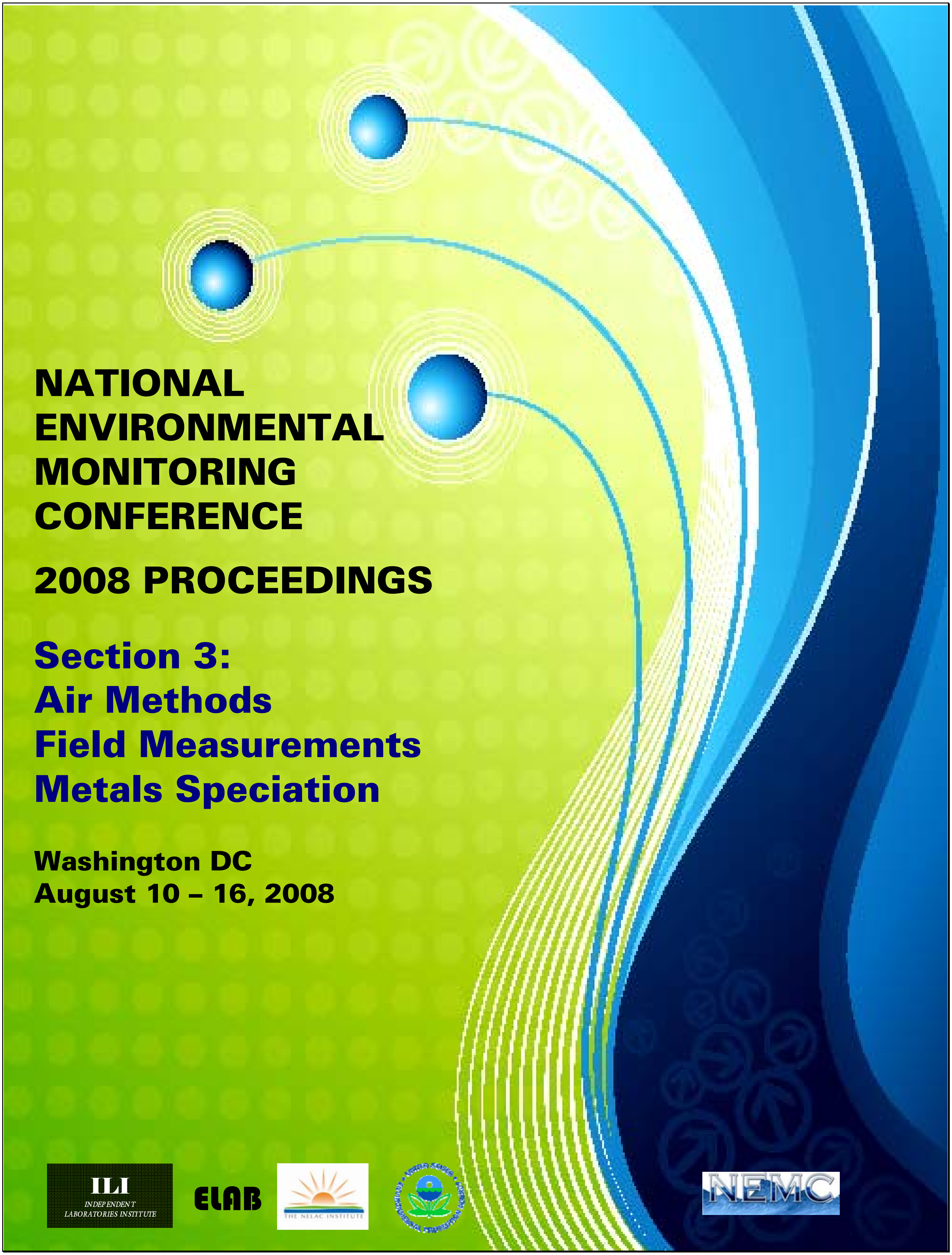

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

2008 PROCEEDINGS

Section 3:
Air Methods
Field Measurements
Metals Speciation

Washington DC
August 10 – 16, 2008

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NEMC 2008
CONFERENCE HIGHLIGHTS

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

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

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

Highlights of the week included the following keynote speakers:

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

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

SECTION 3 TABLE OF CONTENTS

AIR METHODS

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE
PROCEEDINGS 2008

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FIELD MEASUREMENTS

METALS SPECIATION

SECTION 3 TABLE OF CONTENTS cont.

2008 NEMC Proceedings

AIR METHODS

Vapor Intrusion Investigations and Site Assessment Using Passive Sampling Techniques

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ABSTRACT

Chemicals having sufficient volatility can partition to the vapor state and be present in concentrations in air, soil gas, and sub-slab soil gas that may pose a risk to humans. The sampling of soil gas and air provides a direct measurement of the chemicals in those media, while inhalation represents the most direct exposure route to those chemicals. Numerous technical bulletins, methods, and guidance documents have been and are being produced by state and national organizations, technology vendors, consultants, and service providers to inform the investigator on the complexities of vapor sampling in terms of the sampling procedures and the data interpretation. These documents tend to be focused on active sampling techniques whereby a vapor sample is mechanically withdrawn from soil and air.

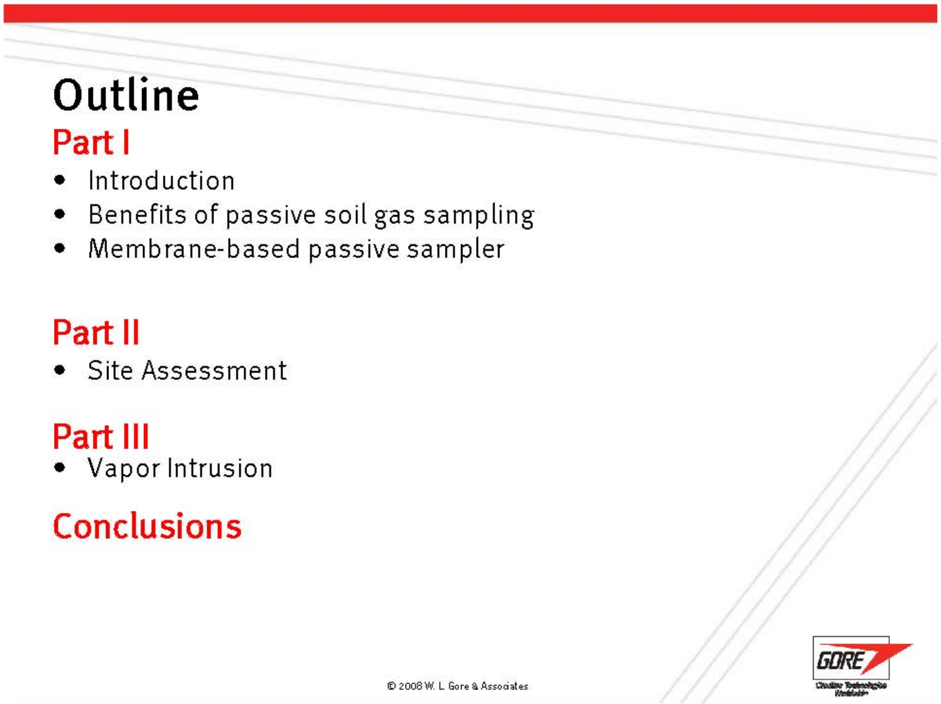
Passive sampling is an alternative method used to collect volatile and semi-volatile organic compounds in vapor, with potentially less variability, more accuracy, and at significantly reduced costs. Passive samplers are generally minimally intrusive, easier to deploy and operate, report a wider range of volatile and semi-volatile organic compounds, and can be used in challenging geological settings, when compared to active techniques. Passive vapor sampling is a time-integrated approach, and when coupled with an appropriate analytical method, allows for the detection of compounds not only at site screening levels (e.g., in soil gas), but at concentrations low enough (ppb, ppt) to address vapor intrusion risk-based screening levels.

Passive soil gas sampling has been used for decades in site screening applications, and has provided a proven, cost-effective method to focus subsequent more invasive and expensive site sampling, while optimizing remedial programs and reducing long-term monitoring costs. The use of passive samplers in vapor intrusion investigations is also growing, where the benefits of passive sampling are being realized beyond a simple site screening tool. This presentation includes examples on how passive sampling is used in site assessments, and how it is now being utilized in vapor intrusion investigations. The presentation will also include a description of a versatile, membrane-based, adsorbent passive sampler.

Vapor Intrusion and Site Assessment Using Passive Sampling Techniques

Jim Whetzel and Jay W. Hodny, Ph.D.
W.L. Gore & Associates, Inc.

National Environmental Monitoring Conference
August 11, 2008



Outline

Part I

- Introduction
- Benefits of passive soil gas sampling
- Membrane-based passive sampler

Part II

- Site Assessment

Part III

- Vapor Intrusion

Conclusions

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Passive Vapor Sampling Techniques

Passive Sampling

- Adsorbent deployment
- Simple operation
- No forced extraction
- Reduction in error

Adsorbent inside glass vial open on end

Adsorbent inside hygiene badge

Source: www.skcinc.com

Adsorbent inside vapor permeable, waterproof membrane

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Benefits of Passive Soil Gas Sampling

- Rapid, inexpensive, unobtrusive installation & retrieval
  - Minimal operator & field sampling error
- Minimal access limitations
- Time-integrated sampling
  - Sensitivity to low concentrations (sub ppb-ppm)
  - Sensitivity to broad range of compounds: VOCs, SVOCs, PAHs
  - Minimizes sampling variability
- Virtually any soil and moisture condition
- No forced extraction
- No mechanical parts or connections
- No energy required

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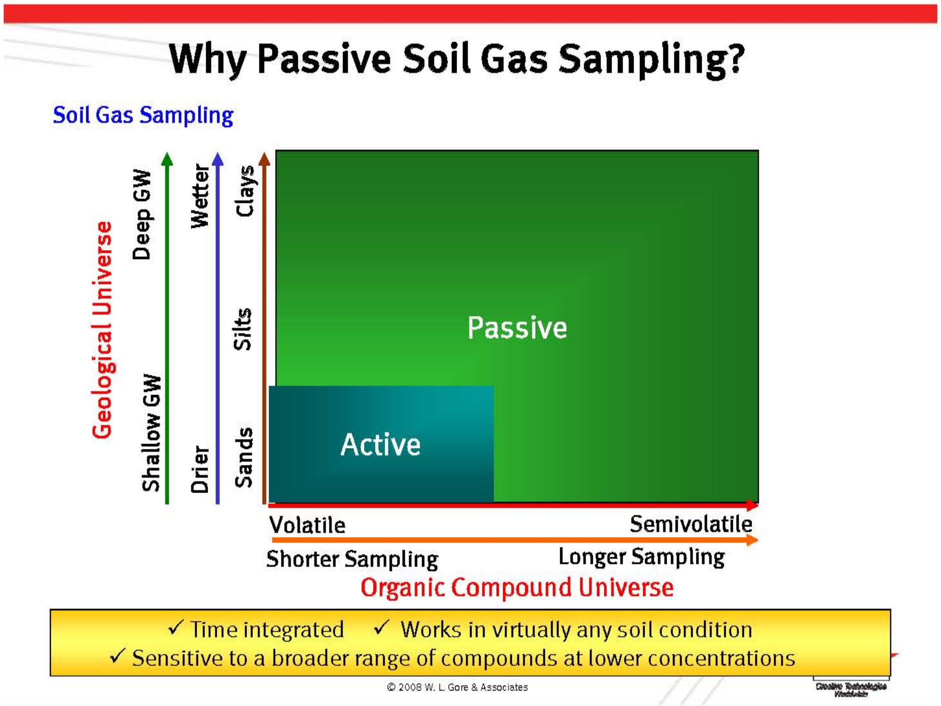

Why Passive Soil Gas Sampling?

Soil Gas Sampling

Geological Universe

Shallow GW
Deep GW

Drier
Wetter

Sands
Silts
Clays

Passive

Active

Volatile
Semivolatile

Shorter Sampling
Longer Sampling

Organic Compound Universe

✓ Time integrated ✓ Works in virtually any soil condition
✓ Sensitive to a broader range of compounds at lower concentrations

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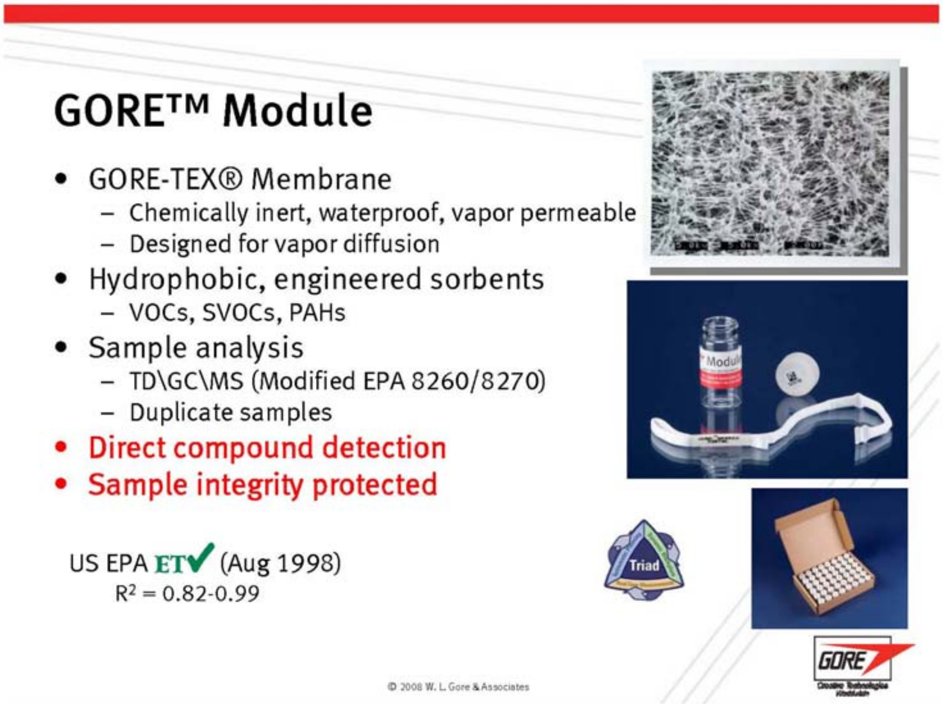

GORE™ Module

- GORE-TEX® Membrane
  - Chemically inert, waterproof, vapor permeable
  - Designed for vapor diffusion
- Hydrophobic, engineered sorbents
  - VOCs, SVOCs, PAHs
- Sample analysis
  - TD\GC\MS (Modified EPA 8260/8270)
  - Duplicate samples
- Direct compound detection
- Sample integrity protected

US EPA ETV (Aug 1998)
$R^2 = 0.82\text{-}0.99$

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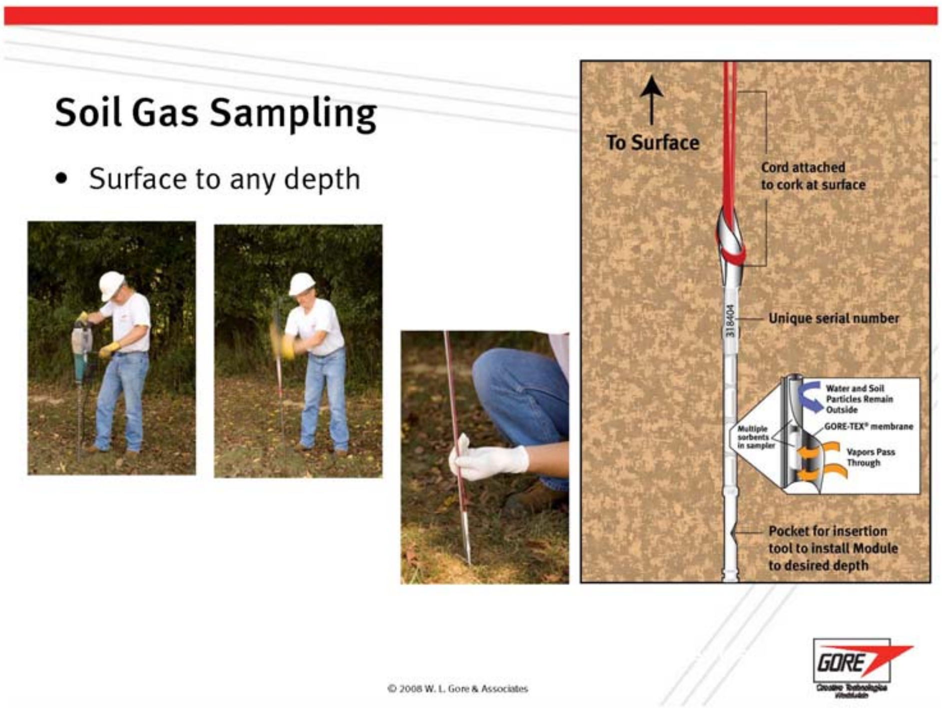

Soil Gas Sampling

- Surface to any depth

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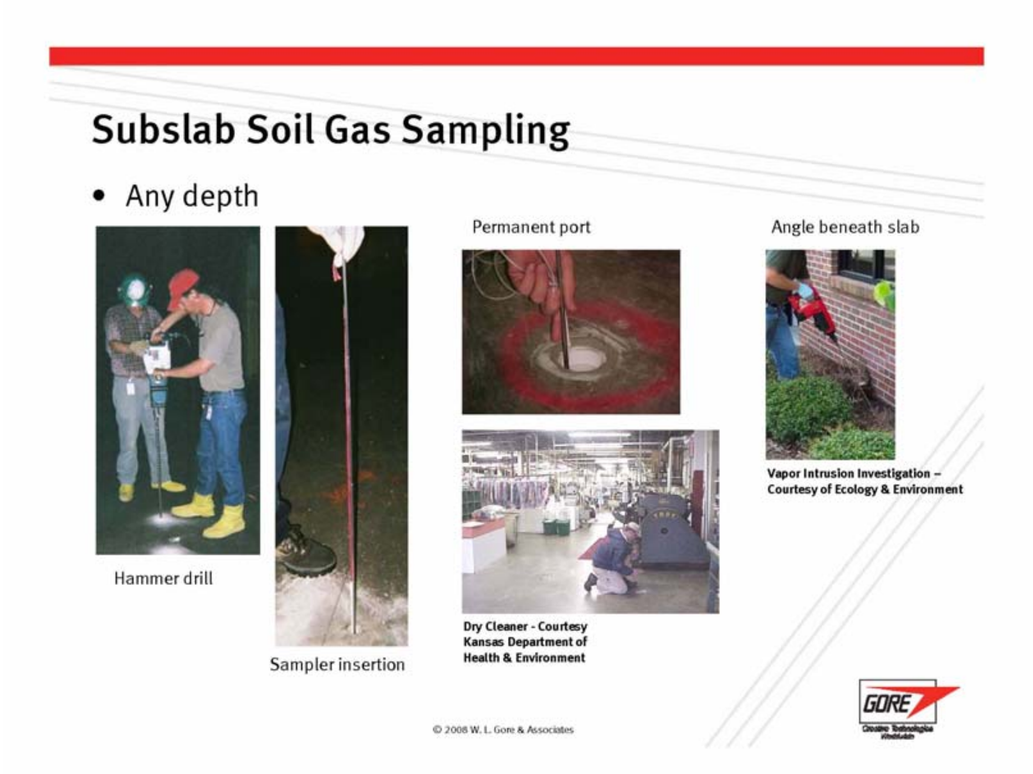

Subslab Soil Gas Sampling

- Any depth

Hammer drill

Sampler insertion

Permanent port

Dry Cleaner - Courtesy Kansas Department of Health & Environment

Angle beneath slab

Vapor Intrusion Investigation – Courtesy of Ecology & Environment

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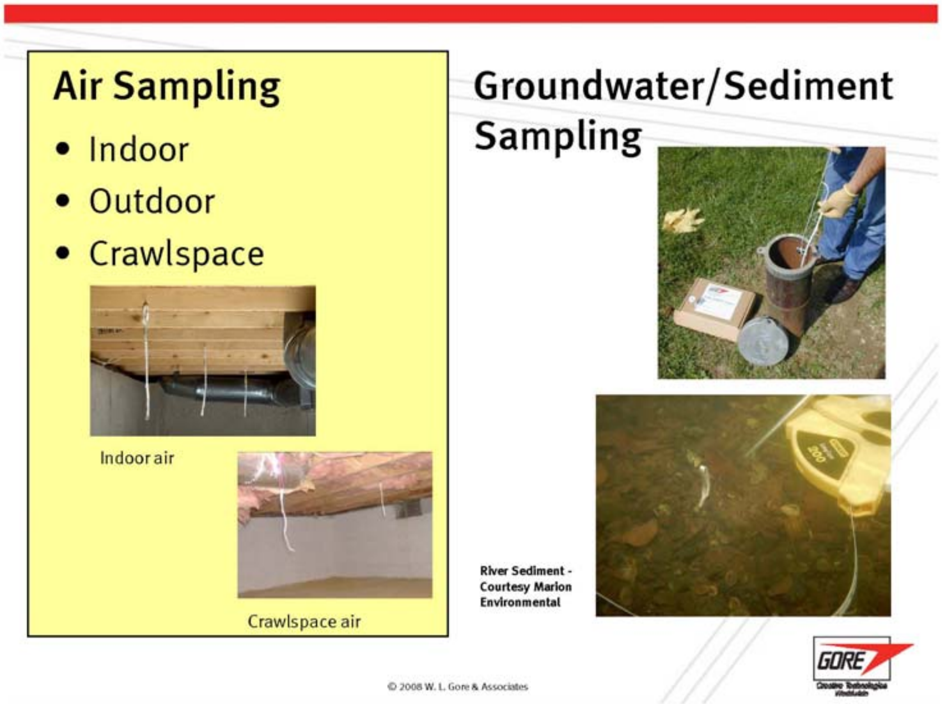

Air Sampling

- Indoor
- Outdoor
- Crawlspace

Indoor air

Crawlspace air

Groundwater/Sediment Sampling

River Sediment - Courtesy Marion Environmental

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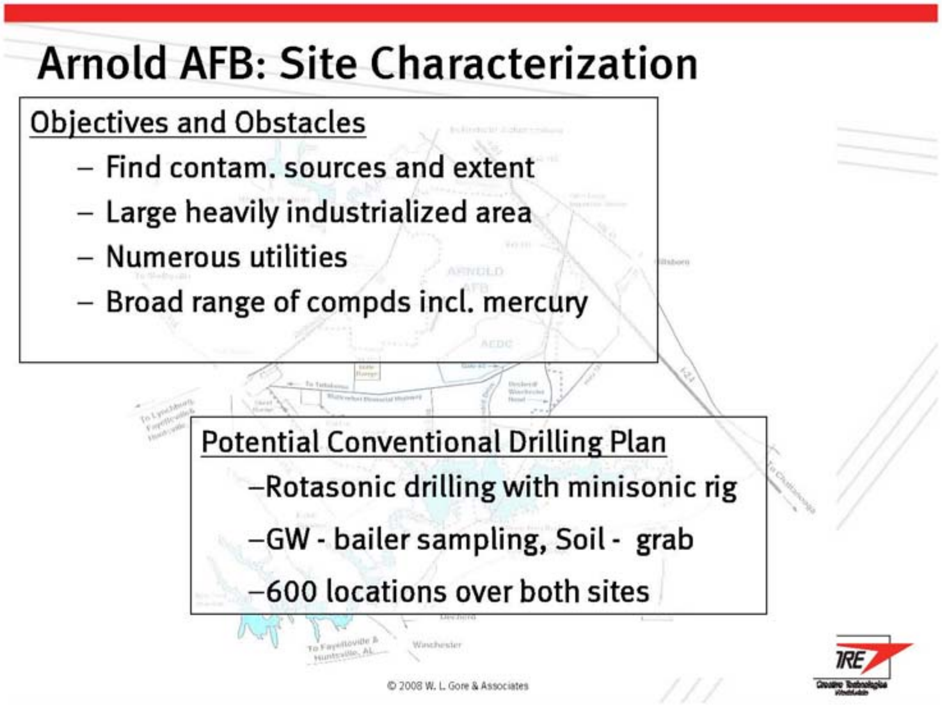

Arnold AFB: Site Characterization

Objectives and Obstacles

- Find contam. sources and extent
- Large heavily industrialized area
- Numerous utilities
- Broad range of compds incl. mercury

Potential Conventional Drilling Plan

- Rotasonic drilling with minisonic rig
- GW - bailer sampling, Soil - grab
- 600 locations over both sites

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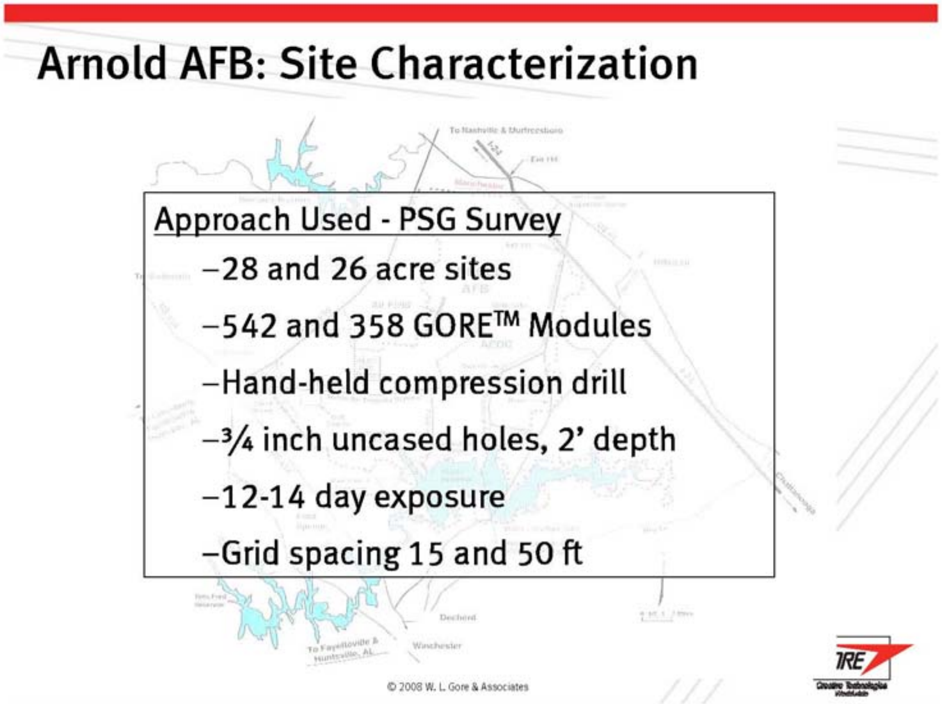

Arnold AFB: Site Characterization

Approach Used - PSG Survey

- –28 and 26 acre sites
- –542 and 358 GORE™ Modules
- –Hand-held compression drill
- –¾ inch uncased holes, 2' depth
- –12-14 day exposure
- –Grid spacing 15 and 50 ft

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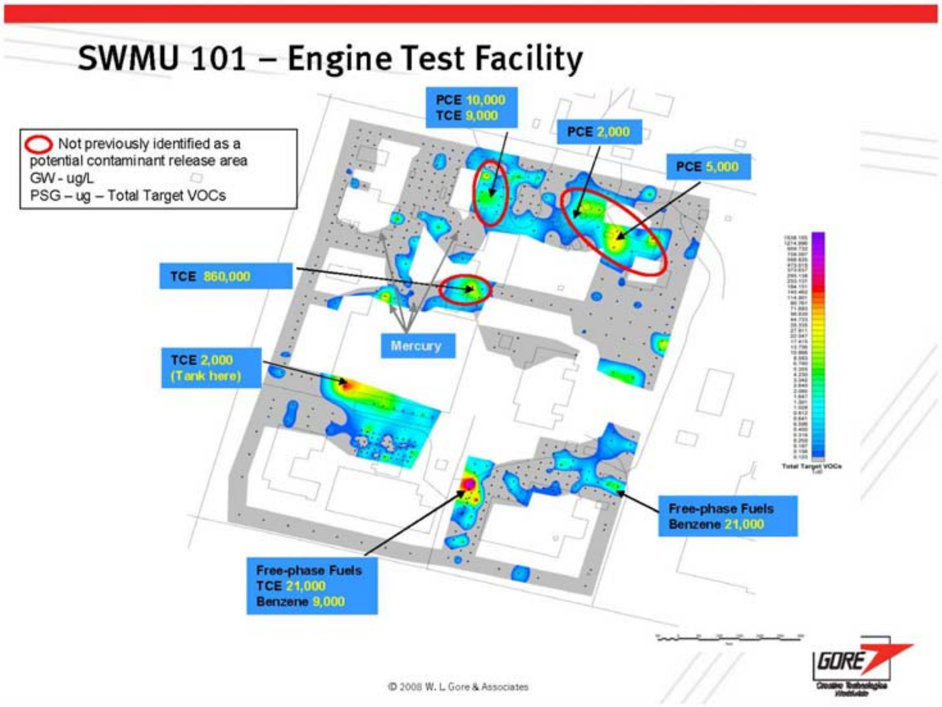

SWMU 101 – Engine Test Facility

○ Not previously identified as a potential contaminant release area
GW - ug/L
PSG – ug – Total Target VOCs

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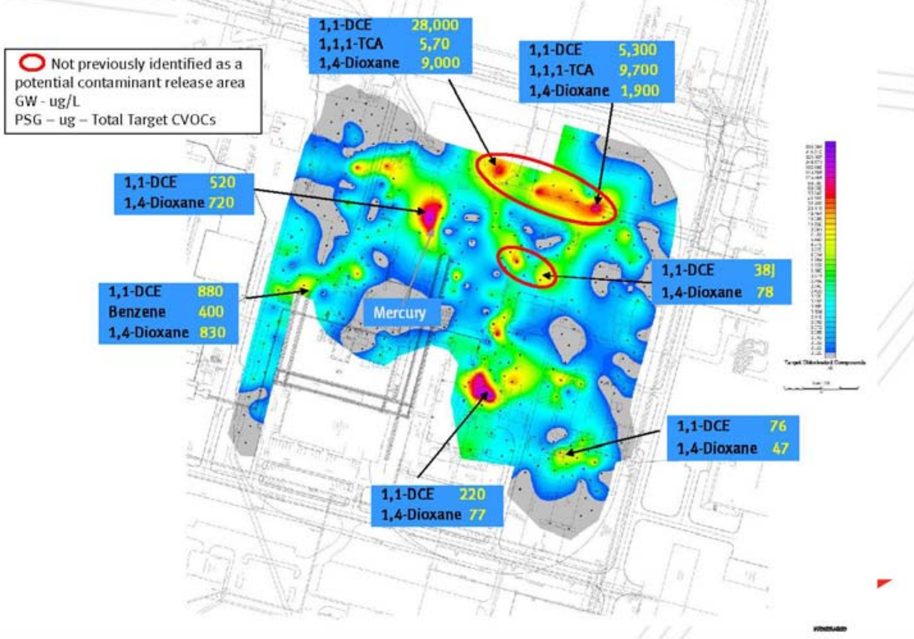
SWMU 102 – Propulsion Wind Tunnel



Arnold AFB - Survey Results

- High resolution delineation
- Solvents, fuels, and mercury detected
- Less labor, reduced utility risk, data collection in limited access areas
  - Eliminated >550 conventional sampling locations
  - > $1 Million saved
  - 75% Cost Reduction (field sampling alone)
  - Remediation program optimized and costs reduced
  - Long term monitoring cost reduced

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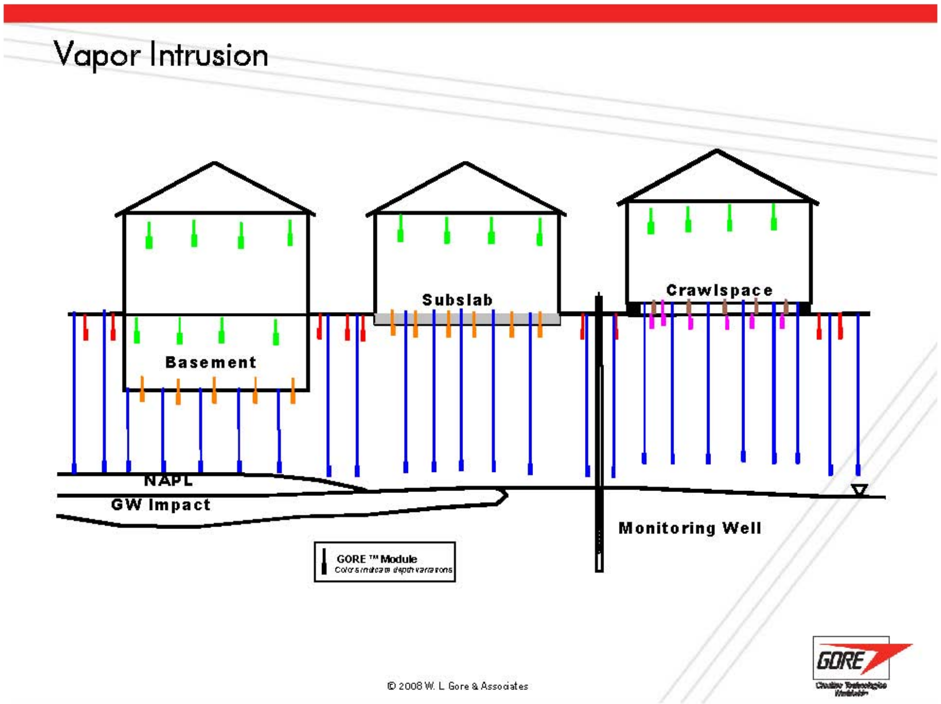

Vapor Intrusion

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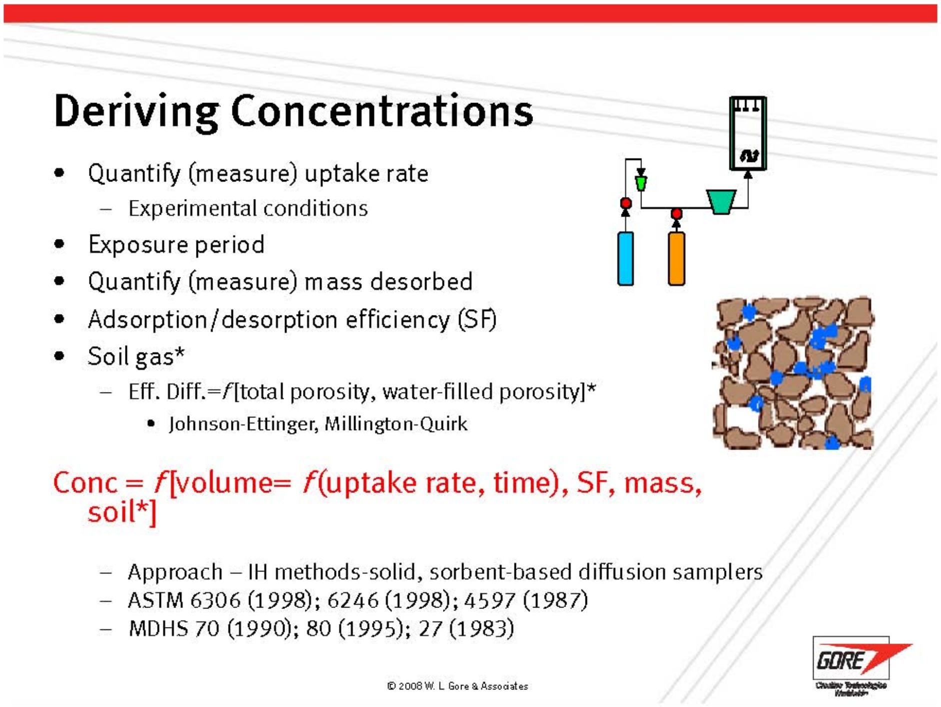

Deriving Concentrations

- Quantify (measure) uptake rate
  - Experimental conditions
- Exposure period
- Quantify (measure) mass desorbed
- Adsorption/desorption efficiency (SF)
- Soil gas*
  - Eff. Diff.=*f*[total porosity, water-filled porosity]*
    - Johnson-Ettinger, Millington-Quirk

Conc = *f*[volume= *f*(uptake rate, time), SF, mass, soil*]

- Approach – IH methods-solid, sorbent-based diffusion samplers
- ASTM 6306 (1998); 6246 (1998); 4597 (1987)
- MDHS 70 (1990); 80 (1995); 27 (1983)

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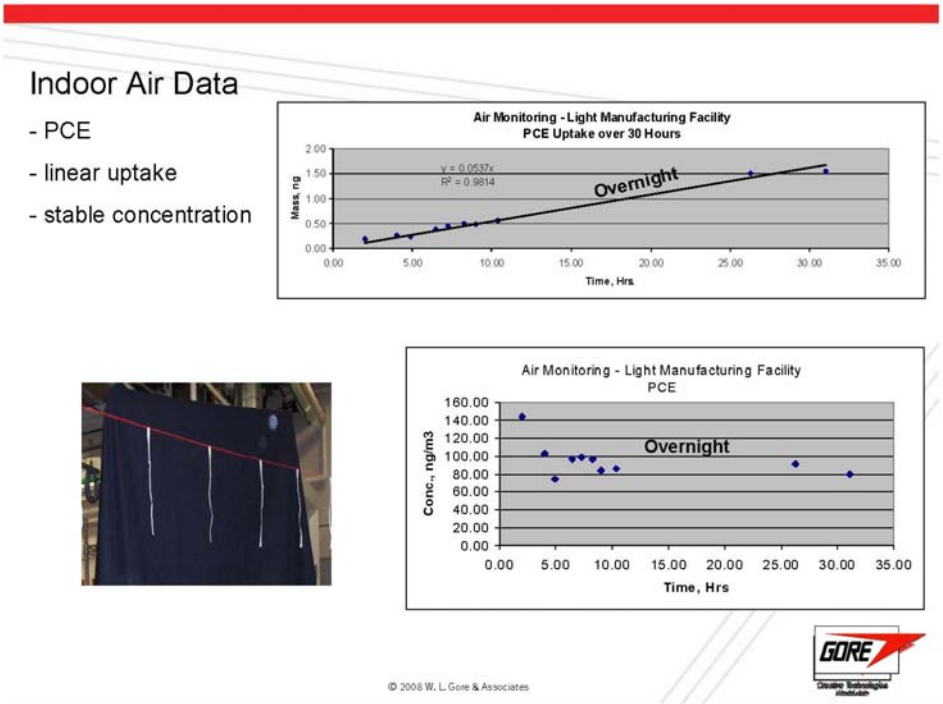

Indoor Air Data

- PCE
- linear uptake
- stable concentration

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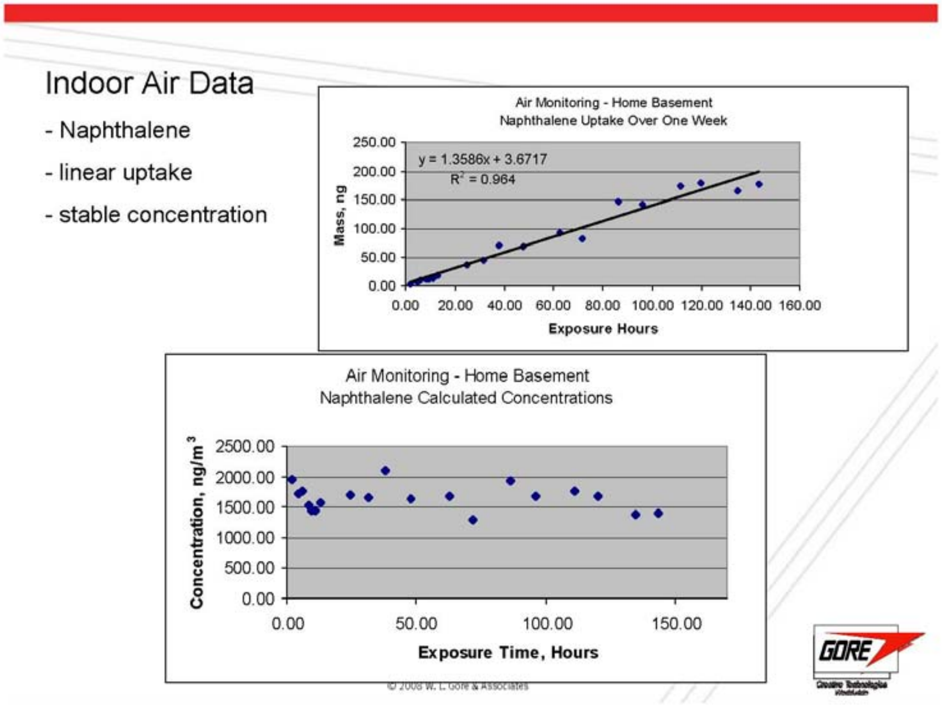

Indoor Air Data

- Naphthalene
- linear uptake
- stable concentration

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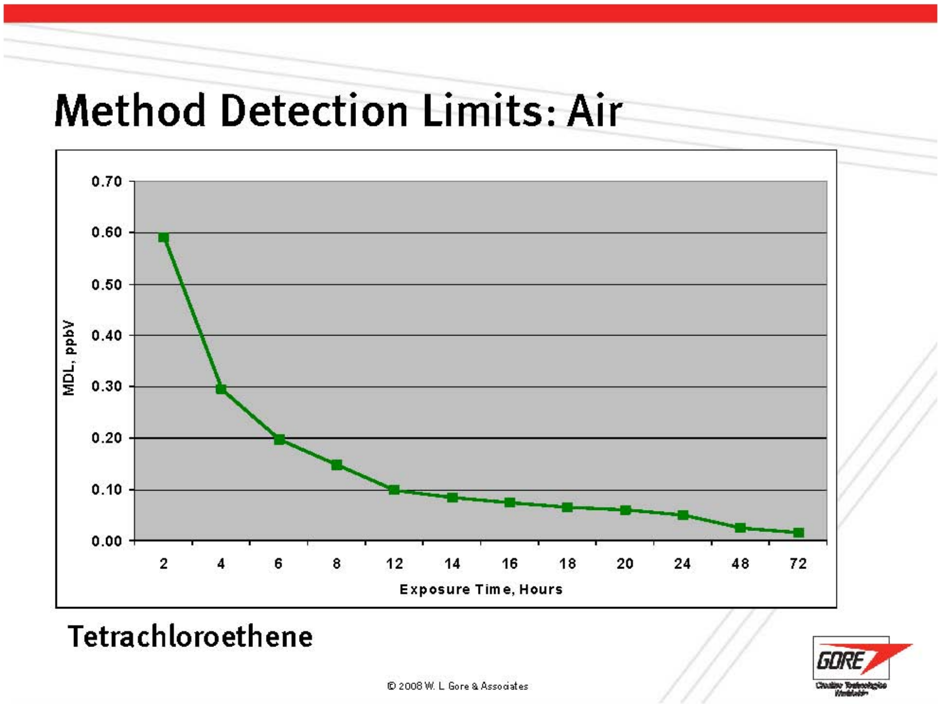

