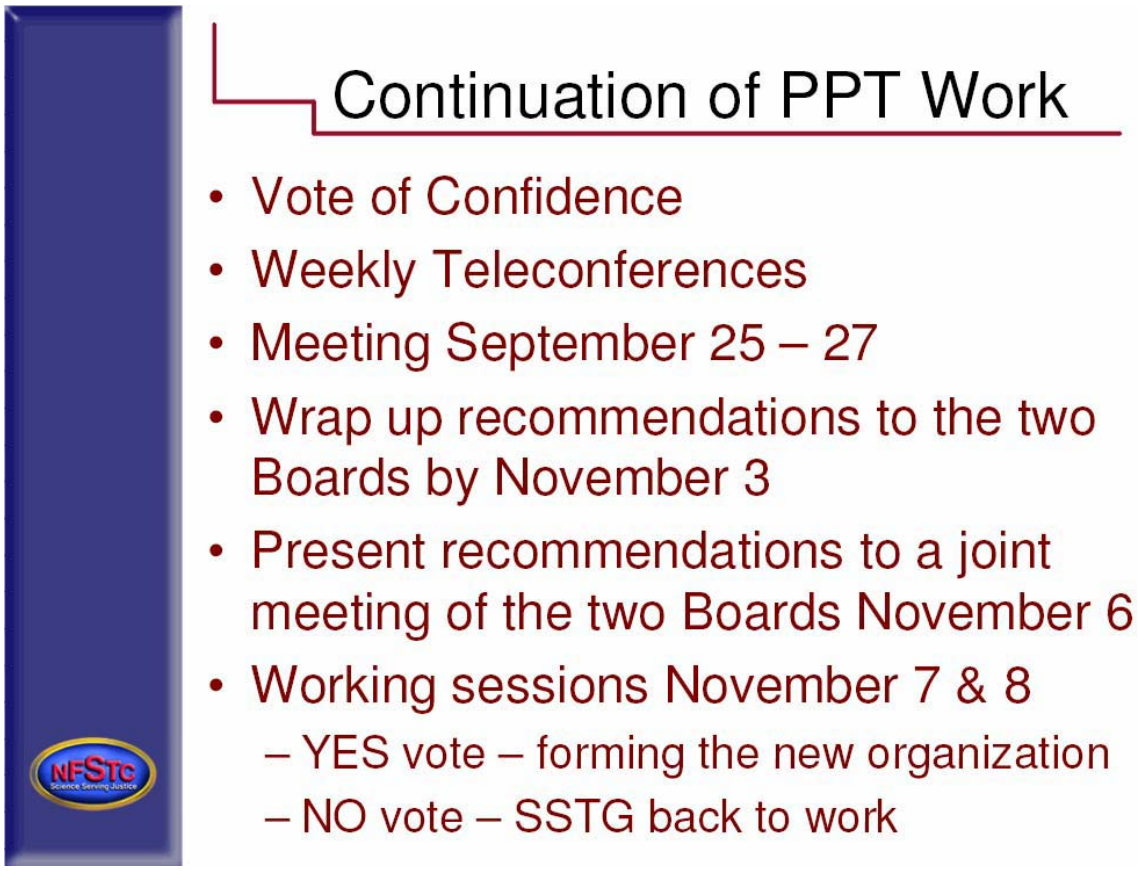
The NELAC Board of Directors recognizes that NELAP AAs and Laboratories will need time to implement changes and proposes a 2 year transition period of the use of the NELAC/NELAP name to give states and laboratories enough time to make these changes.

Transition Plan

This NELAC conference expresses confidence in the NELAC Board of Directors for the Transition Plan.

Continuation of PPT Work

The NELAC conference expresses confidence in the NELAC Board of Directors for the PPT to move forward with their work for the formation of a new organization.


Continuation of PPT Work
• Vote of Confidence
• Weekly Teleconferences
• Meeting September 25 – 27
• Wrap up recommendations to the two Boards by November 3
• Present recommendations to a joint meeting of the two Boards November 6
• Working sessions November 7 & 8
– YES vote – forming the new organization
– NO vote – SSTG back to work
NFSTC
Science Serving Justice

WEDNESDAY P.M., AUGUST 30, 2006

CONCURRENT SESSIONS

Perchlorate

ANALYSIS OF PERCHLORATE IN DRINKING WATER

Munch, D.J.; U.S. Environmental Protection Agency
Pepich, Barry V.; Shaw Environmental, Inc.

Four U.S. Environmental Protection Agency (EPA) methods have been published for the analysis of perchlorate in drinking water. A fifth, which employs Dionex's new 2-D technology, is being validated and should be published shortly. The first method, EPA Method 314.0 supports a minimum reporting level (MRL) of 4.0 µg/L and was used during the first Unregulated Contaminant Monitoring Regulation (UCMR) cycle (2001-2005).

Perchlorate concentrations above 4.0 µg/L were reported in approximately 4% of the public water systems tested. Based on these data, together with concerns regarding relative source contributions for perchlorate and available health effects data, EPA is considering whether perchlorate should be regulated in drinking water and/or if additional occurrence data needs to be collected at lower concentrations.

To alleviate potential impediments associated with the availability of appropriate analytical methods, EPA's Office of Ground Water and Drinking Water (OGWDW) initiated method development projects that were aimed at developing new perchlorate methods that offer improved sensitivity, selectivity and method robustness. A central goal was also to take full advantage of the available instrument base in the drinking water community, thereby offering the analytical laboratories the greatest flexibility in method selection. The new methods employ both ion chromatographic (IC) and liquid chromatographic (LC) separation, and detect perchlorate using either conductivity or mass spectrometric techniques.

This paper describes all four OGWDW methods for the analysis of perchlorate in drinking water, specifically Methods 314.0, 314.1, 331.0 and 332.0, and introduces the fifth 2-D method. The most significant challenge remaining in the area of perchlorate analysis may be deciding which method to use.

A Review of the USEPA Methods for the Analysis of Perchlorate in Drinking Water

Barry V. Pepich[1] and David J. Munch[2]

[1]Shaw Environmental, Inc., 26 West Martin Luther King Drive, Cincinnati, OH 45219

[2]U.S. EPA, Office of Ground Water and Drinking Water Technical Support Center, 26 West Martin Luther King Drive, Cincinnati, OH 45219

BACKGROUND

- Perchlorate is an oxidant used primarily in the manufacture of solid propellants. It inhibits the uptake of iodine by the thyroid gland affecting thyroid hormone production
- Perchlorate was added to the Contaminant Candidate List in 1998 but was listed as "reserved" in List 1 of the proposed UCMR (4/1999)
- Perchlorate was added to List 1 in the final UCMR (9/1999) following publication of EPA Method 314.0

BACKGROUND

- UCMR survey for perchlorate included 2800 large systems and 800 small systems
  - Samples collected at the entry points to the distribution system
- Perchlorate was detected in about 4% of the PWS surveyed at 4 ug/L or greater
  - Perchlorate detected in 26 states and Puerto Rico

BACKGROUND

- USEPA completed a Toxicological Review and Risk Characterization for perchlorate in 2002
  - Proposed oral reference dose (RfD) was 0.00003 mg/kg per day or 1 ug/L (for 70 kg adult consuming 2 L water per day)
- OGWDW sought additional methods with improved sensitivity and selectivity that could potentially be used in UCMR2
  - Method 314.0 and 3 new EPA methods were proposed under UCMR2 in August 2005

BACKGROUND

- During the same period USEPA, in conjunction with the DoD, DoE, and NASA, requested the NAS to review the science associated with the health impacts of perchlorate
  - In January 2005, NAS recommended a RfD of 0.0007 mg/kg per day (or 24.5 ug/L)
  - Less than 0.25% of the surveyed PWS reported concentrations > 20 ug/L
  - Relative source contribution may play a role in final considerations
- The final UCMR2 is scheduled to be published later this year

OUTLINE

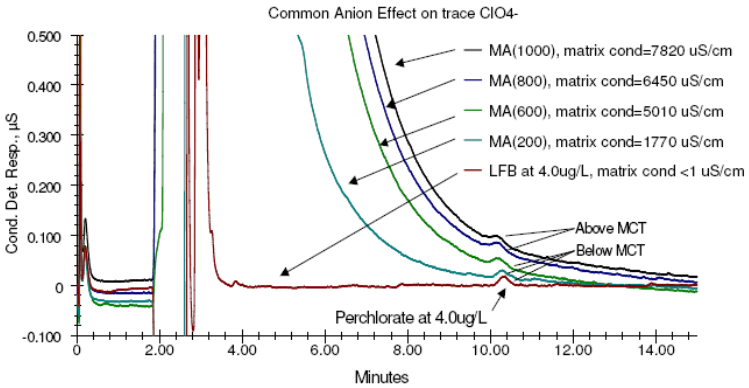
- Method for UCMR1
  - Method 314.0 – IC/Conductivity (D. Hautman)
- Methods for UCMR2
  - Common requirements: sample preservation and LCMRL
  - Method 314.1 – IC/Conductivity with column concentration & matrix elimination (H. Wagner)
    - 2-D Method for perchlorate (Dionex lead, Method 314.2)
  - Method 331.0 – LC/MS or LC/MS/MS (S. Wendelken)
  - Method 332.0 – IC/MS or IC/MS/MS (E. Hedrick)

Method 314.0 – IC/Conductivity

- Method 314.0 detection levels for perchlorate are : MDL= 0.53 ug/L; MRL = 4 ug/L
  - Uses a 4-mm AS-16, 50 uM NaOH and a 1-mL injection
- Samples with high levels of common anions (sulfate, carbonate, and chloride) can challenge method
  - Matrix Conductivity Threshold (MCT) establishes the highest permitted conductance
  - Samples above MCT require either a 10-fold dilution (raises the MRL) or a 3-cartridge clean up
  - Positive sample from unfamiliar sources must be fortified to confirm identification

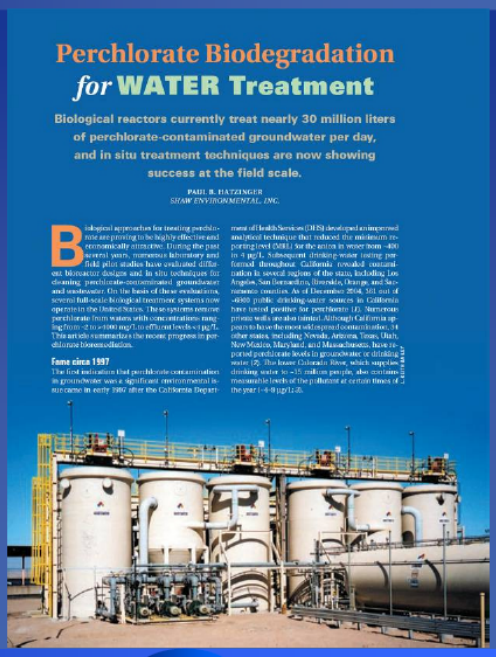
Method 314.0 – IC/Conductivity

The effect of matrix anion (MA) concentration (mg/L) on conductivity background (uS/cm) and perchlorate peakshape at 4.0 µg/L using Method 314.0 without sample clean-up.



UCMR2 Common Requirements – Preservation

- Perchlorate can be readily degraded by perchlorate respiring bacteria (PRB)
- Shaw bioreactor in Henderson, NV is currently remediating water that feeds Lake Mead using PRB
  - Influent 250 mg/L
  - Effluent < 4 mg/L
  - 1,000 gal/min throughput
  - Removing about 1 kg/min



Perchlorate Biodegradation *for* WATER Treatment

Biological reactors currently treat nearly 30 million liters of perchlorate-contaminated groundwater per day, and in situ treatment techniques are now showing success at the field scale.

PAUL B. HATZINGER
SHAW ENVIRONMENTAL, INC.

Biological approaches for treating perchlorate are proving to be highly effective and economically attractive. During the past several years, numerous laboratory and field pilot studies have evaluated different bioreactor designs and in situ techniques for cleaning perchlorate-contaminated groundwater and wastewater. On the basis of these evaluations, several full-scale biological treatment systems now operate in the United States. These systems remove perchlorate from waters with concentrations ranging from <2 to >100 mg/L to effluent levels <4 µg/L. This article summarizes the recent progress in perchlorate bioremediation.

Fame circa 1997

The first indication that perchlorate contamination in groundwater was a significant environmental issue came in early 1997 after the California Department of Health Services (DHS) developed an improved analytical technique that reduced the minimum reporting level (MRL) for the anion in water from ~400 to 4 µg/L. Subsequent drinking-water testing performed throughout California revealed contamination in several regions of the state, including Los Angeles, San Bernardino, Riverside, Orange, and Sacramento counties. As of December 2004, 381 out of ~4000 public drinking-water sources in California have tested positive for perchlorate [1]. Stormwater, process wells are also tainted. Although California appears to have the most widespread contamination, 14 other states, including Nevada, Arizona, Texas, Utah, New Mexico, Maryland, and Massachusetts, have reported perchlorate levels in groundwater or drinking water [2]. The lower Colorado River, which supplies drinking water to ~15 million people, also contains measurable levels of the pollutant at certain times of the year (~4–9 µg/L) [3].

UCMR2 Common Requirements – Preservation

- A large number of PRB have been characterized, most are Grahm-negative anaerobes
- The reduction pathway for perchlorate is:

$$ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow Cl^- + O_2$$

  - Requires an organic (or inorganic) electron donor and low levels of O_2
  - may require trace metals like Fe
- Surface waters with high TOC and BOD collected without headspace could degrade upon storage
  - Nitrate is reduced first

UCMR2 Common Requirements – Preservation

- All 4 UCMR2 methods require sample collection using sterile, disposable plastic syringes and 0.2 um filters
- Samples are stored in sterile, HDPE bottles with headspace

UCMR2 Common Requirements – Lowest Concentration Minimum Reporting Level

- The lowest concentration minimum reporting level (LCMRL) is the lowest true concentration for which future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery
- Developed by OGWDW after thorough evaluation of literature
- Simultaneously considers precision and accuracy
- Performed during method development (only) and requires 7 replicates at 4 concentrations
- The MRL is confirmed using a simple technique (7 samples at 1 concentration) by labs using the methods – NO ITERATION

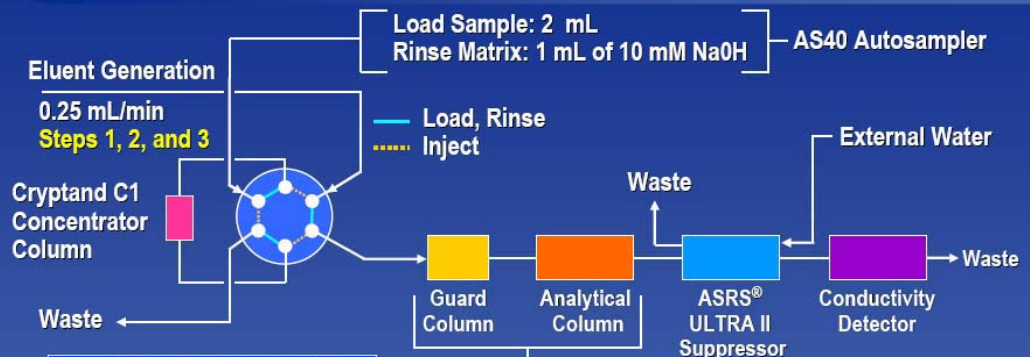
UCMR2 Common Requirements – Lowest Concentration Minimum Reporting Level

- Published as an EPA document and in ES & T:
  - *Statistical Protocol for the Determination of the Single-Laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of Laboratory Performance at or Below the Minimum Reporting Level* (EPA Document #: 815-R-05-006)
  - Winslow, et al. Environ. Sci. Technol. 2006, 40, 281-288
- LCMRL Calculator available on-line at: http://www.epa.gov/OGWDW/methods/sourcalt.html

Method 314.1 IC/Conductivity

- This method employs column concentration and matrix elimination. It has 3 key steps:
  1. Trapping perchlorate from a large volume injection on a Cryptand column
  2. Removing the common interfering anions with a dilute NaOH rinse, and
  3. Quantitatively transferring and refocusing the analytes on the head of the analytical column
- Cryptand column uses manipulation of column capacity (set with Na) to achieve separation

Method 314.1 – IC/Conductivity



NaOH Eluent Generation			
Steps	Function	Conc.	Time
1.	Perchlorate Transfer	0.5 mM	12 Min
2.	Analysis	65 mM	13 Min
3.	Column Cleanup	100 mM	5 Min

Primary Method — AG16, AS16 (2 x 250 mm)

Confirmatory Method — AG20, AS20 (2 x 250 mm)

* Schematic courtesy of Dionex

20590

Method 314.1 LCMRL

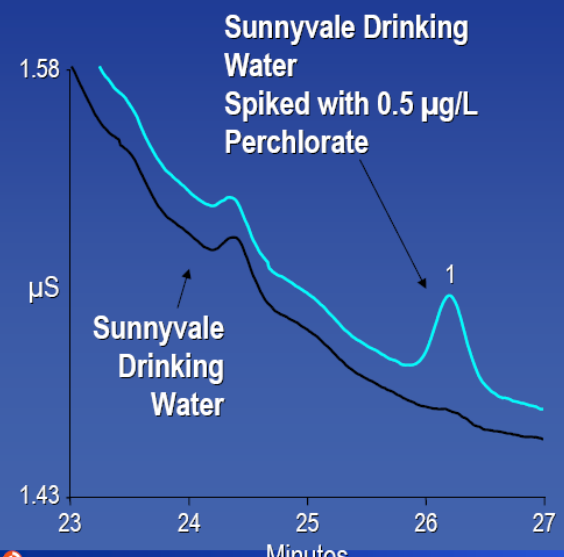
Analytical Column	Analyte	LCMRL (µg/L)	MDL (µg/L)
AS16	ClO_4^-	0.14	0.031
AS20	ClO_4^-	0.13	0.025

Method 314.1 Precision and Accuracy

Matrix	Native Conc. (µg/L)	Fortified Conc. (µg/L)	Mean %Rec.	% RSD
Reagent Water	< LCMRL	0.50	102	2.6
	< LCMRL	5.0	90.0	3.2
Chlorinated Surface Water	0.63	1.0	82.6	2.7
	0.63	5.0	85.8	2.0
Chloraminated Surface Water	< LCMRL	1.0	83.1	3.6
	< LCMRL	5.0	89.3	1.8
Chlorinated Ground Water	< LCMRL	1.0	75.9	5.4
	< LCMRL	5.0	92.4	3.3
RW with 1000 mg/L common anions (TDS = 4450 mg/L)	< LCMRL	0.50	102	2.8
	< LCMRL	5.0	80.9	1.3

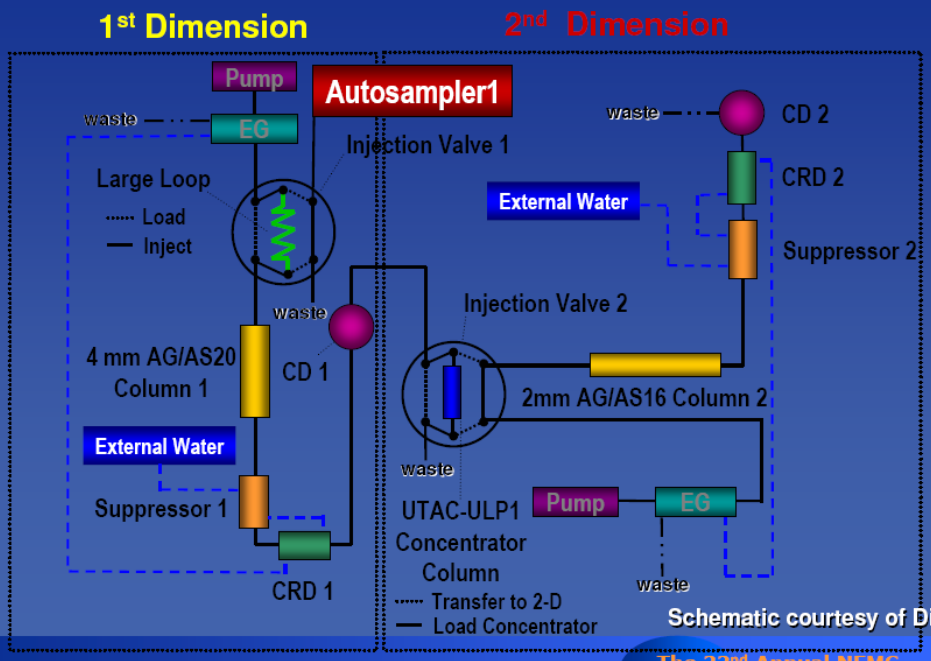
LCMRL = 0.14 ug/L

Method 314.1 – Surface Water Fortified at Low Level



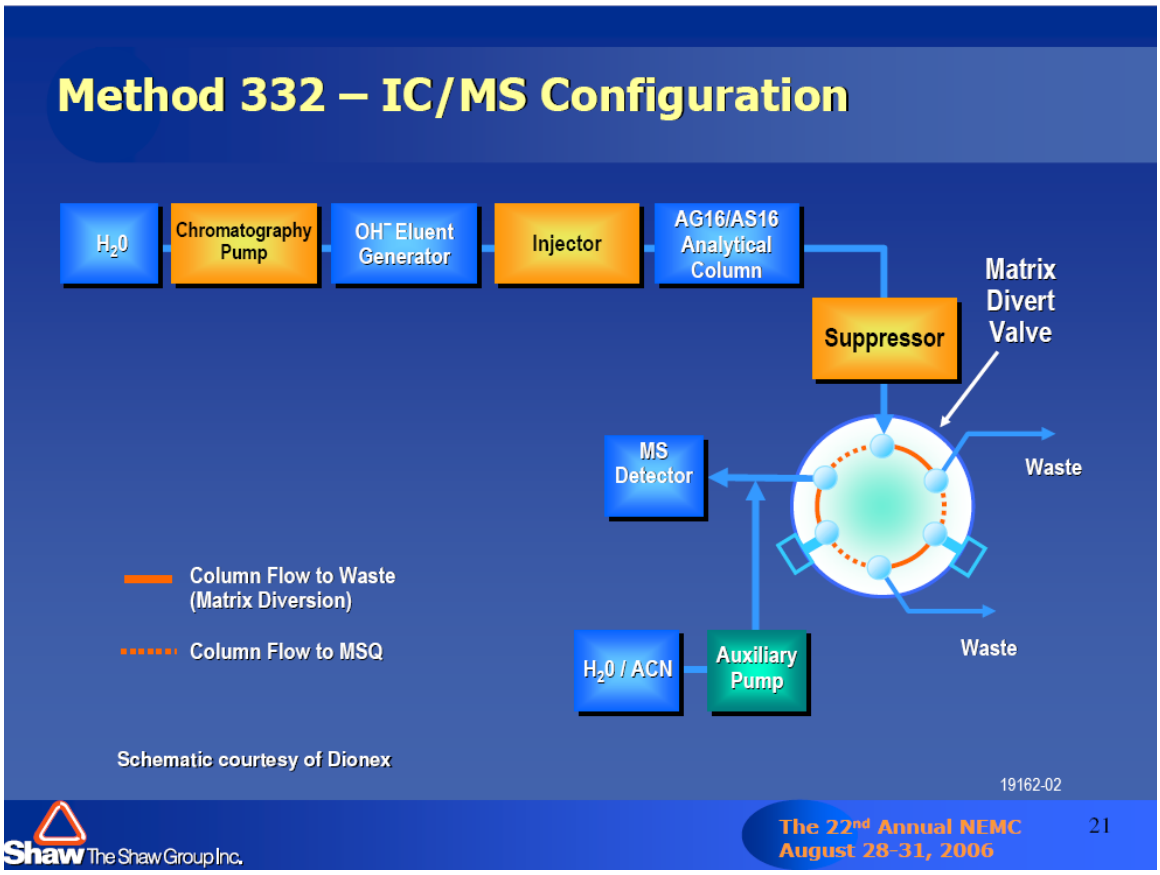
Column:	IonPac® AG20, AS20, 2 mm
Conc.Column:	IonPac Cryptand C1, 4 x 35 mm
Eluent:	Sodium hydroxide: 0.5 mM from 0–12 min, 65 mM from 12.1–28 min, 100 mM from 28.1–30 min.
Eluent Source:	EGC II NaOH cartridge with CR-ATC
Temperature:	35 °C
Flow Rate:	0.25 mL/min
Inj. Volume:	2 mL
Rinse Volume:	1 mL (10 mM NaOH)
Detection:	Suppressed conductivity, ASRS® ULTRA II, 2 mm, AutoSupression® external water mode, 100 mA
Peak:	1. Perchlorate 0.5 µg/L (ppb) Recovery 92%

Perchlorate Analysis by 2-D IC with Conductivity Detection



Method 331.0 and 332.0

- Both methods have a liquid phase separation and detect perchlorate using ESI with MS or MS/MS detection techniques – instrumentation is similar
- ESI techniques are subject to suppression and/or enhancement
- Method robustness and performance improve as chromatography is optimized
- Perchlorate elutes after the common anions on both separation systems


Method 332 – IC/MS Configuration
H_2O
Chromatography Pump
OH^- Eluent Generator
Injector
AG16/AS16 Analytical Column
Suppressor
Matrix Divert Valve
MS Detector
Waste
Waste
H_2O / ACN
Auxiliary Pump
Column Flow to Waste (Matrix Diversion)
Column Flow to MSQ
Schematic courtesy of Dionex
19162-02
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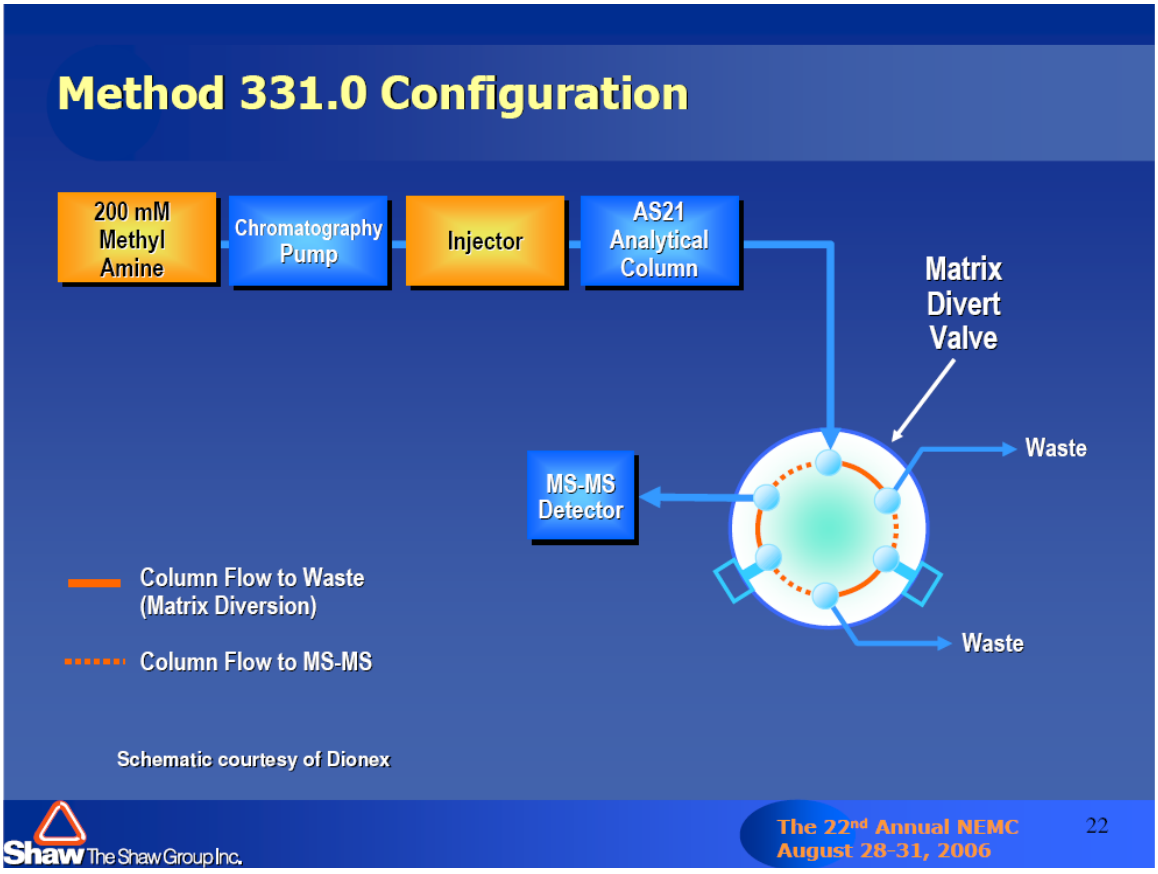
Method 331.0 Configuration
200 mM Methyl Amine
Chromatography Pump
Injector
AS21 Analytical Column
Matrix Divert Valve
MS-MS Detector
Waste
Waste
Column Flow to Waste (Matrix Diversion)
Column Flow to MS-MS
Schematic courtesy of Dionex
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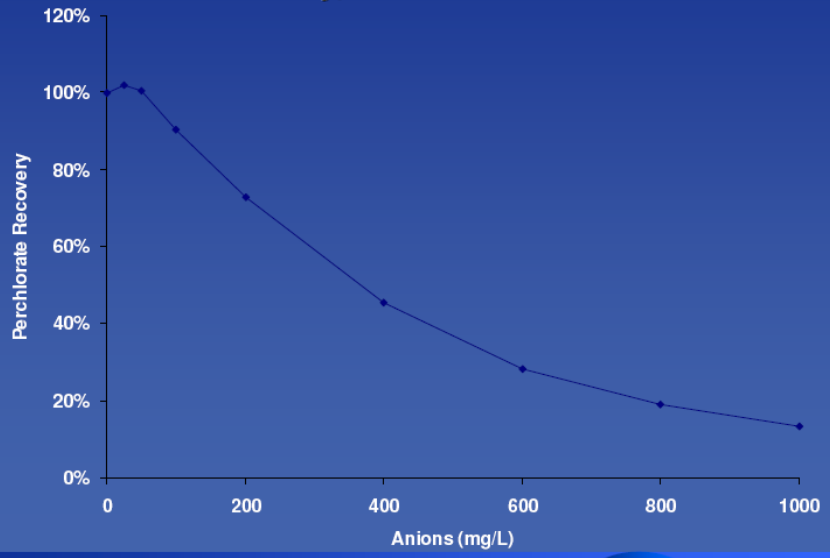
Method 331 and 332 – Suppression

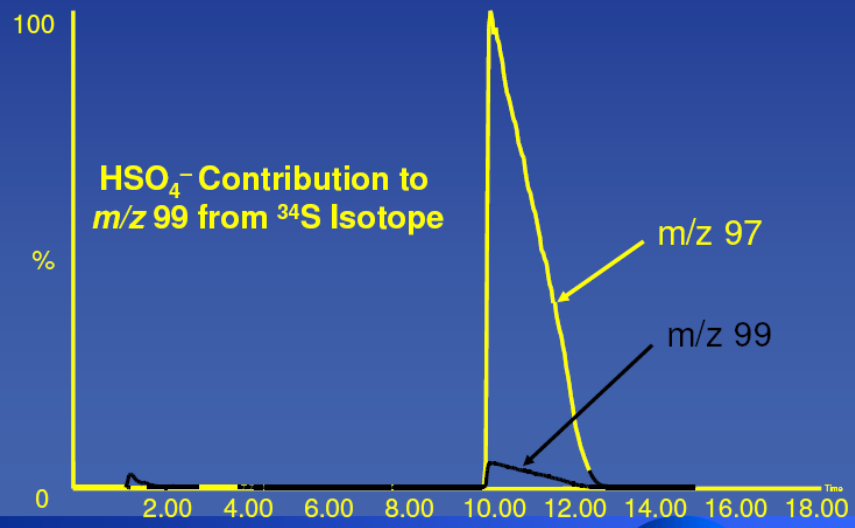
- The effect of common anion concentration on signal suppression (expressed as %Recovery) in SIM mode



Method 331.0 and 332.0 - Internal Standard

- $^{35}Cl^{18}O_4^-$ - *m/z* 107
- Source
  - Isotech, Inc., Miamisburg, OH
  - Dionex (1 mg/L standard solution)
- ISTD has been tested for oxygen exchange in both distilled water and in sodium hydroxide and has acceptable stability
- ISTD does not fully compensate for poor chromatography!

Method 332 – Sulfate Interference in SIM



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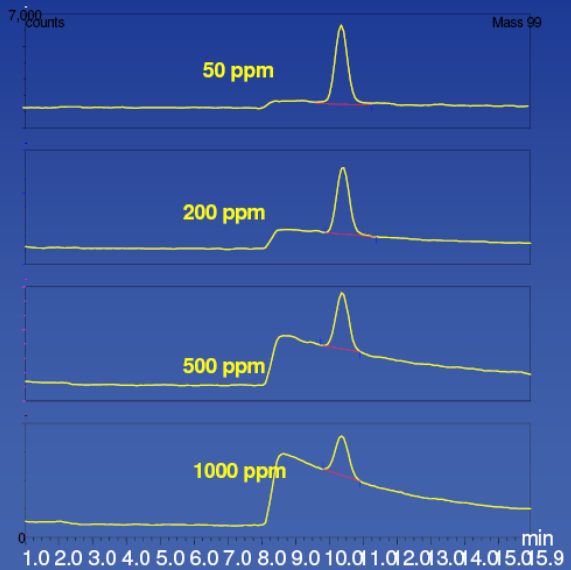
Method 332 – Effect of Common Anion Concentration on Background (m/z 99)



- SIM for m/z 99 for 1.0 ug/L perchlorate in reagent water containing varying concentrations of common ainons
- Martix diverted until 2 min prior to perchlorate elution
- AS 16 separation fully optimized

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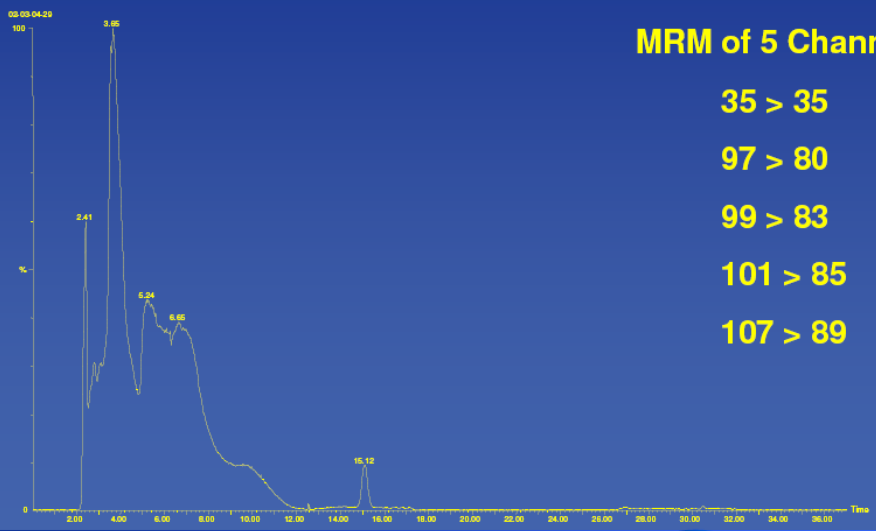
Method 331.0 – Separation Fully Optimized

- 1.0 ug/L perchlorate in 1000 mg/L common anions under optimal separation conditions



MRM of 5 Channels

35 > 35

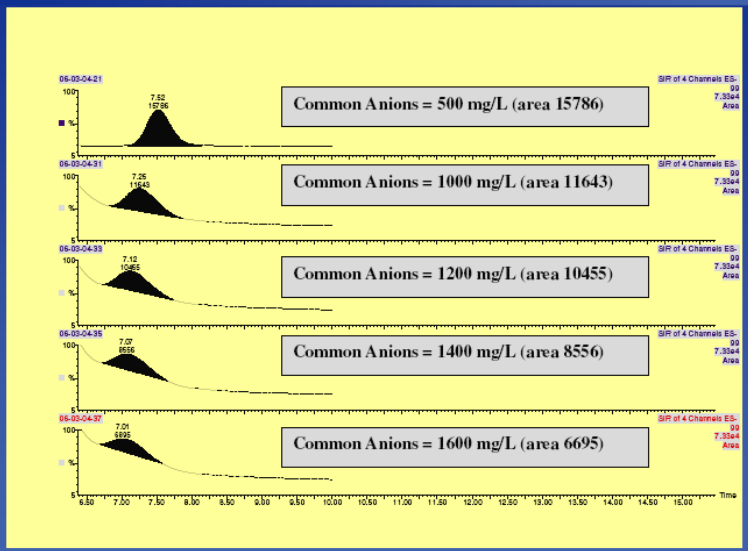
97 > 80

99 > 83

101 > 85

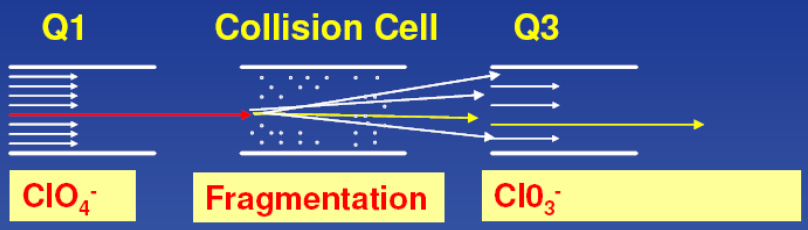
107 > 89

Method 331.0 – Effect of Common Anion Concentration on Background (m/z 99)



- To optimize accuracy and robustness both methods specify that SIM quantitation be performed using *m/z* 101

Multiple Reaction Monitoring Improves Selectivity of Method 331.0 and 332.0



- MRM increases instrument cost and complexity
- However, it dramatically improves selectivity and background
- Alleviates sulfate interference problem

Method 331.0 and 332.0 Quantitation Ions

Precursor Ion (m/z) SIM Mode	Fragment Lost (m/z)	Product Ion (m/z) MRM Mode
$^{35}ClO_4$ (99)	^{16}O (16)	$^{35}ClO_3$ (83)
$^{37}ClO_4$ (101)	^{16}O (16)	$^{37}ClO_3$ (85)
$^{35}Cl^{18}O_4$ (107)	^{18}O (18)	$^{35}Cl^{18}O_3$ (89)

- The sulfate ion interference at *m/z* 99 ($H^{34}SO_4^-$) looses an OH to form a product ion at *m/z* 82
- Both forms of the methods require monitoring the ratio of m/z 99/101 (SIM) and 83/85 (MRM) to confirm the presence of perchlorate and ensure instrument performance (criterion is ± 25 % of 3.08)

Method 331.0 and 332.0 – LCMRL

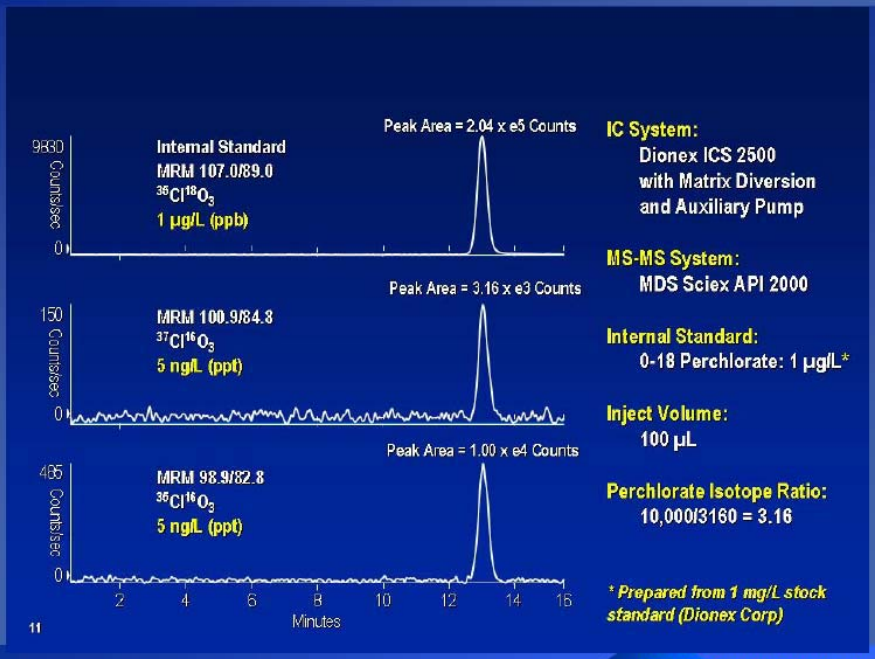
Analysis Method	Analyte	LCMRL (µg/L)	MDL (µg/L)
LC/MS/MS (Method 331.0)	ClO_4^-	0.022	0.005
LC/SIM (Method 331.0)	ClO_4^-	0.056	0.008
IC/SIM (Method 332.0)	ClO_4^-	0.10	0.02

Method 331.0 and 332.0 – Typical Performance in Using SIM

Matrix	Unfortified Conc. (µg/L)	Fortified Conc. (µg/L)	Ratio $^{35}Cl/^{37}Cl$	Mean %Rec.	% RSD
Method 332.0 IC/SIM					
Reagent Water	<LCMRL	0.050	2.77	105	14
	<LCMRL	0.50	3.05	102	3.6
Surface Water	<LCMRL	0.20	2.93	104	8.6
	<LCMRL	1.0	3.04	95	1.5
Ground Water	<LCMRL	0.20	2.83	99	7.4
	<LCMRL	1.0	2.99	93	2.4
Synthetic High Ionic Water	<LCMRL	0.20	2.64	90	11
	<LCMRL	1.0	2.70	90	3.0

LCMRL = 0.10 ug/L

Method 331.0 and 332.0 – Example Chromatogram



CONCLUSIONS

- Method 314.0 met EPA's UCMR1 objectives and helped characterize perchlorate occurrence in PWS
- Three additional methods have been developed that have from 10 to 100 times more sensitivity, offer analyte confirmation, and can analyze relatively high TDS samples without additional sample clean-up
- The most difficult task remaining may be choosing which method to use

Acknowledgements

- Work was supported on-site at the USEPA's Drinking Water Laboratory located in Cincinnati, Ohio. This work has been funded wholly or in part by the United States Environmental Protection Agency under contract 68-C-01-098 to Shaw Environmental, Inc.
- Partner in these projects included: EPA NERL (Cincinnati, OH); Dionex (Sunnyvale, CA); EPA NRMRL (Ada, OK); and EPA Region 2 (Edison, NJ)

New EPA Office of Solid Waste SW 846 Methods for the Analysis of Perchlorate in Various Environmental Matrices

Shen-yi Yang[1] and Sharon M. Drop[2]
[1]U.S. EPA Office of Solid Waste; [2] Science Applications International Corporation

ABSTRACT

Perchlorate is a high profile non-regulated contaminant and is being detected in many soils, aquifers, vegetables, cow milk, beers and wines in the United States (U.S.). The existing SW-846 method for perchlorate in soil has several limitations. The EPA Office of Solid Waste (OSW) is now developing two new improved methods to provide better quantitative and qualitative capabilities for the analysis of perchlorate in various environmental media. These new methods will be used for perchlorate monitoring and cleanup activities. This paper introduces the two new SW 846 methods under development for perchlorate, and reports the results of a round robin validation study involving multiple laboratories and a variety of environmental media.

INTRODUCTION

Perchlorate (ClO_4^-) is a both natural occurring and man-made material. Most of the perchlorate manufactured in the U.S. is being used as a primary ingredient of solid rocket propellant, missiles, and fireworks. Wastes from the manufacture and improper disposal of perchlorate containing chemicals are being increasingly detected in various environmental media. Perchlorate inhibits the uptake of iodine by thyroid gland, thus affects thyroid hormone production and thyroid regulation of metabolism; impairs neurological development of fetus and newborn; and changes in thyroid hormone levels may result in thyroid gland tumors[1].

Perchlorate contamination has been detected in various soils, aquifers, crops, milk and beers in Puerto Rico and in 35 states of the U.S. Perchlorate is very mobile in aqueous systems and it is persistent under typical ground water and surface water conditions. Perchlorate absorbs weakly to most soil minerals and it may degrade in certain environmental conditions[2]. The rate of perchlorate degradation depends on the presence of perchlorate reducing bacteria (PRB) and the environment that favors the growth of PRB (e.g., anaerobic conditions, carbon sources, presence of particular nutrients)[3].

Previously published methods for perchlorate (including Method 9058 for perchlorate in solids), based on ion chromatography (IC) separation and conductivity detection, are not capable of confirming the presence of perchlorate due to chromatographic interferences[4,5]. In addition, the existing Method 9058 has no written procedure for extracting perchlorate from solids. OSW is now developing two new improved methods to provide better quantitative and qualitative capabilities for perchlorate in soil, sludge, wastewater and high salt water. The two new methods determine perchlorate using (HPLC, Method 6850; IC, Method 6860) chromatographic separation followed by negative electrospray ionization (ESI) mass spectrometry (MS). Perchlorate is separated (by HPLC or IC) from the sample matrix, partially fragmented via negative electrospray ionization and detected by MS (with in-source fragmentation) or MS/MS using mass-to-charge (m/z) ratios 83, 85 and 89. Quantitation is performed using m/z 83 and

internal standard calibration. Isotopically-labeled perchlorate, ($Cl^{18}O_4^-$), m/z 89, serves as the internal standard. The 83/85 isotopic ratio reflects the isotopic ratio of naturally occurring $^{35}Cl/^{37}Cl$ and is used for additional confirmation of perchlorate identification. In the absence of interferences a single stage mass spectrometer may be used. In that case the perchlorate is detected and quantified using m/z 99, 101 and 107.

The EPA OSW Perchlorate Task Force, lead by OSW, includes members from EPA Office of Research and Development (ORD), EPA Regional Laboratories, Department of Defense (DOD), instrument vendors and commercial laboratories. The OSW Perchlorate Task Force has provided tremendous support in reviewing/validating these two methods. The Phase I initial demonstration of proficiency (IDP) study was completed in September 2005 and the Phase II methods validation study was completed in July 2006. Information and data collected from our studies are being evaluated and statistically analyzed.

EXPERIMENTAL PROCEDURE

Our validation study was carried out in two phases. Phase I was conducted as an initial demonstration of proficiency (IDP) to identify candidate analytical procedures as well as capable volunteer laboratories for carrying out the actual Phase II method validation. Each of the two developmental methods contains only one analytical system, HPLC/MS for Method 6850 and IC/MS/MS for Method 6860, respectively. In accordance with the Agency's Methods Innovation Rule and in keeping with the original intention of SW-846 Methods as guidance methods[6], a wide range of HPLC and IC columns, single and dual MS systems, and their respective analytical conditions are being evaluated for inclusion in Methods 6850 and 6860 via large-scale, multi-laboratory round robin studies. Our validation study was devised to compare several different analytical systems and identify those capable of accurately determining perchlorate in a variety of real world matrices. Examples of technologies evaluated in this study are shown in Table 1.

Table 1: Examples of Technologies Evaluated in the Validation Study for Methods 6850 & 6850

Method	Column	Mobile Phase	Detection	Quantitation Ions (*m/z*)
6850	K'(Prime) RP	• 10 M CH_3CN • 35 mM CH_3COOH	LC/MS	83, 85, 89
	IC Pak™ Anion/HR	• 25 mM NH_4HCO_3 • 50% CH_3CN • NH_4OH (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	• 30 mM NaOH • 30% CH_3OH	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

Phase I: Initial Demonstration of Proficiency

Twenty four laboratories participated in the Phase I IDP study involving two spiked reagent waters. Each reagent water was initially prepared as a single sample, which was subdivided into individual aliquots and shipped to the respective participating laboratories. Laboratories were instructed to analyze daily replicates of each IDP solution over the course of 3 days. In addition to evaluating analytical precision and bias, the capability to accurately determine perchlorate in the presence of a high conductivity background, relative to drinking water, was also assessed.

Phase II: Method Validation Study on Real World Matrices

Twenty laboratories participated in the Phase II study. The Phase II study consisted of a blind, multi-laboratory round robin study involving real world matrices, including soil, sludge and high salt water (synthetic sea water). Each matrix was spiked at 3, 3 and 2 different perchlorate levels, respectively, for a total of 8 samples. The conductivities of samples ranged from 240 – 45,000 µS/cm. For solids, the matrix conductivity was based on the 1 g/10 mL extract solution. All laboratories were instructed to adhere to the extraction procedure included in the developmental Methods 6850 and 6860 for solid samples. Several laboratories employed the analytical systems described in the developmental methods. Laboratories that have different analytical systems were free to follow their established standard operating procedures for the study. Additionally, a municipal wastewater was collected and spiked at 2 different perchlorate levels and analyzed by a single laboratory in a non-blind study. The Phase II study evaluated: 1) analytical bias and precision between sample replicates and over time (week-to-week); 2) the efficacy of the extraction procedure for perchlorate in solids; 3) a blind single laboratory holding time (HT) study for high salt water; 4) a non-blind HT study for wastewater; and 5) 0.45 µm vs. 0.1 µm filtration for preservation of wastewater samples from biological degradation of perchlorate.

RESULTS AND DISCUSSION

Table 2 summarizes the results of the Phase I study. The study results demonstrate that all laboratories were capable of following the methods and their performance were within acceptable range. All laboratories were allowed to continue in participating in the Phase II study.

Table 2: EPA OSW Phase I IDP Results for Perchlorate Analysis Using Draft Methods 6850 and 6860

IDP Sol'n	$[ClO_4^-]$ (µg/L)	Conductivity (µS/cm)	Precision		Bias
			Sample-to-Sample RSD (%)	Day-to-Day RSD (%)	Based on Spiked Value (%)
1	1.75	< 0.5	0.4 - 7	0.3 - 37	-21 - 6
2	4.0	10,000[a]	0.3 – 9	0.4 - 28	-19 - 6

[a] The sample was spiked with 1400 mg/L each of Cl^-, SO_4^{2-}, and CO_3^{2-} anions.

Figures 2 and 3 present the results of our Phase II study. All laboratories performed well on the salt water and soil samples. Precision between aqueous sample replicates (salt waters and soil extract solutions) replicate soil extractions as well as week-to-week precision for aqueous analytical replicates all averaged less than 20% relative standard deviation (RSD). Similarly, the average bias for the saltwater and soil matrices was less than -40%. These results were

considered to be acceptable, given the complexity and high conductivity of the matrices. The overall trend in negative biases was thought to be indicative of competition for active sites on the chromatographic resin from constituents in the matrices.

Both precision and bias were significantly reduced for the wastewater and sludge matrices. Components of these matrices in some cases, presented deleterious effects to the chromatography, and may have possibly suppressed ionization in the mass spectrometer. We are continuing to investigate the basis for the low recoveries in these matrices. Our studies and those of others suggest that anaerobic perchlorate-reducing bacteria colonies must be established for active perchlorate biological degradation to occur[7]. Thus, perchlorate would be expected to be stable after being spiked into real world samples that did not originally contain perchlorate. The sludge matrix used in the Phase II study was known to originally contain active perchlorate-reducing bacteria. We are investigating whether favorable conditions may have been present during the time that the sludge matrices were originally spiked, that could possibly have induced degradation of the spiked perchlorate.

Figure 2: Analysis and Extraction Precision from EPA OSW Phase II Perchlorate Validation Study for Draft Methods 6850 and 6860
(Error bars represent 1 standard deviation)

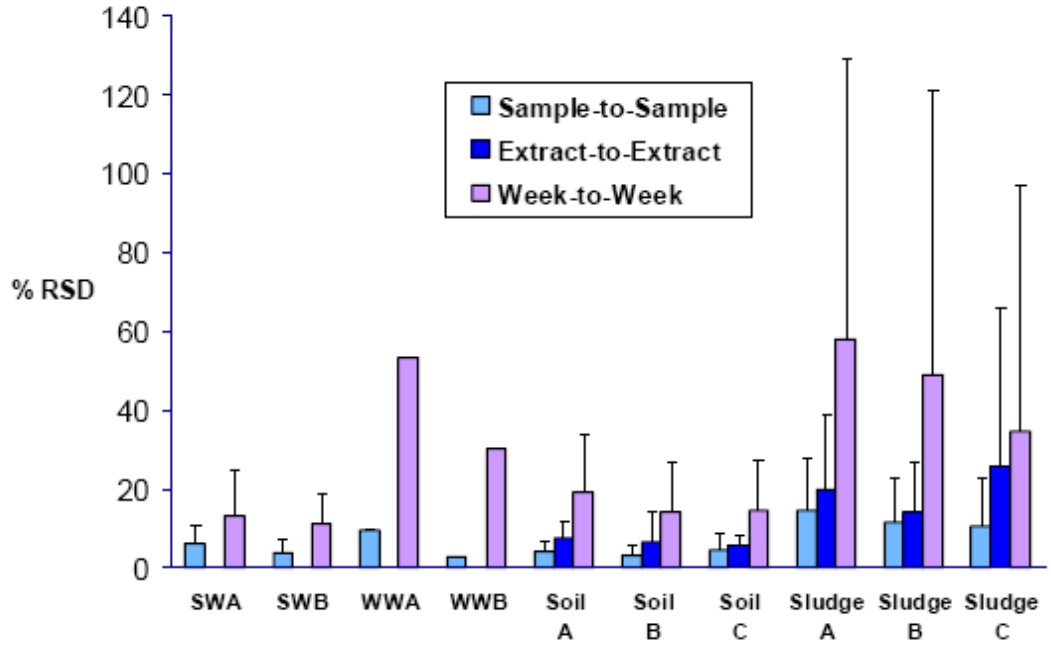
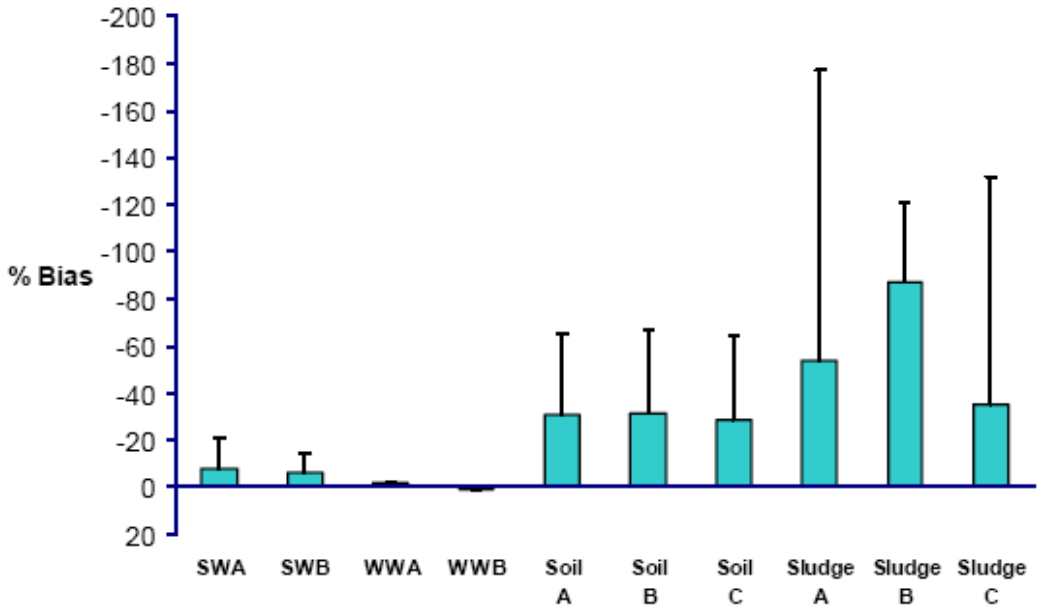


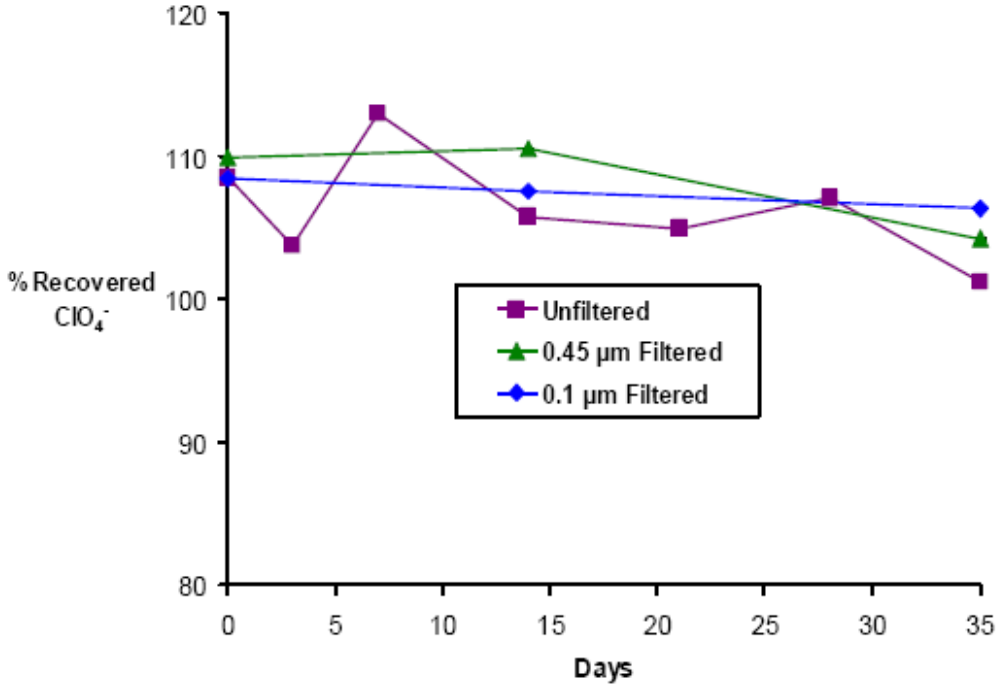
Figure 3: Analytical Bias from EPA OSW Phase II Perchlorate Validation Study for Draft Methods 6850 and 6860
(Error bars represent 1 standard deviation)



We are also evaluating more rigorous extraction procedures such as the Dionex ASE® system which uses elevated temperatures and pressures, the use of alternate extraction solutions, such as 50:50 acetonitrile[8], and/or cleanup steps in an effort to improve perchlorate recovery in more complicated matrices such as wastewater and sludges.

Figure 4 shows the results of the HT study in salt water indicating that perchlorate does not appreciably degrade in salt water. The results of the wastewater HT study are still under investigation. Previous recommendations for membrane filtration and headspace to minimize microbial growth under anaerobic conditions in aqueous samples appear to be a reasonable approach to deterring biological degradation of perchlorate[9,10].

Figure 4: Perchlorate Stability in Synthetic Sea Water under Different Preservation Conditions



CONCLUSION

Our research has demonstrated the precision, accuracy and applicability of several candidate IC/MS and HPLC/MS technologies capable of providing confirmatory analysis of perchlorate in complex matrices, such as high salt waters and soils. Based on the performances demonstrated in our multi-laboratory method validation, we expect to include a number of analytical systems in the final published versions of Methods 6850/6860 for perchlorate analysis in various environmental matrices. Our investigations into the stability of perchlorate in various samples, have suggested at this time that perchlorate is stable in samples that do not contain perchlorate-reducing microorganisms. However as a precautionary measure, membrane filtration and headspace appear to be prudent practices for preserving aqueous samples. We will continue to evaluate and optimize the sample extraction procedure for more complicated matrices such as waste sludges, through the use of alternate solvents, extraction conditions, and cleanup. From these additional optimization studies, we expect to develop improved recommendations in Methods 6850 and 6860 for extracting and analyzing perchlorate in sludges.

ACKNOWLEDGEMENT

We thank the OSW Perchlorate Task Force for their technical contributions to the development of these methods. We also thank the numerous voluntary laboratory participants for their time, effort and technical input.

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DoD PERCHLORATE HANDBOOK

Ingersoll, William S.; NAVSEA 04XQ (LABS)
McLean, Fred S.; NAVSEA 04XQ (LABS)

The Department of Defense (DoD) Environmental Data Quality Workgroup (EDQW) prepared the DoD Perchlorate Handbook to assist DoD facilities in complying with current DoD policy governing perchlorate sampling and testing activities for both environmental restoration/cleanup and compliance monitoring programs. Intended users of this document include DoD Remedial Project Managers (RPMs), contractor project managers, and field-sampling personnel. This handbook includes guidance on using conceptual site models (CSMs) to develop project quality objectives (PQOs) associated with sampling and analysis for perchlorate, designing sampling strategies and implementing appropriate sampling techniques. Other topics include selecting qualified analytical laboratories and analytical methods based on required performance objectives and documenting the above in project planning documents in accordance with the Uniform Federal Policy for Quality Assurance Project Plans, March 2005 (UFP-QAPP).

The DoD Perchlorate Handbook was signed out by the Assistant Deputy Under Secretary for Defense, (Environment, Safety and Occupational Health), on May 1 2006.

Sound Strategies for Collecting Environmental Data on Emerging Contaminants DoD Perchlorate Handbook

Presented to:
National Environmental Monitoring Conference
August 2006

Navy Laboratory Quality & Accreditation Office

Constituents of Emerging Concern
Topics

- Data Quality Challenges
  - Sampling
  - Analytical
  - Data Interpretation
- Emerging Contaminants
- DoD Perchlorate Handbook

Data Quality Challenges Sampling

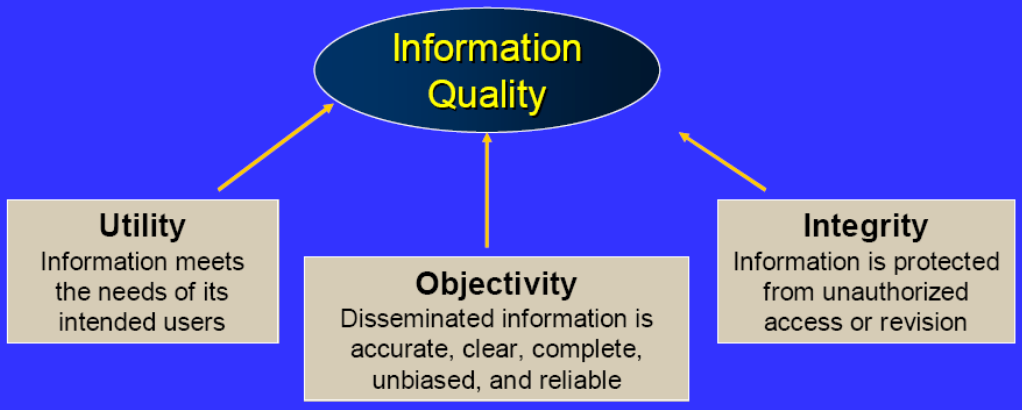
- Sample design
  - When to sample
  - Where to sample
  - How to sample
- Complex Matrices
- Constituent mobility

Data Quality Challenges Analytical

- Appropriate methods
  - Specificity
  - Matrix
  - Interferences
  - MRL
  - Cost
  - Availability
- Laboratory selection
  - Accreditations/approvals
  - Component assessment
  - Compliance with DoD-QSM

Data Quality Challenges

Ensuring Quality of Information Disseminated to the Public by the Department of Defense (UO1678-03) February 2003



Information must be capable of being substantially reproduced

Data Quality Challenges

Emerging Contaminants

- Standards (specific concentrations of concern) do not yet exist
- Laboratories differ in skill, services, equipment, and technology offered
- Methods vary in their ability to detect and recover target analytes
- Analytical methods are not optimized for analyte, matrix, and concentration ranges of interest

Emerging Contaminants
Selecting Appropriate Methods

- Do methods exist that will satisfy your MPCs?
- Is the method suited to your matrix, and concentration range of interest?
- If an existing method does not meet all MPCs, can one be modified?
- Do specific regulatory requirements limit choice of method?

Emerging Contaminants
Selecting Qualified Laboratories

- Does the laboratory have appropriate qualifications and credentials?
- Does it offer your selected method?
- Can it document acceptable method performance *in the matrix of concern, at the concentration of concern?*

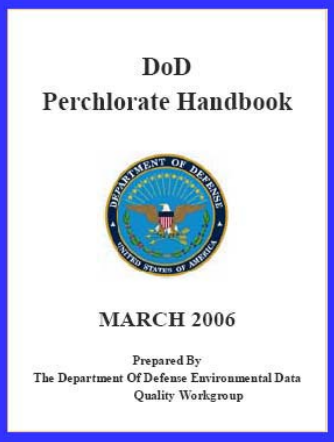
Emerging Contaminants
Developing Sampling Designs

- Are sample locations and timing appropriate for evaluation of the problem?
- How will you distinguish contaminated media from background?
- Will sample collection and handling procedures protect the integrity of the samples?

Example
Perchlorate

- *Improper method application*
  - Method 314.0 developed/validated for use in drinking water
  - Non-specific/subject to interferences
  - MRL in drinking water = 4 ppb
  - Generally not suitable for use in other matrices

DoD Perchlorate Handbook



- Designed to be policy independent
- Facilitates preparation of project-planning documents
- Guides development of sampling designs
- Assists selection of appropriate methods and qualified laboratories

Cost-effective and consistent approach

DoD Perchlorate Handbook
Document

- Intended audience
  - DoD RPMs
  - Contractor project managers
  - Field-sampling personnel
- Perchlorate specific sampling and testing concerns

Policy on DoD Required Actions Related to Perchlorate, January 26, 2006

- Establishes level of concern - 24 ppb
- Comply with state or federal standards whichever is more stringent.
- Addresses sampling policy for:
  - **Environmental Restoration**
  - **Operational Ranges**
  - **DoD-owned Drinking Water Systems**
  - **DoD Wastewater Effluent Discharges**

DoD Perchlorate Handbook *Provides Guidance*

- Use of CSMs to develop PQOs
- Sampling strategies
- Appropriate sampling techniques
- Laboratories and analytical method selection
- Project planning
  - UFP-QAPP

DoD Perchlorate Handbook
Key Requirements

- Implement Environmental Quality Systems
  - UFP-QS
  - UFP-QAPP
- Select Qualified Environmental Testing Laboratories
  - Compliance with DoD QSM
- Develop Conceptual Site Models
- Develop Project Quality Objective

DoD Perchlorate Handbook
Sampling and Sample Designs

- Sample Collection Devices
- Potential Source Areas
- Determine Migration Pathways
- High-Density Perchlorate Solution
- DNAPLS or LNAPLS

DoD Perchlorate Handbook

Laboratory Analysis, Data Deliverables, Data Review and Reporting

- Sampling and Testing for:
  - Regulatory Compliance
  - Environmental Restoration
  - Cleanup and Range Assessments
- Data Deliverable Requirements
- Data Review
- Data Reporting

DoD Perchlorate Handbook

APPENDICES

- Sources and Resources
- UFP-QAPP Worksheets
- Agreements to be Reached During Project Scoping

DoD Perchlorate Handbook
APPENDICES

- Guidance on Developing Conceptual Site Models for Perchlorate Investigations
  - Information to assist in developing CSM for environmental restoration/cleanup sites and ranges
  - Guidance on systematically addressing the site-specific: sources, pathways, receptors

DoD Perchlorate Handbook
APPENDICES

- Guidance on Developing Project Quality Objectives for Perchlorate Investigations
  - PQOs describe the types, amount, and quality of data that will be necessary to support defensible decisions.

DoD Perchlorate Handbook

APPENDICES

- Technical Guides for Sample Collection
  - Provides specific concerns when collecting samples for perchlorate analysis (i.e. interferences from detergents)
  - Drinking water
  - Groundwater
  - Wastewater and surface water
  - Solid samples

DoD Perchlorate Handbook

APPENDICES

- Guidance on Selecting Analytical Services
  - Selection of appropriate analytical methods for the analysis of perchlorate
  - Preparation of solid samples for perchlorate analysis
  - Specification of analytical method performance criteria
  - Table of Recommended Methods for Perchlorate Analysis

DoD Perchlorate Handbook

- Developed by Multi-Component Committee
- Coordinated Across Components
- Posted:

  www.navylabs.navy.mil

  www.denix.osd.mil/denix/Public/Library/Compliance/EDQW/edqw.html

DoD Perchlorate SOPs

- To assist laboratories until EPA releases SW-846 Mass Spec methods the DoD EDQW is publishing two SOPs for:
  - HPLC/ESI/MS
  - IC/MS OR IC/MS/MS
- Use of these SOPs is not mandatory
- All procedures used must meet the quality control criteria specified in Appendix G of the DoD Perchlorate Handbook.

Benefits

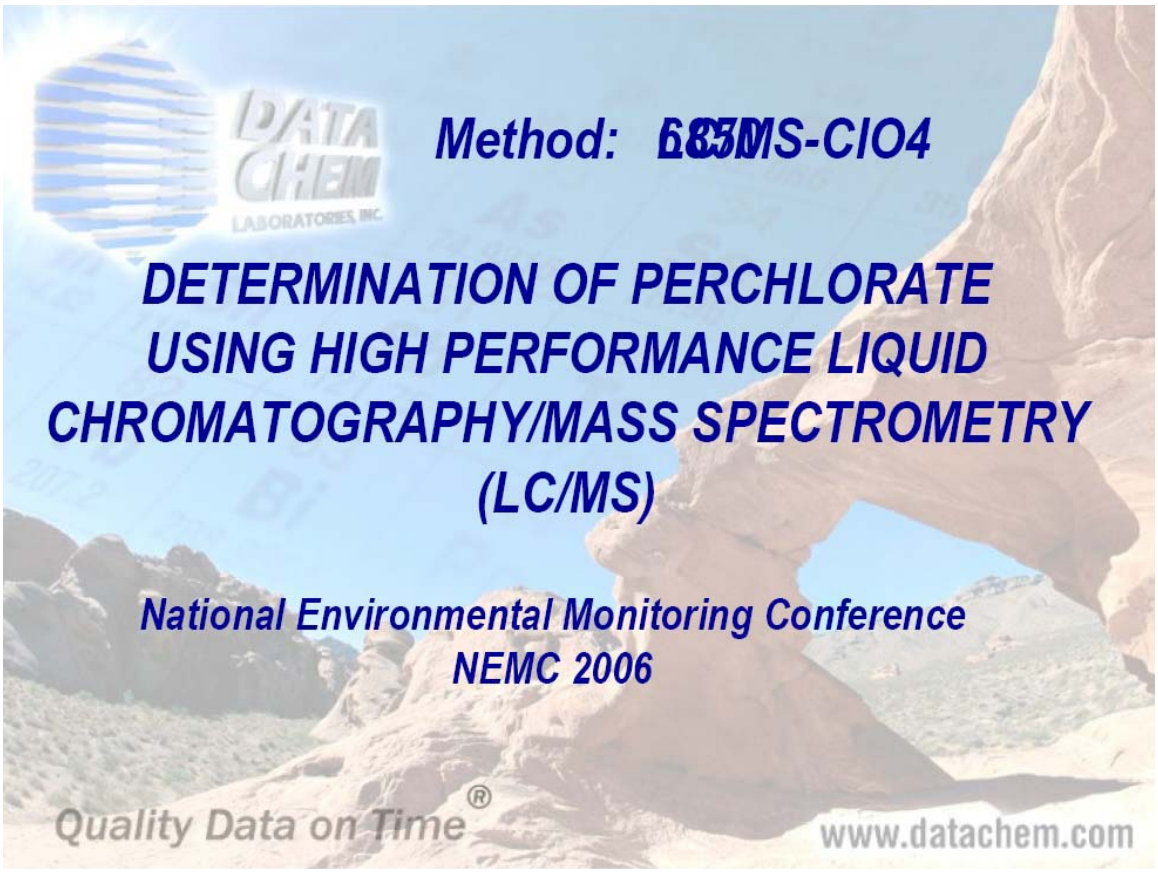
- Approach of Handbook applicable to other emerging contaminants
- Handbook Format Specifies:
  - Concerns associated with sampling and testing for that contaminant
  - Analytical method requirements
  - Application of the Systematic Planning Process
  - Implementation of UFP-QAPP

Ensures decisions are based on data of known and documented quality, appropriate for their intended use

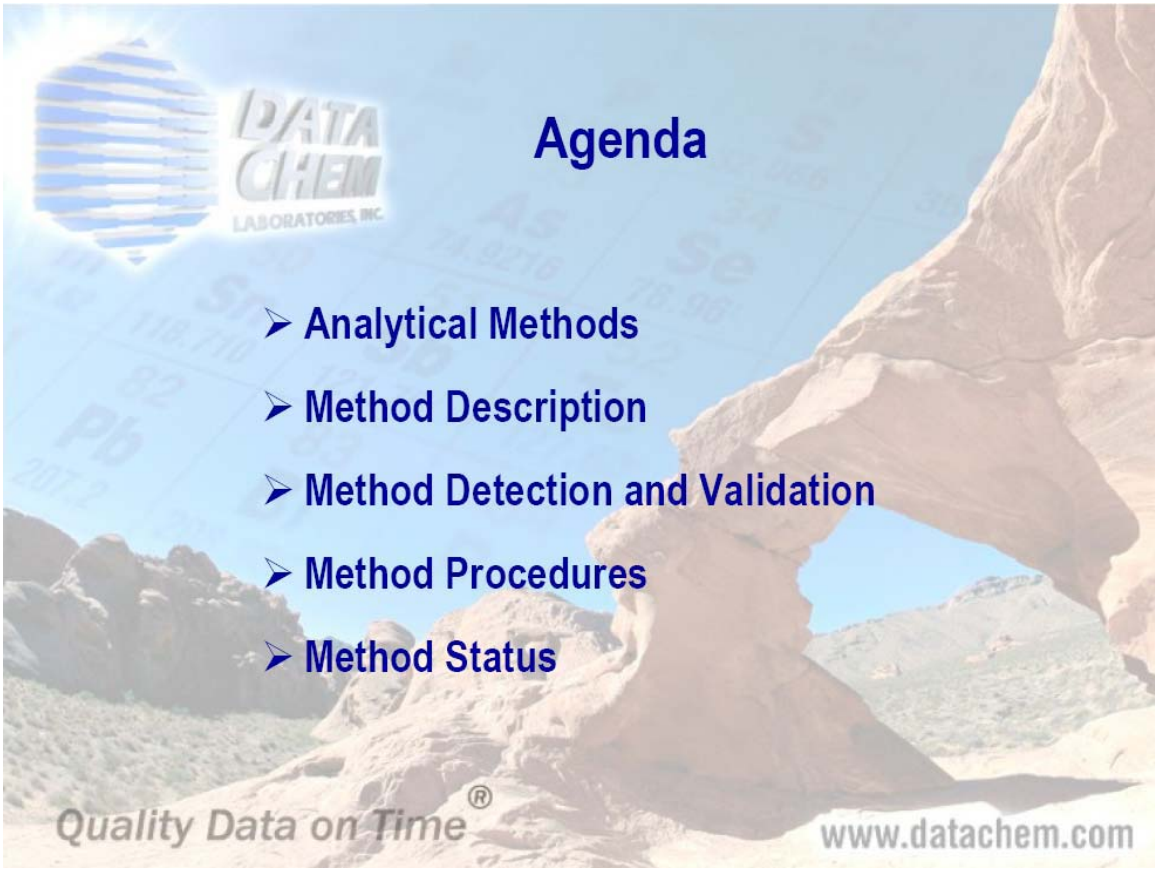
Improving Environmental Data Quality

... Because the Right Decisions Require Quality Data

www.navylabs.navy.mil
www.denix.osd.mil/denix/DOD/Working/EDQW/edqw.html


Method: 6850/6530/LC/MS-ClO4
DETERMINATION OF PERCHLORATE USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS)
National Environmental Monitoring Conference
NEMC 2006
Quality Data on Time®
www.datachem.com


Robert P. Di Rienzo
DataChem Laboratories, Inc.
Kham Lin
K'(Prime) Technologies, Inc.
USEPA OSW
Inorganics Method Development
Quality Data on Time®
www.datachem.com


DATA CHEM
LABORATORIES, INC.
Agenda
Analytical Methods
Method Description
Method Detection and Validation
Method Procedures
Method Status
Quality Data on Time®
www.datachem.com


DATA CHEM
LABORATORIES, INC.
References
DoD Quality Assurance Handbook DoD Quality Assurance Handbook for Perchlorate Investigations
http://www.navylabs.navy.mil./Perchlorate.htm
Treatment Technologies
https://www.denix.osd.mil/denix/denix.html
Quality Data on Time®
www.datachem.com

Analytical Methods

Technology	Published Methods Drinking Water Only	Proposed Methods Water, Soil and Waste
Ion Chromatography (IC)	314.0	314.1 9058
HPLC/MS and HPLC/MS/MS	331.0	6850
IC/MS and IC/MS/MS	332.0	6860

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Method Description

Analysis of Perchlorate utilizes liquid chromatography to separate Perchlorate from interferences and mass spectrometry to detect, confirm and quantify

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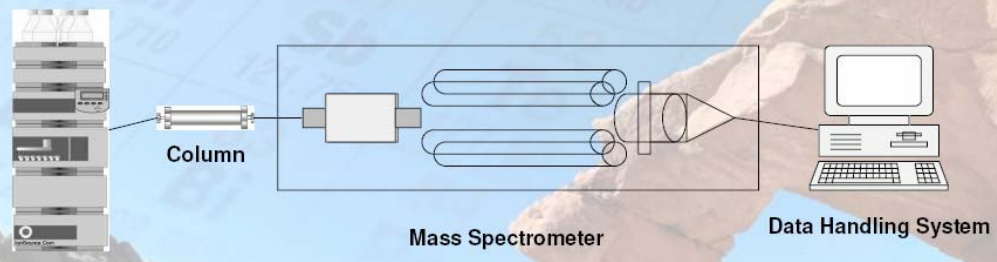
Method Description

- Agilent 1100 LC/MSD
- Mobile phase: Acetonitrile, Water, Acetic Acid
- Column: K'(Prime) Technologies, Inc, KP-RPPX series

Quality Data on Time®

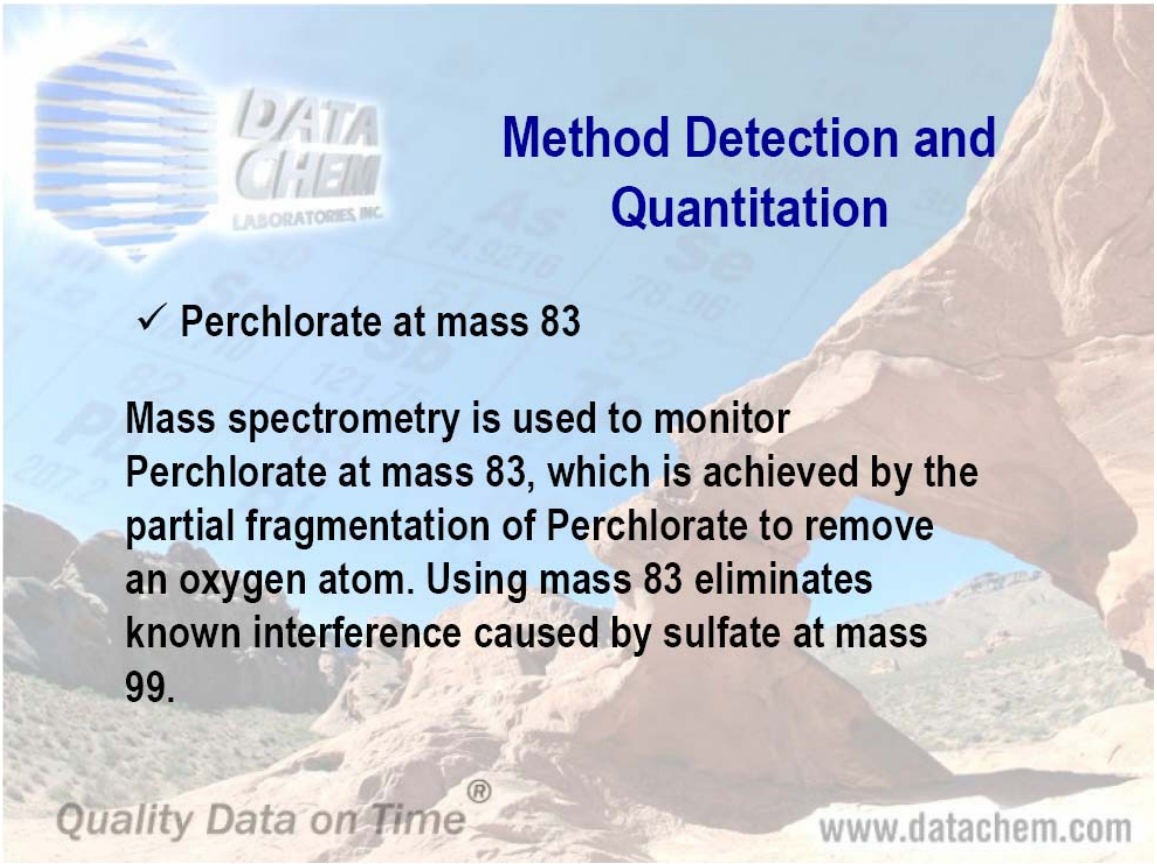
www.datachem.com

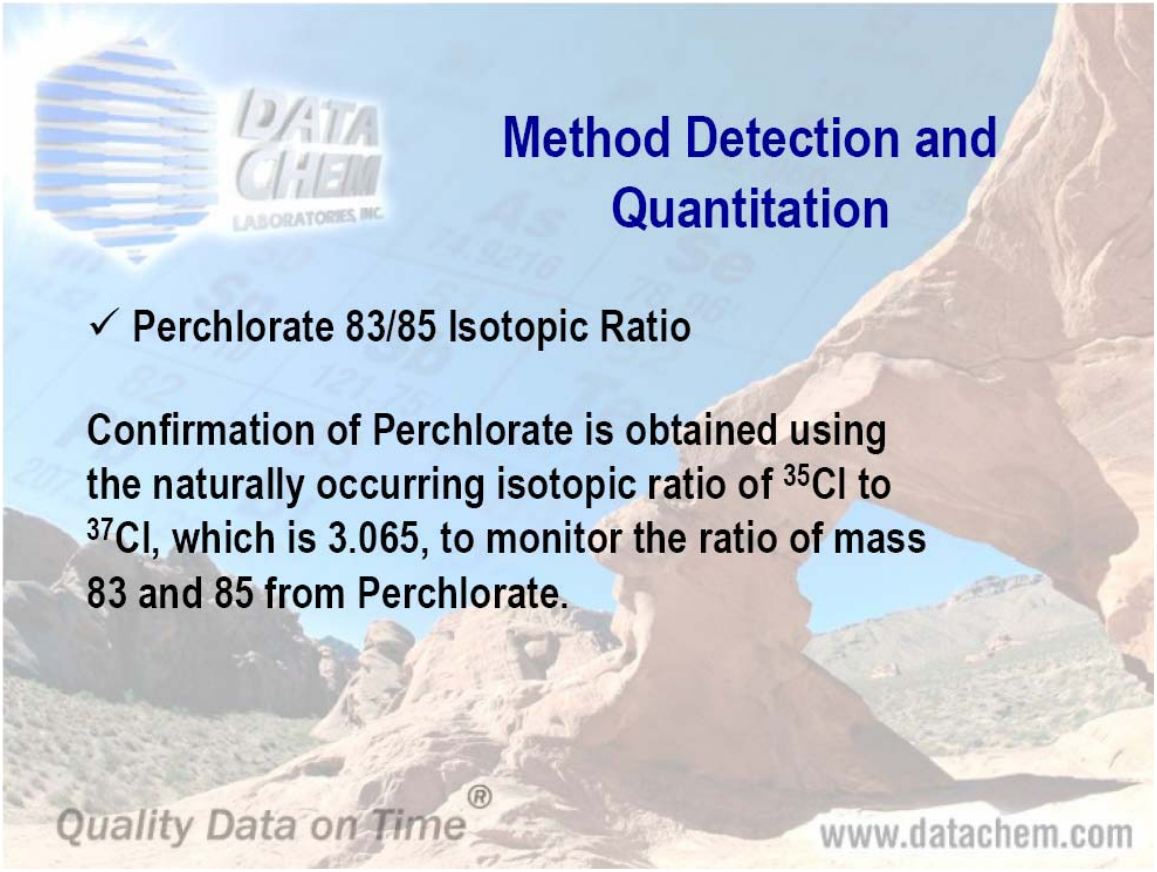
Method Description

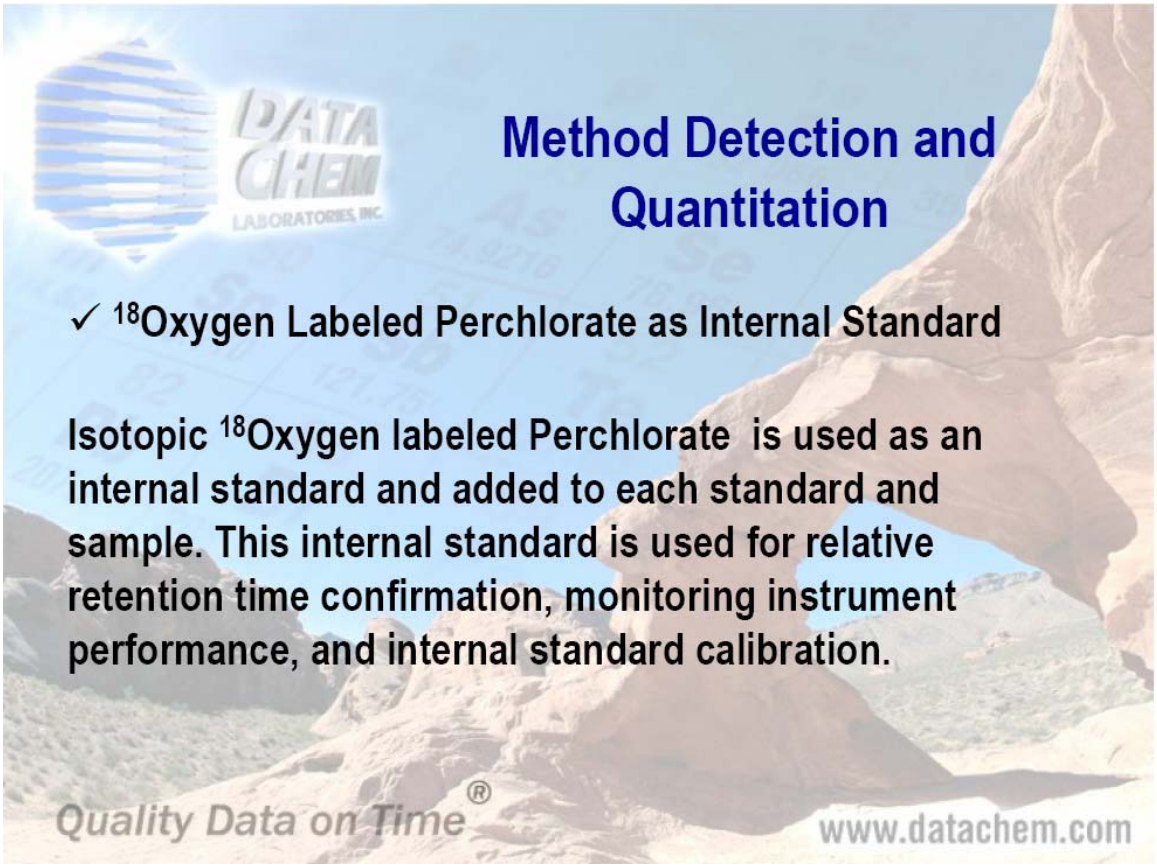


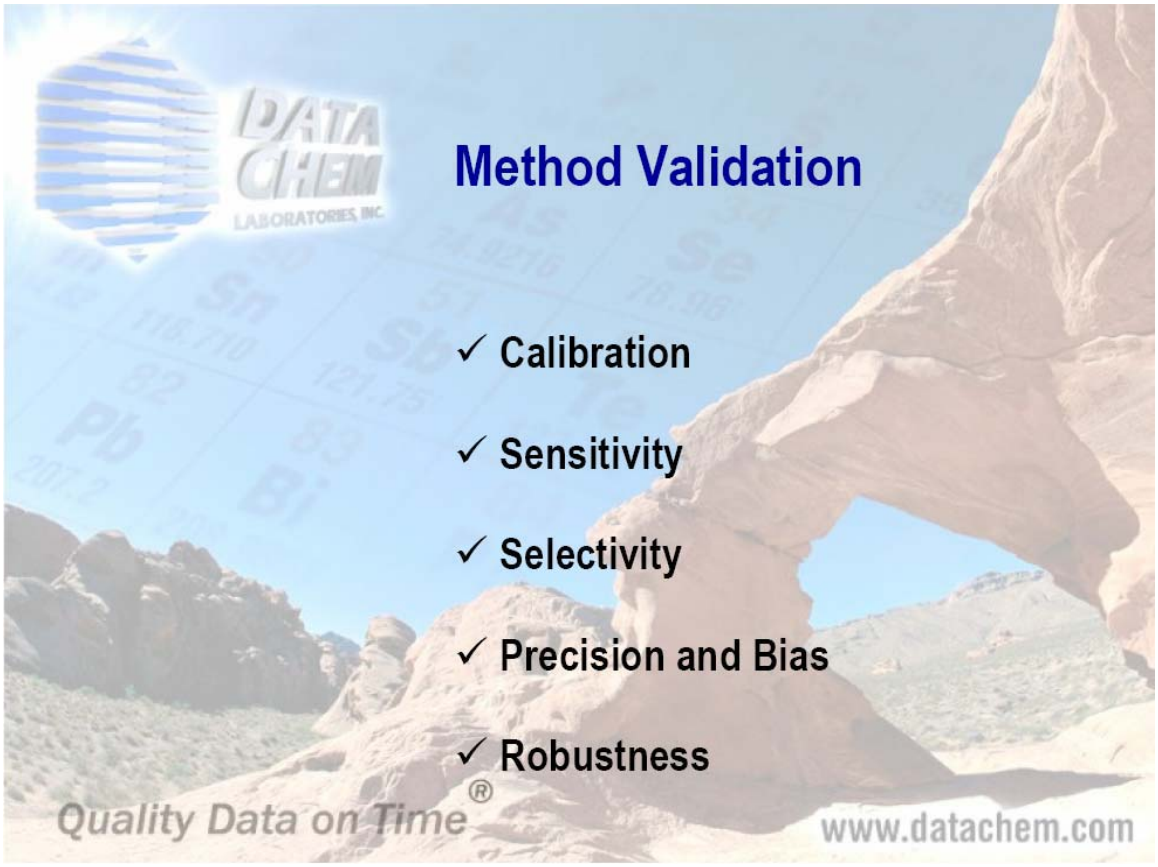
Quality Data on Time®

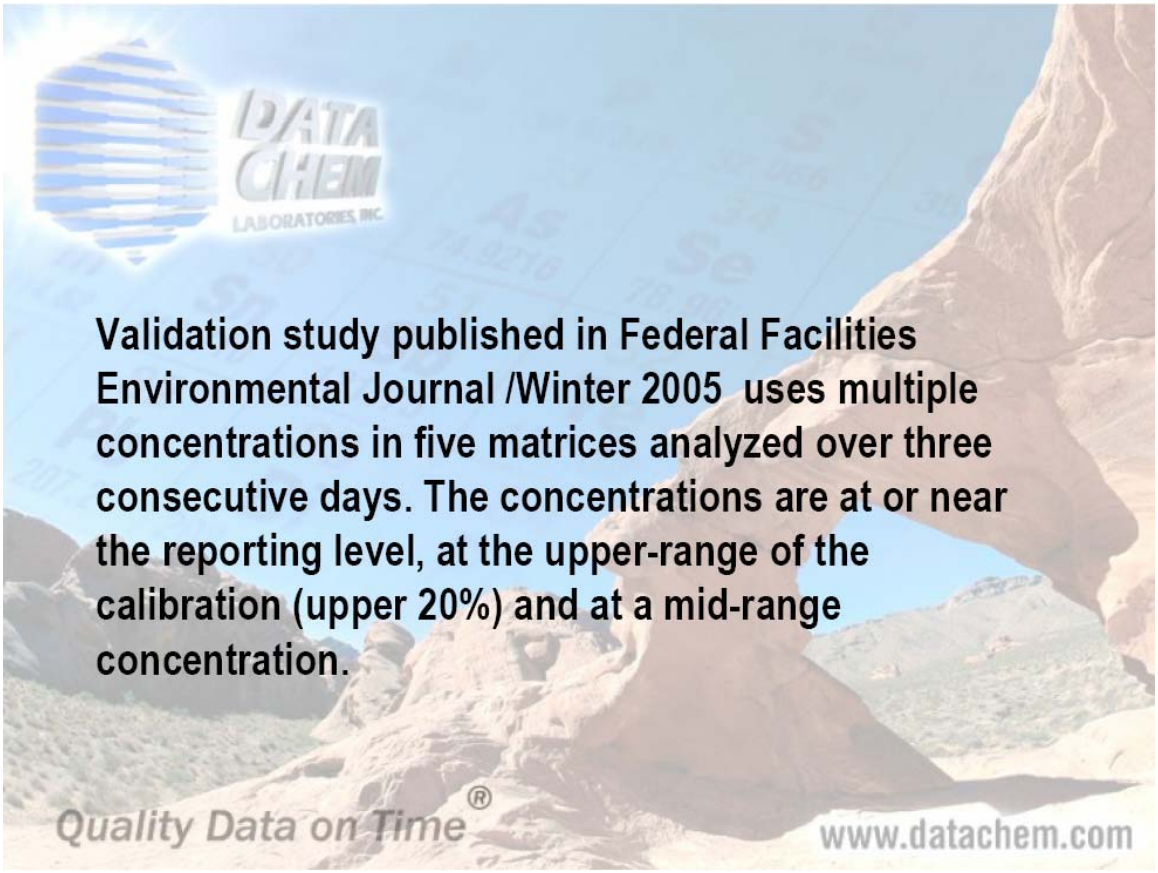
www.datachem.com

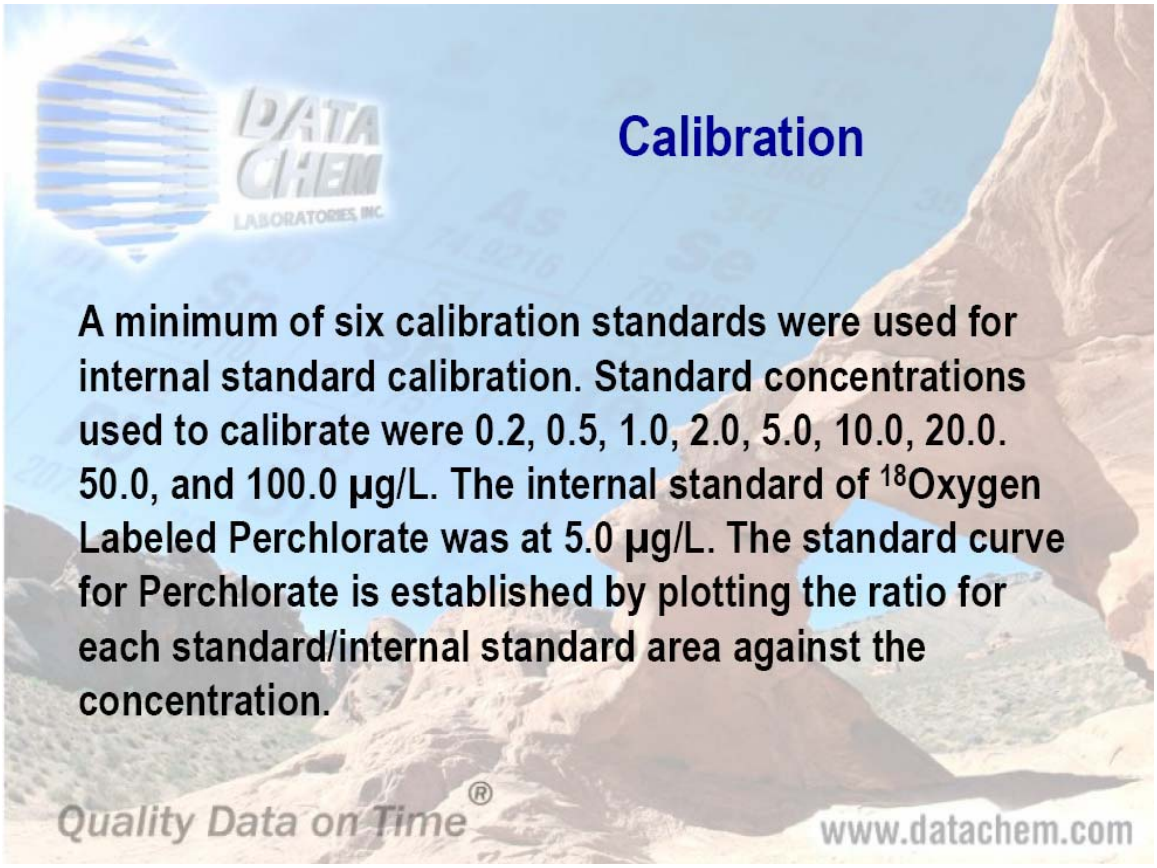

DATA CHEM LABORATORIES, INC.
Method Detection and Quantitation
✓ Perchlorate at mass 83
Mass spectrometry is used to monitor Perchlorate at mass 83, which is achieved by the partial fragmentation of Perchlorate to remove an oxygen atom. Using mass 83 eliminates known interference caused by sulfate at mass 99.
Quality Data on Time®
www.datachem.com


DATA CHEM LABORATORIES, INC.
Method Detection and Quantitation
✓ Perchlorate 83/85 Isotopic Ratio
Confirmation of Perchlorate is obtained using the naturally occurring isotopic ratio of ^{35}Cl to ^{37}Cl, which is 3.065, to monitor the ratio of mass 83 and 85 from Perchlorate.
Quality Data on Time®
www.datachem.com


DATA CHEM LABORATORIES, INC.
Method Detection and Quantitation
✓ 18Oxygen Labeled Perchlorate as Internal Standard
Isotopic 18Oxygen labeled Perchlorate is used as an internal standard and added to each standard and sample. This internal standard is used for relative retention time confirmation, monitoring instrument performance, and internal standard calibration.
Quality Data on Time®
www.datachem.com


DATA CHEM LABORATORIES, INC.
Method Validation
✓ Calibration
✓ Sensitivity
✓ Selectivity
✓ Precision and Bias
✓ Robustness
Quality Data on Time®
www.datachem.com


DATA CHEM
LABORATORIES, INC.
Validation study published in Federal Facilities Environmental Journal /Winter 2005 uses multiple concentrations in five matrices analyzed over three consecutive days. The concentrations are at or near the reporting level, at the upper-range of the calibration (upper 20%) and at a mid-range concentration.
Quality Data on Time®
www.datachem.com


DATA CHEM
LABORATORIES, INC.
Calibration
A minimum of six calibration standards were used for internal standard calibration. Standard concentrations used to calibrate were 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0. 50.0, and 100.0 µg/L. The internal standard of ^{18}Oxygen Labeled Perchlorate was at 5.0 µg/L. The standard curve for Perchlorate is established by plotting the ratio for each standard/internal standard area against the concentration.
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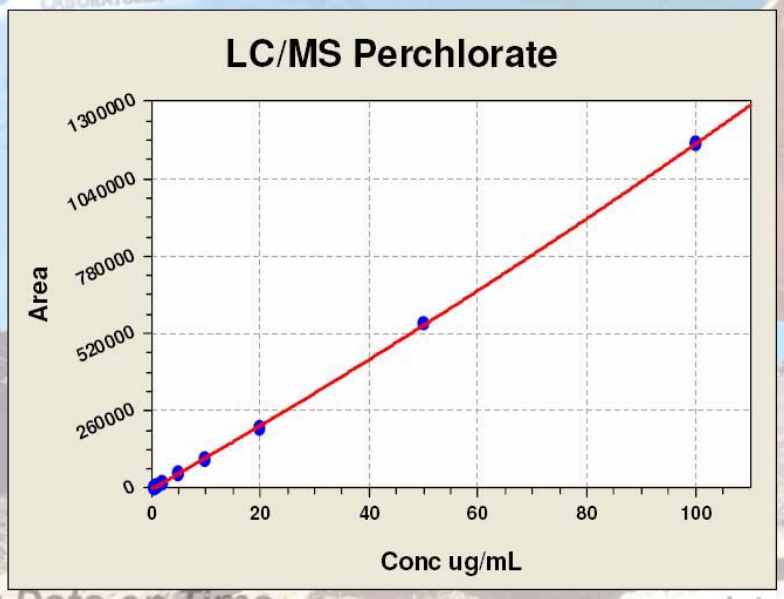
Calibration

Quadratic Fit: y=a+bx+cx^2
Correlation Coefficient: 0.9999599
Calibration Date: June, 2005



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www.datachem.com

Sensitivity and Quantitation

Matrix	MDL	RL
Water	0.0612 µg/L	0.2 µg/L
Soil	0.415 ug/Kg	2.0 ug/Kg

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www.datachem.com

Sensitivity and Quantitation

Matrix	MDL Verification Concentration	MDL Verification Result
Water	0.10 ug/L	0.14 ug/L
Soil	1.0 ug/Kg	1.1 ug/Kg

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www.datachem.com

Selectivity

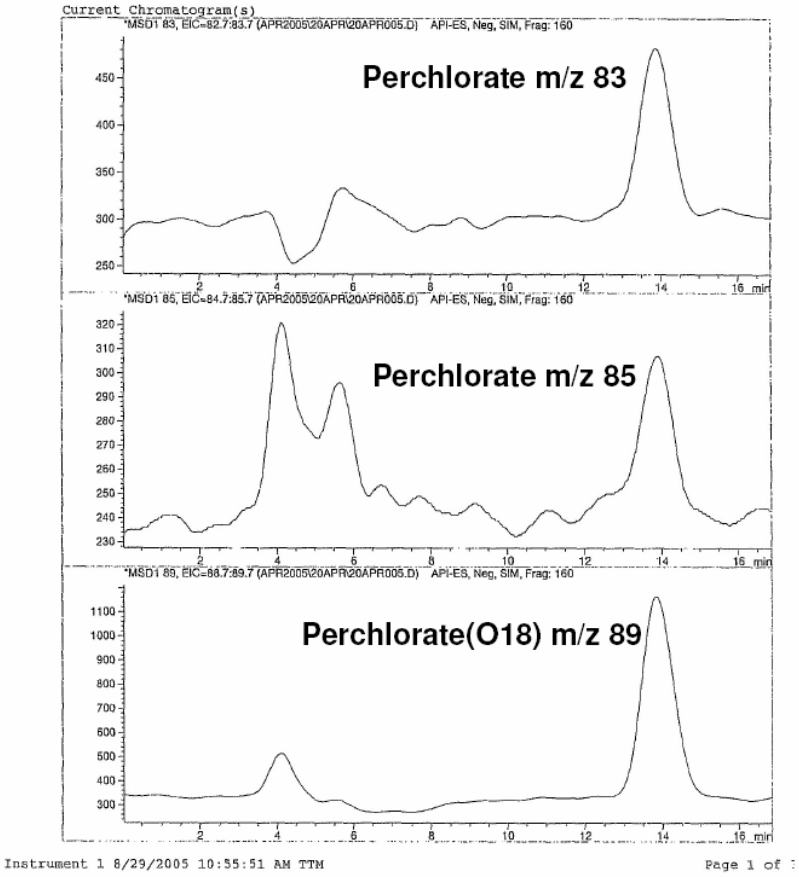
- ✓ Perchlorate 83/85 Isotopic Ratio
- ✓ ^{18}Oxygen Labeled Perchlorate Internal Standard

Quality Data on Time®

www.datachem.com

10 ug/Kg

Soil



Precision and Bias

PT Study	Result 314.0	Result LC/MS	True Value
WS04-1	47.3 µg/L	51.2 µg/L	52.7 µg/L
Potable WatR™ 052004A	NA	5.64 µg/L	5.48 µg/L
WS04-3	89.7 µg/L	83.8 µg/L	90.0 µg/L
WS05-1	114 µg/L	111 µg/L	118 µg/L
WS05-3B	49.7 µg/L	53.3 µg/L	51.5 µg/L
WS06-1	12.2 µg/L	13.2 µg/L	11.5 µg/L

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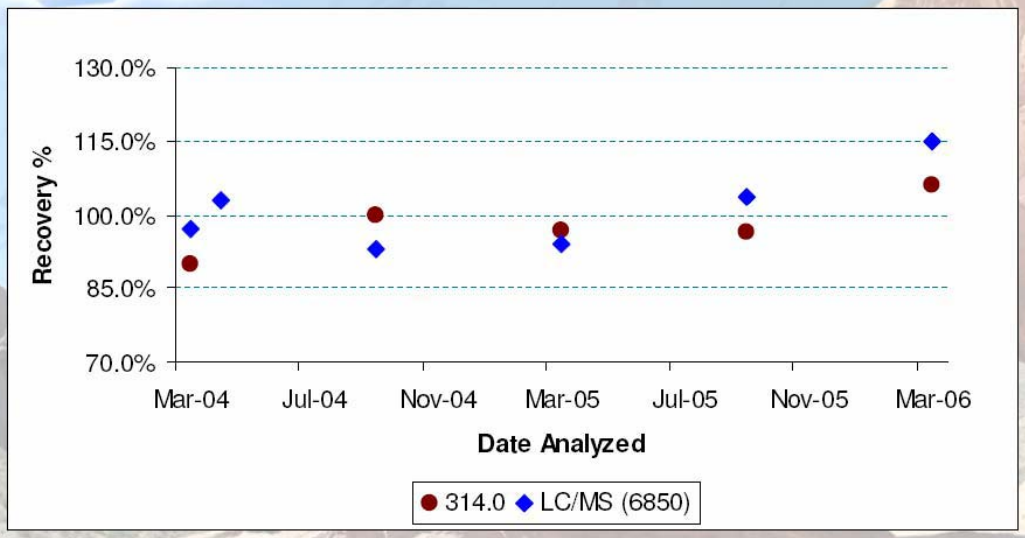
Precision and Bias

PT Results from 2004 to 2006



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Precision and Bias

PT Study	LC/MS Result	Assigned Value[1]
Freeze Dried Spinach Vegetation (ERA Sample 1895) Prep 1 K' Prime Technologies	713 µg/Kg	870 µg/Kg
Freeze Dried Spinach Vegetation (ERA Sample 1895) Prep 2 K' Prime Technologies	748 µg/Kg	870 µg/Kg
Freeze Dried Spinach Vegetation (ERA Sample 1895) Prep 1 Sierra Foothill Laboratory, Inc.	782 µg/Kg	870 µg/Kg
Freeze Dried Spinach Vegetation (ERA Sample 1895) Prep 2 Sierra Foothill Laboratory, Inc.	741 µg/Kg	870 µg/Kg

Assigned Value = Study Mean

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Robustness

Initial Calibration: June, 2005

Date	CCV Low	CCV Low Target	CCV Low Recovery	CCV Mid	CCV Mid Target	CCV Mid Recovery
7/17/05	0.26	0.2	130	9.1	10	91
7/26/05	0.29	0.2	145	9.4	10	94
8/11/05	0.28	0.2	140	9.1	10	91
8/20/05	0.15	0.2	75	10.6	10	106
8/22/05	0.22	0.2	110	10.5	10	105
8/23/05	0.20	0.2	100	10.6	10	106
9/8/05	0.28	0.2	140	10.7	10	107
9/21/05	0.21	0.2	105	9.8	10	98
10/12/05	0.19	0.2	95	10.0	10	100
10/22/05	0.20	0.2	100	9.6	10	96
12/05/05	0.20	0.2	100	10.1	10	101
12/19/05	0.27	0.2	135	9.0	10	90
1/2/06	0.17	0.2	85	9.3	10	93
1/9/06	0.19	0.2	95	10.1	10	101
1/11/06	0.21	0.2	105	9.1	10	91
2/6/06	0.12	0.2	60	10.0	10	100
2/13/06	0.18	0.2	90	10.5	10	105
3/13/05	0.44	0.5	88	9.0	10	90
3/27/06	0.51	0.5	102	9.4	10	94

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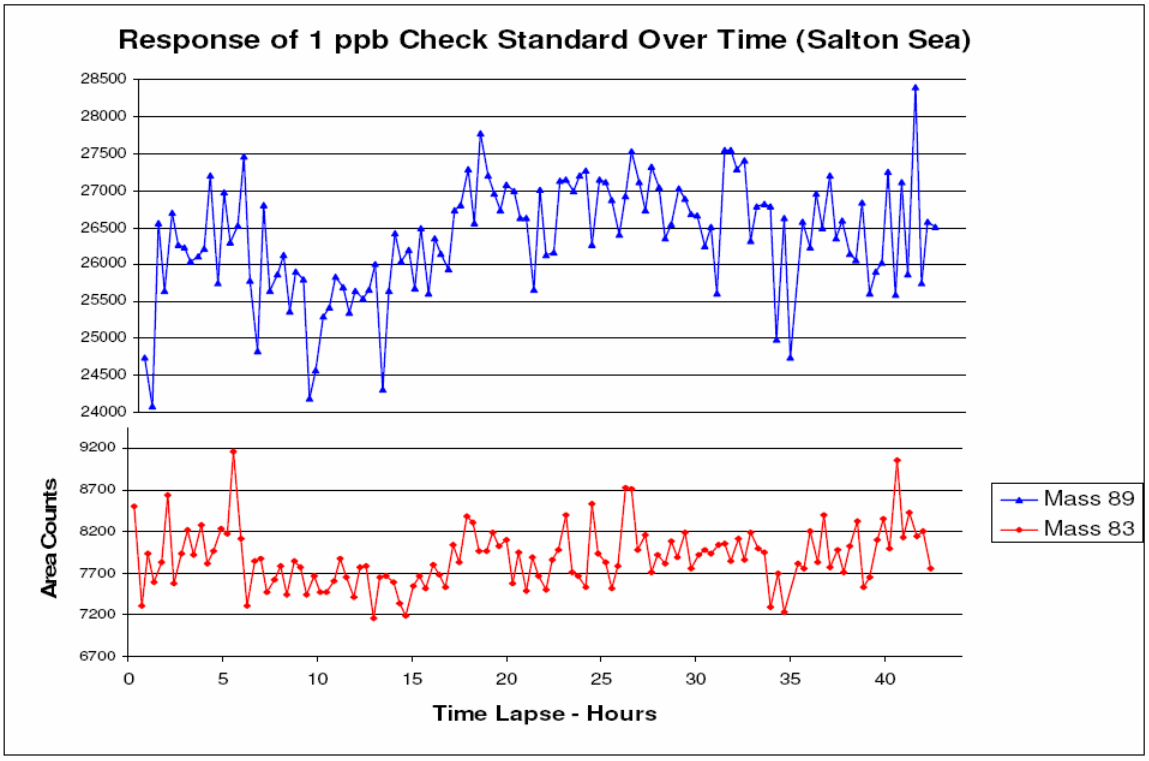
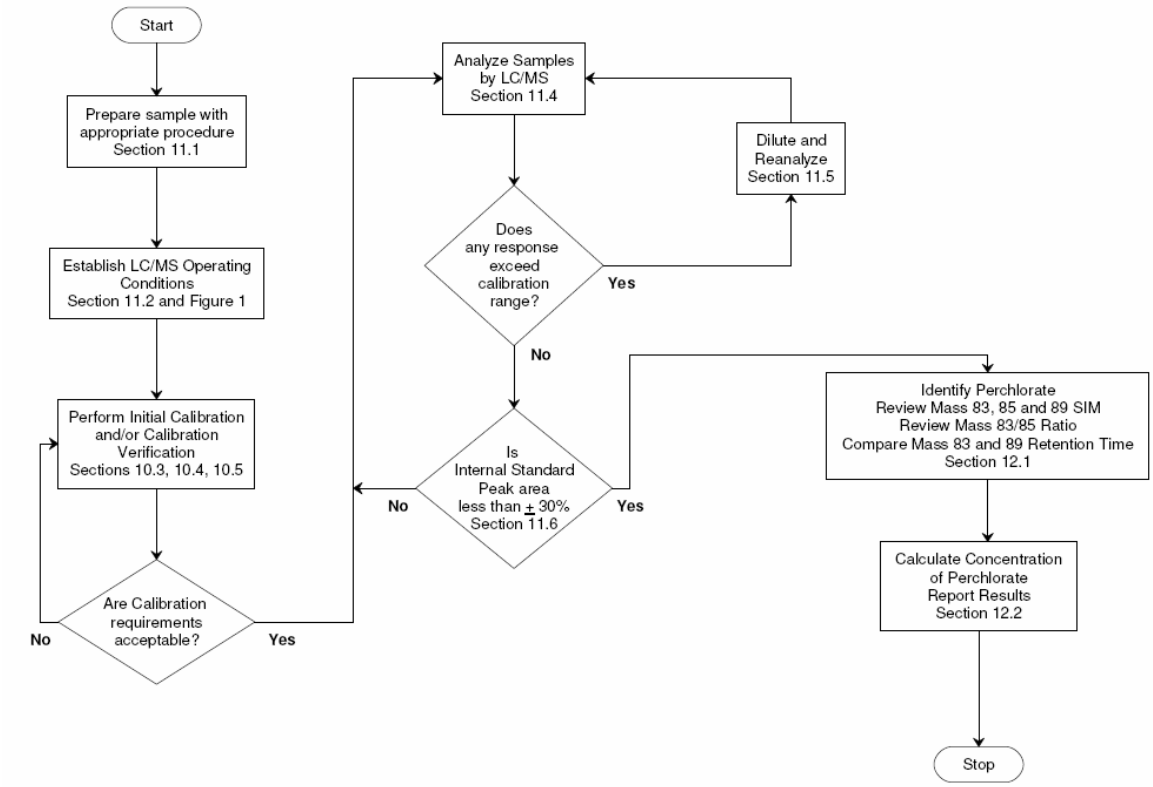
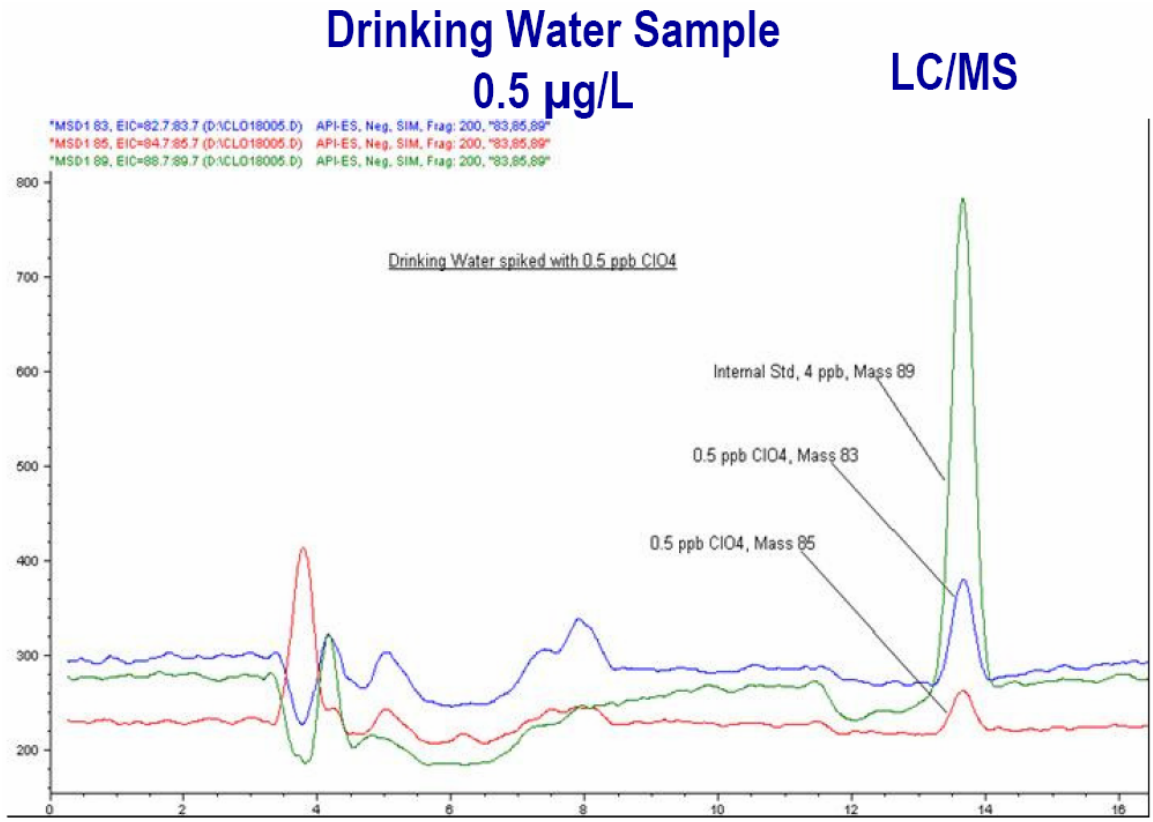
Robustness

Sierra Foothill Laboratory, Inc.



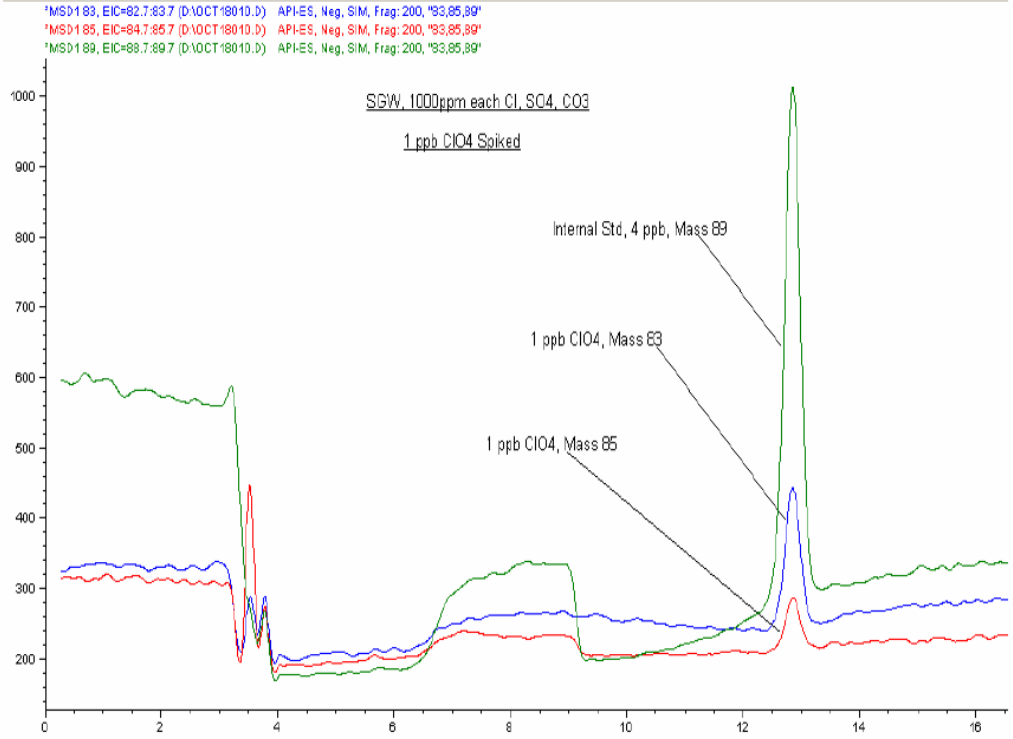


Method Procedures



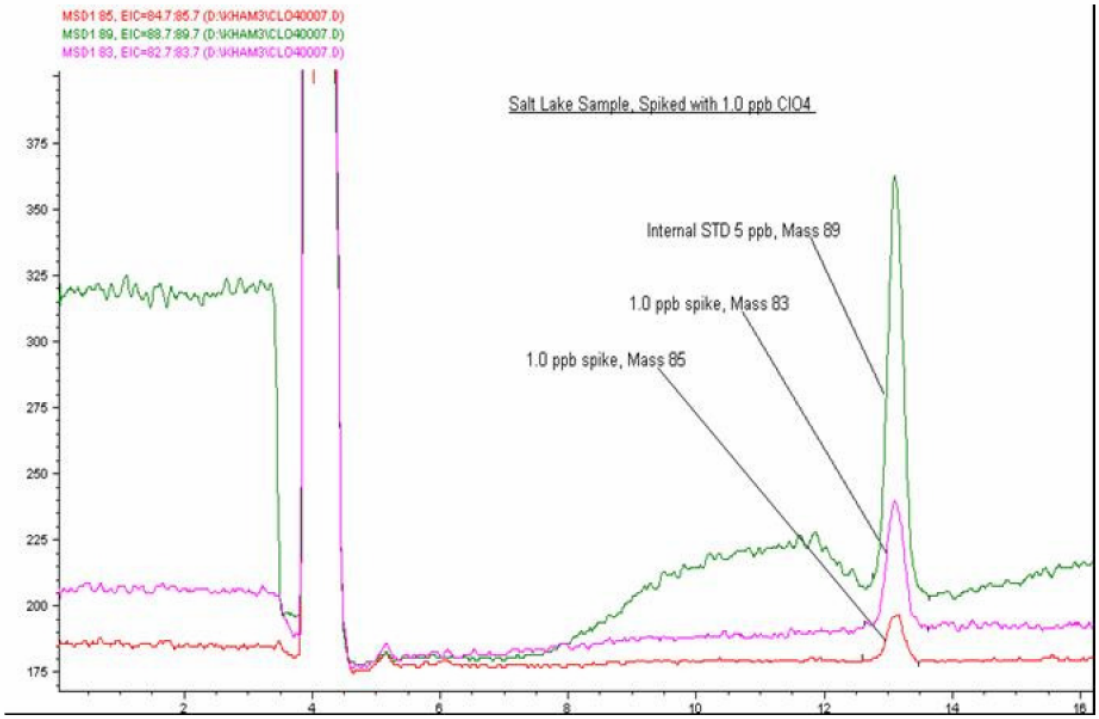
Simulated Ground Water Sample
1 µg/L

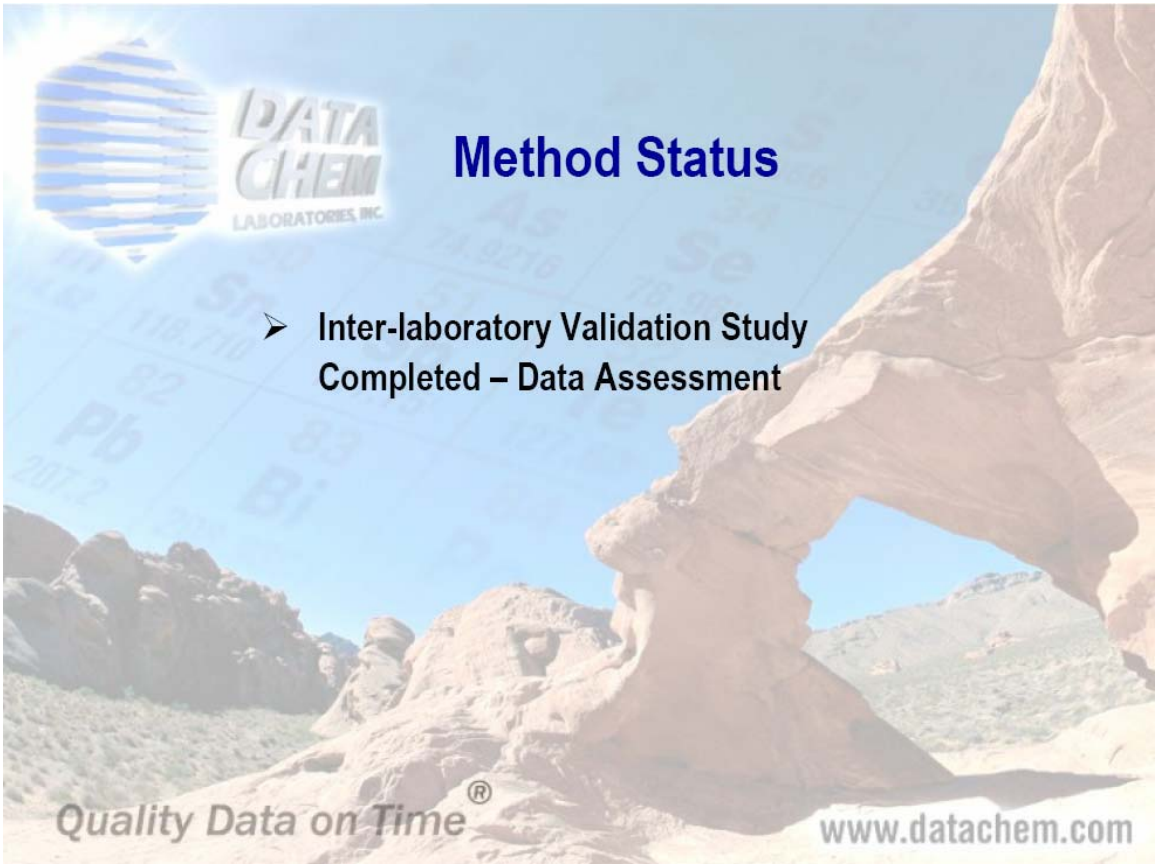
LC/MS

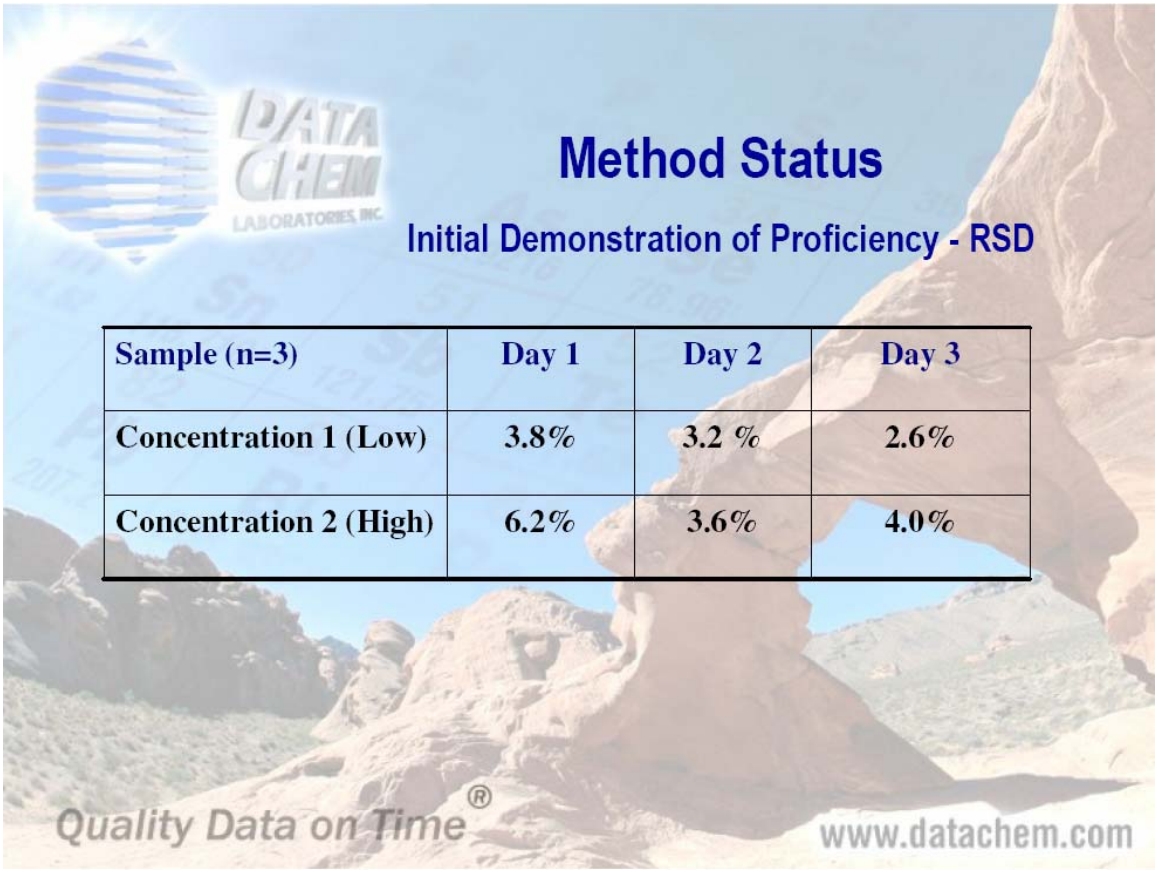


Great Salt Lake Water Sample
1 µg/L

LC/MS







Sample (n=3)	Day 1	Day 2	Day 3
Concentration 1 (Low)	3.8%	3.2 %	2.6%
Concentration 2 (High)	6.2%	3.6%	4.0%

Method Status

Phase II - RSD

Sample	Week 1	Week 2	Week 3
Salt Water A (n=3)	18.8%	18.4 %	14.6%
Salt Water B (n=3)	14.6%	15.3%	7.3%
Soil A (n=9)	11.2%	19.7%	11.1%
Soil B (n=9)	3.4%	6.7%	11.1%
Soil C (n=9)*	7.0%	22.2%	15.7%
Sludge C (n=9)	14.3%	29.1%	18.7%

* Soil C on Week 1 (n=12)

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Method Status

- Last Draft of #### – April 2006
- Published Method – End of 2006

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DATA CHEM
LABORATORIES, INC.
Thank You
Questions?
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THURSDAY A.M., AUGUST 31, 2006

CONCURRENT SESSIONS

Superfund Analytical Services

How to Win a CLP Contract

Presented By: Keith Stewart, CLP Contracting Officer

August 31, 2006

Annual Requirements

- INORGANIC
  - 70,000 Analysis Per Year
- ORGANIC
  - 50,000 Analysis Per Year

Award Criteria

- Pre-Award Performance Evaluation Sample (PA-PES)
  - Pass/Fail
  - Score >85%
- Contract Compliance Screening Audit
  - Pass/Fail
  - Score >85%
- Past Performance
  - Acceptable Performance Rating
- On-Site Audit
  - Pass/Fail
  - Quality Assurance Plan & Standard Operating Procedures
- Price
  - Unit Price Per Sample

Maintaining CLP Status

- Pass Base/Qualification Phase
  - 180 days
  - Minimum of 2 samples
- Deliverables
  - 7,14, 21 day Delivery Schedule
- Pass Quarterly Blind
  - Score > 80
- Receive an Acceptable Performance Rating
  - Annual Rating

Solicitation Notifications

- FEDBIZOPPS
  - www.fedbizopps.gov
- FORECAST DATABASE
  - http://yosemite1.epa.gov/oarm/oam/forecastdatabase.nsf

Upcoming CLP Solicitations & Amendments

- ORGANIC
  - September 2006
  - Solicitation Posted on EPA's Website
    - http://www.epa.gov/oamsrpod/lasc/0614186/index.htm
- INORGANIC
  - March 2007
  - Solicitation Posted on EPA's Website
    - http://www.epa.gov/oamsrpod/lasc

Contacts

- Keith Stewart – CLP Contracting Officer
  Email: stewart.keith@epa.gov
  Phone: 202-564-1286

- Keith Upah – CLP Contracting Officer
  Email: upah.keith@epa.gov
  Phone: 202-564-0870

Contacts Con't

- John Nebelsick – Inorganic Program Manager
  Email- nebelsick.john@epa.gov
  Phone - 402-697-2572

- Phil Cocuzza – Organic Program Manager
  Email – cocuzza.phil@epa.gov
  Phone – 732-632-4765

Questions

Modernization of the Superfund Contract Laboratory Program (CLP)

2006 National Environmental Monitoring Conference (NEMC)
Presented by John Nebelsick, Inorganic Program Manager

Phil Cocuzza, Organic Program Manager

August 31, 2006

What Is the CLP?