Method Detection Limits: Air

Tetrachloroethene

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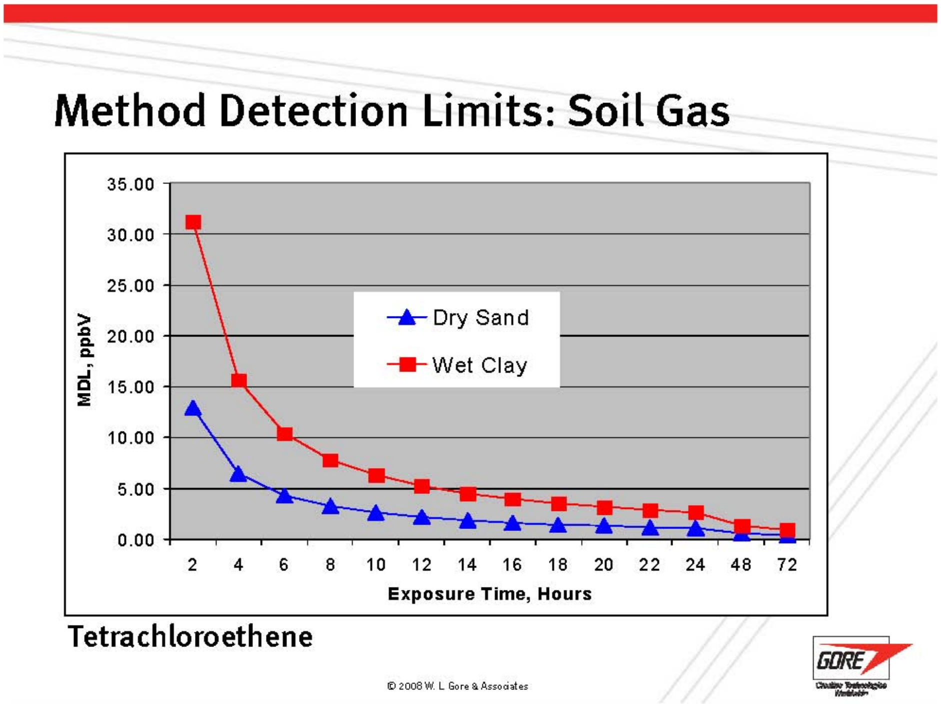

Method Detection Limits: Soil Gas

Tetrachloroethene

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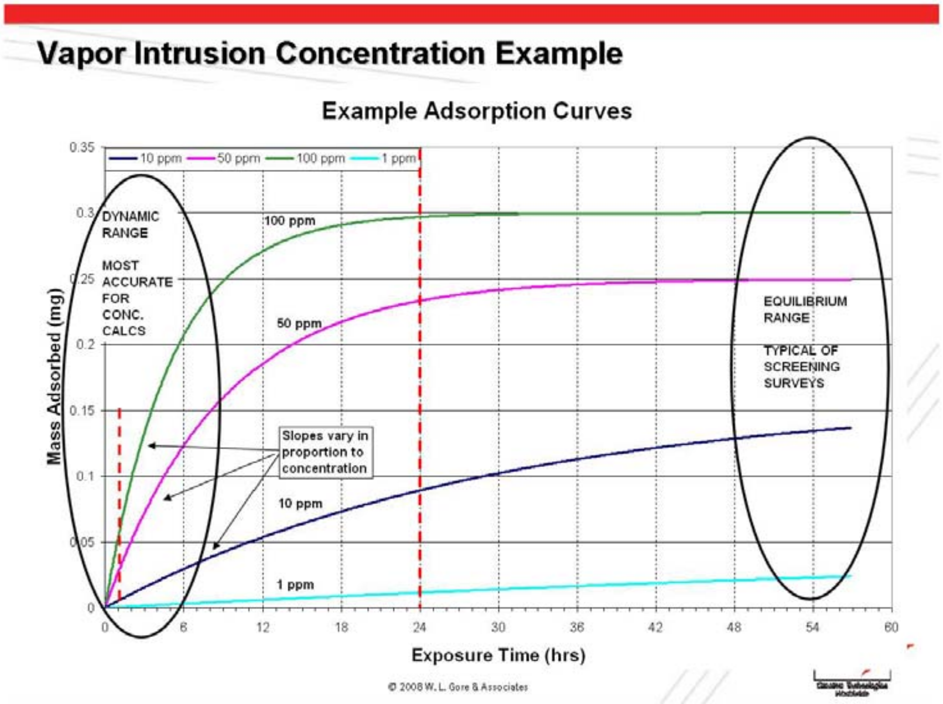

Vapor Intrusion Concentration Example

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Dry Cleaner Sites, Kansas

- Passive Soil Gas Surveys
  - Three foot depth, exterior
  - Base of slab – tight clay
  - Two-day exposure
  - Indoor air and sump air sampled
- Active (Subslab) Soil Gas Surveys
  - One month later
  - Permanent, sealed ports
  - 1L canisters, no flow controllers
  - Grab samples - 3 to 4 minutes
  - No tracer check

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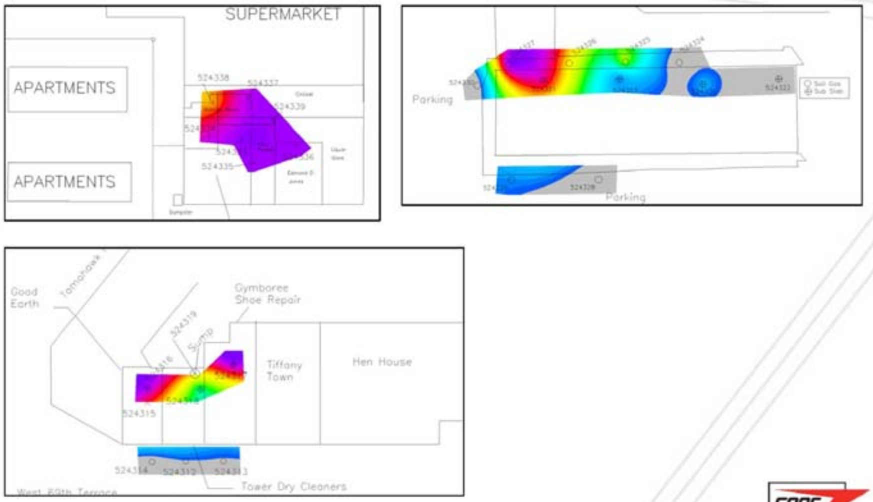
Dry Cleaner Sites, Kansas



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Dry Cleaner Sites, Kansas

	PCE			TCE		cis-1,2-DCE	
#	Media	Passive	Active	Passive	Active	Passive	Active
1	air	2.4	tbs	nd	tbs	nd	tbs
2	sump air	586	tbs	37.3	tbs	33.8	tbs
3	subslab	2,209	1,680	79.5	98.9	107	158
4	subslab	2,904	2,280	65.9	61.2	253	219
5	subslab	14.6	ns-water	nd	ns-water	nd	ns-water
6	subslab	1.9	nd	nd	nd	nd	nd
7	subslab	184	96.5	nd	nd	nd	nd
8	subslab	nd	nd	nd	nd	nd	nd
9	subslab	1.4	nd	nd	nd	nd	nd
10	subslab	>138,000	2,760,000	9,440	81,400	6,720	324,000
11	subslab	>51,100	113,000	142	378	12.8	nd
12	subslab	>91,200	85,500	1,310	2,670	183	nd
13	subslab	>96,200	75,100	314	1,460	nd	nd
14	subslab	>73,200	56,300	190	699	nd	nd
15	subslab	6,420	3,840	303	557	nd	nd
16	subslab	>107,000	125,000	772	2,750	73.6	nd

nd-non detect
tbs - to be sampled
ns - not sampled

SS>420 ug/m3

Air>42 ug/m3

Source: Kansas DHE

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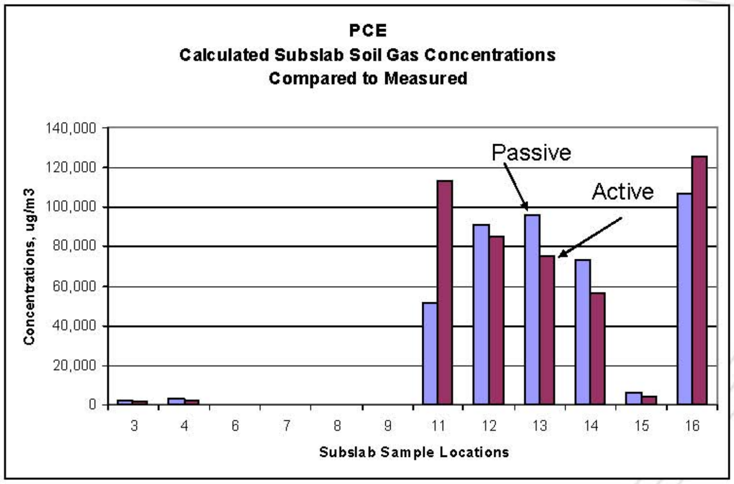
Dry Cleaner Sites, Kansas



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Conclusions

Site Assessment

- High resolution image
- Identify previously unknown release areas
- Focus RFI sampling
- **Overcome access limitations**
- **Significant time savings**

Vapor Intrusion

- Simple installation
  - Minimize field errors
- Versatile
  - ground water, soil gas, sub-slab, crawl-space, indoor air
- Very Sensitive First look
- Estimated vapor concentrations

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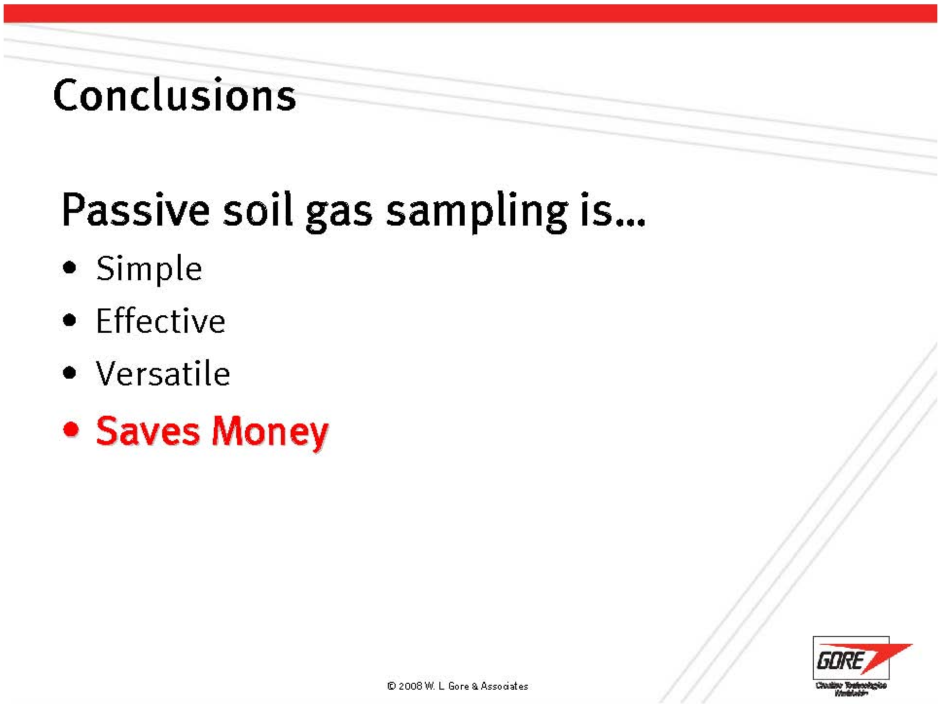

Conclusions

Passive soil gas sampling is...

- Simple
- Effective
- Versatile
- Saves Money

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THANK YOU!

CH2M Hill

KDHE

For more information, contact:

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EPA Method TO-15, EPA Method TO-17 and British MDHS 80 Comparisons: DoD Regional Groundwater Plume and Residential Vapor Intrusion Measurements

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ABSTRACT

Sampling indoor air for potential vapor intrusion impacts using current standard 24-hour sample collection methods may not adequately account for temporal variability and detect contamination best represented by long-term sampling periods. Mr. Henry Schuver of the U.S. EPA OSW stated at the September 2007 A&WMA vapor intrusion conference that EPA may consider recommending longer-term sampling to achieve more accurate time-weighted-average detections.

Investigations at Hill AFB, Utah, have evaluated vapor-intrusion-to-indoor-air impacts originating from groundwater plumes contaminated with volatile organic compounds (predominantly trichloroethene [TCE]) emanating from the Base and migrating beneath adjacent residential communities. To date, over 5,000 24-hour indoor air samples have been collected in residences.

In November 2007, indoor air at four residences was sampled to measure TCE concentrations over short- and long-duration intervals. A carefully designed investigation was conducted consisting of triplicate samplers for three different investigatory methods: dedicated 6-liter Summa canisters (EPA Method TO-15), pump/sorbent tubes (EPA Method TO-17), and passive diffusion samplers (MDHS 80). The first two methods collected samples simultaneously for a 24-hour period, and the third method collected samples for two weeks. The testing began November 12, 2007, and at the time of abstract submission the results from passive diffusion samplers were not completed.

Data collected using Methods TO-15 (canisters) and TO-17 (tubes) provided reliable short-duration TCE concentrations that agree with prior 24-hour sampling events in each of the residences; however, the passive diffusion samplers may provide a more representative time-weighted measurement. The ratio of measured TCE concentrations between the canisters and tubes are consistent with previous results and as much as 28.0ug/m3 was measured.

A comparison of the sampling procedures, and findings of the three methods used in this study will be presented.

INTRODUCTION

For the past several years, Summa canisters have been used routinely in the United States for air quality studies, including indoor air vapor intrusion studies. They have become the reference standard used for quantifying volatile organic compounds in investigations and risk assessment. To date, sorbent tubes and passive diffusion samplers are less commonly used as a tool for indoor air and vapor intrusion assessment in the United States, however, they are used routinely throughout Europe. The subject study was designed to compare these three methods at four residential locations suspected of being impacted by groundwater-to-indoor air vapor intrusion. Sorbent tubes with constant air flow and passive diffusion tubes are likely to become mainstays of air sampling in the United States because of several issues associated with the use of Summa canisters that will be presented later in this paper. Vapor intrusion guidance documents for the U.S. EPA, as well as leading state environmental agencies, recommend collection of gas samples by either Method TO-15 (canisters) or Method TO-17 (sorbent tubes).

There is a growing concern that the current standard 24-hour collection period used to sample indoor air for potential vapor intrusion impacts may not adequately account for temporal variability and detect contamination best represented by longer-term sampling periods. Mr. Henry Schuver of the U.S. EPA OSW stated at the September 2007 A&WMA vapor intrusion conference in Providence, RI that EPA may consider recommending longer-term sampling to achieve more accurate time-weighted-average detections. The purpose of the research described in this paper is to examine the longer sampling time using passive diffusion tubes and to compare these results to shorter-term testing periods using canisters and sorbent tubes. In order to set the stage for where the research was conducted and how the necessity of the testing came to be, the following paragraphs provide some background on the setting and scope.

Areas of groundwater contamination at Hill Air Force Base (AFB), Utah have been organized into 12 Operable Units[1]. Nine of the 12 Hill AFB OUs contaminated with volatile organic compounds (VOCs) have portions of shallow groundwater plumes that underlie Hill AFB buildings and seven residential communities. Previous indoor air quality sampling in areas of shallow groundwater indicates vapor phase contaminants are more likely to be present in the indoor air of overlying buildings. Up to 2,900 homes may be impacted by vapors emanating from the soil gas above these groundwater plumes, and some residences even have indoor sumps containing the contaminated groundwater from these plumes.

Residential indoor air sampling has been conducted at off-base residential locations since 1997 in the seven communities surrounding Hill AFB. The sampling has been conducted to test for the presence of indoor air vapors potentially originating from dissolved volatile organic compounds (VOCs) in groundwater plumes. The VOCs dissolved in the groundwater originating from nine operable units (OUs) on Base are capable of moving upward through the soil and posing a potential long-term human health risk in residential indoor air if those vapors enter homes above the plume. Over 1,500 individual residential locations have been tested using over 5,000 individual 6-liter stainless steel Summa sample canisters.

Hill AFB communicates indoor air results with homeowner/residents, discussing the level of risk present and options for installing a mitigation system if contaminants are above mitigation action levels. Indoor air monitoring programs are implemented, with a focus of collecting at least one sample during the winter, at residences overlying or in proximity to contaminated groundwater.

The frequency and schedule of the monitoring program is dependent on the concentrations measured and whether a mitigation system is installed in the residence.

OVERVIEW OF EXPERIMENTAL METHODS

Investigations at Hill AFB, Utah have evaluated vapor-intrusion-to-indoor-air impacts originating from groundwater plumes contaminated with volatile organic compounds (predominantly trichloroethene [TCE]) emanating from the Base and migrating beneath adjacent residential communities. To date, over 5,000 24-hour indoor air samples have been collected in residences.

In November 2007, indoor air at four residences was sampled to measure TCE concentrations over short- and long-duration intervals. A carefully designed investigation was conducted consisting of triplicate samplers for three different investigatory methods: dedicated 6-liter Summa canisters (EPA Method TO-15), pump/sorbent tubes (EPA Method TO-17), and passive diffusion samplers (British Method for the Determination of Hazardous Substances [MDHS] 80).

It has been established in numerous studies since 1992 that Summa canisters are the reference standard for air sampling in the United States. Sorbent tubes with pumps, however, are also approved and/or suggested for use in vapor intrusion testing by the U.S. EPA[2], the ITRC[3] and the State of New Jersey[4]. It should also be noted that Dr. DiGiulio of the U.S. EPA states[5] Method TO-17 "has several advantages including, rigorous QA/QC requirements, commercially available thermal desorption units and a large selection of sorbents, small size and weight of the sorbent and equipment, and the possibility of moisture management by dry purging and sample splitting prior to injection into the gas chromatograph.." The ITRC[3] Guidance Document states that passive diffusion sampling is a viable alternative for vapor intrusion assessment.

FIELD SAMPLING PROGRAM

MWH contracted Beacon Environmental Services, Inc. (Beacon) to collect air samples using three different sample collection media/equipment at four different residences. Three units (triplicate) of each sample collection device were set up simultaneously in each of four homes and run for either 24 hours or two weeks. The first two methods (EPA Methods TO-15 & -17) collected samples simultaneously for a 24-hour period, and the third method (MDHS 80) collected samples for two weeks. The testing began November 12, 2007.

The first sample method incorporated 6-liter stainless steel Summa canisters and flow controllers already dedicated to the Hill AFB residential sampling program at each site. All flow controllers were set to collect whole air for 24 hours at elevations of approximately 4,200 feet above sea level. The canisters were dedicated to the Hill AFB residential sampling program after they were individually certified clean. Following dedication to the program, canisters have been batch-certified clean. All Summa canisters and flow controllers have been tracked since the dedication of these canisters over four years ago. An historical review of the sample data from the twelve canisters used in this study show no TCE detections over 242ug/m^3; and no evidence of carryover was seen in any of the canisters used for this air sampling method study. The Summa canister analyses for this study were performed at an analytical laboratory located in Simi Valley, California using Method TO-15. Sample canisters are pressurized with humidified nitrogen to drive the sample from the canister and into the gas chromatograph/mass spectrometer for analysis in scan mode. Reporting limits in an undiluted sample for TCE is 0.7ug/m^3.

The second sample method utilized PAS 500 low-flow mini-pumps that drew indoor air at a flow rate of 20 mL/min for 24 hours through special sorbent-packed ¼-inch diameter stainless steel tubes. The flow rates of the pumps were measured using a NIST traceable flow meter at the beginning of the sampling event and then again at the end of the sampling event. The sorbent tubes were analyzed by U.S. EPA Method TO-17 by Beacon, using a Thermal Desorption System connected to a gas chromatograph/mass spectrometer (TD-GC/MS). The TD system allows for the recollection during analysis of the sample split onto a secondary, clean sorbent tube. This advanced feature eliminates the prior "one-shot" limitation of Method TO-17 where duplicate or confirmatory analyses were not possible. The reporting limit for TCE is 0.3ug/m3.

The third sample method utilized passive diffusion samplers (PDS), consisting of ¼-inch diameter stainless steel tubes packed with a custom adsorbent. During sample collection, one end of the tube remained sealed and the other end was fitted with a sampling cap to allow for the free diffusion of compounds onto the adsorbent without the need for a porous membrane. These tubes were exposed to indoor air for two weeks and were analyzed following U.S. EPA Method TO-17 by Beacon using the above mentioned Thermal Desorption System connected to a gas chromatograph/mass spectrometer (TD-GC/MS). The reporting limit for TCE is 0.5ug/m3.

RESULTS/DISCUSSION

Data collected using Methods TO-15 (canisters) and TO-17 (sorbent tubes with pumps) provided reliable short-duration TCE concentrations that agree with prior 24-hour sampling events in each of the residences and the passive diffusion sampler (PDS) time-weighted measurements tracked very closely to the TO-17 results. The results of the testing program are presented below in Table 1. The measured TCE concentrations are consistent with previous results with as much as 28ug/m^3 measured. The PDS results are consistently lower (on the average) than both the TO-15 & -17 concentrations and the effects of time-weighting of the samplers are more evident at increasing concentrations. The effects of time-weighting the sampling process over a two week period reproduced the relative change from residence to residence. The TO-17 results more closely track the PDS concentrations with a range of 3.5 to 30% lower concentrations for the two-week versus 24-hour sampling periods, respectively.

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Table 1. Results of Indoor Air Testing Near Hill AFB, Utah Nov. 12-26, 2007

Compound	TCE		
Units	ug/m3		
Lab	Beacon	Air Lab	Beacon
Method	TO-17	TO-15	MDHS 80
Exposure	24 hr Tube	24 hr Can	2 wk PDS
Location			
8158	**20.4**	**28**	**12.1**
8158	**18.1**	**27**	**11.7**
8158	**10.9**	**19**	**10.8**
8016	**1.9**	**3.3**	**1.8**
8016	**2.0**	**3.6**	**1.7**
8016	**2.2**	**3.6**	**1.8**
8116	<0.3	<0.7	<0.5
8116	<0.3	<0.7	<0.5
8116	<0.3	<0.7	<0.5
8078	**1.2**	**1.8**	**1.0**
8078	**1.1**	**1.8**	**1.0**
8078	**0.9**	**1.7**	**1.1**

The data collected using Methods TO-15 (canisters) and TO-17 (tubes) provided reliable short-duration TCE concentrations that agree with prior 24-hour sampling events in each of the residences, and the passive diffusion samplers provide time-weighted measurements over a two-week period. The ratio of measured TCE concentrations between the canisters and tubes are consistent with on-going research[6].

The following is a summary of the research completed in the study and are not in any particular order of importance.

- The purpose of the indoor air sampling study was to compare the side-by-side testing results of 24-hour Summa canisters, 24-hour active sorbent tubes (using small low-flow pumps), and 14-day passive diffusion sample tubes. The field-based study took place in four residential locations in triplicate near Hill Air Force Base, Utah.
- The active sorbent tubes, Summa canisters and the long-term passive diffusion tubes (PDS) all measured the same trends relative to each residence.
- The PDS results are consistently lower (on the average) than both the TO-15 & -17 concentrations and the effects of time-weighting of the samplers are more evident at increasing concentrations. The effects of time-weighting the sampling process over a two week period reproduced the relative change from residence to residence.
- Regardless of the method used, each had strong agreement among the three reported concentrations within each home for each method.

ACKNOWLEDGEMENTS

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The Importance of Air Sampling Media Cleanliness for Vapor Intrusion Investigations

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ABSTRACT

The increase in regulatory oversight at vapor intrusion sites nationwide, as well as recent publication of Federal and local vapor intrusion guidance documents and screening levels has led to a need for reliable air phase (indoor air and sub-slab/soil vapor) data at extremely low concentrations. This paper will explore and discuss the importance of media cleanliness and certification to achieve typical low level data quality objectives.

Several potential pathways of media contamination will be examined, including: canisters, flow controllers/critical orifice assemblies, vacuum gauges, and canister pressurization/fill stations in the laboratory.

Several contamination situations will be explored and quantified. The resulting data will be used to support laboratory and field sampling best practice recommendations.

INTRODUCTION

Thorough cleaning and certification of canister media has long been an accepted practice in the laboratory community. However, similar cleaning, certification and general care with the associated canister sampling media (e.g. flow controllers and vacuum gauges) has been less commonly discussed and practiced. Since all of this equipment is cleaned and reused, it is critical, especially for ultra low level projects, to ensure that every piece of equipment used to collect a sample has been properly cleaned and certified by the laboratory performing the analysis.

In addition to being described in detail in the EPA TO-15 method[1], the importance of canister cleaning and/or the canister cleaning technique itself has been described in several historical documents, such as canister stability studies by Batterman et. al[4], Ochai et. al[5], and Brymer et. al[6]. These documents all describe a cleaning procedure using steam cleaning & heat. More recently, canister cleaning has been briefly described in the South Coast Air Quality Management District (SCAQMD) Multiple Air Toxics Exposure Study III (MATES III)[7], in the literature by Wang et. al[8], and at technical conferences[9]. To date, cleaning and other maintenance of associated canister sampling equipment (e.g. flow controllers, vacuum gauges) has not been described in great detail in the literature.

The EPA TO-15 method mentions cleaning of the "sampling system components" by rinsing with HPLC grade water and drying in a vacuum oven at 80°C[1]. Restek Corporation recommends cleaning "the entire sampling train as you would the can to minimize introduction of contaminants into a clean can"[2]. Entech Instruments recommends backflushing of flow controllers with nitrogen/zero air and/or baking the flow controllers in a 70°C oven for higher level applications.[3]

Since most commercial air analysis laboratories analyze canister samples from a variety of applications, including indoor/ambient air monitoring (typically lower concentration samples, sometimes in the low ppbV/high pptV range) and soil vapor/soil vapor extraction (SVE) system monitoring (typically higher concentration samples, sometimes in the high ppmV range), the potential exists for cross contamination and false positive results. The purpose of this paper is to explore the potential data quality implications of equipment cleaning & segregation practices (or the lack thereof) in the laboratory. Specifically, the issue of "carryover" or "memory" in air sampling equipment will be addressed.

PROCEDURE

One test sample was created in a 6L electropolished stainless steel (SUMMA) canister with elevated concentrations of a mixture of petroleum hydrocarbons and tetrachloroethene (this sample is referred to as Sample A). The study was split into two areas: contamination of flow controllers (defined as mechanical devices containing an orifice to restrict flow and a diaphragm to maintain consistent flow rate, used for passive time integrated sample collection) and contamination of vacuum gauges (used to check pressure upon receipt at the laboratory after sampling).

Flow Controllers

Sample A was pressurized to 29.4 psig (3 atmospheres) and allowed to equilibrate for 24 hours. It was then analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) via EPA TO-15 to confirm the actual concentrations of selected target volatile organic compounds (VOCs) and to obtain a visual qualitative "fingerprint". Refer to Tables 1 & 2 for instrument conditions; refer to Figure 1 for a GC/MS total ion chromatogram (TIC) fingerprint of Sample A.

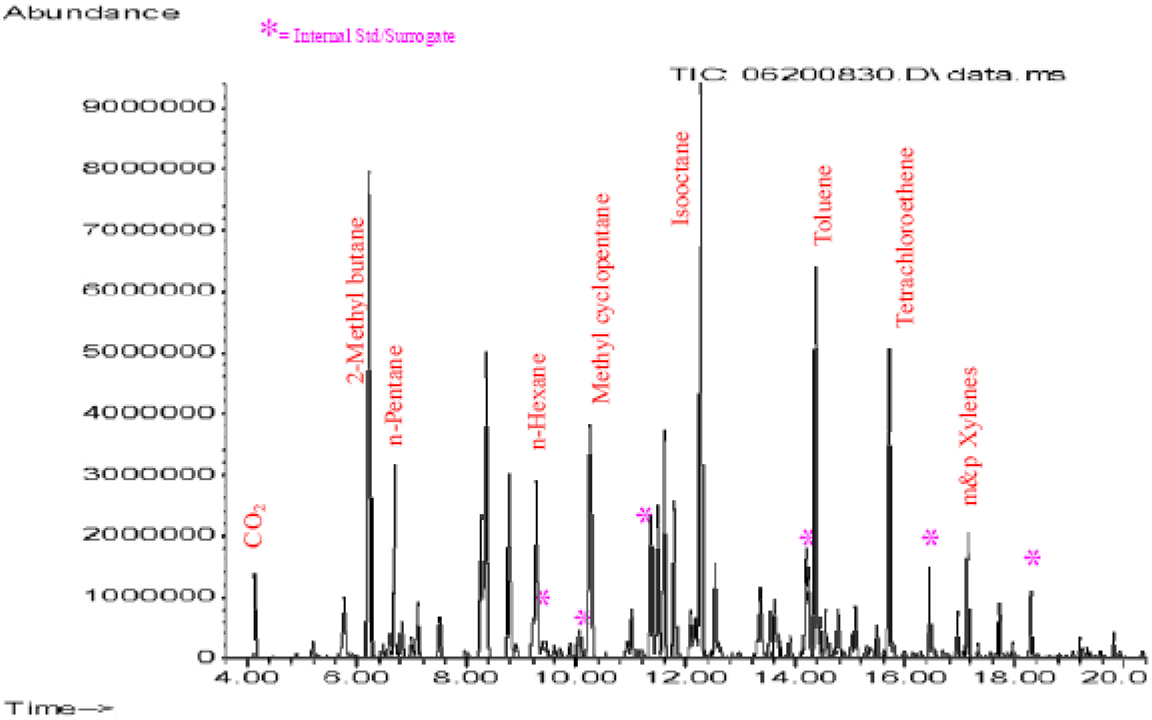
Table 1. Autosampler/Concentrator Conditions (EPA TO-15)

Instrument	Tekmar-Dohrmann AUTOCan Autosampler, equipped with Concentrating Trap, Cryofocusing Module, and Vacuum Pump
Adsorbent Trap	
Set Point	35C
Sample Volume	Up to 1L
Dry Purge	400 mL
Sampling Rate	40-100 mL/min
Desorb Temp	230C
Desorb Flow Rate	10 mL/min Helium
Desorb Time	3 minutes
Bakeout after each run	8 minutes at 260C
Refocusing Trap	
Temperature	-180C
Injection Temperature	120C
Injection Time	1 minute

Table 2. GC/MS Conditions (EPA TO-15)

Instrument	GC/MS #16 (Agilent 6890 GC/5975C MS)
Column	J&W DB-1 MS 60m x 0.32mm ID, 1 µm film thickness
Carrier Gas	UHP Helium
Flow Rate	1 mL/min
Temperature Program	Initial Temperature: 35°C
	Initial Hold: 3 minutes
	Ramp Rate: 5°C/min to 125°C
	2nd Ramp Rate: 20°C/min to 240°C; hold for 6 minutes
MSD Interface Temperature	280°C
Electron Energy	70 volts (nominal)
Mass Range	34-280 amu (SCAN mode)
Scan Time	Minimum 10 scans/peak, not to exceed 1 second per scan

Figure 1. GC/MS TIC Chromatogram of Highly Contaminated Sample (Sample A)
(0.5 mL analysis volume: 2000x dilution)

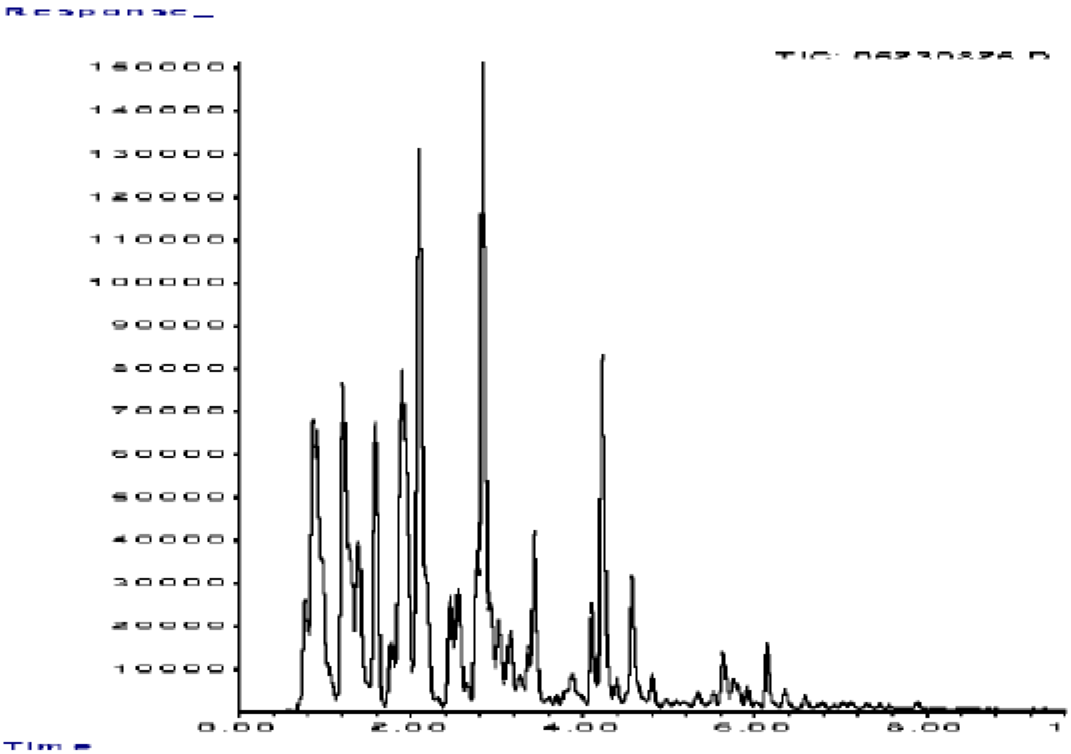


In addition, Sample A was analyzed by gas chromatography/flame ionization detection (GC/FID) to obtain a fingerprint. Table 3 lists GC/FID conditions used and Figure 2 presents the GC/FID fingerprint. For the purposes of this study, selected petroleum indicator compounds (n-hexane, benzene, isooctane, and 1,2,4-trimethylbenzene (1,2,4-TMB), n-decane, n-undecane, and naphthalene) were tracked in the forthcoming data tables and/or chromatgrams.

Table 3. GC/FID Conditions

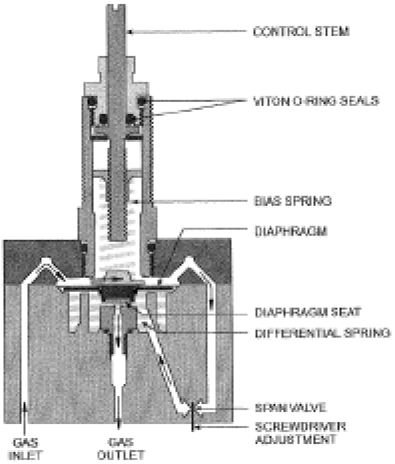
Instrument	GC/FID #19 (Agilent 5890A GC equipped with Flame Ionization Detector
Column	Restek Coroporation RTX-1, 60m x 0.53mm ID, 5 µm film thickness
Carrier Gas	UHP Helium
Temperature Program	Initial Temperature: 60°C
	Initial Hold: 1 minute
	Ramp Rate: 12°C/min to 220°C; hold for 1.5 minutes
Injection Type	Manual (1 mL gas tight syringe)

Figure 2. GC/FID Fingerprint Chromatogram of Highly Contaminated Sample (Sample A)



Contaminated air from Sample A was forced through two flow controllers (Vici Condyne Model 202, see Figure 3 for schematic) at a rate of 65 mL/min for 62 minutes (total volume passed through each flow controller was 4L). One of the flow controllers was then subjected to our laboratory's normal cleaning procedures (purged with high purity air at 30 mL/min in a 60°C oven for 2.5 hours); the other flow controller was used immediately to fill a cleaned and evacuated canister (Sample B) with humidified zero air over approximately one hour. After the first flow controller was cleaned, it was then used to fill a cleaned and evacuated canister (Sample C) with humidified zero air over approximately one hour. Both Sample B and Sample C (having final pressures of approximately 5.0"Hg) were then slightly pressurized with humidified zero air (to 3.5 psig) analyzed via EPA TO-15. Concentrations above the reporting limit (0.1-0.5 $\mu g/m^3$) of target 91 target compounds were reported.

Figure 3. Schematic of Vici Condyne Model 202 Flow Controller



Vacuum Gauges

The pressure of Sample A was adjusted to approximately 10 psig. The pressure of Sample A was then checked with a TIF 9675 digital pressure/vacuum gauge (with necessary NPT/Swagelok tube adapting fittings attached, estimated dead volume in fittings is 0.5 mL), simulating the check done during sample log-in. Immediately after the high concentration sample, the pressure of a fully evacuated simulated "trip blank" canister was checked on the same vacuum gauge. This mock trip blank canister (Sample D)was immediately filled to 3.5 psig with humidified ultra zero air and analyzed via EPA TO-15. The process was repeated, only after reading the pressure of Sample A and before reading the pressure of the next mock trip blank, the gauge and fittings were evacuated with a vacuum pump three times, essentially flushing the dead volume with room air. After the flushing, the pressure of a fully evacuated mock trip blank canister (Sample E) was checked on the flushed vacuum gauge. Sample E was immediately filled to 3.5 psig with humidified ultra zero air and analyzed via EPA TO-15. Samples D & E (associated with Sample A at 10 psig) represent a "worst case" situation, since most real world samples are received at pressures <10 psig.

The entire procedure described above was repeated with Sample A adjusted to 0 psig, to simulate the receipt pressure of typical real world samples. Sample F is the mock trip blank without flushing; Sample G is the mock trip blank with flushing.

For clarity, a complete listing of all sample names/descriptions analyzed in this study is presented in Table 4.

Table 4. Sample Names and Descriptions

Sample Name	Description
Sample A	Highly Contaminated Canister
Sample B	Canister filled via uncleaned flow controller
Sample C	Canister filled via cleaned flow controller
Sample D	Mock trip blank, pressure measured after measuring pressure of 10psig Sample A (not flushed)
Sample E	Mock trip blank, pressure measured after measuring pressure of 10psig Sample A (flushed)
Sample F	Mock trip blank, pressure measured after measuring pressure of 0psig Sample A (not flushed)
Sample G	Mock trip blank, pressure measured after measuring pressure of 0psig Sample A (flushed)

RESULTS

A distinct difference was observed in the quantitative and qualitative analysis of samples from cleaned and uncleaned flow controllers, and flushed and non-flushed vacuum gauges. Figure 4 shows the GC/MS TIC chromatogram for Sample B (uncleaned flow controller); to contrast, Figure 5 shows the GC/MS TIC chromatogram for Sample C (cleaned flow controller). Figure 6 shows the GC/MS TIC chromatogram for Sample D (mock trip blank, not flushed, 10 psig); to contrast, Figure 7 shows the GC/MS TIC chromatogram for Sample E (mock trip blank, flushed, 10 psig). Results from Samples F (mock trip blank, not flushed, 0 psig) & G (mock trip blank, flushed, 0 psig) are presented in Figures 8 & 9, respectively. Numerical results and evaluations follow in the forthcoming subsections.

Figure 4. GC/MS TIC Chromatogram: Sample B
(Uncleaned Flow Controller)

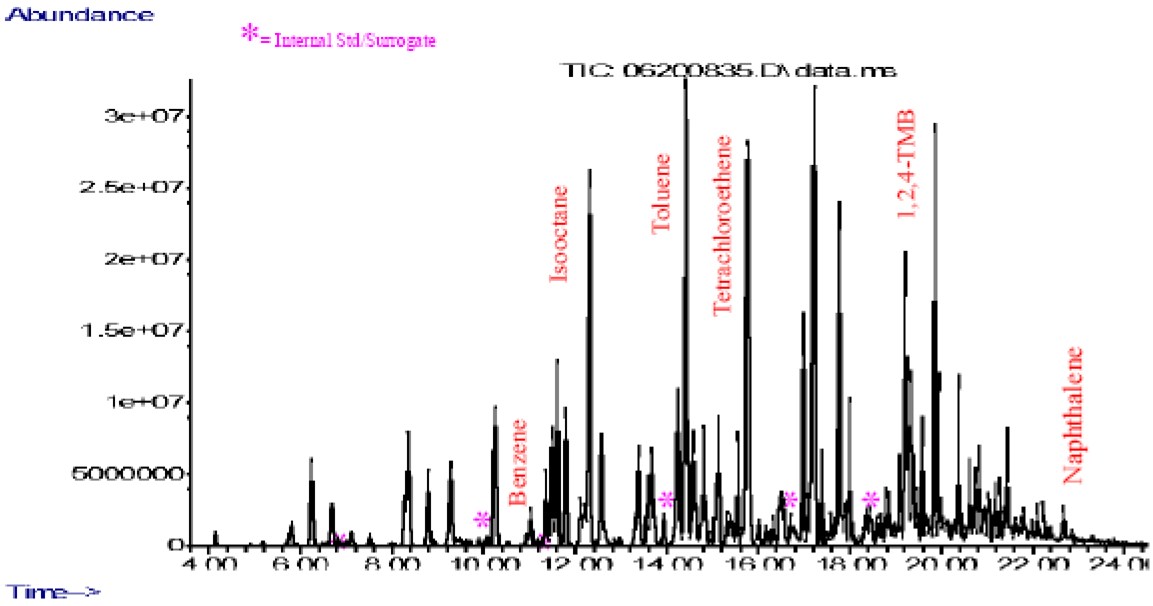


Figure 5. GC/MS TIC Chromatogram: Sample C
(Cleaned Flow Controller)

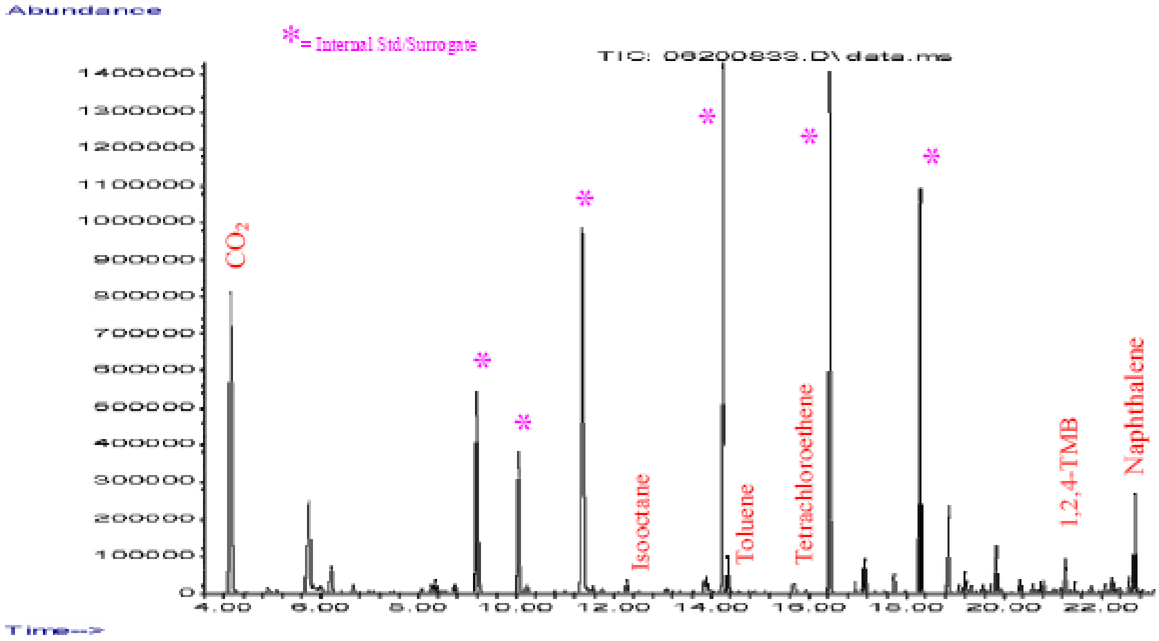


Figure 6. GC/MS TIC Chromatogram: Sample D
(Mock Trip Blank, not flushed, 10psig)

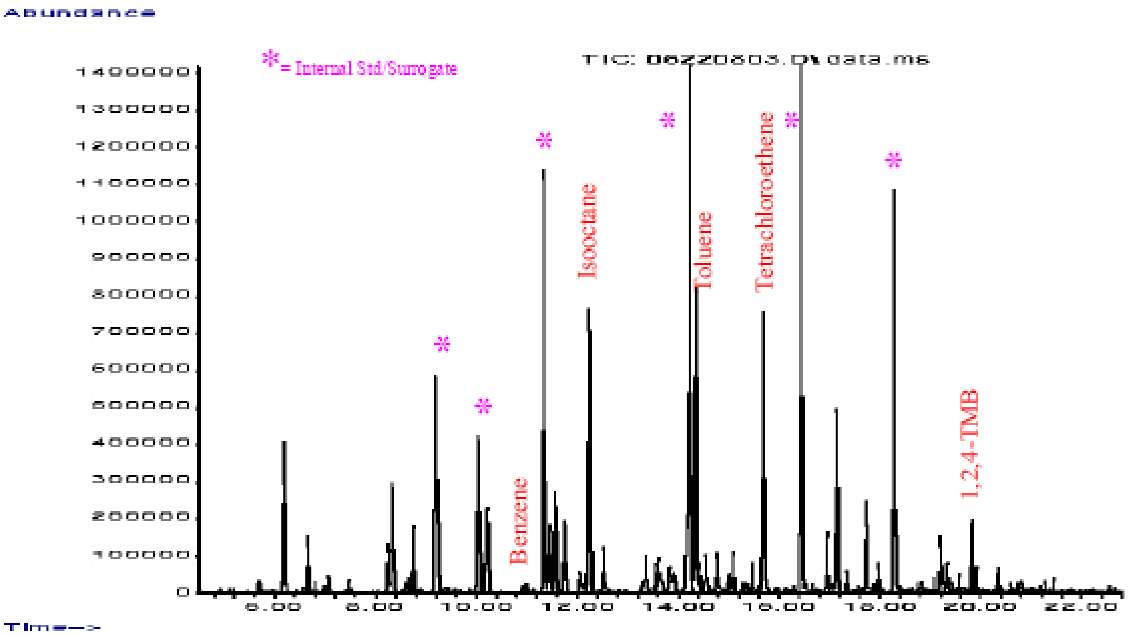


Figure 7. GC/MS TIC Chromatogram: Sample E
(Mock Trip Blank, flushed, 10psig)

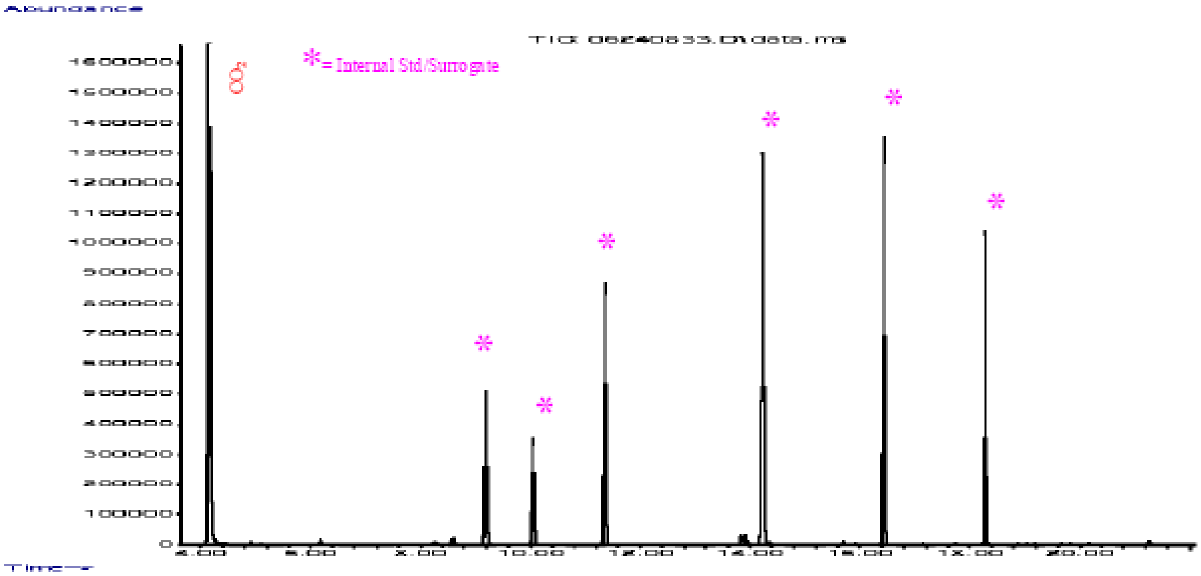


Figure 8. GC/MS TIC Chromatogram: Sample F
(Mock Trip Blank, not flushed, 0psig)

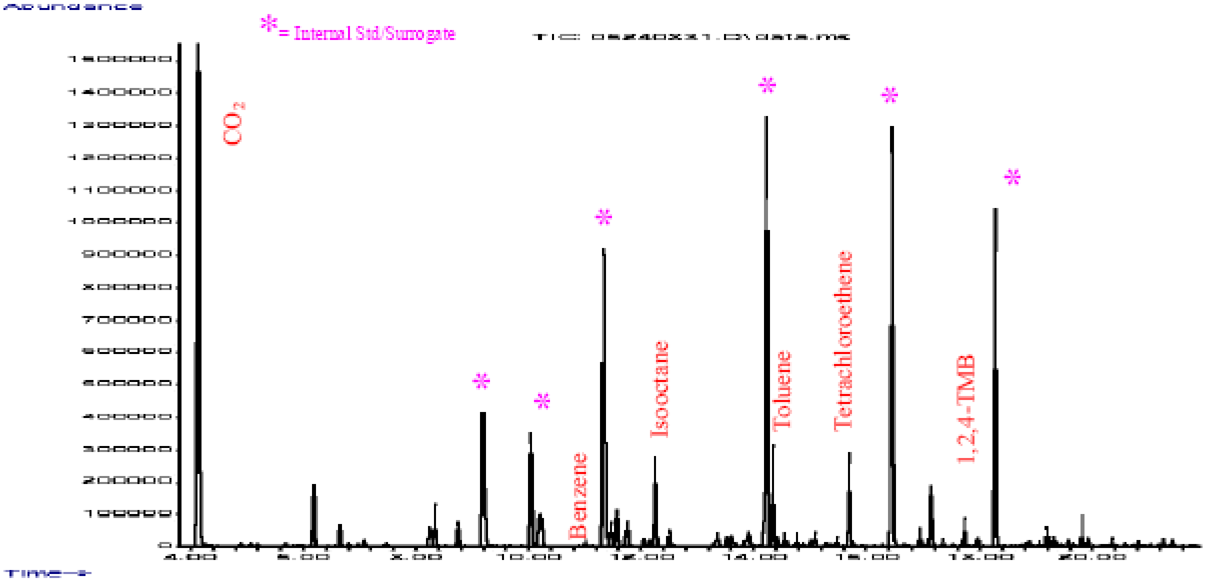
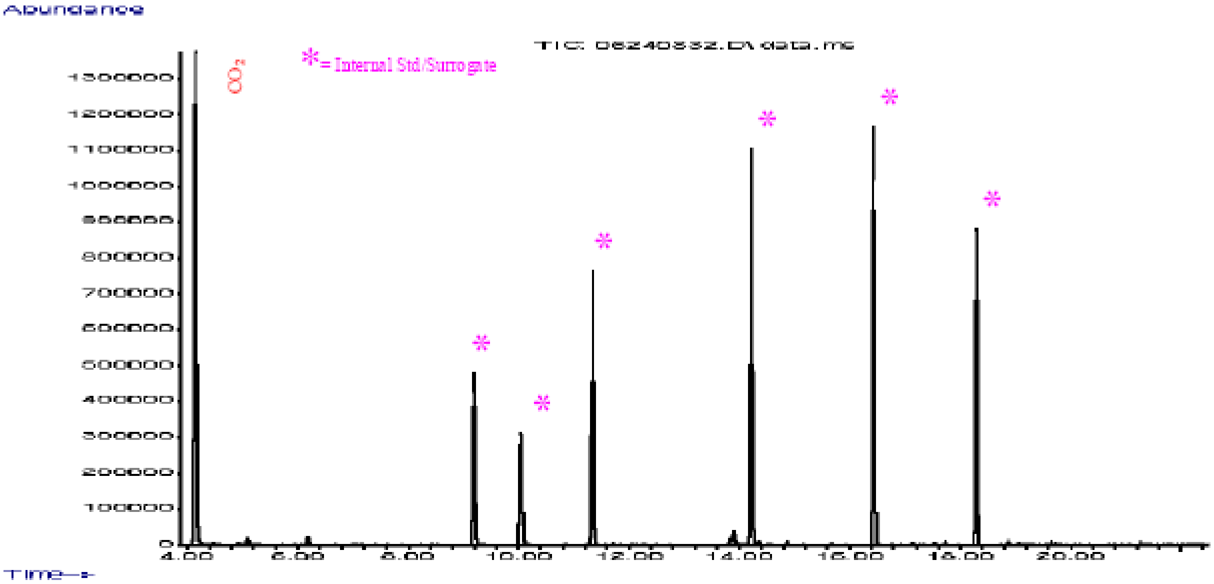


Figure 9. GC/MS TIC Chromatogram: Sample G
(Mock Trip Blank, flushed, 0psig)



Flow Controllers

Tetrachloroethene (PCE)

Tetrachloroethene carryover was seen in Sample B (uncleaned flow controller). Assuming a concentration of 250,000 µg/m^3 in Sample A, 10^6 ng tetrachloroethene were pulled through each flow controller; thus, Sample B (uncleaned flow controller) had 0.20% carryover and Sample C (cleaned flow controller) had 0.0002% carryover. While the percentages of carryover observed were very small, the nominal concentrations seen in the canisters as a result of this carryover exceed many established risk based concentrations for indoor air. Table 5 presents the concentrations seen in these samples, as well as the percent reduction in concentration between the cleaned and uncleaned flow controller samples.

Table 5. Tetrachloroethene Flow Controller Results

Sample A Concentration (µg/m^3)	Sample C Concentration (µg/m^3)	Sample B Concentration (µg/m^3)	% Reduction in Concentration from Cleaning
250,000 (E)	2.2	2000 (E)	99.89%

E=Estimated over calibration range

Petroleum Constituents

Petroleum product carryover was seen in Sample B (uncleaned flow controller). Looking at the eight individual marker compounds, Table 6 presents chemical information (molecular weight (MW) and boiling point (BP)), carryover information, and cleaning effectiveness information.

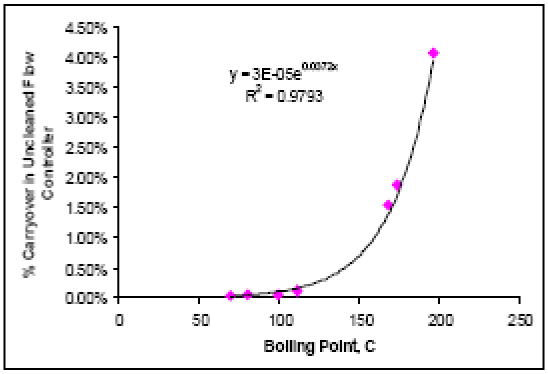
Table 6. Gasoline & Diesel Constituents Flow Controller Results

Compound	MW	BP (°C)	Sample A Concentration(µg/m^3)	Sample C Concentration (µg/m^3), % Carryover		Sample B Concentration (µg/m^3), % Carryover		% Reduction from Cleaning
n-Hexane	86.17	69	140,000	ND (0.75)	NC	250 (E)	0.04%	99.8%
Benzene	78.11	80	36,000	0.23	0.0002%	100	0.07%	99.8%
Isooctane	114.23	99	300,000 (E)	0.84	0.0001%	810 (E)	0.07%	99.9%
Toluene	92.14	111	190,000	2.4	0.0003%	950 (E)	0.13%	99.8%
1,2,4-TMB	120.2	168	8,400	2.2	0.0065%	520 (E)	1.6%	99.6%
n-Decane	142.28	174	2,400	ND (0.75)	NC	180 (E)	1.9%	99.9%
n-Undecane	156.31	196	610	ND (0.75)	NC	99	4.1%	99.6%
Naphthalene	128.17	218	ND (1000)	4.7	NC	12	NC	61.3%

ND= Not detected (above reporting limit), NC= Not calculable, E=Estimated over calibration range

When plotting boiling point versus the percent carryover (Figure 10), the relationship appears to be exponential in nature. Thus, as the boiling point of the contaminant compound increases, the degree of carryover or memory in a flow controller appears to increase exponentially.

Figure 10. Plot of Boiling Point versus Percent Carryover in Sample B



Vacuum Gauges

Tetrachloroethene (PCE)

Tetrachloroethene carryover was seen in Sample D (mock trip blank, not flushed, 10 psig). The carryover concentration seen in Sample F (mock trip blank, not flushed, 0 psig) was reduced by approximately 50%. When the gauge was flushed out in between readings, the carryover concentrations seen in Samples E (10 psig) and G (0 psig) dropped dramatically, but low levels of tetrachloroethene were still seen. The ratio between the 10 psig and 0 psig readings remained similar (the 0 psig reading being approximately half of the 10 psig reading). Table 7 presents the numerical results of this experiment.

Table 7. Tetrachloroethene Vacuum Gauge (Mock Trip Blank) Carryover Results

Sample A Concentration (µg/m^3)	Sample D Concentration (not flushed, 10 psig) (µg/m^3)	Sample E Concentration (flushed, 10 psig) (µg/m^3)	Sample F Concentration (not flushed, 0 psig) (µg/m^3)	Sample G Concentration (flushed, 0 psig) (µg/m^3)
250,000(E)	19	0.36	8.0	0.24

E=Estimated over calibration range

Petroleum Constituents

Petroleum product carryover was seen in Sample D (mock trip blank, not flushed, 10 psig). The carryover concentration seen in Sample F (mock trip blank, not flushed, 0 psig) was reduced by approximately 50%. When the gauge was flushed out in between readings, the carryover concentrations seen in Samples E (10 psig) and G (0 psig) dropped to below the reporting limit. Tables 8A and 8B present the numerical results of this experiment.

Table 8A. Petroleum Constituent Vacuum Gauge (Mock Trip Blank) Carryover Results (Not Flushed)

Compound	Sample A Concentration ($\mu g/m^3$)	Sample D Concentration (not flushed, 10 psig) ($\mu g/m^3$)	Sample F Concentration (not flushed, 0 psig) ($\mu g/m^3$)
n-Hexane	140,000	3.4	1.7
Benzene	36,000	1.0	0.52
Isooctane	300,000 (E)	11	5.2
Toluene	190,000	10	4.6
1,2,4-TMB	8,400	2.4	1.1
n-Decane	2,400	0.78	0.32
n-Undecane	610	0.38	0.22
Naphthalene	ND (1000)	ND	ND

ND= Not detected (above reporting limit), E=Estimated over calibration range

Table 8B. Petroleum Constituent Vacuum Gauge (Mock Trip Blank) Carryover Results (Flushed)

Compound	Sample A Concentration ($\mu g/m^3$)	Sample E Concentration (flushed, 10 psig) ($\mu g/m^3$)	Sample G Concentration (flushed, 0 psig) ($\mu g/m^3$)
n-Hexane	140,000	ND (0.50)	ND (0.50)
Benzene	36,000	ND (0.10)	ND (0.10)
Isooctane	300,000 (E)	ND (0.50)	ND (0.50)
Toluene	190,000	ND (0.50)	ND (0.50)
1,2,4-TMB	8,400	ND (0.50)	ND (0.50)
n-Decane	2,400	ND (0.50)	ND (0.50)
n-Undecane	610	ND (0.50)	ND (0.50)
Naphthalene	ND (1000)	ND (0.50)	ND (0.50)

ND= Not detected (above reporting limit), E=Estimated over calibration range

CONCLUSIONS

The data demonstrate that laboratory best practices should include some type of decontamination for all canister sampling equipment, especially after exposure (or potential exposure) to elevated concentrations. The elevated concentrations of Sample A shown in this study (mg/m^3 range) are not atypical for samples collected from a SVE system or soil vapor samples collected near a subsurface contamination source. Thus, the potential exists for carryover and cross contamination of samples, unless care is taken by the laboratory to properly decontaminate and segregate equipment based on concentration level/application.

Even with very small percent carryover (as seen in Sample C), the nominal concentrations that may result from any type of equipment carryover can exceed human health risk based target levels for vapor intrusion investigations, resulting in false positives and potentially resulting in unnecessary cleanup work. The data demonstrate that this widely used style of flow controller (orifice/diaphragm assembly) has the potential for carryover, even after cleaning, when exposed to elevated concentrations. In fact, for very boiling point contaminants (e.g. naphthalene), carryover may occur even at lower concentrations; this effect can be observed in the data presented in Table 6 (i.e. even with a moderate concentration less than 1000 µg/m^3 in Sample A, we observed naphthalene carryover in Samples B & C). To ensure optimum performance, this equipment should be used for low level (ambient/indoor) applications only. A simpler and less expensive critical orifice device (with less internal surface area and a less convoluted flow path) may be used for higher concentration applications.

Flushing out of the vacuum gauge in between sample pressure readings appears to be an effective practice to prevent carryover from highly contaminated samples to less contaminated samples. However, the data show that even after flushing, a low concentration carryover of tetrachloroethene was present (Samples E & G). This may present a problem for vapor intrusion investigations for human health risk assessments where ultra low level reporting limits are required. Therefore, to minimize the chances of this phenomenon occurring, the laboratory may segregate pressure gauges for low level vs. higher level work. On a related note, the data show that the issue of carryover from pressure gauges is exaggerated with positive pressure samples; under these circumstances, care should be taken by the laboratory to thoroughly decontaminate the system to prevent potential carryover.

It should be noted that additional sources/sinks of volatile organic compounds (VOCs) may exist in typical vapor intrusion sampling/analytical systems. There have been several recent technical presentations at national vapor intrusion conferences that have mentioned the influence of tubing type on VOC samples, including a comprehensive study performed by Hayes et. al.[10] In addition, particulate matter or condensed VOCs entering a canister may act as a source or a sink for VOCs. On the canisters themselves, some older styles of canisters may have pipe thread (NPT) fittings connecting the valve stem to the canister body. These NPT fittings are wrapped with Teflon tape; over time and exposure to elevated concentration samples, this Teflon tape can also act as a source or a sink of VOCs.

To conclude, for low level vapor intrusion work, it is critical for the data user to consider each of these analytical issues and insist that proper decontamination and/or segregation of equipment occurs in the laboratory.

FUTURE WORK

Additional types of sampling equipment may be evaluated, including different brands, designs/configurations, and coating types of flow controller/critical orifice devices. Additional compounds may also be evaluated (other chlorinated VOCs, a better assessment of diesel/heavier hydrocarbons, etc).

ACKNOWLEDGEMENTS

We would like to acknowledge Christopher Parnell, Wida Ang, and the entire TO-15 GC/MS staff at Columbia Analytical Services for providing the analytical support necessary for this paper. Special thanks to Christopher Parnell for his dedicated support on this project and to Maryam Azad for her peer review of this paper.

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The Importance of Air Sampling Media Cleanliness for Vapor Intrusion Investigations

Alyson Fortune
Columbia Analytical Services
Air Quality Laboratory

Presented at NEMC | August 11, 2008 | Washington D.C.

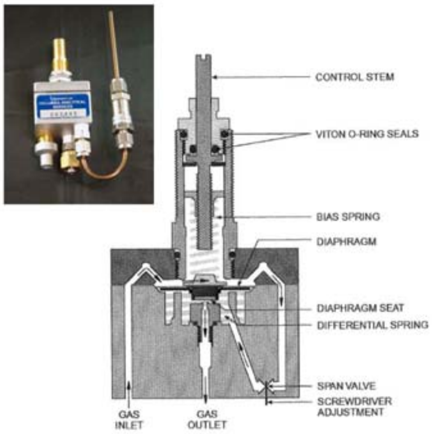
Overview

- ☐ Background
- ☐ Experimental Design
- ☐ Flow Controllers
  - Uncleaned
  - Cleaned
- ☐ Vacuum Gauge
  - Not Flushed
  - Flushed
- ☐ Summary & Recommended Practices

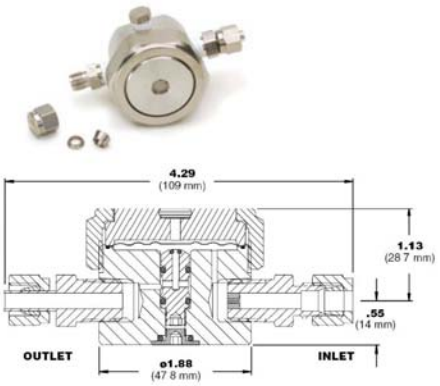
Background

- ☐ Canister cleaning widely accepted and practiced
- ☐ Cleaning/certification of other related equipment equally important but less widely practiced
- ☐ Most commercial labs analyze a variety of samples: pptV levels - % levels: Potential for cross contamination & carryover exists

Background: Flow Controllers



Vici Condyne Model 202



Veriflo SC423XL Series

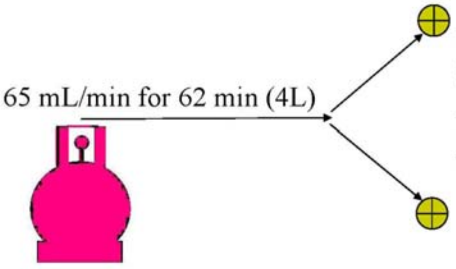
Background: Vacuum Gauge

- Canister samples have pressure checked upon receipt at laboratory with vacuum gauge
- Potential for cross contamination between high concentration & lower concentration samples

Experimental Design

- Test Sample "A" created with elevated concentrations of both tetrachloroethene & petroleum hydrocarbons (6L canister)
- Test Sample "A" pressurized and used for two main sections of this experiment:
  - Flow controllers
    - Evaluate potential carryover from cleaning/not cleaning
  - Vacuum gauge
    - Evaluate potential carryover when checking canister pressures

Flow Controllers



65 mL/min for 62 min (4L)

Test Sample
“A”

Pressurized

Flow Controller #1

Uncleaned after exposure to Test Sample “A”

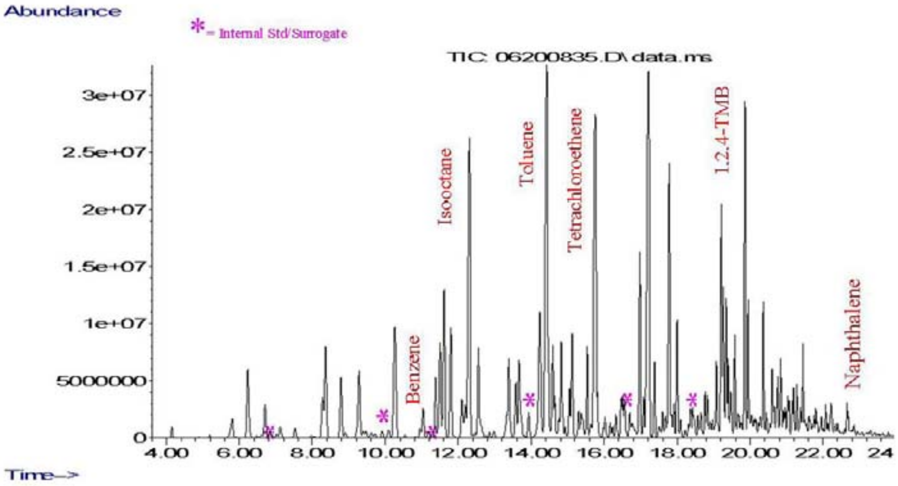
Used to fill clean 6L can over 1 hr with humidified ultra zero air

Flow Controller #2

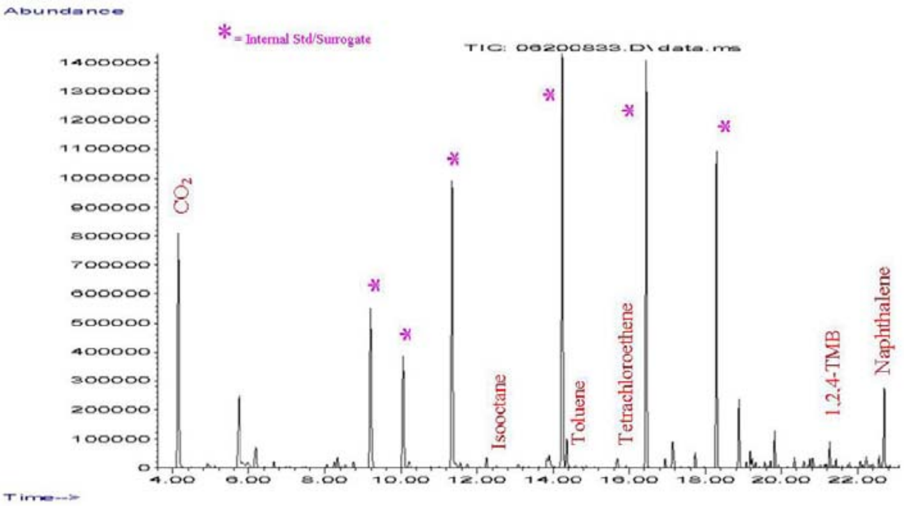
Cleaned after exposure to Test Sample “A”: 60ºC, purge air, 2.5 hrs

Used to fill clean 6L can over 1 hr with humidified ultra zero air

Uncleaned Flow Controller



Cleaned Flow Controller



Flow Controllers Summary

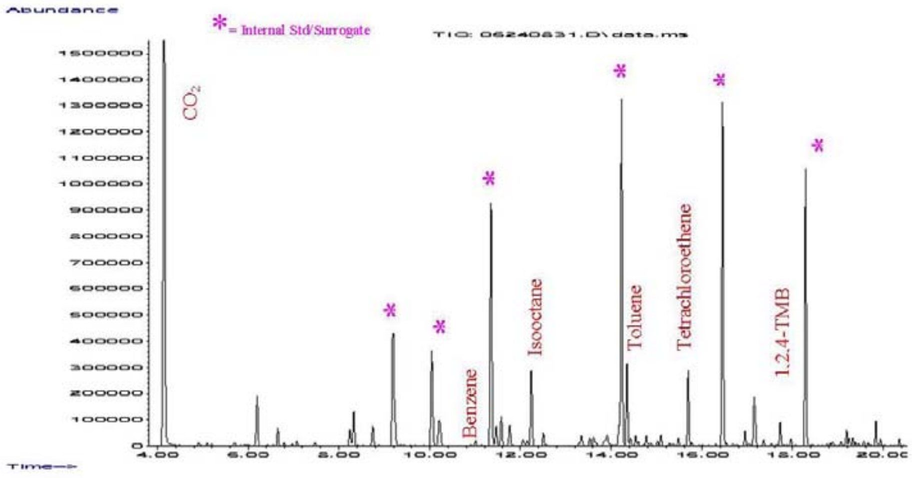
Compound	Sample A	Uncleaned	Cleaned
n-Hexane	140,000	250	ND (0.75)
Benzene	36,000	100	0.23
Isooctane	300,000	810	0.84
Toluene	190,000	950	2.4
1,2,4-TMB	8,400	520	2.2
n-Decane	2,400	180	ND (0.75)
n-Undecane	610	99	ND (0.75)
Naphthalene	ND (1000)	12	4.7
PCE	250,000	2000	2.2

Units= $\mu g/m^3$, ND= Not detected (above reporting limit)

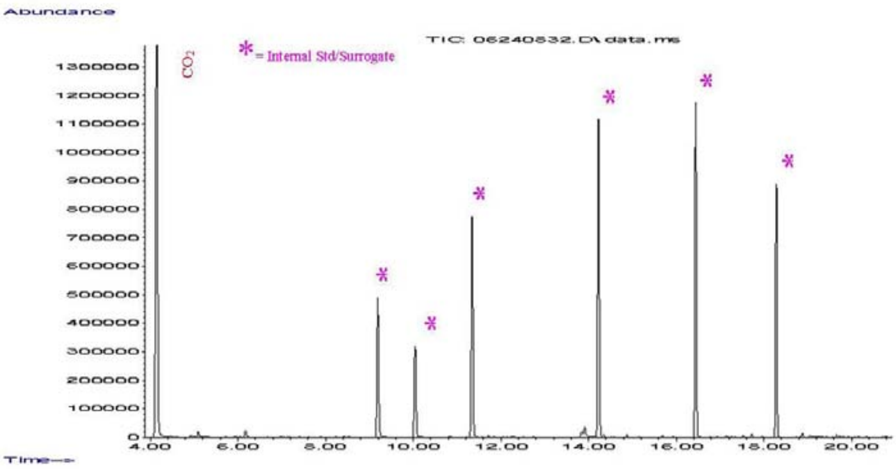
Vacuum Gauge

- Sample "A" pressure adjusted to 0 psig
  - Pressure of Sample "A" canister checked with vacuum gauge. Gauge then immediately used to check mock "trip blank" canister sample (fully evacuated canister)
  - Pressure of Sample "A" canister checked with vacuum gauge. Gauge evacuated three times, flushing apparatus. Gauge then used to check mock "trip blank" canister sample

Vacuum Gauge (Not Flushed)



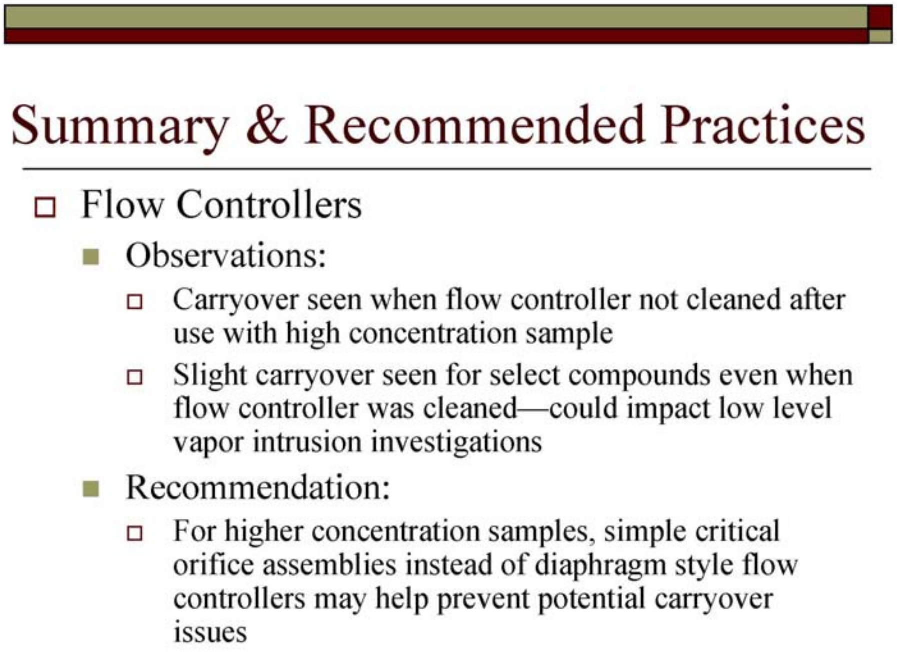
Vacuum Gauge (Flushed)



Vacuum Gauge Summary

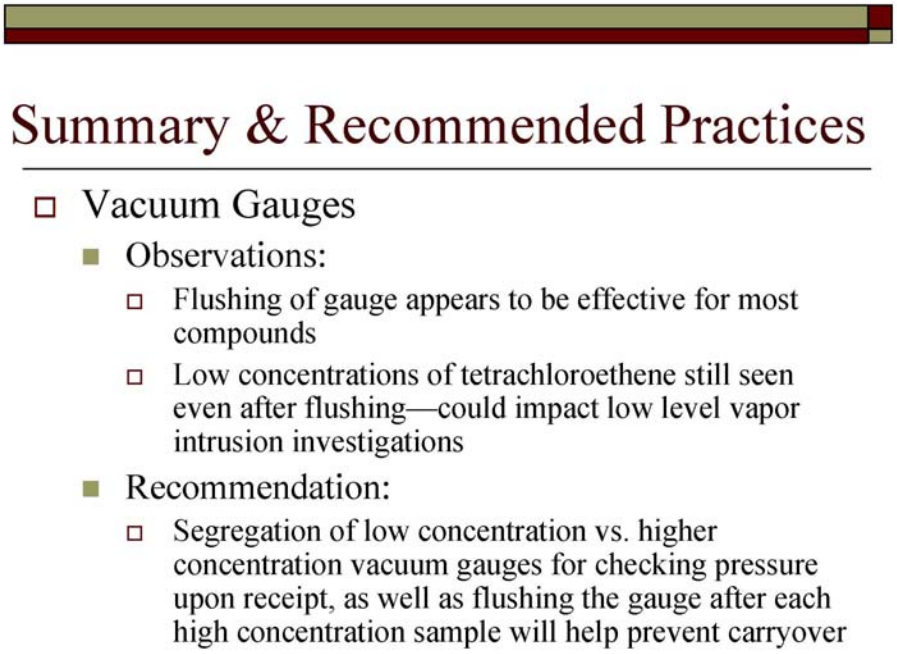
Compound	Sample A	Not Flushed	Flushed
n-Hexane	140,000	1.7	ND (0.50)
Benzene	36,000	0.52	ND (0.10)
Isooctane	300,000	5.2	ND (0.50)
Toluene	190,000	4.6	ND (0.50)
1,2,4-TMB	8,400	1.1	ND (0.50)
n-Decane	2,400	0.32	ND (0.50)
n-Undecane	610	0.22	ND (0.50)
Naphthalene	ND (1000)	ND (0.50)	ND (0.50)
PCE	250,000	8.0	0.24

Units= $\mu g/m^3$, ND= Not detected (above reporting limit)



Summary & Recommended Practices

- Flow Controllers
  - Observations:
    - Carryover seen when flow controller not cleaned after use with high concentration sample
    - Slight carryover seen for select compounds even when flow controller was cleaned—could impact low level vapor intrusion investigations
  - Recommendation:
    - For higher concentration samples, simple critical orifice assemblies instead of diaphragm style flow controllers may help prevent potential carryover issues



Summary & Recommended Practices

- Vacuum Gauges
  - Observations:
    - Flushing of gauge appears to be effective for most compounds
    - Low concentrations of tetrachloroethene still seen even after flushing—could impact low level vapor intrusion investigations
  - Recommendation:
    - Segregation of low concentration vs. higher concentration vacuum gauges for checking pressure upon receipt, as well as flushing the gauge after each high concentration sample will help prevent carryover

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- ☐ Experimental Design, Implementation & Sample Analysis: *Chris Parnell & Columbia Analytical Air Quality lab staff*
- ☐ *Document Review: Maryam Azad*

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Impact of Recent Vapor Intrusion Guidance Documents on Laboratory Methodology and Data Usability

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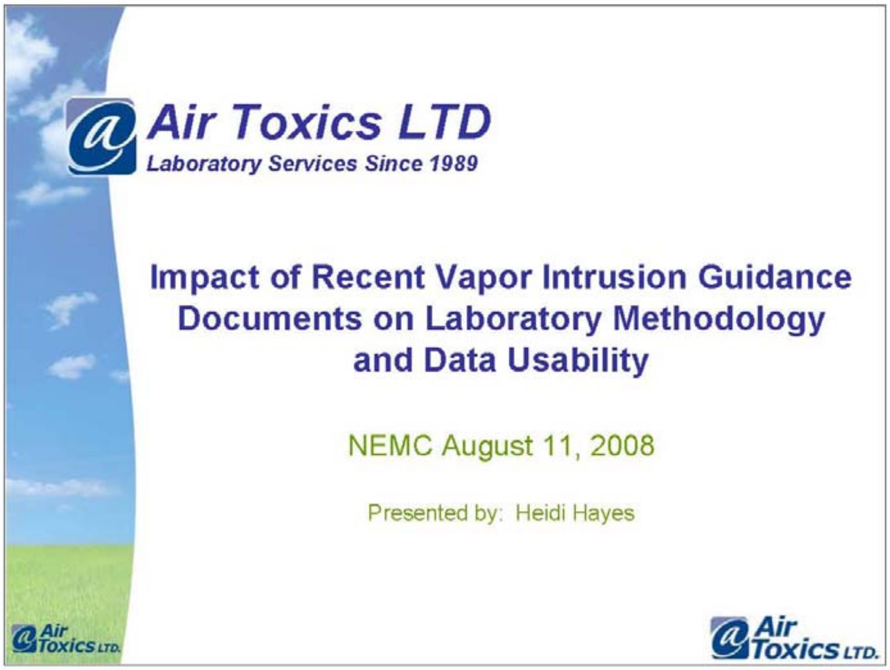
ABSTRACT

The landscape for environmental air analysis in the latter part of the 1990's was guided by the performance based research efforts that lead to the EPA's Compendium of Air Methods (1999). The EPA's OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance) dated 2002 changed the landscape almost overnight with major indoor air and soil gas sampling programs springing up near documented industrial waste sites with subsurface contamination. This paper will review the impact of various State and Federal vapor intrusion guidance documents on sample collection and analytical introduction approaches along with a summary of recent drivers such as lower reporting limits and expanded target compounds (naphthalene and related semi-volatiles). In many cases, the needs of the data user exceeded the scope of the analytical methodologies referenced. Data will be presented from current laboratory validation studies relating to the use of sample collection containers and sampling media for a variety of VOCs, commonly and uncommonly monitored as human health risk drivers. In some cases, guidance documents have had direct bearing on the misapplication of seemingly validated methodologies such as EPA TO15 and SW-846 8260B with minimal consideration for data impact or usability.



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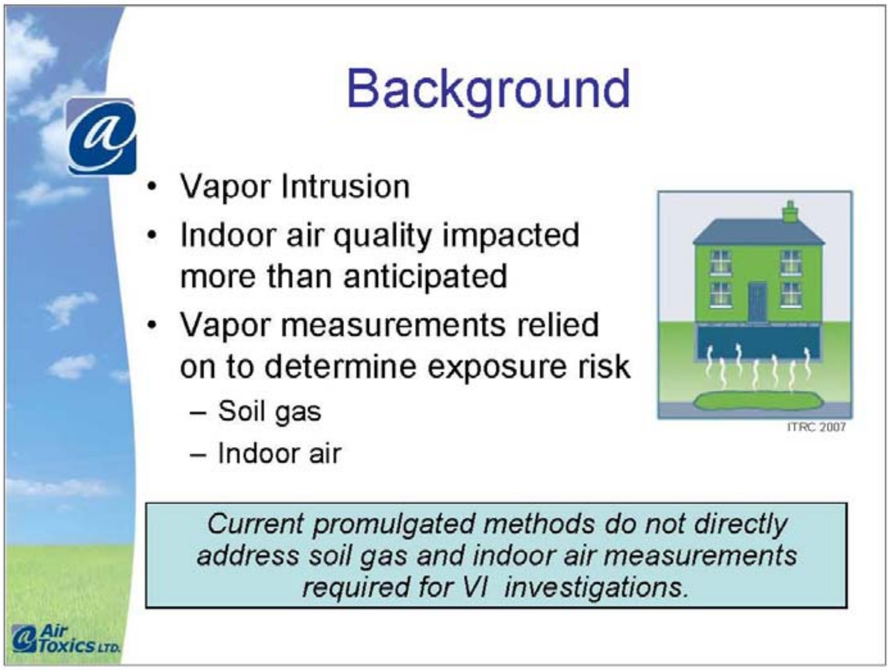
Impact of Recent Vapor Intrusion Guidance Documents on Laboratory Methodology and Data Usability

NEMC August 11, 2008

Presented by: Heidi Hayes



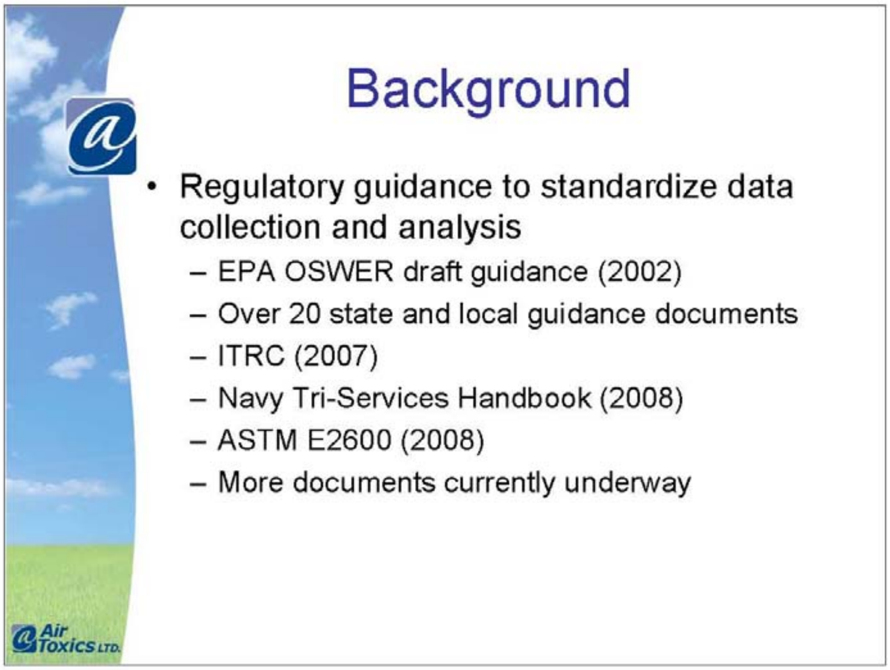
Background

- Vapor Intrusion
- Indoor air quality impacted more than anticipated
- Vapor measurements relied on to determine exposure risk
  - Soil gas
  - Indoor air

ITRC 2007

Current promulgated methods do not directly address soil gas and indoor air measurements required for VI investigations.