- The CLP is a national network of EPA personnel, commercial laboratories, and support contractors.
- The CLP is the preferred mechanism for the Superfund program for providing routine analytical services.

What Is the CLP? (Cont.)

- Over the last 25 years, the CLP has provided:
  - Data of known and documented quality for more than 1,865,000 samples for EPA data users;
  - Support for more than 18,000 projects; and
  - An expense of $483,000,000.
- The CLP has grown from about 69,000 analyses in the past to more than 126,000 analyses in a year.

Issues with the "Old" CLP

- Historically for "routine analytical services", as specified in prescriptive Statements of Work (SOWs).
- No flexibility within the methods.
- Superfund sites are no longer routine.
- The CLP was not meeting the needs of Superfund Regional site managers.

Features of the New CLP

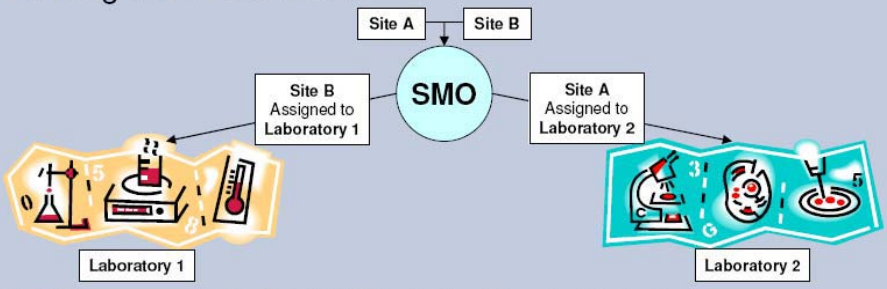
- The CLP provides quick and easy access to a national network of laboratories, available to accept samples 365 days of the year.
- Access begins in the field via the CLP's Field Operations and Records Management System (FORMS II Lite).

Features of the New CLP (Cont.)

- FORMS II Lite allows site samplers to conveniently log completed field sample information, including Geographic Information System (GIS) information.
- Samplers can then generate both hardcopy and electronic Chain-of-Custody Forms, and printed sample labels.

Features of the New CLP (Cont.)

- Field personnel coordinate sample shipment to CLP laboratories through Superfund's Sample Management Office (SMO).
- SMO assigns a CLP laboratory(ies) to each site project based upon scope of project, capacity, and laboratory ranking within the CLP.



Features of the New CLP (Cont.)

- For matching a CLP laboratory with the client's project "scope", the CLP's flexible menu of analytical services provides data users a variety of analyses, data turnarounds, and customized electronic deliverables.
- The CLP's Modified Analysis (MA) option enables users to customize analyte lists, reporting levels, and analytical procedures.

Features of the New CLP (Cont.)

- SMO develops laboratory rankings through a process that begins with the monitoring of all laboratory-generated data for timeliness, completeness, adherence to the SOW, and accuracy.
- Up to 4,000 (Organic) and 2,000 (Inorganic) checks are made for each group of laboratory data.

Features of the New CLP (Cont.)

- Laboratory "performance" results are then weight-factored for laboratory price to determine a final laboratory ranking.
- Laboratory rankings are updated on a monthly basis.

Features of the New CLP (Cont.)

- Results of the performance monitoring of each set of data is also delivered to the data user within 24-48 hours of delivery of data by the CLP laboratory.
- These results are used for Regional data validation of laboratory data.
- Upon request by the data user, SMO also offers specialized computer-aided data review, formatted to user needs.

Features of the New CLP (Cont.)

- SMO provides further service to Superfund clients by coordinating invoice and payment processes between a CLP laboratory and the EPA Regions.
  - A CLP laboratory submits an invoice to SMO through Superfund's Web-Based Invoicing System (WIS).
  - This invoice is then adjusted by SMO for any financial penalties (for late data, etc.), and then electronically sent to the Regional client for approval.

Features of the New CLP (Cont.)

- To complete the full turn-key service provided by the CLP, the Quality Assurance Technical Services (QATS) contractor provides a number of functions:
  - Provides services for annual on-site audits of CLP laboratories;
  - Provides quarterly blind Performance Evaluation (PE) samples to all CLP laboratories;

Features of the New CLP (Cont.)

- Provides specialized Regional requested PE samples;
- Provides a complete audit of raw analytical data supplied by CLP laboratories;
- Provides statistical analysis of CLP laboratory results; and
- Provides limited method development.

CLP Buy-In

- Utilization of the CLP and its support contractors can be procured through a Buy-In program.
- The Buy-In program allows non-Superfund analytical work to be processed through the CLP.
- Analytical work is not restricted to the CLP SOW. SW-846 and modified CLP methods are available through the use of the MA Request.

Today's CLP Goal

- CLP staff, Regional technical experts, and support contractors work continuously to provide state-of-the-art and timely analytical services to Regional clients.

Total Inorganic Analyses FY06 (10 Months)

	FY06 (10 Months)	Per Month
Routine Analyses	33,183	3,318
Modified Analyses (MAs)	25,980	2,598

- 44% of total analyses are MAs.
- However, if we remove two large projects, then 10% of total analyses are MAs.

Inorganic Laboratory Status

- Re-Solicited ILM05.3 Contract
  - Combines Both Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
- Capacity Increased to 5,600 Analyses per Month for All Methods
- Seven Laboratories Are Currently in the Program
- MAs Available Following A Qualification Phase

Inorganic Future Steps (Cont.)

- Solicit ILM06.X
- Staged Electronic Data Deliverable (SEDD)
- Target a Total Inorganic Capacity of 9,600 Samples per Month for All Methods
- Provide Sufficient Overlap of Contracts

Inorganic Future Steps (Cont.)

- Include Method Updates:
  - New Approach to Limits of Detection and Limits of Quantitation;
  - Revised Contract Required Quantitation Limits (CRQLs);
  - ICP-MS Soils Analysis;
  - Cyanide Micro-Distillation Preparation;
  - Multi-Point Calibration;
  - Linear Range at Top of Calibration Curve; and
  - Continuing Calibration Verification/ Continuing Calibration Blank (CCV/CCB) Frequency Now Every Two Hours.

Inorganic Future Steps (Cont.)

- Address Additional Issues from Regions/CLP Laboratories
- New Name
  - e.g., SIM01.X, SIAM01.X, SMA01.X
- Anticipated Award in Spring 2007
- Web Site at http://www.epa.gov/superfund/programs/clp/ilm6.htm

Total Organic Analyses FY06 (10 Months)

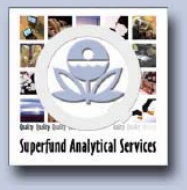
	FY06 (10 Months)	Per Month
Routine Analyses	29,901	2,990
Modified Analyses (MAs)	6,435	644

- 18% of total analyses are MAs.

Features of the New Organic (SOM01.1) Method

- New contract combines OLC & OLM methods (soil/water).
- SOW details methods of analyses contemporary to SW-846.
- Incorporates an expanded surrogate list [referenced in the CLP as Deuterated Monitoring Compounds (DMCs)] for Volatiles (VOAs) and Semivolatiles (SVOAs).
- Divides the historical combined Pesticide/Aroclor analytical protocol into separate analyses.

Features of the New Organic (SOM01.1) Method (Cont.)



- Requires an ending CCV for VOAs and SVOAs analysis.
- Provides options for Low/Medium or Trace-level Volatiles (TVOAs) analysis.
- Provides an option to perform Selected Ion Monitoring (SIM) for TVOA and SVOA compounds.

Features of the New Organic (SOM01.1) Method (Cont.)

- New requirement to submit electronic data through the SEDD protocol.
- The Data Assessment Tool (DAT) is a software-driven process designed to produce enhanced CLP deliverables and more usable reports in standard format.
- The DAT is flexible and may be adapted to meet unique requirements.

Organic Future Steps

- Re-Solicit SOM01.1. Target a total Organic capacity of 4,000 analyses per month.
- A la carte SOWs [e.g., optional Tentatively Identified Compounds (TICs)]. Use a staged SOW with a supporting SEDD & National Functional Guidelines (NFG) to offer flexible options.
- Stand-alone SIM method for the VOA target compound list.

Future CLP

- The Analytical Services Branch (ASB) runs a CLP sister program for Non-Routine Analysis.
- Air analysis by TO-14, TO-15.
- Dioxin by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS).
- Polychlorinated Biphenyl (PCB) Congeners (all 209) via an analytical protocol developed from the Office of Water Method 1668A.
- The goal is to incorporate these Non-Routine Analyses into CLP use.

August 31, 2006 Phil Cocuzza/Modernization of Superfund Contract Laboratory Program 27

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August 31, 2006 John Nebelsick & Phil Cocuzza/Modernization of Superfund Contract Laboratory Program 28

Automated Review of Staged Electronic Data Deliverable (SEDD) Stage 3 Deliverables

NEMC 2006
Anand Mudambi,
SEDD Program Manager
US Environmental Protection Agency
August 31, 2006

Contract Laboratory Program (CLP)

- Established in 1980
- Has Processed More than One Million Samples for the US EPA Superfund Program
- Analyses for Metals, Volatile Organics, Semivolatiles, Pesticides, and Polychlorinated Biphenyl (PCB) Aroclors
- Electronic Deliverables Required since Late 1980s

Issues with Current CLP Electronic Reporting Format

- CLP has used the Agency Standard Format (ASF) since the early 1990s.
- Inflexibility of ASF has made it difficult to add new analytical methods or Quality Control (QC) requirements.
- Line length limits have imposed strict requirements on field length.
- Nearly impossible to accommodate "non-CLP" data.

CLP Interest in SEDD

- ASF Format Not Readily "Human Readable", Therefore Not Suited for Long-Term Storage
- Began Looking for More Flexible Data Formats
- Interest in Formats that "Tagged" Data Rather than Relying on Sequence and Position
- eXtensible Markup Language (XML) and SEDD Meets These Needs

Joint Development of SEDD Requirements

- US EPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB)
- US Army Corps of Engineers (USACE) HTRW Center of Expertise (CX)
- Input from Other US Government Agencies and the Private Sector

Electronic Format Requirements

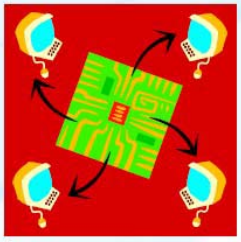
- Must Clearly Define and Identify Each Data Element
- Must Define Relationships within Data
- Must Allow for Change
- Must Not Be Proprietary
- Content Should Be "Human-Readable"

CLP Requirements

- The CLP's need to check calculations from peak areas up to final result.
- The CLP's need to link all analyses to calibration, verification, and preparation and cleanup procedures.
- The CLP's need to clearly and uniquely identify all field and QC samples.

The Result – SEDD Stage 3

- SEDD Stage 3 meets the CLP requirements for Format and Content.
- Stage 3 builds on SEDD Stage 2 currently required in US EPA Emergency Response and USACE Contracts.



CLP SOM01.1

- Statement Of Work (SOW) SOM01.1 Awarded in 2005
- Volatiles, Trace Volatiles, Semivolatiles, Pesticides, Aroclors, and SIM
- Laboratories Now Delivering Compliant Data in SEDD Stage 3 Format

How Laboratories Produced Stage 3 Files

- Laboratories able to generate compliant deliverables in at least three different ways:
  - use own software and data systems;
  - use external vendor software; or
  - use the SEDD Generator Tool developed for US EPA/ASB.

What Is the CLP Doing with the Stage 3 Data?

- CLP Has Developed an Automated Assessment System to review SEDD Stage 3 Data
- Data Is Assessed for Compliance (Complete, Valid, Accurate, Performed as Specified)
- Data Is Qualified Based on National Functional Guidelines (NFG) Document for SOM01.1 (Posted on EPA Website)
- The System is Web-Accessible
- Allows CLP Laboratories to Perform Self-Inspection Prior to Delivery of Data to Government

Electronic Checks Done By the CLP System

- The CLP EDD is processed through an automated data assessment system that performs two main types of evaluation:
  - Initial Assessment (IA); and
  - Full Assessment (FA).

Initial Assessment

- A subset of SOW requirements that must be complete and correct before the data can be accepted. These requirements include:
  - Data completeness to ensure all data requested by user is delivered;
  - Completeness of EDD to ensure all required data elements and nodes are present; and
  - Conformance of EDD to the DTD, to ensure the EDD structure is correct and usable for Full Assessment purposes.
- The laboratory is notified if the EDD fails IA, and asked to submit a corrected EDD via the Web.

Full Assessment

- Preformed After a Laboratory Passes IA
- Two Types of Checks:
  - Completeness – checks for presence and adherence to all SOW reporting requirements; and
  - Compliance – checks to ensure all SOW QC limits are met.
- More than 3,200 Automated QA/QC Checks Performed on Each Deliverable

FA Completeness Checks

- Stage 3 SEDD allows for reporting down to the Peak Level, which includes all data from instrument outputs.
- All required data elements checked for presence and content.
- System-generated defect reports which point out if a required data element is missing or if the value present in it is incorrect.

FA Compliance Checks

- Forms the largest portion of the checks.
- All results and values reported by the laboratory in the EDD are recalculated from the instrument data (e.g., integrated peak areas from a pesticide run).
- Accuracy of all reported results verified by recalculation of values starting with the initial calibration curve.

FA Checks on Samples

- Contract Holding Time for Extraction and Analysis
- Technical Holding Time for Extraction and Analysis
- Verification of results reported for Field and QC Sample Data

Examples of FA Recalculations for Pesticides

- Initial Calibration Curve
  - Calibration Factor for Each Standard
  - Mean Calibration Factor for Each 5 Point Calibration
  - % RSD for Each 5 Point Calibration
- Continuing Calibration
  - Relative Percent Difference
- Performance Evaluation Mixture (PEM)
  - Percent Difference
  - Percent Breakdown
- DDT and Endrin Percent Breakdown

Examples of FA Recalculations for Pesticides (cont'd.)

- Surrogate Results
- Surrogate Recoveries
- Retention Time Windows for All Analytes and Surrogates
- Quantitation Limits
- Reported Results for All Analytes

National Functional Guidelines (NFG) Document Checks

- All NFG Calculation checks are performed in FA.
- Results from these NFG checks are used to flag data.
- Generates an overall assessment summary report.

Future System Enhancements

- CLP Developing Modifications to System to Assess Stage 3 Data from Other Programs:
  - Adding Tests;
  - Deleting Tests; and
  - Adding Reference Tables.

CLP Requirements under Development

- Electronic Reporting for Upcoming Inorganic Statement Of Work (ICP-AES, ICP-MS, CVAA, CN)

SEDD CLP Requirements Under Development (Potential)

- Asbestos by TEM
- Isotope Dilution HRGC/HRMS for Dioxins/Furans and PCB Congeners

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  www.epa.gov/superfund/programs/clp/sedd.htm

PERFORMING AUTOMATED DATA REVIEW AND DATA QUALITY ASSESSMENT ON SEDD FILES

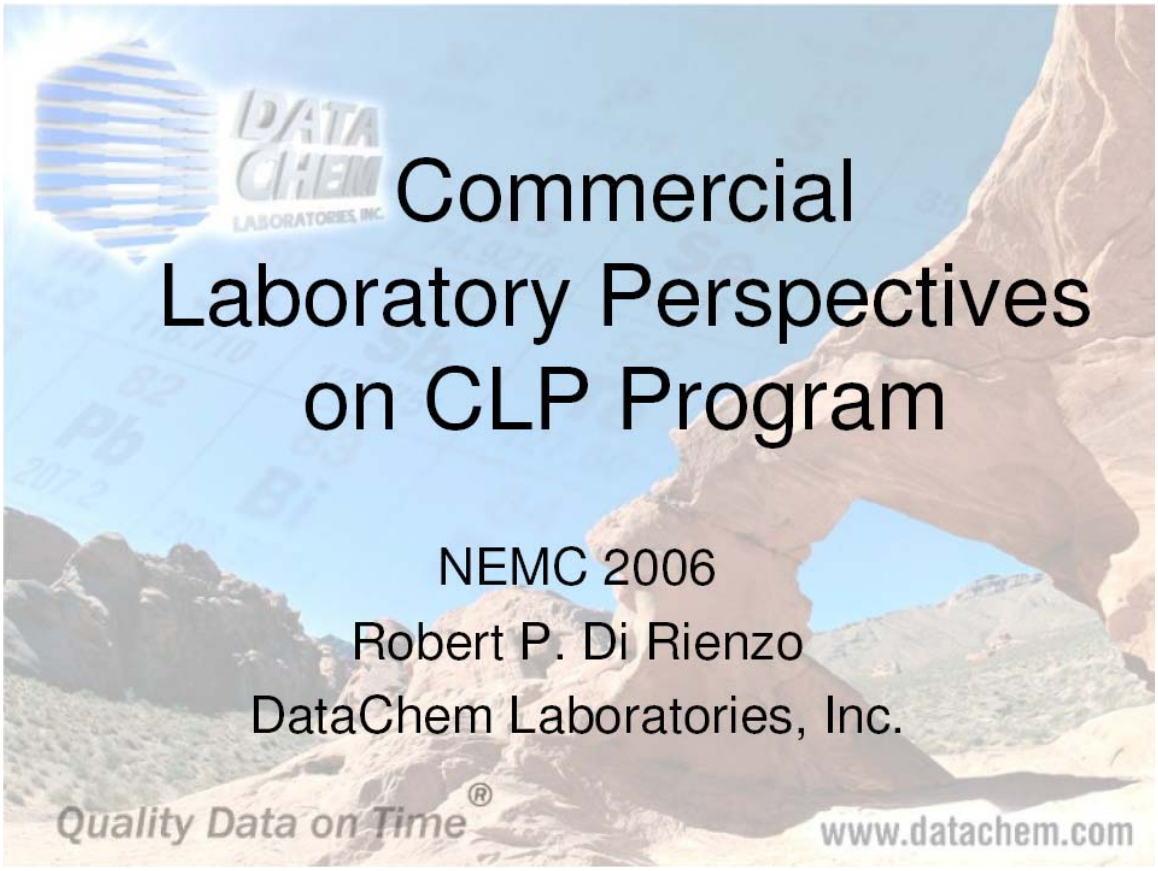
Denzer, Scott M.; Laboratory Consultants, Inc.

This presentation discusses software applications for viewing and utilizing data transmitted in the Staged Electronic Data Deliverable (SEDD) format. Discussion will focus on parsing data from SEDD files, performing automated data review and mechanisms to move and store data to meet project specific electronic data management goals.

One of the software tools, the Automated Data Review (ADR) software, was developed under contract with the Army Corps of Engineers in order to capture and review data in a timely and cost efficient manner. The ADR software allows laboratories to verify compliance with project-specific data format and content rules and allows data users to evaluate and qualify data based on project specific criteria.

Project-specific data requirements are developed as a library within ADR and electronically transferred to the laboratory. Requirements include specific data quality objectives (i.e., required reporting limits) for each analyte within the various analytical methods for a project. This library is used by the laboratory to ensure the contents of a SEDD file meet project electronic deliverable requirements and is also used by the data user to perform an automated review and qualification of data.

Data movement and storage will also be discussed, including recent developments allowing transfer of reviewed data and ADR project library information in XML format for portability and long term storage.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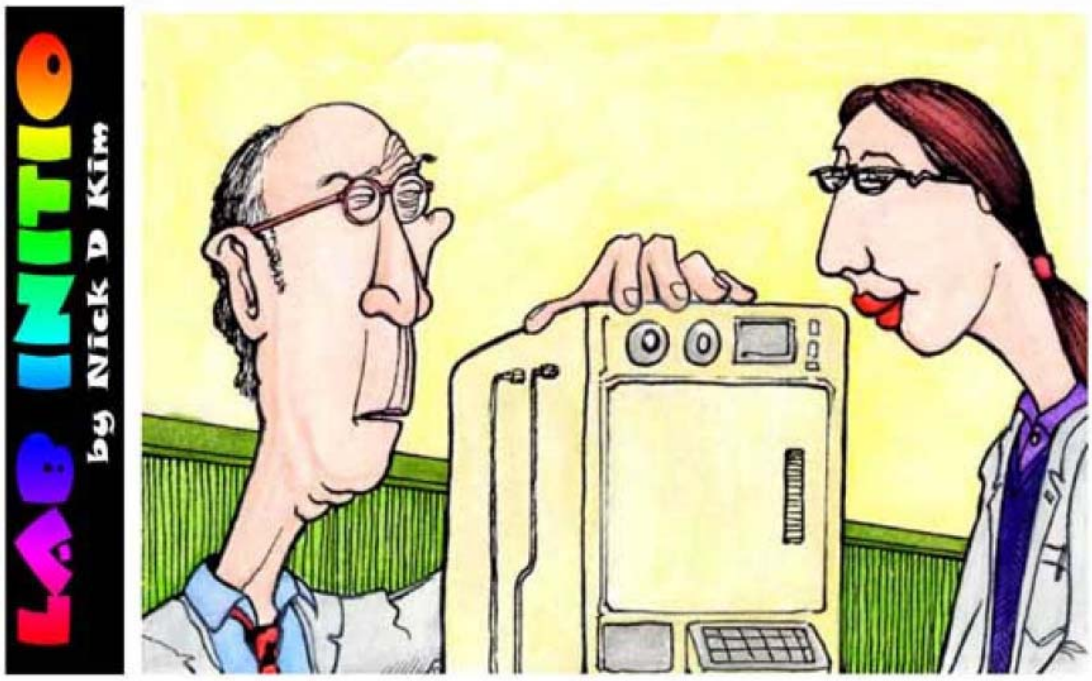
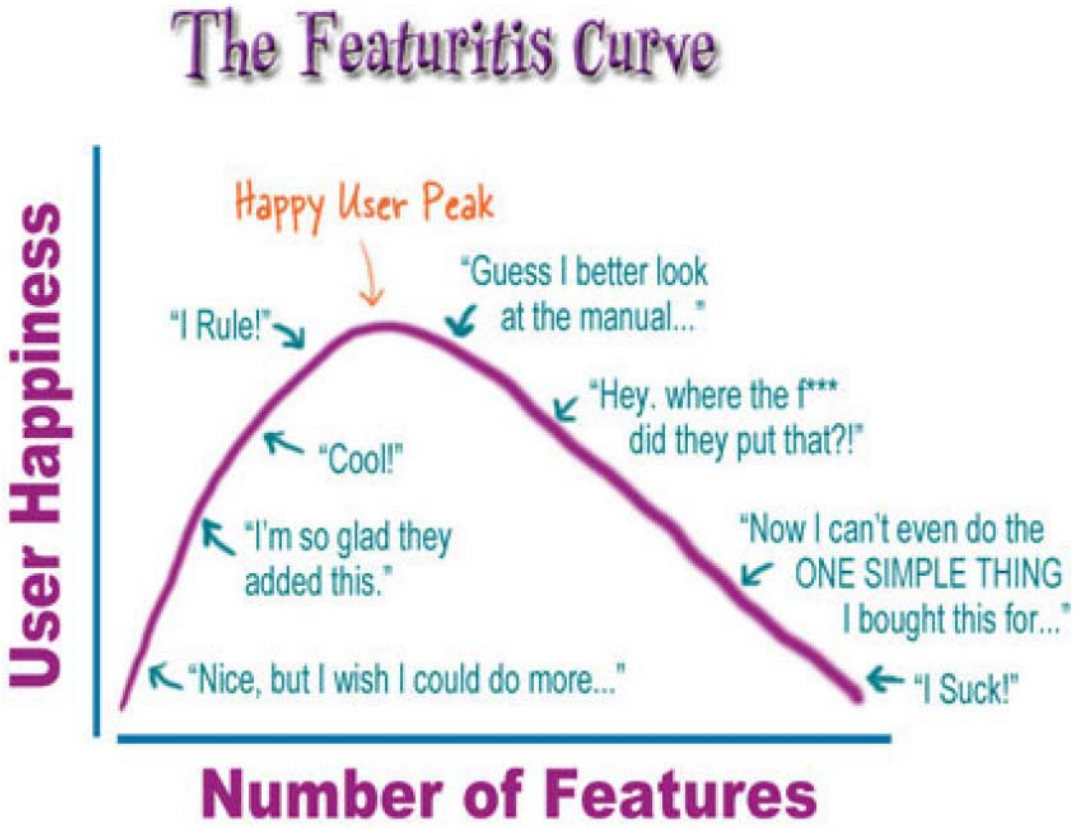


"Yes, love is a potent drug indeed, Miss Cruickshank... But I still don't think we can analyze it using Gas Chromatography..."

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CONCURRENT SESSIONS

Information Management

Staged Electronic Data Deliverable (SEDD) – Overview and Implementation Status

Anand R. Mudambi
US EPA Office of Superfund Remediation and Technology Innovation, Washington, DC 20460

ABSTRACT

The Staged Electronic Data Deliverable (SEDD) is a program neutral format for the delivery of analytical data. It supports multiple requesters' needs depending on the level of reporting requirements as the format clearly reports both simple and complex laboratory processes. The main advantage of SEDD is that laboratories do not have to completely overhaul their Electronic Data Deliverable (EDD) generating systems as data requester needs become more complex, but can simply add additional elements to their current system. Using SEDD as the basis of electronic delivery of analytical data will decrease costs by reducing the number of EDDs laboratories currently have to support and ease data exchange between various programs and agencies.

SEDD files are delivered as XML (eXtensible Markup Language) files. XML is sponsored by the World Wide Web Consortium (W3C) and is a license free, platform independent, final recommended standard. It is well supported by freely available third party tools.

At the present time different Stages for SEDD have been developed based on the complexity of data reporting requirements needed. Valid values for certain key data elements have also been defined.

Delivery of analytical data in the SEDD format is now a requirement for certain Federal Agencies including the U.S. Environmental Protection Agency and the U.S. Army Corps of Engineers. Laboratories are already delivering data using the SEDD format to these agencies under certain programs.

Interagency efforts are underway with the U.S. Navy, U.S. Air Force, some states, and the Department of Energy to promote the use of SEDD.

INTRDUCTION

The Federal Agencies including the US Environmental Protection Agency, US Department of Defense and US Department of Energy collect large amounts of data to make environmental decisions like extent of site contamination, cleanup remedies, and site remediation end points. In order for this information collection to be efficient and cost effective, data collected in electronic formats are the preferred option due the ease of transmission, receipt, evaluation, storage, and retrieval.

Many of the benefits of electronic data are nullified if they are transmitted in proprietary formats since data cannot be exchanged between various groups. This data exchange is very important since many environmental decisions are taken based on data that is collected by one Federal entity and then reviewed by many others.

There is thus a strong Federal need to receive electronic data used for environmental decisions in:

a. A non-proprietary open data standard formats like HTML (Hyper Text Markup Language) and XML (eXtensbile Markup Language)

b. A uniform electronic format especially for environmental data that needs to be exchanged.

OPEN DATA STANDARD – ADVANTAGES AND EXAMPLES

Open data standards have been many significant advantages. They ease data exchange between parties and allow vendors to compete on a level playing field. One big advantage for the Federal Government is that use of open data standards prevents individual monopolies from locking a large market share into their proprietary formats. These standards also are forced to evolve to meet as future needs change and provide incentives for market forces to ensure backward compatibility.

Examples of open data standards are the Hyper Text Markup Language (HTML) used for creating web pages on the Internet and the Extensible Markup Language (XML) which is becoming the standard for data exchange. XML provides a common approach for transmitting information over the Web. This language is a Final Standard recommended by the World Wide Web Consortium (W3C).

THE PROBLEM – TOO MANY ELECTRONIC DATA DELIVERABLES FOR ENVIRONMENTAL LABORATORIES

In today's information age, the environmental laboratories have to report data to most of their clients (including Federal Agencies) in an electronic format. These formats can range from simple electronic spreadsheets to complex ones like the US Air Force Installation Restoration Program Management System (IRPMS) and US EPA's Agency Standard Format (ASF) electronic deliverables. The information conveyed by the electronic data deliverables (EDDs) also varies widely depending on client needs. Laboratories routinely have to support a myriad of reporting formats (in some cases over 100 electronic formats), which increases their operating costs. These formats are also constantly changing as client requirements and methods change adding even more costs to an already burdened industry.

The proprietary nature of many electronic formats also limit the number of laboratories that can be accessed by clients and similarly limit the number of clients that can be accessed by laboratories.

The different types of electronic deliverables also pose problems for the laboratory clients (including Federal and State Agencies), which have to create different electronic tools to evaluate the quality of the data present in the EDDs. It is very expensive to develop and maintain these evaluation tools, which can then be used only for the EDDs for which they were created. Because of the cost of developing the data quality review tools, the electronic deliverable is used mainly for populating client databases, while the data quality review is done manually using the hard copy deliverables. The data in the client database is then changed based on the hard copy

review resulting in a two step process of data entry before the data from the EDD can be used.

Finally with decreasing budgets, it becomes even more vital for Federal Agencies to share electronic information and this becomes difficult (if not impossible) if the EDDs are proprietary.

THE SOLUTION - SEDD

SEDD stands for Staged Electronic Data Deliverable. The SEDD Specification provides a common structure and data element dictionary to report a wide variety of data (chemical, radio chemical, biological, etc.) to multiple customers. The SEDD Specification allows for reporting of analytical data in multiple formats ranging from simple sample concentrations all the way to a CLP type data package and beyond. The SEDD Specification views reporting of analytical data in the same manner as the laboratory produces it - i.e., it is based on the way data is generated in the laboratory for the analysis of a sample. The SEDD Specification is thus designed for reporting the laboratory analytical data and results along with enough information to be able to connect this laboratory results to the site specific sample information taken during the collection of the sample in the field.

The SEDD Specification consists of the following documents:

- An Overview Guide which gives the specifications and structure of creating a SEDD file. Creating a SEDD file requires the use of XML technology and EDDs created using the SEDD Specification are transmitted as XML documents. XML is an open Data Standard and stands for eXtensible Markup Language. It provides a common approach for transmitting information over the Web. This language is a Final Standard recommended by the World Wide Web Consortium (W3C).

- A Data Element Dictionary that gives the SEDD data elements, their corresponding definitions, and allowed valid values.

The latest versions of these documents are available at the following website: [www.epa.gov/superfund/programs/clp/sedd.htm].

Both the Overview Guide and Data Element Dictionary are agency and program neutral - i.e., they do not contain biases or requirements for any particular agency or program.

WHAT IS A SEDD FILE?

1. A SEDD file is a hierarchal electronic file created by a laboratory from their information management system (a single or multiple databases) and is based on the SEDD Specification.

2. A SEDD file is a XML document (with an .xml extension).

3. The SEDD XML Document contains information regarding the chemical analysis of sample(s).

COMMON SEDD MISCONCEPTIONS

Thus the SEDD XML document is not a database used for generating electronic reporting formats like Laboratory Information Management Systems (LIMS) or used for receiving, storing and retrieving environmental data like the US EPA's STORET (STOrage and RETrieval) and SDWIS (Safe Drinking Water Information System). It is also not a file or a parser.

SEDD STAGES

From the SEDD Specification four (4) specific EDD formats (stages) have been created. These individual formats are unique in that each stage directly builds on the previous stage allowing the user to specify the level of detail as needed for a given program or project. These SEDD stages lay out the reporting requirements for a SEDD electronic data deliverable that is agency and program neutral. Thus it can be used for data exchange between agencies and programs.

Stage 1 only uses a small part of the overall SEDD structure and contains a minimum number of data elements to transmit results only data.

Stage 2 contains all of the Stage 1 structure and data elements but adds additional structural and data elements to report method quality control (Stage 2a) and instrument quality control (Stage 2b) information.

Stage 3 contains all of the Stage 2 structure and data elements but adds additional structural and data elements to allow for the independent recalculation of the reported results (e.g., as required by CLP).

A fifth format (Stage 4) is now under development that would build on Stage 3 and allow for the reporting of all raw instrument data files.

ADVANTAGES OF USING SEDD (INCLUDING COST SAVINGS)

SEDD offers significant advantages to all parties that have to generate, receive, or review analytical data. Use of SEDD will reduce the number of EDDs laboratories have to support as the same EDD format based on SEDD can meet multiple client needs.

Data requesters can build common automated tools to review SEDD files. SEDD files being delivered by laboratories are already being reviewed using electronic tools. Preliminary results show a 30-50% cost savings when compared to the same level of manual review.

Finally SEDD files are XML documents – hence they are non-proprietary and can be used for long term storage of data.

SEDD STATUS AND IMPLEMENTATION

US EPA now requires that all analytical data delivered for the Superfund Technical Assessment and Response Team (START) and Response Action Contracts (RACS) well as the Contract Laboratory Program (CLP) be delivered in the SEDD format. The CLP requires the delivery of a Stage 3 EDD, which will allow for a full independent recalculation of the reported results from raw data.

The US Army Corps of Engineers (USACE) now requires the delivery of SEDD files for the FUDS (Formerly Used Defense Sites) Program. USACE contracts are being modified to meet this requirement. Several projects have been competed which successfully parsed these EDDs into various data assessment systems and databases.

SEDD INTER AGENCY EFFORTS AND OUTREACH

US EPA is now also working with other agencies and states to ensure SEDD can meet their requirements. Implementation projects are underway in all 10 US EPA Regions to ensure a smooth transition from the creation of SEDD files by laboratories to electronic evaluation of these files by clients.

SEDD IMPLEMENTATION SUPPORT

US EPA is providing implementation support to all parties interested in using SEDD. The following tools are available for free from the US EPA SEDD Implementation page website: [http://www.epa.gov/superfund/programs/clp/sedd-labs.htm].

a. The SEDD Generator Tool that assists laboratories in creating SEDD files (SEDD files can also be created using vendor support or in-house systems).

b. The SEDD Parser Tool that converts SEDD files for review by electronic tools.

c. A FORM I generator which allows users to view the data results on a hard copy form.

This website also has a SEDD/Automated Data Review (ADR) Project Implementation Overview document which assists personnel who are interested in implementing SEDD along with electronic review tools for their projects.

The following website gives the names of laboratories and vendors supporting SEDD: [http://www.epa.gov/superfund/programs/clp/sedd2.htm]. US EPA can also provide contract language for implementing or requiring to interested parties.

CONCLUSION

The public and private sector can no longer afford to deal with the hundreds of electronic reporting formats from laboratories. SEDD is a versatile format that can meet multiple program and agency reporting requirements. It is now a contract requirement for the delivery of analytical data for some EPA and USACE programs. Using SEDD along with electronic tools can save both time and money in the area of analytical data delivery and review as well as usher in an era of easy data exchange between multiple parties. Please contact Anand R. Mudambi (US EPA) or Joseph Solsky (US Army Corps of Engineers) for more information regarding the SEDD Specification, SEDD Pilot Projects, SEDD Interagency Efforts or development of tools for evaluating and processing EDDs based on the SEDD Specification.

Staged Electronic Data Deliverable (SEDD): Overview and Implementation Status

NEMC 2006
Anand R. Mudambi
US Environmental Protection Agency
(USEPA)
August 31, 2006

Federal Agency Need for Data in Electronic Format

- Collection of Large Amounts of Data Required to Make Various Environmental Decisions, Including:
  - Cleanup Remedies
  - Site Remediation End Points
- Ease of Transmission, Receipt, Evaluation, Storage, and Retrieval
- Efficient and Cost-Effective

XML – A Self Defining Data Format

- Final Recommended Standard by the World Wide Web Consortium.
- Each Piece of Data in XML Has a Tag (or Is Tagged) so the Electronic Data Deliverable (EDD) Is Self-Defined.
- Under SEDD, the EDD From the Laboratory Is Transmitted as an XML Document Based on a Document Type Definition (DTD) or a Schema.

What is SEDD?

- SEDD is a hierarchal file created by a Laboratory Information Management System (LIMS) or any other database.
- A SEDD file contains information regarding the chemical analysis of sample(s).
- Information (analytical results) from a SEDD file can be reviewed and then input into customer databases using parsing routines.
- Parsing routines need to be written ONLY once for each database type.

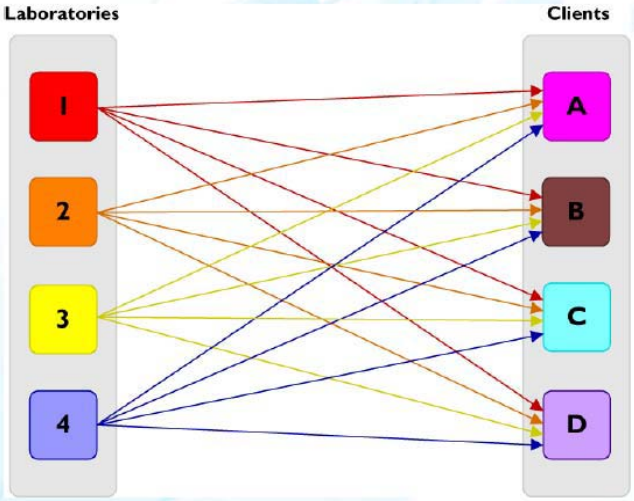
Common SEDD Misconceptions

SEDD Is NOT:

- A Database
- A Flat File
- A Parser

August 31, 2006 Staged Electronic Data Deliverable (SEDD) Overview/Anand R. Mudambi 5

The Current Electronic Data Flow

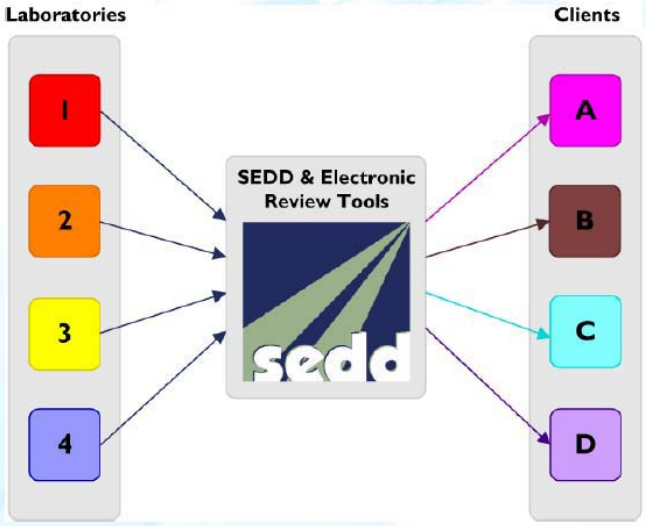


August 31, 2006 Staged Electronic Data Deliverable (SEDD) Overview/Anand R. Mudambi 6

DISADVANTAGES

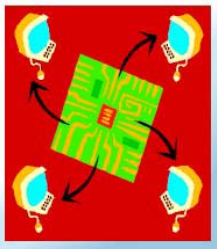
- Proprietary formats limit the number of labs that can be used by clients and vice versa
- Labs have too many EDDs (up to a 100)
- Labs become focused on their EDD and IT departments instead of sample analysis
- EDDs cannot be readily exchanged between various clients

With SEDD and Electronic Review Tools

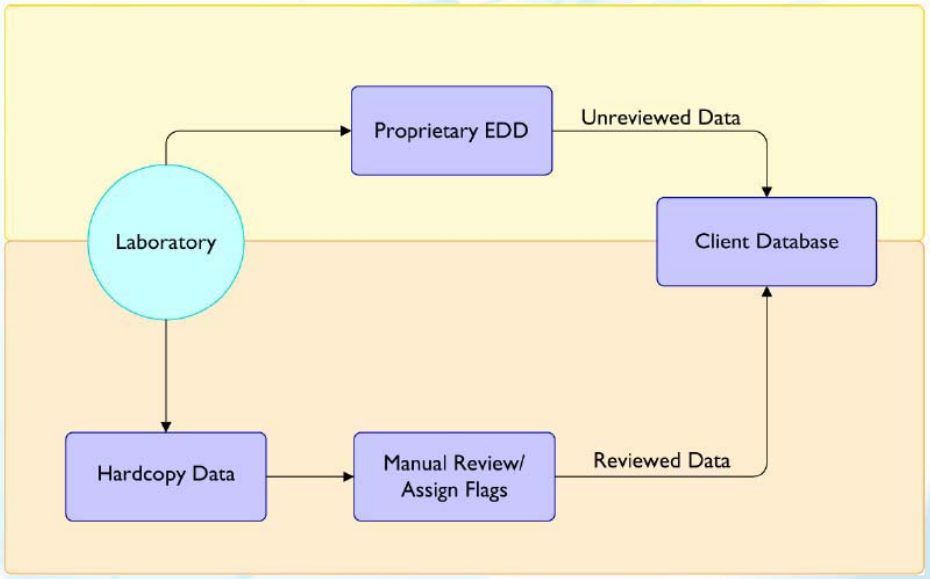


ADVANTAGES

- Many more labs can be accessed by Clients and vice versa
- Staged approach allows for meeting diverse Client Reporting Requirements
- All lab data can be reviewed using electronic tools prior to delivery to/acceptance by Clients



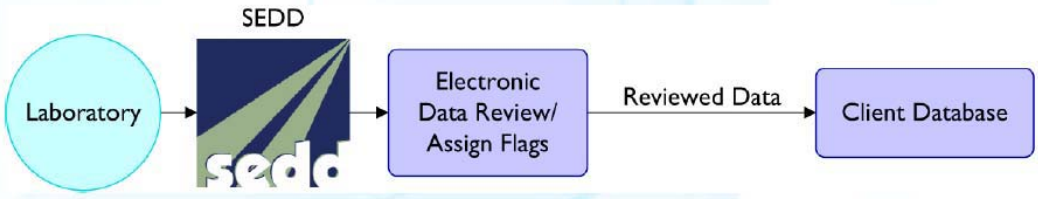
Typical Analytical Data Review Model



DISADVANTAGES

- Review of data is mostly done on the hardcopy by the client
- All data cannot be reviewed in a timely manner
- Proprietary/program specific EDDs are generally not suitable format for long term data storage or retrieval

Analytical Data Review Model using SEDD



ADVANTAGES

- All lab data can be reviewed prior to input into client database using electronic tools (already developed and in development)
- More confidence in the quality of data for the client since 100% of received data is reviewed
- Analytical Data Delivered in XML Format (Non-Proprietary)- suitable for long term storage and later retrieval

SEDD Status

- Many laboratories (including at least one major network) are already delivering compliant SEDD Stage 2 and Stage 3 files.
- Two LIMS vendors now support SEDD.
- SEDD files are now being input and checked by Automated Data Review (ADR) software (EPA, USACE and other private sector vendors).

SEDD Outreach

- Working with other EPA Offices (RCRA, Water)
- Working with US Navy
- Working with US DOE
- Working with States
- Working with the Private Sector

What's Upcoming with SEDD!

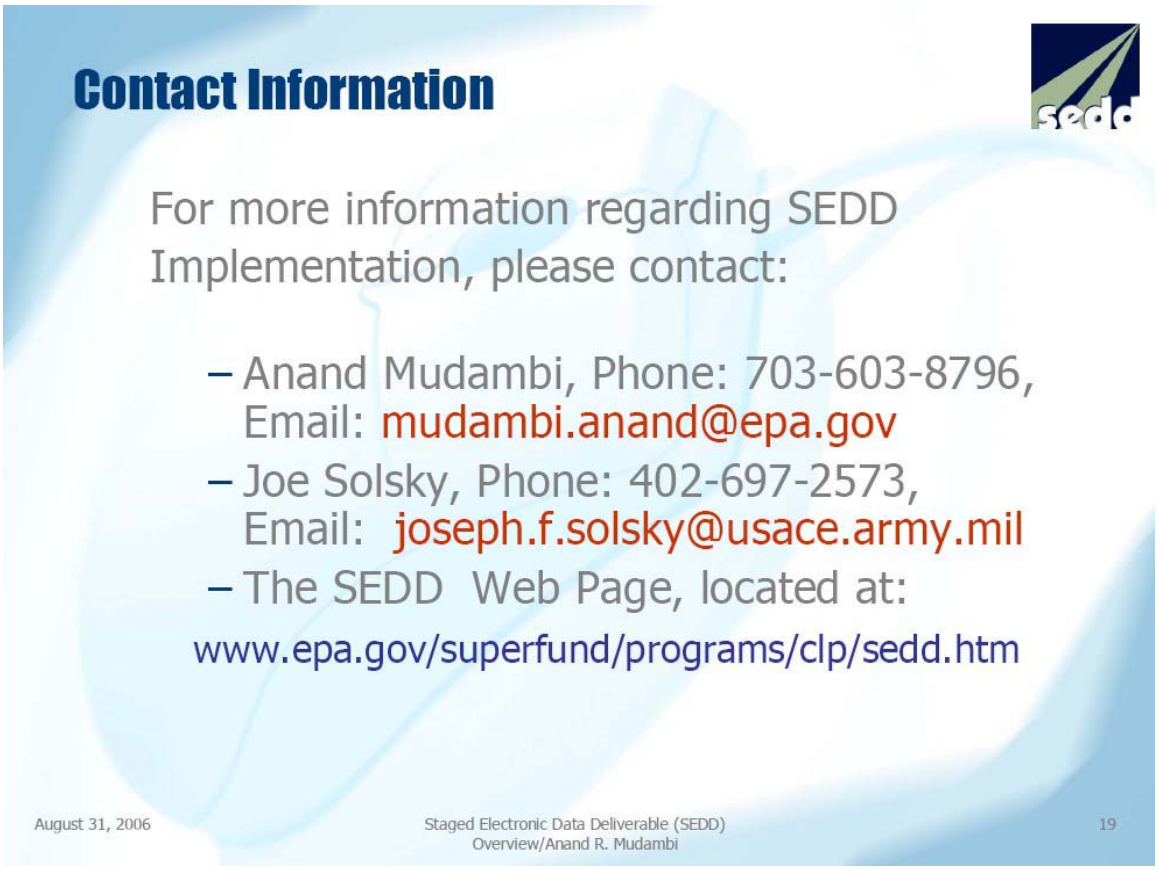
- EPA Website to Allow Generation of Hard Copy Reports from SEDD Files (XSL Style Sheets)
  – Completed (See SEDD web page for details)
- EPA Website to Allow Automated Checking of SEDD files for Compliance
  – In Development

SEDD Implementation Support

- For Laboratories, SEDD Generator Tool Provided by US EPA (FREE) to Create SEDD Files
  - SEDD Files Can Also Be Created Using Vendor Support or by In-House Systems
- For Federal Agencies and Contractors Working on Federal Projects, Automated Data Review (ADR) Software Is Available (FREE*)

SEDD Implementation Support on the Web

- A Web Page for SEDD Implementers
- A List of States, Contractors, Laboratories and Vendors Who Support SEDD
- A 10 Step Process for SEDD/ADR Implementation


Contact Information
sedd
For more information regarding SEDD Implementation, please contact:
– Anand Mudambi, Phone: 703-603-8796, Email: mudambi.anand@epa.gov
– Joe Solsky, Phone: 402-697-2573, Email: joseph.f.solsky@usace.army.mil
– The SEDD Web Page, located at:
www.epa.gov/superfund/programs/clp/sedd.htm
August 31, 2006
Staged Electronic Data Deliverable (SEDD) Overview/Anand R. Mudambi
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A Technical Overview of the Staged Electronic Data Deliverable (SEDD)

Joseph Solsky
U.S. Army Corps of Engineers (CENWO-HX-C), 12565 W Center Rd, Omaha, NE 68144

ABSTRACT

Due to the various levels of data complexity and reporting required by requesters, it is impossible for one single electronic data deliverable (EDD) format to be able to meet the needs of the multiple data users. The Staged Electronic Data Deliverable (SEDD) solves this problem by reporting data using multiple formats known as 'Stages', with each stage building on the next. Currently, three stages have been defined for SEDD. A common structure has been developed that will allow for the reporting of all types of data. SEDD allows for the complete linking of all samples to their associated QC samples, the complete linking of all samples to their associated continuing and initial calibration data, and the complete linking of all reported results to the specific analysis that was used to derive that specific result.

SEDD delivers data in the form of an XML document. In order to create or use a SEDD file, a Document Type Definition (DTD) or Schema file from the U.S. EPA SEDD website is required. Another problem with current EDDs is the existence of client specified valid values within these EDDs. These valid values can be significantly different to the point where the methods used or the analytes being reported would not be recognizable to anyone other then the original data requester, thus making data exchange between parties difficult. The latest version of SEDD (Draft Version 5.1) addresses this and other issues.

INTRODUCTION

Most commercial laboratories are now delivering data to their customers in both hard copy and electronic formats. More and more emphasis is being placed on these electronic formats and it is not uncommon for an average sized commercial laboratory to deliver data to various clients in over one hundred (100) different electronic formats. This is both time consuming and costly. Most of these electronic formats are customer specific and proprietary and were designed to directly import the reported data into customer-specific databases. The proliferation of these customer-specific and proprietary formats makes it very difficult to share data between customers and develop software to further review and process the reported data.

WHAT IS SEDD?

No one single electronic data deliverable format would be able to meet the needs of the multiple data users due to the various levels of data complexity and reporting as required by those users. Some users require only that the final testing result(s) be reported along with some general sample information. Other users require that the laboratory report summary method Quality Control (QC) data while other users require the reporting of sufficient information to independently recalculate all reported data. As a consequence, SEDD accommodates the reporting of data in 'Stages', with each stage building on the next using XML technology. Currently, three stages or unique electronic data deliverable formats have been defined for SEDD. Stage 1 contains the minimum number of analytical data elements to report 'Results Only'

data to the end user. Stage 2 builds on Stage 1 and adds method (Stage 2a) and instrument (Stage 2b) Quality Control (QC) data. Stage 3 builds on Stage 2 and adds additional measurement data to allow for the independent recalculation of the reported results.

SEDD delivers data in the form of an XML document. XML (eXtensible Mark-up Language) was originally developed by the World Wide Web Consortium (W3C) and was initially published in early 1998. It was designed to ease data exchange between various parties, especially between various databases. Today's databases can readily import and export XML. An Electronic Data Deliverable (EDD) that is based on XML is self-defining since each piece of data is 'tagged'.

A common structure has been developed for SEDD that will allow for the reporting of all types of data. SEDD allows for the complete linking of all samples to their associated QC samples and the complete linking of all samples to their associated continuing and initial calibration data. Various non-target analytes, such as internal standards and surrogates, can be linked to their associated target analytes. All reported results can be linked to the specific analysis or analyses that was used to derive that specific result. SEDD also provides a means for the reporting of complex analytical relationships. For example, the reporting of data can be difficult for the Polychlorinated Biphenyls (PCBs). PCB results can be calculated by establishing separate calibration curves for each peak chosen and averaging the separate calculated peak results together. PCB results can also be calculated by summing up selected or all chromatographic peaks together to establish a single calibration curve and then reporting the final result from this single curve. SEDD does not dictate which specific approach a laboratory must use but can readily capture what the laboratory did and report the results to the data user. SEDD can readily report data that is generated by summing various analytes together, averaging results together from two or more analyses, results that are derived from the Method of Standard Additions and other techniques.

A typical SEDD file is structured as a hierarchial file. An example of what part of a typical file might look like follows:

```
<ReportedResult>
        <AnalyteName>Benzene</AnalyteName>
        <CASRegistryNumber>71-43-2</CASRegistryNumber>
        <Result>24.2</Result>
        <ResultUnits>ug/L</ResultUnits>
</ReportedResult>
```

The above file is described as 'self-defining' since all of the reported data is identified with 'tags'. For example, the data element 'AnalyteName' is located within the 'ReportedResult' node and contains the value 'Benzene'. Each reported value is preceded and followed by an associated data element name 'tag'. Nodes are simply data elements that contain other data elements instead of specific values. Typical SEDD files can become rather large. These files can be easily viewed and edited using commercial software. One such Freeware product is XML Notepad. XML Notepad is a Microsoft product that is no longer supported or available from Microsoft, however, it is still freely available over the internet.

In order to create or use a SEDD file, an associated Document Type Definition (DTD) file would be required. For each Stage of SEDD, the DTD would specify what parts (nodes) of the overall SEDD structure would be required and what specific data elements would be available for use within each part (node) of the SEDD structure. Thus, a DTD can be used to 'validate' a SEDD file to ensure that it meets the structural requirements as specified in the corresponding DTD. Currently, generic DTDs have been developed for Stages 1, 2a, 2b and 3 of SEDD. Recently, DTDs are being replaced by Schemas. Schemas are similar to DTDs but offer additional content checking and validation features. Schemas will soon be adopted for use with SEDD in the near future.

In addition to the multitudes of noncompatible EDDs that currently exist, another significant issue that exists are the client specified values that are contained within these EDDs. These 'valid values' can also be significantly different to the point where the methods used or the analytes being reported would not be recognizable to anyone other than the original data user. The latest version of SEDD (Draft Version 5.1) addresses this problem. For the data elements that identify the methods used or the analytes reported, SEDD uses three tiers of data elements. Methods and analytes are identified at the laboratory level, at the client level and at a national reference level. SEDD will not prescribe valid values at the laboratory or client level but will require them at the national reference level. The SEDD valid values not only report the valid value but the reference from which the valid value was derived. By reporting data in this manner, the data can now be recognized by multiple clients. Many of the data elements within SEDD use valid values that can be directly referenced to nationally or internationally recognized sources.

SEDD STAGE 3 FILES AND BEYOND

A SEDD Stage 3 file captures and reports all of the data needed to independently recalculate all final results by capturing this data in the manner in which in was generated. By capturing the data in this manner, the data can be reported and reviewed against the requirements of many different programs. For initial calibrations, average calibration/relative-response factors, linear regressions, quadratic regressions, and other techniques can all be used. These calibration strategies can be applied on a per peak basis or applied when peaks are summed together. Various weighting factors can also be used when regressions are performed. In addition, either 'external standard' or 'internal standard' procedures can be used for any analyte using any method. This same type of flexibility that is used for the reporting of initial calibrations is used throughout the sample preparation and analysis process.

This independent recalculation is performed by starting with an integrated area count for a typical organic chromatographic method or by starting with a background corrected spectral intensity measurement for a typical inorganic spectroscopic method. Data for each standard used is captured. This would include the standard's concentration and amount used, its identification, and the original vendor and lot number of the standard. Each step of the sample preparation, sample cleanup and sample analysis is captured such that the entire analytical process can be recreated.

At the present time, a SEDD Stage 3 file cannot deliver raw instrument data, such as chromatograms, or other laboratory documents, such as Chain-of-Custody forms. Due to the

proprietary nature of most instrument raw data files, the storage and long term archiving of this data has become a problem. Laboratories must often save older copies of software and/or instrument hardware to access these files. As these older systems age or when laboratories close, this raw data is often lost forever.

A SEDD Stage 4 file would have the identical structure as a SEDD Stage 3 file except that it now contains all of the instrument raw data. To address the items that were mentioned in the previous paragraph, a stage 4 file would store the data in an XML format. ASTM (American Standard for Testing and Materials) Subcommittee E13.15 is currently developing the requirements for the storage of raw instrument data files in an XML format called AnIML (Analytical Information Markup Language). More information can be obtained on AnIML at their website (http://animl.sourceforge.net/). The SEDD Stage 4 has not yet been developed, however, information interchange is now taking place between EPA and this ASTM group.

In addition, SEDD is expected to grow to include other areas, such as reporting of data for the radiochemical methods, reporting of field geological data, reporting of overall project data. Once a standardized EDD format is accepted, private vendors can now develop additional software to review, assess, and validate the data.

CONCLUSIONS

SEDD has the potential to replace many of the client-specific proprietary Electronic Data Deliverable formats that are in current use throughout the environmental testing and other industries. Several programs with the Environmental Protection Agency (EPA), notably the Contract Laboratory Program (CLP), and within the Department of Defense, notably the Formerly Used Defense Sites (FUDS) program as implemented by the U.S. Army Corps of Engineers, now require the use of SEDD. More than two dozen testing laboratories now have the capability to generate SEDD files. In addition, two LIMS vendors now have the capability of exporting data in the SEDD format. Additional information on SEDD can be found at the following web site: www.epa.gov/superfund/programs/clp/sedd.htm.

A Technical Overview of Staged Electronic Data Deliverable (SEDD)

NEMC 2006

Joseph F. Solsky
US Army Corps of Engineers (USACE)
August 31, 2006

The Problem with Today's EDDs

- Laboratories produce more than 300 different Electronic Data Deliverables (EDDs).
- Most EDDs to date are customer-specific.
- Most EDDs are proprietary.
- No stand-alone, self-defining EDD present - a must in case of another national emergency.
- No EDD present that meets diverse customer needs for detailed analytical chemistry reporting.

The Solution - SEDD

- SEDD - Staged Electronic Data Deliverable
- Staged Approach Allows for Meeting Diverse Reporting Requirements
- Eases Data Exchange between Various Parties
- Analytical Data Delivered in eXtensible Markup Language (XML) Format (Non-Proprietary)
- XML Is Designed for the Creation of Complex Documents and for Input into Various Databases

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XML – A Self-Defining Data Format

- XML - eXtensible Mark-up Language
- Final Recommended Standard by the World Wide Web Consortium
- Each Piece of Data in XML Has a Tag (or Is Tagged) so the Data Set (EDD) is Self-Defined
- Under SEDD, the EDD from the Laboratory Is Transmitted as an XML Document Based on a DTD or Schema

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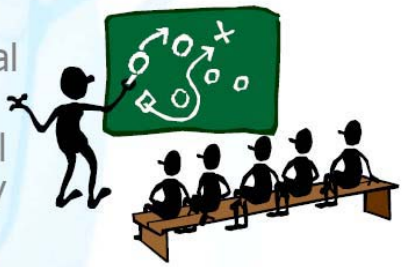
Example XML File

```
<ReportedResult>
   <AnalyteName>Benzene</AnalyteName>
   <CASRegistryNumber>71-43-
   2</CASRegistryNumber>
   <Result>24.2</Result>
   <ResultUnits>ug/L</ResultUnits>
</ReportedResult>
```


What Is SEDD?

- Uses a common syntax to describe diverse laboratory activities and report analytical data electronically.
- Allows users to link analytical data to underlying laboratory activities and processes to provide full traceability.
- Provides a means for reporting complex analytical relationships.



The Stages of SEDD

- Stage 1 - Contains the minimum number of analytical data elements required to transmit results-only data.
- Stage 2 - Data content builds on Stage 1 by adding method (Stage 2a) and instrument (Stage 2b) Quality Control (QC) data.
- Stage 3 - Data content builds on Stage 2 by adding additional measurement data to allow for independent recalculation of the reported results [e.g., Contract Laboratory Program (CLP)].

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Stage 3 SEDD Files

- A SEDD Stage 3 file contains enough data to allow for the independent recalculation of the reported results.
- Raw instrument data would generally not be used. Corrected instrument data, such as peak areas or corrected intensity readings, would normally be captured.
- This file contains all of the linkages to relate all calibration data and other data to each reported result.
- This file contains information to associate all standards used to their original vendors and lot numbers.

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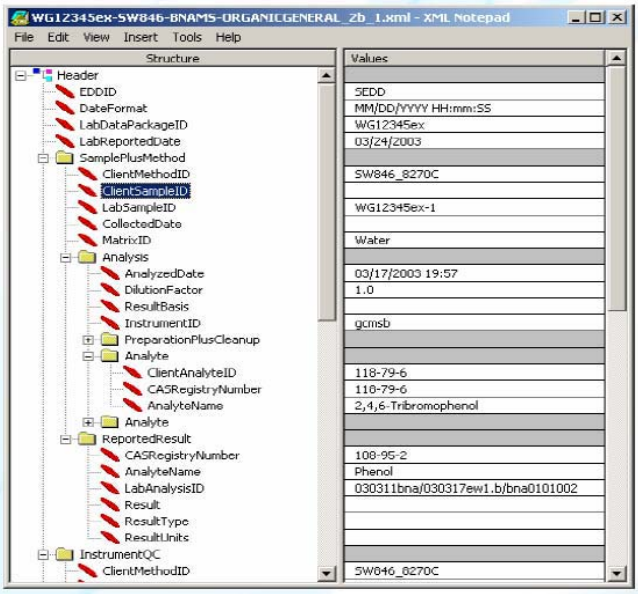
The Future – SEDD Stage 4

- A Stage 4 file uses the same structure as Stage 3 but includes all instrument raw data files that were generated during the analysis of the sample. Other supporting files could also be included.
- These instrument raw data files are stored in a non-proprietary XML format.
- Significant advantages can be realized when data is delivered at this level.

Example XML File (As Viewed in XML Notepad)



What Are Document Type Definitions (DTDs)?

- Would specify what parts of the SEDD structure (nodes) are required.
- Would specify what data elements are required for each node.
- Three stages have now been defined. Data can be delivered based on the amount and complexity of the data required by the user. Generic DTDs are developed for Stage 2a, 2b and 3.
- Schemas can also be used in place of DTDs.

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The Valid Value Issue

- SEDD now includes a set of valid values.
- Whenever possible, all valid values were tied to an existing standard or recognized database of values. When valid values are reported, they are reported with the appropriate source identified.
- All critical data, such as analyte and method IDs, can be identified using laboratory, client, and referenced values.