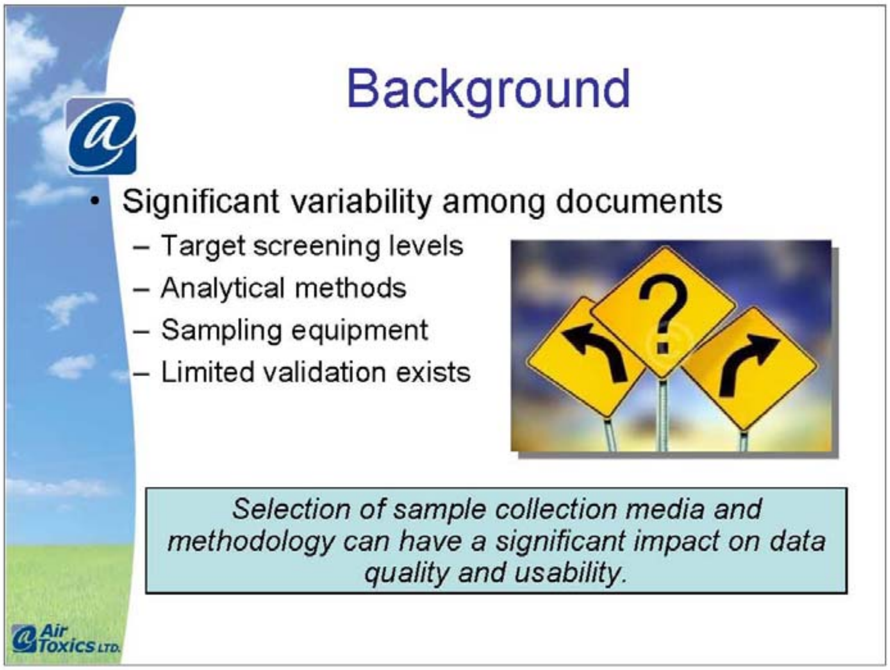
Vapor intrusion is the migration of VOCs from contaminated ground water or soil into nearby buildings or homes. VI has been a growing concern over the past decade due to well-publicized sites in which indoor air quality was impacted more than anticipated. (Redfield, CO and Endicott, NY). To determine whether vapor intrusion poses a risk to residents or workers, soil gas (exterior and sub-slab) and indoor air are typically collected for VOC measurements. Current promulgated methods do not directly address soil gas and indoor air measurements required for VI investigations. Historically, the development of methods have been largely funded by the EPA including the original compendium methods which were written in the late 80s and updated again in the 90s. The loss of federal research funding and the large scale health risk Vapor Intrusion sampling programs have forced some states and organizations to establish their own guidance documents on their own and without the benefit of consensus scientific practice.



Background

- Regulatory guidance to standardize data collection and analysis
  - EPA OSWER draft guidance (2002)
  - Over 20 state and local guidance documents
  - ITRC (2007)
  - Navy Tri-Services Handbook (2008)
  - ASTM E2600 (2008)
  - More documents currently underway

The goal of each document is the same: to produce quality measurements to support VI investigations and support decisions regarding human health risks. EPA was one of the first to set the stage with the draft guidance published in 2002. Since then over 20 state and local agencies have written documents, as well as ITRC, Navy, ASTM and more are currently underway.

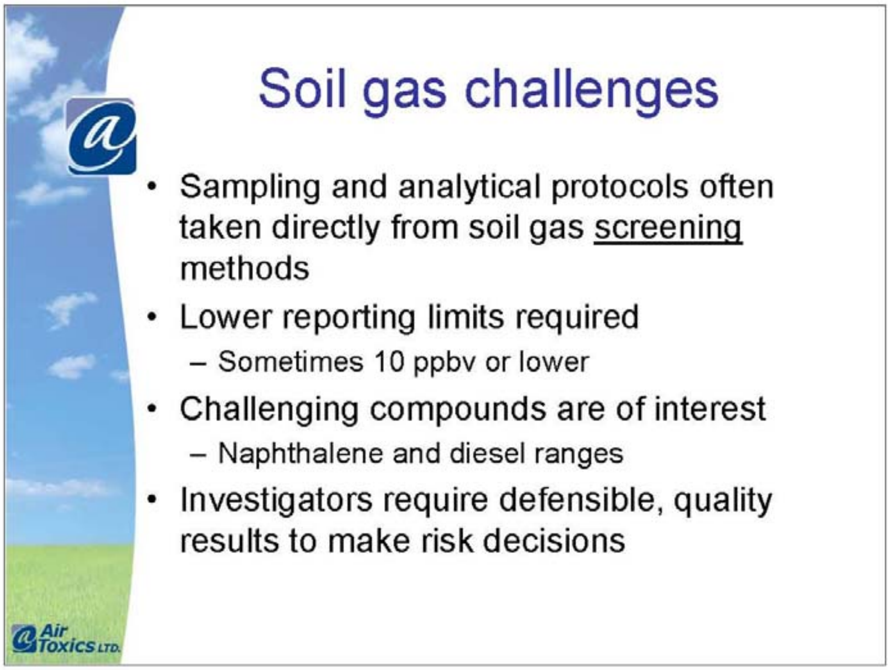


Background

- Significant variability among documents
  - Target screening levels
  - Analytical methods
  - Sampling equipment
  - Limited validation exists

Selection of sample collection media and methodology can have a significant impact on data quality and usability.

Although each of these documents have the same goal, there is significant variability among the documents in the overall approach to VI and screening levels can vary by several orders of magnitude. The focus on my presentation is on the variability in the sampling and analytical protocols. These protocols are described in many of the documents with limited validation supporting the procedures. However, the selection of sample collection media and methodology can have a significant impact on data quality and usability. Today I will be presenting several examples of how protocols described in existing VI guidance documents do not stand up against the rigor of validation.



Soil gas challenges

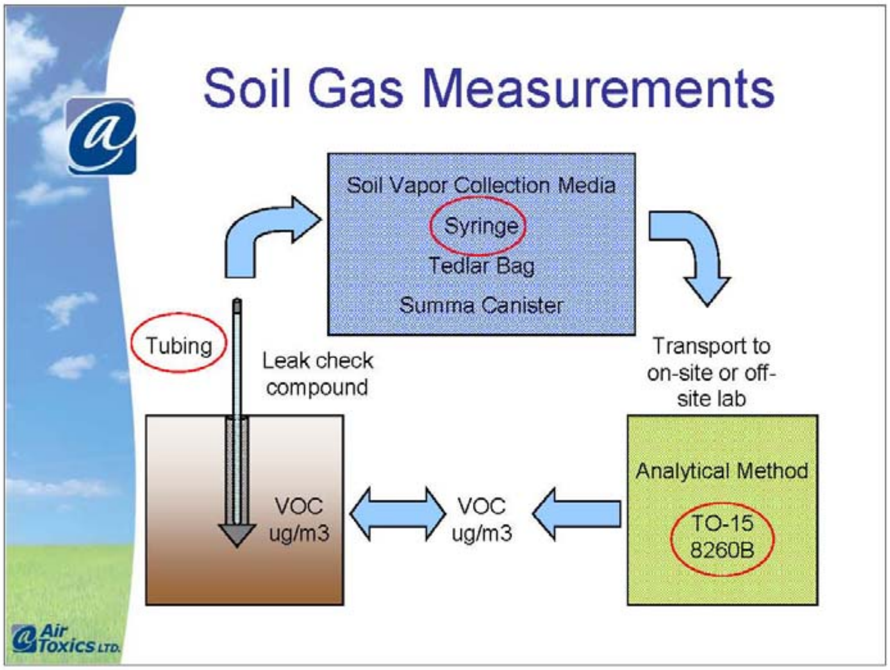
- Sampling and analytical protocols often taken directly from soil gas screening methods
- Lower reporting limits required
  - Sometimes 10 ppbv or lower
- Challenging compounds are of interest
  - Naphthalene and diesel ranges
- Investigators require defensible, quality results to make risk decisions

Let's start with soil gas measurements which have become one of the primary tools for VI investigations. Historically, soil gas was primarily used as a screening tool to map GW plume and delineate sub-surface contamination. Reporting limits were on the order of ppmv and several key VOCs were monitored (BTEX, chlorinated VOCs). Many of the guidance documents rely on the protocols developed for screening for VI investigations. However, VI investigations require much lower RLs, may require quantitation of challenging compounds with low vapor pressures. In addition, a higher level of quality is required as the soil gas measurements may be used to make risk decisions.

Methods used to map GW plumes and delineate sub-surface contamination

RLs 10 ug/L (ppmv levels)

Focused on a limited list BTEX/Chlorinated VOCs



Soil Gas Measurements

Soil Vapor Collection Media

Syringe

Tedlar Bag

Summa Canister

Tubing

Leak check compound

Transport to on-site or off-site lab

Analytical Method

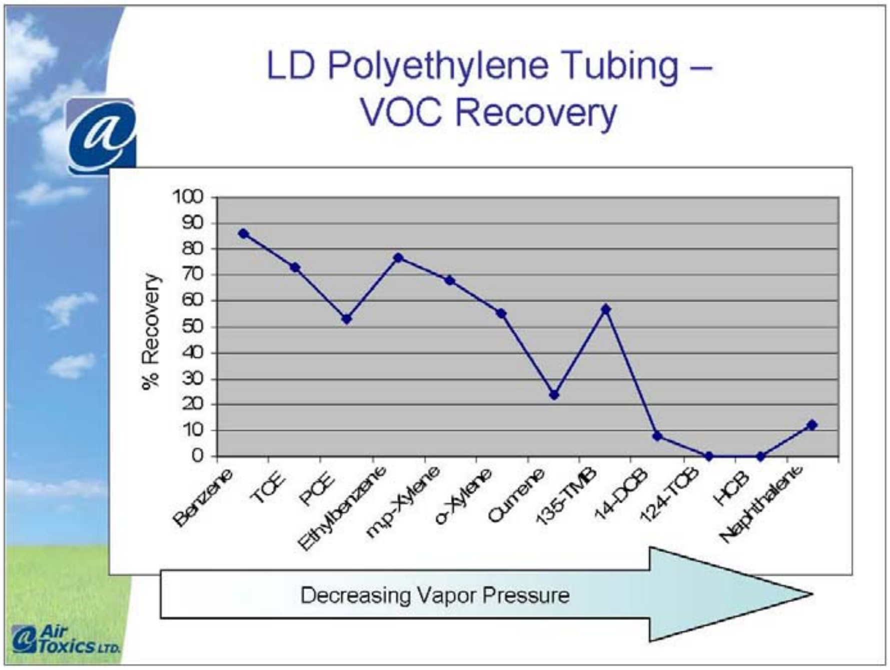
TO-15

8260B

VOC ug/m3

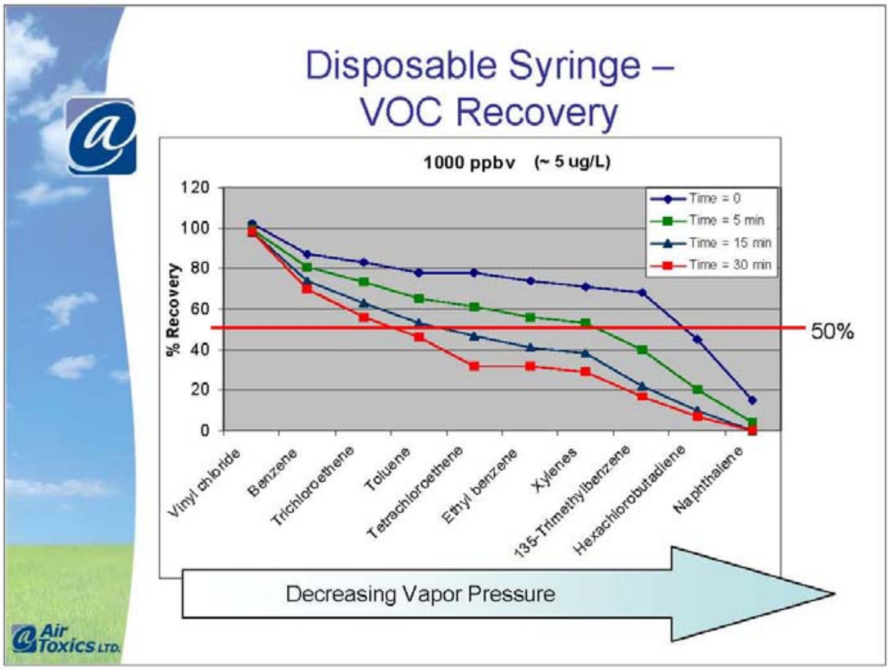
VOC ug/m3

Through tests in the laboratory, we have identified several commonly used techniques described in existing guidance documents which result in significant recovery issues. I will briefly review the results of 3 examples – tubing type used to extract the soil vapor from the subsurface, the collection media used to store and transport the soil gas sample, and the analytical method selected to analyze the soil vapor.



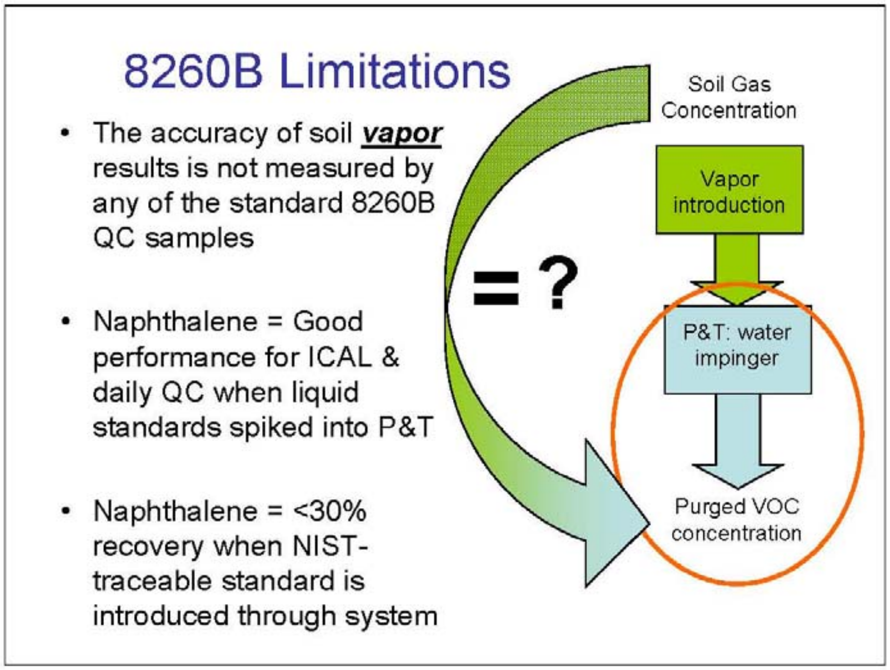
LD Polyethylene Tubing – VOC Recovery

One of the validation tests we performed was the evaluation of tubing, a significant part of the soil gas sampling train. We evaluated various types of tubing looking at both background VOCs as well as recovery. We found that one of the commonly used tubing types LD polyethylene tubing yielded poor recoveries for many of the VOCs. You can see that the recovery for each VOC through the tubing drops as a function of decreasing vapor pressure. The LD polyethylene tubing is commonly described in guidance documents and is the standard tubing provided by some of the direct push manufacturers.



Disposable Syringe – VOC Recovery

Moving from tubing to sample collection media, we evaluated the use of disposable syringes for soil gas measurements. Disposable syringes are described for example in the California DTSC soil gas advisory with a required maximum storage time of 30 minutes. When we evaluated these syringes for the storage of a multi-component VOC standard, we observed significant losses in recovery as a function of decreasing vapor pressure and as a function of increasing storage time.



8260B Limitations

- The accuracy of soil ***vapor*** results is not measured by any of the standard 8260B QC samples
- Naphthalene = Good performance for ICAL & daily QC when liquid standards spiked into P&T
- Naphthalene = <30% recovery when NIST-traceable standard is introduced through system

Soil Gas Concentration

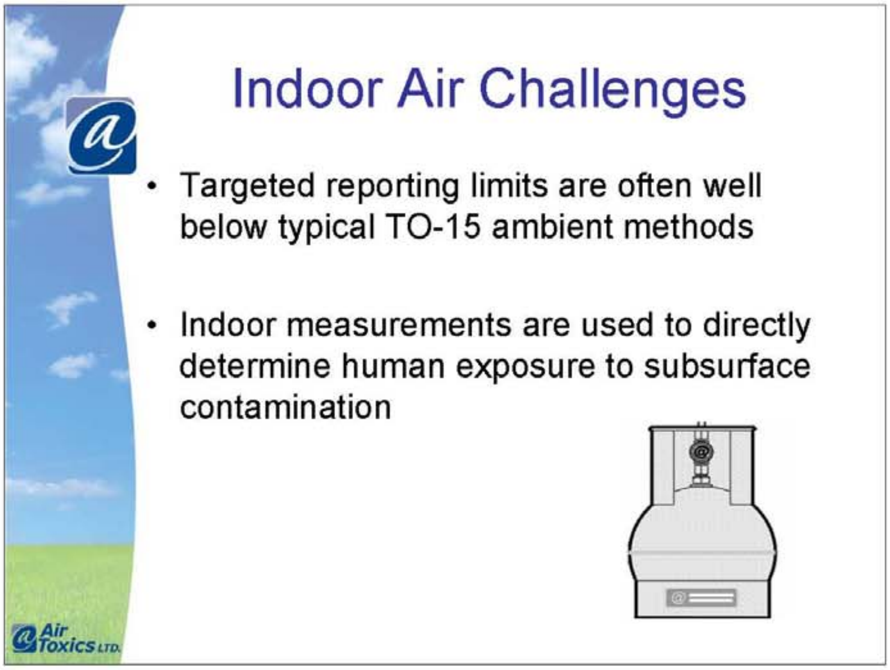
Vapor introduction

P&T: water impinger

Purged VOC concentration

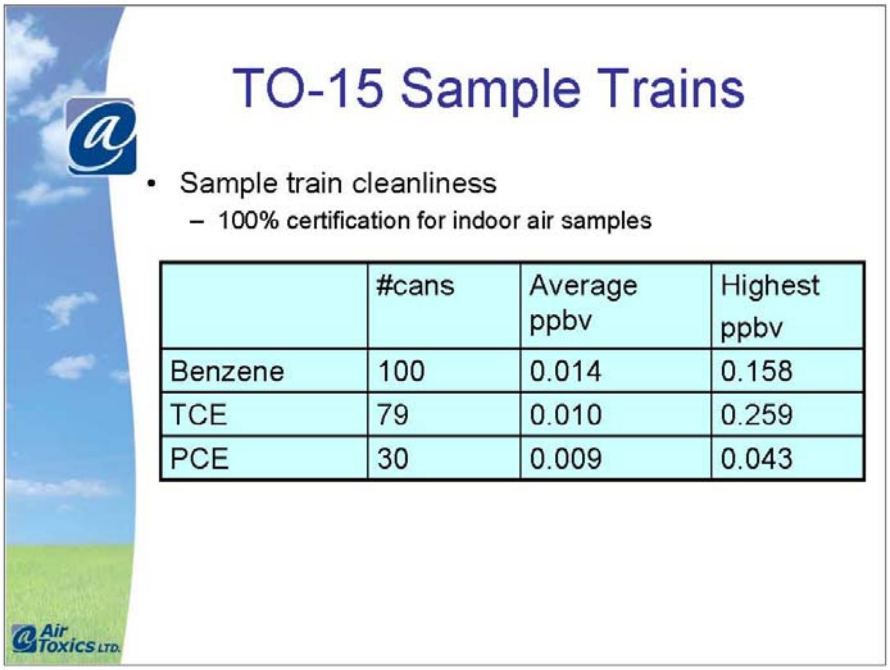
= ?

Moving on to the analytical method utilized for soil gas, several guidance documents allow for the use of SW-846 8260B for the analysis of soil gas. SW-846 was written for soil and water and as such, there are no written protocols in 8260 describing how to introduce vapor samples into P&T, leaving it up to each lab to set up their own approach. The QC reported by 8260B only provides accuracy and precision of part of the analytical system. The vapor introduction step is not evaluated. As an example, on our 8260B unit modified for soil gas analysis, naphthalene performs very well when injecting the methanolic standard in the P&T. We get a beautiful ICAL, second source recovery and daily CCV recovery. However, when we inject a NIST-traceable naphthalene standard through our vapor introduction step and through the P&T system, recovery of naphthalene is very poor, typically less than 30%. Since the required protocols do not require validation of the vapor introduction step, the accuracy of the lab may be suspect.



Indoor Air Challenges

- Targeted reporting limits are often well below typical TO-15 ambient methods
- Indoor measurements are used to directly determine human exposure to subsurface contamination

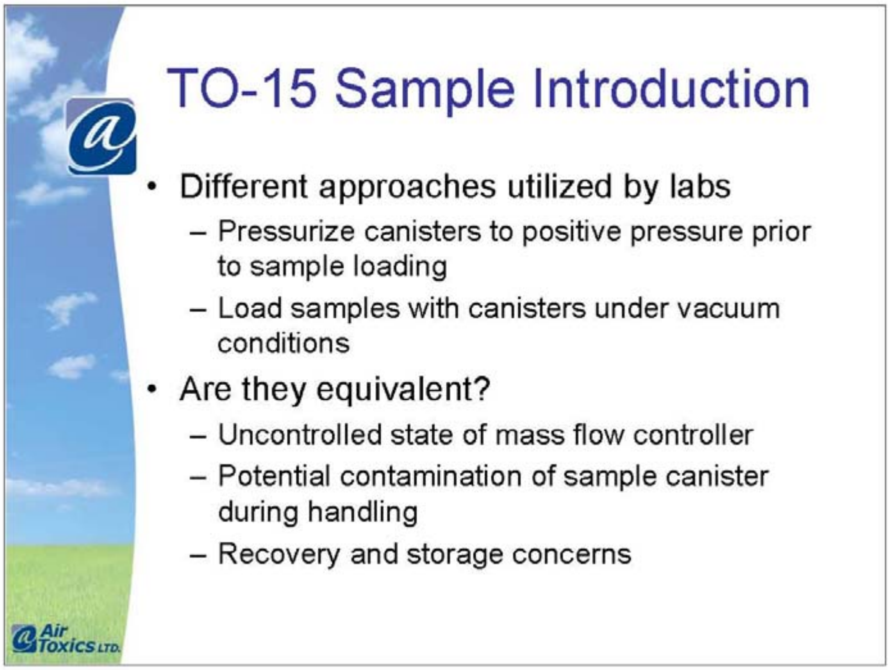


TO-15 Sample Trains

- Sample train cleanliness
  - 100% certification for indoor air samples

	#cans	Average ppbv	Highest ppbv
Benzene	100	0.014	0.158
TCE	79	0.010	0.259
PCE	30	0.009	0.043

Many of the guidance document do not directly address media cleanliness and if they do, they often allow for batch certification. With indoor air screening levels below 0.2 ppbv, batch certification is not sufficient to insure quality data. Evaluating a set of 100 canisters certified after standard TO-15 cleaning protocols, you can see that benzene was present in each canister at 0.014 pbv with the highest concentration of 0.158 ppbv; TCE which can have a screening level as low as 0.003 ppbv shows a detection in 79% of the canisters with an average concentration of 0.010 ppbv. Clearly batch certification protocols fall short.

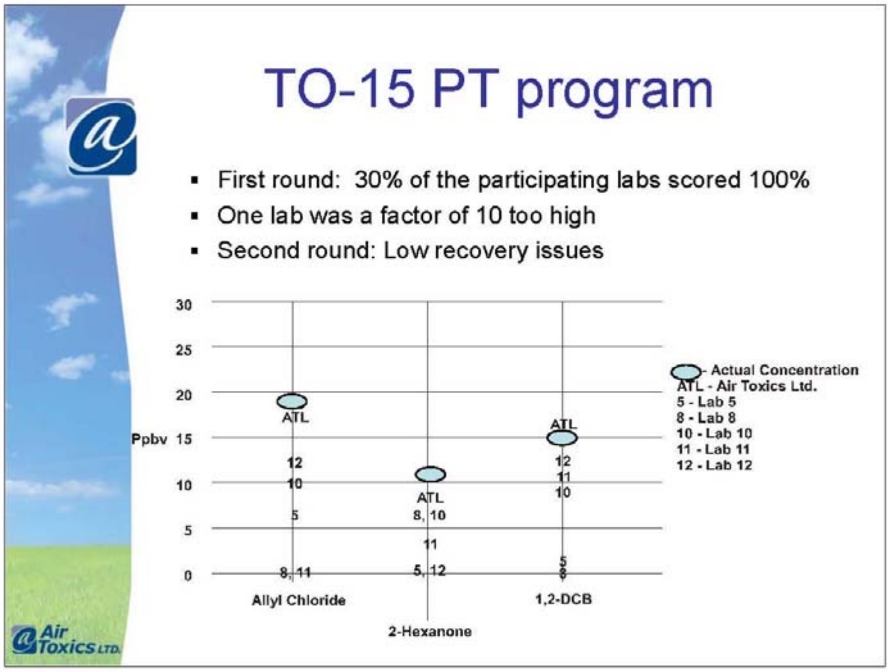


TO-15 Sample Introduction

- Different approaches utilized by labs
  - – Pressurize canisters to positive pressure prior to sample loading
  - – Load samples with canisters under vacuum conditions
- Are they equivalent?
  - – Uncontrolled state of mass flow controller
  - – Potential contamination of sample canister during handling
  - – Recovery and storage concerns

There is also some debate regarding sample introduction protocols for indoor air samples. The TO-15 method does not provide much detail regarding the protocols for loading. The latest NJDEP document restricts the practice of pressurizing canisters. Air laboratories are not consistent as to their approach.

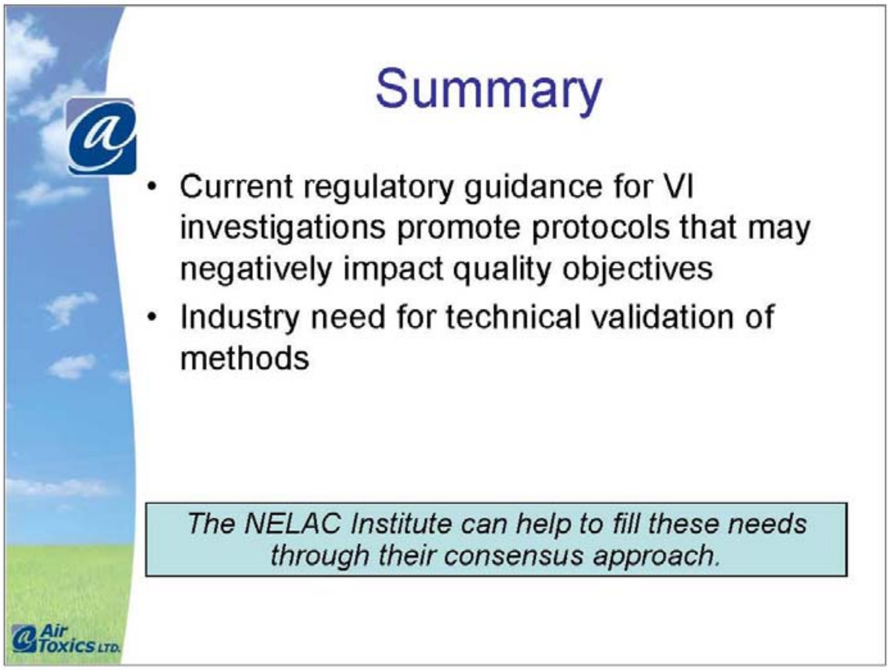
Are they equivalent? Does one approach provide more defensible results? There is very little validation in the literature regarding this practice. The audit sample programs and storage studies in the literature are at ambient or pressurized conditions. There are a few concerns that should be addressed before the practice of loading canisters with sub-ambient pressure becomes a requirement for indoor air samples. 1) Is an accurate volume of sample being measured during the loading step onto the concentrator? Mass flow controllers are typically designed to operate with a specific pressure differential across the device. If the canister vacuum is too high, we have seen our mass flow controllers unable to reach its set point for the flow rate. With time, the flow rate drops and the specific sample volume loaded may not be accurate. 2) Is there a greater chance for contamination when handling a sample canister is under vacuum? Either introduction of laboratory air due to improper connection of the canister to the equipment or cross-contamination from a previous sample loaded on the equipment.



TO-15 PT program

- First round: 30% of the participating labs scored 100%
- One lab was a factor of 10 too high
- Second round: Low recovery issues

And finally, few programs require audit samples for laboratories that are performing indoor air analysis for VI investigations and no mandatory air PT program exists through NELAP. On a voluntary basis, we have participated in several rounds of some preliminary programs, and the results of the several of the participating labs are extremely concerning. Results can vary from the actual concentration by an order of magnitude and some cases, compounds were not detected. This should be very concerning to data users who rely on TO-15 results to make decisions on whether vapor intrusion is exposing people to unacceptable levels of VOCs.



Summary

- Current regulatory guidance for VI investigations promote protocols that may negatively impact quality objectives
- Industry need for technical validation of methods

The NELAC Institute can help to fill these needs through their consensus approach.

Throughout this presentation I provided examples of protocols within guidance documents that fall short of the quality objective required for a VI assessment. These data are being used to make decisions on whether a school is safe, whether a family is safe, and whether a community is safe. The industry needs our assistance, experts in air testing who can validate protocols under the rigor of scientific scrutiny. The mission statement of TNI states that "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."

We suggest assisting with the current state VI guidance documents is consistent with TNI's mission and is in fact critical without the research programs of the EPA

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Questions?

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Comparison of Air Toxics Inter-Laboratory Experiments in Region 5

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ABSTRACT

The US EPA Region 5 Air and Radiation Division has been conducting a semi-annual inter-laboratory comparison experiment for various air pollutants consisting of carbonyl, metals and volatile organic compounds with the various state and EPA federal laboratories within the region. In 2004 Eastern Research Group has started to collect the samples using a multi-port sampling manifold to minimize any sampling differences between samples. The results provide a record of the spread of the analytical results and the improvements made in the analytical results from the laboratories. Compounds that have specific sampling and analytical difficulties will be identified.

EPA's National Dioxin Air Monitoring Network: Analytical Issues

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ABSTRACT

The USEPA has established a National Dioxin Air Monitoring Network (NDAMN) to determine the temporal and geographical variability of atmospheric chlorinated dibenzo-p-dioxins (CDDs), -furans (CDFs), and coplanar polychlorinated biphenyls (PCBs) at rural and non-impacted locations throughout the United States. NDAMN had 32 sampling stations and had three primary purposes: (1) to determine the atmospheric levels and occurrences of dioxin-like compounds in rural and agricultural areas where livestock, poultry and animal feed crops are grown; (2) to provide measurements of atmospheric levels of dioxin-like compounds in different geographic regions of the U.S.; and (3) to provide information regarding the long-range transport of dioxin-like-compounds in air over the U.S. Designed in 1997, NDAMN was implemented in phases, with the first phase consisting of 9 monitoring stations and achieved congener-specific detection limits of 0.1 fg/m3 for 2,3,7,8-TCDD and 10fg/m3 for OCDD. With respect to the coplanar PCBs, the detection limits are generally higher due to the presence of background levels in the air during the preparation and processing of the samples. Achieving these extremely low levels of detection presented a host of analytical issues. Among these issues are the methods used to establish ultra-trace detection limits, measures to ensure against and monitor for breakthrough of native analytes when sampling large volumes of air, and procedures for handling field blanks. Despite such procedural difficulties, these methods made it possible to measure dioxin-like compounds at extraordinarily low concentrations.

The National Dioxin Ambient Air Monitoring Network (NDAMN): Sampling Methods and Results of Measuring Dioxin-Like Compounds in Rural and Remote Areas of the United States

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Joseph Ferrario; Environmental Chemistry Lab, Office of Pesticide Programs, Stennis Space Center, MS 39529

ABSTRACT

Long-term measurements of the atmospheric concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (PCBs) were taken in rural, remote and urban areas of the United States by the National Dioxin Air Monitoring Network (NDAMN). The aim of NDAMN was to provide a general indication of background air concentrations of PCDDs, PCDFs, and cp-PCBs in rural and remote areas of the United States. A total of 29 quarterly sampling moments occurred from June, 1998 to December, 2004 at 34 locations geographically distributed throughout the United States. The rural sites were chosen in order to obtain air concentrations in areas where crops and livestock are grown, and that encompassed a range of geographic locations in terms of latitudinal and longitudinal positions. Remote sites were selected on the basis that they were relatively free of human habitation and >100 km away from human dioxin sources. The locations of sampling sites covered a wide range of climate conditions from tropical sub-humid to sub-Arctic climates. Ambient air sampling was conducted with a TE 1000-PUF (polyurethane foam) sampler in accordance with EPA Method TO-9A as modified in the Quality Assurance Project Plan. The sampler consisted of a sampling head, a meter equipped with a magnehelic gauge to measure air flow, and a blower type vacuum pump. The sampling head assembly consisted of a quartz-fiber filter (QFF) and a glass sample cartridge containing a PUF absorbent plug. A regulated air flow was drawn into the top of the sampling head assembly, and the particle-bound phase of the contaminants in the air stream was collected on the filter surface (porosity down to 0.1 μm), while the vapor phase was absorbed into the PUF. Each sampling moment consisted of 20-24 days of active sampling over a28-day period, on a weekly schedule of 5 or 6 days of continuous operation followed by 1 or 2 days of inactivity. In this manner approximately 6000 to 8000 m3 of air passed through the sampling head assembly. This allowed for the sensitivity of air measurement of individual congeners of dioxin-like compounds in the fg m-3 range of detection. This paper will present details of the NDAMN air sampling protocol, report results of the special and temporal measurement of dioxin-like compounds in ambient air over rural and remote areas of the U.S. for monitoring periods 1998 through 2004.

Polycyclic Aromatic Hydrocarbons Method Development and Data Analysis

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ABSTRACT

Semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), have received increased attention due to interest from the U.S. Environmental Protection Agency (EPA) and the National Air Toxic Trends Stations (NATTS) program. Many of these compounds are highly carcinogenic or mutagenic. Eastern Research Group, Inc. (ERG) has demonstrated exceptional performance of SVOC analysis using Compendium Method TO-13A1 with Gas Chromatography/Mass Spectroscopy (GC/MS) and selective ion monitoring (SIM). The sensitivity and selectivity of GC/MS SIM allows comparison of rural, suburban, and urban PAH content in ambient air. The following will be discussed: data using Method TO-13A collection and analysis of ambient air across the United States will be presented to show amounts of PAHs in the ambient air; data will be presented to show compound stability; data to determine the breakthrough volume for naphthalene; the collection efficiency of naphthalene using a high volume sampler.

Proficiency Testing (PT) for Low Metal Concentration Ambient Air Sample Analysis in Support of the National Air Toxics and Trends Stations (NATTS) Program

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ABSTRACT

Under the Clean Air Act (CAA), the U.S. Environmental Protection Agency regulates 188 hazardous air pollutants (HAPs) which are associated with a wide variety of adverse human health and ecological effects. These air toxics originate from various sources including point, area, and mobile sources that result in population exposure to a single or multiple HAPs. Current Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics by 75% from 1993 levels to significantly reduce human exposure. The National Air Toxics Trends Station (NATTS) network consisting of 27 stations within the contiguous 48 states has been established to provide data to assess the trends. To ensure collected data are of desired quality and to provide a broad understanding of the error inherent in the data, EPA's Quality System (QS) for NATTS provides performance evaluation or proficiency testing (PT) samples to participating laboratories on a quarterly or semi-annual basis. These PT samples consist of volatile organic compounds (VOCs) in a passivated stainless container, aldehyde compounds on a 2,4-dinitrophenylhydrazine-coated cartridge, polycyclic aromatic hydrocarbons (PAHs) in a PUF/XAD-2 sandwich housed in a glass cartridge with retaining screens, and selected HAP metals on a 47-mm quartz filter. The preferred method of analysis of metals in ambient air samples is based on inductively coupled plasma mass spectrometry (ICP-MS). Some laboratories also have used X-ray fluorescence (XRF) spectrometry. Although the concentrations of HAP metals in ambient air samples vary over a wide range, usually most of the concentrations are closer to the instrument detection limits. Hence it becomes critical that the laboratories develop proficiency in analyzing metal samples at low concentrations. The desired characteristics that have evolved in this program for the low-concentration metal PT samples are that concentrations of the metals on PT filters reflect concentrations normally encountered in ambient air samples; that a large number of uniform samples be available; that the matrix or filter material of the PT samples be the same as for the field samples; and that the method of preparation of PT samples be comparable to the method of sample collection. Instead of using the conventional method of preparing PT samples by injecting low-concentration HAPs solutions on filters and drying them under a heat lamp, this program has adopted aerosol deposition technology developed by KulTech Incorporated for making XRF calibration samples. Sample generation involves preparing aerosols from a solution of HAP metal salts, drying the aerosols in a simulated stack, and collecting the aerosol on 47-mm-diameter filters by drawing the aerosol flow through the filter after a steady-state concentration is reached. Multiple samples are made using a sample manifold, and uniformity of samples is ensured by analyzing a randomly selected, statistically significant number of samples. The analytical results of the participating laboratory

are compared to the mean results obtained from a referee laboratory for each element. Currently, the typical concentration for blind HAP metals in the PT program is between 0.5 µg and 5 µg per filter. Because the laboratories find it very challenging to meet the acceptance criteria for the metals analysis, the PT program is generating positive feedback. The laboratories get to compare their own performance with the group performance and implement improvements. The analysis of the reported results by the laboratories over the last 10 quarters indicates there has been marked improvement in performance as analysts become more experienced in analysis of these PT samples.

Sampling Study of Hexavalent Chromium in Ambient Air

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ABSTRACT

Hexavalent chromium (Cr6+) 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 Cr6+ monitoring. Attempts to sample and analyze Cr6+ at NATTS with improved sensitivity uncovered challenges in the sampling procedures. Studies performed by ERG show a significant loss of Cr6+ as samples are taken at ambient temperatures. A stability study was performed was performed to determine the best sampling conditions to maintain Cr6+ stability with less than 30 Relative Percent Difference (RPD). The stability of Cr6+ was evaluated using collocated samplers in conjunction with Texas Commission of Environmental Quality (TCEQ). Data, using improvements to the Cr6+ sampling and analysis procedure for the NATTS, will be presented to show Cr6+ recovery from these field samples.

Sampling Study & Data Results of Hexavalent Chromium in Ambient Air

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Overview of Presentation

- Why are we concerned?
- What method do we use?
- What are the restrictions to current method?
- How can we improve?
- What data have we reported?
- Conclusions

Health Effects

- Penetrates biological membranes
- Highly toxic, even at low mass concentrations and emissions
- Inhalation irritant and associated with respiratory cancer
- EPA Screening level – 0.000083 µg/m^3 or 0.083 ng/m^3
- Intermediate Risk Factor (15 to 365 days) – 1 µg/m^3 or 1000 ng/m^3

Method Development Overview

To reduce the risk of Cr^{6+} loss prior to analysis:

- Collects on cellulose filters
- Acid wash
- Coat with sodium bicarbonate solution
- Collect day after sampling
- Freeze immediately after sample collection

Cr6+ Filter Stability Study

Spiked Samples	Cellulose Filters (spiked 2.5 total ng)			
	Average Concentration (total ng)	**Percent Recovery**	**Average Relative Percent Difference (RPD)**	**Coefficient of Variation (CV)**
Next day pickup (33 hrs)	1.76	70.2%	**29.8%**	8.4%
Pickup 2 days after (57 hrs)	1.27	**50.9%**	**49.1%**	12.7%
Pickup 3 days after (81 hrs)	1.19	**47.5%**	**52.5%**	9.3%
Pickup 4 days after (105 hrs)	1.05	**41.8%**	**58.2%**	11.2%

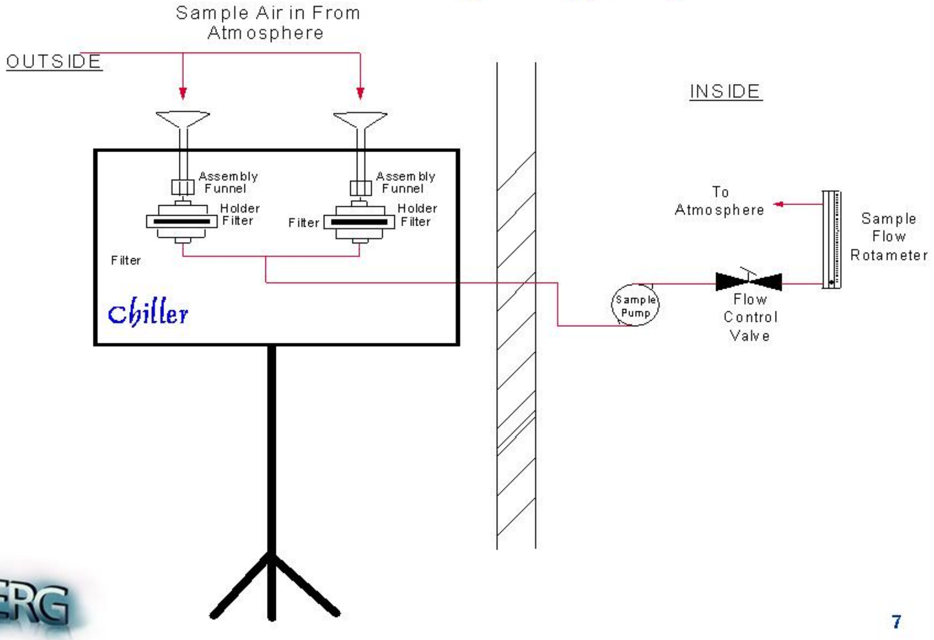
Temperatures ranged from 54 to 79°F

How can we improve the Method?

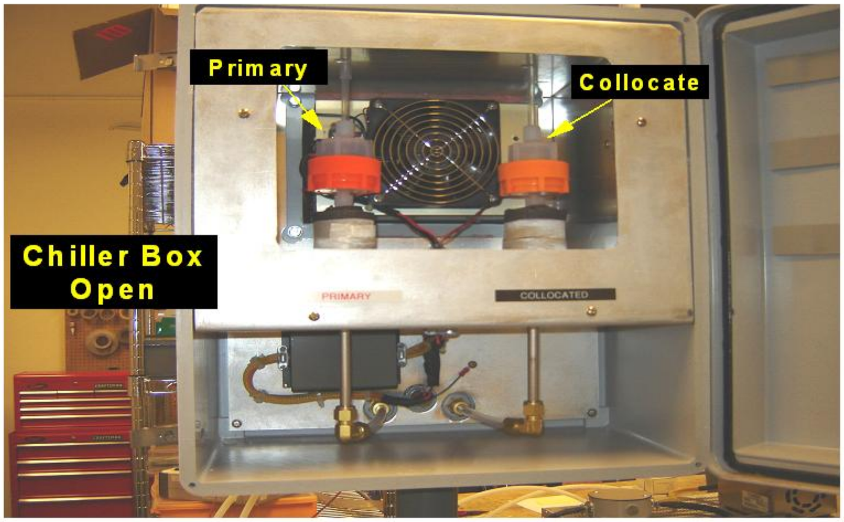
- Fabricated sampler with chiller
  - ☐ Collects samples at constant temperature (started study at 15°C)
  - ☐ Holds samples at constant temperatures until retrieved from the field (15°C)

Chiller is attached to current sampling unit.