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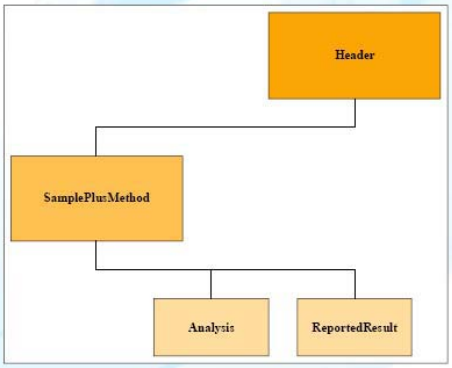
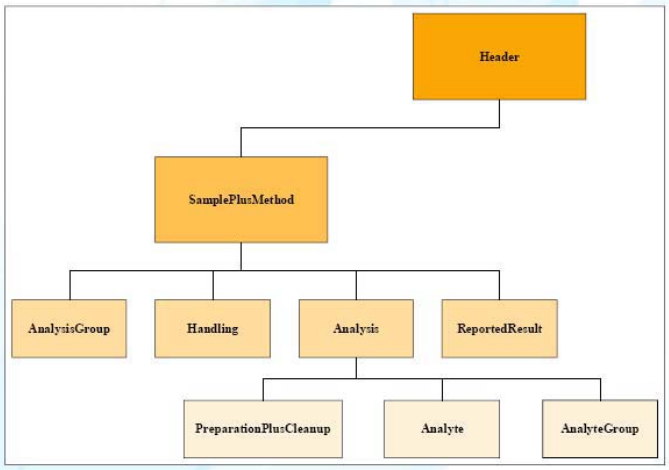
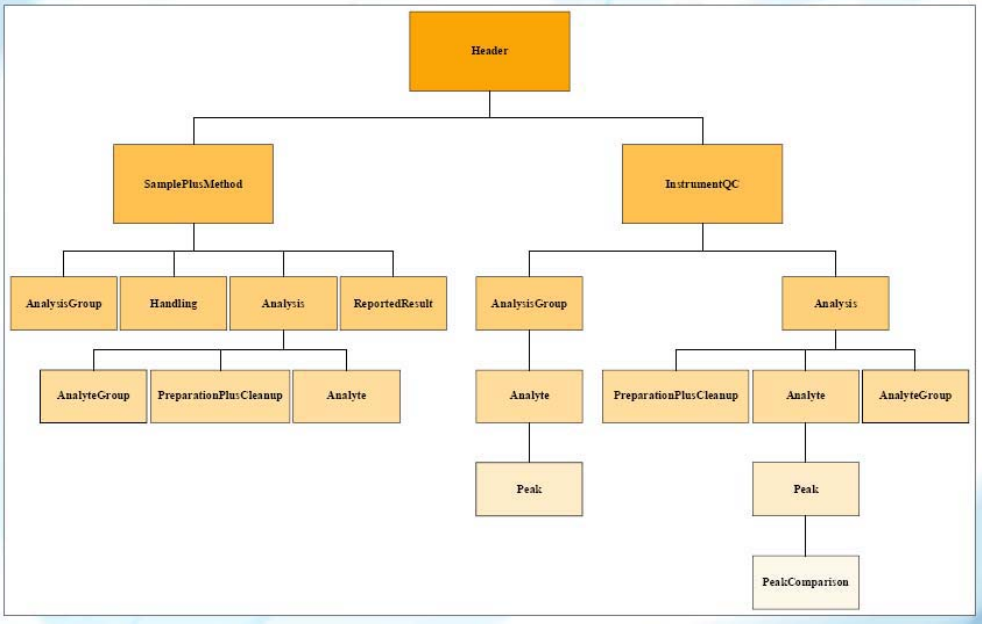
SEDD Stage 1 Structure



SEDD Stage 2a Structure



SEDD Stage 2b Structure



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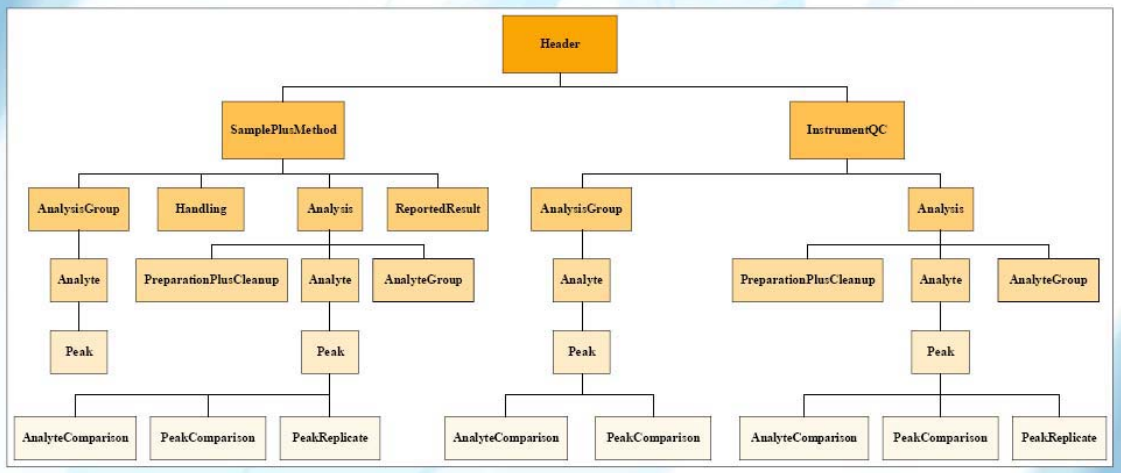
SEDD Stage 3 Structure



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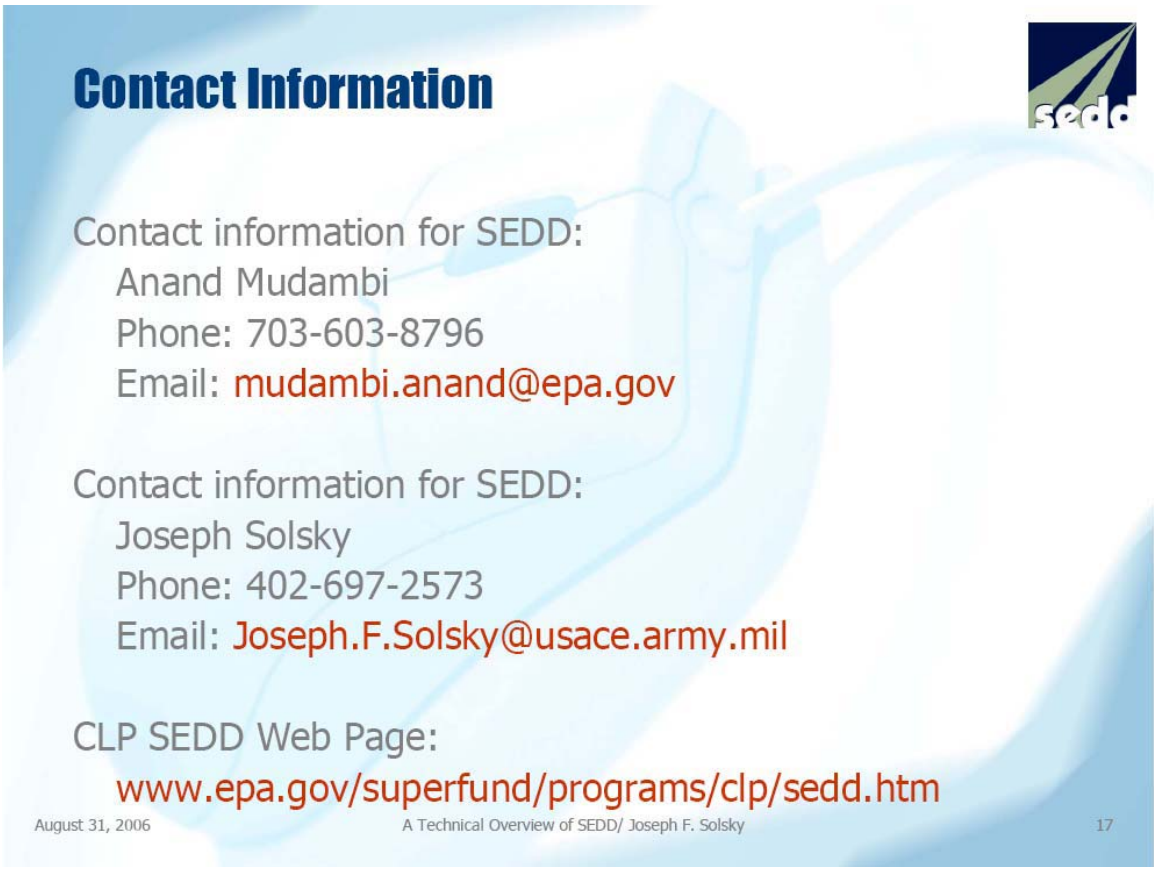
Contact Information
sedd
Contact information for SEDD:
Anand Mudambi
Phone: 703-603-8796
Email: mudambi.anand@epa.gov
Contact information for SEDD:
Joseph Solsky
Phone: 402-697-2573
Email: Joseph.F.Solsky@usace.army.mil
CLP SEDD Web Page:
www.epa.gov/superfund/programs/clp/sedd.htm
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AnIML FOR INTERCHANGING ANALYTICAL DATA

Kramer, Gary W.; National Institute of Standards and Technology

Interchanging analytical data and their associated "scientific metadata" across space and time, from instrument to application, application to application, and applications to/from databases has often been hampered by multiple, incompatible data formats. The rapid pace of information technology and computing hardware innovation has exacerbated this problem. Analytical information stored on early digital media (let's say 8-inch floppy disks) 20 years ago may be less accessible today than such information stored on paper 20 years before.

ASTM SubCommittee E13.15 on Analytical Data is creating AnIML to describe chromatography and spectroscopy data and metadata. Based on XML (eXtensible Markup Language) and its associated technologies, AnIML facilitates access to analytical data by building in descriptions of the data and metadata with delimited tags in the same way that HTML (HyperText Markup Language) describes the display of items on a webpage. AnIML is built around a core schema that defines ways for describing almost any data. Technique Definition files are created to constrain the data description mechanisms for a given analytical technique to those commonly accepted for a given technique, to delineate the metadata items commonly associated with such domain data, and to permit content extension by vendors and users without changing the core schema. Once in AnIML format, analytical data can be interchanged over the web, converted to other formats, validated, or visualized in multiple formats using existing XML-based tools. AnIML ensures the integrity of the data through the use of digital signatures and provides for the data tracking, verification, and validation necessary for use in regulated industries.

Analytical Information Markup Language

A New Mechanism for Interchanging and Archiving Analytical Chemistry Data

Gary W. Kramer

Biochemical Science Division
National Institute of Standards and Technology

NIST

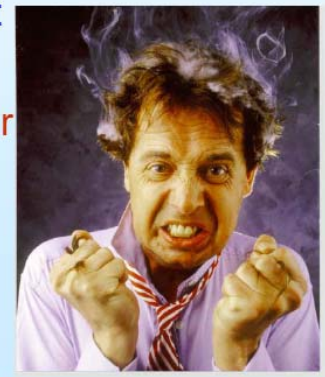
In the beginning...

- Consortium on Automated Analytical Laboratory Systems (CAALS)
  - CAALS-I Communication Protocol
  - High-Level Communications Protocol
  - Common Command Set
  - Device Capability Dataset
- Laboratory Equipment Control Interface Specification (LECIS) - ASTM E1989-1998.
- System Capability Dataset
- How to Deal with Result Data?
- NIST In-House Data Interchange/Archiving Needs

NIST

Why should I care? Scenario 1

- I just want to paste a chromatogram from our data system into a Word document. But the @#$%& thing seems to be stored in some kind of in binary format.
- I just want to copy a peak table into a spreadsheet. What happened? It looks like the transporter beam scrambled my data.
- I'd like to be able to look at, expand, plot,… that xyzoscopy data that my colleague at EJU sent me. What do you mean I have to buy the vendor's $5K softwar package? I just want to look at the @#$%& data.



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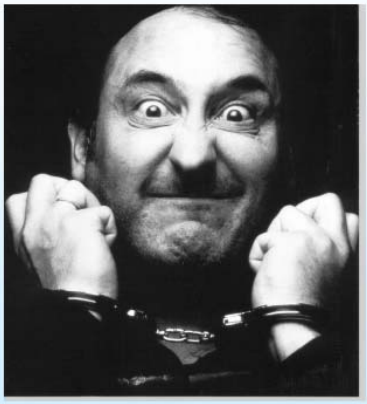
Why should I care? Scenario 2

- We did that study before. The data are all here… on these DEC 8 inch floppy disks…
- If I could just open & read this file, I wouldn't have to…. But it's a Visicalc file that requires the CP/M operating system.
- This old NMR data "might" be valuable, but the tapes on this shelf take up too much room. I'll bet all their contents would fit onto a a couple of DVDs. Know anybody that has a 9-track tape reader interfaced to a PC?

NIST

Problems with Current Result Data Handling Mechanisms

- Native Data Formats
  - Proprietary Formats
  - "Metadata" Separated from Result Data
    - Metadata & Data in Multiple Files
    - Metadata Not Available in Electronically
    - No Way to Link Metadata with Result Data
- Interchange Data Formats
  - Available for Only a Few Important Techniques
    - ANDI — GC, LC, MS
    - JCAMP-DX — IR/FTIR, NMR, UV/Vis, IMS
  - Fixed Order, Fixed Syntax, Immutable Formats
  - Content Limitations
  - Inconsistent Implementations
- Formats Incompatible with Modern Network Technologies



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Goals for New Result Data Handing

- Extensible
  - Easy to Add New Elements without Breaking Existing Applications
- Flexible
  - Useful for Diverse Needs: Interchange, Interconversion, Archiving...
- Useable & Maintainable
  - Easy to Create, Use, Adapt, Maintain...
  - Readily Available Tools
- Acceptable
  - Use Standard Mechanisms Accepted by Mainstream Computing
- Network Friendly

☞ Extensible Markup Language

NIST

What is a markup language?

- Markup is a way using delimiting tags to tell a computer program something about a data element.
- Hypertext Markup Language (HTML) is used for describing text on a page.

```
<head>
    <title>What is a markup language?</title>
</head>
```

- Extensible Markup Language (XML) is used for describing data.

```
<date>2006-03-25-05:00</date>
```

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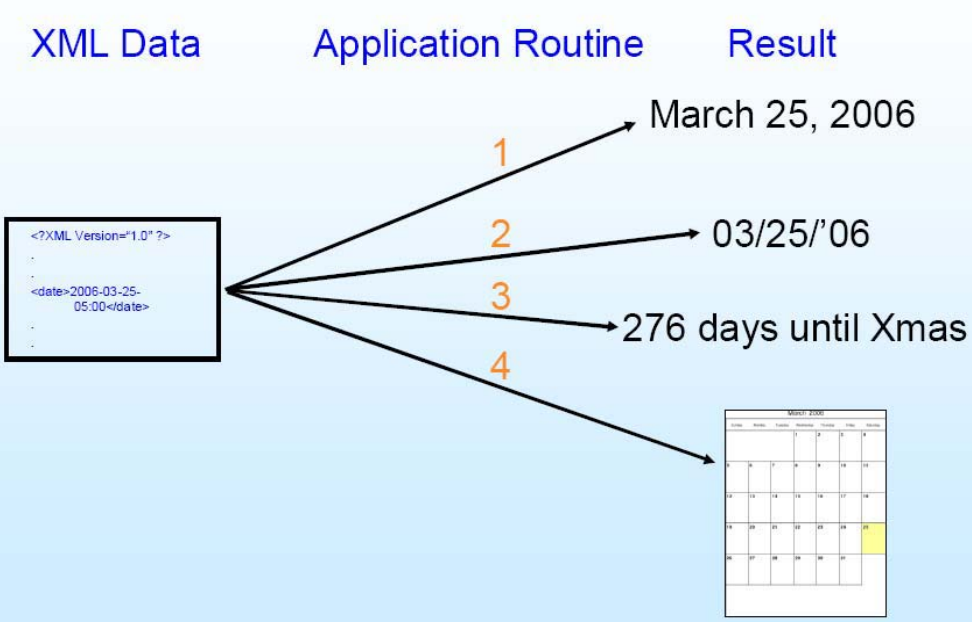
So what!



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XML in 10 Points

- XML is for structuring data
- XML looks like HTML
- XML is text, but is not meant to be read
- XML is designed to be verbose
- XML is a family of technologies
- XML is new, but it has a history & a heritage
- XML turns HTML into XHTML
- XML is modular
- XML is license-free, platform-independent, and well-supported
- XML is a standard maintained by the W3C

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www.w3.org/XML/1999/XML-in-10-points

SpectroML

- SpectroML is a markup language for spectroscopy data based upon:
  - XML
  - JCAMP-DX (IUPAC)
  - ANDI/NetCDF (ASTM)
  - Thermo-Galactic GRAMS and SPC file format
  - Data definitions from instrument manufacturers
  - ASTM Definitions
- SpectroML is defined for UV-Visible spectral data

Galactic GALACTIC INDUSTRIES CORPORATION

PerkinElmer VARIAN Agilent

SHIMADZU XML

SPECTROML XML for Molecular Spectrometry Data

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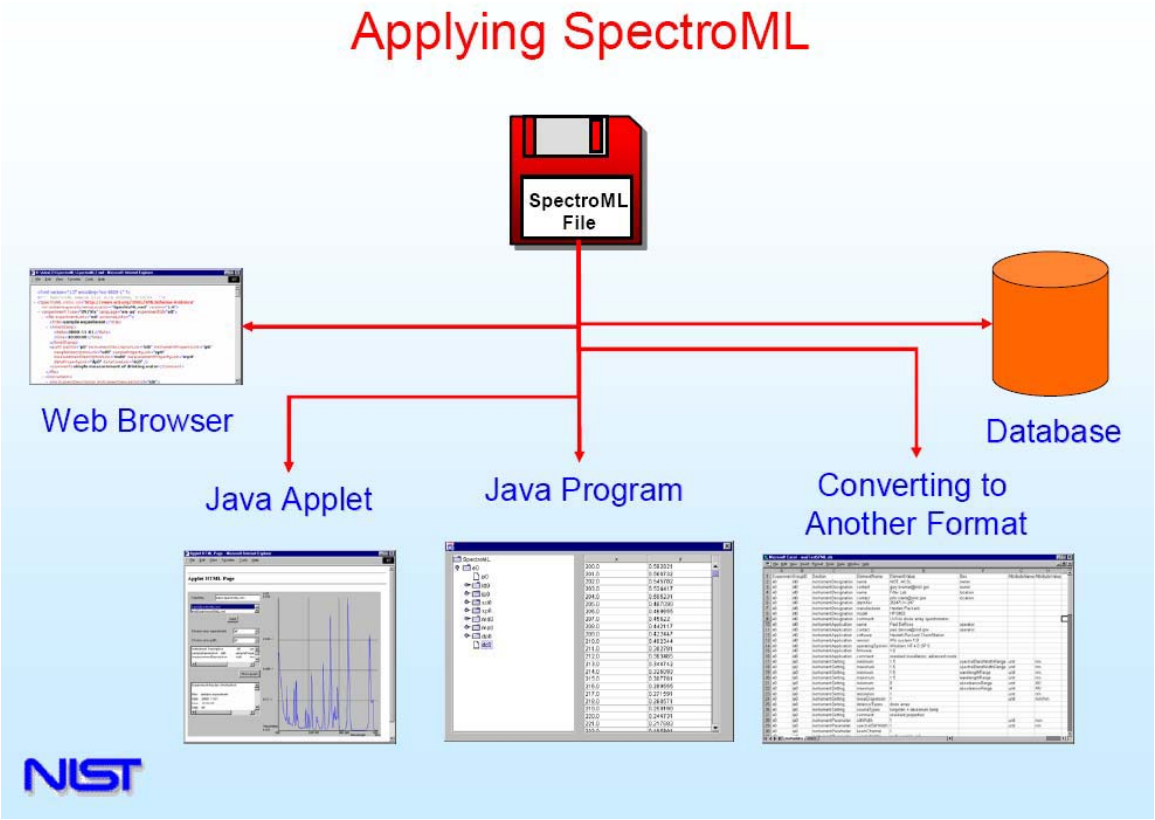
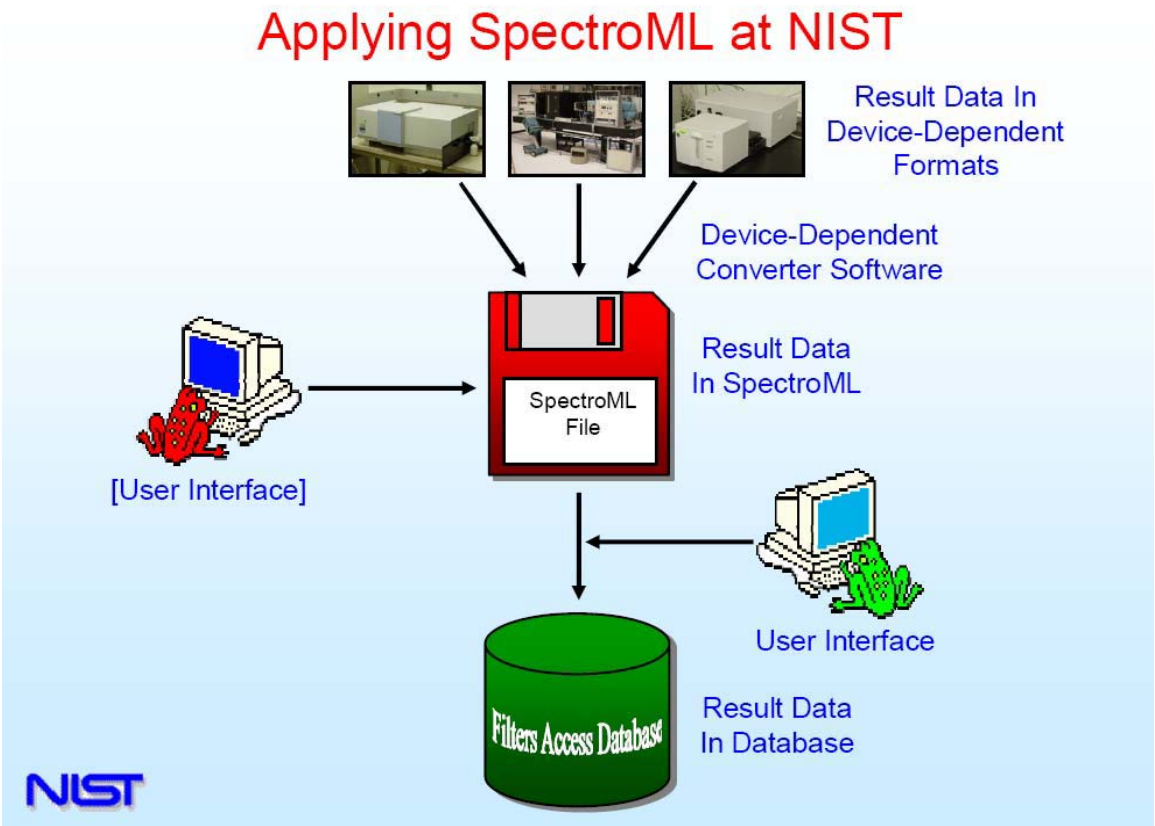

Applying SpectroML
SpectroML File
Web Browser
Database
Java Applet
Java Program
Converting to Another Format
NIST


Applying SpectroML at NIST
Result Data In Device-Dependent Formats
Device-Dependent Converter Software
SpectroML File
Result Data In SpectroML
[User Interface]
User Interface
Filters Access Database
Result Data In Database
NIST

Generalized Analytical Markup Language (GAML)

- Represent Analytical Data from Multiple Spectroscopy & Chromatography Techniques
- Compact, Simple Dictionary & Hierarchy (Schema)
- Use XML Datatypes & Hierarchical Structure to Mimic Relationships in Data Sources
- Avoid Parameter "Mapping" Problem
- Minimize the Need for Complex Dictionaries
- Permit Future Expansion
- Keep File Sizes Small

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James Duckworth, Thermo LabSystems

An XML-Based Standard for Molecular Spectrometry and Chromatography Result Data

- Possibility of XML-Based Approach Raised
  - ASTM E01.25 and E13.02 Meetings PittCon '00 Atlanta
- Demo of SpectroML and Applications
  - ASTM E13.01 Meeting PittCon '01 New Orleans
- First Organizational Meeting Held
  - ASTM E13.01 Meeting EAS '01 Atlantic City
- Task Group Organizational Meeting
  - ASTM E13.01.03 Meeting PittCon '02 New Orleans
- Task Group Working Meeting
  - ASTM E13.01.03 Meeting Shimadzu, Inc. 9/'02
- New Subcommittee Meeting
  - ASTM E13.15 Meeting PittCon 3/'03 Orlando
- E13.15 Meets at EAS and PittCon
  - AnIML Working Group Meets "Virtually" ~biweekly

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ASTM INTERNATIONAL Standards Worldwide

AnIML an XML-Based Standard for Analytical Result Data

- SpectroML and GAML serve as starting points for an XML-based standard interchange format for molecular spectrometry and chromatography.
- Instrument manufacturers, data system & LIMS developers, software developers, end-users, consensus standards organizations, regulatory agencies, and other interested parties are invited to participate in this effort.

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XML in Chemistry

ASTM INTERNATIONAL Standards Worldwide

Creating Analytical Information Markup Language (AnIML)

- Creating AnIML does NOT mean "starting over."
- AnIML should be built on existing ASTM, IUPAC, instrument vendor, and LIMS-developer efforts to define common data dictionaries.
- Once the schemas for AnIML are in place, straight-forward translators can be written to bridge current datasets to the new standard.
- AnIML should be developed in a way that makes it extensible to multiple techniques, yet avoids duplication of effort and dictionary entries.

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Key Features of AnIML

- Extensible
- Can Accommodate ANY Type of Data
- Validateable
- Traceable through Audit Trails
- Verifiable Using Digital Signatures

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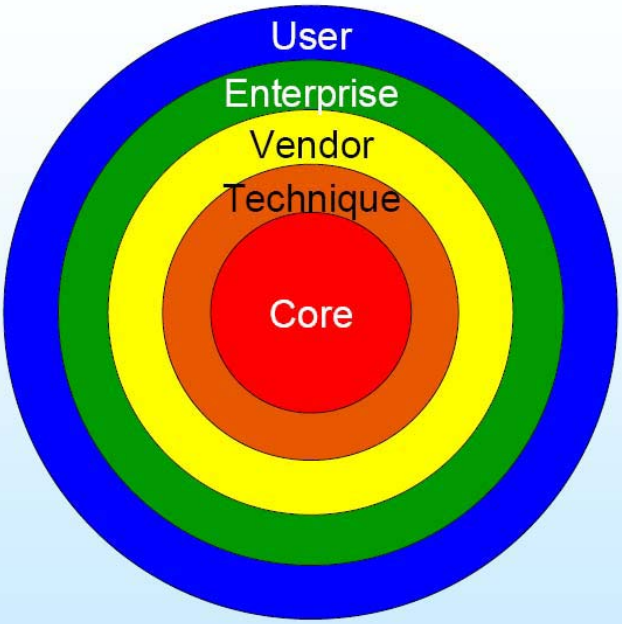
AnIML Conceptual Model



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AnIML Components

- AnIML Core Schema
  - One Schema
  - Maintained by ASTM E13.15
- AnIML Technique Schema
  - One Schema
  - Maintained by ASTM E13.15
- AnIML Base Technique Documents
  - One Instance Document per Technique
  - Maintained by ASTM E13 or Appropriate Domain Expert Organization
- AnIML Extended Technique Documents
  - One Instance Document per Technique Created from the Appropriate Base Technique Document
  - Maintained by Vendor, Organization, User, or Whoever Extends the Technique
- AnIML Result Data Files

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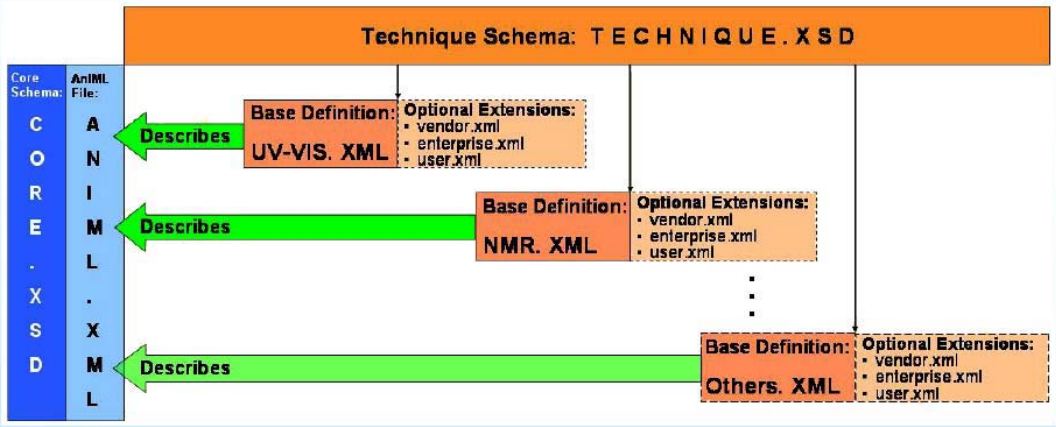
AnIML Components



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Considerations for Terms & Concepts in the Core

- Is the term/concept shared by most spectroscopy and chromatography techniques?
- Is the term/concept used in most datasets collected by most spectroscopy and chromatography techniques?
- Items that software needs to "understand" must be fundamental elements.
- Items that software only need for display and/or reporting can be more generically represented.
- Representations must be consistent with the requirements of FDA's US 21CFR11 and ISO 17025.

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MakeUp of Core

- Sample Information
  - Name
  - Identifier
  - Solvent
- Basic System Information
  - Technique
  - System Name
- Basic QA Information
  - (AnIML Version)
  - Title/Experiment Name
  - Date
  - Time
  - Operator/User/System Name
- Basic Units

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AnIML Core Data Representation

- Variable or Axis-Centric Approach
  - Variables
    - Independent Indexing
    - Independent
    - Dependent
  - Peak Tables
- Data Continuity Types
  - Continuous (Sampled)
  - Discrete
  - Sparse
- Result Data
  - Data Type
    - IEEE 32-Bit Floating Point little endian
    - IEEE 64-Bit Floating Point little endian
  - Data Encoding
    - Base64 Binary

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AnIML Core Data Terminology and Taxonomy

Collection

Page-Set

Page (1 or more)

Vector (sequence of data) (1 or more)

Attribute: independent indexing | non-indexing

Attribute: dependent

Attribute: continuous | discrete | sparse

Parameter (single values applies to entire page) (1 or more)

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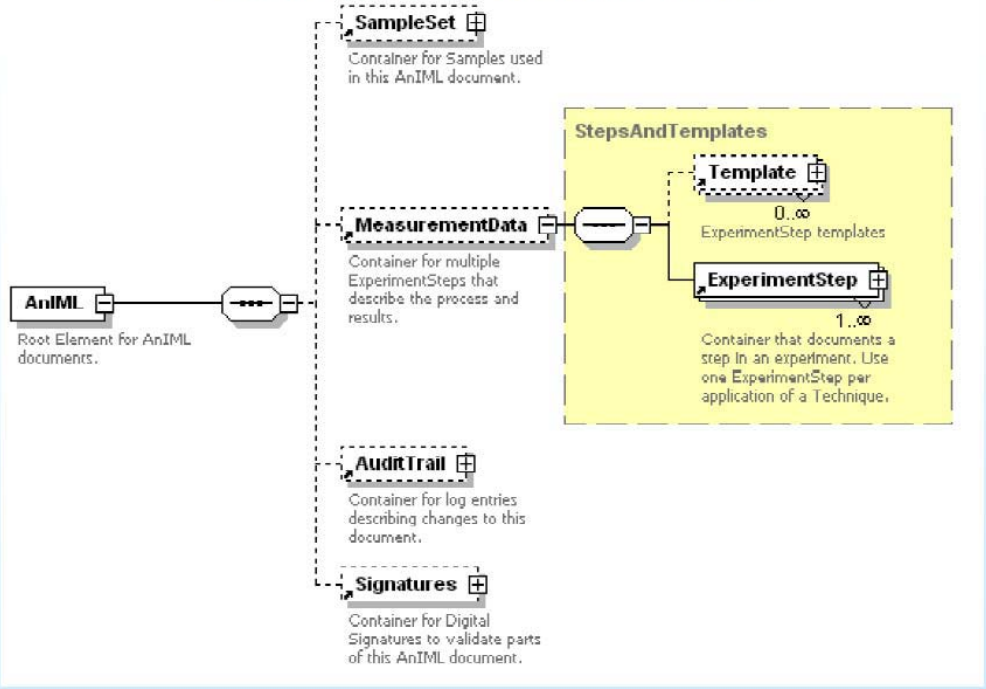
Structure of AnIML Core



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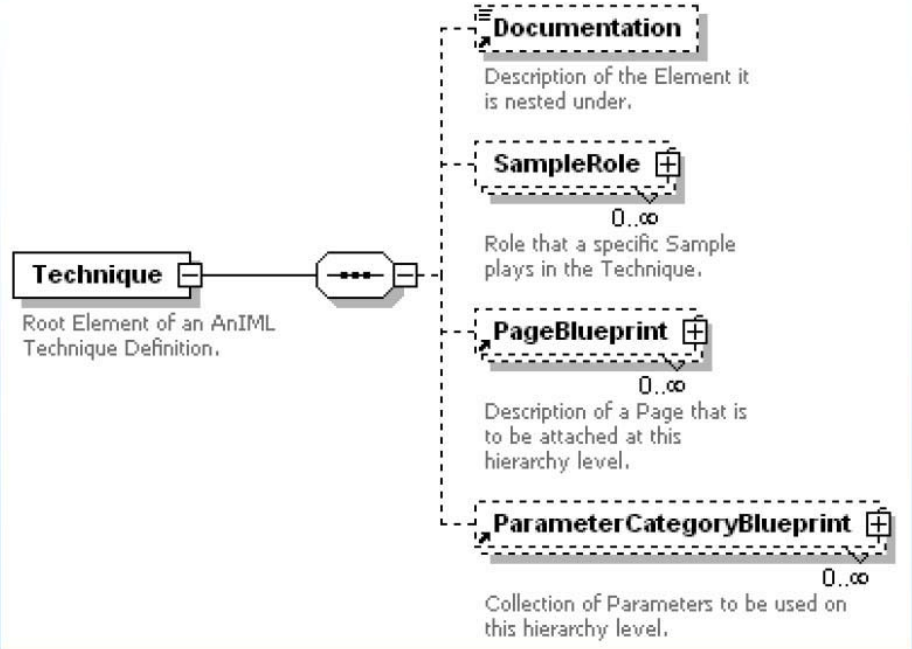
Structure of AnIML Technique Schema



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Phase 1 AnIML Techniques

Must have defined, agreed upon ontology
Must have defined, agreed upon data dictionary

- UV/Vis - SpectroML (& JCAMP-DX)
- NMR - JCAMP-DX
- IR - JCAMP-DX
- MS - Andi
- Chromatography - Andi
- IMS - JCAMP-DX

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AnIML Element Sources

- JCAMP-DX Elements
- Andi Elements
- IUPAC Gold Book Definitions
- ASTM Terminology

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AnIML Naming & Design Rules

- Rules for organizing content
- Rules for generating element names
- Rules permit reuse, minimize duplication
- Rules limit ambiguities of human language
- Rules simplify design of applications
- Rules enhance interoperability
- Rules versus "Guidance"
- Encoding rules to permit automatic validation

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UnitsML

- Most markup languages need to deal with quantities & units
- Why not create a definitive markup language & schema to encode units into XML that can be used with all other markup languages?
- UnitsML allows the unambiguous storage, interchange, & processing of numeric data
- Using UnitsML
  - Incorporation
    - Import
    - Include
  - Referencing
- OASIS Units Markup Language (UnitsML) Technical Committee (coming soon)

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Validating AnIML Files

- Syntactic Validation
  - Checks Document Against Schemas
  - Done by XML-Aware Applications (e.g., web browsers)
    - Format Checking (Matching Tags, etc.)
    - Element Completeness
    - Data Type Checking
- Bounds/Limits Checking
  - Done by Database Front Ends
    - Data ≤ or ≥ a Limiting Value
    - Data Between or Outside of Ranges of Values
- Semantic Validation
  - Checks for Correct Unit Types
  - Checks for Inclusion or Exclusion of Values in Sets
  - Checks for "Appropriateness"
- NIST AnIML *Semantic Validator* Program

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Creating, Modifying, and Extending AnIML Technique Documents

- Requirements:
  - Domain Expertise
  - XML Expertise
- Problem: The requirements seem to be nearly mutually exclusive.
- Solution: The WICIL/NIST *Technique Creator* Program
  - Utilizes the AnIML Core Schema, AnIML Technique Schema, and AnIML Base Technique Documents
  - Provides Graphic Visualization of Technique Document Structure
  - Provides Step-by-Step Editing Guidance
  - Creates the XML Code

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WI CIL

E13.15 Deliverables (Software)

- AnIML Core Schema
- AnIML Technique Schema
- AnIML Technique Definition Documents for:
  - UV/Vis
  - IR
  - NMR
  - Mass Spec
  - Chromatography
  - IMS
- AnIML File Validator
- Generic AnIML Viewer
- AnIML Example Files

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E13.15 Deliverables (Documentation)

- AnIML Core Standard
- AnIML Core User Guide
- AnIML Technique Standard
- AnIML Technique User Guide
- Naming and Design Rules for the AnIML Core
- Naming and Design Rules for AnIML Techniques
- AnIML Technique Definition Documents for:
  - UV/Vis
  - IR
  - NMR
  - Mass Spec
  - Chromatography
  - IMS

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FAQs

- What if we don't get it right the first time?
- What happens when more "definitive" schemas appear?
- We/I don't like the definitions in the lower levels.
- What if new extensions of the technique emerge, new techniques are invented, or techniques are "hyphenated?"
- Can XML handle my variable temperature, pH-gradient, LC-MS-MS-MS/PDA/NMR data?
- Since XML is text, how can data tampering be avoided?
- What do we do with our bazillions of JCAMP (or ANDI or…) spectra?
- Is XML the ultimate solution?

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More Information

- XML
  - http://www.w3c.org
  - http://www.xml.org
  - http://www.xml.com
  - http://www.xmlfiles.com
- SpectroML
  - ftp://caals.nist.gov/pub/download/spectroml
  - http://www.xml.org…registry...schemas DTDs…chemistry
- GAML
  - http://www.xml.org…registry ...schemas DTDs …chemistry
- ANIML
  - http://animl.sourceforge.net
  - http://www.iupac.org/standing/cpep.html

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Acknowledgements

- NIST Systems Integration for Manufacturing Applications (SIMA) Program
- SpectroML
  - Professor Reinhold Schäfer - Fachhochschule Wiesbaden
  - Alexander Rühl - Definition, DTD, & Schema
  - Martin Peschke - Applications, Applets, C++ & Java APIs
  - Aykut Arslan - Instrument-to-SpectroML Applications
  - Anh Dao Nguyen - SpectroML-to-Database Application
- GAML
  - James Duckworth - Thermo Electron Corporation

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Acknowledgements

- ANIML
  - Burkhard Schäfer - BSS&N - AnIML Core & Technique Schemas
  - Dominik Pötz - SAP, AG - AnIML Core & Technique Schemas, AnIML Validator, & Technique Creator
  - Maren Fiege - Waters Informatics - AnIML Technique Definition Base Documents
  - Tony Davies - Waters Informatics - Chair, IUPAC SubCommittee on Electronic Data Standards
  - David Martinsen - American Chemical Society - E13.15 Secretary
  - Anh Dao Nguyen - AnIML Example Data Files, Technique Base Documents for UV/Vis and IR, & Generic AnIML Viewer
  - Peter Linstrom - NIST
  - Mark Bean - GlaxoSmithKline
  - Bob McDonald - JCAMP-DX
  - Ronny Jopp & Alexander Roth - Incorporating UnitsML & NDRs for AnIML

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Long Term Storage of Chromatographic Data

Dale O'Neill
Agilent Technologies, 6612 Owens Dr., Pleasanton, CA 94588

INTRODUCTION

Imagine you are in a court room and are facing litigation. The court rules for the opposing party, saying that you are to produce records for the last 20 years of data. In the past, companies that have found themselves in this predicament have spent millions of dollars extracting information from old tapes. Others extracted information only to have their findings rejected because they did not understand the difference between an electronic file and electronic data. If a court demands records and you spend hours retrieving, printing, and reviewing documents, and then turn this over to a court, a savvy lawyer might ask, "What about the hidden data?" He might add, either this company is incompetent or they are hiding something. Your company might complain that to go back and retrieve the data again is costly and burdensome, but the courts will insist it is your data, you organized it that way, and therefore it is your responsibility to collect it and turn it over to the court.

Since over 50% of data is not printed, lawyers on both sides must be able to look into the computer, and you are responsible for retrieving that data and giving it to the courts or regulators. If you have not taken care to properly preserve the data, you will be forced to hire Information Technology specialist, software developers, and data reviewers to extract this information for you. This could be an economic hardship on the company.

Whether it is litigation, or to validate HIPAA, Sarbanes-Oxley, or FDA's 21 CFR Part 11 compliance, the need for data preservation is important. Even if you are not concerned at this time about data preservation and litigation, your customers are, and they will in the future come and ask you to be part of a solution.

Data Preservation is important. It covers Electronic Discovery, Record management, Application and Data Life Cycle, Maintenance, and Migratory patterns. My focus is on Application and Data Life Cycle and how this contributes to the solution of data preservation.

MORE DATA

According to a report by UC Berkley's School of Information Management and Systems, over the next several years more data will be created than in the previous 300 years combined.

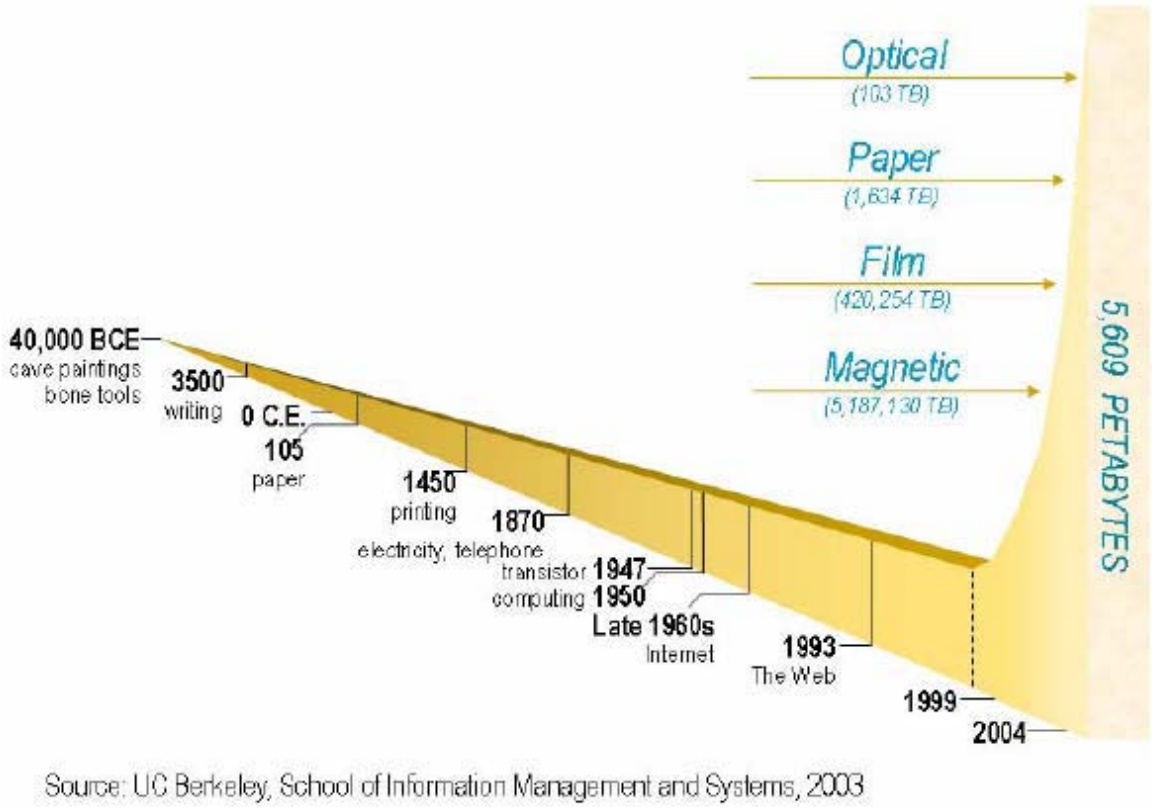


Figure 1

DIFFERENT SOURCES AND DATA TYPES

This data is in various proprietary formats of which some is well structured and others not structured. Some data is stored on disks and others in databases.

RETENTION PERIODS

Because of this mass amount of data and the many proprietary formats, regulations are now surfacing requiring companies to make their data retrievable for the next 10 to 30 years. Some SOP's require the data to be accessible for up to the next 100 years.

This has created many headaches in the industry. With many vendors continuing to create new applications and new data formats while at the same time not given adequate support for old applications and old data formats, the problem will only continue to grow.

APPLICATION LIFE CYCLES

When a new need arises, applications are created and released. Shortly after release bug fixes are made and service packs distributed. Next, enhancements are made in minor revisions. And then the application peaks and a new OS is in sight. New and wonderful technology is promoted, a new compiler is made, and shortly therein the old application has started to be forgotten.

But what happens to all this data that has just been created from this old application? Do we archive or delete it? Where is the old application and is it still being supported by the creating

company? Will the new application be able to import the old data? Can another application import this data? How easy or difficult is it to import this data? Where is our retention policy manual and can anyone understand it?

THE NEED FOR TECHNOLOGY NEUTRAL FORMAT (TNF)

Critical data must be preserved in its entirety. Partial data like electronic paper is not good enough. The data must be "brought forward" and useable for viewing and analysis. This means it must be OS independent and outlive the original application. It must be human readable, that is, not in binary or proprietary format.

THE PROBLEMS WITH MULTIPLE TNF FORMATS

There are current applications meeting some of these requirements. They create a standard that is OS independent, and can be human readable, and can even be imported into the next version of the software. And of course it is the best format because "we did it and we know best, as our sales people have already pointed this out to you".

Unfortunately, this happens all too often in the technology world and the side affects are costly. These proprietary formats have little or no interoperability. Multiple viewers and analysis tools must be created and supported. Proliferation of yet another format is created and sometime in the future this data will have to be imported/exported along with the other proprietary formats.

THE ADVANTAGES OF A STANDARDIZED FORMAT

On the other hand, when using a standard format, the exchange of data is made tremendously easier. You don't have to send a request to engineering to write a converter. There is a consistent and well-known architecture. All the vendors you could say talk the same language. Tools can be used and designed to work across versions. Generic tool sets can now be made available and used. This would be equivalent to email. There are many email applications available, but the standard for sharing email is well defined. How these applications work are proprietary, but the data is well described so all can view, reply, and exchange information. If vendor X stops making his email application, there are many other applications that will continue to support and maintain your email capability.

AnIML TO THE RESCUE

To help solve these problems Analytical Information Markup Language called AnIML has been developed. AnIML is an XML standard for analytical chemistry data. It is the collaborative effort between many groups and individuals and is sanctioned by the ASTM.

AnIML is a standard format that is a structured text file using xml technologies. AnIML is generic and not vendor specific. You can view AnIML with any text editor, like Notepad. AnIML is all-inclusive. Every bit of data from an entire experiment can be represented and stored in an AnIML file.

MAPPING DATA INTO AnIML

To begin using AnIML you need to start mapping your data. To do this you need to start educating yourself on the following two topics, AnIML Core Schema and AnIML Technique Documents.

AnIML Core Schema

The AnIML core schema is the heart of AnIML, and ultimately defines all structure and data types found in an AnIML file.

AnIML Technique Documents

AnIML technique documents are schemas that define a particular analytical technique. A technique is similar to describing a type of automobile such as a truck, bus, or passenger vehicle. All these vehicles work off a core premise of an engine, wheels, seats, mirrors, etc. But where you place these items in the different vehicles is the "technique". A technique specifies the type of AnIML document you are creating.

For example, if you were to map Peak Position and Peak Height into AnIML, several locations would be acceptable to the AnIML schema. The figure below shows the data being placed in either a Vector or Parameter Category Set. So the question begs, "Which one is correct," or "Where should I place my Chromatography data?"

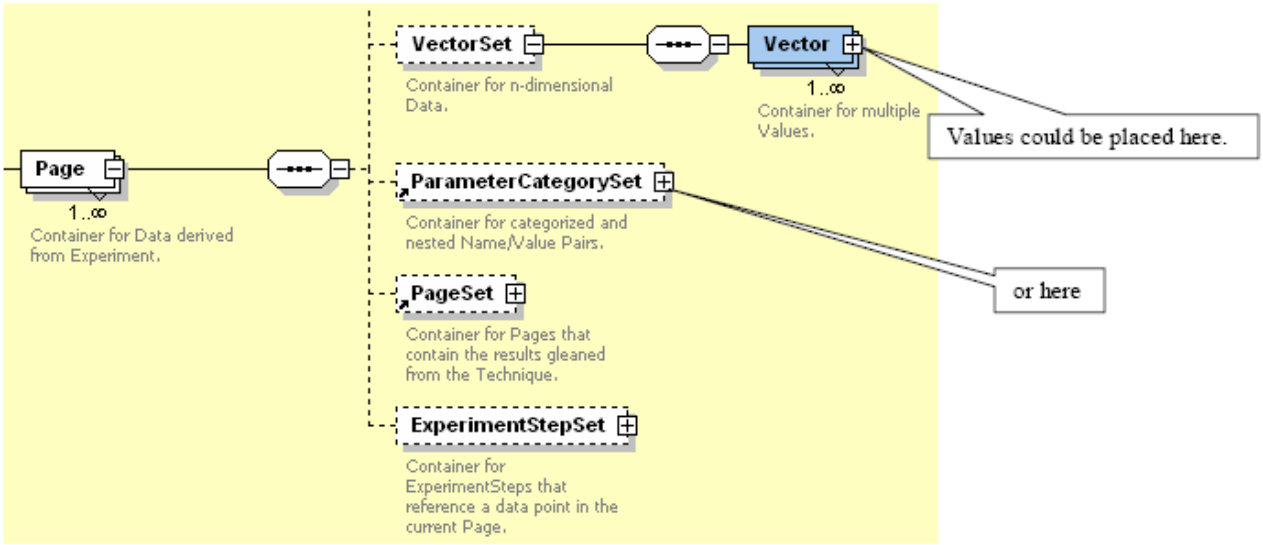


Figure 2: Location of Values without Technique

The answer is found in the Technique document. The Technique document for Chromatography data tells us to place these items inside a Vector and to call them PeakPosition and PeakHeight.

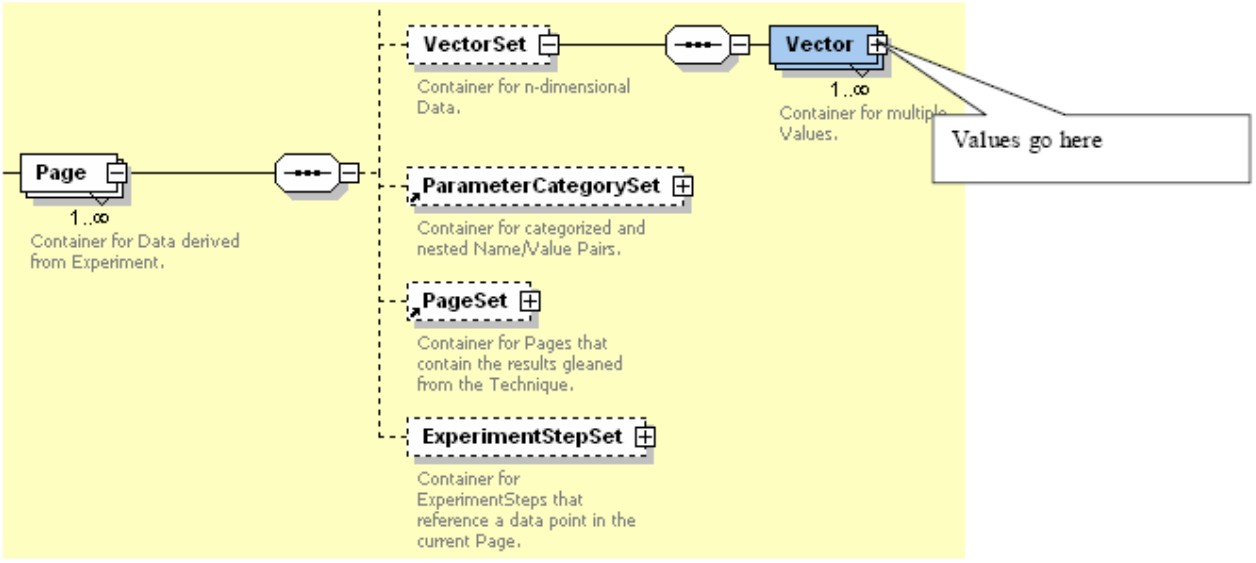


Figure 3: Location of Values Based on Technique

CUSTOMIZABLE ARCHITECTURE

Technique documents cover common values such as PeakNumber, PeakPosition, PeakArea, etc. So what do you do with custom data system values such as Area to Height ratio or Peak Integration Events?

The core schema of AnIML provides for storage of custom data through a concept called ParameterCategorySets. The data stored here is still structured and can be viewed by generic viewers. Below is a generic viewer displaying Custom Results. Although the viewer does not understand custom data, it does understand how to display an AnIML CustomParameterCategorySet.

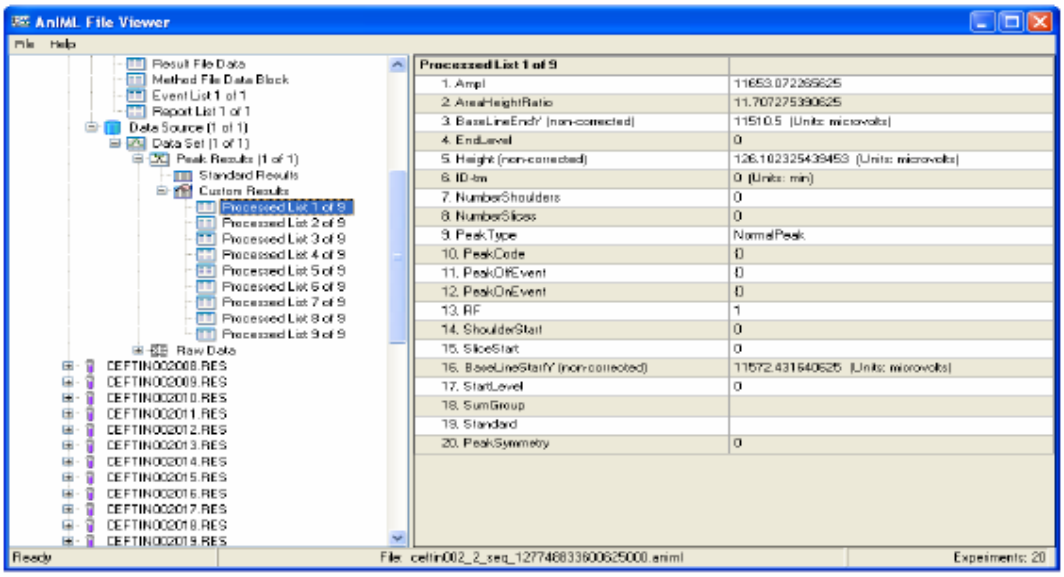


Figure 4: TNF Viewer

LARGE AnIML FILES

It should also be noted that a typical Chromatograph AnIML file can easily contain 50,000 plus lines of text. These lines include such information as:

- General File Information
- Method Configuration
- Instrument Configuration
- Injector Configuration
- Calibration Information
- Raw Data Results
- Peak Results
- Revision Information
- Other Data

Developers need to be aware of the size requirements, and design tools/viewers for speed from the ground up.

BEST PROGRAMMING PRACTICES

Encapsulate Logic to Write Sections of the AnIML File into Object Classes

AnIML core is made up of defined structures/objects such as ParamaterCategorySets, PageSets, Pages, Templates, etc. Creating these known objects encourages code reuse and makes enhancements easy.

Maintain a Level of Indirection between Source Data and the AnIML File

When maintaining a level of indirection between source data and the AnIML file you put yourself in a position to handle future changes. If a new feature and/or version of the AnIML schema is released, changes are easily accommodated.

Tools, Applications, and Viewers Should Operate on the Indirect Data

Tools, Applications, and Viewers, created should operate on the indirect data. When changes occur upstream, these applications will continue to work unmodified, once the intermediate object classes are changed.

SUMMARY

It is important that we do not leave key data in irreconcilable formats. Saving or storing data might seem like a simple act. But how will today's data appear to those in the future. We need to 'future-proof' today's digital data so that it can be regenerated in the computer applications of tomorrow.

Analytical Instrument Markup Language (AnIML)

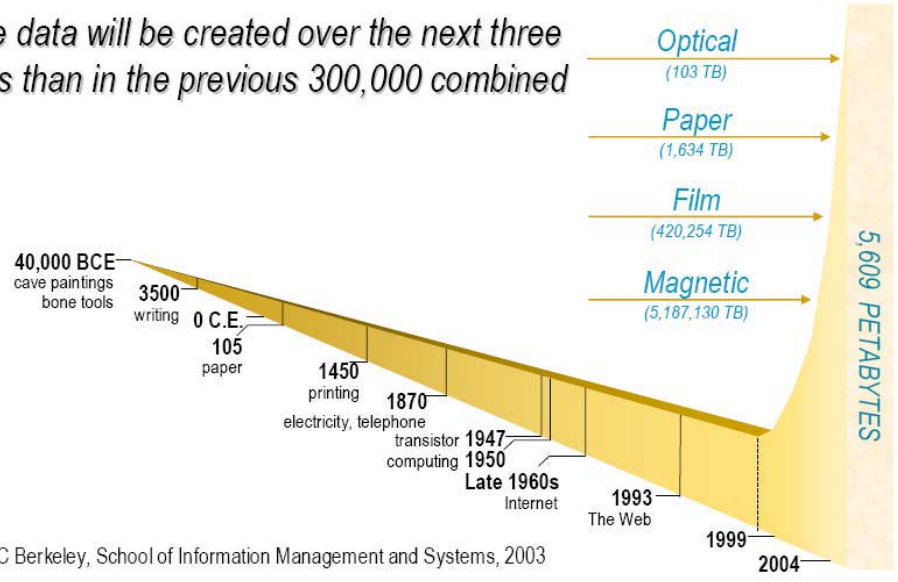
Long Term Storage of Chromatographic Data...

AnIML, TNF, Viewers, and Plenty of Challenges!

Dale O'Neill
Agilent Technologies

More and more data…

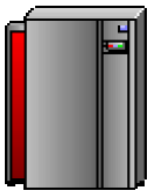
More data will be created over the next three years than in the previous 300,000 combined



Source: UC Berkeley, School of Information Management and Systems, 2003

Different sources and types of data…

Files



Databases

Structured Data

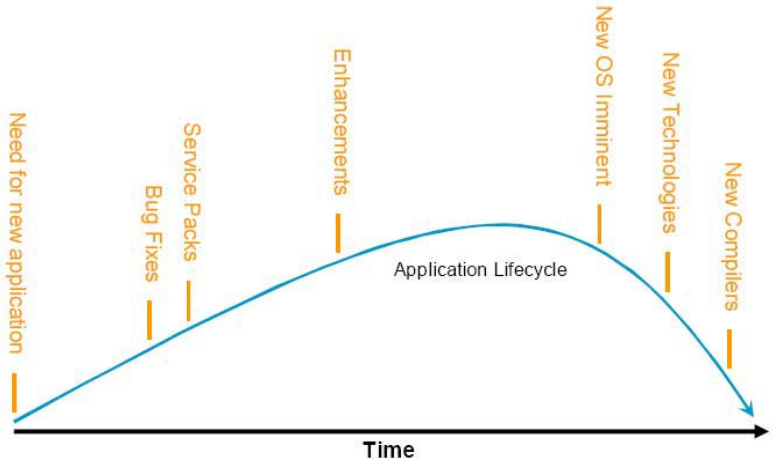
Unstructured Data

Retention periods…

- **Regulations**
  - 10, 20, 30 years
- **SOPs**
  - 40, 50… sometimes upwards of 100 years!

Application lifecycles

All applications progress through a natural lifecycle.



The need for Technology Neutral File (TNF) formats

Critical data must:

- **Be preserved in its entirety**
- **Be OS independent**
- **Outlive the creating application**
- **Must be human readable (not binary or proprietary formats)**
- **Must be usable today (viewing and analysis)**

Structured Text Files

The problems with multiple TNF formats

- Little or no interoperability
- Must create multiple viewing and analysis tools
- Proliferation of more formats
- Maintenance and versioning nightmare for developers
- New applications must support all previous formats
- "Our format is best" syndrome

The advantages of a standardized format

- Easy exchange of data between applications
- Consistent and well known architecture
- Tools can be designed to work across versions
- Generic tools can be developed and shared
- Shared vendor support for standard format
- Format will be maintained and supported, even if vendors come and go

AnIML to the rescue

- AnIML is a standardized file format
- AnIML is a structured text file, using XML technology
- AnIML is generic and is not vendor specific
- AnIML is human readable
- AnIML is all-inclusive. Every bit of data from an entire experiment can be represented and stored in an AnIML file
- AnIML is flexible, while still predictable
- Data in an AnIML file can be tightly constrained for any given analytical technique

Mapping data to AnIML

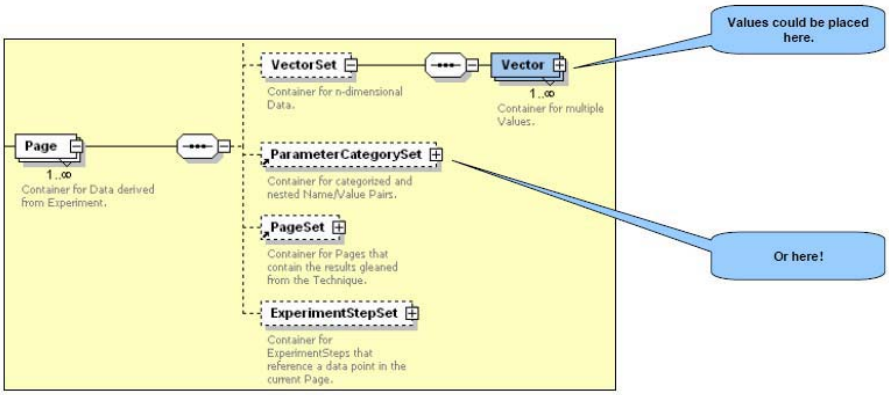
Application developers can begin to map analytical data into AnIML by educating themselves on the following topics:

- **AnIML Core Schema**
  - This schema is the heart of AnIML, and ultimately defines the structure for all data in AnIML XML files
- **AnIML Technique Documents**
  - These schemas define the rules for your structured data, given a particular analytical technique

Mapping data to AnIML

Example

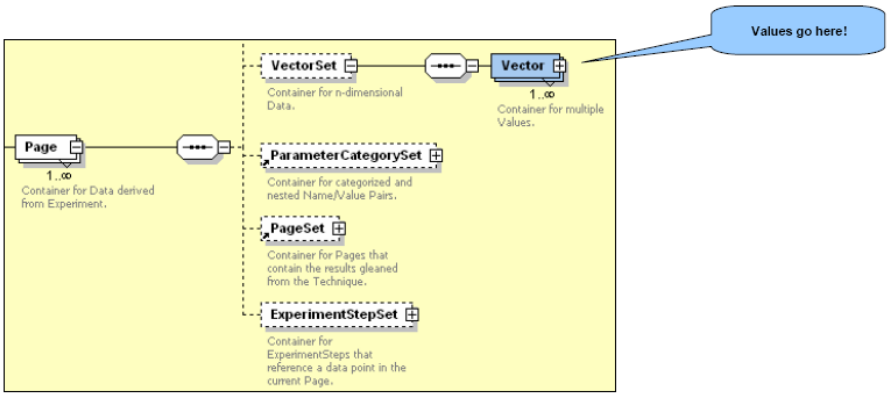
- **Mapping Position of Peak and Height of Peak into the AnIML schema**
- **Without a technique document, where do we put these items, and what are they called?**



Mapping data to AnIML

Example

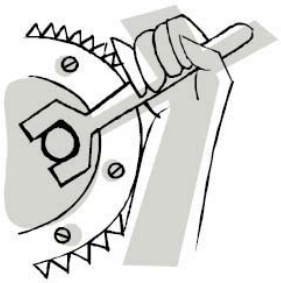
- **The technique document tells us to put these items inside of a Vector, and call them PeakPosition and PeakHeight, respectively**



Customizable Architecture

Technique documents cover common values only

Peak Number
Peak Position
Peak Height
Peak Width
Peak Area
Peak Amount
etc.