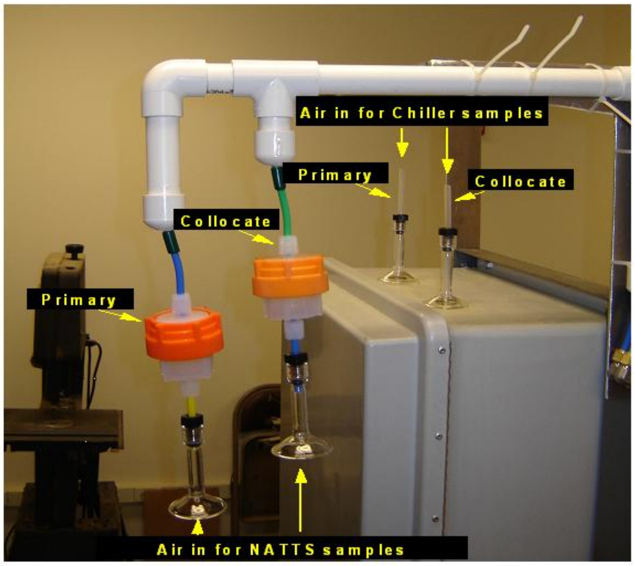
ERG Cr^{6+} Sampling System



ERG Cr^{6+} Chiller (open)



ERG Cr^{6+} Chiller & NATTS Sampling Study Design



Chiller Study

- Water collects on filters if sampled @ 0 and 10°C
- Water not collected @ 15°C (59°F)
- Conditions were considered acceptable during the study if:
  - ☐ Filters spiked and placed in cassettes, no flow (Control Spikes)
    - within 80-120% Recovery
  - ☐ Filters spiked and placed in filter holders, with flow (Matrix Spikes)
    - within 75-125% Recovery
- Filters spiked by liquid solution

Chiller Recovery – 0 hour hold

Test	Date Samples Setup	% Recovery Collocated Samples (Spikes w/Flow)	% Recovery Spikes w/o Flow *	Temp	
				High (°F)	Low (°F)
0hr – 1	10/31/2007	98.6%	99.2%	74	38
0hr – 2	11/7/2007	102.8%	97.3%	55	30
0hr – 3	11/14/2007	64.4%	111%	78	49
0hr - 4	11/28/2007	100.6%	118%	57	32
Average		**91.6%**	**107%**	66	37

* No flow through filters

Chiller Recovery – 24 hour hold

Test	Date Samples Setup	% Recovery Collocated Samples (Spikes w/Flow)	% Recovery Spikes w/o Flow *	Temp	
				High (°F)	Low (°F)
24hr – 1	10/22/2007	97.5%	100%	83	64
24hr – 2	10/29/2007	104.5%	101%	61	37
24hr – 3	11/12/2007	60.8%	116%	66	37
24hr – 4	11/26/2007	92.4%	112%	64	44
Average		**88.8%**	**107%**	69	46

* No flow through filters

Chiller Recovery – 72 hour hold

Test	Date Samples Setup	% Recovery Collocated Samples (Spikes w/Flow)	% Recovery Spikes w/o Flow *	Temp	
				High (°F)	Low (°F)
72hr – 1	10/25/2007	107.2%	100%	70	59
72hr – 2	11/1/2007	70.2%	102%	78	53
72hr – 3	11/15/2007	87.8%	126%	66	39
72hr – 4	11/19/2007	42.9%	104%	61	46
Average		**91.6%**	**107%**	69	49

* No flow through filters

Next Steps…

- Take sampler to the field
- Find the hottest, most humid sampling location
  - ☐ Overcome the humidity factor – 15°C does not work anymore!!
  - ☐ Study ERG NATTS vs. Converted PM10 vs. ERG Chiller Samplers.

TCEQ and ERG are conducting a study in Houston

Cr^{6+} Data Collection

- Over 3 years of sample data (January 1, 2005 to March 31, 2008)
- 21 sites across the country – 16 NATTS, 5 UATMP
- Samples collected every 6 days, 10% collocated, 1 field blank every month

NATTS – National Air Toxics Trends Station
UATMP – Urban Air Toxics Monitoring Program

Cr^{6+} Monitoring Site Locations

Current Method Description

- Collect 21.6 m^3 sample in 24 hours
- Detection limits below risk level (2008 DLs are 0.0065 ng/m^3)
- DISADVANTAGE: All samples must be recovered the day after sampling to reduce the loss of Cr^{6+}

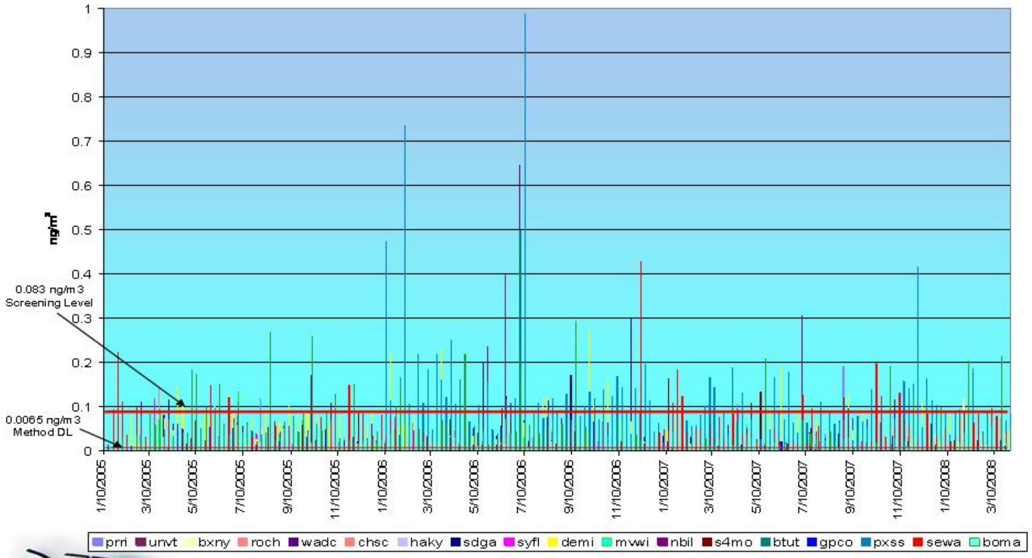
Daily Average Mass Concentration Variation

- Highest three:
  - Phoenix, AZ (0.067 ng/m3)
  - Detroit, MI (0.049 ng/m3)
  - Boston, MA (0.041 ng/m3)
- Lowest three:
  - Providence, AL (0.0019 ng/m3)
  - Portland, OR (0.0028 ng/m3)
  - Austin, TX (0.0035 ng/m3)

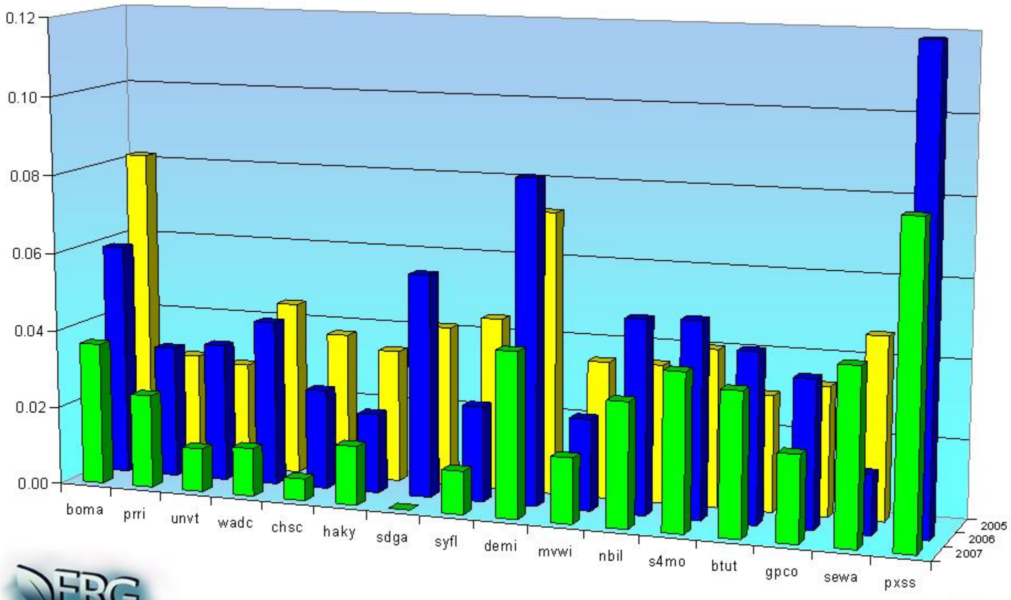
Seasonal Variation

- Seasons
  - Winter – December to February
  - Spring – March to May
  - Summer – June to August
  - Fall – September to November
- Thirty-nine months of data allows us to compare years as well as seasons
- No global trends but site trends were noted

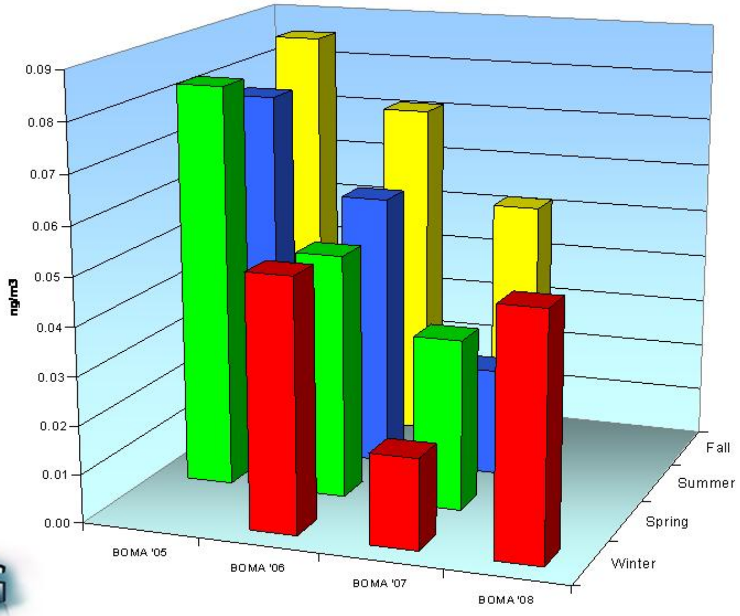
Results from Jan ’05 to Mar ‘08



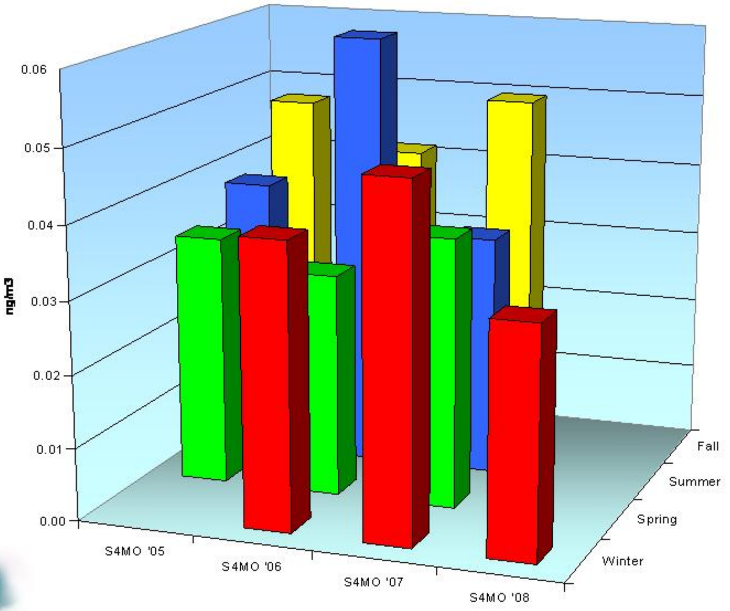
Annual Trends (ng/m^3)



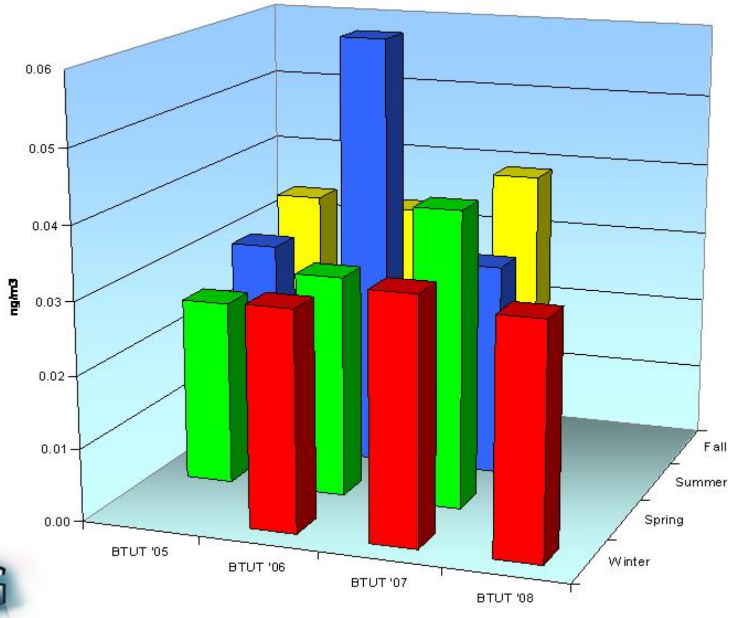
Roxbury, MA Seasonal Trends



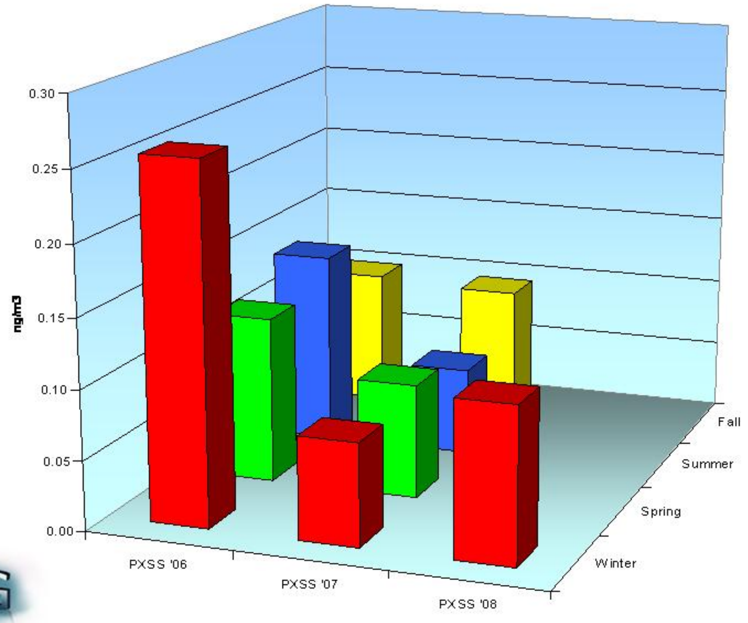
St. Louis, MO Seasonal Trends



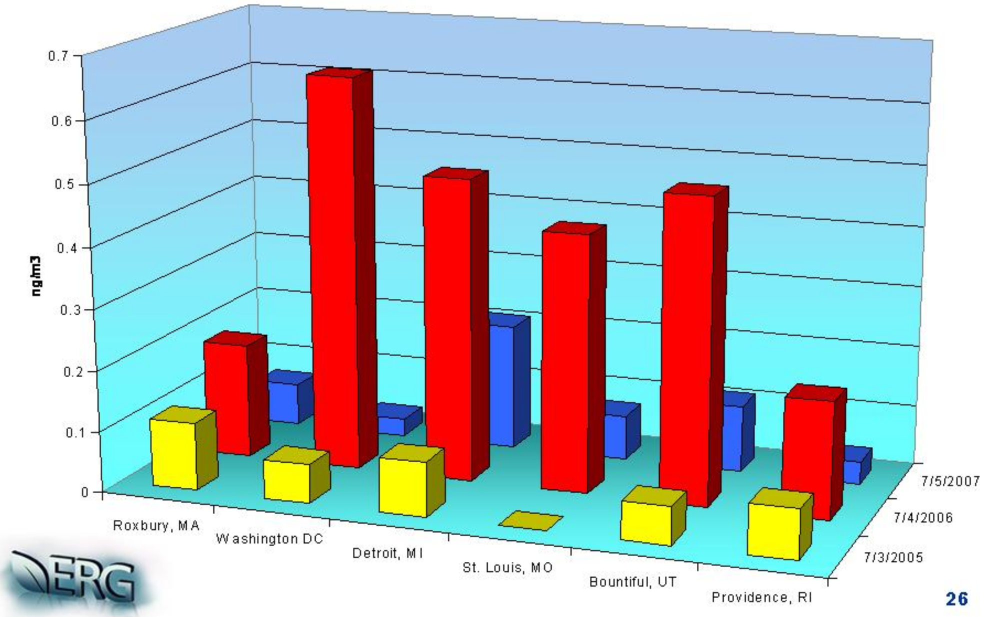
Bountiful, UT Seasonal Trends



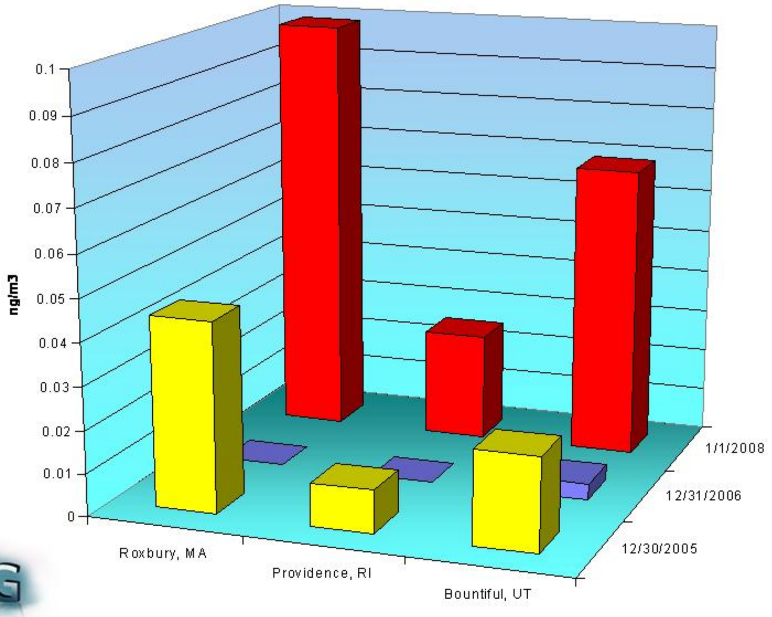
Phoenix, AZ Seasonal Trends



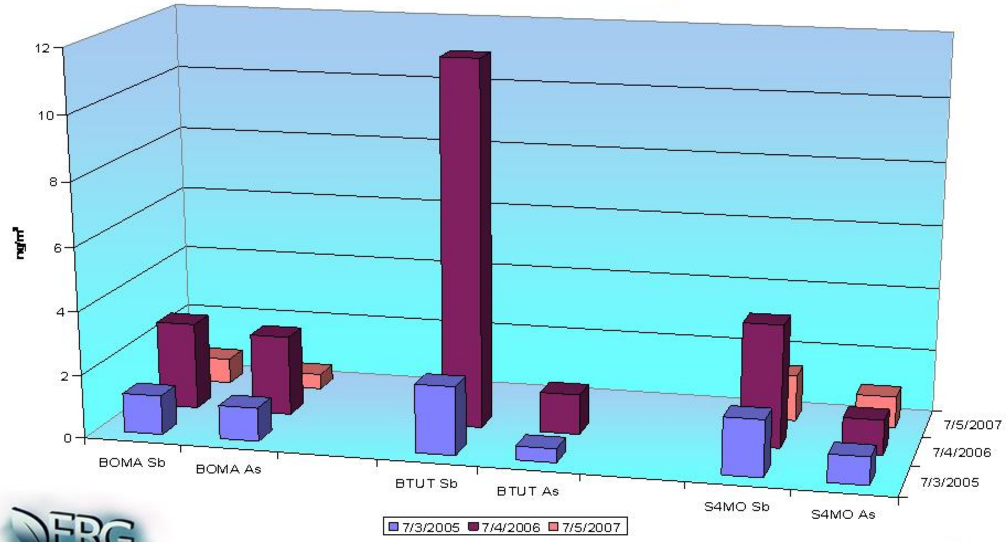
July 4th Celebration!



New Years Celebration!



4th of July Celebration (Other Metals)!



Conclusions

- Cr^{6+} is highly toxic and a health concern
- Late pickup provides reduced concentrations
- Chiller sampler shows promise
- Data results varied from site to site
- No global trends, but trends noticed within sites seasonally and annually
- July 4th & New Year pyrotechnic displays may be potential Cr^{6+} (and other pollutant) emitters?

Acknowledgments

- US EPA, OAQPS
  - ☐ Mike Jones
  - ☐ Dennis Mikel
  - ☐ Joann Rice

- ERG
  - ☐ Mitch Howell
  - ☐ Chris Kopp
  - ☐ Mark Owens
  - ☐ Dave Dayton
  - ☐ Pearl Kaplan

Continuous Monitoring of Ambient Air Toxic Metals at Low PG/DSCM Concentrations

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ABSTRACT

Eight of the 33 ambient air toxic elements (ATE) identified by the U. S. Environmental Protection Agency (EPA) as posing the greatest potential environmental health threat in urban areas are metals and their compounds. EPA's Air Toxics Component of the National Monitoring Strategy calls for monitoring of ambient air toxic elements (ATE) to improve our understanding of these pollutants and air quality issues at the national and local level. However, sampling and analysis procedures currently being used to measure ambient ATE in particulate matter (PM) are inadequate to consistently quantify many of the ATE at their typical concentrations. X-Ray Fluorescence (XRF) is commonly used for measuring ambient ATE in PM, but the method's detection limits as currently applied are insufficient. Inductively Coupled Plasma Mass Spectrometry (ICPMS) is an alternative approach being considered with detection limits approaching typical ambient concentrations. However, ICPMS is limited in that it requires 24-hour high volume samples, quartz fiber filters used have relatively high and variable blank concentrations, analytical procedures generate hazardous waste and the method is not applicable to automated and remote measurements. Conversely, XRF is readily applicable to automated measurements, and its full potential for ATE quantification has not been achieved. For example, conventional sampling and analysis methods have not been optimized for PM deposits on thin membrane filters, and recent sampling and analysis advances have not been incorporated into current instruments and methods. Phase I of this study evaluated the potential of XRF for quantifying ATE at their typical concentrations using contemporary field sampling and laboratory analysis technology optimized for PM deposits on thin membrane filters. Phase II consisted of implementing Phase I advances in a field-deployable, real time monitor for ATE using a 50 watt air-cooled X-ray tube. Phase II results for this field-deployable monitor demonstrated detection limits of 4, 110, 9, 5, and 5 pg/dscm for As, Cd, Cr, Pb, and Hg, respectively, with automated four hour sampling and analysis times. This field monitor developed in this study represents a major advance in ATE measurement capabilities over currently-available methods and could contribute greatly to surveys of hazardous elemental concentrations in ambient air. This paper presents (1) an overview of Phase I improvements to XRF sampling and analysis procedures, and demonstrated detection limits; (2) a description of the ATE monitor developed in Phase II; and (3) an evaluation of the monitor's performance.

Preconcentrator Method Development for the Analysis of Microbial Volatile Organic Chemicals from Mold Using Air Canisters and Gas Chromatography – Mass Spectrometry

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ABSTRACT

Hurricanes and other events that cause flooding, as well as high humidity environments, lead to mold growth in houses and other building structures. Because the presence of mold can be harmful to human health (leading to a version of sick building syndrome) and its visual detection is not always possible analysts are turning to alternate ways to detect its presence, including chemical detection with gas chromatography – mass spectrometry (GC-MS). Mold produces volatile organic chemicals (VOCs) that in addition to giving a characteristic musty odor can be used to indicate its growth or perhaps even to fingerprint the type of mold. Geosmin and 2-methylisoborneol are well-known "earthy" smelling microbial VOCs, but there are a wide variety of other components representing alcohol, ketone, furan, and other mainly polar functionalities.

Because of their polarity and what may be very low concentrations of the compounds in a home, an inert and large volume collection device is needed for sampling. Air canisters that have been passivated are ideal for sampling microbial VOCs. VOC introduction is via a preconcentrator to a GC-MS for qualitative and quantitative determinations, but the preconcentrator must be able to manage moisture effectively to give acceptable chromatographic results.

This paper will show the method development involved in tuning a commercial preconcentrator for the analysis of microbial VOCs with an air canister and GC-MS. Various attempts to reduce water that leads to poor chromatographic results, will be discussed in detail.

Preconcentrator Method Development for the Analysis of Microbial Volatile Organic Chemicals from Mold Using Air Canisters and Gas Chromatography – Mass Spectrometry

Michelle Misselwitz, Jack Cochran, Irene DeGraff, Dave Shelow, and Silvia Martinez
Restek Corporation
Bellefonte, PA

Mold and the Media

- Hazards of mold are much publicized
  - 60 Minutes and other news magazines
- Lawsuits pursued

Silent Killers: Toxic Mold

Stachybotrys Can Infest A House

July 26, 2002

Workers are now trying to save Brockovich's house from toxic mold. It is an expensive job. **(CBS)**

RELATED

INTERACTIVE

Home Health Hazards

Discover what hazards your home may be harboring and find out how to get rid of them.

AnswerTips™ enabled (What's this?)

(CBS) Since the movie bearing her name appeared, everyone knows who Erin Brockovich is: the working mother who traced illnesses in a small California town to groundwater contaminated by Pacific Gas and Electric.

After the case was settled for hundreds of millions of dollars, Brockovich got a big promotion, and now divides her time between her job and motivational speaking.

She lives in a million-dollar home near Los Angeles, with her third husband, Eric Ellis, and the youngest of her 3 children - 11-year-old Beth.

Brockovich says it is the house she always wanted. The bonus she got from winning the lawsuit made her dream possible. But then it turned into a nightmare, ***48 Hours*** **Correspondent Susan Spencer** reports.

For months, touring her home required a hazmat suit. The house was filled with slimy black mold called Stachybotrys

Traducción española por Inspector del Molde Website
Site Web de Inspetor de Molde de Tradução Português
La Traduction française pour l'Inspecteur de Moisissure le Site Internet
Besuchen Sie deutsche Übersetzung des Form-Inspektors Website
Посетите российский перевод Инспектора Почвы вебсайт

Mold Inspector Black Toxic Mold, Household Mold, Mold Allergy, & Mold Symptom Information & Help, plus Mold Laboratory for Toxic Mold Analysis & Toxic Mold Species Identification, plus Mold Training and Mold Certification

The Internet's first mold self-help website online since 1999, this _Mold Inspector_ website includes over 300 pages of "how to" guidance & advice on black toxic mold, household mold, mold species, mold infestation, mold health problems & treatments, mold inspection, mold testing, toxic mold testing, mold removal, mold remediation, mold legal claims, mold legal defenses, mold training, mold certification, mold products, plus Certified Mold Inspector & Certified Mold Remediator Directories. *Visit the Site Map at the bottom of this page to explore this website to learn how to deal with mold infestation problems in the USA, Canada, Central America, South America, the Caribbean, Asia, Australia, New Zealand, Europe, the Middle East, & Africa.*

Use MoldZyme enzyme-action mold cleaner, the most environmentally-friendly, safe, and effective mold, mold smell, and mold stain remover.

Solve Your Home Mold Problems for $199 anywhere in the world with the UNLIMITED (60 days) expert email & phone guidance, direction, and assistance of Phillip Fry, Certified Mold Inspector, Certified Environmental Inspector, Certified Mold Remediator, and Certified Environmental Hygienist!

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The Artistic Side of Mold

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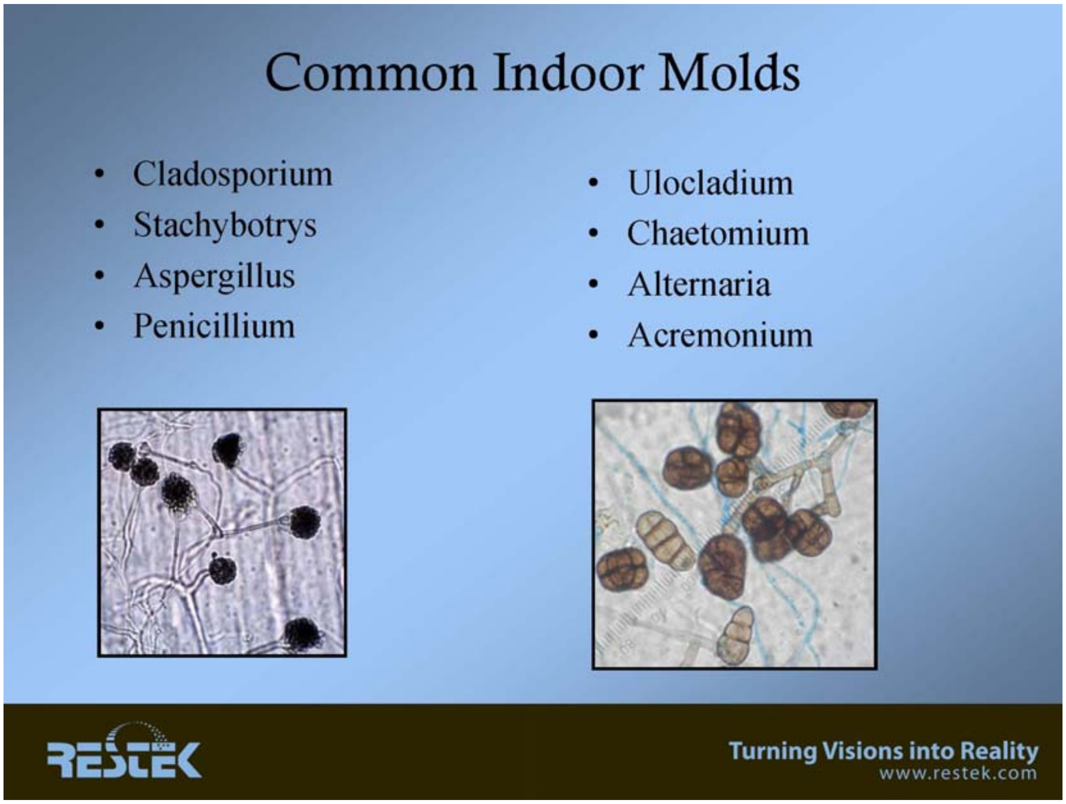

Common Indoor Molds

- Cladosporium
- Stachybotrys
- Aspergillus
- Penicillium

- Ulocladium
- Chaetomium
- Alternaria
- Acremonium

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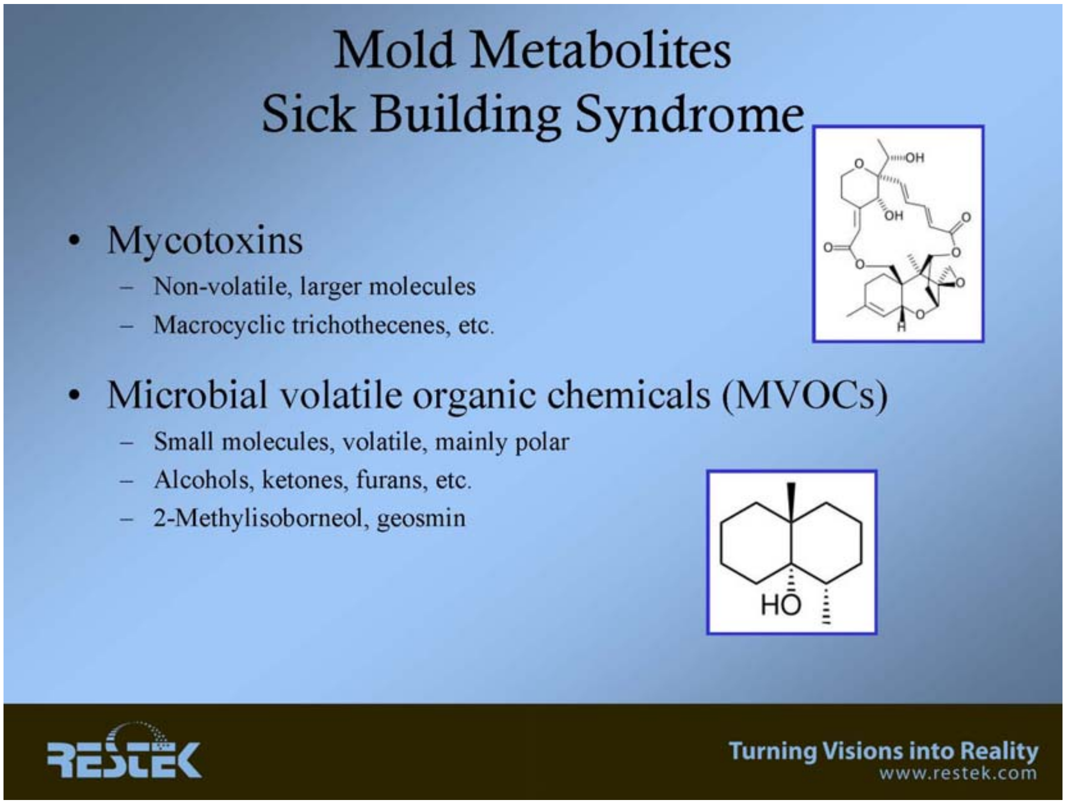

Mold Metabolites
Sick Building Syndrome

- Mycotoxins
  - Non-volatile, larger molecules
  - Macrocyclic trichothecenes, etc.
- Microbial volatile organic chemicals (MVOCs)
  - Small molecules, volatile, mainly polar
  - Alcohols, ketones, furans, etc.
  - 2-Methylisoborneol, geosmin

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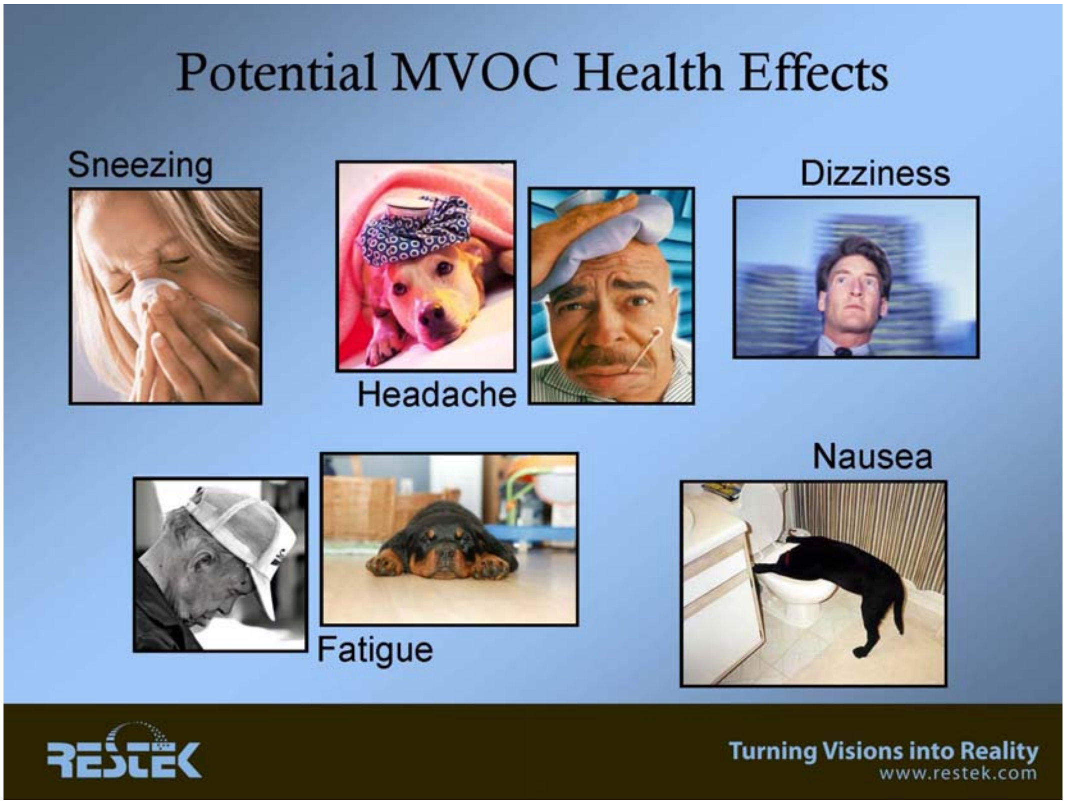

Potential MVOC Health Effects

Sneezing

Headache

Dizziness

Fatigue

Nausea

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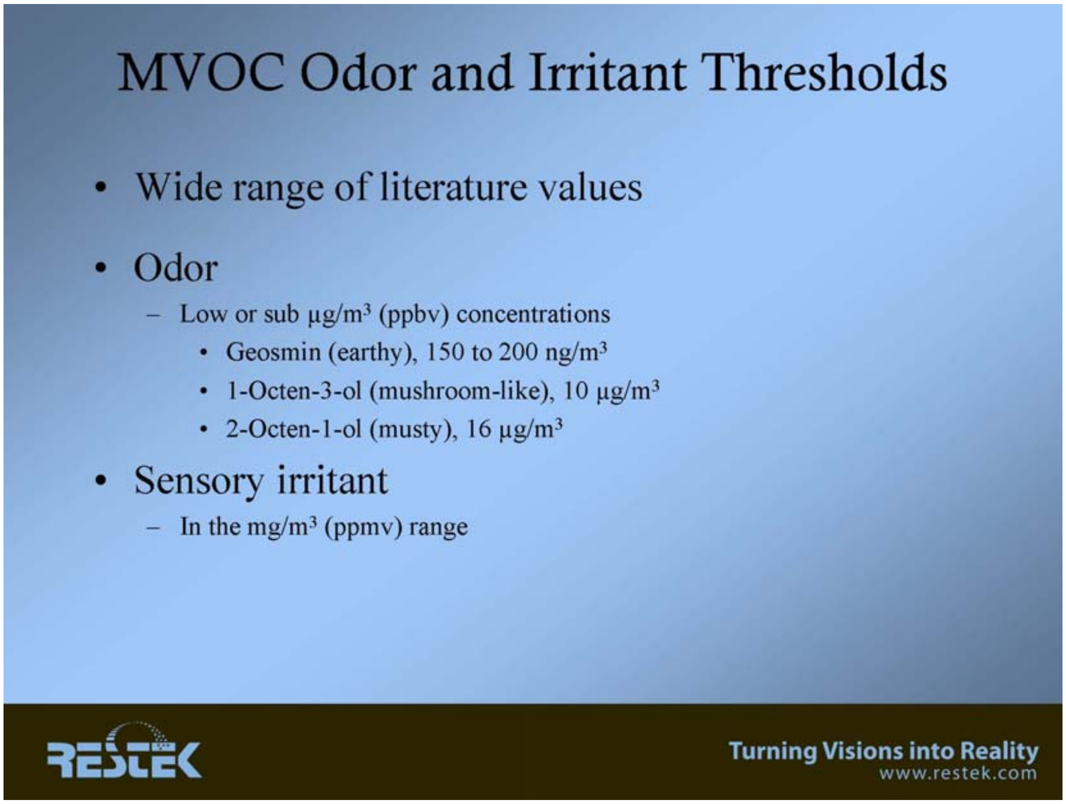

MVOC Odor and Irritant Thresholds

- Wide range of literature values
- Odor
  - Low or sub µg/m³ (ppbv) concentrations
    - Geosmin (earthy), 150 to 200 ng/m³
    - 1-Octen-3-ol (mushroom-like), 10 µg/m³
    - 2-Octen-1-ol (musty), 16 µg/m³
- Sensory irritant
  - In the mg/m³ (ppmv) range

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Why Determine MVOCs?