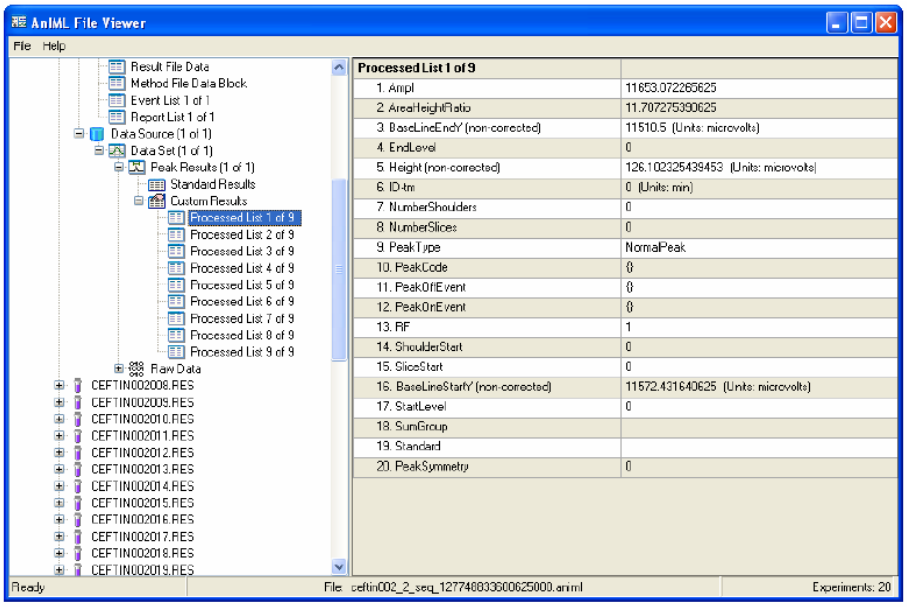
What to do with custom data system values?

Area to Height Ratio
Number of Shoulders
Peak Integration Events
etc.

Answer…

- **The core schema provides for storage of custom data through a concept called ParameterCategorySets**
- **The data is still structured, and can be discovered and viewed by generic viewers**

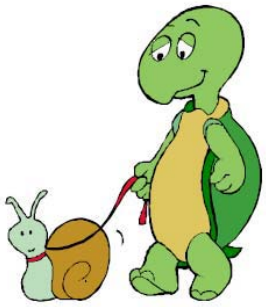
Customizable Architecture



A typical AnIML file can be quite LARGE

A typical Chromatograph AnIML file can easily be 50,000+ lines of text. Includes items such as:

- **General file information**
- **Method configuration**
- **Instrument configuration**
- **Injector configuration**
- **Calibration information**
- **Raw data results**
- **Peak results**
- **Revision information**
- **etc.**



Developers need to be aware of the size requirements, and design tools/viewers for speed from the ground up.

Best programming practices

- **Encapsulate logic to write sections of the AnIML file into object classes**
  - Encourages code reuse, and allows bugs to be fixed in one place
  - Enhancements and changes are easy to make
- **Maintain a level of indirection between source data and the AnIML file**
  - If new features and/or versions of the AnIML schema are released, changes are easily accommodated

- **Tools, applications, viewers should operate on the indirect data**
  - When changes occur upstream, the tools will continue to work unmodified, once the intermediate object classes are changed

Demo

- View real AnIML XML file
- View same AnIML file in Agilent's AnIML File Viewer

Summary

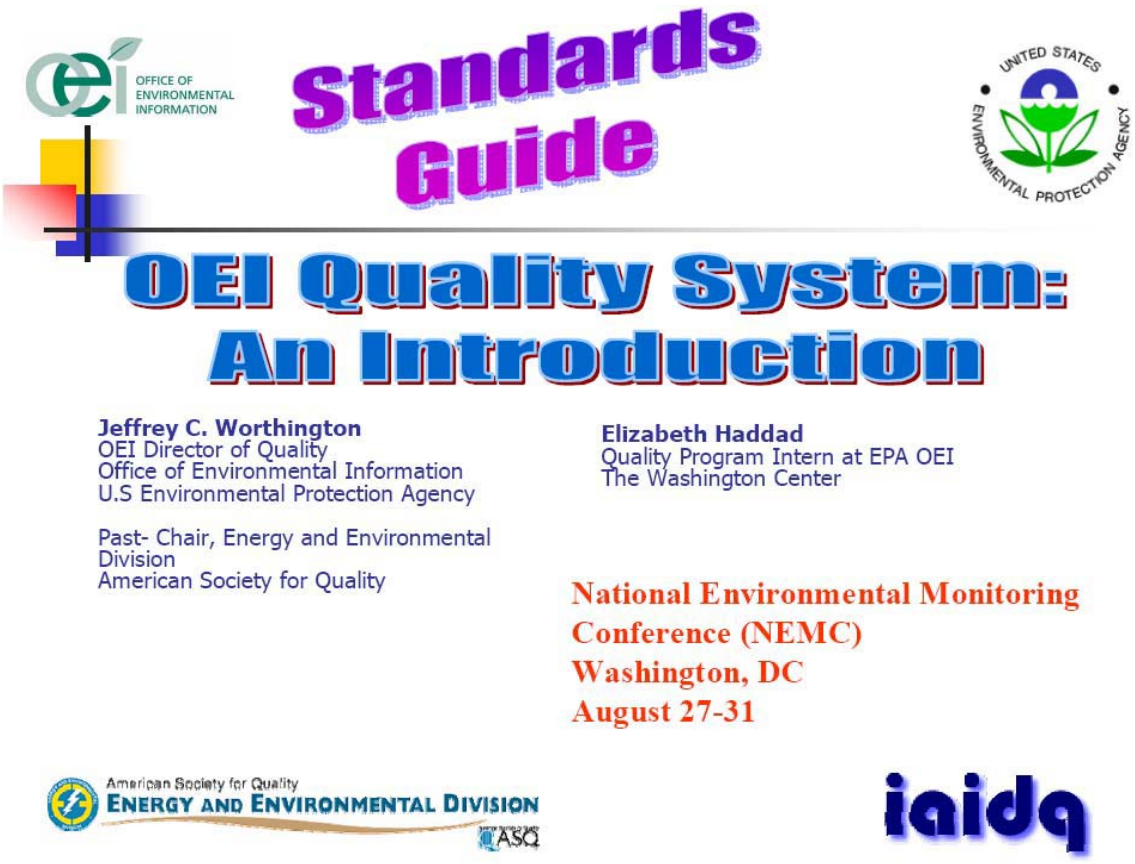
- Massive amounts of data are being generated
- Much of this data must be kept for 30+ years
- Applications retire, but the data must live on, in a TNF format
- AnIML is being created by the ASTM subcommittee E13.15, and is the standard for TNF representations of analytical data
- AnIML is a highly structured, but flexible file format
- Tools, applications, and viewers are already being generated around AnIML

Questions

DEVELOPING AN INTRANET-BASED QUALITY MANAGEMENT SYSTEM TO INCORPORATE MEASUREMENT AND REPORTING

Haddad, Elizabeth – United States Environmental Protection Agency; Worthington, Jeffrey – United States Environmental Protection Agency; Policy and Program Development Staff – U.S. Office of Environmental Information

Quality planning has focused primarily on outputs for many quality management systems resulting in quality documents such as management plans, project plans, assessment reports, and the like. Placing the quality system in an electronic application allows the quality manager and data developer to incorporate the reporting function into the on-site processes. This approach provides for increased manager interaction and encourages the development and use of measurements of the performance of the quality system AND through the quality system, measurements of performance of the enterprise operations. The EPA Office of Environmental Information recently developed their quality system as an intranet web site and is using this approach to manage and report quality for the office. This presentation reviews the advantages of the approach, demonstrates how the OEI quality system is constructed in an electronic environment, and demonstrates how measurements are incorporated into the system.



Jeffrey Worthington- BIO

- **Director of Quality for the USEPA Office of Environmental Information**. Jeff served as the Director of Quality USEPA ORD National Risk Management Research Laboratory (NRMRL) and as the Director of Quality Assurance for TechLaw, Inc. He is an American Society for Quality (ASQ) Certified Quality Manager and ASQ Certified Quality Auditor. Jeff, Senior ASQ member, founding member of the Education Division, is the Past-Chair of the ASQ Energy and Environment Division and participates on the ASQ Division Affairs Council. He is a founding member and past Director for the recently established International Association for Information and Data Quality (IAIDQ). Jeff served as Editorial Board member for Quality Assurance, Science, and the Law, the Journal of Environmental Forensics, Environmental Laboratory magazine, and Environmental Testing and Analysis magazine.

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Elizabeth Haddad - BIO

Elizabeth Haddad is a Quality Program and Regulatory Program intern for The Washington Center. Elizabeth is assigned to the USEPA Office of Environmental Information, Office of Planning, Resources, and Outreach, Policy and Program Development Staff. In her short tenure as an intern, Elizabeth has participated in developing the innovative and interactive web-based OEI quality system, supports quality and information policy development, assists in implementing the OEI quality system, and analyzes Agency policy to facilitate potential integration. Elizabeth is a graduate of Tufts University where she double-majored in International Relations and Middle Eastern Studies.

DISCLAIMER

The opinions expressed in this technical presentation are those of the authors and do not necessarily reflect the views of the US EPA or The Washington Center.

Purpose of Presentation

- Describe OEI's newly approved (2/06) Intranet-based Quality Management Plan
- Demonstrate some of its capabilities

What Is OEI's Quality Policy?

OEI will ensure the quality of the OEI products, services, and procedures addressed in this quality system and will meet customer's needs and expectations.

What Are OEI's Quality Principles?

- Principle 1 - Information quality includes that part of CONTENT for which we are responsible, as well as DELIVERY.
- Principle 2 - We define quality for OEI PRODUCTS and SERVICES to include four basic areas.
- Principle 3 - Customer Satisfaction means "Do they respect us? Would they come back to us for products and services?"

What Is a Quality Management Plan (QMP)?

A document that describes an organization's system in terms of its organizational structure, policy and procedures, staff functional responsibilities, lines of authority, and interfaces for those planning, implementing, documenting, and assessing all activities conducted.

Why Does OEI Need a QMP?

- It's required for EPA organizations by Quality Order 5360.1 A2.
- It's a sound business practice that is expected by OEI's internal and external customers.

Why Does OEI Need a *New* QMP?

- All EPA Quality Requirements Documents are valid for a period of five years, and then must be revised/renewed.
- OEI's previous QMP was due to expire in 2006.

OEI QMP 2006-2011: What's New?

- It's on-line (EPA Intranet)!
- It offers interactive features (e.g., a QAPP template)
- It incorporates reporting features on the same site as the Plan

OEI QMP 2006-2011: What's New? (cont.)

- It features annual agreements with OEI Office Directors on program priorities
- It includes information on new topics (e.g., Information Quality Guidelines compliance)

Major Challenges of an On-Line QMP

- Creating it:
  - Existing EPA guidance and practice assumes a stand-alone document
  - "Go back to basics" to reinvent the essence of a QMP
  - Create an integrated (nested) system rather than a collection of pdf files

Major Challenges of an On-Line QMP (cont.)

- Reviewing/approving it:
  - Following links
  - Tracking processes
  - Ensuring completeness
- The EPA Quality Staff did an admirable and thorough job

Key Elements of OEI QMP

- Description
- Tools
- Reports
- Records
- Resources
- Training
- Processes

Pending Quality Policy Changes

- Like every other Agency QMP, this will change due to upcoming broadening of the Agency's quality policy
- We have a head start – this QMP points in the direction the Agency is heading

For More Information

Contact:

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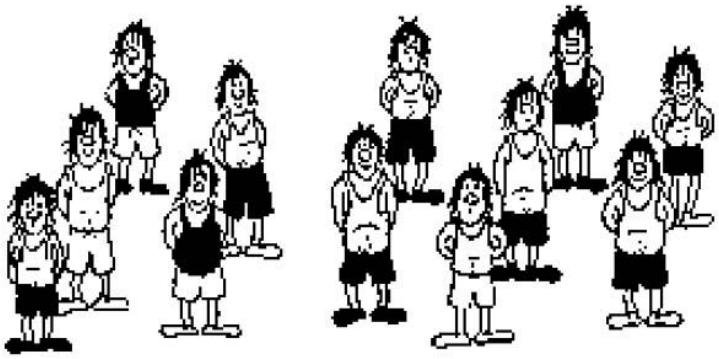
THURSDAY A.M., AUGUST 31, 2006

CONCURRENT SESSIONS

The Performance Approach



12 or 13 people???

How a Concensus Measurement Model Will Improve Overall Environmental Monitoring

Jeffrey C. Worthington
OEI Director of Quality
Office of Environmental Information
U.S Environmental Protection Agency

Past- Chair, Energy and Environmental Division
American Society for Quality

Elizabeth Haddad
Quality Program Intern at EPA OEI
The Washington Center

22nd Annual National Environmental Monitoring Conference
Arlington, VA
August 27-31, 2006

American Society for Quality
ENERGY AND ENVIRONMENTAL DIVISION
ASQ

iaidq

2

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You Can't Manage What You Can't SEE!

You Can't Manage What You Can't SEE!

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You Can't Manage What
You Can't SEE!


You Can't Manage What
You Can't SEE!


You Can't Manage What
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You Can't Manage What
You Can't SEE!

OVERVIEW

You can't manage what you can't see.

I. Introduction: What is needed to move toward a consensus measurement model

II. Basic concepts of information quality

III. Basic concepts of environmental measurement models

IV. EPA needs and perspectives

V. The impact of current EPA quality and information policies and standards

VI. A model for EPA

VII. Next steps

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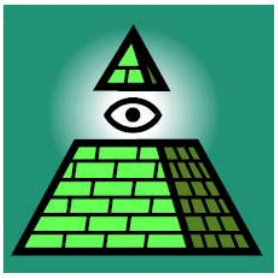
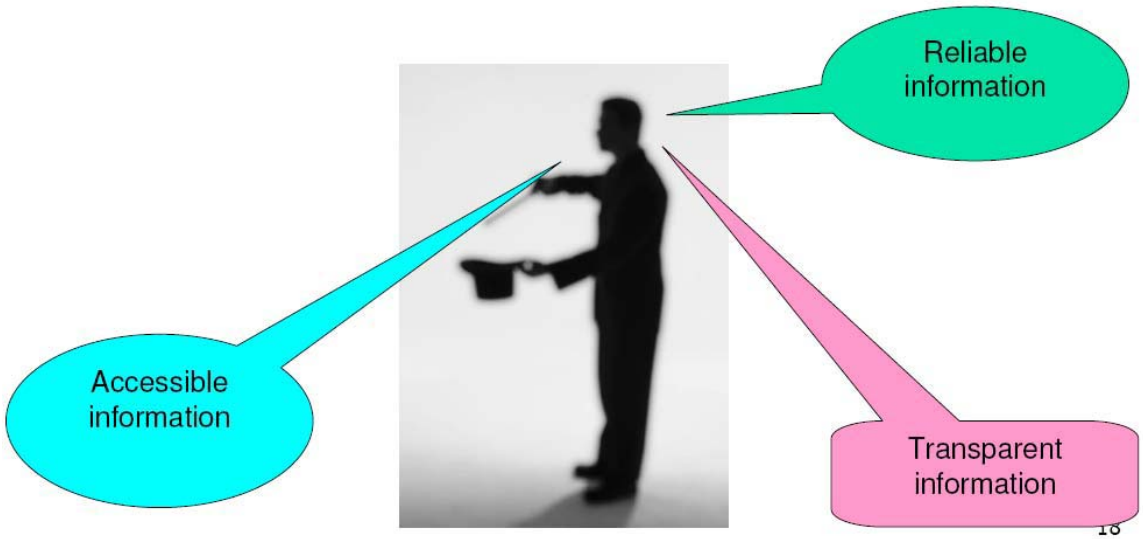
You Can't Manage What You Can't SEE!



"Any sufficiently advanced technology is indistinguishable from magic."
-- Arthur C. Clarke, English physicist and science fiction author, (1917 -)



You Can't Manage What You Can't SEE!

- Eye of Providence – "builders of the past"
- All-Seeing Eye (of Deity) – Masonic reference
- Obverse of Great Seal of the U.S.
  - *Novus Ordo Seclorum* – A new order of the ages
- DaVinci Code movie
- National Treasure movie

Obverse of
The United States
Great Seal

The basic tool for the manipulation of reality is the manipulation of words. If you can control the meaning of words, you can control the people who must use the words.

- Philip K. Dick, American writer, *I Hope I Shall Arrive Soon*, 1986

You Can't Manage What You Can't SEE!

The basic tool for the manipulation of data is……

The basic tool for the manipulation of data is the manipulation of the words that describe the data……

To give environmental measurements value:

The basic tools for capturing, recording, manipulating, using, disseminating, and archiving information are:

- ***Standard procedures and process to develop information content***
- ***Standard procedures and processes to ensure consistent information format, and***
- ***Standard procedures and processes to ensure consistent information functionality.***

If you can control all these processes, you can control and ensure effective use of the information – including environmental measurements.

Why would a national consensus model improve environmental measurements?

Standard content, format, and function of information in environmental measurements leads to improved:

- Consistency
- Completeness
- comparability

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What changes might take place?

- Need to accommodate consensus approach during planning
- Recognition that data and information (environmental measurements) have a lifecycle

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If you don't control the information aspect of your environmental measurements – format, content, and functionality –

Floccinaucinihilipilification of the environmental measurements will occur

OFFICE OF ENVIRONMENTAL INFORMATION

Floccinaucinihilipilification

"estimating something as worthless"

Floccinaucinihilipilification

FLOK-si-NO-si-NY-HIL-i-PIL-i-fi-KY-shuhn

Flocci+nocci+nihili+pili+fication

What is needed to move towards a national consensus model for environmental information measurement?

What is needed?

An understanding of what has changed

EPA before

- Env. Data to support decisions
- A receiver of data
- A provide of data reports
- Flexibility in formats for improved quality

EPA now

- An information resource
- A conduit to data owned by others
- A provide of tools to self-select your own reports
- Flexibility for you access, but not in formats

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What is needed? For consensus

- Standard language
- Recognition of key components
- Agreement on what is important
- Agreement on why it is important and what is its value
- Identification and involvement of stakeholders
- Recognition of challenges and approach to resolve
- Systematic approach to implement AND maintain

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A Standard Approach for:

- Relevant policies
- Procedures
- Data and other standards
- Guidelines
- (increased interoperability between users)

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Does quality come in flavors like ice cream?

- Environmental measurements are a type of information
- Information quality is more than just the environmental measures
- EPA is already actively dealing with the concept of information quality

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EPA already has drivers for information quality in the Federal Government

- General – accountability to the public
- Support the enterprise mission
- Meet required enterprise program statutory specifications
- Federal information quality requirements
- Clinger-Cohen Act (Chief Information Officer Responsibilities)
- President's (electronic government) E-Government Strategy, E-government Act of 2002
- OMB information policies
- Enterprise's information policies

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EXAMPLE

Office of Management and Budget and Information

- Office of Management and Budget
  - Information and Regulatory Affairs
    - Information Policy, E-Gov & IT
      - E-government initiatives
      - Information quality government-wide initiatives
        - Final Information Quality Bulletin on Peer Review (12.16.04)
        - Federal Information Quality Guidelines (12.22.02)
      - IT policy documents
        - M-06-02, Improving Public Access to and Dissemination of Government Information and Using the Federal Enterprise Architecture Model (12.16.05)
        - M-05-23, Improving Information Technology (IT) Project Planning and Execution (08.04.05)
        - OMB Circular A-119: Federal Participation in the Development and use of Voluntary Consensus Standards and in Conformity Assessment Activities (02.10.98)
      - IT spending
      - Computer security
      - Privacy guidance
      - Privacy reference materials
      - Government Paperwork Elimination Act (GPEA)
      - Freedom of Information Reform Act

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M-06-02, Improving Public Access to and Dissemination of Government Information and Using the Federal Enterprise Architecture Model (12.16.05)

3 new requirements

1. Organize and categorize your information for public access, make it searchable across agencies, and describe how you use formal information models to assist your dissemination activities
2. Review the performance and results of your information dissemination program and describe the review in your Information Resources Management (IRM) Strategic Plan
3. Publish you IRM Strategic Plan on your public website

   (if not doing this now, do this by 09.01.06)

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PART 2

M-06-02, Improving Public Access to and Dissemination of Government Information and Using the Federal Enterprise Architecture Model (12.16.05)

Using the Federal Enterprise Architecture Data Reference Model – the DRM can help you to:

1. Identify how information and data are created, maintained, accessed, and used.
2. Define agency data and describe relationships between missions and program performance and information resources to improve the efficiency of mission performance, and
3. Define data and describe relationships among data elements used in the agency's information systems and related information systems of other agencies, State, and local governments and the private sector.

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Basic concepts of information quality

Basic concepts of information quality

Ensure the quality of:

- the real processes (science and technology) before production of information AND
- The quality of the resulting information

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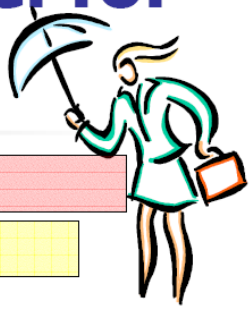
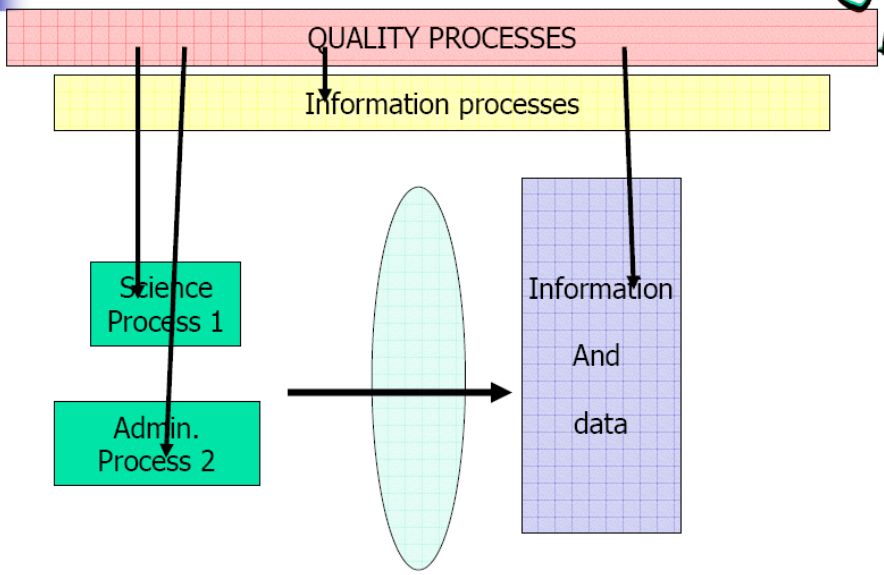
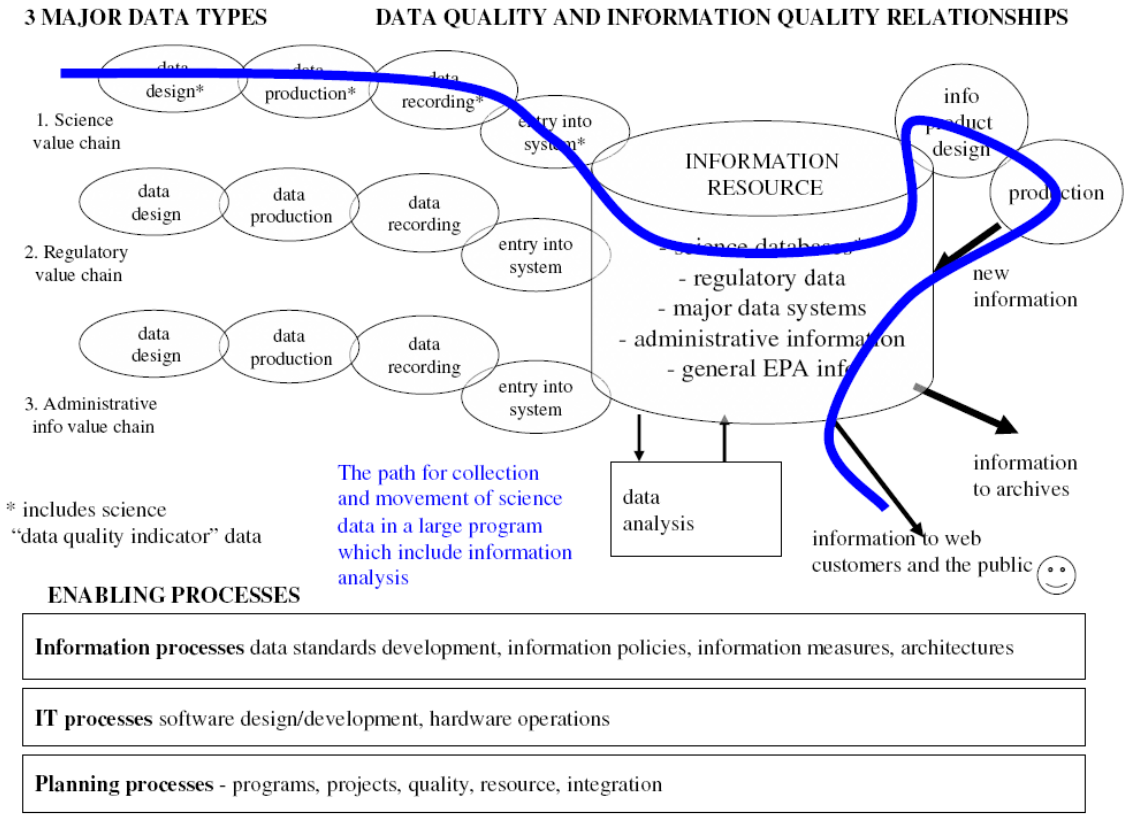
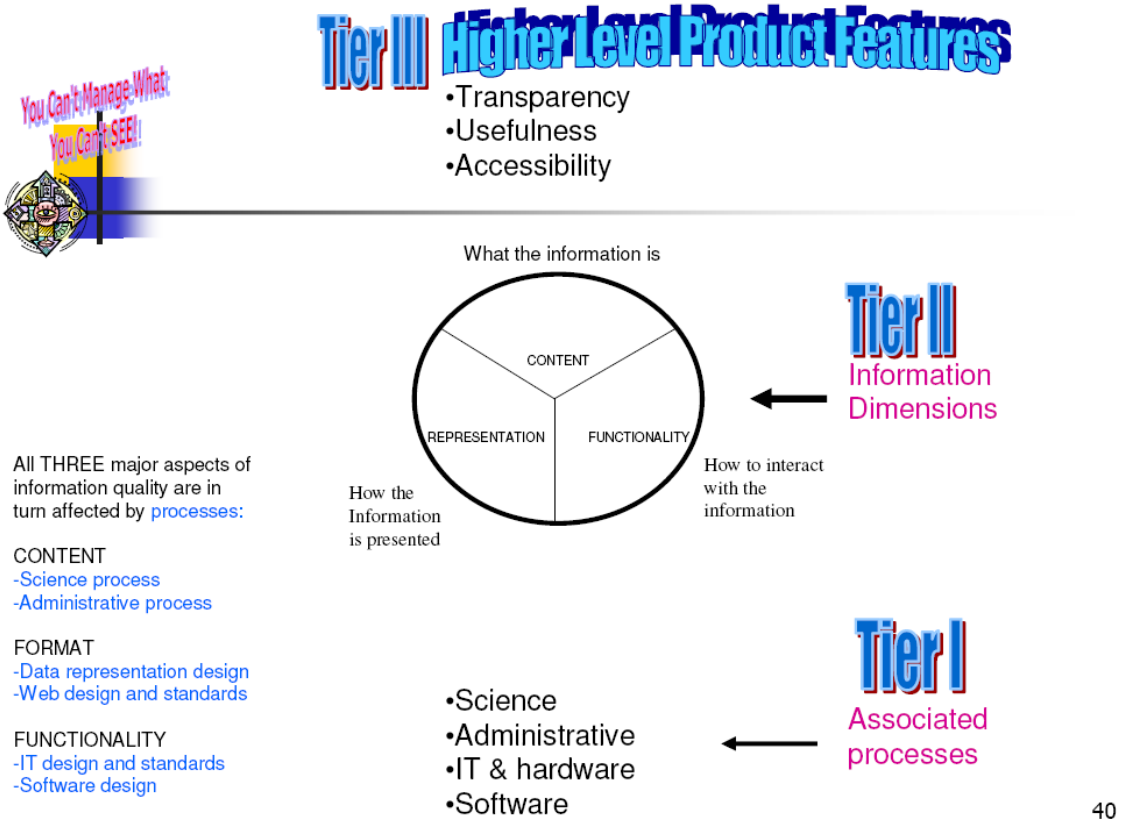
A Heirarchial Model for *QUALITY*





38


3 MAJOR DATA TYPES
DATA QUALITY AND INFORMATION QUALITY RELATIONSHIPS
data design*
data production*
data recording*
entry into system*
1. Science value chain
data design
data production
data recording
entry into system
2. Regulatory value chain
data design
data production
data recording
entry into system
3. Administrative info value chain
INFORMATION RESOURCE
- regulatory data
- major data systems
- administrative information
- general EPA inf
info product design
production
new information
information to archives
information to web customers and the public
data analysis
* includes science "data quality indicator" data
The path for collection and movement of science data in a large program which include information analysis
ENABLING PROCESSES
Information processes data standards development, information policies, information measures, architectures
IT processes software design/development, hardware operations
Planning processes - programs, projects, quality, resource, integration


You Can't Manage What You Can't SEE!
Tier III
Higher Level Product Features
•Transparency
•Usefulness
•Accessibility
What the information is
CONTENT
REPRESENTATION
FUNCTIONALITY
How the Information is presented
How to interact with the information
Tier II
Information Dimensions
All THREE major aspects of information quality are in turn affected by processes:
CONTENT
-Science process
-Administrative process
FORMAT
-Data representation design
-Web design and standards
FUNCTIONALITY
-IT design and standards
-Software design
•Science
•Administrative
•IT & hardware
•Software
Tier I
Associated processes

EPA needs and perspectives

EPA Quality Needs

Traditionally focused on:

- Decisions about the environment
- Measurements of the environment to support those decisions

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EPA Quality Needs - refocused

Areas that also must be addressed:

- EPA serves as a owner of historical information in large data sets
- EPA serves as a pathway to access information and data of others
- EPA serves as a provider on information services that allow citizens to access information and data through "information products" or "information tools."
- EPA must understand data and information needs from the stakeholders perspective

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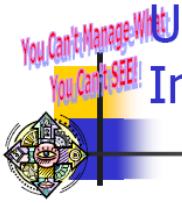
Example Quality Policy



USEPA Office of Environmental Information

1. Information quality includes that part of CONTENT for which we are responsible, as well as DELIVERY.

2. We define quality for OEI PRODUCTS and SERVICES to include 4 basic areas:
   - *Functions: Does it have the functions and features I want?*
   - *Internal Controls: Does it work? Do we have adequate internal controls to avoid errors or defects? Do defects prevent me from using it?*
   - *Customer service: Do customers get the service that they expect, and is it on time?*
   - *Efficiency: Did I effectively use my resources in the process? Are we on time and on budget?*

3. Customer Satisfaction means "Do they respect us? Would they come back to us for products and services?"

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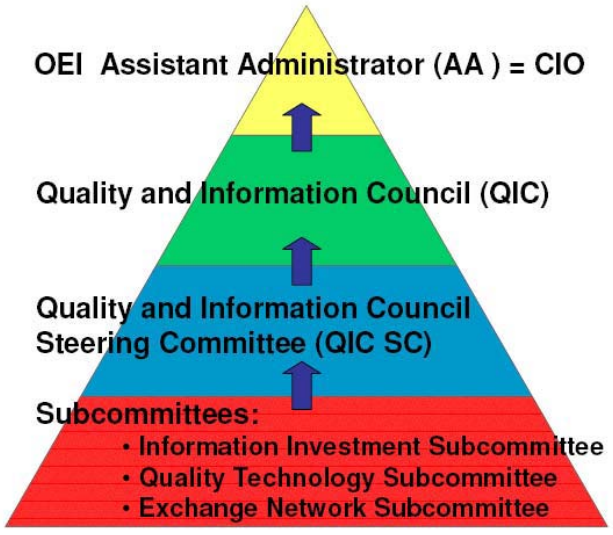
What is EPA's model now for planning and controlling the quality of Agency information?

Information Policy Development Process



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What drives the development of information policies?

- General – E-government information laws and regulations
  - OMB sitewww.estrategy.gov/drilldown.cfm?action=it_policy_documents
  - Chief Information Officers www.cio.gov/index.cfm?function=documents
- EPA Program needs
- Selected EPA IT/IRM Programs (Internet Available)
  - Central Data Exchange
  - EPA Dockets – now within the Federal Documents Management System (FDMS)
  - Environmental Data Registry (EDR)
  - Facility Registry System
  - EPA Geospatial Blueprint
  - Locational Data Improvement (locational data standard)
  - EPA National Records Management Program
  - Privacy Act
  - Quality System
  - System of Registries

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Information Policies

(available on the intranet)

- Information Resources Management (IRM) Policy Manual
- Accessible Electronic and Information Technology
- Policy on limited Personal Use of Government Office Equipment
- Senior Information Officials
- EPA's Forms Management Policy
- National Geospatial Data Policy
- Library Systems Manual
- Vital Records
- Software Management and Piracy Policy
- Locational Data Policy Implementation Guidance
- Chemical Abstract Service Registry Number Standard
- Data Standards for Electronic Transmission of Laboratory Measurement Results
- Enterprise architecture
- Capitol planning
- System lifecycle management
- Facility Identification Data Standard
- Good Automated Laboratory Practices
- Privacy Act Manual
- "Cookies" and Other User Tracking Methods/Waivers
- Children's Privacy and Copyright Issues
- External Links for the EPA Public Access Website
- Use of Public Access Web Servers External to www.epa.gov Web Site
- Web Site Developmental Web Site
- Web Site Management: Standard EPA "Look and Feel"
- Access to Current and Outdated Information on EPA's Web Site
- EPA Information Security Manual
- Information Security for Personal Computers

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Standards

Standards that support information quality

- Management standards
- Quality standards
- Planning standards
- Environmental standards
- Science standards
- Analysis standards
- Records standards
- Laboratory standards
- Information standards
- Data standards
- Web standards
- Objectivity, presentation standards
- Security standards
- Assessment standards

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Type of Information Standards

- Information technology (IT)
  - standard configuration documents – "procedures" to configure IT system
  - technical standards – the "IT roadmap," all approved hardware and software
  - operational directives – "processes" – management, telecommunications, user registrations, timesharing, etc.
- Information content
  - data standards – agreed upon names, definitions, attributes and structures for shared data
  - codes sets – agreed upon standard codes (OH for Ohio)
  - XML tags – agreed uupon tag names to speed web programming

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Information Technology: Standard Configuration Documents

- Microsoft Windows Server 2003 Standard Configuration Document
- AAA Client Connection Configuration Standard
- Lotus Notes USB Drive Configuration and Use Standard Configuration Document

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Information Technology: Technical Standards

EXAMPLES

- Lotus domino
- Oracle
- Coldfusion
- Java
- Geographic Information System

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Information Technology: Operational Directives

EXAMPLES (more than 30 ODs)

- NTSD operational directives manual review
- Transfer of customer accounts among EPA users
- Archiving tapes and data sets
- Computer security incident response
- National Computer Center (NCC) enterprise server (Mainframe) timeshare accounting
- Headquarters service branch weekend accounting

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Information Content:
Data Standards (current)

- Attached Binary Object
- Bibliographic Reference
- Biological Taxonomy
- Chemical Identification
- Compositing Activity
- Contact Information
- Enforcement/Compliance
- Environmental Sampling, Analysis and Results Data Standard - Overview of Component Data Standards
- Environmental Sampling, Analysis and Results: Analysis and Results
- Environmental Sampling, Analysis and Results: Field Activity Data Standard
- Environmental Sampling, Analysis and Results: Monitoring Location
- Environmental Sampling, Analysis and Results: Project
- Equipment
- Facility Site Identification
- Institutional Control
- Latitude/Longitude
- Measure
- Method
- Permitting Information
- Quality Assurance and Quality Control
- Representation of Date and Time
- SIC/NAICS
- Sample Handling
- Tribal Identifier

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Data Standard Example 1

Chemical Identification data standard: consists of a series of "data elements"

NAME	DEFINITION	TYPE	STATUS
Chemical Abstracts Service Registry Number	The unique number assigned by Chemical Abstracts Service (CAS) to a chemical substance	Alphanumeric (9) Mandatory	Standard /final
Chemical Substance Systematic Name	A standard name assigned to a chemical substance	Alphanumeric (2000) Mandatory	Standard /final
EPA Chemical Identifier	The identifier to be created and placed in the SRS for each chemical substance or chemical group in the SRS for which a SAS Registry Number does not exist and cannot be assigned	Alphanumberic (9) Mandatory	Standard /final
EPA Chemical Internal Tracking Number	The unique record number assigned to a chemical substance or a chemical grouping for tracking within EPA systems	Alphanumberic (9) Mandatory	Standard /final
EPA Chemical Registry Name	The name US EPA has selected as the preferred name for a chemical substance	Alphanumberic (9) Mandatory	Standard /final
Chemical Preferred Acronym Name	The name US EPA has selected as the preferred acronym or otherwise abbreviated name in the SRS for a chemical substance, when use of a shortened name in appropriate	Alphanumeric (2000) Mandatory	Standard /final
14 additional data elements follow			

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Information Content: Code Sets

CODE SETS contain permissible values, value meaning names, and value meaning definitions that can be used in applications. They can be associated with EPA data standards, national/international standards, or contain lists of values commonly used by EPA programs.

Code sets help ensure consistency of content quality.

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Code Set Examples

Examples:

- Country names
- County names
- State names
- State codes
- Geometric type codes
- Verification method codes
- Vertical collection method codes
- Vertical collection method names

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Information Content:

XML and XML Tags
Standard Tags

- XML = Extensible Markup Language
- XML tag = the name for a "data element" used for XML programming in web applications
- XML tags are for each data element in a data standard and for other accepted uses

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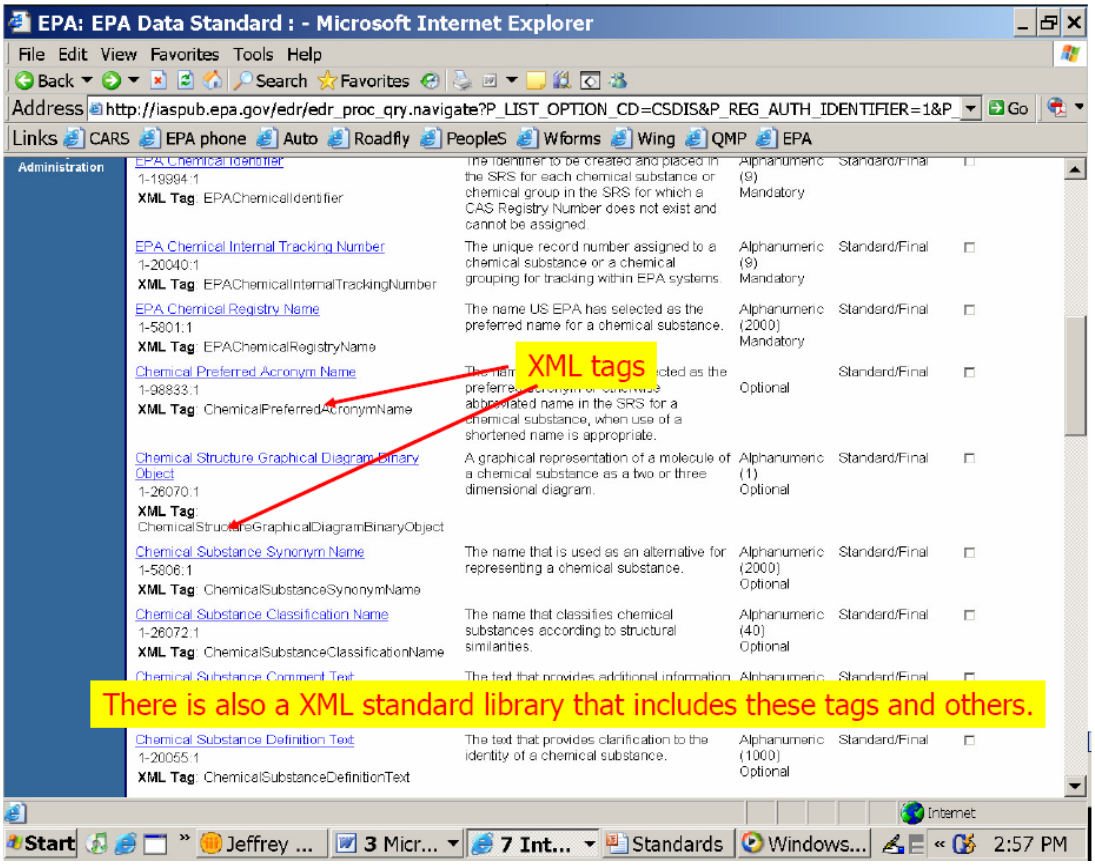

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Does this collection of standards serve now as a national consensus model for environmental measurements?

DISCUSSION

- _____
- _____
- _____

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EPA QUALITY POLICY

- ORDER - Policy and Program Requirements for the Mandatory Agency-wide Quality System (Agency Directive: *EPA Order 5360.1 A2*)
  - MANUAL - EPA Quality Manual for Environmental Progams (Agency Directive: *EPA Manual 5360 A1*)
    - Office-specific Quality Management Plan (QMPs)
      - Contract and Grants Quality Plans
      - Quality Assurance Annual Reports and Work Plans (QAARWPS)

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Re-defining *QUALITY*

Quality addresses all products and services in the following areas:

PROCESSES

- Environmental and related science applications
- Engineering applications associated with environmental applications
- Administrative operations that result in information and data that are considered to be a resource of the organization

INFORMATION TECHNOLOGY

- Hardware reliability and maintainability
- Software design controls
- Configuration and operational conformity

INFORMATION MANAGEMENT

- Database quality
- Information modeling functionality
- Data standards and associated standards conformity

INFORMATION OPERATIONS

- Web operations
- Web standards conformity

GENERAL INFORMATION QUALITY CONSIDERATIONS

- Information quality include both information content and information delivery
- Information quality covers the following 4 areas
  - Information features
  - (reasonable) freedom of defect
  - Customer service
  - Cost efficiency
- Customer satisfaction

National Consensus Model
ENVIRONMENTAL MEASUREMENTS

INTER-RELATED STANDARDS TO ACCOMMODATE CONTENT, FORMAT, AND FUNCTIONALITY ASPECTS OF ENVIRONMENTAL MEASUREMENTS INCLUDING:

CONTENT – for each environmental measurement type

- Library of data standards for environmental measurements (e.g., measurement values, PARCCS)
- Geospatial data standards (done!!)
- Library of data standards for "associated data" (e.g., location, well information, site conditions, etc.)
- Library of data standards for " metadata" (e.g., data descriptors – contained in data standards)
- Data Provenance standards – to describe possible "levels" or methodology to offer some form of data provenance

FORMAT – (PRESENTATION)

- Information standards for presentation formats (e.g., tabular, map)
- Web presentation standards (e.g., transparency objectivity options)
- .....for its intended purpose
- Standard description methods
- Geospatial formatting

INFORMATION FUNCTIONALITY

- Standard for terminology for naming and interacting with environmental measures
- Standard modeling interactions

DATA BASES AND DATA MANAGEMENT

- Standard methodology for database management functions
- Standard methodology for records management for large data collections

National Consensus Model
ENVIRONMENTAL MEASUREMENTS

WILL LEAD TO IMPROVED UNDERSTANDING AND IMPROVED QUALITY OF ENVIRONMENTAL MEASUREMENTS WHICH CAN BE EXPRESSED UNIFORMLY IN TERMS OF THESE IMPORTANT FEATURE

- Completeness
- Consistency
- Correctness
- Accessibility
- Security
- Privacy
- Authenticity
- Objectivity
- Transparency
- Reliability

Resources
Information and Data Quality

- David Loshin
- Larry English, www.infoimpact.com
- Dr. Tom Redman, www.dataqualitysolutions.com
- Frank Dravis, Business Objects
- Dr. Wang, MIT Data Quality Group
- American Society for Quality (ASQ) Information Integrity Group
- International Organization for Information and Data Quality (IAIDQ.org)
- DAMA

66

CONTACT INFORMATION

- Jeffrey Worthington - EPA

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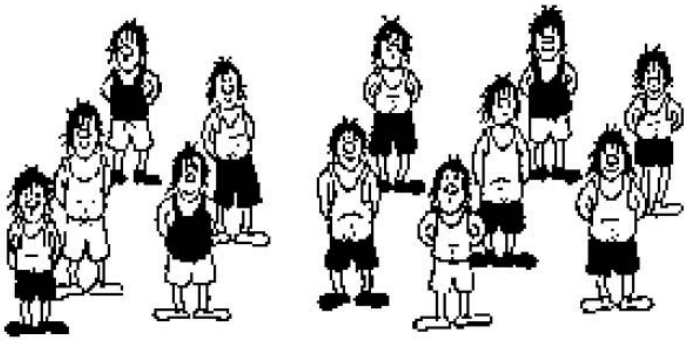


12 or 13 people???

68

IMPROVING THE HEALTH OF ENVIRONMENTAL MONITORING WHEN USING EPA TEST METHODS

Houck, Ronald – Pennsylvania DEP; Parr, Jerry – Catalyst Information Resources; Schrenkel, Carol – Lionville Laboratory, Inc.

Most environmental analyses performed in the US are done using one of the more than 750 test methods published by the US Environmental Protection Agency (EPA) that were developed for trace environmental analyses. An indication of the health of the industry would be to compare the expected performance of these methods to what would be considered a reasonable measure of accuracy. For trace environmental analyses, a measure of good performance is considered to be within 70 to 130 % of the true concentration. Using this measure, many published EPA methods cannot be considered to be healthy. For example, a frequently used method is Method 625, for the determination of semivolatile organics. Of the 64 analytes listed in this method, a recovery of 0% is acceptable for one third of the analytes while a recovery of less than 70% is acceptable for every analyte. To compound this problem, many of these methods were developed many years ago and since that time, new contaminants of concern have been identified. As the methods have not been updated to reflect the additional of new analytes of concern, laboratories are free to use any performance to demonstrate that a method is appropriate.

The accreditation standard developed by the National Environmental Laboratory Accreditation Conference (NELAC) in 2003 has attempted to address this widespread issue by requiring laboratories to demonstrate performance with a method prior to its use and then on an on-going basis continually demonstrate that the method is being used correctly. However, the NELAC standard also allows a 0% recovery to be considered acceptable. In the NELAC program, laboratories are also required to analyze proficiency test (PT) samples. These results are evaluated using well-defined and established criteria, and for many analytes, the acceptance criteria are comparable to those published in EPA methods with the condition that at least a 10% recovery is required. However, the current NELAC PT program cannot always be used to indicate performance because analytes routinely measured in environmental samples are not required to be measured in PT samples. The NELAC program has also compounded this problem in that some state agencies only accredit for analytes listed within a given published method.

A new approach is needed that will ensure that environmental data generated using any test method not only is of "known quality," but that the quality meets a pre-defined level of performance. This presentation will describe some of the problems with the current prescriptive approach in the use of test methods, highlights some of the compounding issues contained in the 2003 NELAC standard, and present some options for a different approach.

Improving the Health of Environmental Monitoring When Using EPA Test Methods

Or All Is Not As It Seems…

Carol Schrenkel, Lionville Laboratory, Inc.
Jerry Parr, Catalyst Information Resources
Steve Arms, Florida Department of Health

Assumptions in the Prescriptive Method Approach

- The methods have been validated and provide acceptable performance
- Laboratory quality control samples monitor the results to ensure acceptable data is being generated
- Laboratory accreditation programs provide an independent check, through PT samples and review of data

Reality 1

- Many EPA methods have not been thoroughly validated and/or do not provide acceptable performance

Method Validation

- If a method indicates an analyte can be determined, experimental data exists to support this statement
- LOD, LOQ, Precision & Bias, Selectivity (NELAC)

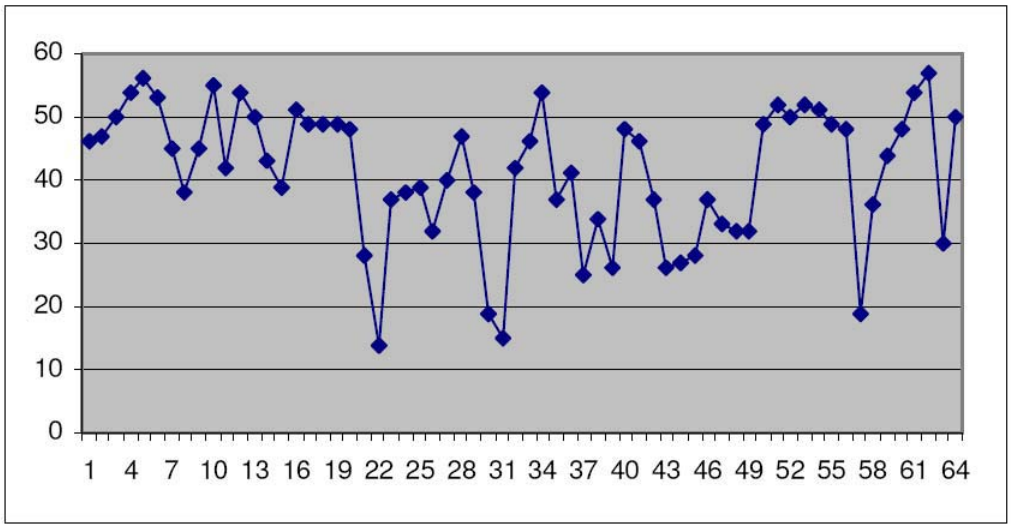
Method 8270

- 240 Analytes
  - "can be determined"
- 136 with footnotes for Method 3520
  - e.g., ND = Not determined
- 64 Analytes with interlaboratory performance data (DOD)
  - 3 "poor performers"
  - 4 "insufficient data"

Acceptable Performance

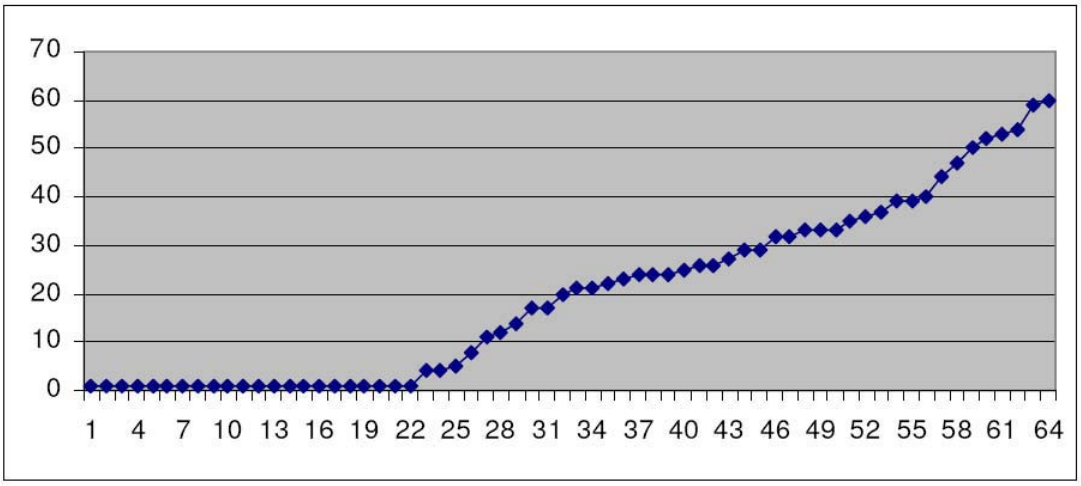
- Mean Recovery of 65-70%
- Mean RSD of 30-35%
- Reason:
  - mean – (2 * SD) = lower QC limit (95% confidence)
  - 65 – (2 * 35) **< 0**

Method 8270 Provides Unacceptable Performance for Every Analyte



Lower LCS Limits Developed by DOD for Analytes in Method 8270

Method 625 Provides Unacceptable Performance for Every Analyte



Lower Acceptance Limits for Analytes in Method 625

Reality 2

- PT samples frequently include 0 as an acceptable score
- Records reviewed by state assessors allow 0% recovery to be acceptable
  - IDOC
    - mean needs to be within control limits
  - LCS
  - MDL
    - A valid MDL study may include a non-detect

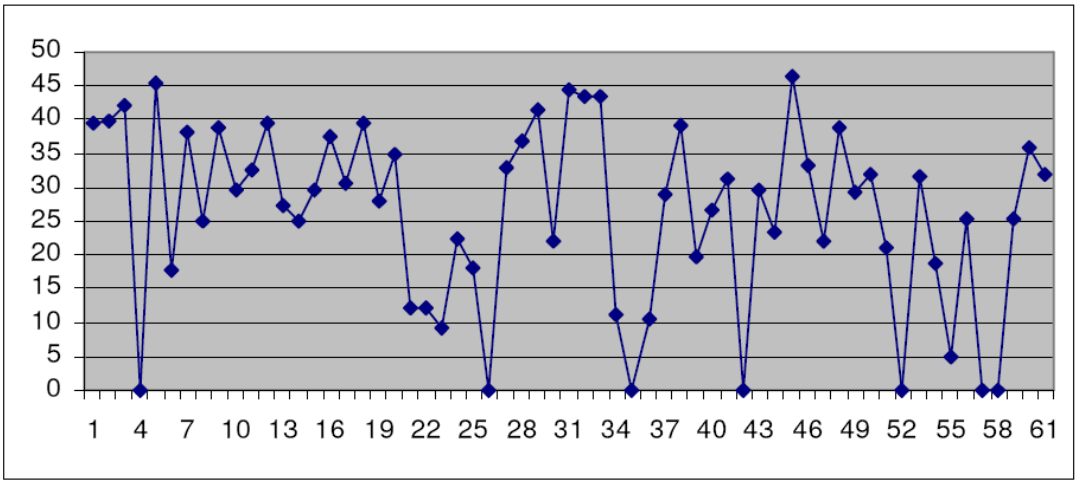
Reality 3

- PT samples do not contain all analytes routinely measured in environmental samples
- A typical BNA PT sample contains 61 Base-Neutrals, 20 Acids
- 19 analytes have not been included since 2001
- Another 10 include 0 as acceptable when they are included

Reality 3 (cont'd)

- 40 CFR Part 264 Appendix IX contains 126 semivolatile analytes
- 45 are not included in the NELAC Fields of Proficiency Testing (FOPT)
- 29 are not included in PT samples or include 0 in the acceptable range
- 59% of Appendix IX semivolatile analytes have no performance data

Many Proficiency Test Samples Have Little Value



Acceptable PT Results for Semivolatiles in Water (100 ug/L)

Potential Method Performance (or lack thereof?)

- 0 % recovery is acceptable for LCS
- 0 % recovery is acceptable for IDOC
- 0 % recovery is acceptable for MDL study
- 0 % recovery is acceptable for PT samples

WHY BOTHER TO RUN THE SAMPLES??

A Case in Point: 1,4-Dioxane

- Listed in Method 8260 with footnote indicating poor purging efficiency
  - No performance data with Method 5030
- Listed in CLP SOW volatiles
  - Notice given of poor performance
- Not listed in Method 8270
  - 8270 might be a better method unless 8260 is modified
- Not contained in NELAC FOPT
- Recent analyte of concern

Method Performance for 1,4-Dioxane

- Neither Method 8260 or 8270 is sensitive enough without modification (FL Groundwater Cleanup Target Level=3.2 ug/L)
- Method 8260, heated purge and trap, SIM
  - Recovery acceptance limits, 70 – 130%
  - RPD limit, 20%
- Method 8270, optimized for 1,4-Dioxane
  - Recovery acceptance limits, 10 – 150%
  - RPD limit, 50%
- Method 8270, Isotope Dilution
  - Recovery acceptance limits, 15 – 110%
  - RPD limit, 30%

Data from field comparison study report, conducted by BBL Environmental Services, Inc. on behalf of Lockheed Martin in May 2006

Accreditation for 1,4-Dioxane

- Laboratory cannot be accredited for this analyte using Method 8260 (method must be modified beyond what is acceptable for accreditation)
  - Ironically, a lab could be accredited by 8260 without the needed modifications
- Laboratory cannot be accredited for this analyte using Method 8270 (analyte not listed)

Florida Laboratories

- 41 labs with 48 accreditations to analyze for 1,4-Dioxane in non-potable water
  - 36 Method 8260
  - 3 Method 8015
  - 1 CLP Volatiles
  - 8 Laboratory SOP
    - 7 based on 8270
    - 1 based on 8260

Time for A Change

Educate Data Users

- MQOs/DQOs should be set *prior* to sampling
- There are method limitations and tradeoffs between # of analytes and cost
- A large # of analytes may be determined by a method, but it was not intended that all could be measured in the same sample and achieve reliable data across the board

Time for A Change
Accrediting Authorities decide:

- Accredit these analytes by method within the laboratory's Quality System and demonstrated capability of the method
  - Recognizing that data will be within method limitations (and continue to include 0!), **OR**
- Accredit only a specific list of analytes for which performance data exists (e.g., FOPT), **BUT**
- Accredit uniformly nationwide to prevent possible unintended competitive advantages

Time for A Change

- Allow labs to use any method that gets reliable data
- Do not accept 0% recovery
  - Remove the analyte or modify the method
- Accredit labs based on SOP and not on a method which may or may not be appropriate

THE GOOD, THE BAD AND THE UGLY REVISITED ENVIRONMENTAL TESTING IN THE 21ST CENTURY

Burrows, Richard; Severn Trent Laboratories

At this meeting in 1998, I presented a paper, *The Good, The Bad and The Ugly*, discussing prescriptive vs. performance based methods. This paper will examine progress made since then, examining the causes of some problems in environmental testing and possible solutions:

- Barriers to a performance approach
- Controlling data quality
- Problems with the prescriptive approach
- Widely used performance measures that are bad, or even ugly
- What should a performance approach look like?
- When are prescriptive requirements required?

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The Good, The Bad and The Ugly Revisited

Richard Burrows

NEMC 2006

SEVERN TRENT STL

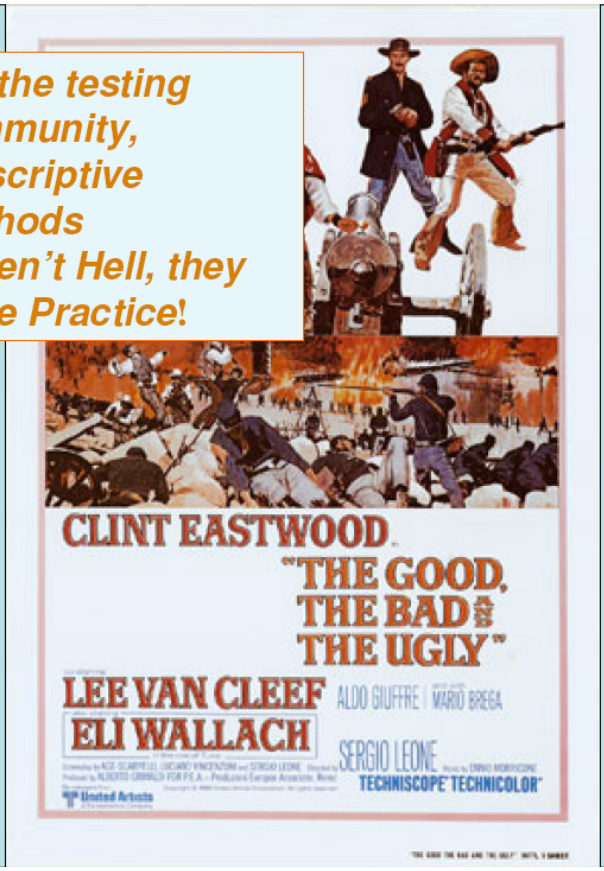
NIST Initiative

- Health, Depth and Breadth of the Environmental Monitoring Industry

Health

Are we using analytical methods that give us the best possible data?

For the testing community, Prescriptive methods Weren't Hell, they Were Practice!



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The Good, the Bad and the Ugly

- PBMS - Three possible results
- Good systems
  - Rugged, reliable and economical analyses
- Bad Systems
  - Proliferation of data user specification of trivial method requirements
- Ugly Systems
  - Poor, biased and unreliable analyses

- How's it going…

1998 hypothetical

- Site investigation
  - PAH known to be present
  - Other toxic compounds possibly present
  - Cleanup goal 500ug/kg for PAH

The Good Method

- Accelerated Soxhlet, CH_2Cl_2/acetone
- GC/MS
- 5 point calibration for PAH, RSD < 15%
- Low standard equivalent to 200ug/kg
- Single point standard at RL for other Appendix IX compounds
- Continuing calibration for PAH only, 15%D
- LCS at mid point for PAH, 60-140%, at RL for other compounds
- MS/MSD is PAH mix

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The Good method

- Similar to 3541 / 8270, but
  - Different calibration and QC criteria
    - Tight quantitative criteria for PAH
    - Detect / non detect for other compounds
    - QC focused on analytes of most interest

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Can the "good" method be implemented?

- 1998
  - NO
- 2006
  - NO

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Why not?

- Method is like 8270, but not 8270, so accreditation is difficult
- Clients, consultants, data validators, states, federal agencies will probably not agree on the details (unless an EPA method is followed exactly)

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How prescriptive are we?

- SPE not acceptable for explosives because it is in Update IV to SW-846
- LCMS not acceptable for explosives because the compounds are not in the analyte list for 8321
- Collision cell not acceptable for 200.8 because 200.8 does not mention collision cells

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Is prescriptive OK?

- Current system makes sense if
  - EPA is best at writing methods
  - EPA can promulgate or make methods available for use in a timely and effective manner
  - The first is debatable. There are definite issues with the second

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Why are we so prescriptive?

- Don't trust the labs

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Barriers to New Methods

- Limited programs
  - 200.8 (only 12 years….)
- Limitations within the programs
  - 331, 332
- Certification

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Which method?

- "Use the latest version of a method"
  - States may of may not approve Update IV methods
  - 8270C Rev 3 December 1996
  - 8270D Rev 4 January 1998 (Update IVA)
  - 8270D Rev 4 February 2006 (New Methods)

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Very Prescriptive, but

- Solvent systems are flexible
  - 3545A and 3550C both specify acetone /hexane or hexane alone for PCBs
  - 3570 specifies 100% methylene chloride

At a minimum…demonstrate proficiency
…using a clean reference matrix.

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Be prescriptive when necessary

- Use QC criteria where these provide a good measure of performance
- Use prescriptive method details where measurement of method performance using routine QC measures is difficult

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QC measures

- Most instrumental details
  - Initial and continuing calibration criteria, peak capacity, internal standard and surrogate recovery

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Difficult to measure using routine QC

- Recovery from sample matrix
  - Solvent system, contact time
- Homogeneity
  - Sample size, particle reduction
- Matrix effects on instrumentation
  - Isotope dilution standards

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PBMS

- New interest at the agency, driven from the highest levels
  - Office of Water proposes restating their "Streamlining" proposal

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Streamlining

- Based on demonstrating equivalent or superior performance to a reference method
  - Determine and compare to reference method
    - MDL
    - Calibration linearity
    - Calibration verification
    - IPR
    - OPR
    - Matrix spike precision and recovery
    - Blanks

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Problems with "Streamlining"

- State auditing procedures (both NELAC and non-NELAC)
- Legal issues
- Problems with marketing non-EPA methods

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An alternative

- Remove all possible method details from EPA methods
- A detailed procedure could still be developed and published (ES&T, Anal. Chem) but would not be in regulation
- Control the performance of the analytical technique for the analyte through QC criteria.

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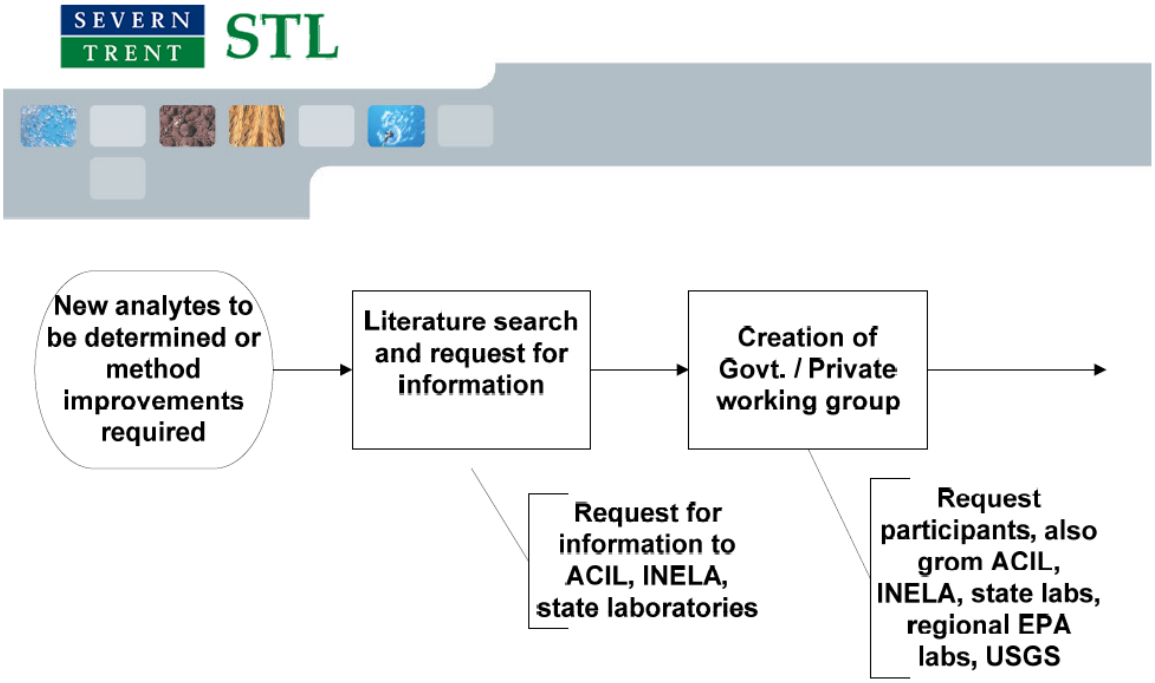
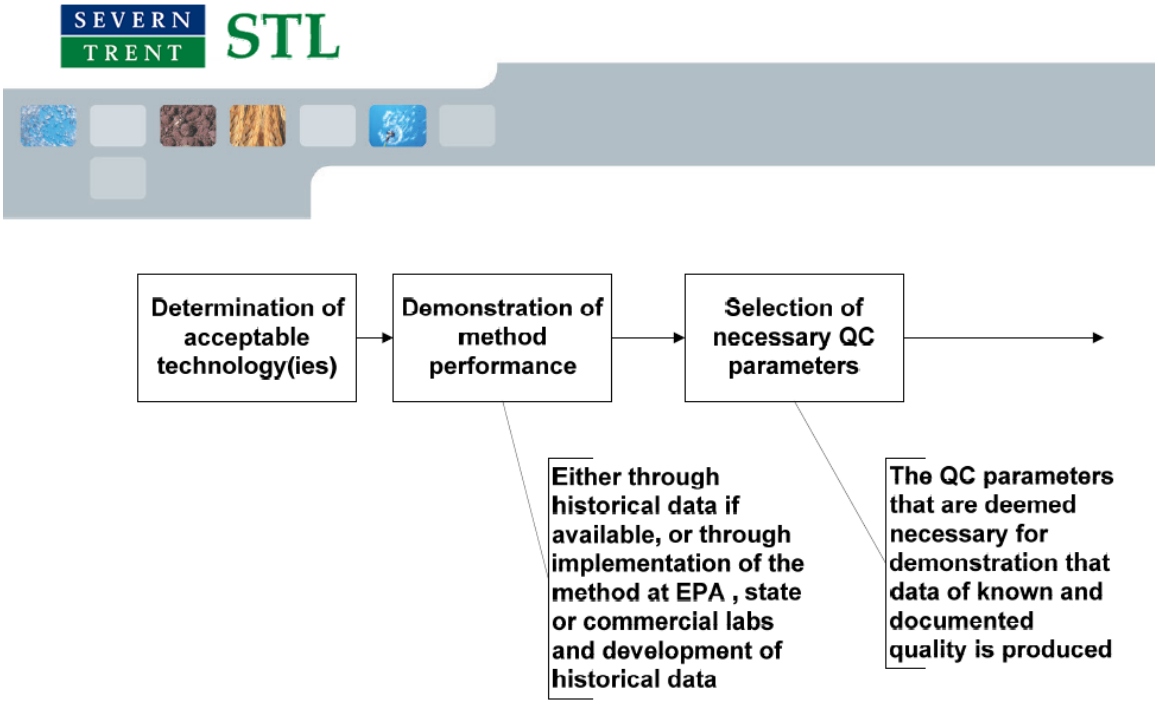
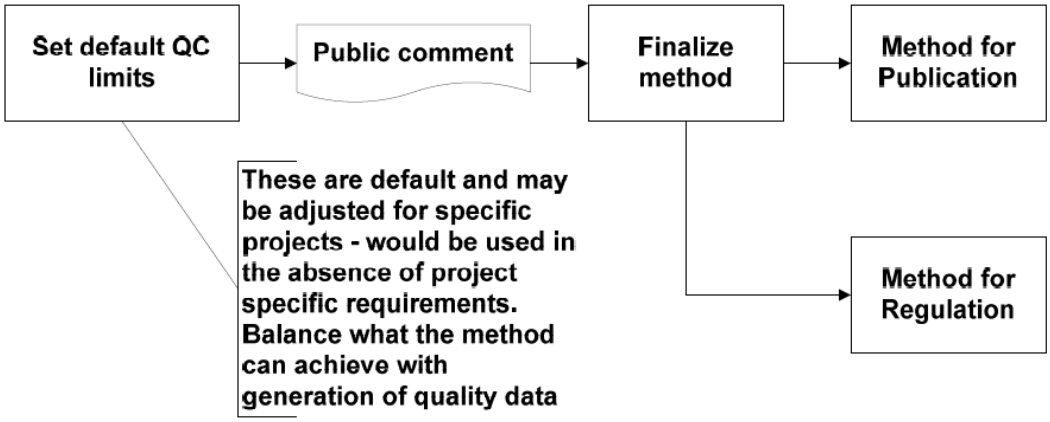
- "SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology."


SEVERN TRENT STL
New analytes to be determined or method improvements required
Literature search and request for information
Creation of Govt. / Private working group
Request for information to ACIL, INELA, state laboratories
Request participants, also grom ACIL, INELA, state labs, regional EPA labs, USGS


SEVERN TRENT STL
Determination of acceptable technology(ies)
Demonstration of method performance
Selection of necessary QC parameters
Either through historical data if available, or through implementation of the method at EPA , state or commercial labs and development of historical data
The QC parameters that are deemed necessary for demonstration that data of known and documented quality is produced

SEVERN TRENT STL



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Why QC criteria in the method?

- It is very difficult to convert a DQO into a MQO, because the MQO needed depends on how far from a regulatory limit the results are.
- After the fact, we can decide whether the data was sufficient to make a decision, but before the fact we can't say what quality is going to be necessary
- Default criteria are needed

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Perchlorate example

- EPA has developed 5 new methods for perchlorate, all have some prescriptive details and are not consistent with each other.
- Total 169 pages – one analyte
  - Not currently useable for compliance monitoring

SEVERN TRENT STL

PBMS perchlorate method

Perchlorate is determined by LC/MS/MS or IC/MS/MS. Mass 83 is used for quantitation and mass 85 for confirmation. In the absence of interferences, single stage mass spectrometry may be used, in which case use mass 99 for quantitation and 101 for confirmation.
^{18}O labeled perchlorate is used as an internal standard. Aqueous samples may be analyzed directly or following clean up on solid phase columns. Solid samples are extracted using an aqueous leach.
Identification of perchlorate requires peaks for the quantitation and qualifier ions to maximize within one scan, and within 0.1 minutes of the labeled perchlorate internal standard.
In the absence of project specific quality control requirements the following must be used:

SEVERN TRENT STL

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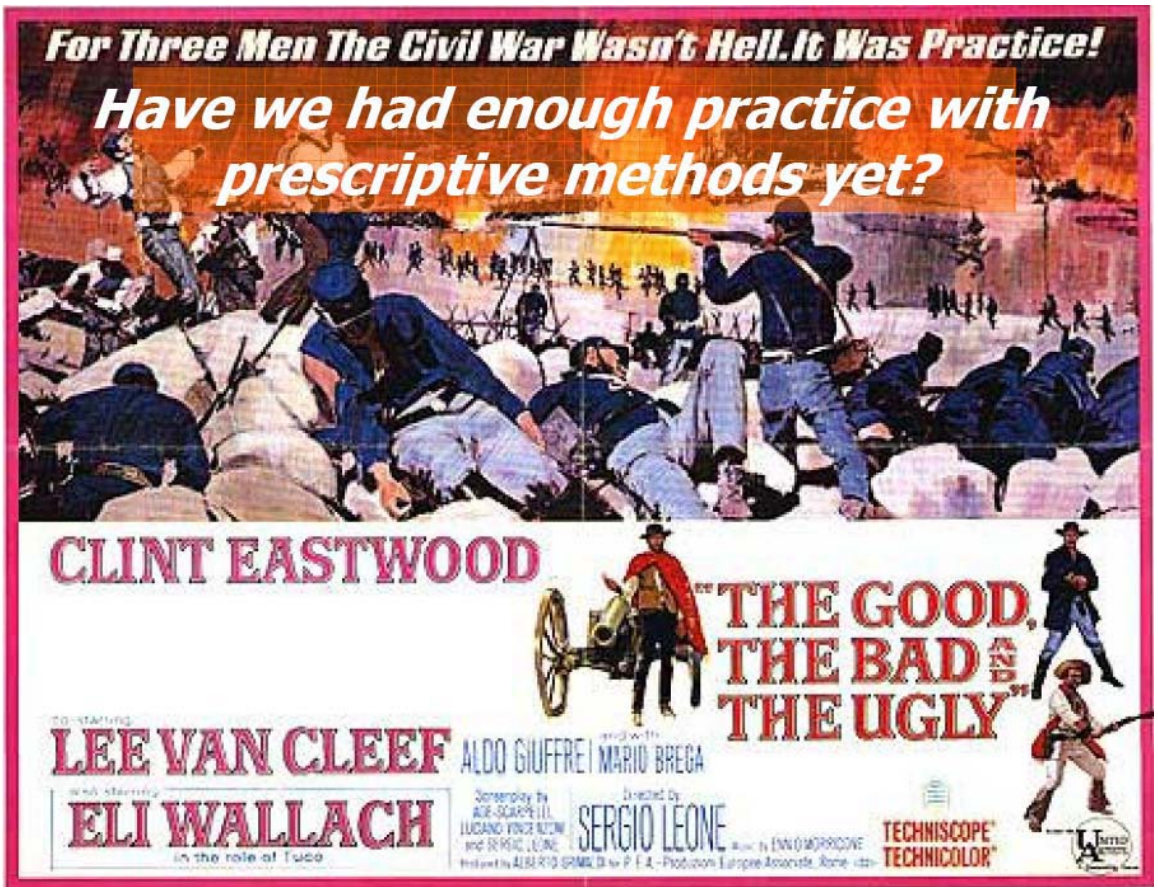

PERFORMANCE BASED MEASUREMENT SYSTEMS

Blye CEAC, David R.; Environmental Standards, Inc.
Vitale CEAC, CPC, Rock J.; Environmental Standards, Inc.

Performance-Based Measurement Systems (PBMS) is an excellent tool by which analytical buyers can develop new or modify existing analytical methods to meet project-specific objectives. Conversely, PBMS has been inappropriately construed as a license to modify existing methods in a manner that enhances laboratory sample through-put, without necessarily generating high-quality analytical data. The proper use of PBMS for the purpose of generating high-quality analytical data requires the buyers of analytical services to be educated in terms of getting generically written methods to "work" for their program and compounds of interest. Unfortunately, the lion's share of analytical buyers are uneducated in terms of purchasing analytical services and tend to purchase services based solely on cost. Because cost is often the overriding factor, some commercial laboratories' offerings, under the misapplied auspices of PBMS, are less desirable in terms of generating an accurate analytical result. This presentation will present "how to do it right."

Performance-Based Measurement Systems
A Double Edged Sword
Buyer Beware

22nd Annual NEMC
August 31, 2006

David R. Blye, CEAC
Rock J. Vitale, CEAC, CPC
Environmental Standards, Inc.

ENVIRONMENTAL STANDARDS

Topics

- PBMS and MIR revisited
- The Double Edged Sword
- Doing it Right!

ENVIRONMENTAL STANDARDS

PBMS and MIR Revisited

- PBMS conveys “what” needs to be accomplished, but not prescriptively “how” to do it.
- PBMS is a 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. (*www.epa.gov/epaoswer/hazwaste/test/pbms.htm)*
- HUH?

3

ENVIRONMENTAL STANDARDS

PBMS and MIR Revisited

- PBMS allows the stakeholders to define what the quantitative MQOs are and provides the flexibility in developing or modifying an analytical method to achieve the criteria.
- Methods Innovation Rule (MIR) – allows the use of other practical test methods other than SW-846 for RCRA regulations with exception of the “method-defined parameters” (ex., TCLP)
- PBMS and MIR – an opportunity for advancement (?)

4

ENVIRONMENTAL STANDARDS

PBMS should be good – right?

- One size fits all.
- Take advantage of technology
  - LC/MS
  - LC/MS/MS
  - IC/MS
- Modify existing methods or develop new methods to improve data quality.
- Potentially reduce costs for the lab and customer by matching a method to a particular data use (ex., screening for presence or absence).

5

ENVIRONMENTAL STANDARDS

The Double Edge Sword

- PBMS *is* good for those reasons, but…CONCERNS
- Can EPA mandate PBMS to compel industry to develop a procedure to look for new Compounds of Emerging Concern (CECs) or a ridiculous sensitivity level?
- Will labs *on the DARK SIDE* use PBMS as a license to take short-cuts to undercut an already commodity-perceived commercial marketplace?
- Do method modifications truly yield quality enhancements? Clearly some do, but can "modifications" being hidden short-cuts?

6

ENVIRONMENTAL STANDARDS

The Double Edge Sword

Concerns:

- Comparability of results generated by varying PBMS-developed techniques? Ours vs. Theirs.
  - Qualitative or quantitative impacts of technique used.
- How can we expect PBMS to take hold when we can't even have a soil VOC method proven to be scientifically better (5035) universally accepted in the industry and mandated by regulators?

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ENVIRONMENTAL STANDARDS

The Double Edge Sword

Concerns:

- Analytical buyers are (unfortunately) generally uneducated and don't know the differences, pit-falls, gaps and limitations with SW-846 methods as they are written. How can we expect them to *get* PBMS?
- Uneducated regulators; knowledgeable individuals in analytical issues at the project level where decisions are made are lacking.

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ENVIRONMENTAL STANDARDS

The Double Edge Sword

Concerns:

- Lack of competent analysts in the commercial laboratories.
  - Many are not chemists
  - Poor understanding of analytical chemistry concepts – calibration techniques, quality control data interpretation etc.
  - Unfamiliar with nomenclature, compound structure and the chemistry behind the current methods.

9

ENVIRONMENTAL STANDARDS

The Double Edge Sword

Concerns:

- Is there is a viable commercial market for enhanced analytical offerings given COST is the current driver.
- Cost involved in developing and validating new project-specific methods.
- Its easy to hide behind EPA “approved” methods. PBMS can be scary.

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ENVIRONMENTAL STANDARDS

Doing it Right!

- The monitoring and analytical community MUST promote EDUCATION of the Stakeholders.
  - Regulated
  - Regulators
  - Lab Community
- Analytical chemistry "short courses."
- Quality Control concepts.
- With some fundamental concepts, stakeholders can begin to use PBMS to their benefit.

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ENVIRONMENTAL STANDARDS

Doing it Right!

- First, method selection is driven by DQOs.
- Does an existing, approved method meet your needs?
- IF NOT, then we consider modification or method development.
- Engage a competent laboratory EARLY in the process.
  - Laboratories with strong technical expertise and that place an emphasize on methods development will embrace PBMS.
- Engage a competent chemistry consultant EARLY in the process.
- Include the regulatory authority in the thought and development process – buy in and concensus.

12

ENVIRONMENTAL STANDARDS

Doing it Right!

Method Modification can be simple!

Example - Purge and Trap Method 8260B for tert-butyl alcohol (TBA) consistently caused "rejection" of data due to a RRF < 0.05 (a stupid validation rule in itself).

- d10-TBA Internal Standard was used for quantitation of native TBA. RRF ~ 1.
- Demonstrate, validate and document.

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ENVIRONMENTAL STANDARDS

Doing it Right!

A PBMS thought related to detection and quantitation:

- Instead of MDL reporting, there should be more emphasis on modifying the calibration range and sensitivity of the method to encompass the concentration of concern.

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ENVIRONMENTAL STANDARDS

Doing it Right!

Method Development

- Clearly define your Method Quality Objectives (MQOs) to satisfy DQOs.
  - Precision
  - Accuracy
  - Sensitivity
- Research and understand the nature of the compound(s) of concern.
- Will one or multiple techniques be necessary?

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ENVIRONMENTAL STANDARDS

Doing it Right!

- Develop and "experiment" with the proposed techniques.
- Test robustness.
- Evaluate selectivity.
- Evaluate potential interferences.
- Refine and document the method (SOP).
- Validate the method.

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ENVIRONMENTAL STANDARDS

Doing it Right!

Method Validation

- Provide objective evidence that the MQOs are achieved.
- Should be as rigorous as necessary for the application (presence/absence vs monitoring at the MCL.)
- MDL and QL determination and confirmation
- Precision and Accuracy/Bias – spikes, spike replicates.

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ENVIRONMENTAL STANDARDS

Summary

- Promote education in PBMS use and concepts.
- Buyer beware. Include technical specifications for all work, even for approved methods.
- Project Teams must account for the time it takes to modify or develop methods in project schedules.
- Labs must insist on a more active role in the project for PBMS to be successful.

18

ENVIRONMENTAL STANDARDS

DEVELOPMENT OF NEW EPA PROMULGATED METHODS

Later, Douglas W.; Dionex Corporation
Munch, David J.; U.S. Environmental Protection Agency

The timely development of new EPA-promulgated methods that are inclusive of the latest technology is of prime interest to all stakeholders in the environmental community, including regulators that develop, promulgate, and enforce use of methods, suppliers that develop and provide analytical instrumentation for performance of methods, and laboratories that are ultimately responsible for using the methods to generate and report scientifically valid and legally defensible data. In the past, there has been much criticism and debate about the difficulty of developing new methods based on state-of-the-art analytical technologies. Timely promulgation of new environmental testing methods has also been a high-energy focal point. Performance-based methods have been advocated by some as the means to address these problems. There is, however, much debate within EPA and the stakeholder community on an appropriate performance-based implementation process that provides flexibility in the development of analytical methods without compromising the integrity of quantification and numeration principles as intended using the traditional reference method approach.

In this paper, a truly functional collaboration paradigm that has evolved over the past few years between Dionex as a supplier and the EPA Office of Ground Water and Drinking Water, Technical Support Center (EPA-OGWDW-TSC) will be described. This collaboration paradigm has been effective in the development of several new methods for drinking water analysis. For example, our two organizations have worked effectively to develop and promulgate two new methods for bromate analysis (Methods 317.0 and 326.0), which have recently been promulgated as part of the Phase II Drinking Water Regulations. Furthermore, 3 new methods have been collaboratively developed for the determination of low-level perchlorate (Methods 314.1, 331.0, and 332.0) and have been proposed as part of the UCMR II Rule (August 2005). Continuing, a new method for the analysis of cations (ASTM 6919) in drinking water has been proposed in the Analytical Methods Update Rule form the Office of Water (April 2004). Currently, EPA-OGWDW-TSC and Dionex are collaborating on the development of many other new methods for the analysis of bromate, perchlorate, oxyhalides, haloacetic acids, paraquat-diquat, and other emerging environmental contaminants using the most recent analytical technologies such as two-dimensional chromatography, IC, LC, IC-MS, IC-MS/MS, LC-MS and LC-MS/MS. This collaboration has also reached out to the testing laboratory community to involve them in the generation of method validation data. In this collaborative manner between agency-supplier-laboratory, new methods that include the latest analytical technology are finding there way into use in a much more timely manner. This paper is intended to present and promote this type of collaboration paradigm in the environmental community.

A Collaborative Approach to the Timely Development of New EPA Promulgated Methods for Emerging Environmental Contaminants

Douglas W. Later, Dionex Corporation
David J. Munch, EPA Office of Ground Water & Drinking Water, Technical Support Center

The 22nd Annual National Environmental Monitoring Conference
Arlington, Virginia
August 28—31, 2006

The 'Dilemma'

- New technology for detection and quantitation of emerging environmental contaminants can quickly outdate traditional reference methods.
- EPA Offices are continually working to keep pace with emerging technologies and new environmental contaminants to keep methods current and published-promulgated in a timely manner.
- High data quality consistent with DQOs must to be available for making scientifically sound regulatory decisions.

The 'Stakeholders'

- U.S. EPA Offices
  - Method Developers and Promulgators
  - Regulators
  - Enforcement Branches
- Technology Innovators
  - Instrument Companies
  - University and Research Institutes
  - Suppliers
- Testing Laboratories- Users of the Methods
- Customers- Reviewers and Users of the Data

The 'Options'

- Develop Methods in Isolation
  - can be slow and not acceptable to most stakeholders
  - may not use the latest technologies
- Performance-Based Measurement Systems (PBMS)
  - too flexible for some, but not all, stakeholders
  - data quality is heavily dependent on competence of users
  - dependent on available resources that can be committed to method development
  - permits method development by laboratories that do not have adequate resources nor expertise
- 3rd-Party Standard Setting Organizations (e.g. ASTM)
  - acceptable to many stakeholders, but can still be slow
  - data quality can be variable and dependent on application
- Collaboratively-Developed Reference Methods (CDRM)
  - improvement in speed of methods development and timely publication
  - provides excellent approach combining experienced method development chemists with the latest technology and technological experts
  - another method development approach– not a panacea

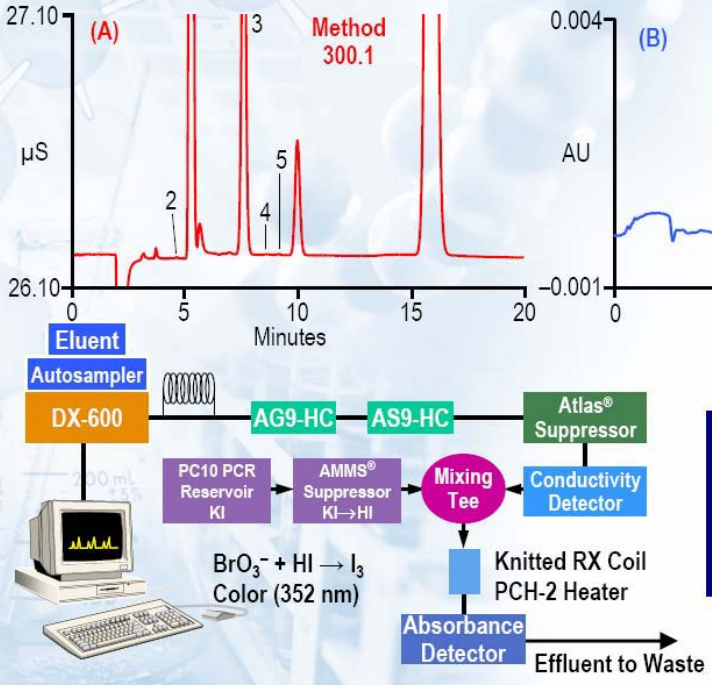
The 'Key Concerns'

- **Flexibility** in analytical method development without compromising the integrity of quantitation and numeration principals of traditional reference methods
- **Resources**
  - Funding
  - Time
  - Staff
  - Expertise
  - Technology
- **Relationship Balance**
  - The agency must maintain a position of neutrality and 'non-endorsement'
  - The commercial method co-developers must not 'over-exploit' their position

EPA-OGWDW – Dionex Collaboration Paradigm

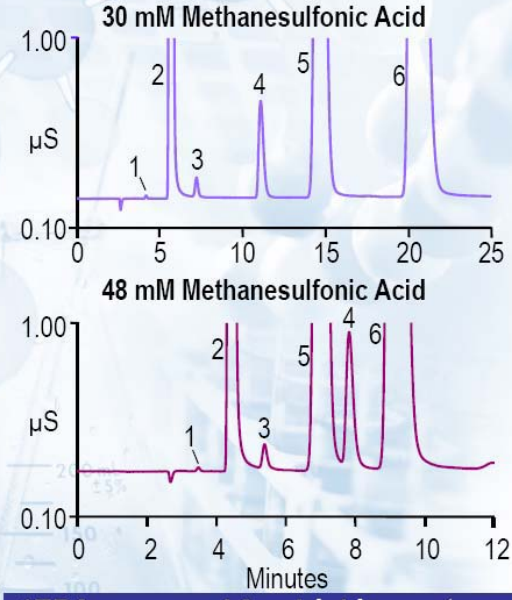
- Collaborators:
  - EPA-OGWDW Technical Support Center
  - Shaw Environmental (EPA Contractor)
  - Dionex Research and Development
  - Dionex Applications Laboratory
  - Dionex Market Development
- Interactions
  - Technology Exchange Days
  - Regular Conference Calls
  - Site Visits
  - On-site Method Development
- Collaboration Modes
  - Passive
  - Proactive
  - Collaborative
- Method Development Approaches
  - Method technology developer
  - Golden Data Generation
  - Second Laboratory Validation Studies
- Method Writing
  - Unilateral
  - Jointly
  - Co-authorship
  - Acknowledgements

Example #1(Dionex-Passive): Bromate by Methods 300.1, 317.0, and 326.0



Methods 317.0 and 326.0 were recently promulgated as part of the Stage 2 Drinking Water Regulations

Example #2 (EPA Passive): ASTM Method D6919-03

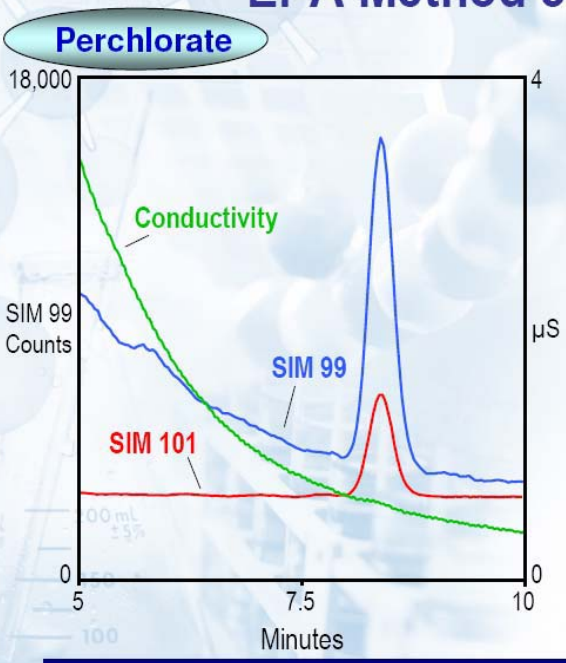


Column:	IonPac® CS16, CS16-5 µm, 5 x 250 mm
Flow Rate:	1.0 mL/min
Eluent Source:	EGC 11 KOH cartridge
Temperature:	40 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, CSRS® ULTRA, 4 mm, AutoSuppression® recycle mode

Peaks	mg/L (ppm)
1. Lithium	0.002
2. Sodium	19.7
3. Ammonium	0.07
4. Potassium	0.99
5. Magnesium	7.2
6. Calcium	18.5

***EPA proposed for drinking water and wastewater compliance monitoring as part of the Analytical Methods Update Rule (April 2004)**

Example #3 (EPA-Dionex Collaborative): EPA Method 332.0 (IC-MS)*



Column:	IonPac® AG16, AS16, 2-mm i.d.
Suppressor:	ASRS® ULTRA, 2 mm
Eluent:	65 mM KOH (EG40)
Flow Rate:	0.30 mL/min
Inj. Volume:	250 µL
Detection:	1. Conductivity
	2. MSQ, SIM 99, $^{35}ClO_4^-$
	3. MSQ, SIM 101, $^{37}ClO_4^-$
MS Conditions:	–ESI, 70 V, 350 °C
Sample:	Groundwater diluted 1/10
Peak:	Perchlorate ~ 7–8 µg/L

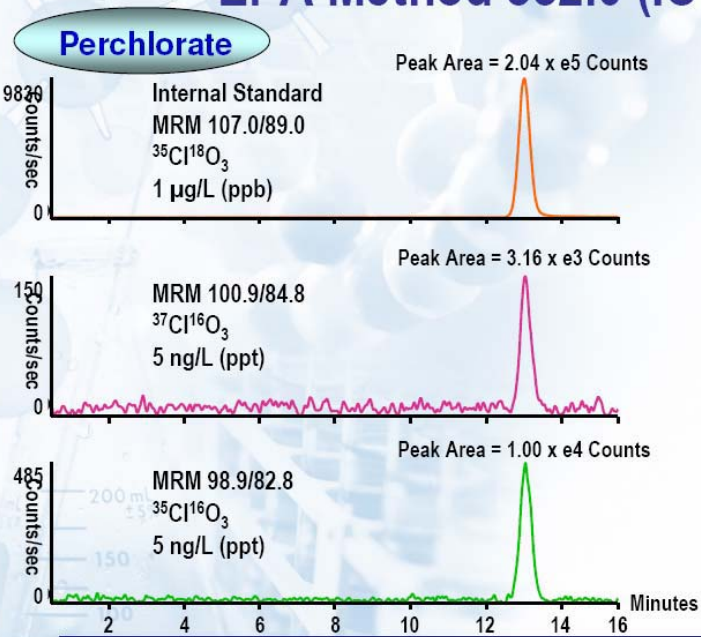
$(MDL)_{99}$** = 0.04 ppb

* Method developed jointly by EPA and Dionex

** MDL = SD x t_s (n = 7), t_s = 3.14

*** UCMR II Method developed jointly by EPA-OGWDW and Dionex**

Example #3 (EPA-Dionex Collaborative): EPA Method 332.0 (IC-MS/MS)*



IC System:
Dionex ICS 2500
with Matrix Diversion
and Auxiliary Pump

MS/MS System:
MDS Sciex API 2000

Internal Standard:
0-18 Perchlorate: 1 µg/L*

Inject Volume:
100 µL

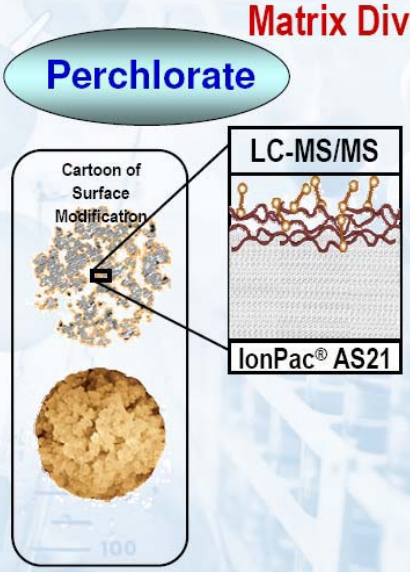
Perchlorate Isotope Ratio:
10,000/3160 = 3.16

** Prepared from 1 mg/L stock standard (Dionex Corp)*

*** UCMR II Method developed jointly by EPA-OGWDW and Dionex**

Example #3 (EPA-Dionex Collaborative): EPA Method 331.0 (LC-MS/MS)*

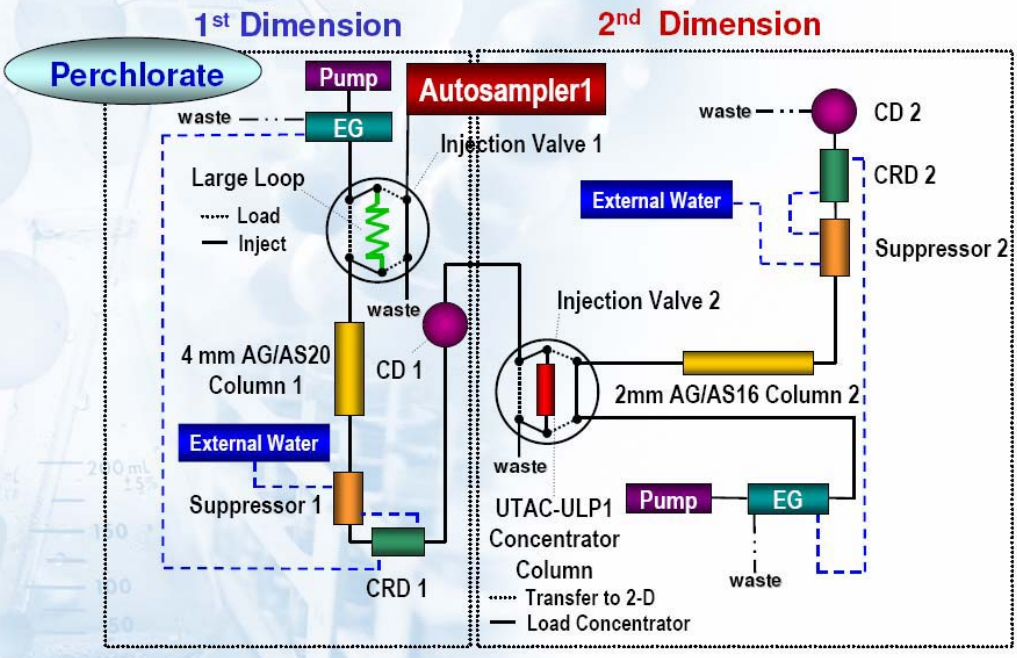
Perchlorate Analysis Using Ion-Exchange Separation, Matrix Diversion, and MS/MS Detection



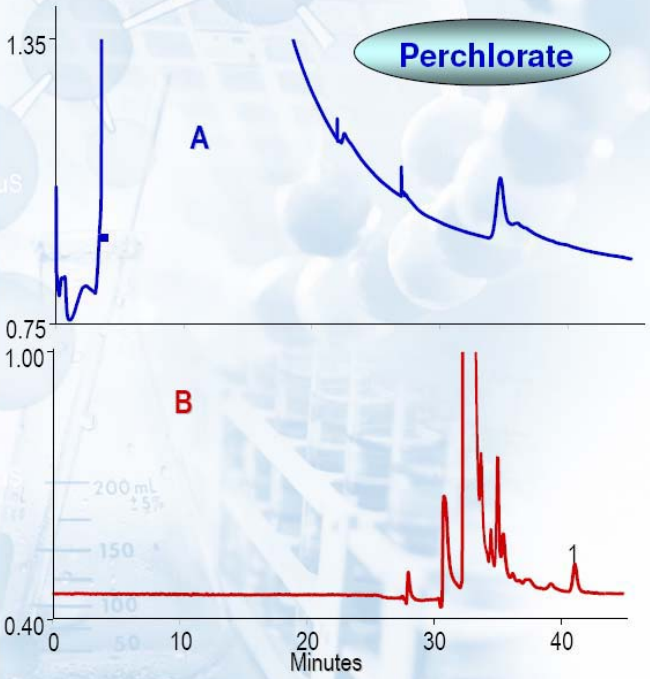
Eluent:	200 mM methyl amine
Flow Rate:	0.35 mL/min
Analysis Column:	IonPac® AS21, 2 mm
Diversion:	Eluent divert valve before detector to send common anions (e.g.,chloride, bicarbonate, sulfate) to waste
Detector:	Triple quadrupole MS/MS

*** UCMR II Method developed jointly by EPA-OGWDW and Dionex**

Example #4a (Proactive-Dionex): 2-D Method 314.2 Instrument Schematic



Example #4a (Proactive-Dionex):
2-D Method 314.2 Instrument Schematic



A) First-Dimension Conditions

Column:	IonPac® AG20, AS20, 4 mm
Flow Rate:	1.0 mL/min
Concentration:	35 mM KOH
Suppressor:	ASRS® Ultra II, 4 mm
Current:	150 mA

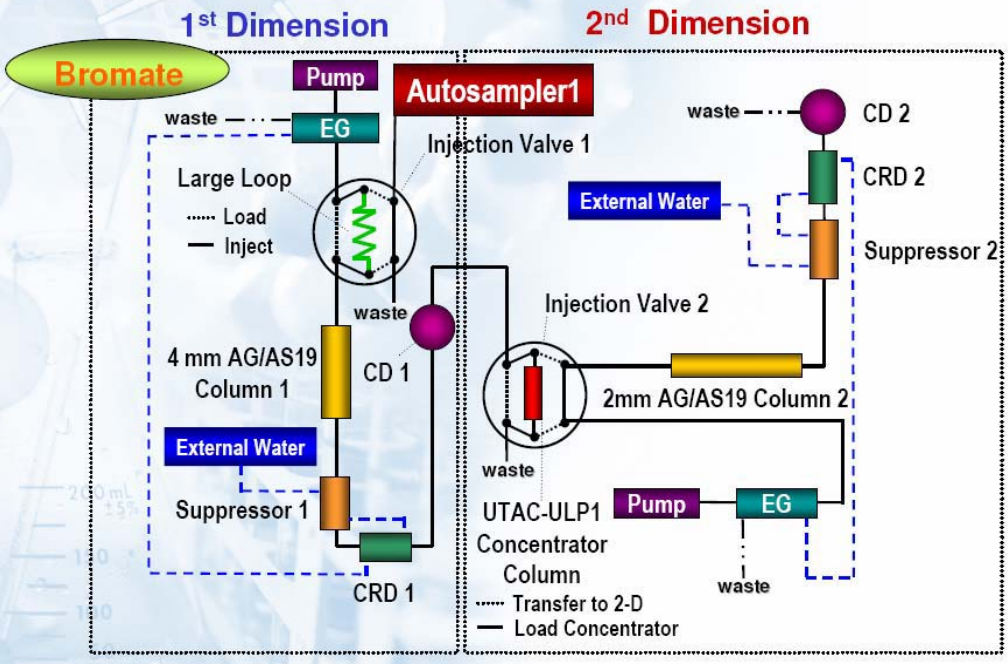
B) Second-Dimension Conditions

Column:	IonPac AG16, AS16, 2 mm
Flow Rate:	0.25 mL/min
Concentration:	65 mM KOH
Suppressor:	ASRS Ultra II, 2 mm
Current:	41 mA
Loop:	4000 µL
Concentrator:	TAC-ULP1 (5 x 35 mm)
Oven:	30 ˚C
Peak:	1. Perchlorate 0.5 µg/L

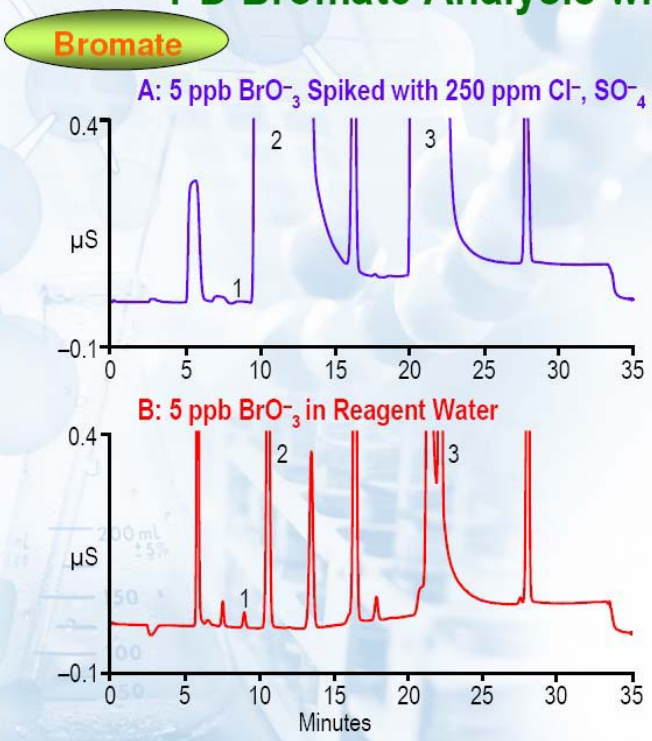
Matrix:

Chloride:	1000 mg/L
Bicarbonate:	1000
Sulfate:	1000

Example #4b (Proactive-Dionex):
2-D Bromate Method Instrument Schematic



Example #4b (Proactive-Dionex):
1-D Bromate Analysis with AS19 Column



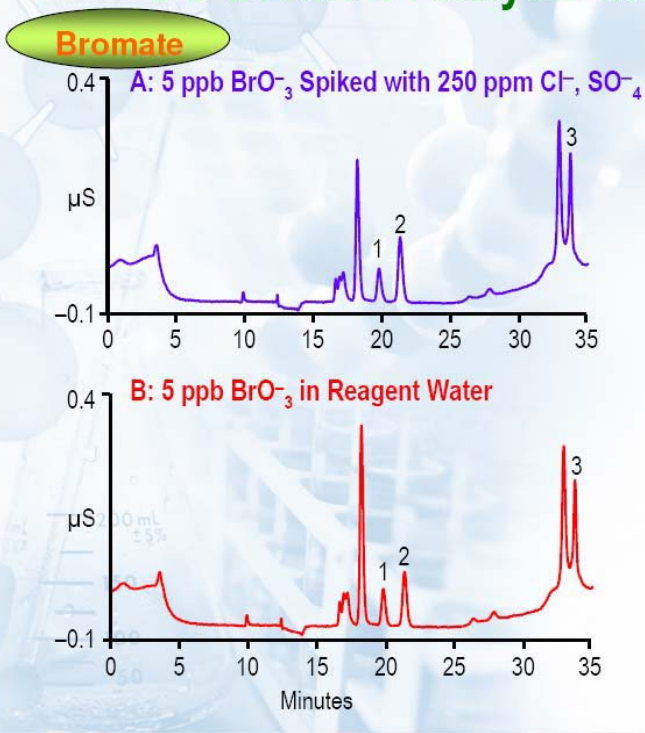
Column:	IonPac® AG19, AS19, 4 mm
Flow Rate:	1.0 mL/min
Suppressor:	ASRS® ULTRA II, 4 mm
Current:	113 mA
Loop:	500 mL
Oven:	30 °C

Time:	KOH Gradient (mM)
0	10
10	10
25	45
30	45
30.1	10
35	10

Peaks:	A	B
1. Bromate	0.005 mg/L	0.005 mg/L
2. Chloride	250	0.030
3. Sulfate	250	0.150

22486

Example #4b (Proactive-Dionex):
2-D Bromate Analysis with AS19 Columns



Primary Condition

Column:	IonPac® AG19, AS19, 4 mm
Flow Rate:	1.0 mL/min
Suppressor:	ASRS® ULTRA II, 4 mm
Current:	113 mA

Secondary Condition

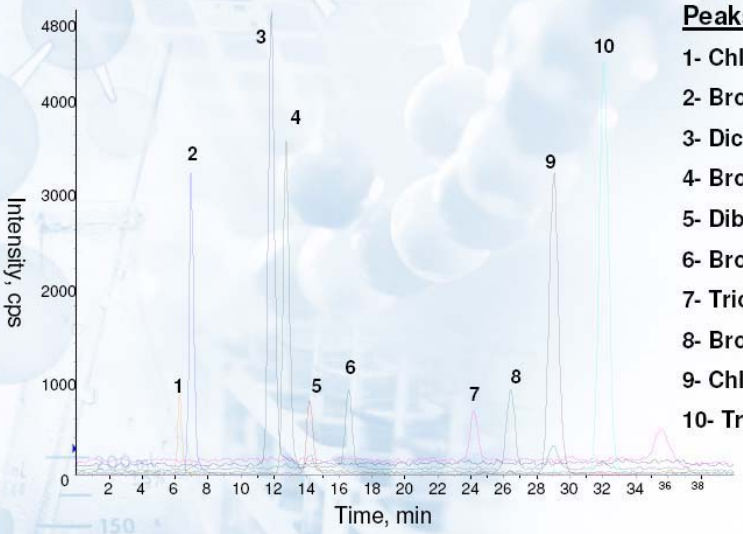
Column:	IonPac AG19, AS19, 2 mm
Flow Rate:	0.25 mL/min
Suppressor:	ASRS ULTRA II, 2 mm
Current:	29 mA
Loop:	500 mL
Concentrator:	TAC-ULP1
Temperature:	30 °C

Time:	Gradient (mM)	Gradient (mM)
0	10	10
10	10	
19.5		10
25	45	
30	45	
30.1	10	
34.5		45
35	10	45

Peaks:	A	B
1. Bromate	0.005 mg/L	0.005 mg/L
2. Chloride	250	0.030
3. Sulfate	250	0.150

22487

Example #5 (EPA-Dionex Collaborative): Haloacetic Acids by IC-MS/MS



Peaks	µg/L (ppb)
1- Chloroacetic acid	6
2- Bromoacetic acid	4
3- Dichloroacetic acid	6
4- Bromochloroacetic acid	4
5- Dibromoacetic acid	2
6- Bromide	2
7- Trichloroacetic acid	2
8- Bromodichloroacetic acid	2
9- Chlorodibromoacetic acid	10
10- Tribromoacetic acid	20

IC-MS/MS

Direct Injection

No Derivatization—No Sample Prep

Collaboration Team Members

- EPA-OGWDW
  - David Munch
  - Steve Wendelken
  - Dan Hautman,
- Shaw Environmental
  - Barry Pepich
  - Herb Wagner
  - Alan Zaffiro
  - Steve Winslow
- Dionex R&D
  - Chris Pohl
  - Kannan Srinivasan
  - Rosanne Slingsby
  - Rida AlHorr
  - Rong Lin
  - Charanjit Saini
- Dionex Applications Laboratory
  - Brian DeBorba
  - Dave Thomas
  - Jeff Rohrer
- Dionex Market Development
  - Doug Later
  - Bob Joyce

Summary of Recently Developed and In-Progress CDRMs

- Methods Developed and Proposed or Promulgated
  - Method 317.0: Bromate by IC-PCR (ODA method)
  - Method 326.0: Bromate by IC-PCR (HI method)
  - ASTM Method D 6919-03: Cations by IC
  - Method 314.1: Perchlorate by Suppressed Conductivity Detection with Cryptand Concentrator
  - Method 331.0: Perchlorate by LC-MS/MS
  - Method 332.0: Perchlorate by IC-MS and IC-MS/MS
- Methods Currently in Development
  - Method 314.2: Perchlorate by Suppressed Conductivity Detection using 2-D IC
  - Bromate by Suppressed Conductivity Detection
  - Paraquat/Diquat by Ion-Pairing LC-MS/MS
  - Haloacetic Acids by IC-MS/MS
  - Oxyhalides by IC-MS

THURSDAY A.M., AUGUST 31, 2006

CONCURRENT SESSIONS

Perchlorate

TWO DIMENSIONAL ION CHROMATOGRAPHIC METHOD

DeBorba, Brian; Dionex Corporation
Later, Douglas W.; Dionex Corporation
Lin, Rong; Dionex Corporation
Pohl, Chris; Dionex Corporation
Srinivasan, Kannan; Dionex Corporation

Bromate is presently regulated in drinking water at an MCL of 10 ug/L using EPA Methods 300.1, 317.0 and 326.0. Perchlorate has been proposed as an UCMR 2 target analyte to be monitored at 0.5 ug/L using EPA Methods 314.0, 314.1, 331.0, and 332.0. Determining emerging ionic environmental contaminants such as perchlorate and bromate at parts-per-billion (ppb) concentrations can be challenging due to other anionic species present in the matrix at high parts-per-million (ppm) level, such as chloride, sulfate, carbonate, etc. The challenge is further magnified by the fact that the matrix ions tend to elute the contaminant ions of interest causing recovery and peak shape anomalies. Suppressed conductivity detection is selective toward ionic species, has adequate sensitivity for detecting trace perchlorate and bromate, offers lower capital cost, and is simple to use in conjunction with an ion chromatographic (IC) instrument. Thus, suppressed conductivity IC is very appealing to many laboratories performing environmental testing. The goal then is to develop a method that eliminates the high concentration matrix anions and minimizes their interferences in the measurement of trace level ionic contaminants.

The objective of this paper is to describe a two-dimensional ion chromatographic (2-D IC) method using suppressed conductivity detection that has recently been developed by this laboratory. A 2-D IC method can be used to provide detection limits for perchlorate and bromate of <1.0 ppb even in the presence of other high-concentration (> 250 ppm) matrix anions, such as chloride, sulfate and carbonate. In the first dimension, up to 4 mL can be injected onto a 4 mm high capacity ion exchange column that is used to separate the contaminant anion of interest from the matrix ions. The contaminant ion is heart-cut using automated valve switching on to a concentrator column while eluting from the first dimension column. In the second dimension, the contaminant ion is further separated on a 1-2 mm microbore anion exchange column. Eluent from the 1st and 2nd dimension separations are suppressed using a self-regenerating suppressor, and the analyte detected and quantified using conductivity detection. The entire 2-D IC system is automated from injection to data reporting under the control of a chromatographic management system (CMS). Separation of the target analyte from the matrix anions in the 1st dimension in conjunction with a sensitivity enhancement that is proportional to the flow rate ratio between the 1st and 2nd dimensions affords detection limits for perchlorate and bromate on the order of 100 parts-per-trillion (ppt). This paper will describe the 2-D IC instrumentation used in these methods, demonstrate method robustness and simplicity, as well as report on data generated for a recently proposed draft EPA Method 314.2 for perchlorate.

A Two-Dimensional Ion Chromatographic Method for the Ultra-low Level Determination of Perchlorate and Bromate Using Suppressed Conductivity Detection

Douglas Later, Rong Lin, Brian DeBorba, Kannan Srinivasan and Chris Pohl

The 22nd Annual National Environmental Monitoring Conference
Arlington, Virginia
August 28—31, 2006

DIONEX

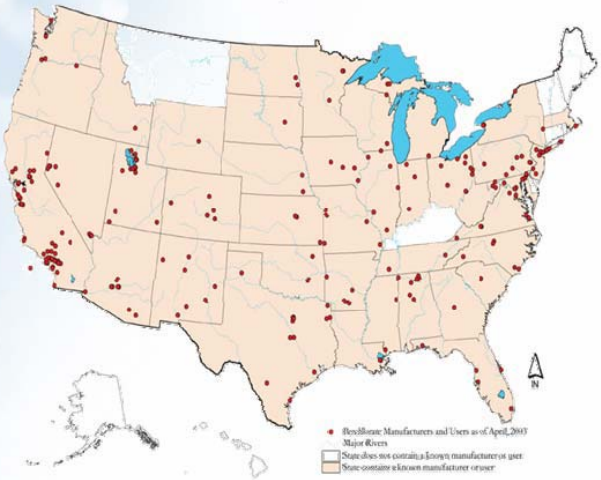
Presentation Outline

- Background Information on Perchlorate and Bromate
  - Occurrence
  - Health Effects
  - Regulatory Status
  - Current Methodologies
- 2-D Ion Chromatography (IC) Technology
- Perchlorate 2-D IC Application
- Bromate 2-D IC Application
- Summary

Sources of Perchlorate Contamination

- Rocket fuel production and waste disposal
- Munitions and explosives production and waste disposal
- Fireworks production, use and disposal
- Road flare production and disposal
- Hazardous waste disposal sites
- Phosphoric acid added to food and beverage products
- Indiscriminate chemical disposal

Perchlorate Manufactures and Users as of April 2003



http://www.epa.gov/fedfac/images/perchlorate_manuf_users_map.jpg

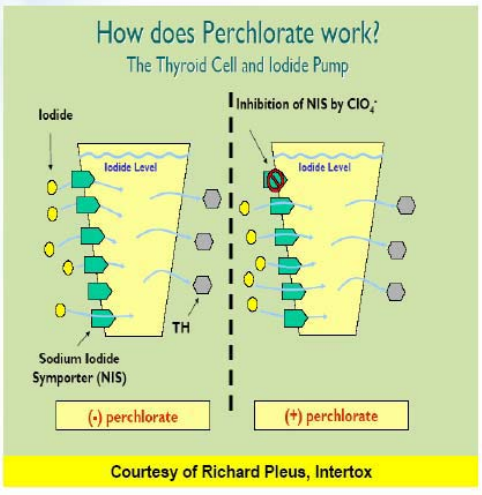
22271

Perchlorate Health Issues*

"Perchlorate interferes with the iodide uptake into the thyroid gland."

- Interferes with thyroid hormone production
- Interferes with thyroid regulation of metabolism
- Interferes with neurological development of fetus and newborn
  - Behavior changes
  - Delayed development
  - Decreased learning capability
- Changes in thyroid hormone levels may result in thyroid gland tumor

* U.S. EPA website (www.epa.gov)



Courtesy of Richard Pleus, Intertox

22273

U.S. EPA Unregulated Contaminant Rule (UCMR)

- Initial UCMR (1999) monitoring requirement
  - Required drinking water utilities to monitor and report perchlorate at levels > 4.0 ppb (January 1, 2001 to December 31, 2003)
  - EPA Method 314.0 required for measuring perchlorate
- UCMR II (2007)
  - Will require major water utilities to again monitor and report perchlorate levels in finished drinking water at >0.50 ppb (starts January 1, 2007)
  - Must use one of these EPA methods*:
    - » Method 314.0—IC with Conductivity Detection
    - » Method 314.1—Preconcentration IC with Conductivity Detection and Second Column Confirmation
    - » Method 332.0—IC-MS or IC- MS-MS
    - » Method 331.0—LC-MSMS
  - Note: Must be able to quantify sub-ppb of perchlorate, even in a matrix with 1000 ppm, each, chloride, bicarbonate, and sulfate

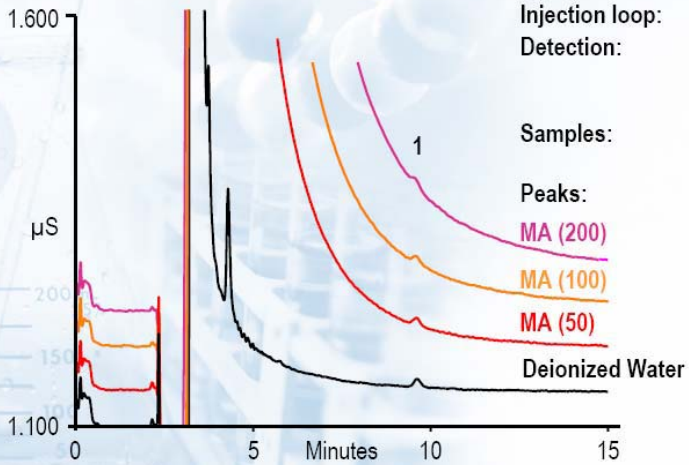
* If Perchlorate > 0.5 ppb, must ensure the value is really Perchlorate by analyzing with a confirmatory method; must demonstrate method used has an LCMRL of < 0.5 ppb

22275

EPA Method 314.0

Determination of 1 µg/L Perchlorate with Increasing Concentrations of Chloride, Sulfate, and Carbonate

Column:	IonPac® AG16, AS16, 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 EG with CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Injection loop:	1000 µL
Detection:	ASRS® ULTRA II, AutoSuppression®, external water mode, 193 mA
Samples:	MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}
Peaks:	1. Perchlorate 1 µg/L



19866

Instrumentation Cost Analysis by Method

Method	Technique	Relative Cost	Cost Range
Method 314.0	IC-CD	+	~$25 - 50K
Method 314.1	IC-CD-SCC	+ +	~$60 - 80K
Method 332.0/6860	IC-MS	+ + +	~$150 - 175K
Method 332.0/6860	IC-MS/MS	+ + +	~$150 - 175K
Method 6850	LC-MS	+ + + +	~$150 - 200K
Method 331.0	LC-MS/MS	+ + + + +	~$175 - 225K

Sources of Bromate in Drinking Water

Disinfection Treatment	Disinfection By-Products
Chlorination	Trihalomethanes Haloacetic Acids Chlorate
Chlorine Dioxide	Chlorite Chlorate
Chloramine	Chlorate
Ozonation	Bromate

20868

Toxicology of Bromate

- Clinical signs of bromate poisoning in humans* include:
  - Anemia, hemolysis, renal failure, hearing loss
- Carcinogenicity:
  - Animals: International Agency for Research on Cancer (IARC) has concluded that bromate is carcinogenic in animals
  - Humans: IARC has assigned bromate to Group 2B (the agent is possibly carcinogenic to humans)

*World Health Organization, Geneva, 2000

22478

Regulation of Bromate in Municipal Drinking Water

- **1993**
  - World Health Organization (WHO) set a guideline of 25 µg/L bromate in drinking water
- **1998**
  - U.S. Environmental Protection Agency established a 10 µg/L bromate maximum contaminant level (MCL) in drinking water and a maximum contaminant level goal (MCLG) of zero under the Stage 1 disinfectants/ disinfection by-products (D/DBP) rule
  - European Union reduced the regulatory value from 50 to 10 µg/L bromate
- **2003**
  - WHO set a provisional value of 10 µg/L bromate in drinking water
- **2004**
  - U.S. Environmental Protection Agency, Stage II D/DBP rule leaves MCL at 10 µg/L
  - The U.S. FDA adopted the U.S. EPA's MCL for bromate in bottled waters

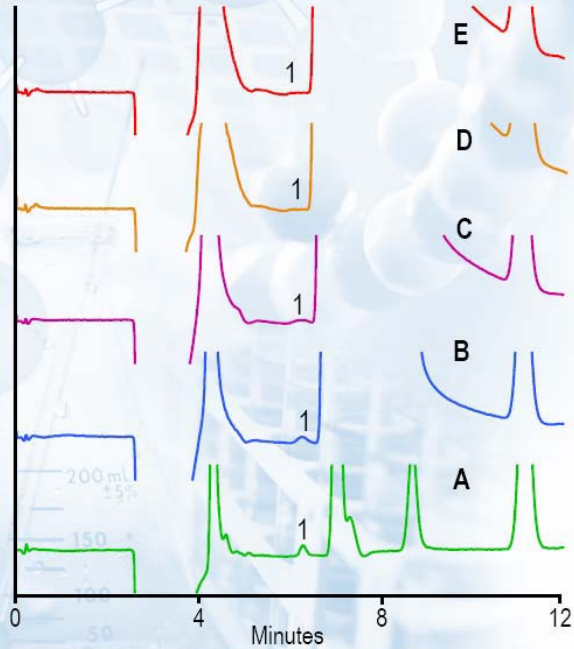
20870

U.S. EPA Methods for Determining Disinfection By-Product Anions

U.S. EPA Method	Analytical Technique	Analytical Column	Analyte(s)
300.0 (B)	IC with Suppressed Conductivity Detection	IonPac® AS9-SC	Chlorite, Bromate, Chlorate
300.1 (B)	IC with Suppressed Conductivity Detection	IonPac AS9-HC	Chlorite, Bromate, Chlorate, Bromide
317.0	IC with Suppressed Conductivity Detection and Postcolumn with ODA	IonPac AS9-HC	Chlorite, Bromate, Chlorate, Bromide
326.0	IC with Suppressed Conductivity Detection and Postcolumn with Acidified KI	IonPac AS9-HC	Chlorite, Bromate, Chlorate, Bromide
321.8	IC-ICP-MS	CarboPac® PA100	Bromate

21392

Effect of Matrix Concentration on Bromate Peak Shape and Recovery



Column: IonPac® AG9-HC, AS9-HC, 4 mm
Flow Rate: 1.0 mL/min
Concentration: 9.0 mM carbonate
Suppressor: AAES®
Current: 58 mA
Loop: 500 µL
Oven: 30 °C

Peaks: 1. Bromate 0.005 mg/L

Matrix Concentration: (ppm of Cl^- and SO_4^{-2})

A	0
B	50
C	100
D	150
E	200

22481

New 2-D Method—Features

- Allows for large loop injection in the first dimension (4-mm column)
  - Possible to inject a larger loop than the standard approach since the capacity and selectivity of the analytical column in the first dimension dictates the recovery and the analyte of interest is analyzed in the second dimension
- Focus the ions of interest in a concentrator column after suppression in the first dimension
  - Hydroxide eluent suppressed to D.I. water thus providing an ideal environment for focusing or concentrating the ions of interest
- Pursue analysis in the second dimension using a smaller column format operated at a lower flow rate leading to sensitivity enhancement that is proportional to the flow rate ratio
  - For a 4-mm column operated in the first dimension at 1 mL/min and a 2-mm column operated in the second dimension at 0.25 mL/min, the enhancement factor is 4
- Easy implementation on through state-of-the-art IC instrumentation

22483

ICS-3000 System for Automated 2-D IC

Software Automation

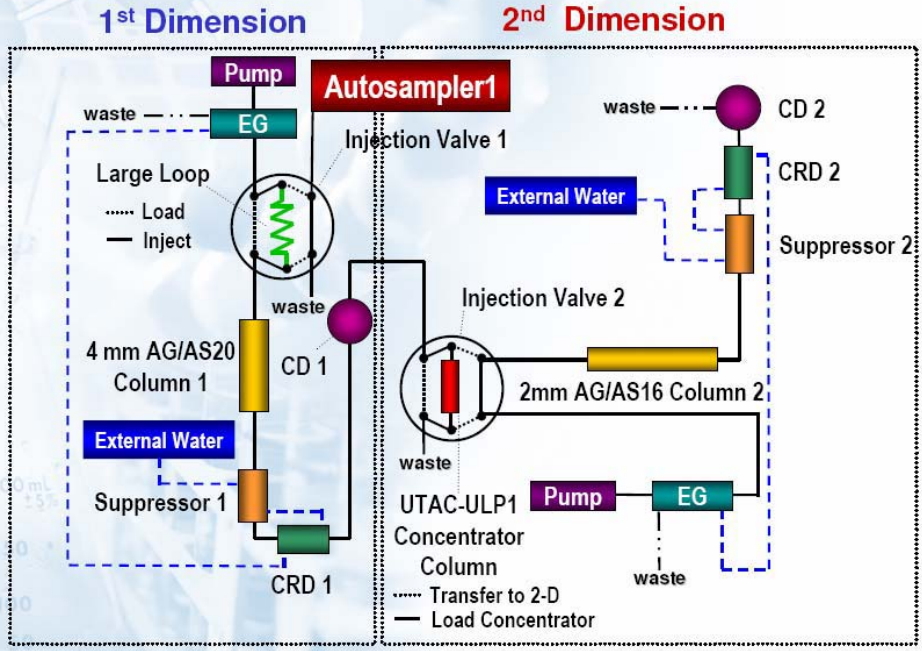
Hardware Automation

Dual Pump

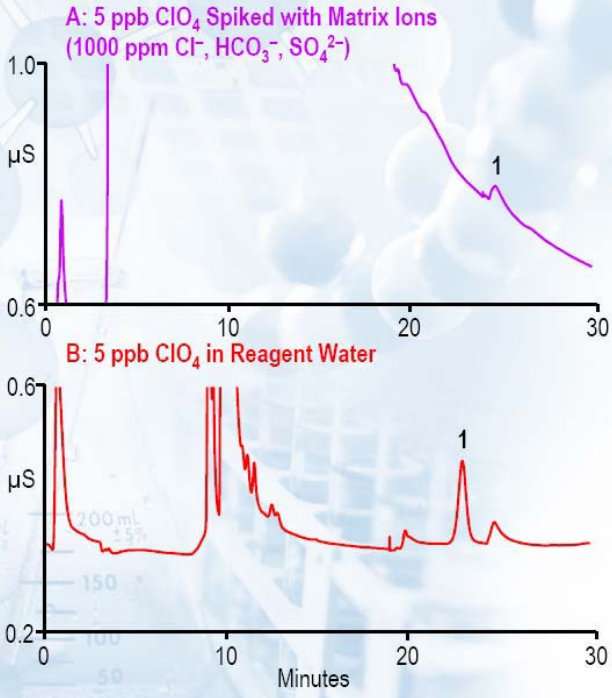
Autosampler DC Module Eluent Generator

22484

Perchlorate: 2-D Method 314.2 Instrument Schematic



1-D Perchlorate Analysis with AS20 Chemistry



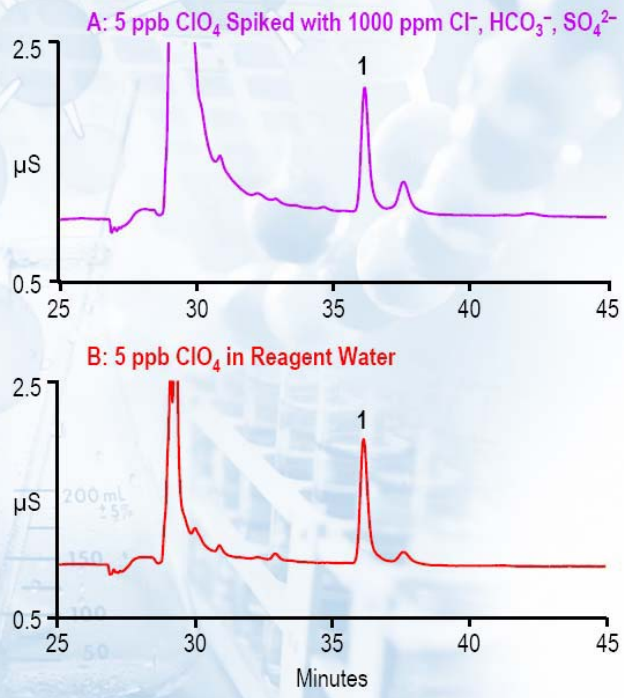
Column:	IonPac® AG20, AS20, 4 mm
Flow Rate:	1.0 mL/min
Concentration:	35 mM KOH
Suppressor:	ASRS® Ultra II, 4 mm
Current:	87 mA
Loop:	4000 µL
Oven:	30 °C
Peak:	1. Perchlorate 0.005 mg/L