- Indicator of mold growth
  - Even when mold is not visible
  - May be possible to fingerprint mold type
    - Marker compounds
    - Ratios of certain MVOCs
- Sick building monitoring
  - Health effects studies
  - Mold remediation efforts

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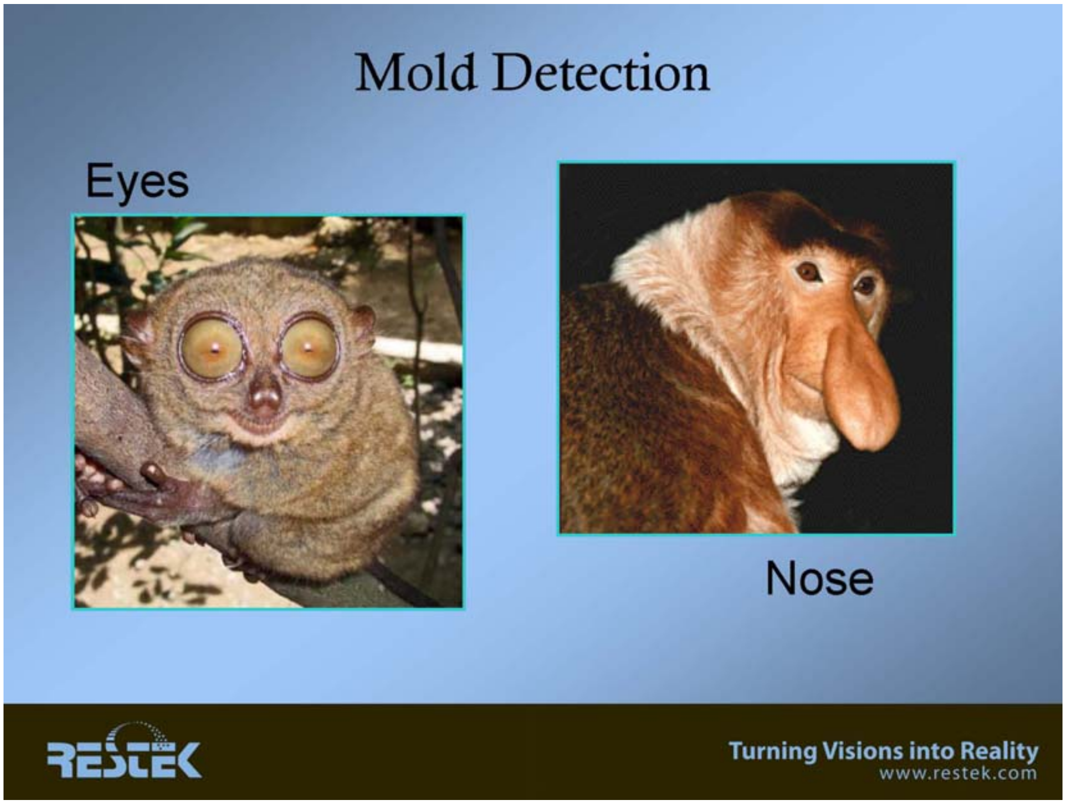

Mold Detection

Eyes

Nose

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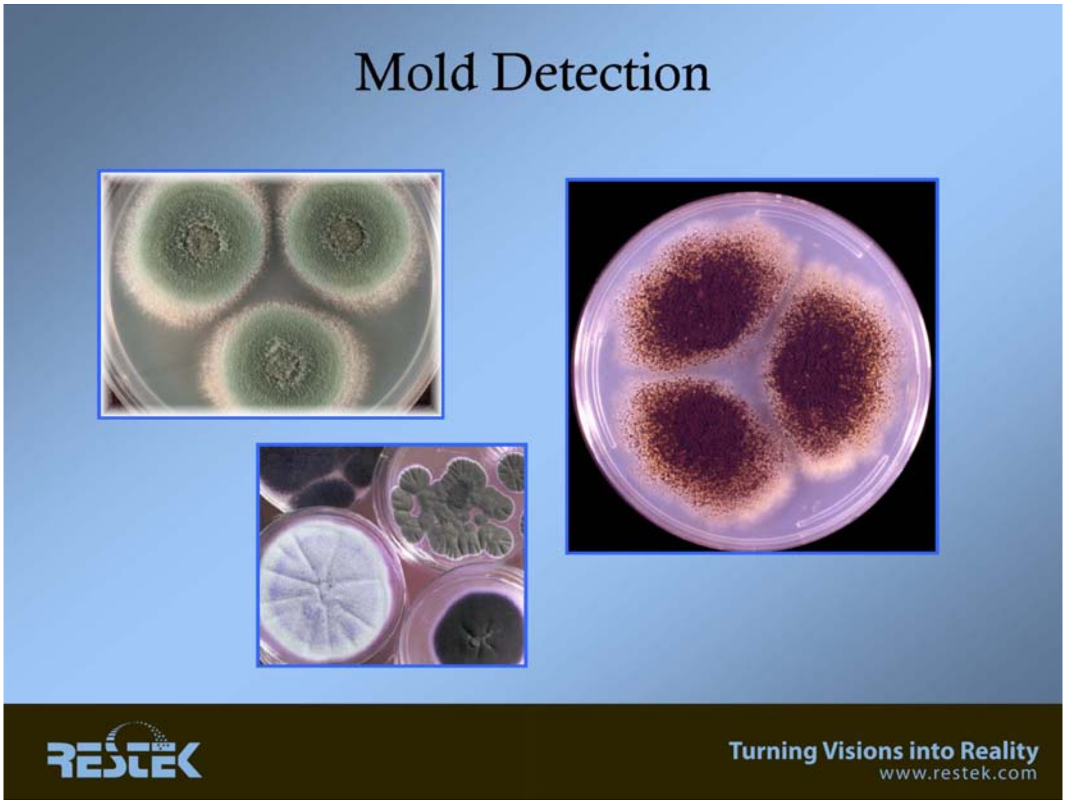

Mold Detection

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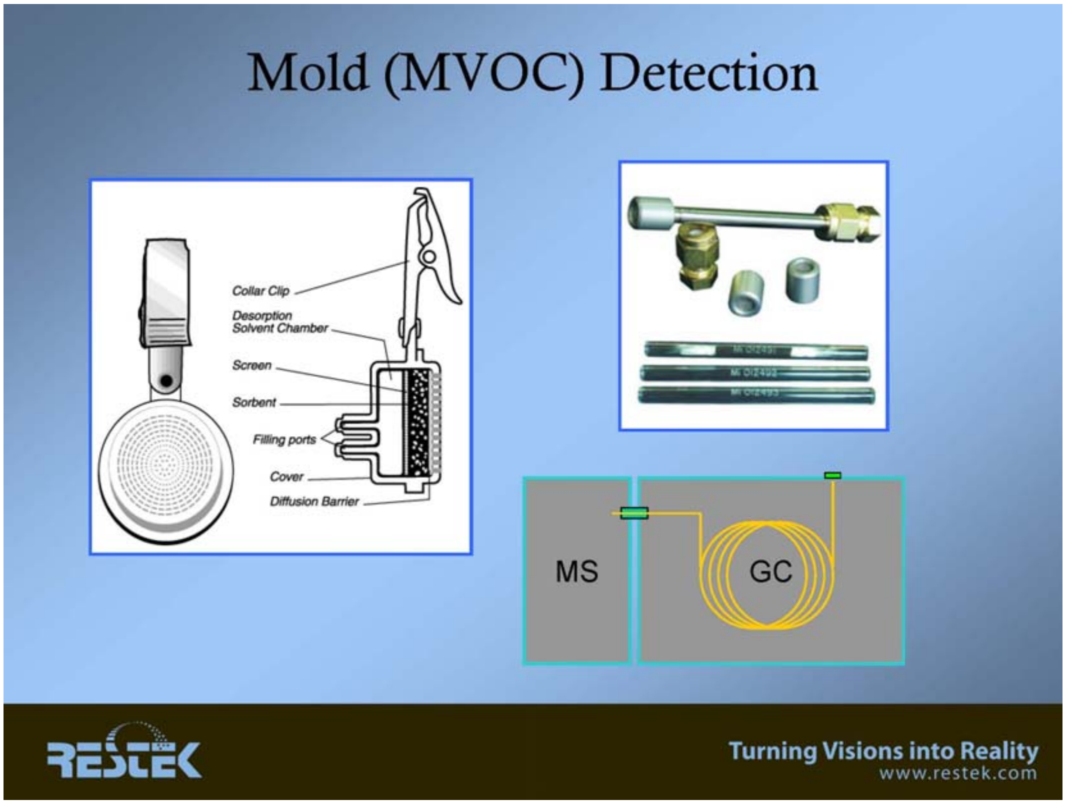

Mold (MVOC) Detection

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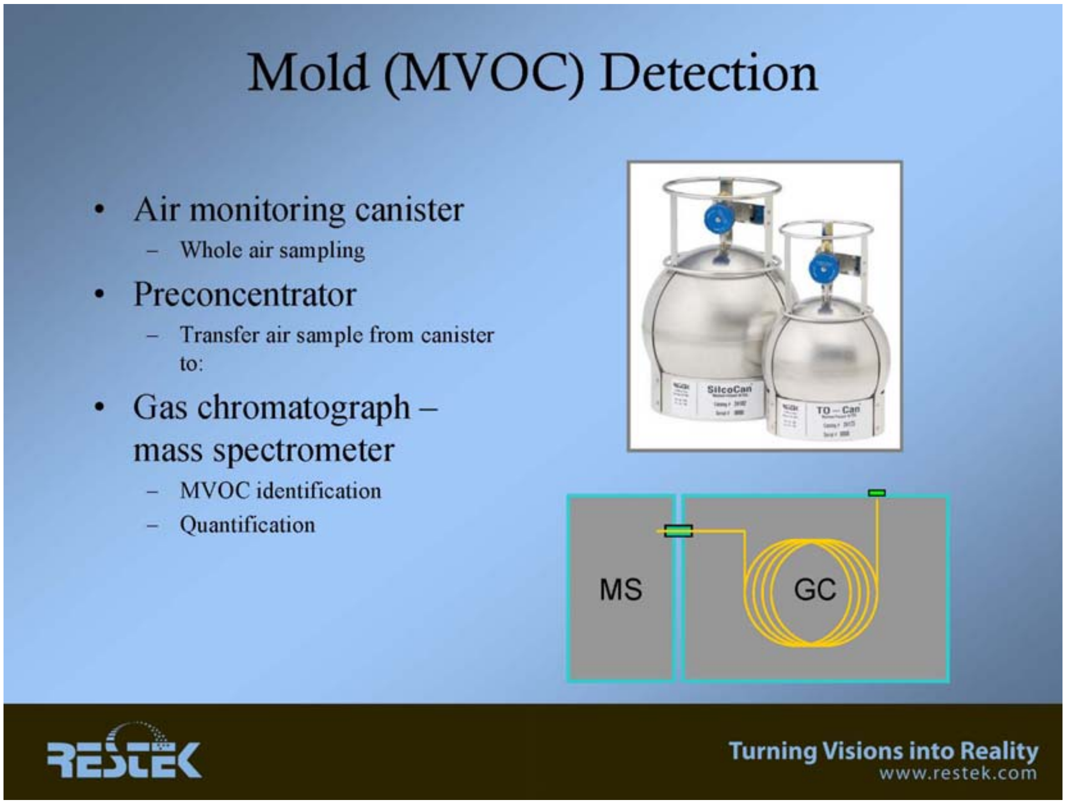

Mold (MVOC) Detection

- Air monitoring canister
  - Whole air sampling
- Preconcentrator
  - Transfer air sample from canister to:
- Gas chromatograph – mass spectrometer
  - MVOC identification
  - Quantification

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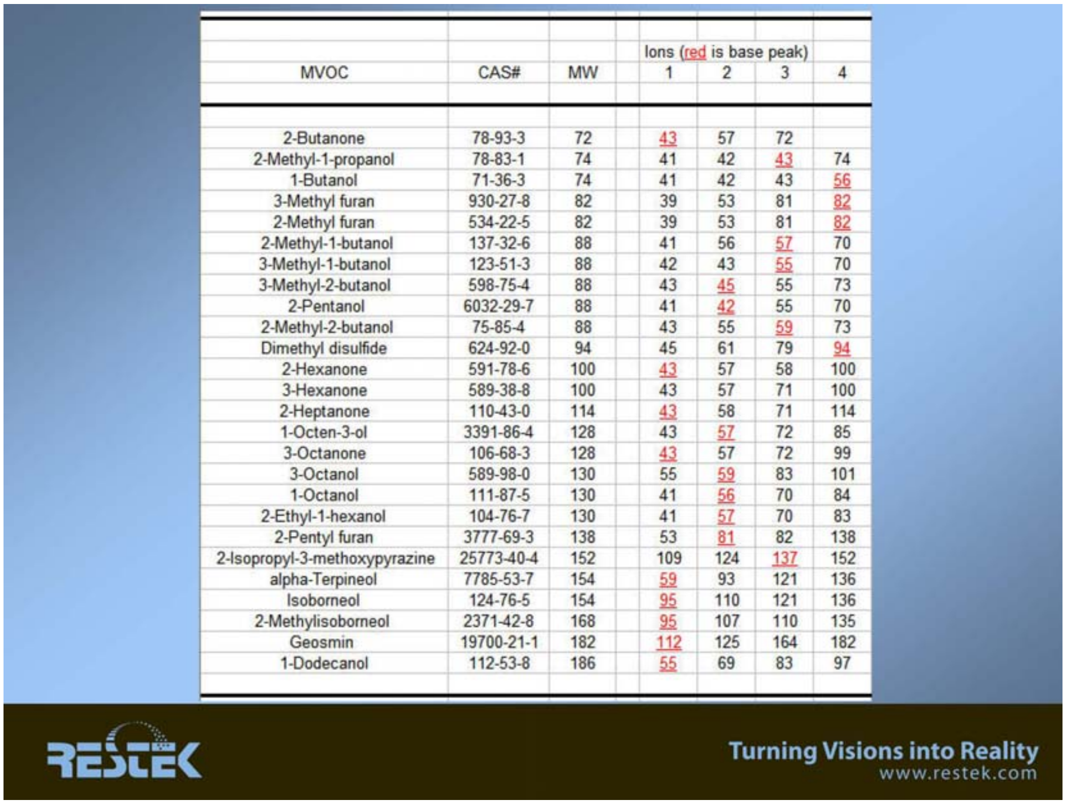

			Ions (red is base peak)			
MVOC	CAS#	MW	1	2	3	4
2-Butanone	78-93-3	72	**43**	57	72	
2-Methyl-1-propanol	78-83-1	74	41	42	**43**	74
1-Butanol	71-36-3	74	41	42	43	**56**
3-Methyl furan	930-27-8	82	39	53	81	**82**
2-Methyl furan	534-22-5	82	39	53	81	**82**
2-Methyl-1-butanol	137-32-6	88	41	56	**57**	70
3-Methyl-1-butanol	123-51-3	88	42	43	**55**	70
3-Methyl-2-butanol	598-75-4	88	43	**45**	55	73
2-Pentanol	6032-29-7	88	41	**42**	55	70
2-Methyl-2-butanol	75-85-4	88	43	55	**59**	73
Dimethyl disulfide	624-92-0	94	45	61	79	**94**
2-Hexanone	591-78-6	100	**43**	57	58	100
3-Hexanone	589-38-8	100	43	57	71	100
2-Heptanone	110-43-0	114	**43**	58	71	114
1-Octen-3-ol	3391-86-4	128	43	**57**	72	85
3-Octanone	106-68-3	128	**43**	57	72	99
3-Octanol	589-98-0	130	55	**59**	83	101
1-Octanol	111-87-5	130	41	**56**	70	84
2-Ethyl-1-hexanol	104-76-7	130	41	**57**	70	83
2-Pentyl furan	3777-69-3	138	53	**81**	82	138
2-Isopropyl-3-methoxypyrazine	25773-40-4	152	109	124	**137**	152
alpha-Terpineol	7785-53-7	154	**59**	93	121	136
Isoborneol	124-76-5	154	**95**	110	121	136
2-Methylisoborneol	2371-42-8	168	**95**	107	110	135
Geosmin	19700-21-1	182	**112**	125	164	182
1-Dodecanol	112-53-8	186	**55**	69	83	97

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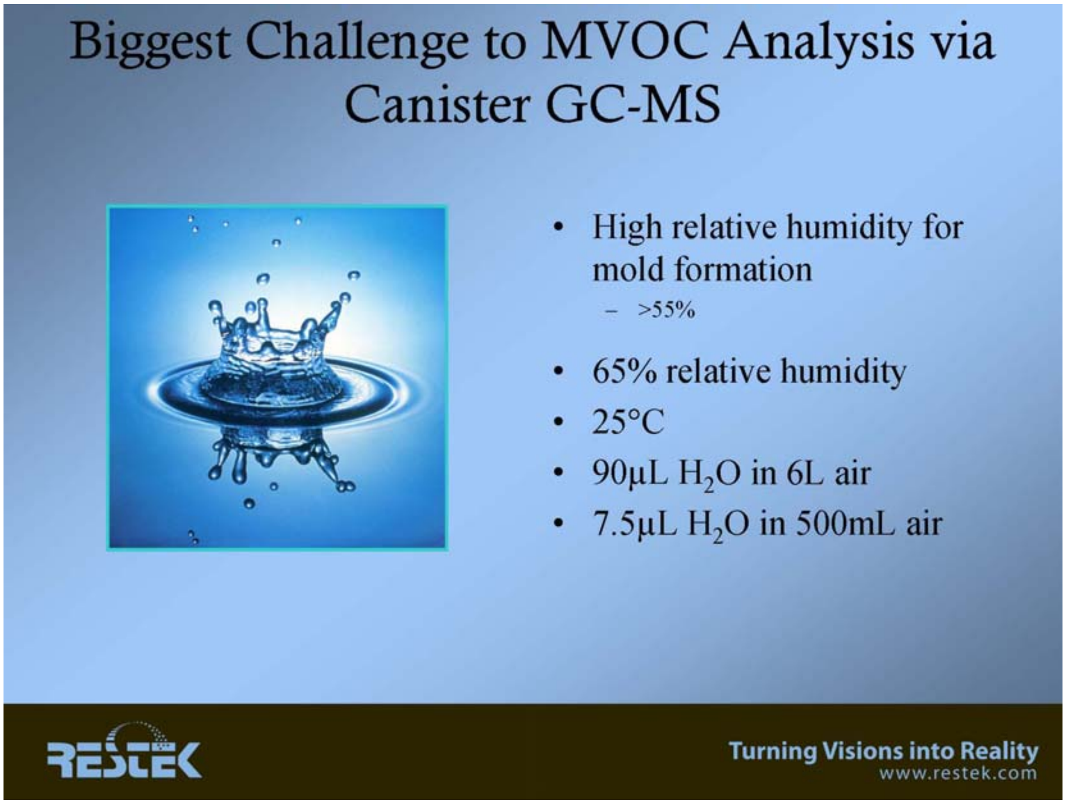

Biggest Challenge to MVOC Analysis via Canister GC-MS

- High relative humidity for mold formation
  - >55%
- 65% relative humidity
- 25°C
- 90µL H_2O in 6L air
- 7.5µL H_2O in 500mL air

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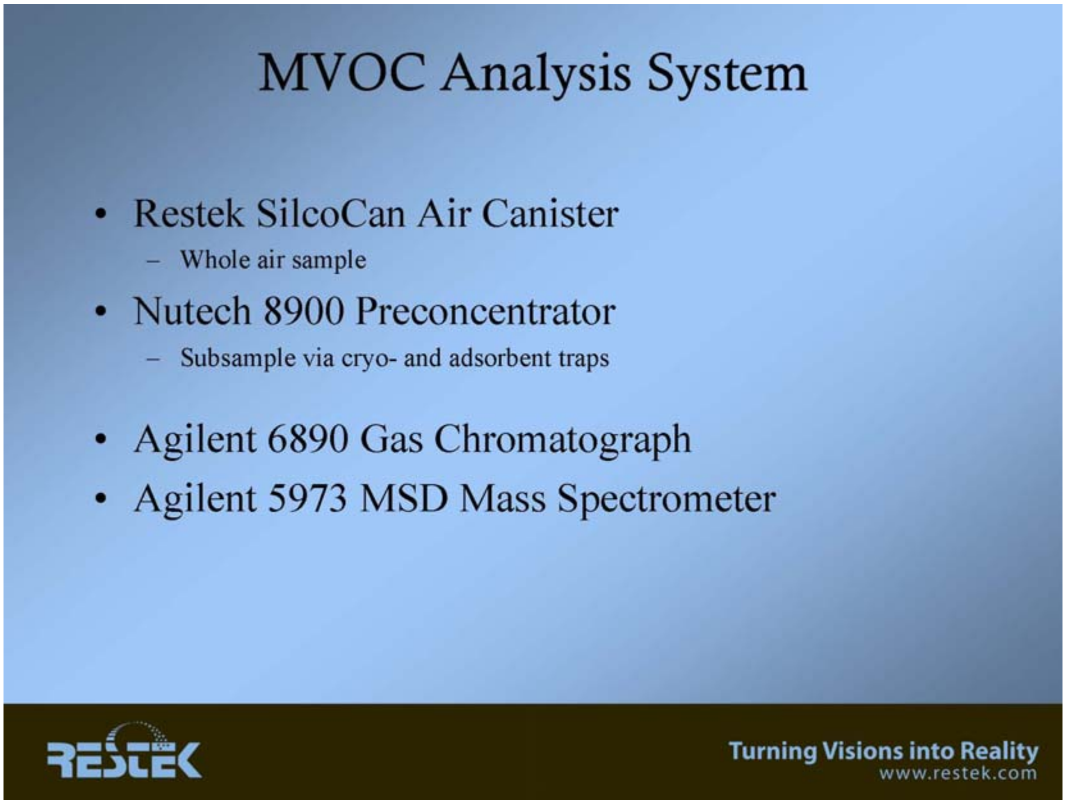

MVOC Analysis System

- Restek SilcoCan Air Canister
  - Whole air sample
- Nutech 8900 Preconcentrator
  - Subsample via cryo- and adsorbent traps
- Agilent 6890 Gas Chromatograph
- Agilent 5973 MSD Mass Spectrometer

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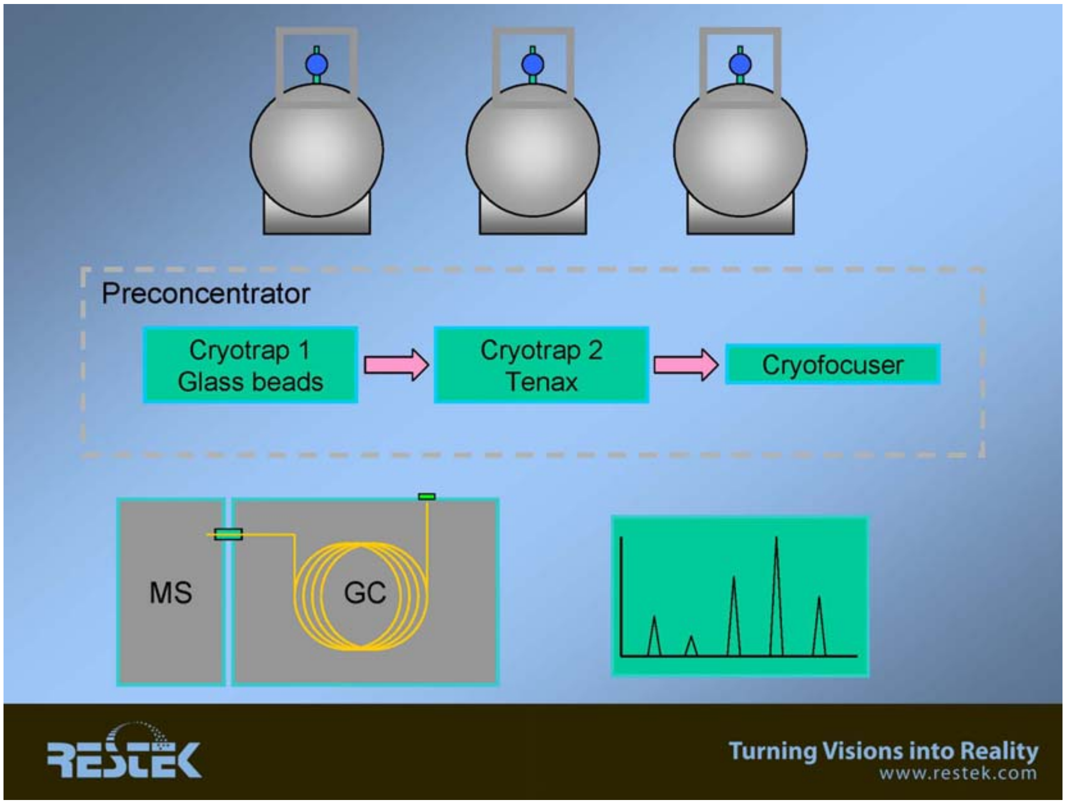

Preconcentrator

Cryotrap 1
Glass beads

Cryotrap 2
Tenax

Cryofocuser

MS

GC

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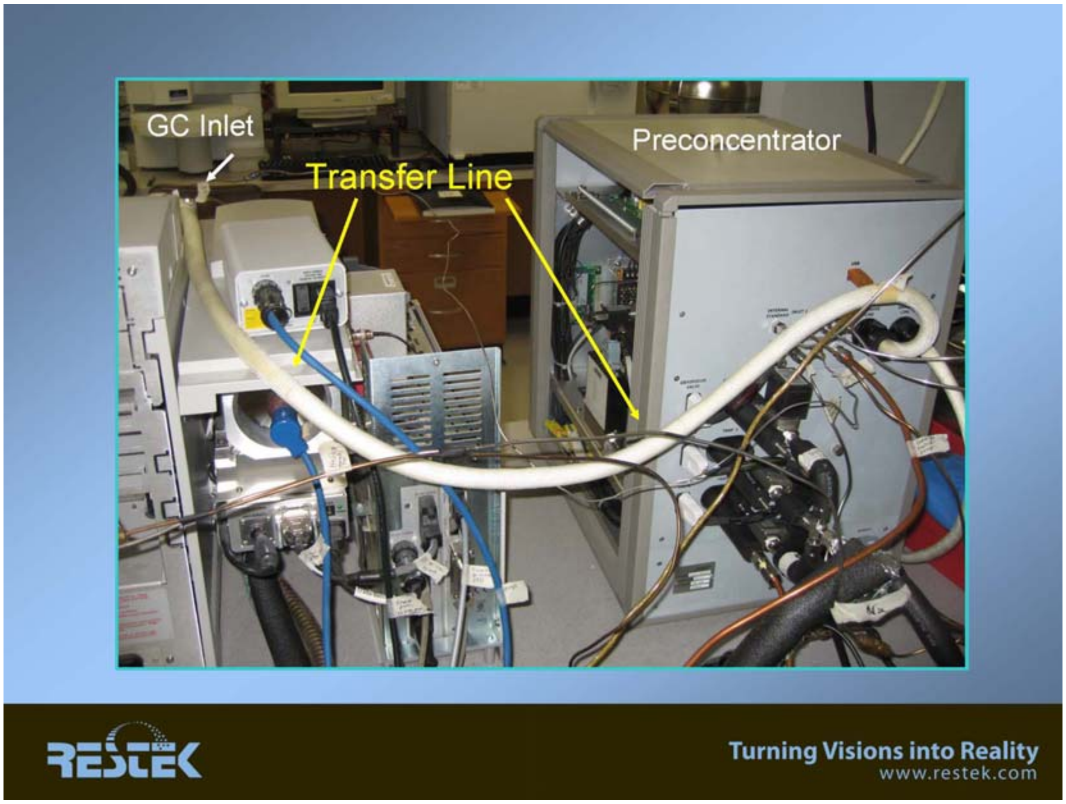

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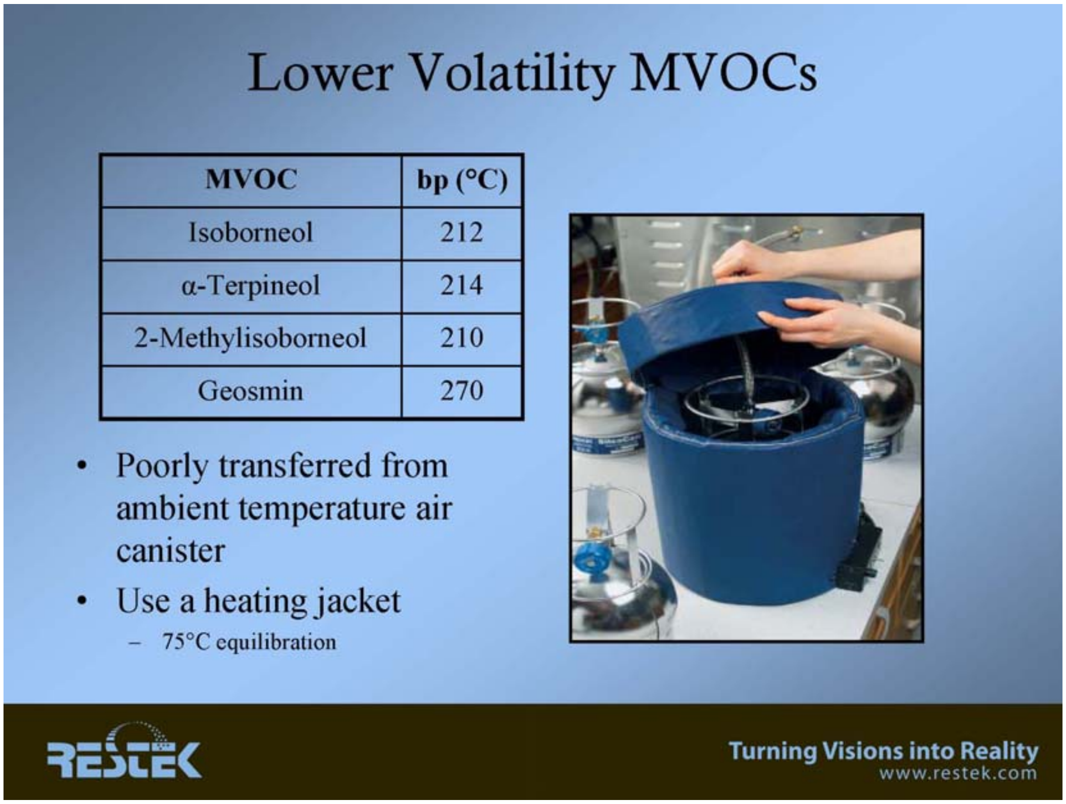

Lower Volatility MVOCs

MVOC	bp (°C)
Isoborneol	212
α-Terpineol	214
2-Methylisoborneol	210
Geosmin	270

- Poorly transferred from ambient temperature air canister
- Use a heating jacket
  - 75°C equilibration

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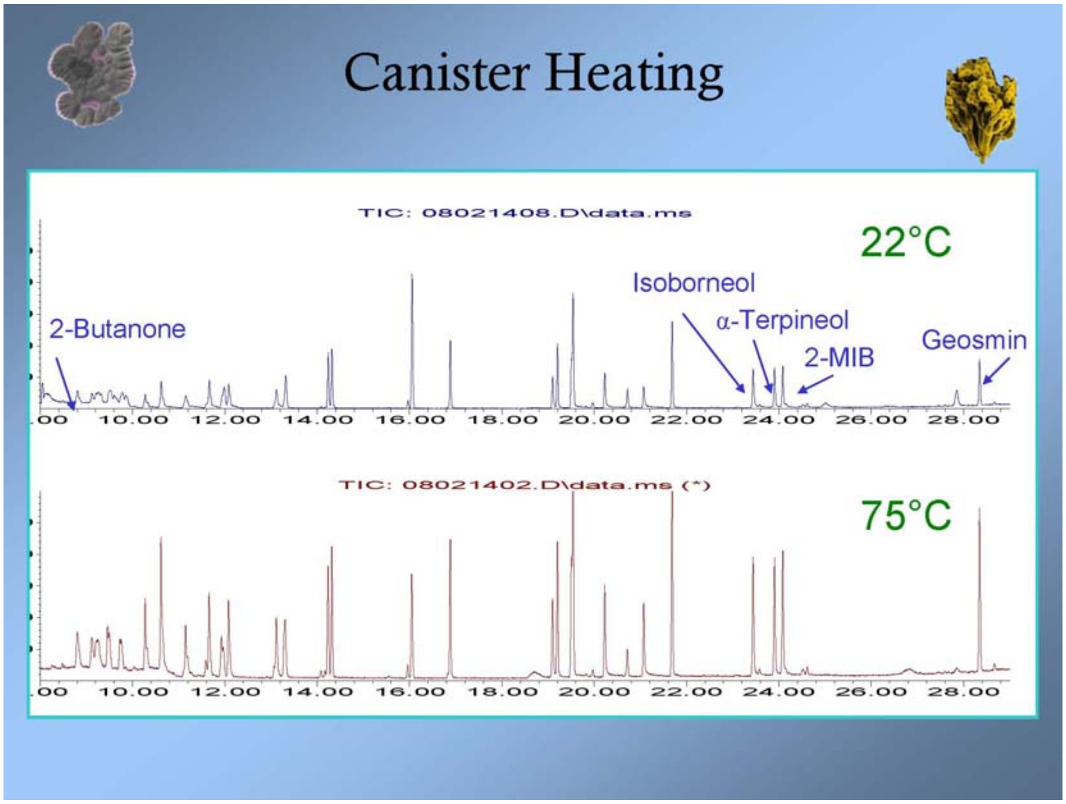
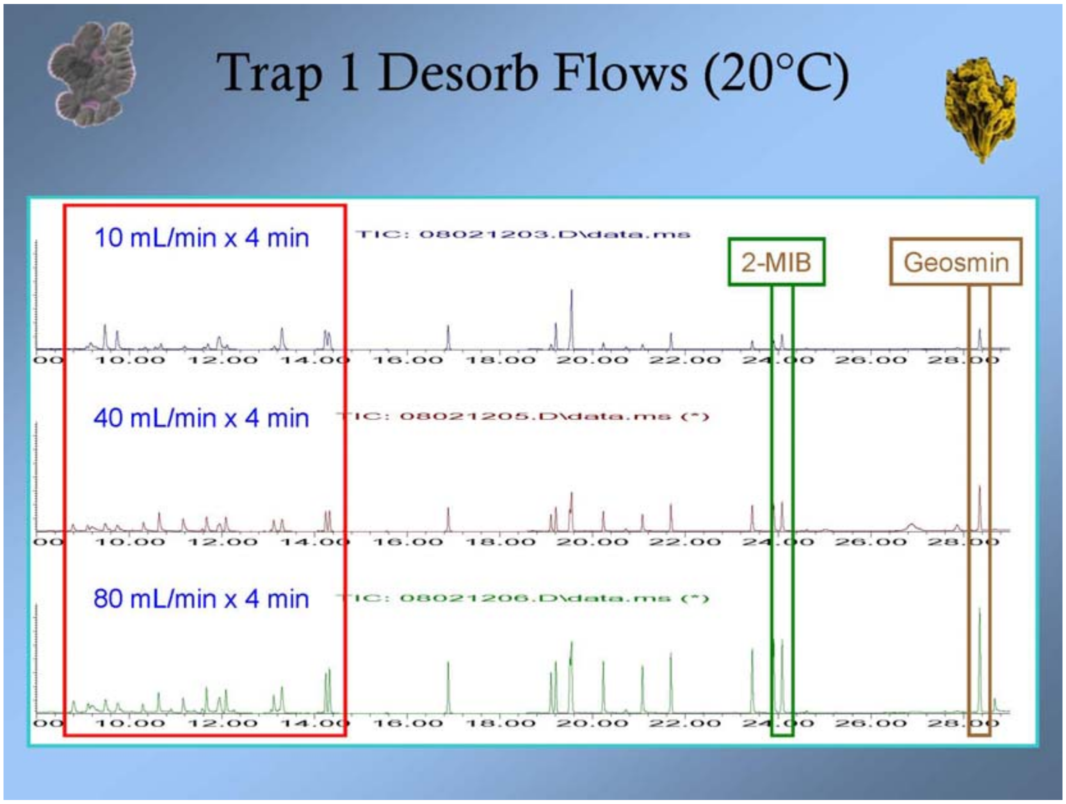
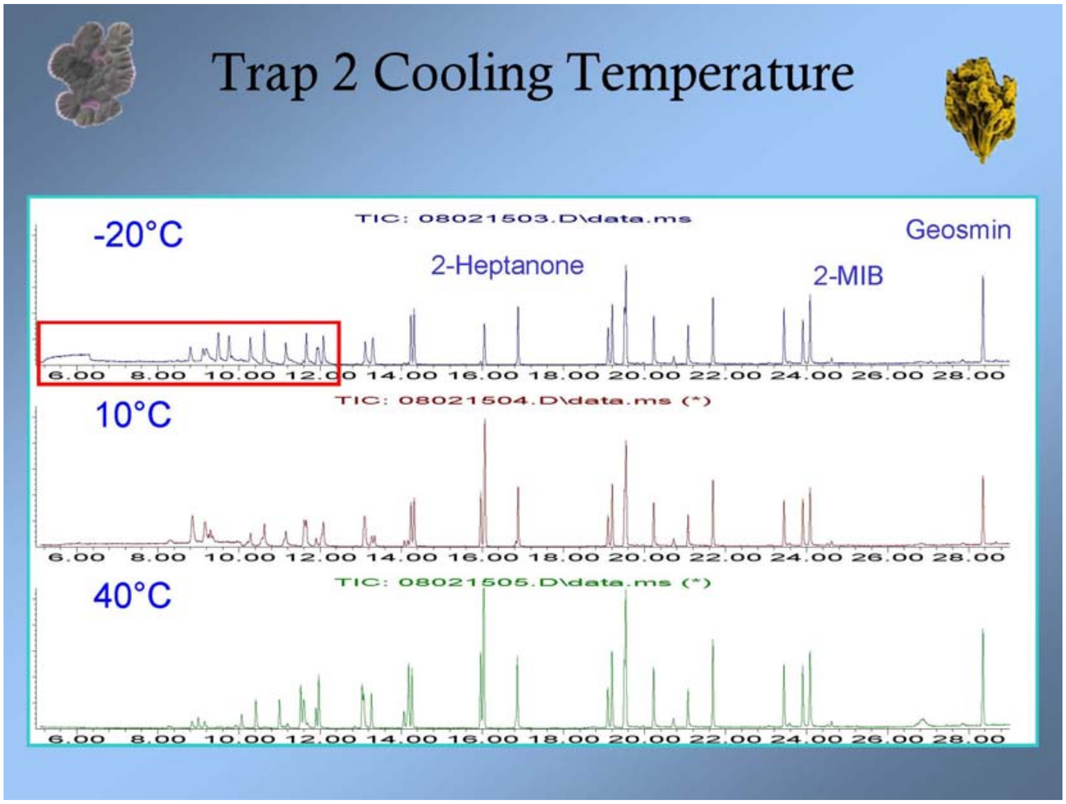


Canister Heating

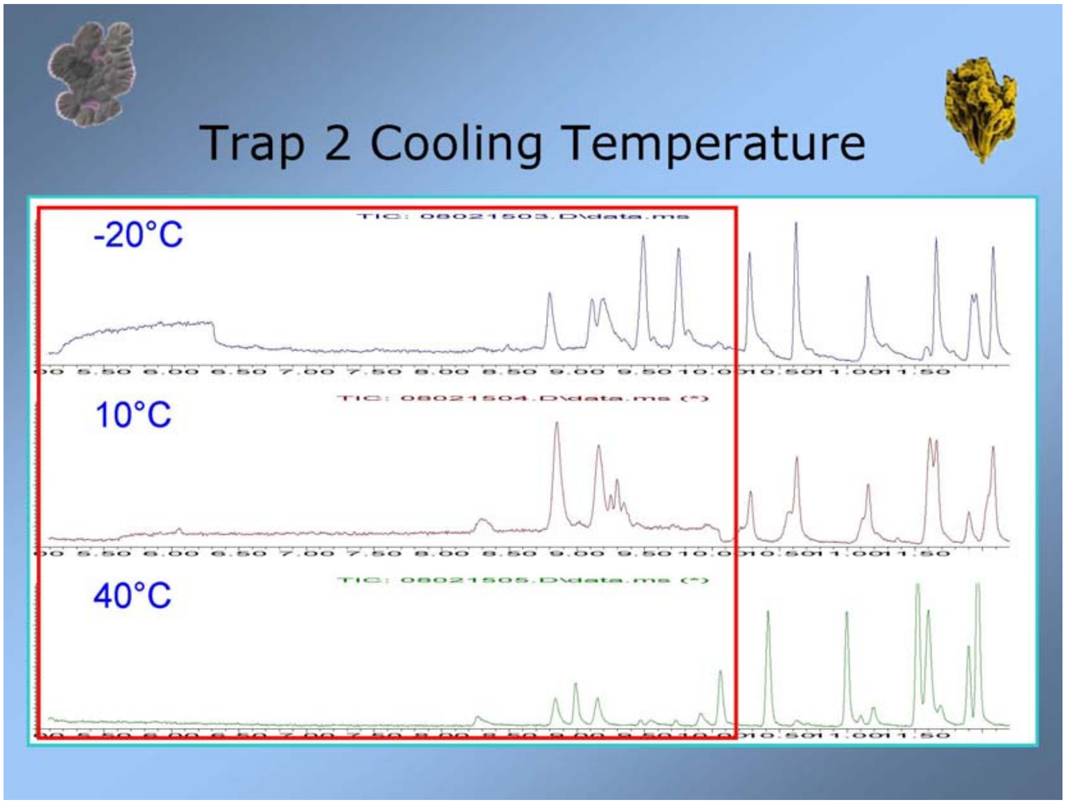
Trap 1	Cooling Temp (°C)	-150	**Glass beads**
	Desorb Temp (°C)	20	
	Desorb Flow (mL/min)	60	
	Desorb Time (min)	1	
Trap 2	Cooling Temp (°C)	-20	**Tenax**
	Desorb Temp (°C)	150	
	Desorb Flow (mL/min)	60	
	Desorb Time (min)	2	
Focuser	Cooling Temp (°C)	-150	
	Desorb Temp (°C)	150	
	Desorb Flow (mL/min)	GC	
	Desorb Time (min)	4	



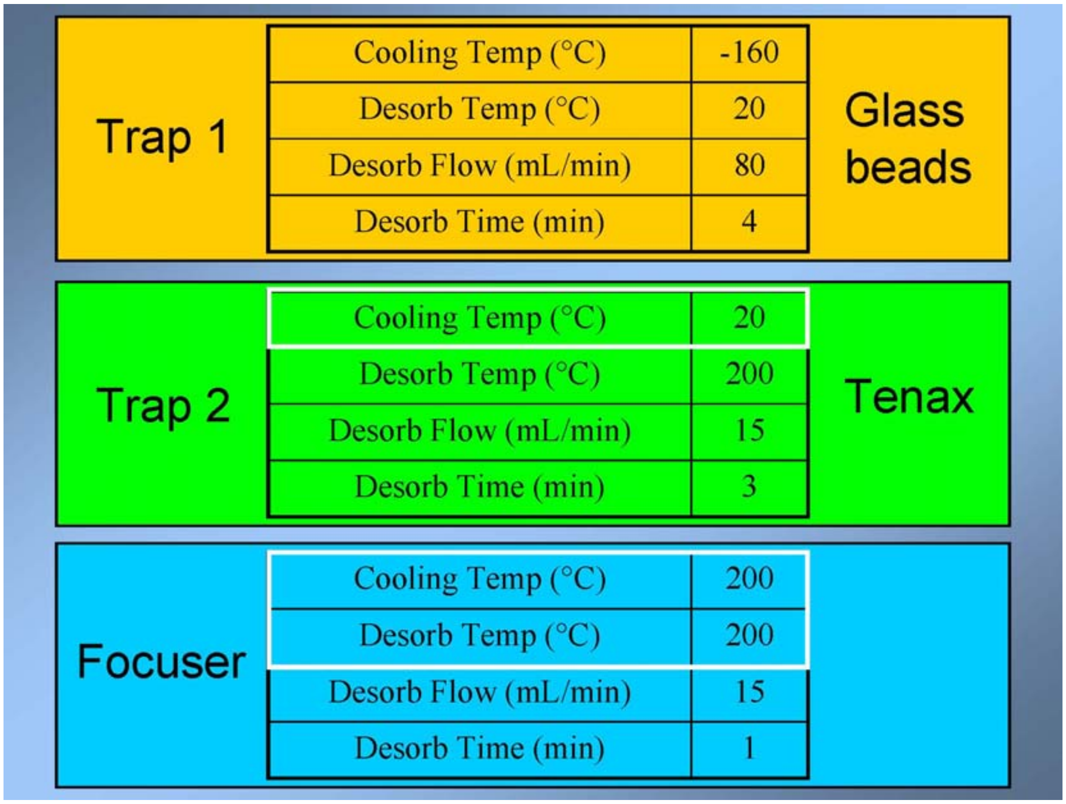
Trap 1 Desorb Flows (20°C)