Matrix:	A	B
Chloride	1000	0
Bicarbonate	1000	0
Sulfate	1000	0

22285

2-D Perchlorate Analysis with AS20 Chemistry

Second Dimension Chromatograms with (A) and without (B) Matrix



Primary Conditions

Column:	IonPac® AG20, AS20, 4 mm
Flow Rate:	1.0 mL min
Concentration:	35 mM KOH
Suppressor:	ASRS® ULTRA II, 4 mm
Current:	87 mA

Secondary Conditions

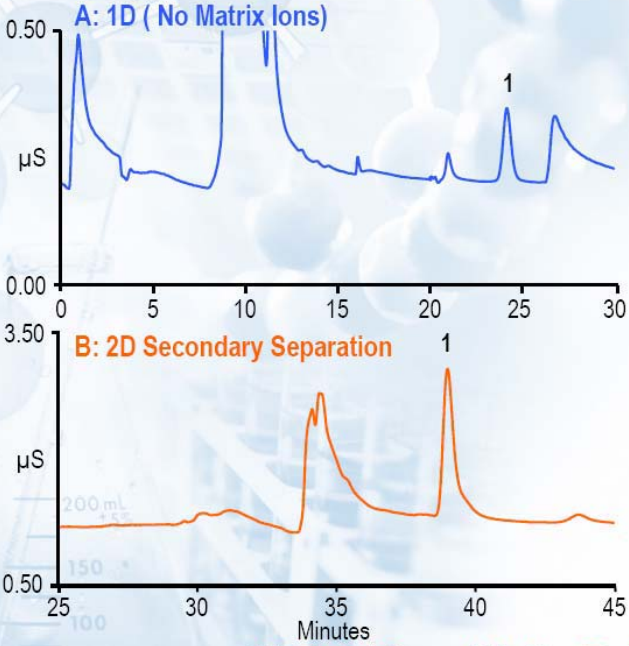
Column:	IonPac AG20, AS20, 2 mm
Flow Rate:	0.25 mL/min
Concentration:	60 mM KOH
Suppressor:	ASRS ULTRA II, 2 mm
Current:	38 mA
Loop:	4000 µL
Concentrator:	TAC-ULP1
Oven:	30 °C
Peak:	1. Perchlorate 0.005 mg/L

Matrix:	A	B
Chloride	1000	0
Bicarbonate	1000	0
Sulfate	1000	0

22286

2-D Perchlorate Analysis with AS16/AS20 Columns

1st (A) and 2nd (B) Dimension Chromatograms



Primary Conditions

Column:	IonPac® AG16, AS16, 4 mm
Flow Rate:	1.0 mL/min
Concentration:	35.0 mM KOH (EG)
Suppressor:	ASRS® ULTRA II, 4 mm
Current:	150 mA
Loop:	4000 µL

Secondary Conditions

Column:	IonPac AS20, 1 mm prototype
Flow Rate:	0.10 mL/min
Concentration:	35.0 mM KOH (EG)
Suppressor:	ASRS ULTRA II, 2 mm
Current:	38 mA
Concentrator:	TAC-ULP1
Peak:	1. Perchlorate 5.0 µg/L

Peak Area	
Primary:	0.0754
Secondary:	0.8799

10-Fold Sensitivity Enhancement

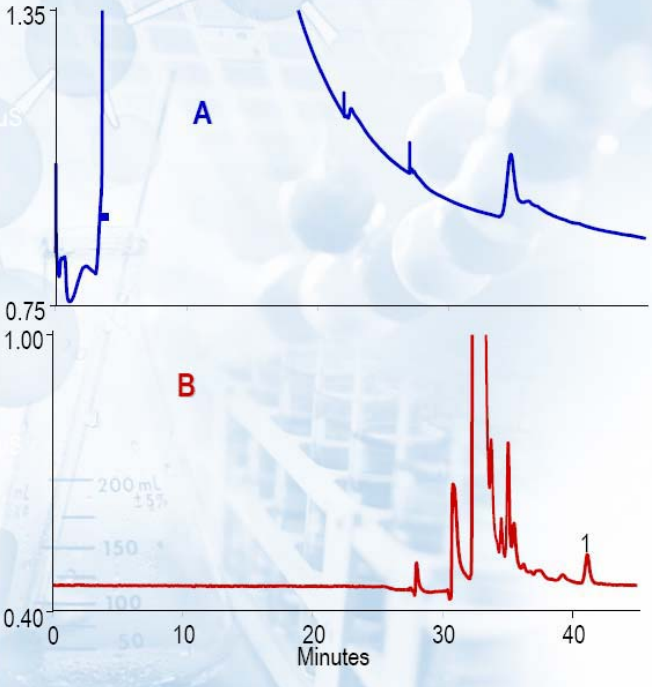
22288

2-D Perchlorate Analysis
Peak Area Recovery at 5 ppb

Matrix Concentration (ppm)	Perchlorate Peak Area	Recovery
0	0.3522	100%
50	0.3560	101.1%
100	0.3567	101.3%
200	0.3509	99.6%
500	0.3505	99.5%
800	0.3468	98.5%
1000	0.3438	97.6%

22287

0.5 ppb Perchlorate Spiked in High Inorganic Water
1st (A) and 2nd (B) Dimension Chromatograms



A) First-Dimension Conditions

Column:	IonPac® AG20, AS20, 4 mm
Flow Rate:	1.0 mL/min
Concentration:	35 mM KOH
Suppressor:	ASRS® Ultra II, 4 mm
Current:	150 mA

B) Second-Dimension Conditions

Column:	IonPac AG16, AS16, 2 mm
Flow Rate:	0.25 mL/min
Concentration:	65 mM KOH
Suppressor:	ASRS Ultra II, 2 mm
Current:	41 mA
Loop:	4000 µL
Concentrator:	TAC-ULP1 (5 x 35 mm)
Oven:	30 °C
Peak:	1. Perchlorate 0.5 µg/L

Matrix:

Chloride:	1000 mg/L
Bicarbonate:	1000
Sulfate:	1000

Calibration and Limit of Detection

Method	Analyte	Range (µg/L)	Linearity[a] (r^2)	MDL[b] (µg/L)	Standard deviation of MDL (µg/L)	Retention Time Precision (%RSD[c])	Peak Area Precision (%RSD)
2D ClO_4	Perchlorate	0.3-10	0.9998	0.016	±0.005	0.02	2.66
Primary (Method 314.1)	Perchlorate	0.5-10	0.9999	0.023	±0.007	0.06	5.15
Confirmatory (Method 314.1)	Perchlorate	0.5-10	0.9999	0.026	±0.008	0.10	5.64

[a]Quadratic fit

[b]MDL = $\sigma t_{S,99}$ where $t_{S,99}$ = 3.14 for n = 7 using a concentration of 0.06 µg/L as the MDL standard

[c]RSD = relative standard deviation, n = 7 for 0.5 µg/L perchlorate standard

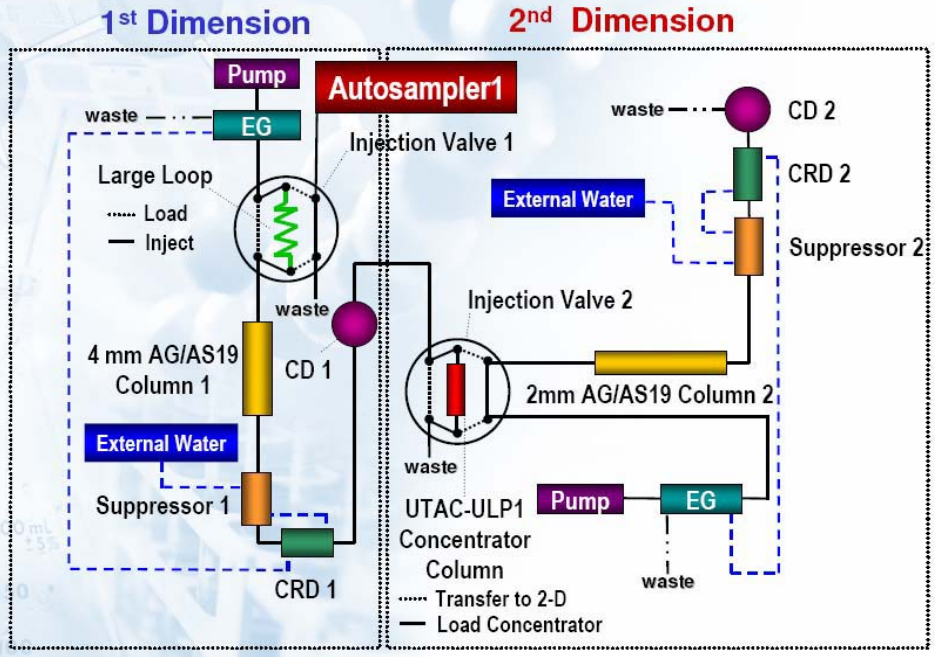
Precision and Accuracy

			Peak Area Precision (%)			Average Recovery (%)		
Matrix	Spiked Perchlorate (µg/L)	# Reps	2D ClO_4	Primary Method (314.1)	Confirm. Method (314.1)	2D ClO_4	Primary Method (314.1)	Confirm. Method (314.1)
HIW	0.5	7	2.07	4.24	4.10	95.8	93.3	95.7
	5.0	7	0.21	2.22	2.22	99.7	106.4	101.8
Sunnyvale Drinking Water	0.5	7	1.40	3.30	N/A	95.9	106.6	N/A
	5.0	7	0.74	1.42	5.96	98.9	97.4	120.1
San Jose Drinking Water	0.5	7	1.77	3.40	2.28	102.0	98.8	103.8
	5.0	7	0.94	2.60	2.21	99.0	108.8	108.7
Scotts Valley Drinking Water	0.5	7	1.53	4.00	N/A	97.1	107.8	N/A
	5.0	7	0.99	2.24	4.95	100.9	112.0	107.3
Palo Alto Drinking Water	0.5	7	1.54	—	—	100.8	—	—
	5.0	7	0.98	—	—	100.9	—	—

N/A = not available due to a co-eluting peak

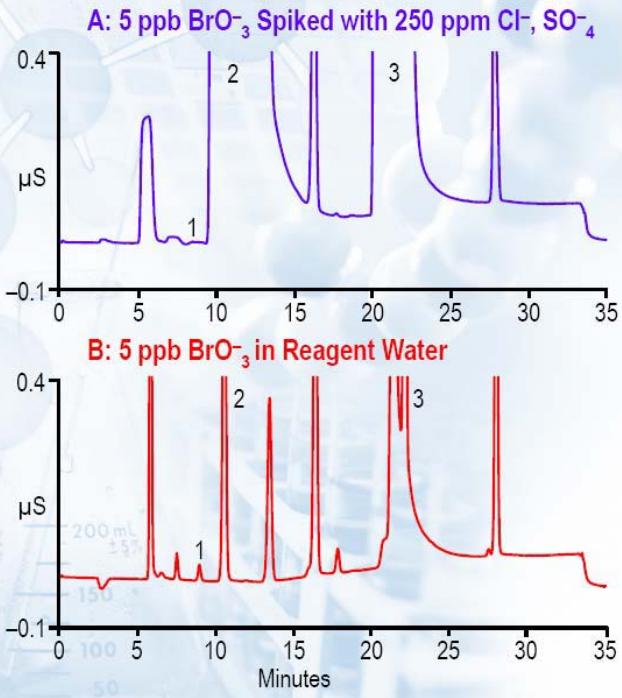
— Samples not analyzed by Method 314.1

Bromate: 2-D Method 314.2 Instrument Schematic



Note: Other columns used in 2nd Dimension: AS23, AS11HC, AS15

1-D Bromate Analysis with AS19 Gradient Chemistry



Column: IonPac® AG19/AS19 4 mm
Flow Rate: 1.0 mL/min
Suppressor: ASRS® ULTRA II, 4 mm
Current: 113 mA
Loop: 500 µL
Oven: 30 °C

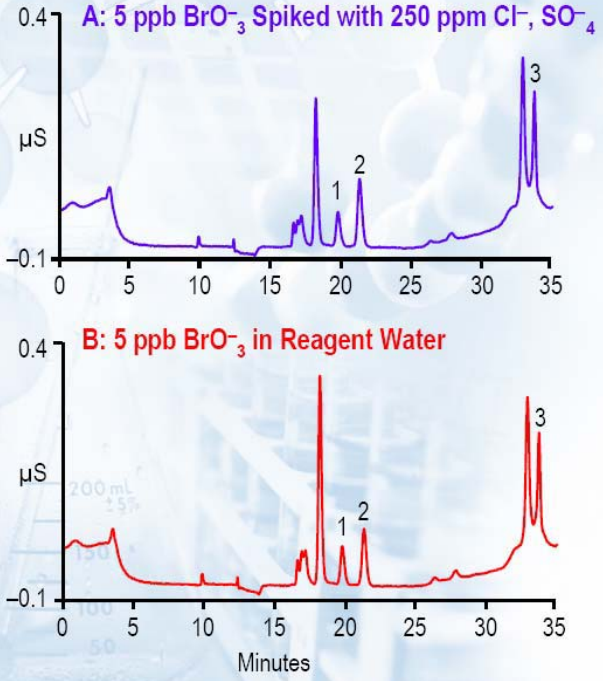
Time:	KOH Gradient (mM)
0	10
10	10
25	45
30	45
30.1	10
35	10

Peaks:	A	B
1. Bromate	0.005 mg/L	0.005 mg/L
2. Chloride	250	0.030
3. Sulfate	250	0.150

22486

2-D Bromate Analysis with AS19 Gradient Chemistry

2nd Dimension Chromatograms with (A) and without (B) Matrix



Primary Condition

Column:	IonPac® AG19, AS19, 4 mm
Flow Rate:	1.0 mL/min
Suppressor:	ASRS® ULTRA II, 4 mm
Current:	113 mA

Secondary Condition

Column:	IonPac AG19, AS19, 2 mm
Flow Rate:	0.25 mL/min
Suppressor:	ASRS ULTRA II, 2 mm
Current:	29 mA
Loop:	500 µL
Concentrator:	TAC-ULP1
Temperature:	30 °C

Time:	Gradient (mM)	Gradient (mM)
0	10	10
10	10	
19.5		10
25	45	
30	45	
30.1	10	
34.5		45
35	10	45

Peaks:	A	B
1. Bromate	0.005 mg/L	0.005 mg/L
2. Chloride	250	0.030
3. Sulfate	250	0.150

22487

Bromate Peak Recovery with the 2-D Method

Chloride & Sulfate Matrix Concentration (ppm)	Bromate Peak Area	Recovery
0	0.0248	100%
50	0.0245	98.8%
100	0.0250	100.8%
150	0.0244	98.4%
200	0.0249	100.4%
250	0.0249	100.4%

22488

2-D Method Sensitivity Enhancement for Bromate

Dimension	Response Peak Area	Flow Rate ml/min	Sensitivity
First (4 mm)	0.0063	1	1
Second (2 mm)	0.0248	0.25	3.936

MDL based on n = 7 runs (students *t* test) 0.2 ppb for a 500-µL injection with 200 ppm of chloride and sulfate using suppressed conductivity detection

22489

Summary

- Trace analysis of environmental contaminants such as perchlorate and bromate push the performance limits of conventional determinant methods such as IC with suppressed conductivity detection.
- Matrix composition is most frequently a factor in trace analysis.
- Confirmation analysis is required for definitive determinations, which normally requires more sensitive and selective detection and quantitation.
- Matrix elimination techniques assist in reducing interferences and enabling better sensitivity using conventional detectors.
- 2-D IC is a cost effective technology that allows confirmatory trace analysis using conventional detection.

TRACE LEVEL DETERMINATION OF PERCHLORATE IN SOILS, SALT WATER BY TANDEM SUPPRESSED CONDUCTIVITY AND MASS SPECTROSCOPY (IC/MS)

Gandhi Sr., Jay; Metrohm-Peak, Inc.

Perchlorate salts are being used as rocket propellants, in fireworks and in the electroplating industry. Recently, it is believed by the scientific community that Perchlorate hinders the iodine absorption ability of the thyroid gland posing higher health risk for the public. Perchlorate can be released into the soils, ground water, surface water and irrigational waters, which in turn contaminate crops of vegetables and fruits. It is critical to identify and quantify levels of Perchlorate contamination in soils, saltwater and waste effluents from Perchlorate manufacturing sites. This presentation demonstrates use of conventional ion chromatography conductivity detection and mass spectrometer in tandem. Difficulties and remedies in sample extractions along with benefits of mass spectrometer will be discussed.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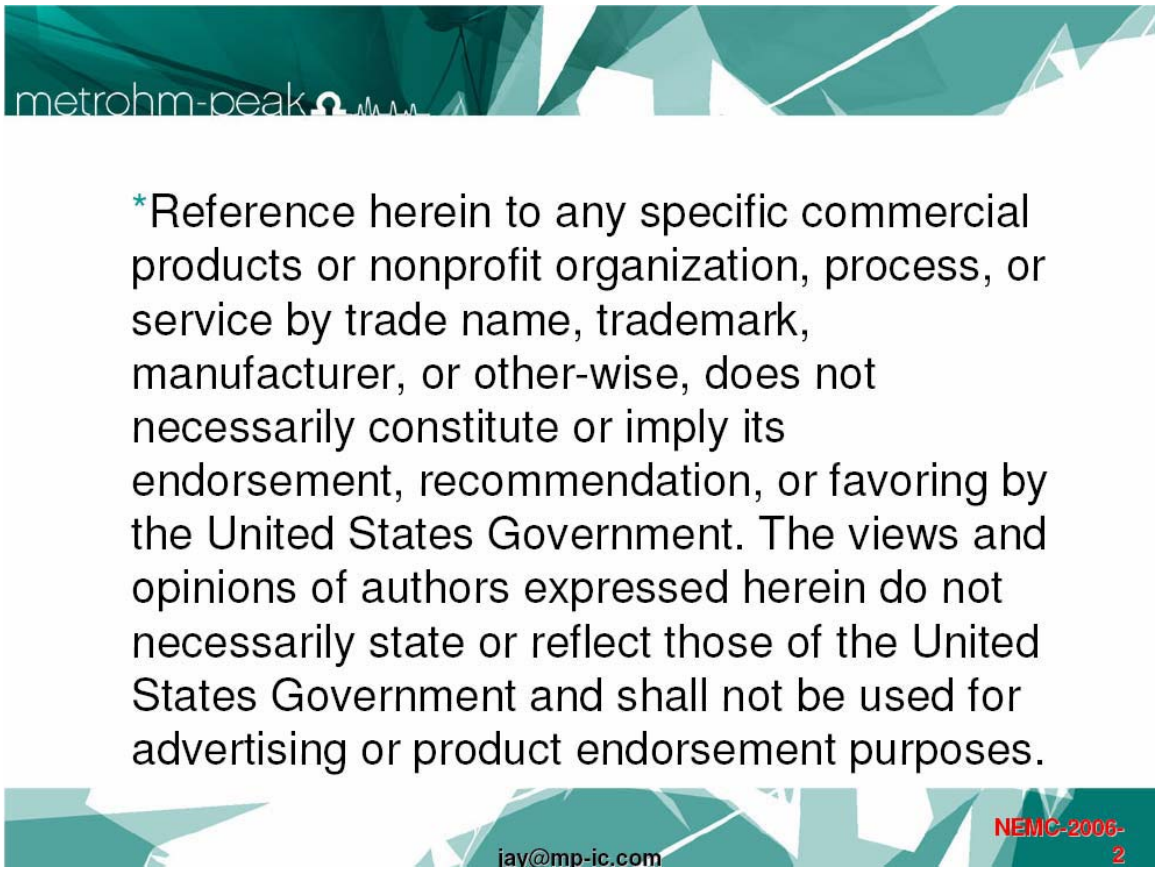
Trace Level Determination of Perchlorate in Soils, Salt Water by Tandem Suppressed Conductivity and Mass Spectroscopy (IC/MS)
Presented by
Jay Gandhi**
Sr. Development Chemist
Metrohm-Peak Inc.,
Houston TX – USA
Johnson Mathew
Env. Scientist
USEPA Region-6
Houston TX - USA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*Reference 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.
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NEMC-2006-2

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Outline

- Perchlorate analysis – a new challenge
- Experimental
- Real World Data
- Summary

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Perchlorate Analysis

- USEPA method 314 – suppressed conductivity
- USEPA method 314.1 – Matrix elimination and pre-concentration
- USEPA method 332.0 – ICMS and ICMSMS
- USEPA method 331.0 – LCMS and LCMSMS

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USEPA method 314.0

Determination of Perchlorate in various water matrix
by suppressed conductivity

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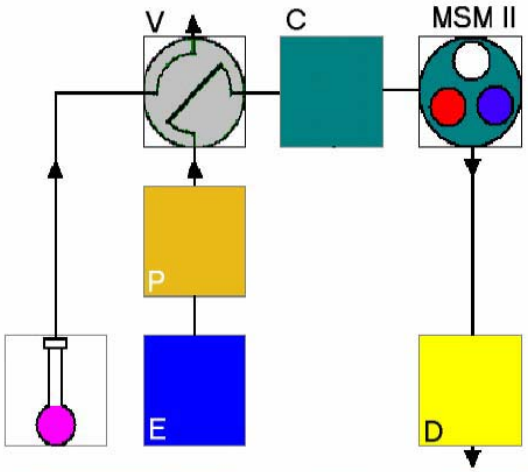
USEPA method 314.0

Using a Functionalized Monolithic Column

Advanced Modular IC	
E	Eluent
P	Pump
V	Valve with loop
C	Column
MSM II	Metrohm Suppressor Module «MSM»
D	Detector



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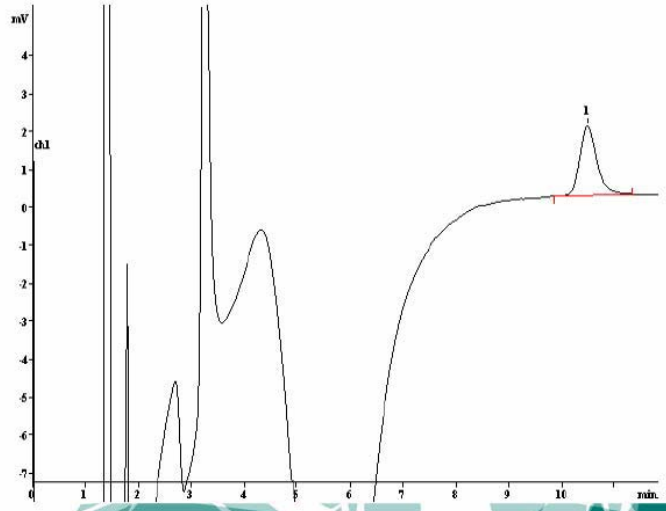
USEPA method 314.0

5 ppb Perchlorate in Ultra Pure Water

Metrosep Dual 4 – 50 mm

1 Perchlorate 5 ppb

LiOH/p-cyanophenol; 5/12 mM; 1.75 mL/min; 750 µL



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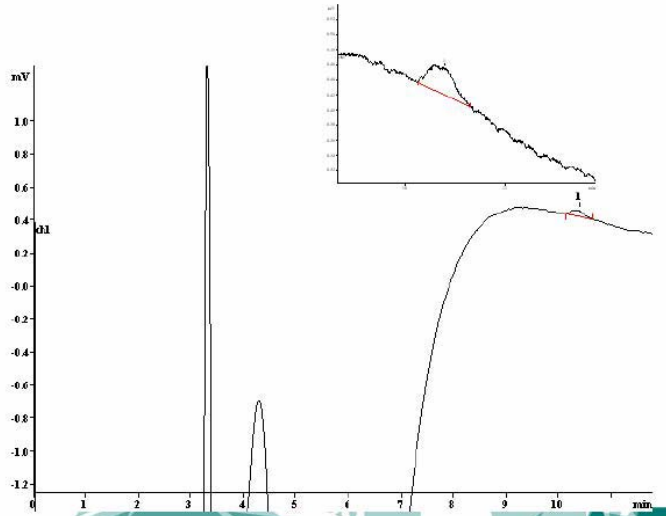
USEPA method 314.0

0.13 ppb Perchlorate in Ultra Pure Water

Metrosep Dual 4 – 50 mm

1 Perchlorate 0.13 ppb

LiOH/p-cyanophenol; 5/12 mM; 1.75 mL/min; 750 µL



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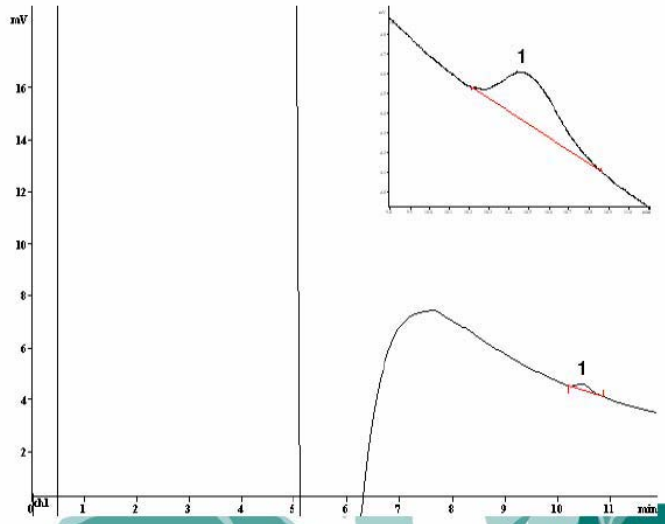
USEPA method 314.0

0.5 ppb Perchlorate in High Ionic Matrix

Metrosep Dual 4 – 50 mm		
	Chloride	1'000 ppm
	Carbonate	1'000 ppm
	Sulfate	1'000 ppm
1	Perchlorate	0.54 ppb



LiOH/p-cyanophenol; 5/12 mM; 1.75 mL/min; 750 µL

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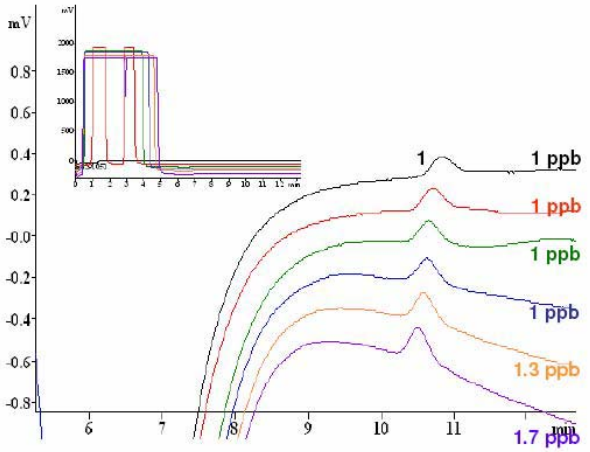
USEPA method 314.0

ppb Levels Perchlorate in High Ionic Matrix

Metrosep Dual 4 – 50 mm

1	Perchlorate in Reagent Water
	50 ppm Cl^-, HCO_3^-, SO_4^{2-}
	250 ppm Cl^-, HCO_3^-, SO_4^{2-}
	500 ppm Cl^-, HCO_3^-, SO_4^{2-}
	750 ppm Cl^-, HCO_3^-, SO_4^{2-}
	1'000 ppm Cl^-, HCO_3^-, SO_4^{2-}



LiOH/p-cyanophenol; 5/12 mM; 1.75 mL/min; 750 µL

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USEPA method 314.0

Calibration

Metrosep Dual 4 - 50

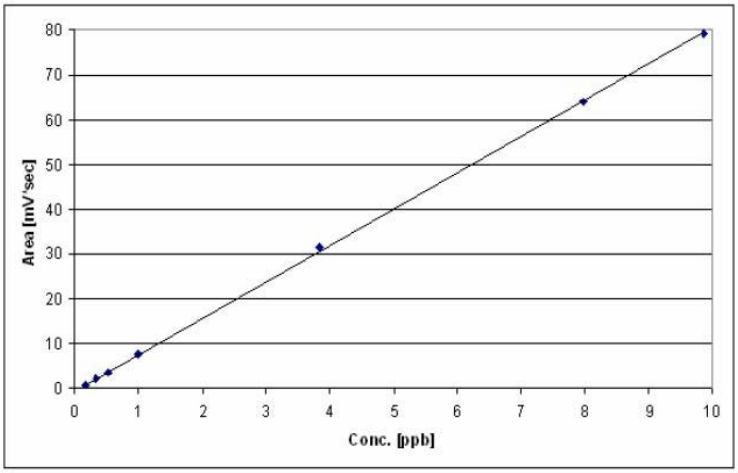
Calibration level

0.17, 0.35, 0.53, 0.99, 3.84, 7.97, 9.87 ppb

Correlation coefficient

$r^2 = 0.9999$

$y = 8.0945x - 0.474$



LiOH/p-cyanophenol; 5/12 mM; 0.8 mL/min; 3.5 mL

USEPA method 314.0

Precision, Recovery and LCMRL

Conc. [ppb]	Mean [n=7]	SD	RSD [%]	Recovery [%]
0.113	0.133	0.0041	3.1	118
0.17	0.168	0.0065	3.8	99
0.345	0.323	0.0078	2.4	94
0.521	0.529	0.0033	0.6	102
0.95	0.959	0.0313	3.3	101
1.976	1.984	0.0772	3.9	100

Lowest Concentration Method Reporting Level: 0.113 ppb

(calculated by the USEPA)

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USEPA method 314.1

Determination of Perchlorate in various water matrix by pre-concentration and matrix elimination suppressed conductivity

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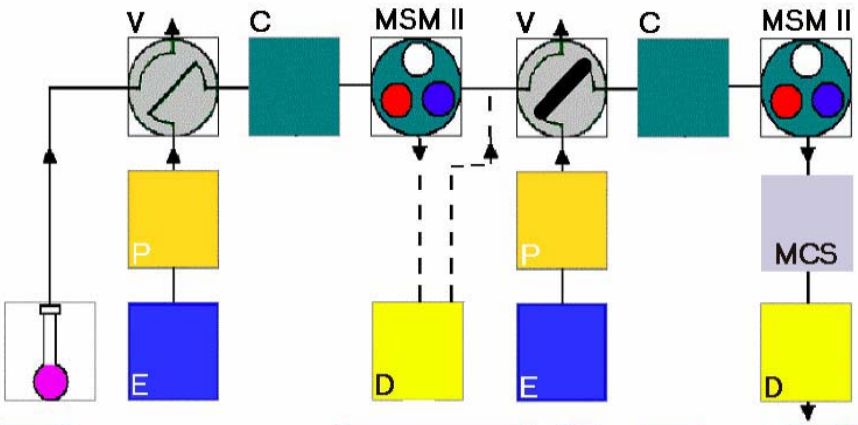
USEPA method 314.1

Using IC Pre-separation Technique

System 1: Pre-separation	System 2: Separation/Determination



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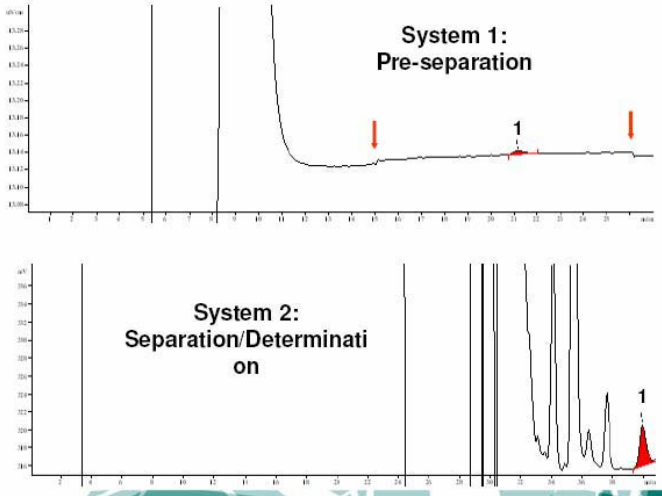
USEPA method 314.1

0.5 ppb Perchlorate in Ultra Pure Water

Metrosep A Supp 5 – 150 mm

1	Perchlorate in UPW	0.5 ppb

Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL



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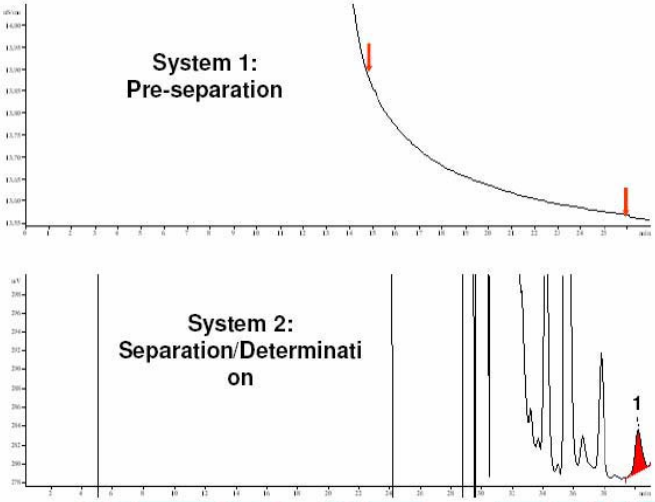
Pre-separation Technique

0.5 ppb Perchlorate in High Ionic Matrix

Metrosep A Supp 5 – 150 mm

	Chloride	1'000 ppm
	Carbonate	1'000 ppm
	Sulfate	1'000 ppm
1	Perchlorate	0.5 ppb

Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL



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USEPA method 314.1

Calibration

Metrosep A Supp 5 – 150

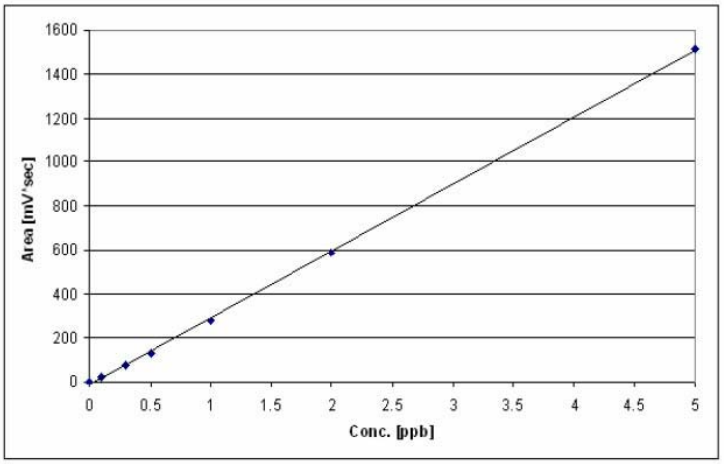
Calibration level

0, 0.1, 0.3, 0.5, 1, 2, 5 ppb

Correlation coefficient

$r^2 = 0.9997$

y = 304.24x - 13.821



Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL

metrohm-peak

USEPA method 314.1

Precision, Recovery and MDL

Conc. [ppb]	Mean [n=7]	SD	RSD [%]	Recovery [%]
0.1	0.116	0.0017	1.4	116
0.3	0.286	0.0088	3.1	95
0.5	0.481	0.0136	2.8	96
1	0.987	0.0143	1.5	99
2	2.020	0.0225	1.1	101
5	5.000	0.0636	1.3	100

Method Detection Limit: 0.1 ppb

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USEPA method 331.0

Determination of Perchlorate in various water matrix
by LCMS, LCMSMS

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Agilent 1100 LC/MSD

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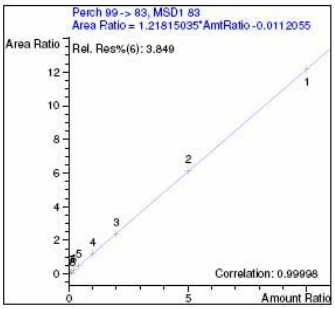
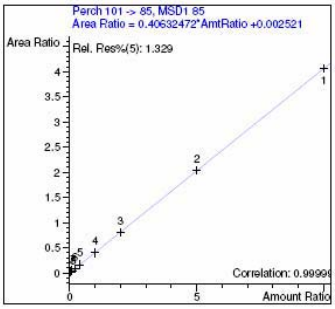
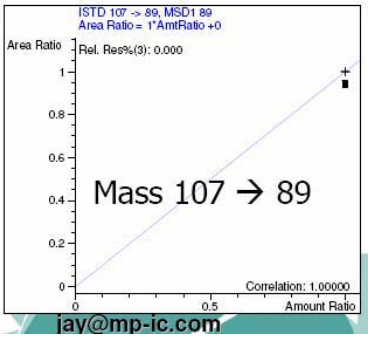
Metrohm LC column



Range for Calibration Standards 0.2ppb to 10ppb (ClO_4^{1-})



Mass 99 → 83



Mass 101 → 85

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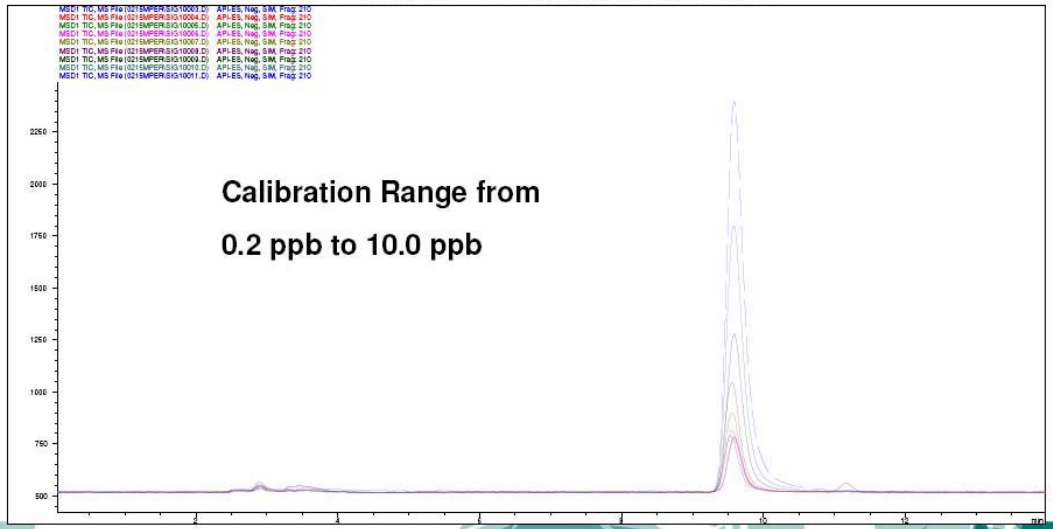
Total Ion Chromatograms (TIC) Calib. Standards



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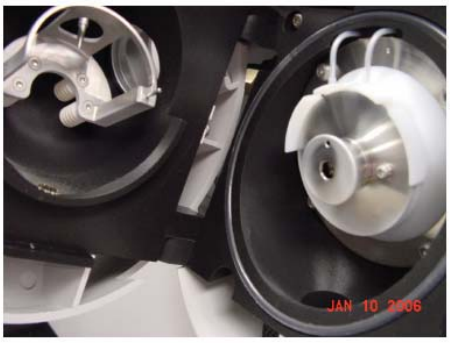
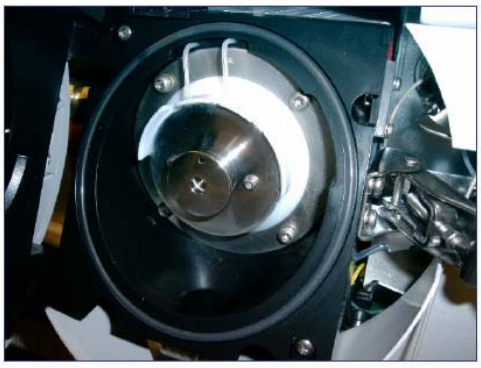
LC-MSD Interface after 40 injections (method 331.0)



Salty interface



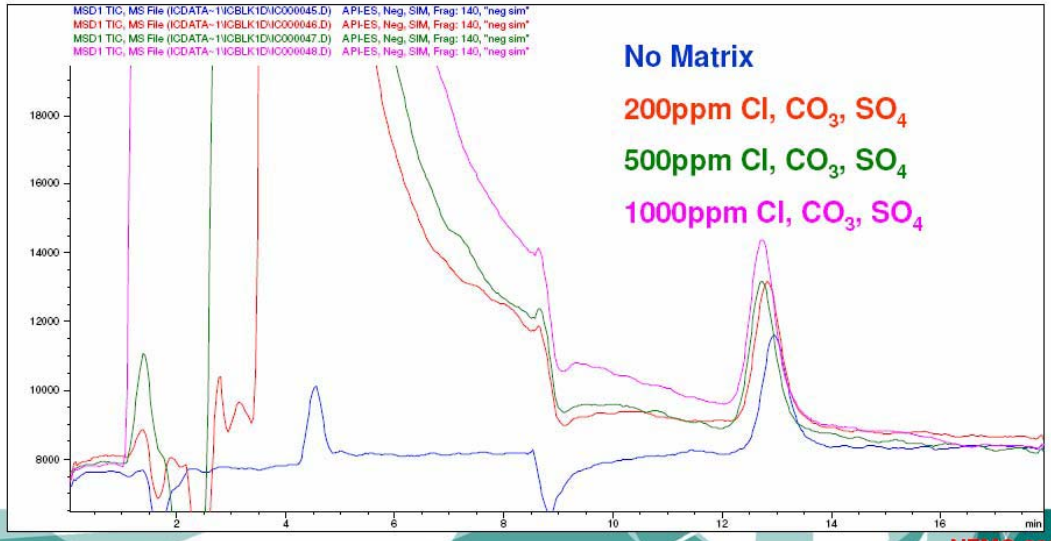
metrohm-peak

USEPA method 332.0

Determination of Perchlorate in various water matrix
by ICMS, ICMSMS

metrohm-peak

Synthetic Water Matrix Spikes Overlaid with 1ppb Standard



jay@mp-ic.com

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Soil Samples

jay@mp-ic.com

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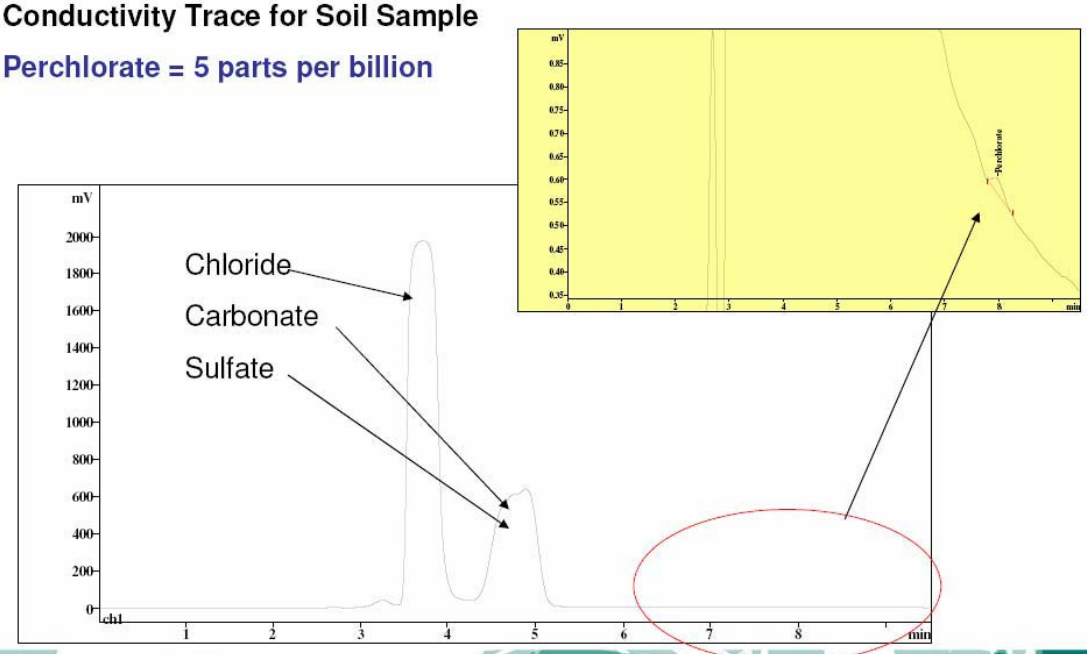
Conductivity Trace for Soil Sample

Perchlorate = 5 parts per billion



jay@mp-ic.com

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Challenges

- **Soil matrix can be**
  - **Very fine (clay)**
  - **Contains high concentration of transition metals**
  - **Contains excessive amount of Calcium and Magnesium etc.**

Remedies for the challenges

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Solution

- 1 gm Sample + 10ml of 20mM (HCl + HNO_3)
  - It removes Carbonates by CO_2↑
  - Converts metals into water soluble salts of Chloride and Nitrates
  - In-line filtration auto-sampler removes particulates and

Metals are removed by…..

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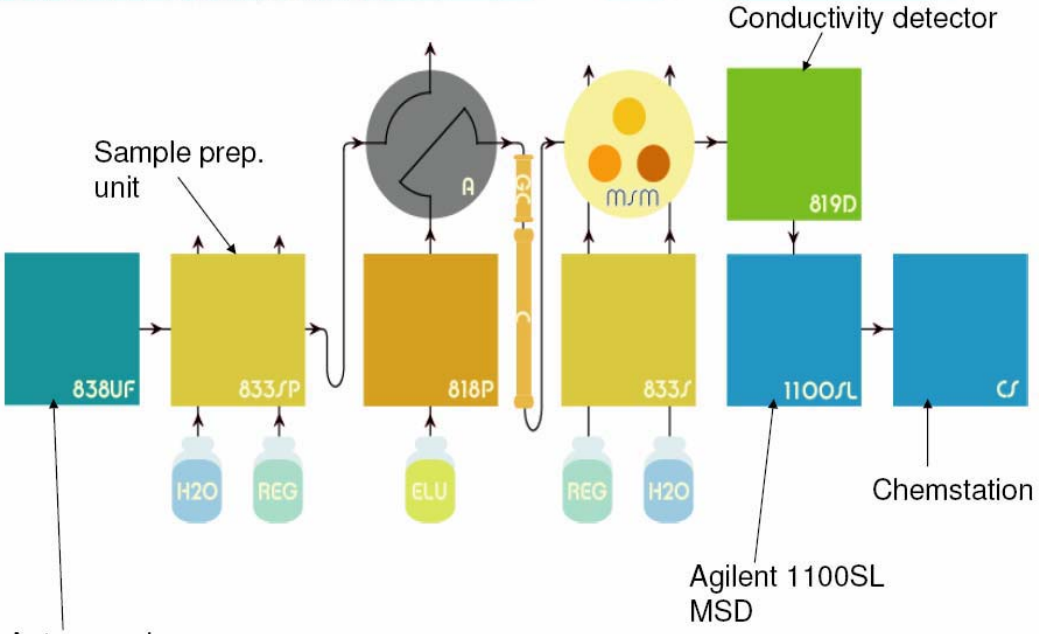

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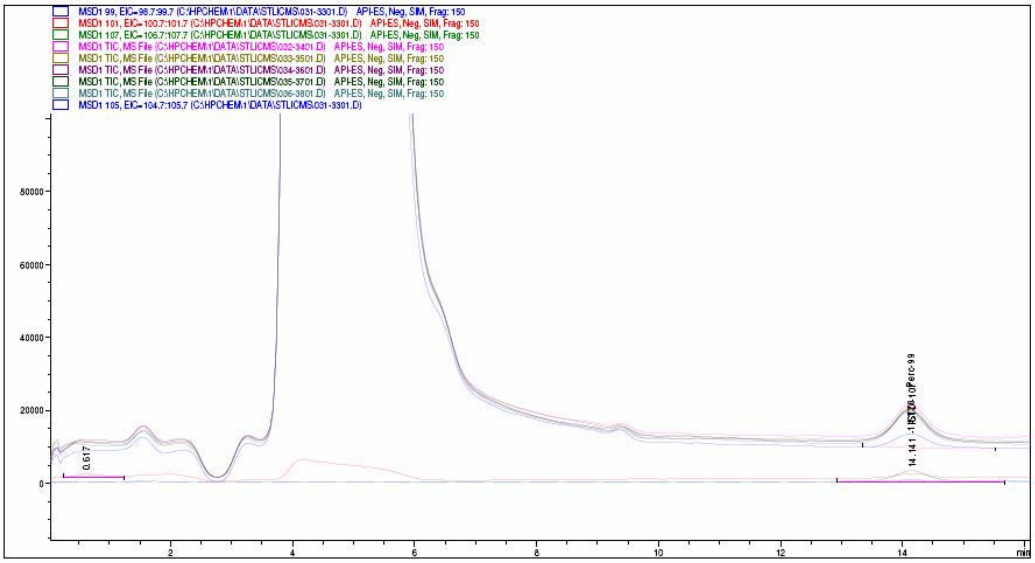
Data of Soil Samples

After implementation of extraction and in-line sample preparation



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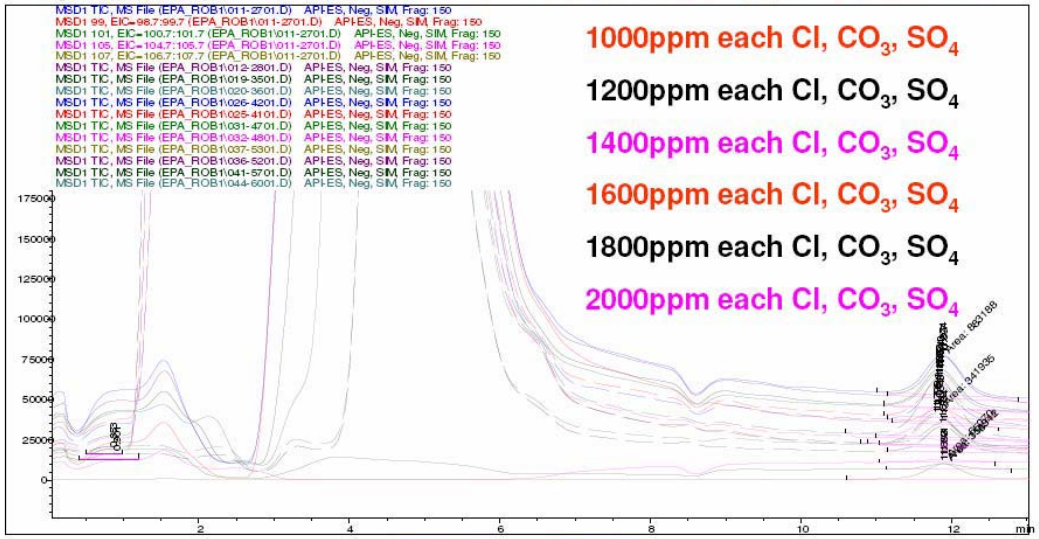
Synthetic Matrix Spikes Overlaid with 1ppb Standard



Simulated Soil Matrix

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MDL Study for Soil Samples

Sample ID	m/z 99, ppb	m/z 101, ppb	m/z 107, ppb	True Value, ppb	m/z 99, % Rec	m/z 101, % Rec
Soil-0.5ppb-1	0.4529	0.4820	1.00	0.502	90.22%	96.02%
Soil-0.5ppb-2	0.4727	0.4892	1.00	0.502	94.16%	97.45%
Soil-0.5ppb-3	0.4698	0.5133	1.00	0.502	93.59%	102.25%
Soil-0.5ppb-4	0.4269	0.5865	1.00	0.502	85.04%	116.83%
Soil-0.5ppb-5	0.5541	0.5176	1.00	0.502	110.38%	103.11%
Soil-0.5ppb-6	0.4916	0.5186	1.00	0.502	97.93%	103.31%
Soil-0.5ppb-7	0.4794	0.5375	1.00	0.502	95.50%	107.07%
Average	0.478	0.521	1.000	0.502	95.26%	103.72%
Std Deviation	0.039	0.035			0.078	0.069
% RSD	8.24%	6.64%			8.24%	6.64%
Calculated MDL, ppb	0.124	0.109				

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MDL Study for Soil Samples

Sample ID	m/z 99, ppb	m/z 101, ppb	m/z 107, ppb	True Value, ppb	m/z 99, % Rec	m/z 101, % Rec
Soil-5.0ppb-1	5.6846	5.8867	1.00	5.99	94.90%	98.27%
Soil-5.0ppb-2	5.6971	5.8566	1.00	5.99	95.11%	97.77%
Soil-5.0ppb-3	5.7143	5.8664	1.00	5.99	95.40%	97.94%
Soil-5.0ppb-4	5.7931	5.8270	1.00	5.99	96.71%	97.28%
Soil-5.0ppb-5	5.6886	5.7892	1.00	5.99	94.97%	96.65%
Soil-5.0ppb-6	5.6702	5.8107	1.00	5.99	94.66%	97.01%
Soil-5.0ppb-7	5.6693	5.8294	1.00	5.99	94.65%	97.32%
Average	5.702	5.838	1.000	5.990	95.20%	97.46%
Std Deviation	0.043	0.034			0.007	0.006
% RSD	0.75%	0.58%			0.75%	0.58%
Calculated MDL, ppb	0.135	0.106				

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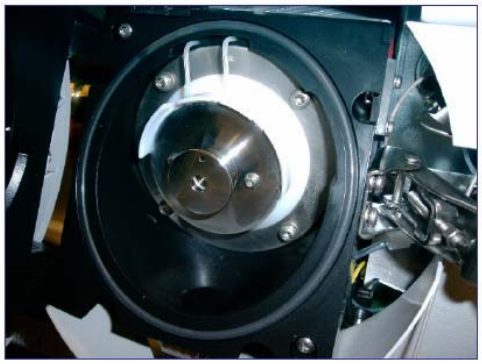
MSD Interface after 150 injections



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Acknowledgements

- USEPA – Region 6
- USEPA – OSW, Washington DC
- Customers of Metrohm-Peak for providing data and soil samples
- STL – Savannah, GA


metrohm-peak
Thank you for Listening
jay@mp-ic.com
NEMC-2006-37

THE HIGHEST LEVELS OF PERCHLORATE DETECTED IN FOODS AND BEVERAGES BY ION CHROMATOGRAPHY COUPLED WITH TANDEM MASS SPECTROMETRY (IC-ESI-MS/MS)

Antonsen, Stephen – Dionex Corporation; El Aribi, H. – MDS Sciex; Le Blanc, Y. – MDS Sciex; Sakuma, T. – MDS Sciex

A new IC-ESI-MS/MS method, with simple sample preparation procedure, has been developed for quantification and confirmation of perchlorate (ClO_4^-) anions in water, fresh and canned food, wine and beer samples at low part-per-trillion (ng l^{-1}) levels. To the best of our knowledge, this is the first time an analytical method is used for determination of perchlorate in wine and beer samples.

The IC-ESI-MS/MS instrumentation consisted of an ICS-2500 ion chromatography system coupled to either an API 2000™ or an API 3200™ mass spectrometer. The IC-ESI-MS/MS system was optimized to monitor two pairs of precursor and fragment ion transitions, i.e., multiple reaction monitoring (MRM). All samples had oxygen-18 isotope labeled perchlorate internal standard added prior to extraction. Chlorine isotope ratio ($^{35}Cl/^{37}Cl$) was used as a confirmation tool. The transition of $^{35}Cl^{16}O_4^-$ (m/z 98.9) into $^{35}Cl^{16}O_3^-$ (m/z 82.9) was monitored for quantifying the main analyte; the transition of $^{37}Cl^{16}O_4^-$ (m/z 100.9) into $^{37}Cl^{16}O_3^-$ (m/z 84.9) was monitored for examining a proper isotopic abundance ratio of $^{35}Cl/^{37}Cl$; and the transition of $^{35}Cl^{18}O_4^-$ (m/z 107.0) into $^{35}Cl^{18}O_3^-$ (m/z 89.0) was monitored for quantifying the internal standard. The minimum detection limit (MDL) for this method in de-ionized water is 5 ng l^{-1} (ppt) using the API 2000™ mass spectrometer and 0.5 ng l^{-1} using the API 3200™ mass spectrometer.

Over 350 food and beverage samples were analyzed mostly in triplicate. Except for four, all samples were found to contain measurable amounts of perchlorate. The levels found ranged from 5 ng l^{-1} to 463.5 ± 6.36 µg kg^{-1} using MRM 98.9 → 82.9 and 100 µl injection.

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NEMC 2006

The Highest Levels of Perchlorate Detected in Foods and Beverages by IC-ESI-MS/MS

World Wide Survey

Houssain El Aribi, Ph. D.

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LC- or IC- MS/MS Topics in Environmental Analysis

- Pesticides (target analysis, screening, very polar pesticides)
- Perchlorate
- Disinfection by-products: haloacetic acids, bromate, trihamethanes, etc…
- Estrogens and endocrine disruptors
- Fluorinated compounds
- Brominated flame retardants
- Polycyclic aromatic hydrocarbons
- Explosives
- Algal toxins and shellfish toxins
- Biogenic amines
- Antibiotics
- Screening for emerging compounds, etc.…

They are found in contaminated water, food, beverages, soils, etc.. .
They could pose a serious threat to human health.

2

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Challenges

- Screening for hundreds of emerging compounds using analytical instruments
  - Sample preparation (*as simple as possible*)
  - Separation (*HPLC, IC, etc…*)
  - Detection *(as sensitive as possible i.e., MS/MS)*
  - Confirmation (*using ISTD and isotope ratios*)
- Analyzing very polar compounds *(IC-MS/MS)*
- Ease-of-use *(software)*

3

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LC- or IC-MS/MS Involves…

- **Chromatography – separation of analytes**
  - Pumps
  - Autosampler
  - Column
- **Ionization – ion production**
  - Electrospray (ESI, TurboIonSpray® source)
  - Atmospheric Pressure Chemical Ionization (APCI)
  - Atmospheric Pressure Photo Ionization (APPI)
- **MS filtering – ion transmission**
  - Q_1 Selected Ion Monitoring (SIM)
  - Q_1-Q_3 parent to product ion transitions (MRM); highly specific
  - Other possibilities as well…
- **Detection – ion detection (signal to peak)**
- **Data analysis**
  - Qualitative (what is it?)
  - Quantitative (how much is present?)

4

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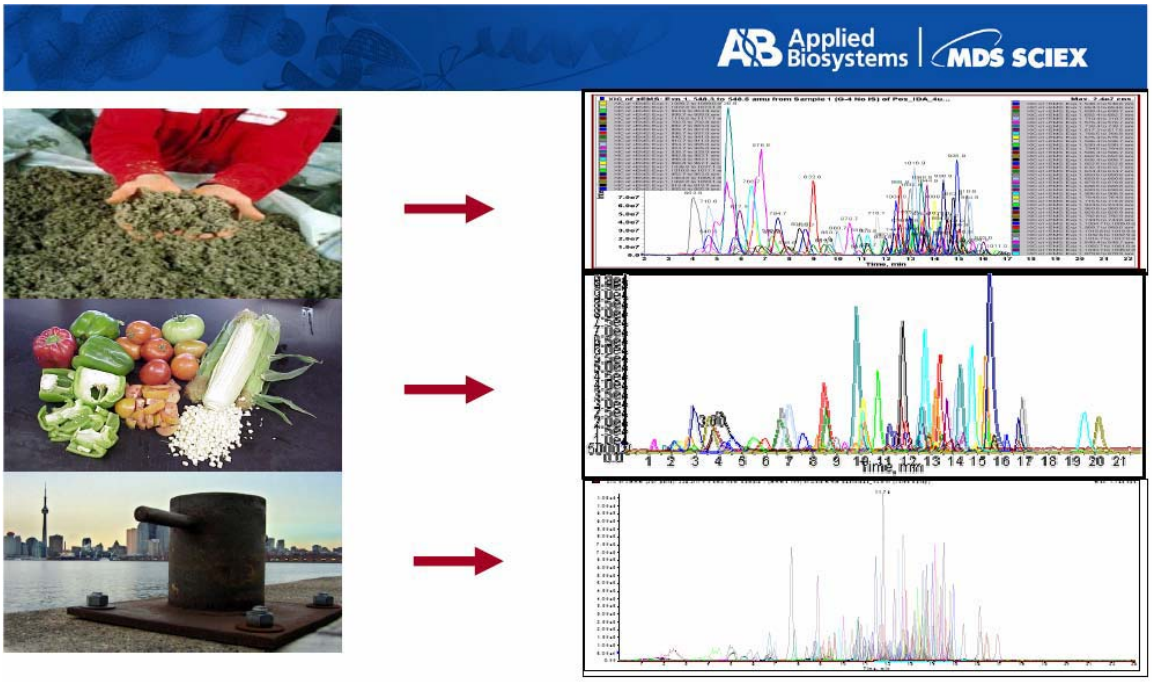

How to go from this .....to this

(Sample xxxxx).....(quantitation with high reliability)

5

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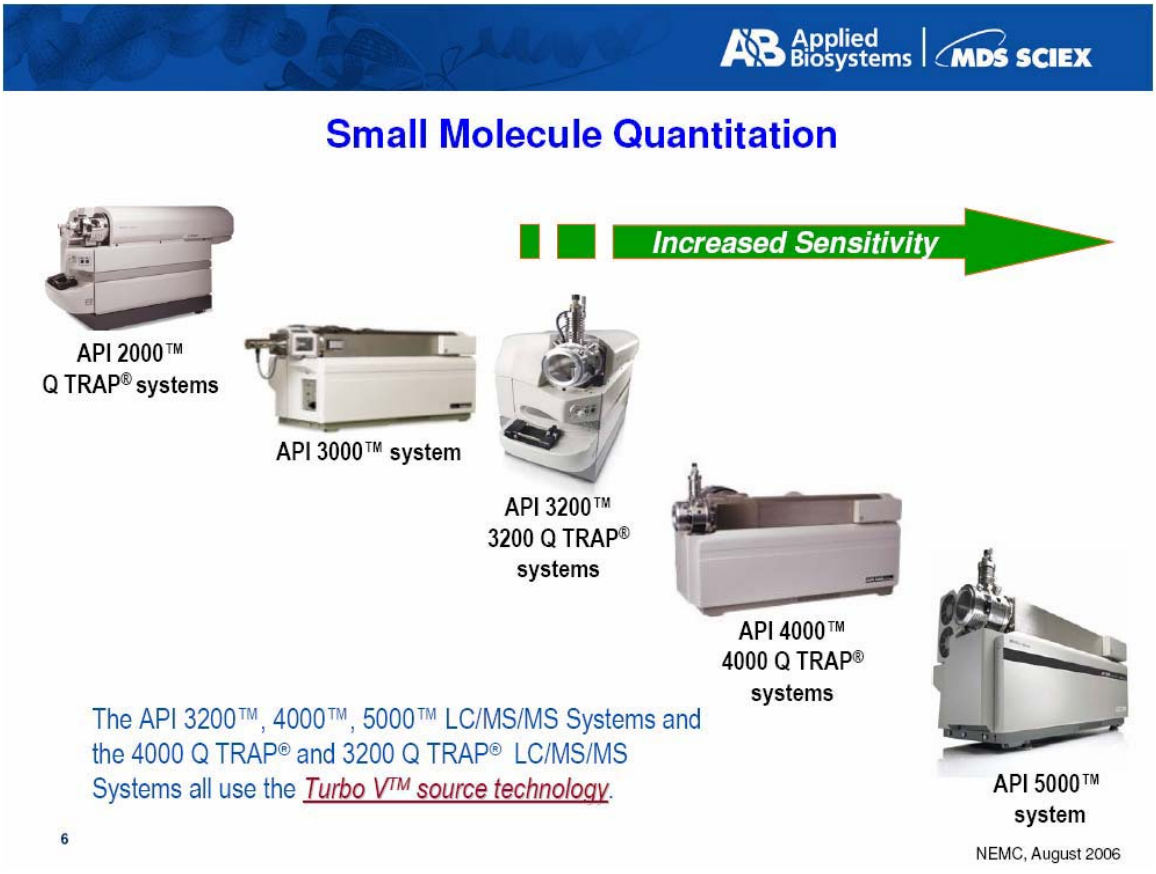

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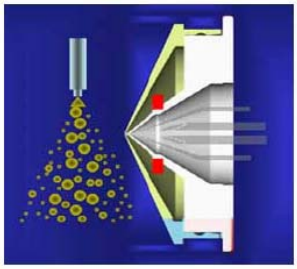
Turbo V™ Source



- Rugged, Reliable, Easily Interchangeable
- Orthogonal Sprayer: Enhance sensitivity and minimize contamination
- Covers a wide range of applications and compounds
- Accommodates diverse range of flow rates up to ***2 mL/min***
- Quick change between ***ESI*** and ***APCI*** probes

7

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Turbo V™ Source and Methods Transfer

API 3200™ and
3200 Q TRAP® Systems

All these platforms can operate with the same software…
Re-optimize your compound dependent parameters using Analyst® software's automated optimization routine, roll up your LC equipment, and run your samples.

API 4000™ &
4000 Q TRAP® Systems

API 5000™ system

…and this can be done in any order or combination…

8

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Shane Snyder, Southern Nevada Water Authority
In studies of over-the-counter vitamins for children, pregnant women, and the general population, researchers found some with high levels of perchlorate.

Winkler *et al*, *Anal. Chem.*, **2004**, *76*, 469473
Krynitsky *et al.*, *Anal. Chem.*, **2004,** *76*, 5518–5522.
Sanchez *et al.*, *Environ. Sci. Technol.* **2005,** *39*, 9391–9397.
El Aribi *et al.*, *Anal. Chim. Acta*, *567*, **2006**, 39-47
Exploratory Data on Perchlorate in Food: http://www.cfsan.fda.gov/~dms/clo4data.html
Rebecca Renner, *ES & T Online News*, **March 8, 2006** and **April 26, 2006**
http://pubs.acs.org/subscribe/journals/esthag-w/2006/mar/science/rr_vitamins.html
http://pubs.acs.org/subscribe/journals/esthag-w/2006/apr/science/rr_produce.html

Analysis of perchlorate using API 3200™

Perchlorate

➢Perchlorate is a powerful thyroid toxin that can affect the thyroid's ability to take up the essential nutrient iodide and make thyroid hormones and thus affects:

- Thyroid hormone production
- Thyroid regulation of metabolism
- Size of brain structures
- Neurological development of fetus and newborn

➢Small disruptions in thyroid hormone levels ***during pregnancy*** can cause lowered IQ and larger disruptions cause mental retardation, loss of hearing and speech, or deficits in motor skills for infants and children.

➢Thyroid hormones control fetal/infantile neurodevelopment. "***Iodine deficiency*** is the single most important preventable cause for mental retardation".

……Thyroid hormones regulate metabolism in adults, but pregnant women face a special risk because these hormones help guide the brain and nerve development of their fetuses.

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Perchlorate Analysis

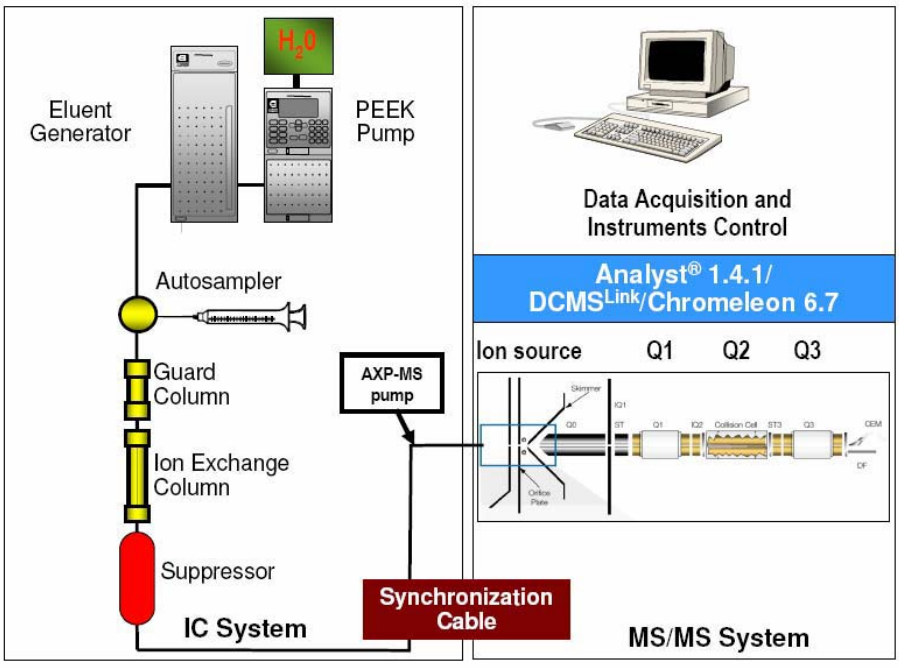
Perchlorate has received widespread attention as an environmental pollutant. This attention has resulted in development of analytical methods to support its measurement.

Methods 314.1, 331.0, and 332.0.

- **Method 314.1** is based on an IC separation preceded by a pre-concentration column matrix removal step and followed by suppressed conductivity detection. *(EPA approved method for drinking water)*
- **Method 332.0** relies on an IC separation and suppression of the IC eluent followed by either mass spectrometry (MS) or tandem mass spectrometry (MS/MS) for detection and quantitation.
- **Method 331.0** is an LC-MS/MS method that relies on a unique LC column specifically designed for separation of perchlorate using a volatile methylamine-based mobile phase followed by unsuppressed Electrospray Ionization (ESI) MS/MS detection and quantitation.

Analysis of perchlorate using API 3200™

IC-MS/MS Schematic



Analyst® 1.4.1 is featured with AAO, which allows the Dionex IC system to be controlled through Analyst. This integration is achieved via the companion software Chromeleon® 6.7/DCMS® link that facilitates control of Dionex chromatography instruments.

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IC Experimental Procedure

- Dionex GS 50 pump (1), EG50 eluent generator (2), AS50 auto-sampler (3), CD25A conductivity detector (4), LC30 chromatography oven with rear-loading Rheodyne injection valve (100-µL loop) (5),
- IC Columns: IonPac® AS16 or AS20; 250 x 2-mm i.d.; guard column: IonPac® AG16 AG20; 50 x 2-mm i.d.
- Suppressors: ASRS® MS, 2-mm
- Analytical flow rate: 0.3 mL/min
- IC oven temperature: 28 °C
- Injection volume: 100 µL.
- Dionex AXP-MS auxiliary pump (6), Eluent: 90% acetonitrile + 10% water at 0.3 mL/min.

ICS-2500™

Reagent-Free™ System

➢**Isocratic 45 mM KOH**

*The post column addition of this solvent **improves** the electrospray process and provides a **better sensitivity** than 100 % water-based run.*

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Analysis of perchlorate using API 3200™

MS Experimental Procedure

- ***Electrospray (negative mode)***
- IonSpray™ Voltage: –4500 V
- Declastering Potential: –40 V
- Entrance Potential: –10 V
- Collision Energy: –35 eV
- Collision Exit Potential: –3 V
- Curtain Gas™: 10 psi
- Gas Supply 1: 60 psi
- Gas Supply 2: 70 psi
- Source Temperature: 550 °C

API 3200™

LC-MS/MS System

Quantitation (MRM)

Q1/Q3:	unit resolution
Dwell Time:	200 ms

An oxygen-18 isotopic labeled perchlorate ($^{35}Cl^{18}O_4^-$) is used as an internal standard

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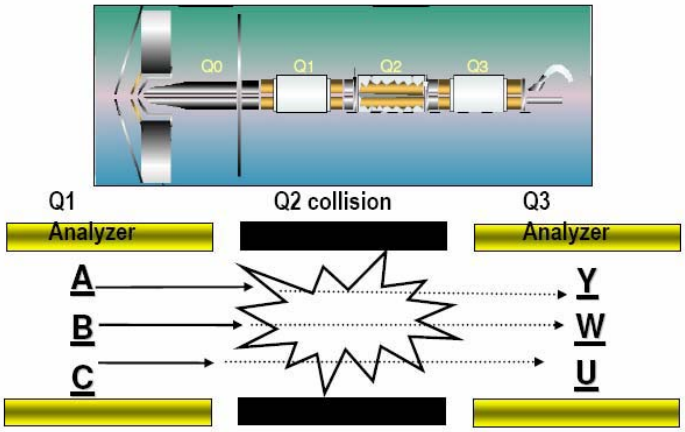
Multiple Reaction Monitoring



Quantitative Analysis

In the case of perchlorate analysis:

A-Y : $^{35}Cl^{16}O_4^-$ (m/z 98.9) - $^{35}Cl^{16}O_3^-$ (m/z 82.9) _ **Quantitation**
B-W : $^{37}Cl^{16}O_4^-$ (m/z 100.9) - $^{37}Cl^{16}O_3^-$ (m/z 84.9) _ **Confirmation**
C-U : $^{35}Cl^{18}O_4^-$ (m/z 107.0) - $^{35}Cl^{18}O_3^-$ (m/z 89.0) _ **ISTD**

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Analysis of perchlorate using API 3200™

Sample Preparation for Perchlorate Analysis

Water and Urine: Drinking water samples were analyzed without preparation. Waste water and urine samples were filtered.

Fruits and Vegetables: Bulk samples were first cut into small, 1 – 2 cm pieces and chopped in a food processor. Samples were prepared by weighing 10 ± 0.10 g of each food samples into separate 50 mL disposable polypropylene centrifuge tubes. 20 mL De-ionized water was added.

Milk products: 5 ± 0.05 mL of each sample was pipetted into separate 50 mL disposable polypropylene centrifuge tubes. 5 mL of de-ionized water and 20 mL of acetonitrile were added.

Wine Samples and other Beverages: Individual sample solutions were prepared by pipetting 5 mL ± 0.05 mL of each samples into separate 50 mL disposable polypropylene centrifuge tubes. 25 mL of de-ionized water was added.

- The centrifuge tubes were capped and shaken with a Vortex-Genie® for 2 min.
- The tubes containing the test portion were then centrifuged at 2,500 rpm for 25 minutes at room temperature.
- The samples were then filtered with a 0.2-µm pore size nylon-mesh syringe filter.
- All samples have internal standard (18O-labeled perchlorate) added prior to extraction. This effectively corrects for any sample losses during preparation, and for any matrix effects in the ionization process.

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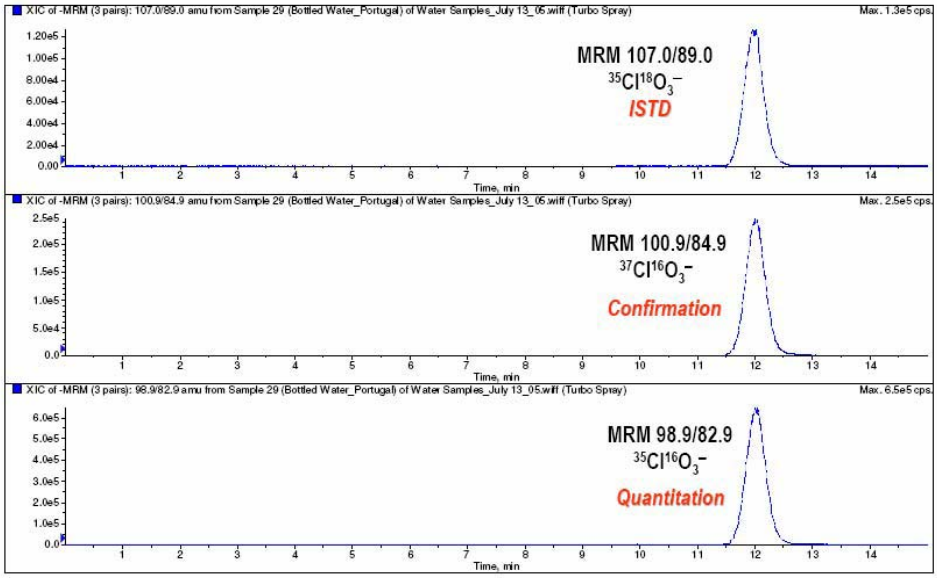
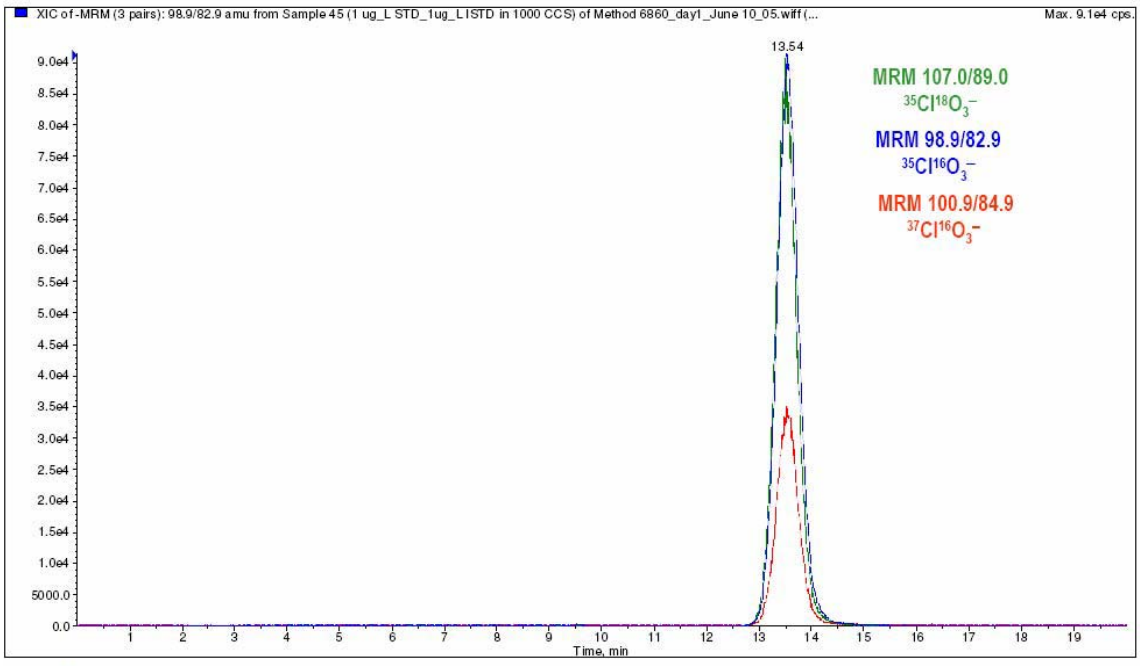
Bottled Water Sample Spiked with 1 µg/L ISTD



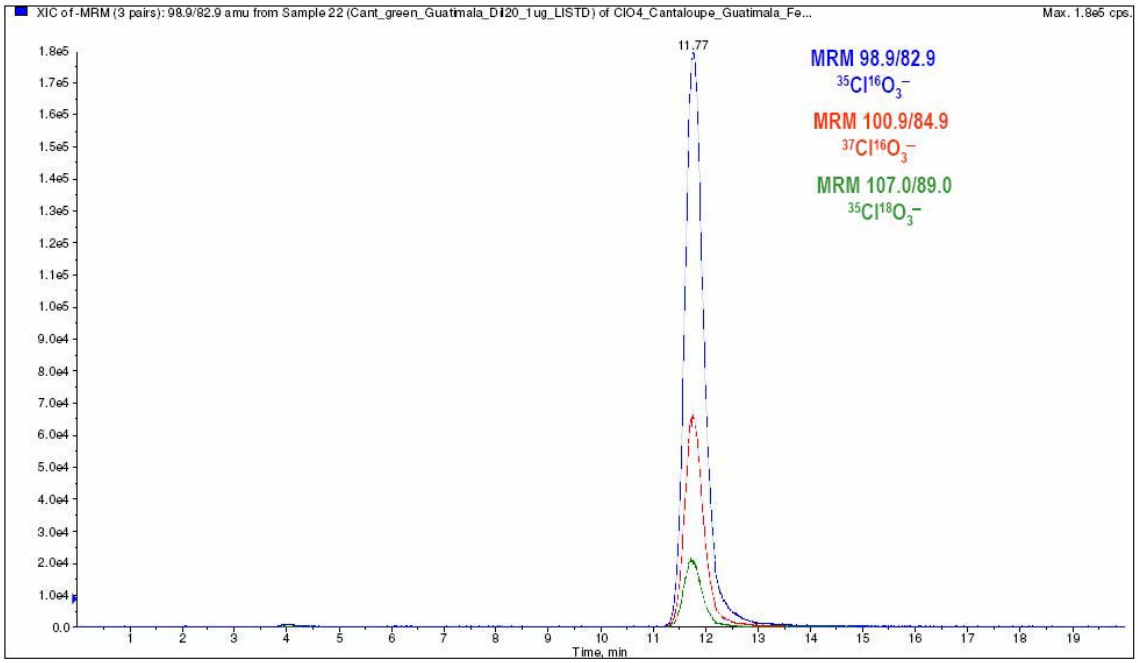
*To confirm the presence of perchlorate, the **82.9/84.9 peak area** count ratio should be between **2.2** and **3.3**. This ratio is derived from the natural abundance of **chlorine-35** and **chlorine-37** isotopes[1].*

1. G.G. Hawley, "The Condensed Chemical Dictionary", 10th ed.; Van Nostrand Reinhold Company Inc., New York, 1981.

Solution of 1000 ppm CCS spiked with 1 µg/L



Cantaloupe Extract spiked with 1 µg/L ISTD



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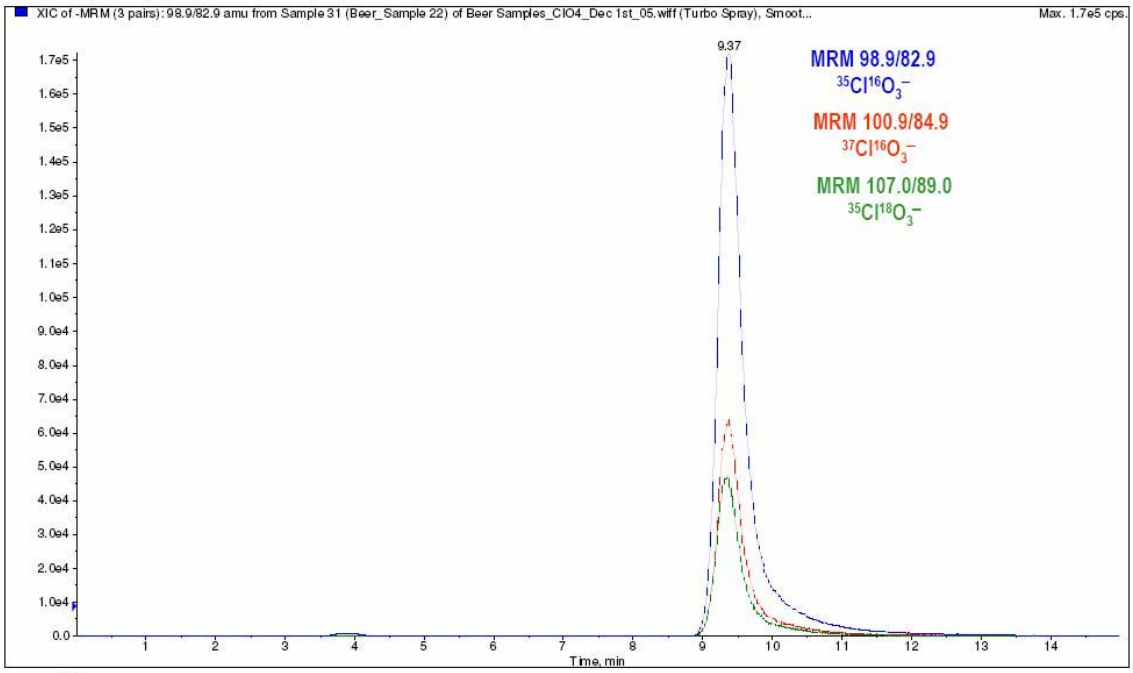
Beer Sample spiked with 1 µg/L ISTD



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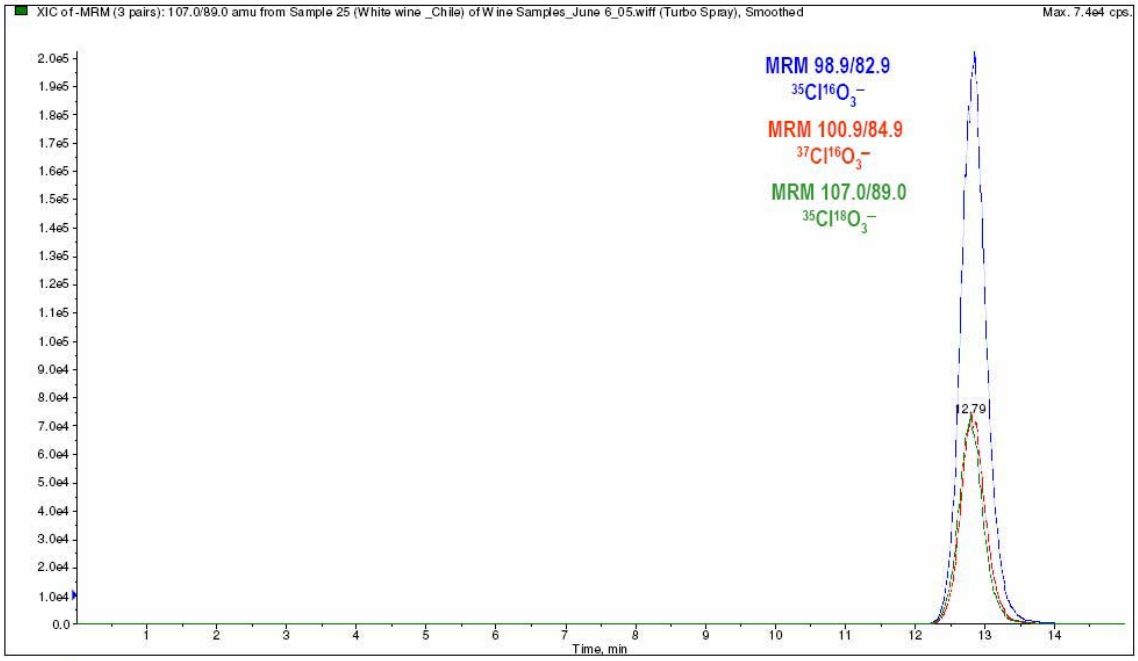
Wine Sample spiked with 1 µg/L ISTD



21

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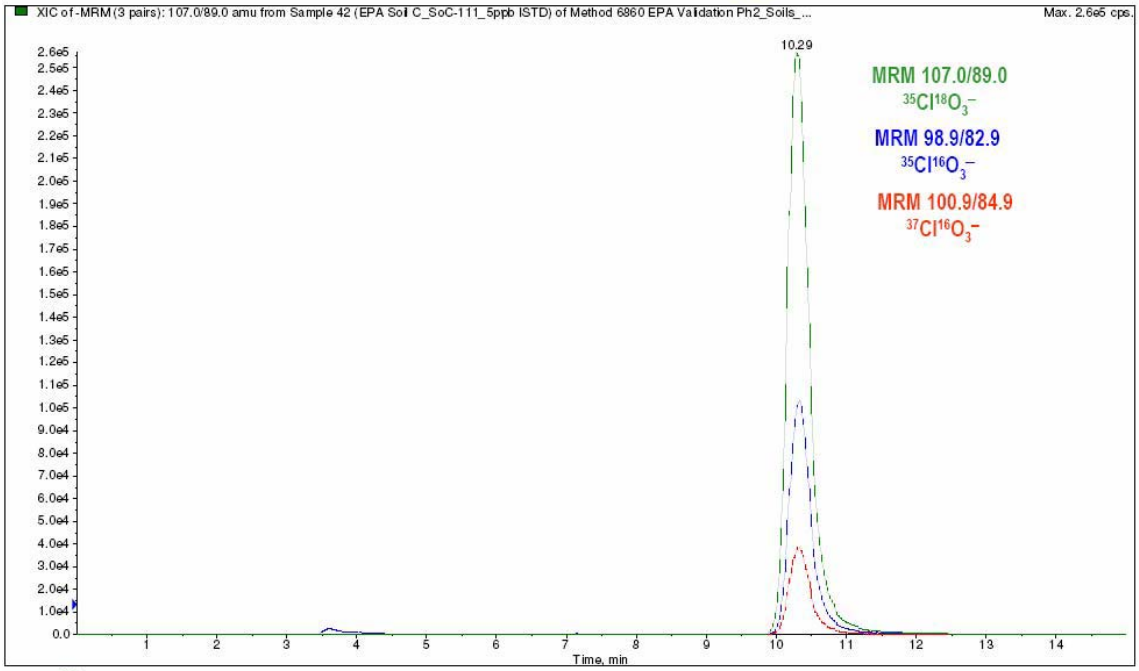
EPA Soil C spiked with 5 µg/L ISTD



22

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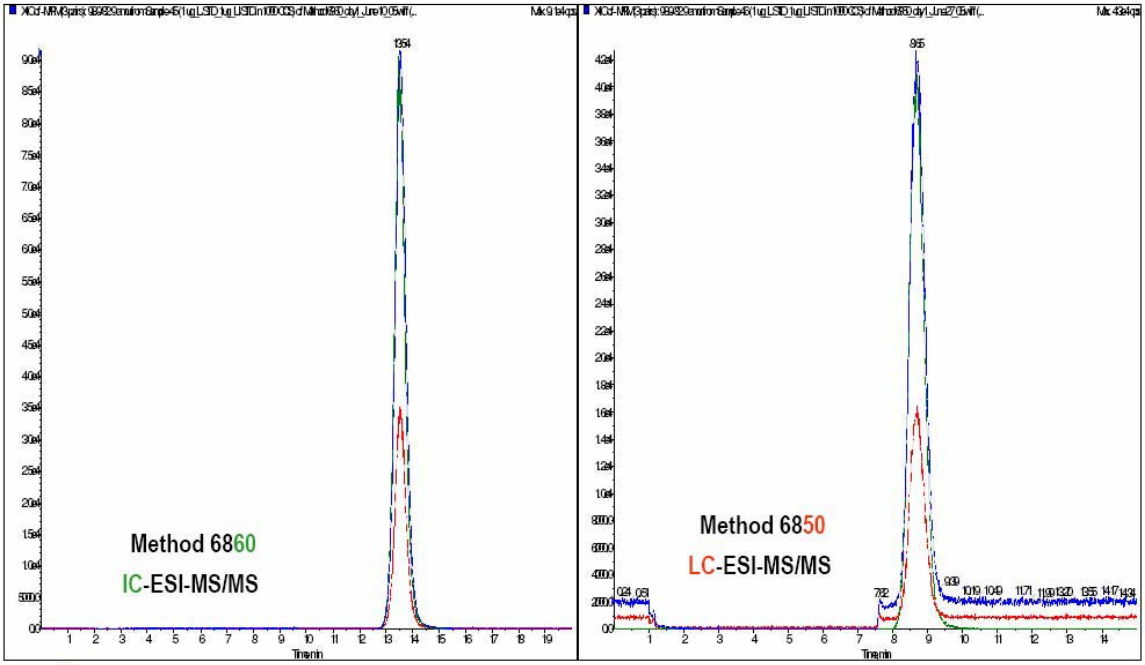
Solution of 1000 ppm CCS spiked with 1 µg/L



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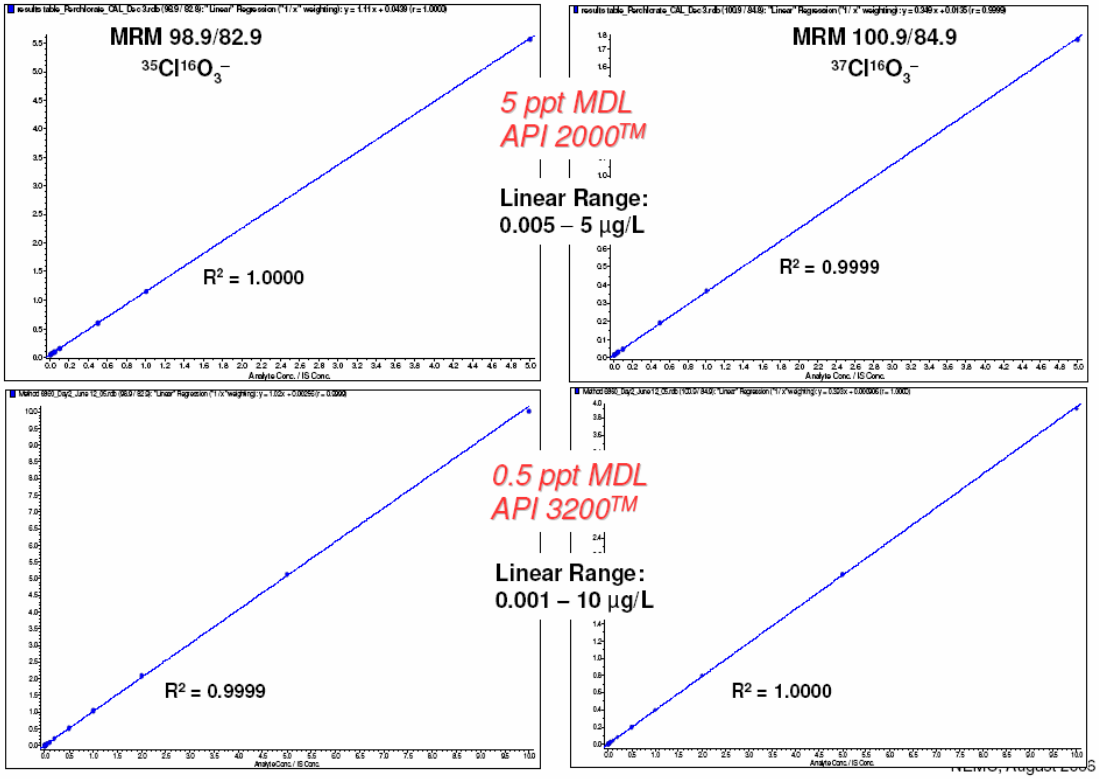
Calibration Curves in DI Water



Perchlorate in Tap and Filtered Water

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Water Sample	Origin	Perchlorate[a] (µg/L)
2	Nobleton, Ontario	0.035 ± 0.001
4	Winnipeg, Manitoba	0.106 ± 0.002
6	Toronto, Ontario	0.061 ± 0.001
9	Dorval, Quebec	0.047 ± 0.001
10	Quebec city, Quebec	0.091 ± 0.001
11	Sunny Vale, California	0.073 ± 0.001
12	Reston, Virginia	0.162 ± 0.001
13	Las Vegas, Nevada	2.983 ± 0.021
14	Porto, Portugal	0.041 ± 0.003
20	Beijing, China	0.035 ± 0.000

Sample/Origin	Filter Type	Perchlorate[a] (µg/L)
32/Nobleton	Reverse osmosis	0.012 ± 0.001
35/Aurora	Brita	0.012 ± 0.001
36/Toronto	Reverse osmosis	0.005 ± 0.000
38/Brooklin	ECO system	0.096 ± 0.001

*At least when **new**, these filters effectively removed most of the perchlorate from the water.*

25

El Aribi *et al.*, *Anal. Chim. Acta*, 567, **2006**, 39-47

NEMC, August 2006

Analysis of perchlorate using API 3200™

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Perchlorate in Bottled Water

Water Sample	Origin	Perchlorate[a] (µg/L)
1	Toronto, Ontario	0.067 ± 0.002
2	Toronto, Ontario	NQ ± NQ
3	Winnipeg, Manitoba	NQ ± NQ
4	Paris, France	0.092 ± 0.002
5	Berlin, Germany	0.198 ± 0.032
6	India	0.105 ± 0.001
7	Porto, Portugal	5.098 ± 0.040

[a] Average of three replicates ± standard deviation.

***52** water samples were analyzed in triplicate and the measured isotopic ratios of ^{35}Cl to ^{37}Cl varies from **2.67** to **3.30** with an average of **2.93 ± 0.17**.*

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NEMC, August 2006

Perchlorate in Produces

Sample	Origin	Perchlorate[a] (µg/Kg)
Oranges	California, USA	9.990 ± 1.350
Oranges	Cyprus	0.079 ± 0.007
Clementines	Morocco	0.446 ± 0.099
Clementines	China	0.093 ± 0.004
Grapes, Green	California, USA	19.290 ± 1.061
Grapes, Green	Chile	21.980 ± 0.763
Tomato	Florida, USA	0.260 ± 0.002
Tomato	Ontario, Canada	0.329 ± 0.016
Tomato	Mexico	62.800 ± 2.706
Apples	Ontario, Canada	0.088 ± 0.007
Apples	Florida, USA	0.116 ± 0.014
Apples	China	0.077 ± 0.014
Plums	Italy	2.795 ± 0.070
Mushrooms	Poland	5.670 ± 0.255
Lyches	South Africa	0.938 ± 0.091
Cantaloupes *(Jan 2005)*	Guatemala	463.500 ± 6.364
Cantaloupes *(Feb 2006)*	Guatemala	308.160 ± 1.427
Cantaloupes	Costa Rica	151.650 ± 1.909

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Perchlorate in Produces, *Conti…*

Sample	Origin	Perchlorate[a] (µg/Kg)
Raspberries	Chile	23.110 ± 2.086
Apricot	Chile	145.650 ± 4.031
Raw Asparagus	Mexico	39.900 ± 0.424
Cooked Asparagus	Mexico	24.345 ± 0.955
Banana	Equador	0.299 ± 0.019
Banana	Colombia	2.432 ± 0.168

[a] Average of three replicates ± standard deviation.

A comparison between level of perchlorate in ***raw*** asparagus and ***cooked*** asparagus clearly showed that perchlorate can survive in food even after processing at a **high temperature**.

66 *produce samples were analyzed in triplicate and the measured isotopic ratios of* ^{35}Cl *to* ^{37}Cl *varies from* ***2.63*** *to* ***3.23*** *with an average of* ***3.07 ± 0.08***.

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Perchlorate in Wines

Applied Biosystems | MDS SCIEX

Sample	Origin	Perchlorate[a] (µg/L)
White	B.C., Canada	0.738 ± 0.000
Red	Ontario, Canada	20.760 ± 0.427
White	Germany	1.437 ± 0.021
White	Germany	1.065 ± 0.021
Red	California, USA	2.856 ± 0.008
White	New York, USA	1.593 ± 0.013
Rose	Portugal	50.250 ± 0.382
White	Australia	1.539 ± 0.013
Red	Australia	1.032 ± 0.000
White	New Zeeland	0.567 ± 0.004
Red	New Zeeland	0.092 ± 0.000
Red	Japan	14.850 ± 0.042
White/Green	Portugal	1.509 ± 0.004
Red	Chile	38.880 ± 0.000
White	Chile	10.800 ± 0.085
White	Spain	2.634 ± 0.008
Red	Spain	6.600 ± 0.000

[a] Average of three replicates ± standard deviation.

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El Aribi *et al.*, *Anal. Chim. Acta*, *567*, **2006**, 39-47

NEMC, August 2006

Perchlorate in Wines, *Conti…*

Applied Biosystems | MDS SCIEX

Sample	Origin	Perchlorate[a] (µg/L)
White	South Africa	6.120 ± 0.000
Red	South Africa	1.002 ± 0.008
Red	Italy	2.980 ± 0.028
White	Italy	1.827 ± 0.004
Red *(May 2005)*	Serbia & Montenegro	27.090 ± 0.127
Red *(January 2006)*	Serbia & Montenegro	27.486 ± 0.066

[a] Average of three replicates ± standard deviation.

***77** wine samples were analyzed in triplicate and the measured isotopic ratios of ^{35}Cl to ^{37}Cl varies from **2.64** to **3.19** with an average of **2.78 ± 0.18**.*

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NEMC, August 2006

Perchlorate in Beer

Sample	Origin	Perchlorate[a] (μg/L)
1	Ontario, Canada	0.956 ± 0.005
2	Quebec, Canada	3.456 ± 0.062
3	Holland	0.210 ± 0.006
4	Oregon, USA	2.014 ± 0.009
5	Chile	8.976 ± 0.069
6	Germany	0.240 ± 0.006
7	Belgium	0.509 ± 0.007
8	Japan	7.570 ± 0.039
9	Singapore	0.118 ± 0.003
10 *(Nov 2005)*	France	21.096 ± 0.083
11 *(Jan 2006)*	France	22.804 ± 0.030
12	China	0.450 ± 0.004
13	Israel	14.204 ± 0.050
14	Denmark	0.081 ± 0.002
15	Mexico	1.215 ± 0.006
16	Russia	0.540 ± 0.005
17	Bungay, UK	0.188 ± 0.005
18	Portugal	1.142 ± 0.011

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Perchlorate in Beer

144 *beer samples were analyzed in triplicate and the measured isotopic ratios of* ^{35}Cl *to* ^{37}Cl *varies from* ***2.66*** *to* ***3.06*** *with an average of* ***2.93 ± 0.07***.

Perchlorate in Urine

Volunteers	Perchlorate (μg/L)[a]
1 – ~ 75 kg_H	16.040 ± 0.015
2 – ~ 75 kg_H	26.320 ± 0.018
3 – ~ 70 kg_D	28.440 ± 0.017
4 – ~ 80 kg_T	1.054 ± 0.005
5 – ~ 85 kg_P	16.530 ± 0.009
6 – ~ 85 kg_M	4.203 ± 0.008
7 – ~ 75 kg_H	21.490 ± 0.015

[a] Average of three replicates ± standard deviation.

This shows that perchlorate is, probably, excreted virtually unchanged in the urine after absorption.

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NEMC, August 2006

Conclusion

- The IC-ESI-MS/MS method was found to be a robust, specific and sensitive system for the determination of perchlorate in various matrices.
- Dionex and Applied Biosystems/MDS Sciex are providing a sensitive validated package for the analysis of polar compounds.

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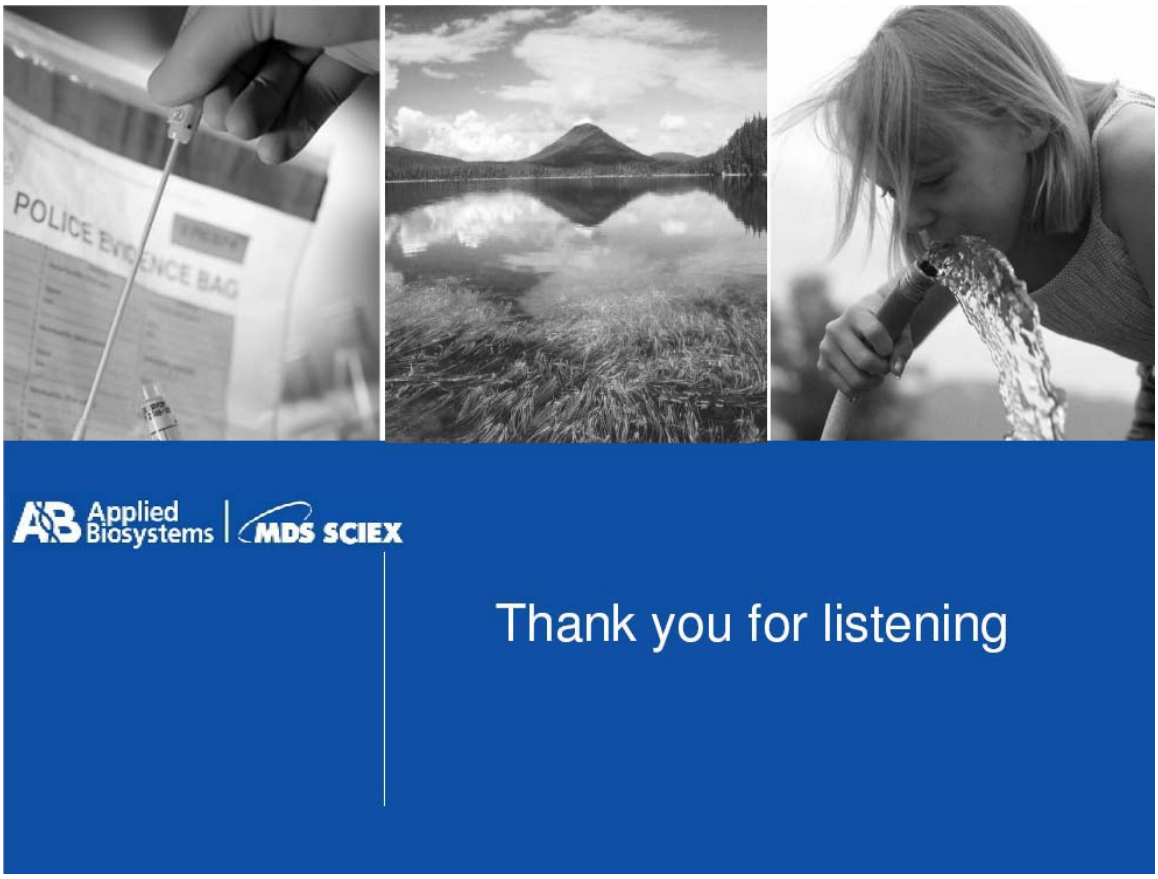
NEMC, August 2006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Applied Biosystems
MDS SCIEX
Thank you for listening

RAPID DETERMINATION OF PERCHLORATE ANION IN FOODS AND ENVIRONMENTAL SAMPLES BY ION CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

Hopper, Marvin L.; Krynitsky, Alexander J.; Niemann, Richard A.; Williams, Anthony D. – U.S. Food and Drug Aministration Center for Food Safety and Applied Nutrition

A rapid, sensitive, and specific method was developed for the determination of perchlorate anion in foods and environmental samples. The foods included fresh fruits and vegetables, whole milk, infant formula, baby foods, grains, and bottled water. The environmental samples included saltwater, soil, and sludge acquired from a recent round robin study conducted by the U.S. Environmental Protection Agency (EPA) Office of Solid Waste. The extraction and cleanup procedures will be discussed for each type of sample matrix and compared to other existing methods. A Waters IC-Pak Anion HR column (4.6 mm x 75 mm) was eluted with 100 mM ammonium acetate in 50:50 (v/v) acetonitrile/water mobile phase at a rate of 0.35 mL/min. A triple stage quadrupole mass spectrometer, equipped with electrospray ionization (ESI) in the negative ion mode, was used to determine perchlorate anion. An $^{18}O_4$-labeled perchlorate anion was used to correct for any matrix effects. Fortified test portions gave recoveries ranging from 80 -120%. Determination of incurred perchlorate anion residues agreed well with results for comparable commodities or products analyzed by published methods.

Rapid Determination of Perchlorate Anion in Foods and Environmental Samples by Ion Chromatography-Tandem Mass Spectrometry

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Potential Food Exposure Pathways

- Crops
  - Irrigation water
  - Soil
- Food-producing animals
  - Water - forage - feed
- Fish
  - Aquatic environment - feed
- Production water containing perchlorate

FDA's Strategy and Goals

- Determine the occurrence of perchlorate in a variety of foods.
- Evaluate exposure to perchlorate from food.
- Support any action that might be needed to protect the public health.

FDA Exploratory Surveys

- FDA surveyed 446 samples for FY04:
  - 137 lettuce
  - 51 bottled water
  - 20 spinach
  - 49 tomatoes
  - 33 carrots
  - 31 cantaloupe
  - 125 milk
- Characterize distribution within product type & product to product variations

FY05 Survey-1,039 Samples

- FY 05 perchlorate survey – 500 targeted sample (domestic and imports)
- Additional tomato, carrot, spinach, cantaloupe samples.
- Wider variety of food samples:
  - Produce (broccoli, onions, cucumbers, peas, green beans, cabbage, collard greens)
  - Fruit and fruit juices (apple, grape, strawberries, watermelon, apple juice, orange juice)
  - Grain products (rice, wheat flour, corn meal, oat meal)
  - Aquaculture catfish and salmon, and shrimp.

FY05 Activities (cont.)

- Farm milk survey – 100 each: raw milk, feed, water.
- Infant formula survey – 21 samples.
- FDA's Total Diet Study (TDS) infant foods.
  - 4 market baskets for FY 05.
  - 57 infant foods per market basket.

FY06 Activities

- FY 06 TDS survey – about 800 food samples (4 market baskets).
  - Dairy and eggs
  - Meat/poultry/fish
  - Mixtures (e.g., casseroles, sandwiches, soups, pizza) and vegetables.
  - Candy/sweets/ sugars/syrups
  - Beverages
  - 100 targeted follow up and food samples

FDA Analytical Method Development

- IC- electro conductivity detection (less expensive method)
- IC-MS/MS; ESI in negative mode
- Miniaturizing extraction and cleanup procedure for IC-MS/MS to facilitate high sample throughput for a large variety of foods

FDA Analytical Method Development

- IC-MS/MS
  - Anion exchange IC column
  - Isotopically labeled internal standard ($^{18}O_4$-labeled perchlorate)
  - 0.5 µg/L LOQ – Bottled Water
  - 1 µg/kg LOQ – Produce, meats, and infant foods
  - 3 µg/L LOQ – Milk, infant formula
  - 3 µg/kg LOQ – Low Moisture Foods
  - Sample prep – extraction/SPE/filtration
  - Minimal matrix effects with IS

Instrumentation

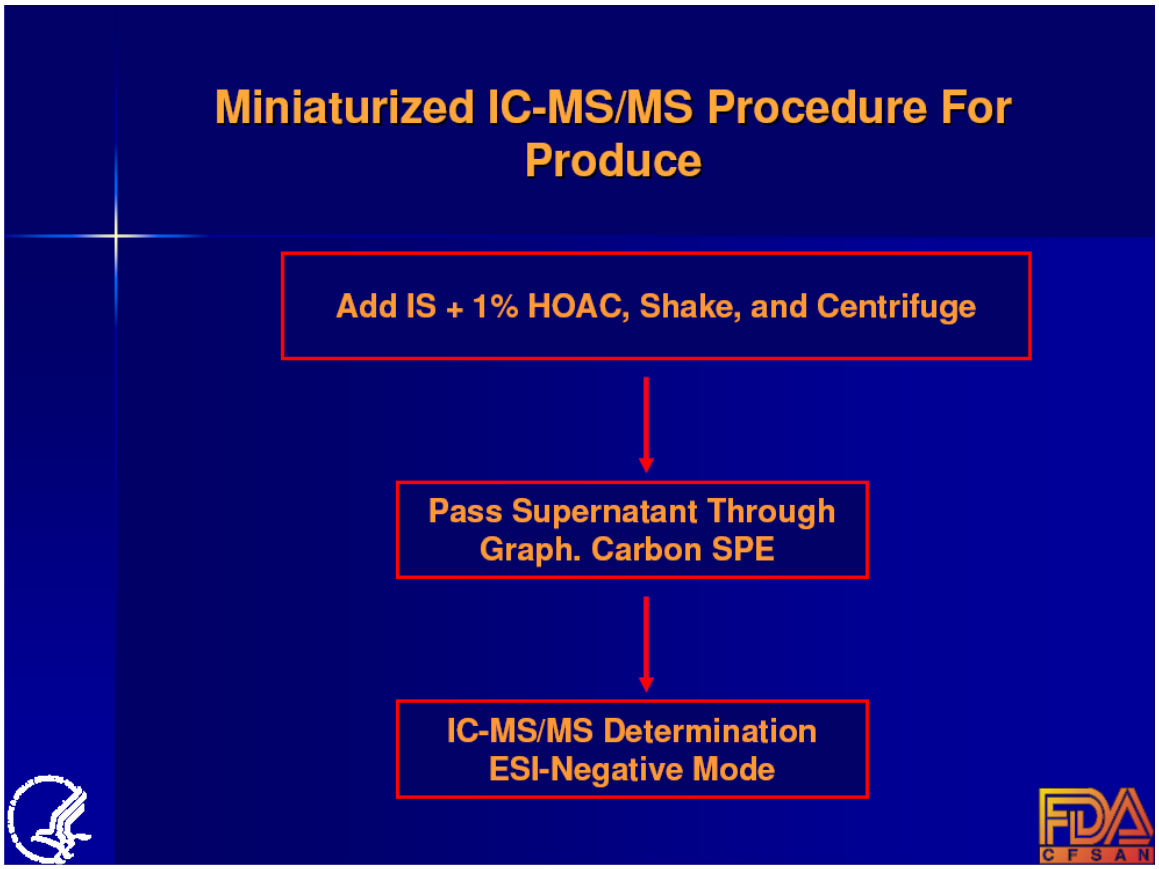
- HPLC – Agilent Model 1100 HPLC
- Mass Spectrometer – Micromass Quattro Micro™ triple stage quadrupole mass spectrometer.

HPLC Conditions For Perchlorate

- IC Column – 4.6 mm x 75 mm Waters IC-Pak™ Anion HR
- Guard Column – Waters IC-Pak™ Anion Guard-Pak™
- Mobile Phase – 100 mM ammonium acetate in 50:50 (v/v) acetonitrile:water
- Flow Rate – 350 µL/min, isocratic
- Injection Volume – 50 µL

MS/MS Ion Transitions Monitored (ESI Neg.)

Compound	Primary Ion Transition	Secondary Ion Transition
Native Perchlorate	m/z 99→83	m/z 101→85
$^{18}O_4$-labeled Perchlorate	m/z 107→89	m/z 109→91



Fortified High-Moisture Foods via Miniaturized Method

Whole Cantaloupes

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
5.0	104	9.5
10.0	97.6	1.3

Spinach

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
10.0	100	7.1
20	101	11.3

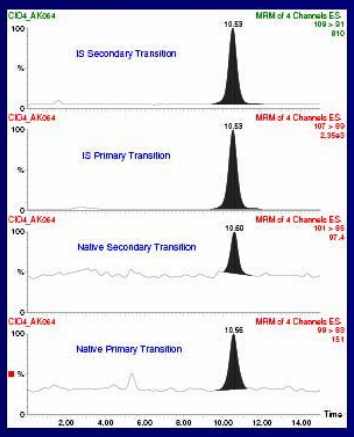
Carrots

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
10.0	102	10.7
20.0	99.4	2.6

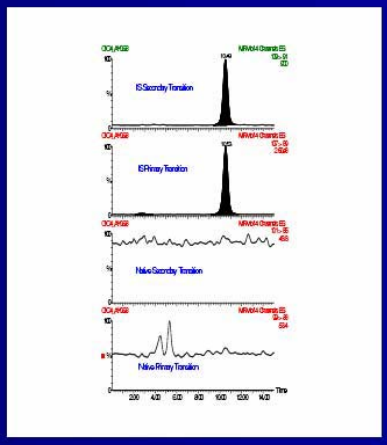
Tomatoes

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
10.0	85.9	5.3
20.0	89.1	4.5

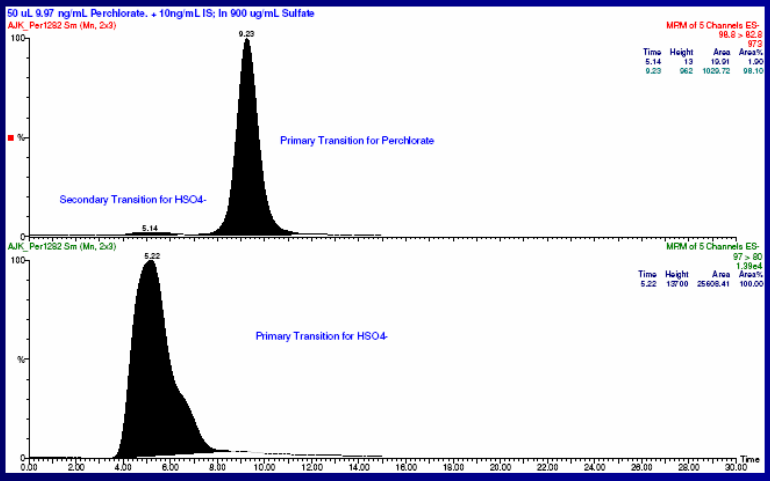
2 µg/kg Perchlorate Fortified in Iceberg Lettuce



Iceberg Lettuce Control



Water Containing: 9.97 ng/mL Native Perchlorate and 900 µg/mL HSO_4^- (Method Overcomes Interferences)

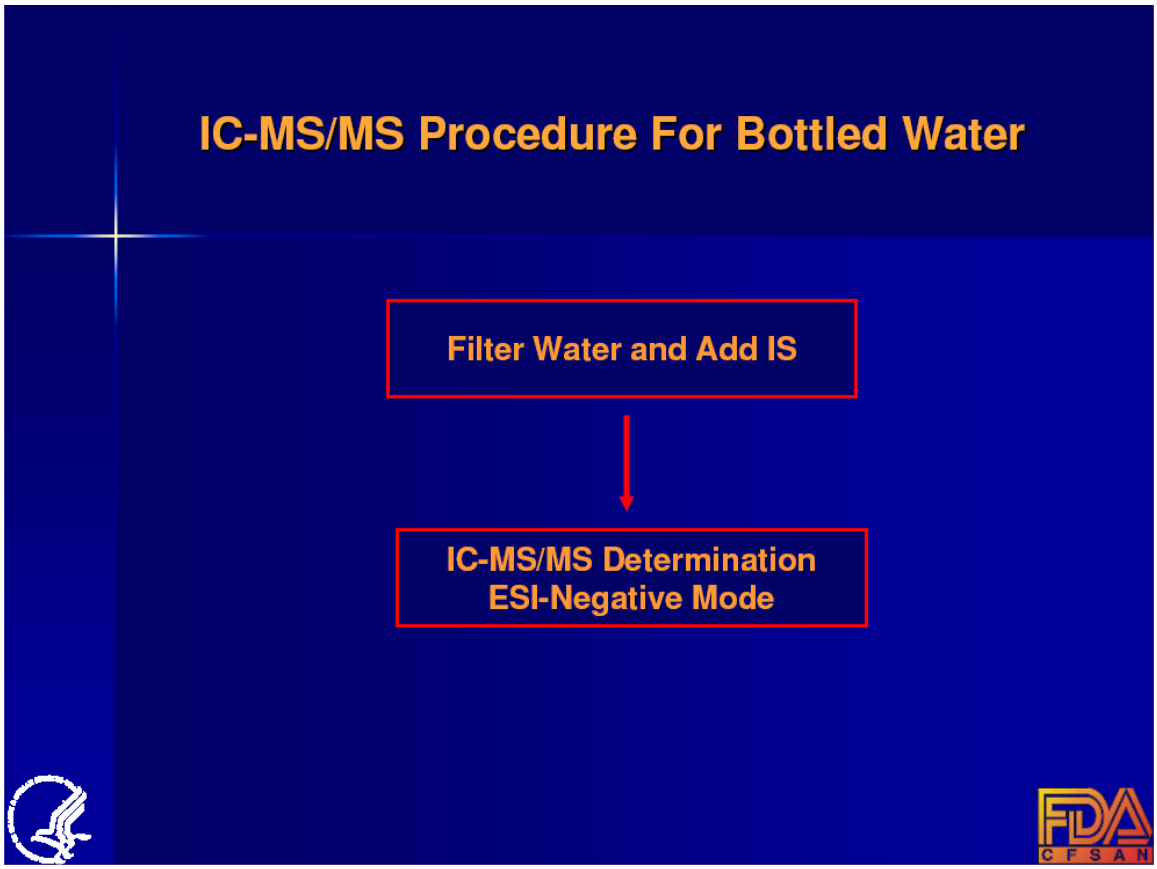


"Mini Method" – IC-MS/MS CFSAN vs. Another FDA Lab Incurred Perchlorate

Commodity	*N*	Concentration Range (µg/kg)	P-value	Significant Difference @ 95% Confidence Interval
Cantaloupe	12	2.8-115	0.56	NO
Carrots	8	3.0-111	0.26	NO
Infant Foods	25	0.89-12.0	0.60	No
Spinach	19	6.1-768	0.098	No

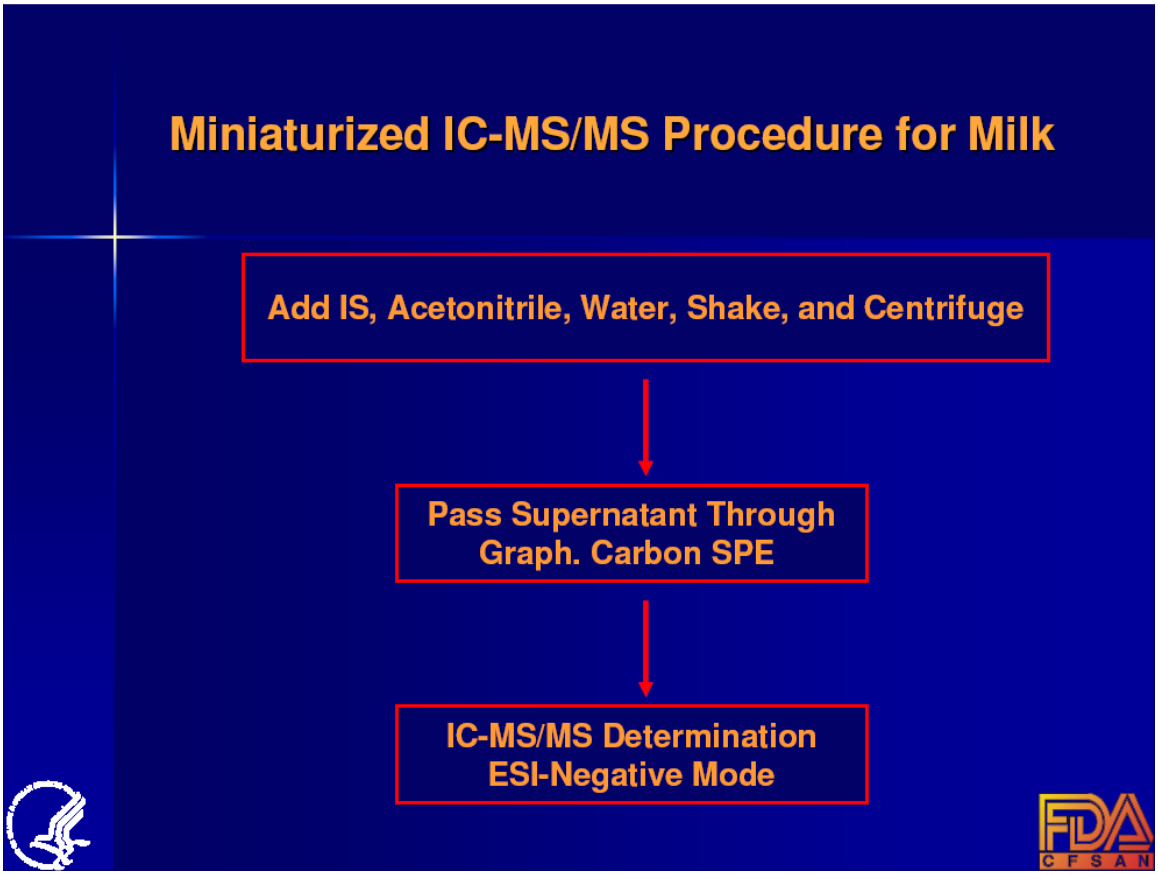
IC-CD (via longer method) vs. IC-MS/MS (via miniaturized method) Incurred Perchlorate

Commodity	*N*	Concentration Range (µg/kg)	P-value	Significant Difference @ 95% Confidence Interval
Lettuce	27	2.9-136	0.32	NO
Cantaloupe	12	2.8-115	0.68	NO
Carrots	9	1.2-111	0.15	NO
Spinach	19	6.1-768	0.29	NO



Fortified Bottled Water

Fortification Level (µg/L)	Average Recovery (n=3)	% RSD
0.50	115	9.9
1.0	104	8.2
5.0	109	4.6
10.0	99.7	6.8



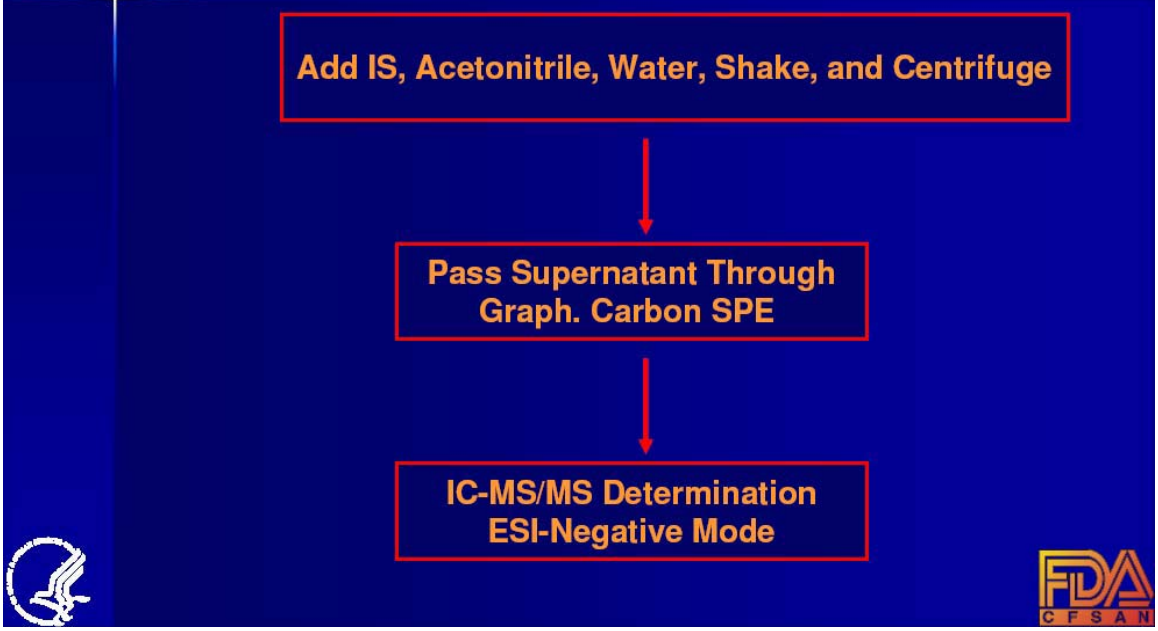
Fortified Whole Milk

Fortification Level (µg/L)	Average Recovery (n=3)	% RSD
5.0	98.9	5.1
10.0	99.7	8.1
20.0	101	6.4

MS/MS Determination of Split Milk Samples From UC-Davis

Sample No.	FDA/CFSAN IC-MS/MS µg/L	UC-Davis RP HPLC-MS/MS µg/L
Milk #1	5.21	5.83
Milk #2	4.59	5.28
Milk #5	4.66	5.28
Milk #7	4.70	4.85
Milk #8	4.59	5.82

Miniaturized IC-MS/MS Procedure for Low Moisture Foods, Meats, and Infant Foods



Fortified Low-Moisture Foods via Miniaturized Method

Corn Meal

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
5.0	107	5.2
10.0	99.5	8.9

Wheat Flour

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
5.0	114	4.6
10.0	93.1	3.6

Soybeans

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
5.0	108	4.9
10.0	103	4.3

Oatmeal

Fortification Level (µg/kg)	Average Recovery (n=3)	% RSD
5.0	107	15.8
10.0	101	13.8

Advantages To Miniaturization

- Faster than traditional methods
- IS added at beginning, thus more accurate.
- All disposable components
- No need for filtration flasks, etc.
- Comparable results to traditional methods even with “Round Robbins”
- Prep 20 samples in < 2 hr

Precautions with Mini Method

- Use 1% HOAC as Extraction Solution: This is needed to suppress active sites on Envi Carb SPE.
- Use PTFE syringe filters and Not nylon: Perchlorate can be retained on nylon syringe filters.
- Losses of perchlorate are not apparent with matrix since sample matrix will suppress active sites on SPE.

Monitoring ESI Matrix Effects With Labeled IS

Commodity	Signal Supression/Enhancement
Milk	+20 %
Lettuce	-10 %
Bottled Water	-10 %
Infant Foods	-70 %
Carrots	-10 %
Cantaloupe	-40 %
Spinach	-70 %
Tomatoes	-70 %

Conclusions

- Advantages with IC-MS/MS:
  - Identification and Confirmation
  - Accurate Quantitation
  - Sensitivity and specificity
  - Eliminates False Positives
  - Less sample cleanup needed
- Disadvantage – Cost ~ $230,000
- Must use isotopically labeled IS for accurate quantitation
- Miniaturized Method is versatile for a variety of foods
- FDA has published some of the results from FY 2004 500 sample survey on website: http://www.cfsan.fda.gov/~dms/clo4data.html
- Analytical method available on same website

Publications

- Krynitsky, A.J.; Niemann, R.A.; Nortrup, D.A. *Analytical Chemistry* **2004**, 76, 5518-5522.
- Krynitsky, A.J.; Niemann, R.A.; Williams, A.D.; Hopper, M.L *Analytica Chimica Acta* **2006**, 567, 94-99.
- Niemann, R.A.; Krynitsky, A.J.: Nortrup, D.A. *Journal of Agricultural and Food Chemistry* **2006**, 54, 1137–1143.
- Exploratory Data on Perchlorate in Food, http://www.cfsan.fda.gov/~dms/clo4data.html

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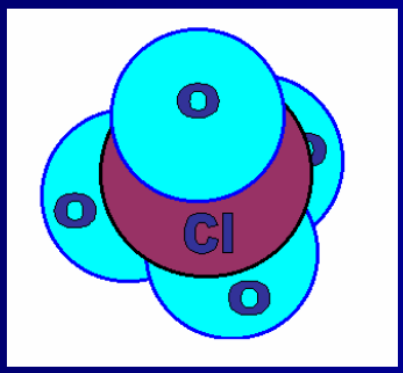

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