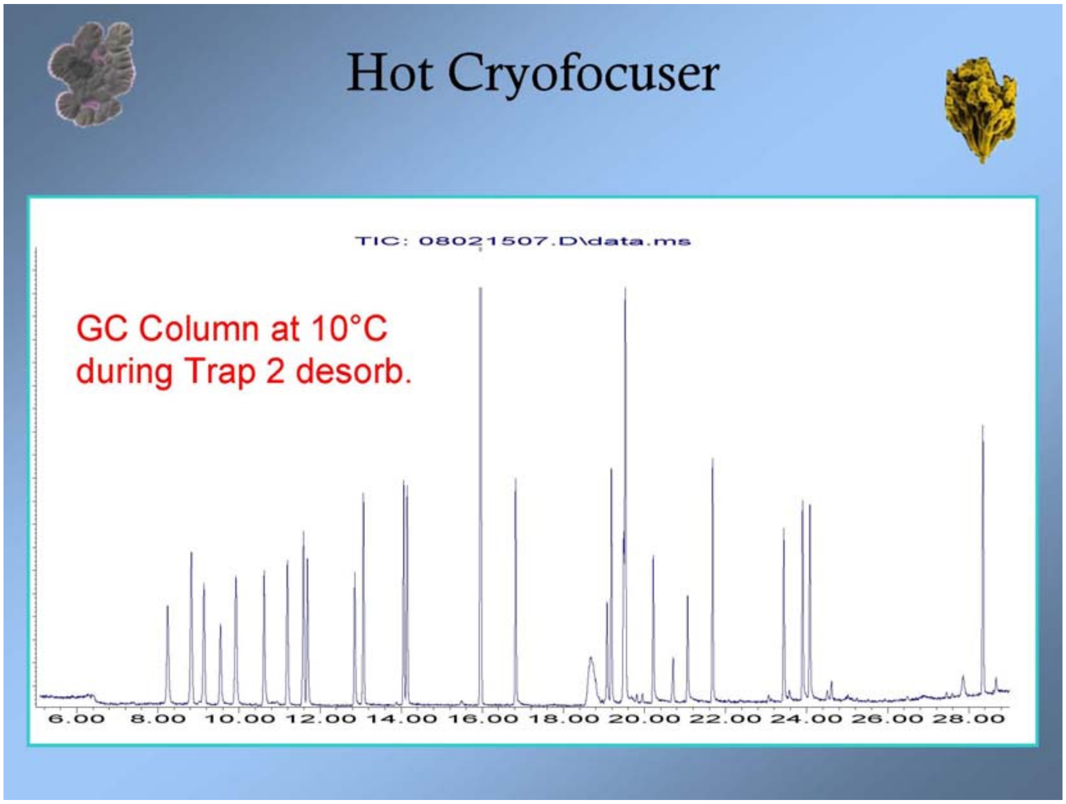
Trap 2 Cooling Temperature



Trap 2 Cooling Temperature

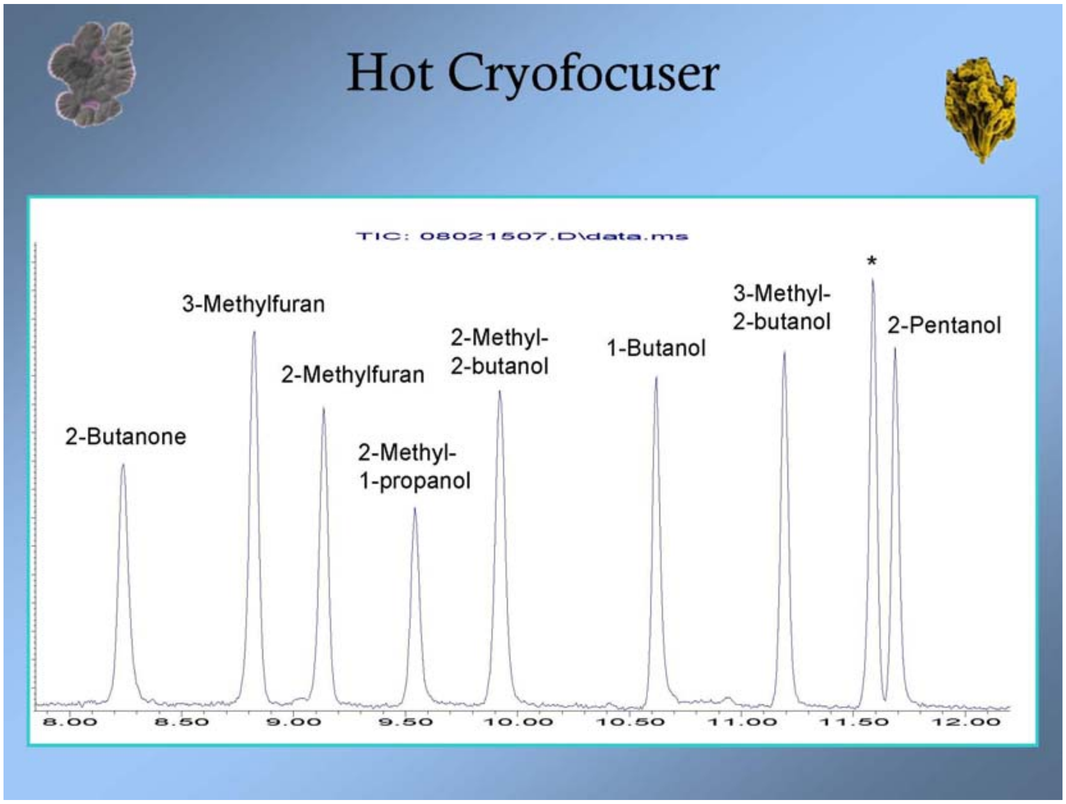


Trap 1	Cooling Temp (°C)	-160	Glass beads
	Desorb Temp (°C)	20	
	Desorb Flow (mL/min)	80	
	Desorb Time (min)	4	
Trap 2	Cooling Temp (°C)	20	Tenax
	Desorb Temp (°C)	200	
	Desorb Flow (mL/min)	15	
	Desorb Time (min)	3	
Focuser	Cooling Temp (°C)	200	
	Desorb Temp (°C)	200	
	Desorb Flow (mL/min)	15	
	Desorb Time (min)	1	

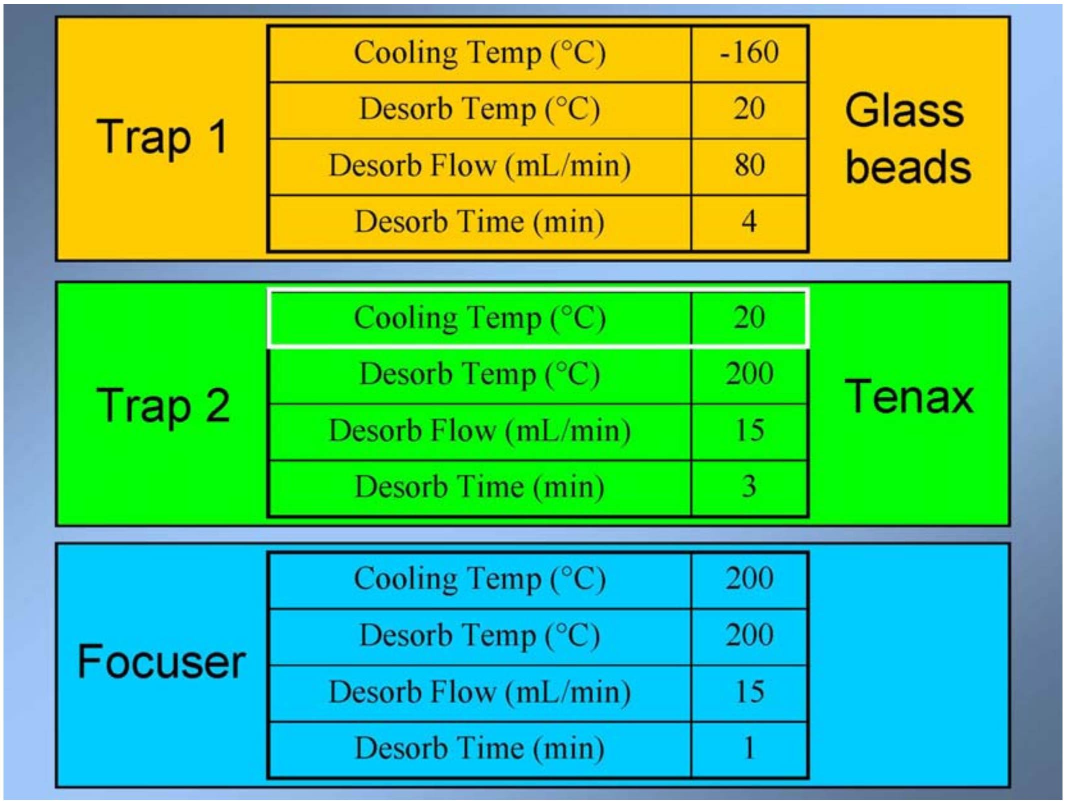


Hot Cryofocuser

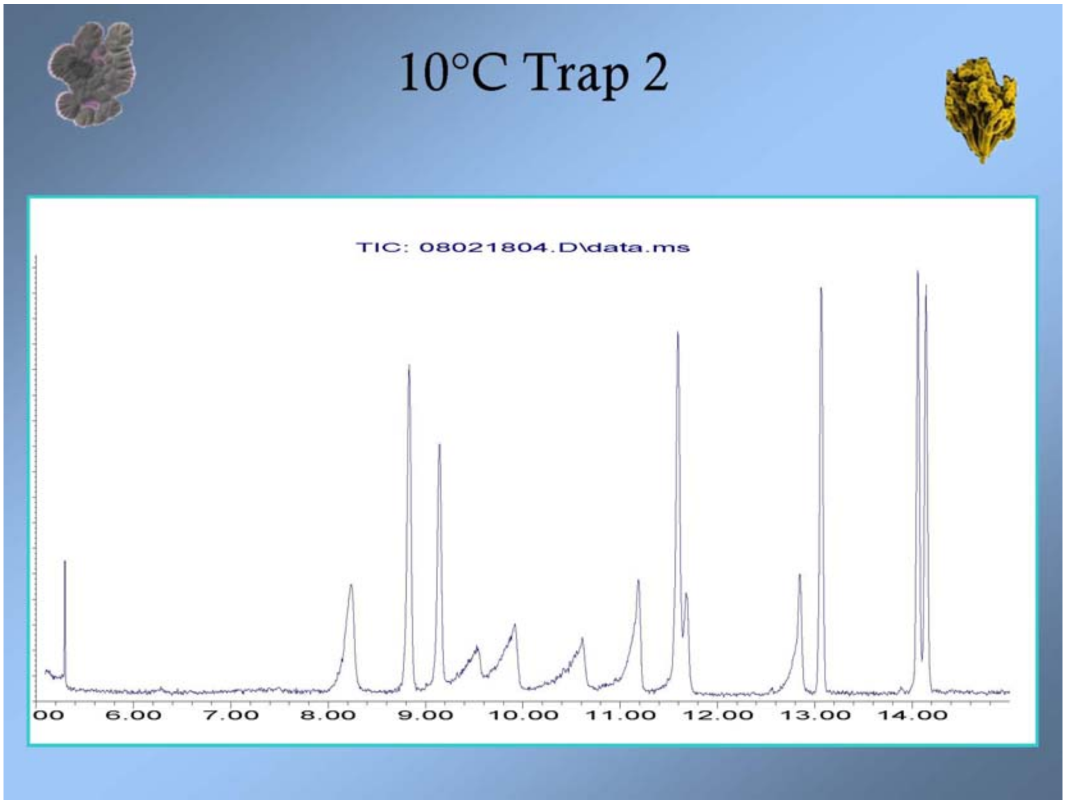
GC Column at 10°C
during Trap 2 desorb.



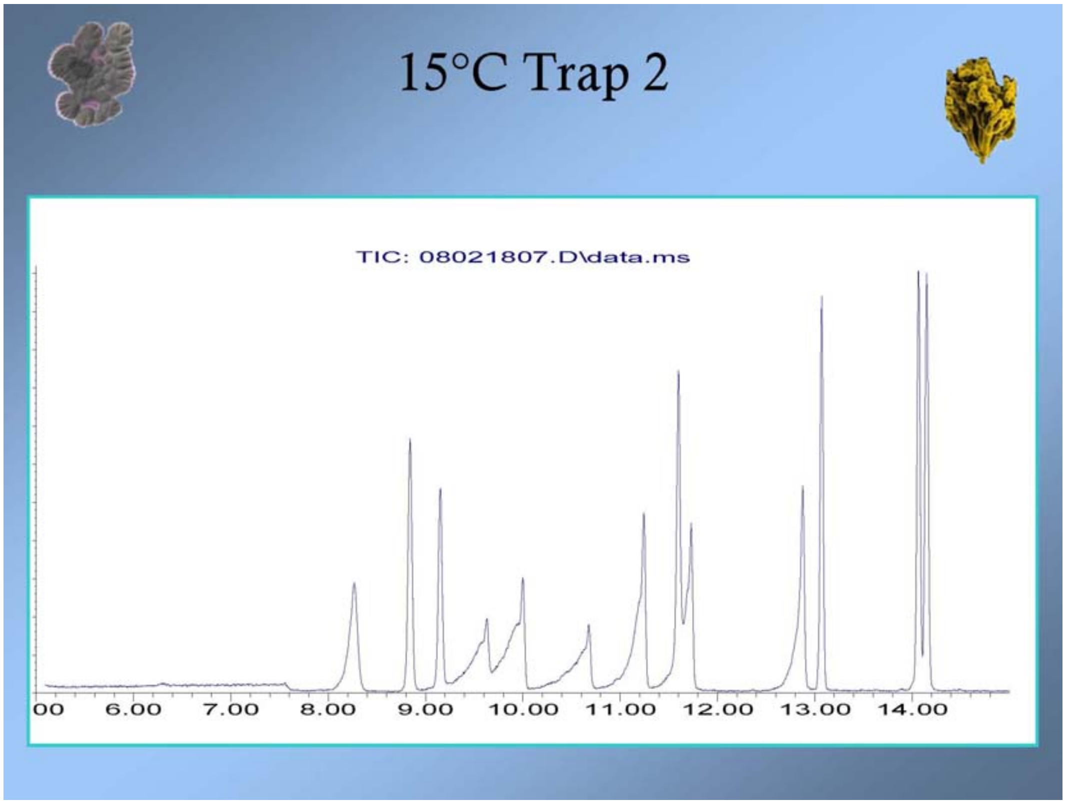
Hot Cryofocuser



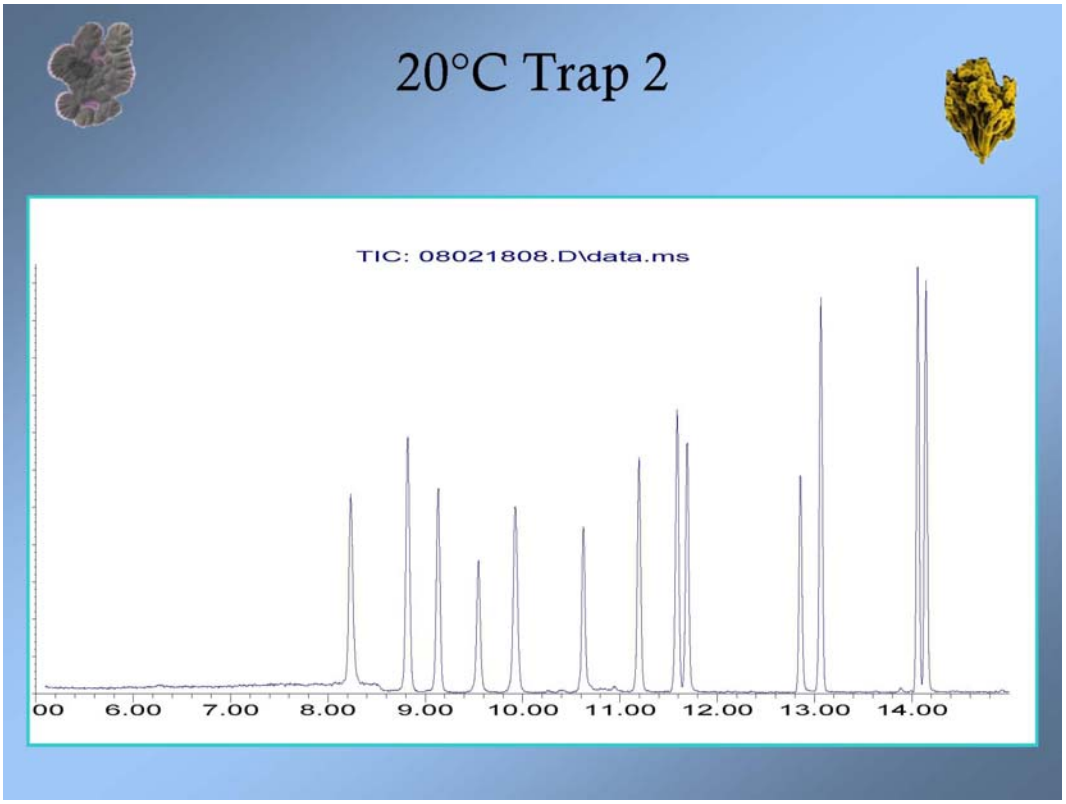
Trap 1	Cooling Temp (°C)	-160	Glass beads
	Desorb Temp (°C)	20	
	Desorb Flow (mL/min)	80	
	Desorb Time (min)	4	
Trap 2	Cooling Temp (°C)	20	Tenax
	Desorb Temp (°C)	200	
	Desorb Flow (mL/min)	15	
	Desorb Time (min)	3	
Focuser	Cooling Temp (°C)	200	
	Desorb Temp (°C)	200	
	Desorb Flow (mL/min)	15	
	Desorb Time (min)	1	



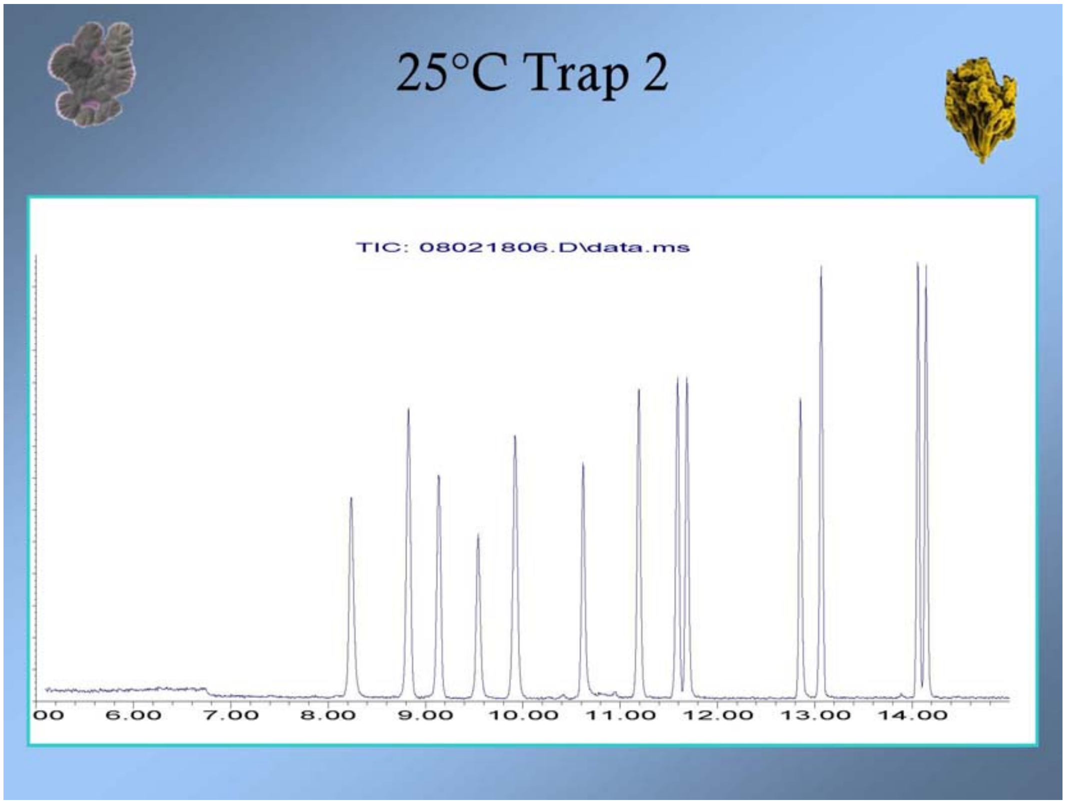
10°C Trap 2



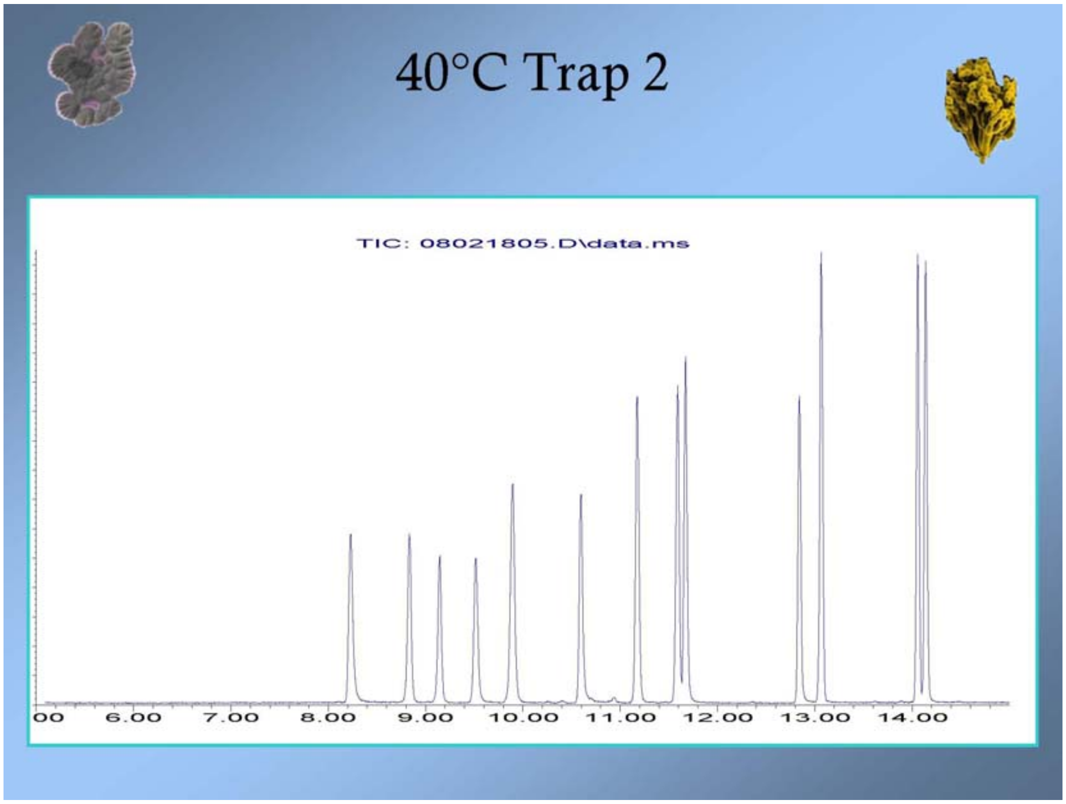
15°C Trap 2



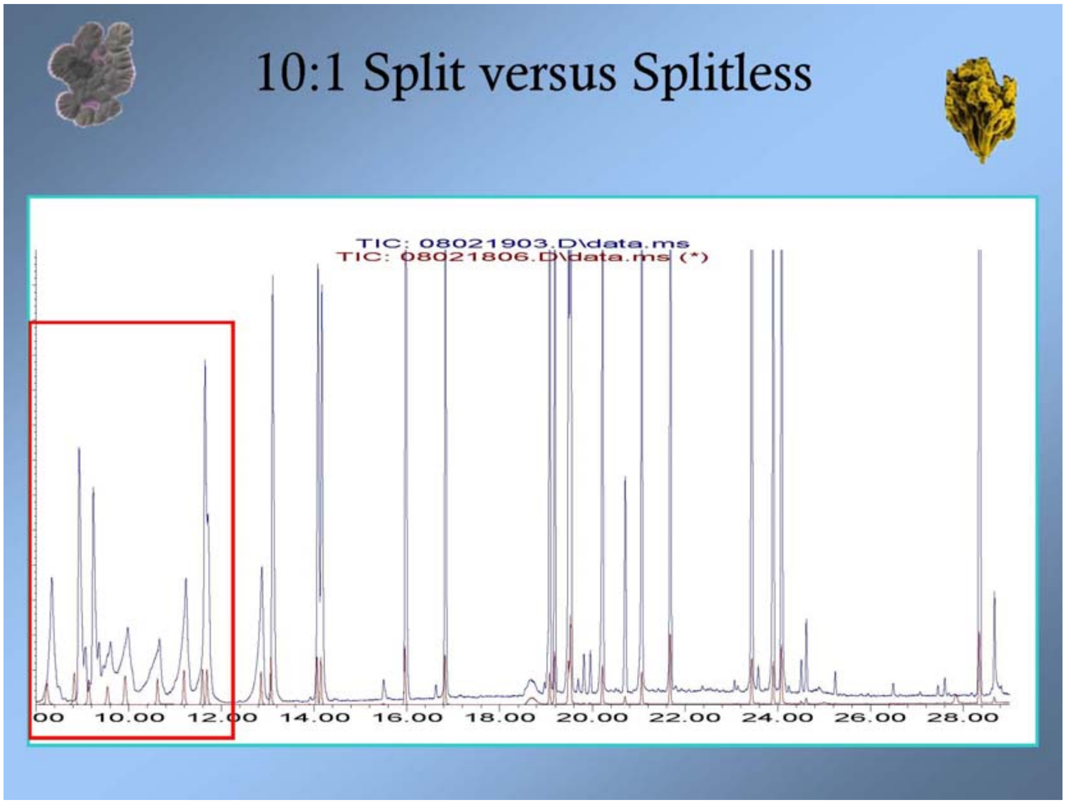
20°C Trap 2



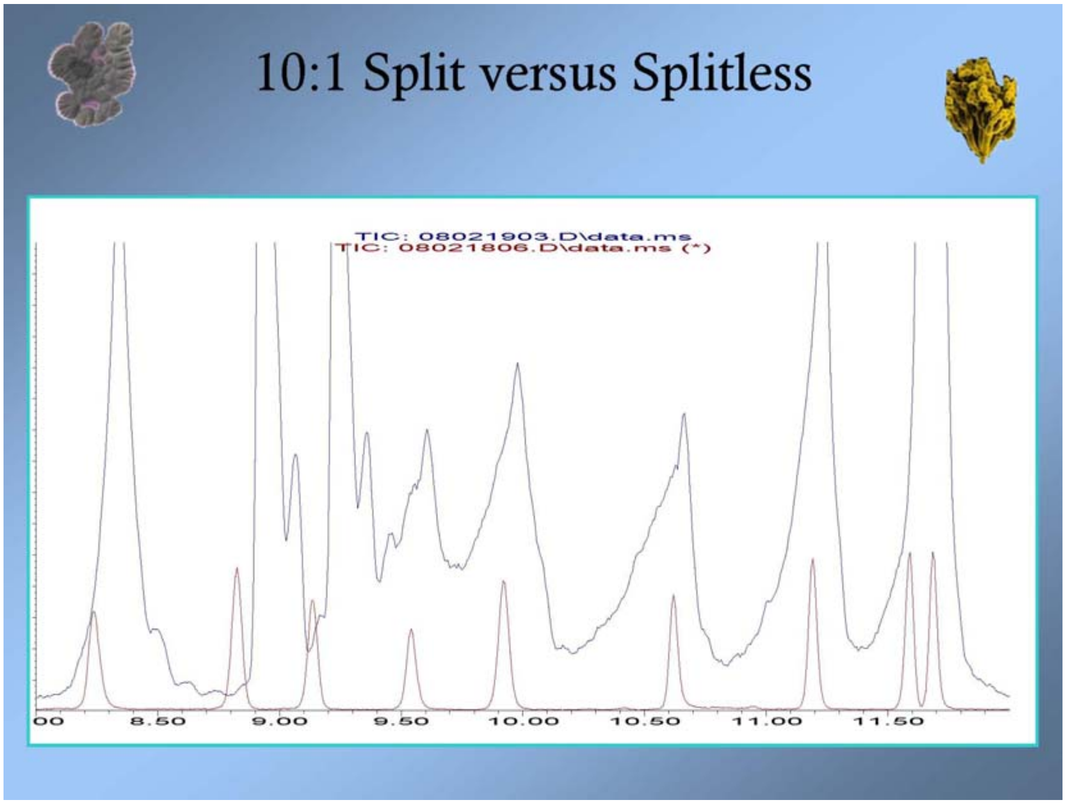
25°C Trap 2



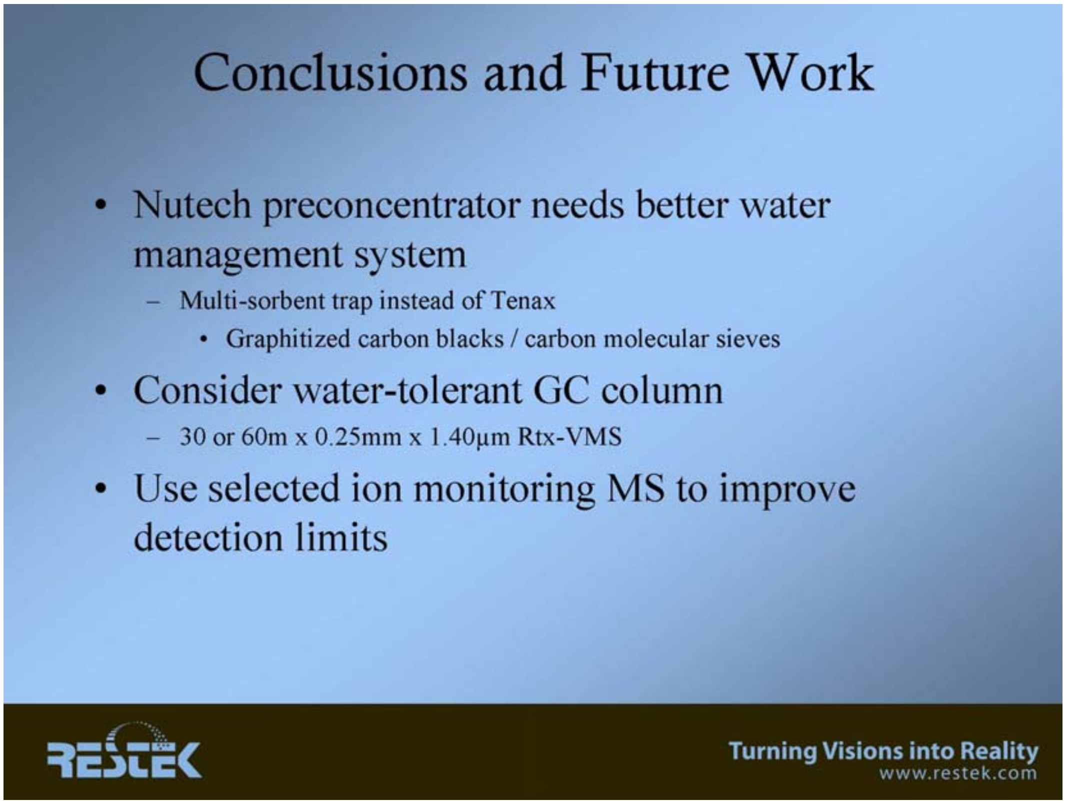
40°C Trap 2



10:1 Split versus Splitless



10:1 Split versus Splitless



Conclusions and Future Work

- Nutech preconcentrator needs better water management system
  - Multi-sorbent trap instead of Tenax
    - Graphitized carbon blacks / carbon molecular sieves
- Consider water-tolerant GC column
  - 30 or 60m x 0.25mm x 1.40µm Rtx-VMS
- Use selected ion monitoring MS to improve detection limits

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2008 NEMC Proceedings

FIELD MEASUREMENTS

Evaluation and Implementation of Sensor Technologies in a Regulatory Environment

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ABSTRACT

Environmental sensors are small, transportable analytical devices that provide data in real time, are ruggedized to withstand a wide range of weather conditions, operate remotely, acquire data continuously or on demand, and provide processed data directly to the user. One example usage of environmental sensors would be for groundwater monitoring. Environmental monitoring of groundwater is a costly process that is accomplished typically by gathering samples from wells, and then shipping them to a fixed laboratory where sample preparation and analysis is performed. This process may not yield data for months after initial sample collection. Cost could be reduced by the use of sensors placed directly in a well, thereby eliminating sample collection and shipment costs, and reducing analytical costs and delays in data acquisition and reporting. There are a variety of technical, logistical and regulatory issues that must be considered for sensors to assume a role in the environmental community for routine monitoring operations. Sensor demonstration projects can evaluate these and other issues.

INTRODUCTION

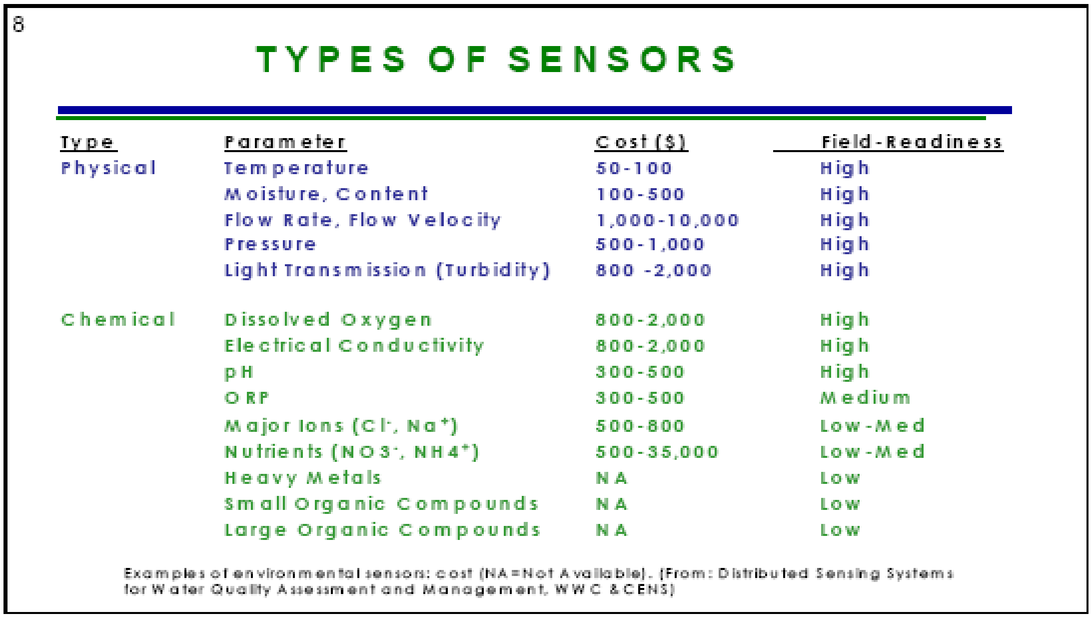
A technical/regulatory guidance document has been prepared by the Interstate Technology Regulatory Council's (ITRC) Sampling, Characterization and Monitoring (SCM) Team (www.itrcweb.org) as an overview of sensors and their use for environmental quality professionals. The value of sensors for monitoring and remediation projects is discussed, and examples of sensor technologies and a comparison to traditional data acquisition methods and instrumentation will be presented. Emphasis upon the ability of sensors to generate legally defensible data for regulatory use, and the regulatory community's perspective on use of sensors for environmental monitoring will presented along with examples of successful use of sensors for regulated sites.

An Environmental Sensor Tool (Sensor) is defined as any device that collects environmental data on water, air or soil, ideally in situ without the need to obtain a discrete sample. Sensors ideally can collect large amounts of data on a continuous basis over time, with the sensor often placed in one location. Sensors are typically small, transportable analytical devices that provide data in real time, are ruggedized to withstand a wide range of weather conditions, operate remotely, acquire data continuously or on demand, and provide processed data directly to the user. Sensors can be used as a stand-alone to replace current methods or to supplement current methods.

When faced with the novelty and assortment of sensors, limited knowledge of their capabilities and overall costs, and concerns about comparability of sensor data with results from conventional analytical methods, project managers and regulators may hesitate to incorporate on-site sensor technology into characterization and monitoring efforts. Sensors can be effective tools for meeting the responsibilities of environmental stewardship but guidance and education are needed for optimal implementation of the new technologies, and understanding and acceptance in State and Federal circles. The goal of the ITRC sensor document is to provide a floor of knowledge on sensor operations, uses, limitations, and regulatory considerations for technology implementers, data users, and regulatory representatives as an aid for selection of appropriate technologies.

TYPES OF SENSORS AND ISSUES WITH THEIR USE

Sensors for environmental applications can be organized into two broad categories: Physical and Chemical. The USEPA has recently compared issues related to these types of sensors:



TYPES OF SENSORS

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

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

Sensors for radiological and biological applications are also commercially available.

While sensors for environmental applications are generally available, there are issues related to the selection, deployment, operation and maintenance that must be considered.

Technical specifications for sensors include issues such as:

- Range
- Accuracy
- Drift
- Resolution

Other questions involving the use of sensors include:

- How often do I need to access the data?
- Where will the sensor be deployed? – Sensors are often beneficial in inaccessible locations
- How durable is the sensor for long-term applications?
- How easy is the sensor to install?
- Is power for the sensor readily available?
- What are the life-cycle costs? – is it justifiable by the greater data density?
- What are the O & M costs?

SENSOR APPLICATIONS

Some potential areas of application of sensor technologies are extremely broad and diverse. It includes issues such as the evaluation of septic systems, non-point source run-off, combined sewerage overflows, beach closures and water usage for golf course maintenance. Schematics of applications to septic systems and non-point runoff are shown below:

Figure 1: Septic Systems

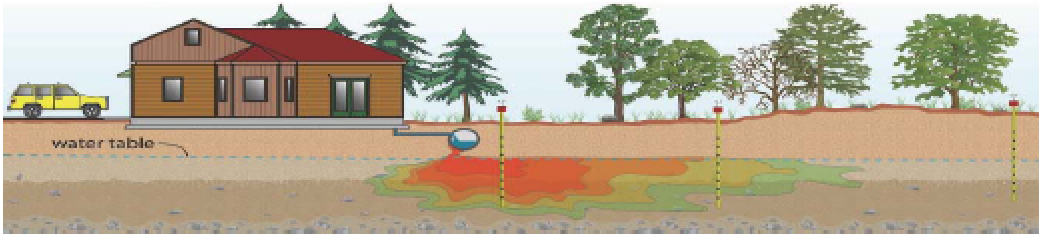
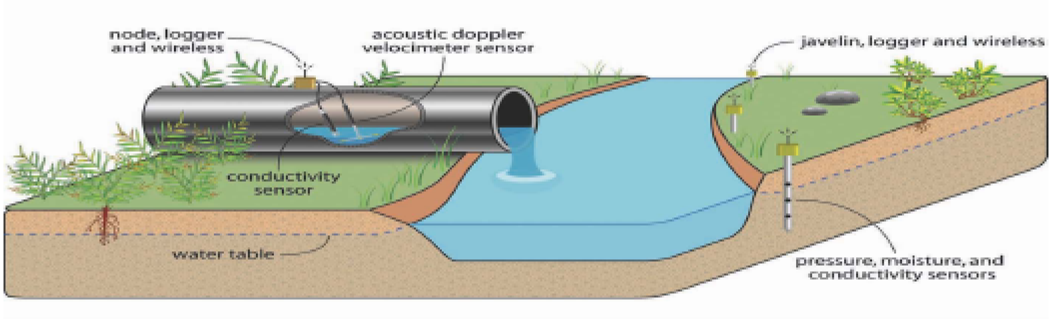


Figure 2: Non-Point Source Run-Off



Figures 1 and 2 provided with permission of the Woodrow International Center for Scholars

SENSORS AND DATA QUALITY

For any of the potential applications, an evaluation of the data quality issues comparing sensors to traditional sampling/analysis protocols must be made if the use of sensors is plausible. Some areas of consideration related to data quality include comparison of limits of detection, percentage agreement between nitrate measurements made by sensor and traditional analyses and comparison of measurements of known standards.

Another important purpose of this study is to see if the increased data density provided by sensors provides enhanced informational value to an environmental regulatory decision-maker. Even if the quality of an individual data point provided by a sensor (as determined by measures such as sensitivity, accuracy or precision) is statistically different than a comparable data point obtained by conventional analytical methodology, the use of sensors may provide useful information regarding the cumulative effect that increased sampling frequency may impart to decisions regarding analytical data.

USING SENSORS IN REGULATORY AGENCIES

A recent survey of State regulatory agencies involving the use or potential use of sensors was encouraging. The major findings of this survey were:

- There are few real or perceived statutory barriers to the use of sensors for regulatory data generation
- Most States can accommodate the potentially large amounts of data that sensors can provide
- Sensor data must be compared directly to traditional data collection approaches using the metrics described above.

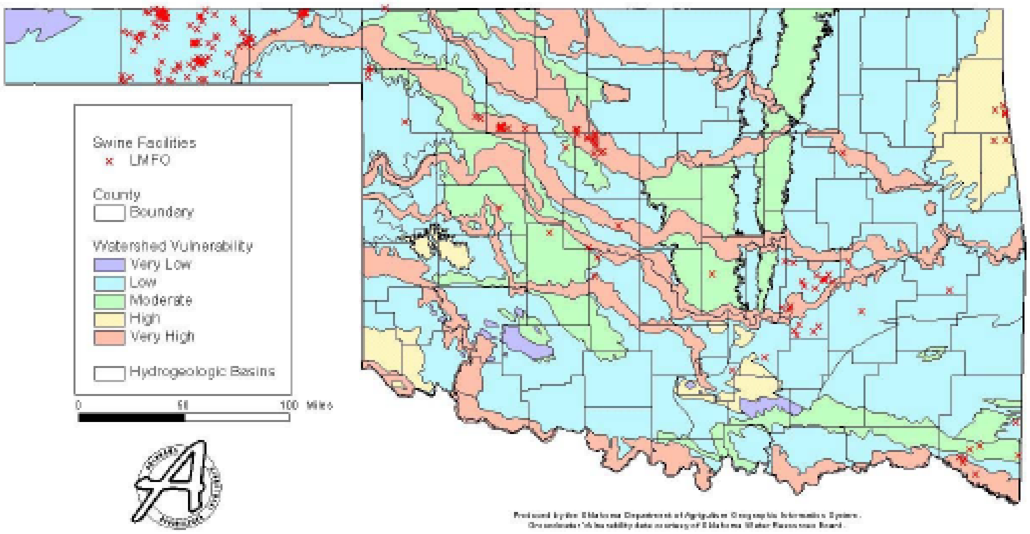
The best way to evaluate the use of sensors is through targeted research or demonstration projects. Objectives of any such project must include that the project conclusions must be of broad national interest and applicable to other types of environmental sampling situations Sensor data must of comparable quality to traditional methods, The overall costs associated with he acquisition of data by sensors must be advantageous when compared to traditional sample/analysis approaches and that the reliability of continuous sensor data collection and transmission must be assured.

Among several promising areas of sensor application is the monitoring of groundwater discharges from Confined Animal Feeding Operations (CAFOs). Oklahoma is one of several agrarian States that has numerous CAFOs for cattle, hog, and poultry farming operations. Most of these operations discharge animal wastes into a surface water lagoon. Groundwater is typically monitored around these lagoons with a series of wells consisting of 1 upgradient and 2 downgradient locations. The monitoring operation is currently performed manually using contract labor to obtain the samples, which are then transported to a fixed laboratory for analysis once each year.

The potential for nitrate pollution due to excessive seepage from the bottom of lagoons is enormous. Due to financial constraints, most sites are only sampled and tested annually. The map shown below indicates the scope and potential of this problem due to hog operations in OK:

Swine LMFO's and Groundwater Vulnerability in Oklahoma

March, 2001



Produced by the Oklahoma Department of Agriculture Geographic Information System.
Groundwater Vulnerability data courtesy of Oklahoma Water Resources Board.

Ten percent of 790 wells located near CAFOs in OK showed levels of nitrate above the regulatory limit of 10 mg N/L during the 2001 annual sampling episode. Due to the limited frequency of sampling, a very real potential exists to miss contamination caused by groundwater flux from a significant event such as heavy rainfall. Decisions regarding the operational viability of these CAFOs must be made based on the data available; if high readings occur, quarterly sampling is commenced. This limited amount of information may compromise decision-making and exacerbate existing problems, delaying remediation before issues are identified and defined.

Flush-out events that result from heavy rainfall may be missed with the current annual sampling practice. Continuous recording sensors are the most cost effective and practical way of recording this relatively transient event, providing early identification of potentially harmful pollution. If sensors prove to be a viable option for CAFOs, costs for manual sampling and laboratory testing could potentially be reduced or eliminated.

SUMMARY

Important take-home messages about the potential for the use of sensor technologies in environmental applications are:

- Sensors offer a new way to measure environmental contaminants
- Sensors are an adjunct to, not a direct replacement for, traditional measurement systems
- Sensors can provide an "early-warning" of environmental problems before they become severe
- The life cycle cost of sensors may be less than traditional measurement systems
- Most States will allow the use of sensors if data quality concerns are successfully addressed

- Data collected by sensors can be as selective, sensitive and accurate as those obtained by traditional means
- Sensors need to be "proven" via field research pilots/demonstration studies

ACKNOWLEDMENTS

This work is the collective product of the members of the Interstate Technology and Regulatory Council, Sampling, Characterization and Monitoring Team.

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EVALUATION AND IMPLEMENTATION OF SENSORS IN A REGULATORY ENVIRONMENT

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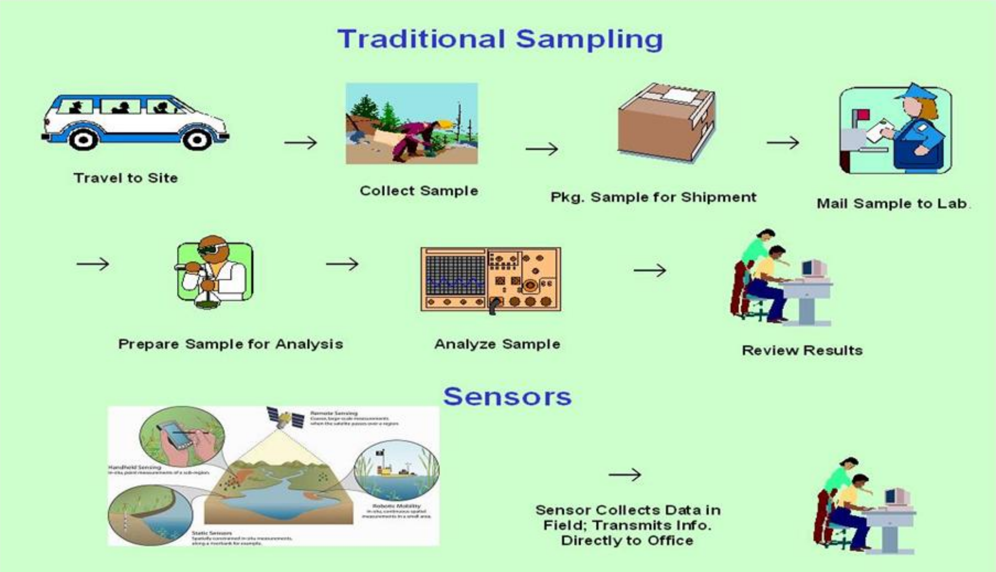
609-292-4945

COMPARISON OF PROCESSES TO COLLECT ENVIRONMENTAL DATA



Traditional Sampling

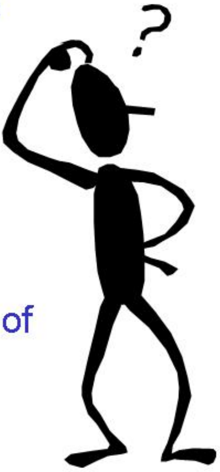
Travel to Site → Collect Sample → Pkg. Sample for Shipment → Mail Sample to Lab. → Prepare Sample for Analysis → Analyze Sample → Review Results

Sensors

→ Sensor Collects Data in Field; Transmits Info. Directly to Office

WHAT IF?

- it was possible to get real-time, continuous environmental data without having to physically obtain a sample
- What are the benefits of this type of data?
- What types of applications would this type of information be useful for?
- What are some of the regulatory concerns regarding the use of sensors?



WHAT DO I MEAN BY"SENSOR" (FOR ENVIRONMENTAL WORK)?

- A sensor is any device that collects environmental data on water or soil in situ without the need to obtain a discrete sample. Sensors collect large amounts of data, potentially on a continuous basis over time, with the sensor often placed in one location.

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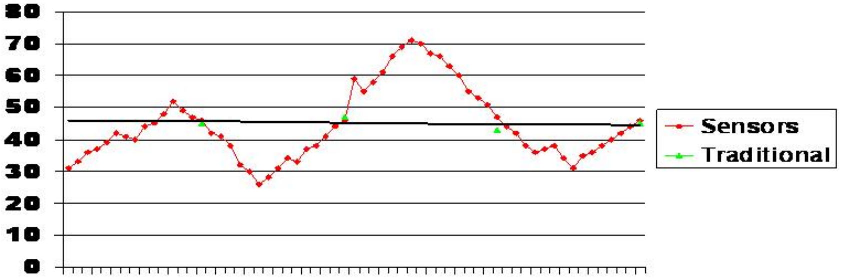
SENSORS/CAR ANALOGY

- These “car sensors help the driver <u>make better decisions</u>
- **Speedometer**
    - Prevent getting a ticket for speeding
  - Fuel gauge
    - Prevent walking for gas
  - Tachometer
    - Gauge most efficient use of engine speed

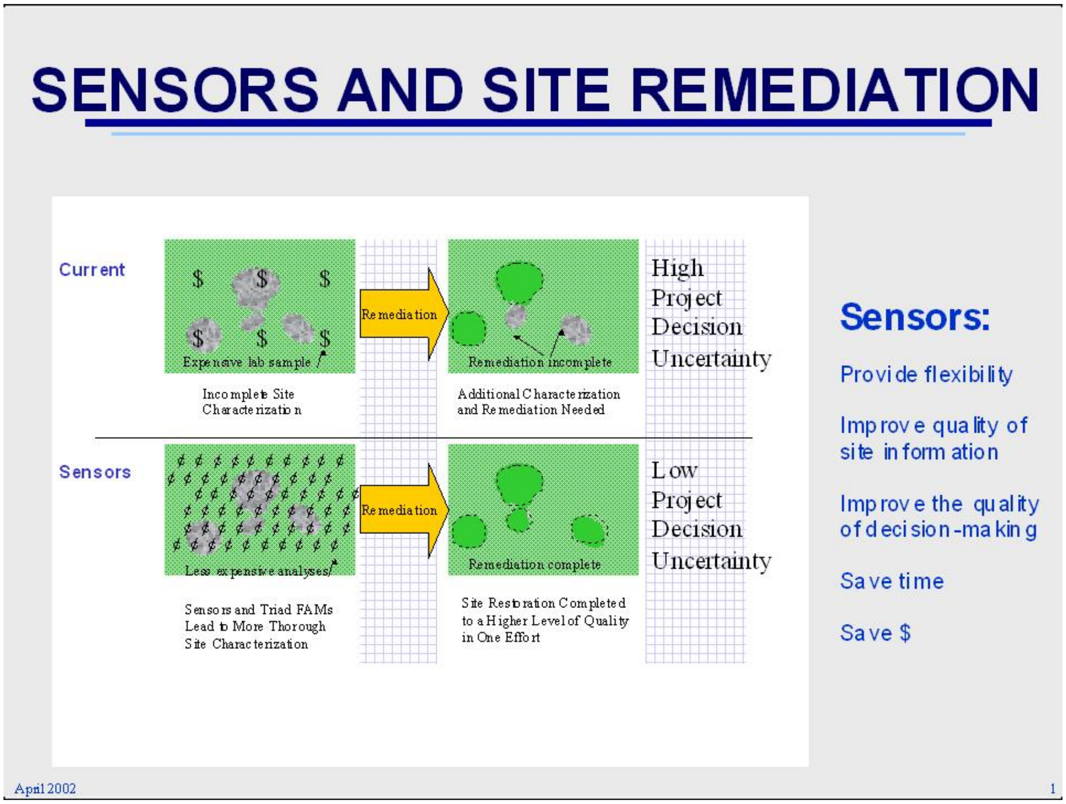
- Sensors can provide similar help with environmental decision-making

SENSORS VS. TRADITIONAL DATA COLLECTION



Traditional sampling and analysis methods only collect a limited amount of data; this can miss trends over time

Sensors gather much more data, providing useful information on temporal variations in contaminant levels that can be clearly defined



SENSORS AND SITE REMEDIATION

Sensors:

Provide flexibility

Improve quality of site information

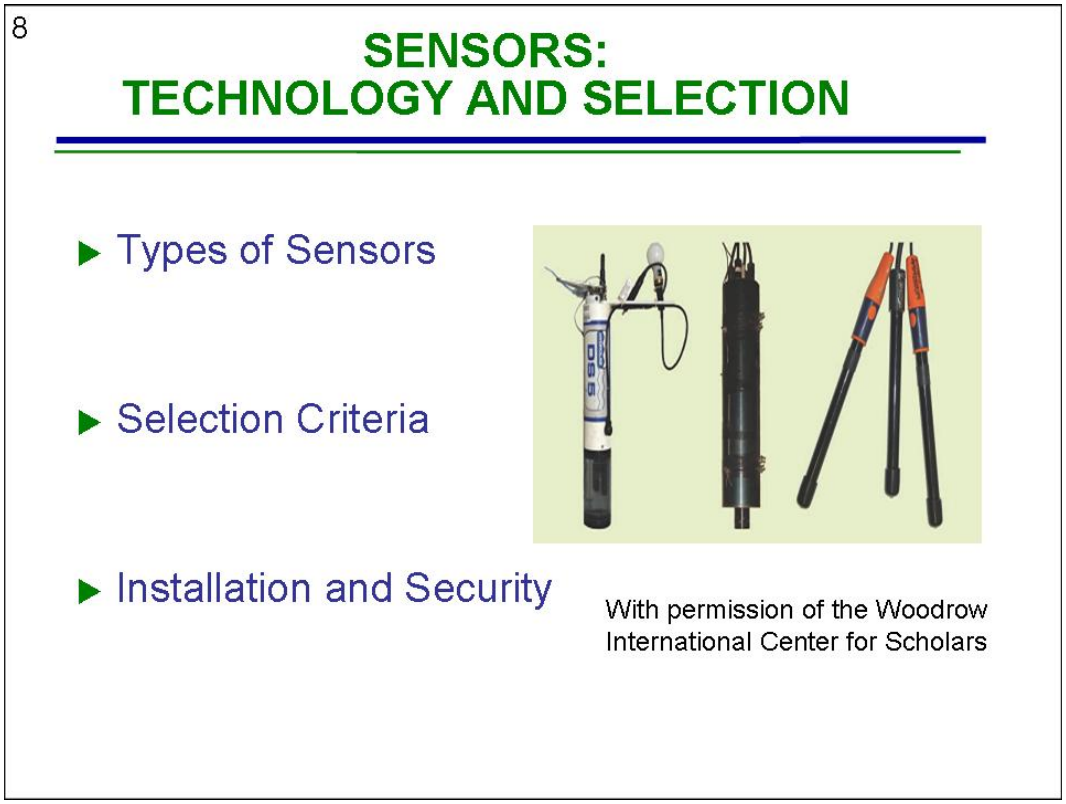
Improve the quality of decision-making

Save time

Save $

April 2002

1



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SENSORS: TECHNOLOGY AND SELECTION

- Types of Sensors
- Selection Criteria
- Installation and Security

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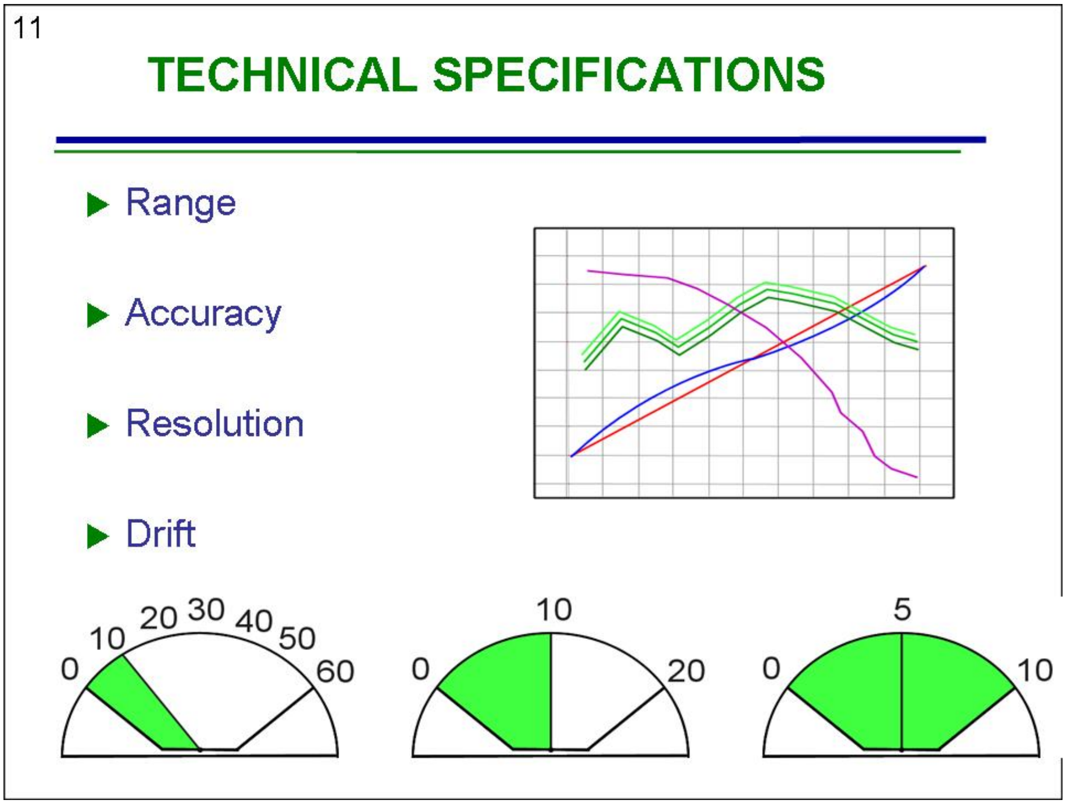
TYPES OF SENSORS

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

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

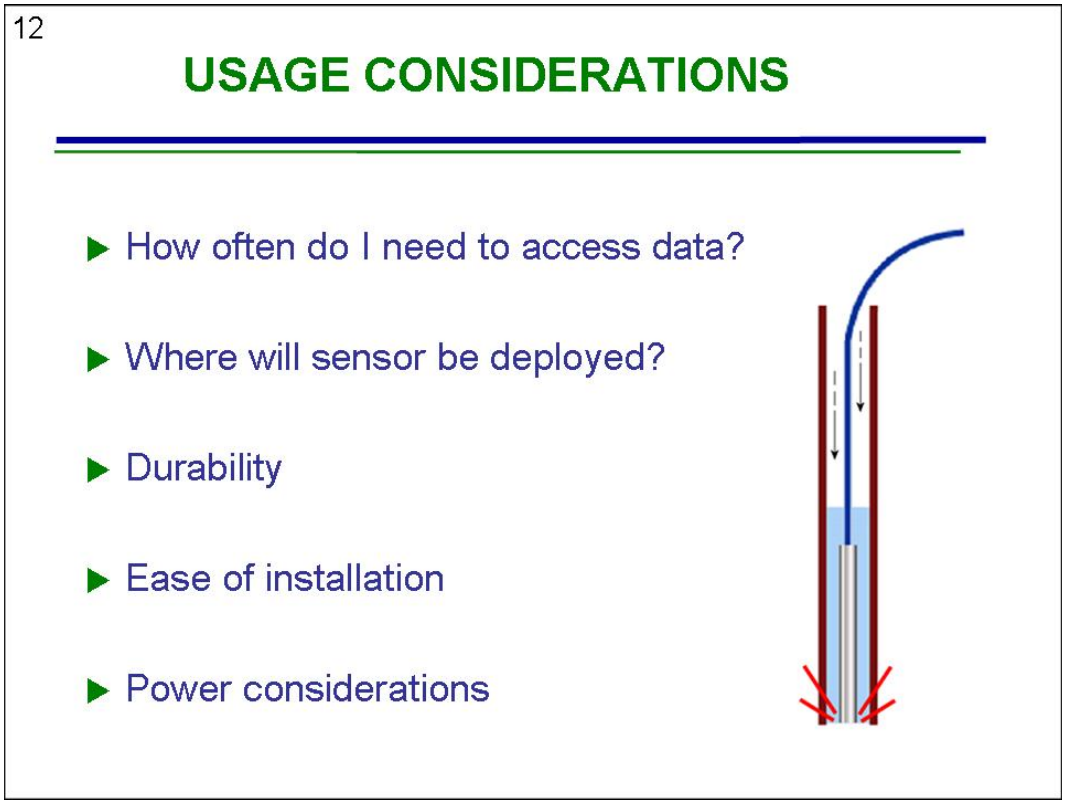
SELECTION CRITERIA

- Technical Specifications
- Usage Considerations
- Capabilities
- Maintenance & Operation
- Cost



TECHNICAL SPECIFICATIONS

- Range
- Accuracy
- Resolution
- Drift



USAGE CONSIDERATIONS

- How often do I need to access data?
- Where will sensor be deployed?
- Durability
- Ease of installation
- Power considerations

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CAPABILITIES

- Built-in datalogging
- Automatic alarming & control
- Portable vs. Dedicated
- Telemetry/wireless capable
- Web based control or data access
- Software

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MAINTENANCE & OPERATION

- Calibration
  - How is it done?
- Service
  - Cleaning
  - Changing desiccant

→ To Factory?

- In the field?
- In my lab?
- Must return to factory?
- How often????

COST CONSIDERATIONSS

- What are the Costs?
  - Initial purchase price
  - Lifecycle costs must be evaluated
  - Are they justified by the greater data density?
- What are the O&M Costs?
  - Installation
  - Calibration
  - Maintenance
  - Training

AREAS OF APPLICATION: SEPTIC SYSTEMS

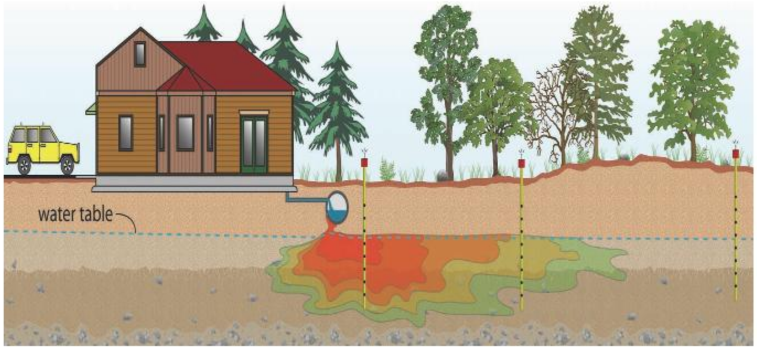

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Illustration of a sensing system used to monitor aqueous contaminants in soil and groundwater. Sensors embedded in the soil and groundwater monitor a chemical plume spreading from a source, such as a septic tank. If concentrations become too high, the system generates an alert. *Illustration: J. Fisher, UC Merced.*

Malfunctions are unpredictable & detrimental effects slow to accumulate

Temporal data provides info. on wastewater composition

“Meter Readers” could monitor septic systems

AREAS OF APPLICATION: NON-POINT SOURCE RUNOFF

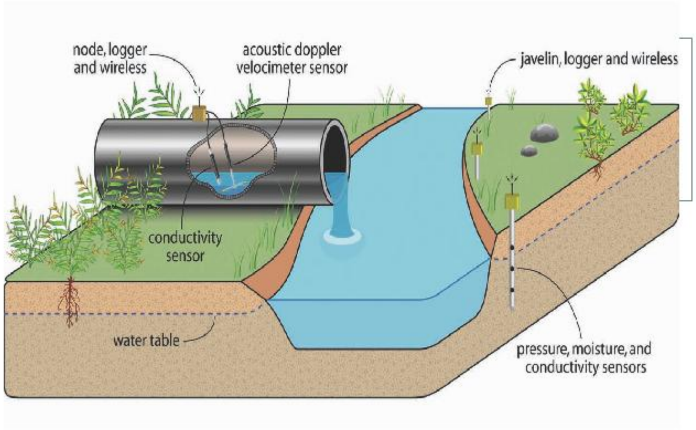

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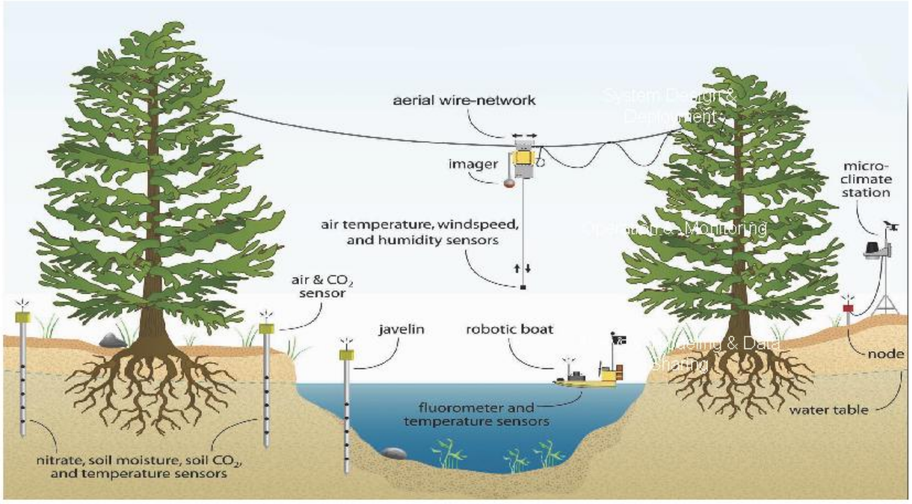
Illustration of hypothetical non-point source runoff drain and javelin-based monitoring system Illustration by J. Fisher U. Merced

MULTI-SCALE SENSOR SYSTEM



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CURRENT SENSOR ACTIVITY

- Commercial marketplace is booming
- Extensive academic and commercial research
- EPA
  - Strategic Plan 2006-2011: Goal 4
- NSF
  - National Ecological Observatory Network (NEON)
  - Sensors for Environmental Observatories report: 2006
- Interstate Technology Regulatory Council (ITRC)

SENSOR IMPLEMENTATION HURDLES

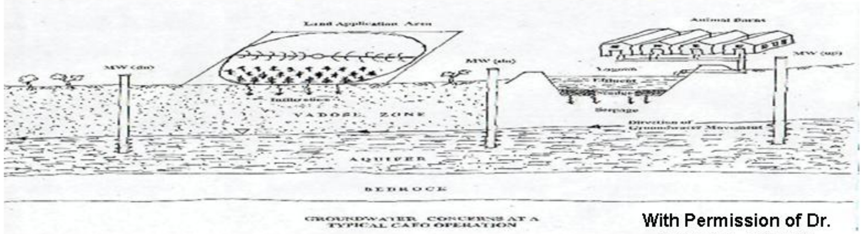
- Do State or Federal regulations prohibit the use of sensors?
  - ITRC State survey shows no real or perceived regulatory barriers
- Can data management and storage issues be addressed?
  - Most organizations can handle the transmission and storage of large amounts of sensor data
- Can sensor data be proven to be equivalent to traditional methodologies?
  - We need to conduct pilot studies where sensors are directly compared to traditional data acquisition systems

POTENTIAL SENSOR RESEARCH PILOTS

- Groundwater monitoring in NJ
  - Evaluate anthropogenic nitrate input above 10 ppm DW std.
- TCE Plume Delineation at Andrews AFB
  - In conjunction with ESTCP, use ORP, conductivity and pH sensors as surrogates to help define extent of TCE plume
- CAFOs in OK
  - Effluents from animal feeding operations to GW and DW sources

SENSOR RESEARCH: CAFOs

- CAFO = **C**onfined **A**nimal **F**eeding **O**peration
- CAFOs discharge to surface water lagoons; $(NO3)^-$ seepage a concern
- Monitoring of wells upgradient (1) & downgradient done annually due to high labor and lab. costs
- Contamination due to groundwater flux from heavy rainfall may be missed



GROUNDWATER CONCERNS AT A TYPICAL CAFO OPERATION

With Permission of Dr. J. Shirazi, OK DOA

WHAT THE CURRENT CAFO DATA SHOWS

- Widely varying (NO3)$^-$-N levels; samples taken every 6-12 months from 2000 - 2007:
  - #1: 0.02 - 0.36 mg/L
  - #2: 0.2 - 100
  - #3: 0.03 - 19.39
  - #4: 0.4 - 142

- Data sometimes taken when wells as “dry”
- Sparse and widely variant data makes any to conduct

SENSOR CAFO RESEARCH PROJECT

- Deploy nitrate sensors at several OK CAFO sites in 2008
- Collect data for 9-12 months
- Compare results and costs to traditional methods of collection and analysis
- Publish documents/present talks describing study results

SOME TAKE-HOME MESSAGES

- Sensors offer a new way to measure environmental contaminants
- Sensors are an adjunct to, not a direct replacement for, traditional measurement systems
- Sensors can provide an “early-warning” of environmental problems before they become severe
- The life cycle cost of sensors may be less than traditional measurement systems
- Most States allow the use of sensors
- Data collected by sensors can be as selective, sensitive and accurate as those obtained by traditional means
- Sensors need to be “proven” via field research pilots/demonstration studies

Addressing the Misconceptions About QA/QC in Triad Projects

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ABSTRACT

The Triad approach addresses the uncertainty associated with site heterogeneity by using field based measurements to assess, generally in real-time or near real-time, the representativeness of samples and sampling strategies. By using predetermined yet flexible sampling protocols (proscribed in the dynamic work strategy), the site investigation converges on the sampling density necessary to reduce the conceptual site model (CSM) uncertainty to acceptable levels that support the site decisions the project was designed to address. Analytical uncertainty is also assessed and controlled to the level necessary to support site specific decisions. All Triad projects have Quality Assurance Project Plans.

Precision and accuracy are very important DQOs with any project. All data used to support site decisions must be of defined quality. There has long been a perception that field measurements can not meet precision and accuracy requirements to provide data of adequate quality for various site decisions (i.e. remedial design/selection, risk assessment). The Triad approach addresses precision and accuracy in terms of whether a technique or system provides data of defined quality which is adequate to support decisions, often in real-time or near real-time. There are many different field measurement technologies available today, all of which can provide data of known quality as long as the analyst performs proper QC procedures. Even relatively qualitative data such as the GeoProbe membrane interface probe, immuno-assay and colorimetric measurements require calibration and periodic calibration check samples to insure they are operating within acceptable precision and accuracy criteria.

In Triad projects, data are generally used in real-time, as often as immediately after the completion of the analysis, to make decisions about the site investigation. It is critical that the field analyst use the QC data as it is collected to access data quality in real-time and to alert the on-site project manager to any QC problems encountered. It is true that data are used in Triad projects to make decisions before third party validation occurs. This is due to the immediate use of the data by the core technical and decision teams. However, this does not mean that the proper QC procedures are not followed or that third party validation is not possible. Field measurement technologies produce data sets that are often validated after the completion of the field portion of the project. The level of QC and data validation required are project specific and are key elements in the systematic planning portion of Triad projects.

A hallmark of Triad project uncertainty management is the use of multiple data streams to evolve the CSM. For example, collecting high resolution geologic data and high resolution contaminant distribution data often allow a very detailed understanding of the contaminant distribution relative to groundwater flow. The convergence of the collaborative data sets adds to their ability to manage project decision uncertainty. It should be remembered that the objective of QA/QC procedures for any project is to insure that data quality is adequate to support project specific decisions. Although not a traditional form of project QC, the convergence of collaborative data sets is a strong component of all Triad projects that is used to manage decision uncertainty.

This paper will discuss the implementation of QA/QC procedures during a recent Triad investigation that used semi-quantitative data (MIP) and both on site quantitative (EPA Method 8265) and off-site quantitative (EPA Method 8260b) data to address uncertainty in the CSM.

Quality Assurance/Quality Control and the Triad Approach

2008 National Environmental Monitoring and
Analytical Conference

William M. Davis
Triad Environmental Solutions, Inc.

QA/QC and the Triad Approach

Overview

- **Definitions**
- **Planning for QA/QC: How much is enough?**
- **Executing the QA/QC program**
- **How is QA/QC is different in a Triad project?**
- **Summary**

QA/QC and the Triad Approach

Definitions continued:

Validation: confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. In design and development, validation concerns the process of examining a product or results to determine conformance to user needs.

Verification: confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. In design and development, verification concerns the process of examining a result of a given activity to determine conformance to the stated requirements for that activity.

PARCC: Precision, Accuracy, Representativeness, Comparability Completeness

Source: US EPA 2002, "*Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8)*"

QA/QC and the Triad Approach

Planning for QA/QC: How much is enough?

- QA/QC are addressed during **systematic planning** & address specific DQO requirements!!!
  - This includes:
  - Selection of methods with appropriate LOD, selectivity…
  - Specifying QC acceptance criteria to meet project objectives
  - Level of verification/validation required
- QA/QC are documented in the **Dynamic Work Strategies WP**; this includes an integrated or stand alone QAPP!!!
- QC (and some QA) are executed, documented and reported **during field execution**
- QA is reported in the data verification/validation report in the **final project report**

QA/QC and the Triad Approach

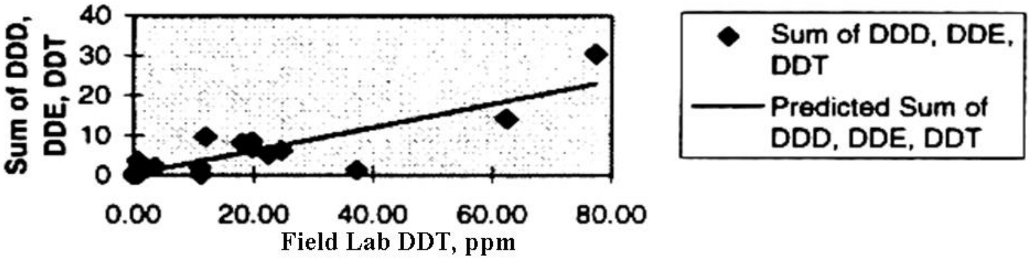
Planning for QA/QC: How much is enough?

- Semi-quantitative methods require a QA/QC plan!

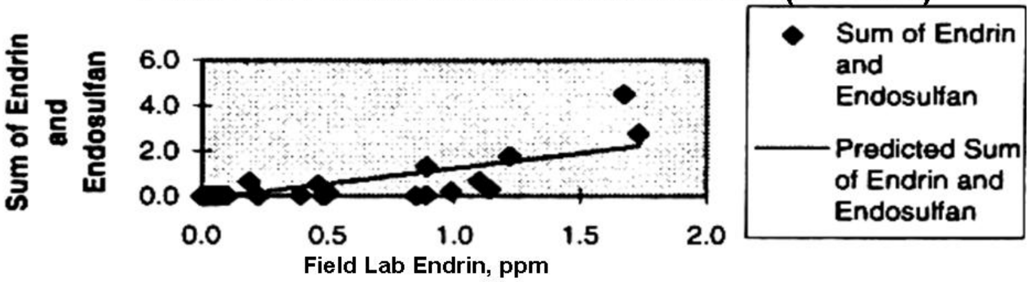
X-ray Fluorescence, MIP and Immuno Assay system checks
w/ specified performance criteria

Pre-deployment data comparability study Immuno Assay

Field Lab DDT Regression Analysis (R2 = .79)

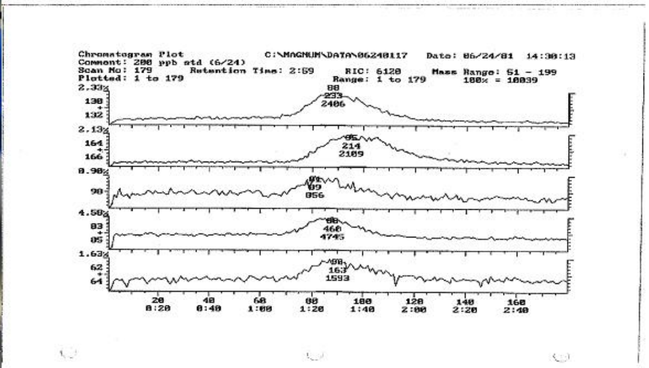


Field Lab Endrin Regression Analysis (R^2 = .60)

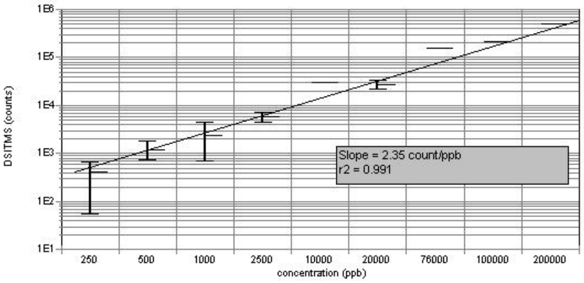


Tri-Corders Environmental, Inc.

MIP/DSITMS Calibration

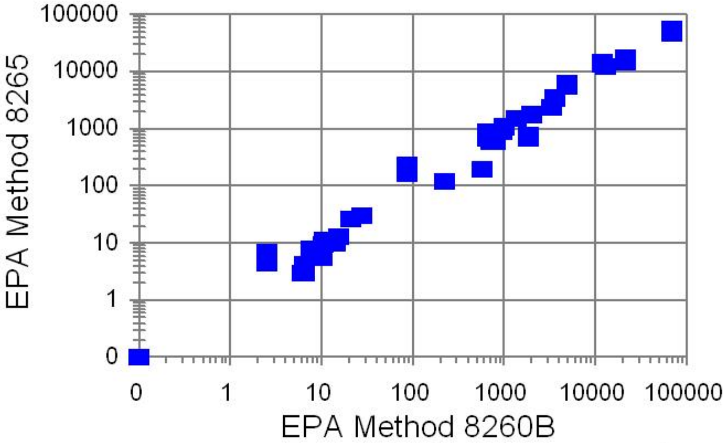


```
Chromatogram Plot          C:\MAGNUM\DATA\06240117   Date: 06/24/01   14:30:13
Comment: 200 ppb std (6/24)
Scan No: 179        Retention Time: 2:59    RIC: 6120       Mass Range: 51 - 199
Plotted: 1 to 179                          Range: 1 to 179    100% = 10039
```



Slope = 2.35 count/ppb
r2 = 0.991

Data Collaboration

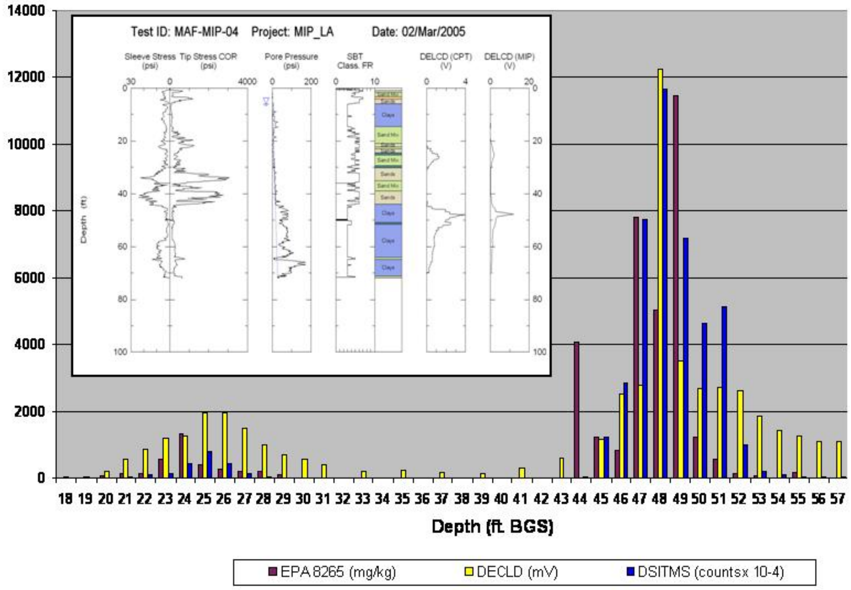


Split sample results EPA Method 8265 and EPA Method 8260B

EPA 8265 = 0.75 EPA Method 8260B + 93; r^2 = 0.98, n = 207

Data Collaboration

MIP04 MIP and EPA Method 8265 C0llaboration



QA/QC and the Triad Approach

Planning for QA/QC: How much is enough?

- Field deployed quantitative methods require a QA/QC plan!

The amount of QA/QC may be lower than the same method executed in the lab, it may be the same or it may be more.

McGuire AFB, NJ, 14 working days, 15 MIP, 640 analyses (234 client soil, 162 client groundwater, (244 QC samples)

Vandenberg Air Force Base, CA, 3.5 working days, 352 analyses of passive diffusion bags samples (290 client samples, 62 QC samples)

Hill Air Force Base, UT 9.5 working days, 840 analyses (609 client samples, 231 QC samples)

QA/QC and the Triad Approach

Planning for QA/QC: How much is enough?

- Verification of data required in real-time in Triad projects

  Field analyst MUST verify data
  Off-site near real time verification as require by project DQOs

- Validation can be performed in real-time or after project field execution

- Blind performance check standards for real-time validation

QA/QC and the Triad Approach

Executing the QA/QC program

“The best laid plans ……….”
You must be diligent in the execution!!!

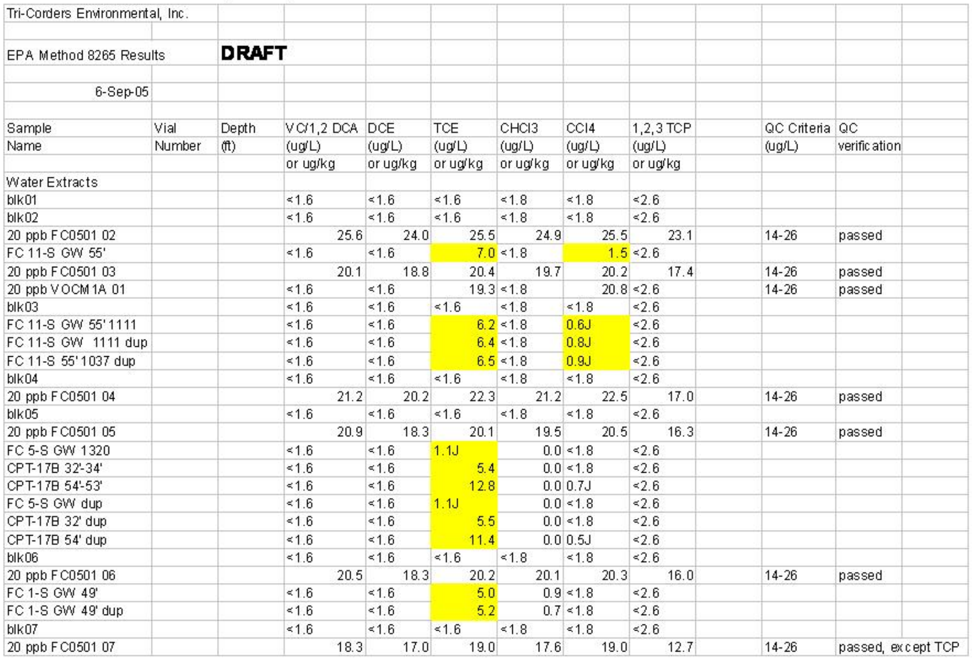
Depending on level of QA/QC to meet project objectives, your QC officer may need to review data daily during field execution.

Real-time decisions require real-time data, therefore real-time QA/QC.

Real-time and near real-time availability of QC data to decision makers.

QA/QC and the Triad Approach

QA/QC in real-time and near real-time



Tri-Corders Environmental, Inc.

EPA Method 8265 Results **DRAFT**

6-Sep-05

Sample Name	Vial Number	Depth (ft)	VC/1,2 DCA (ug/L) or ug/kg	DCE (ug/L) or ug/kg	TCE (ug/L) or ug/kg	CHCl3 (ug/L) or ug/kg	CCl4 (ug/L) or ug/kg	1,2,3 TCP (ug/L) or ug/kg		QC Criteria (ug/L)	QC verification
Water Extracts											
blk01			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
blk02			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
20 ppb FC0501 02			25.6	24.0	25.5	24.9	25.5	23.1		14-26	passed
FC 11-S GW 55'			<1.6	<1.6	7.0	<1.8	1.5	<2.6			
20 ppb FC0501 03			20.1	18.8	20.4	19.7	20.2	17.4		14-26	passed
20 ppb VOCM1A 01			<1.6	<1.6	19.3	<1.8	20.8	<2.6		14-26	passed
blk03			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
FC 11-S GW 55' 1111			<1.6	<1.6	6.2	<1.8	0.6J	<2.6			
FC 11-S GW 1111 dup			<1.6	<1.6	6.4	<1.8	0.8J	<2.6			
FC 11-S 55' 1037 dup			<1.6	<1.6	6.5	<1.8	0.9J	<2.6			
blk04			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
20 ppb FC0501 04			21.2	20.2	22.3	21.2	22.5	17.0		14-26	passed
blk05			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
20 ppb FC0501 05			20.9	18.3	20.1	19.5	20.5	16.3		14-26	passed
FC 5-S GW 1320			<1.6	<1.6	1.1J	0.0	<1.8	<2.6			
CPT-17B 32'-34'			<1.6	<1.6	5.4	0.0	<1.8	<2.6			
CPT-17B 54'-53'			<1.6	<1.6	12.8	0.0	0.7J	<2.6			
FC 5-S GW dup			<1.6	<1.6	1.1J	0.0	<1.8	<2.6			
CPT-17B 32' dup			<1.6	<1.6	5.5	0.0	<1.8	<2.6			
CPT-17B 54' dup			<1.6	<1.6	11.4	0.0	0.5J	<2.6			
blk06			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
20 ppb FC0501 06			20.5	18.3	20.2	20.1	20.3	16.0		14-26	passed
FC 1-S GW 49'			<1.6	<1.6	5.0	0.9	<1.8	<2.6			
FC 1-S GW 49' dup			<1.6	<1.6	5.2	0.7	<1.8	<2.6			
blk07			<1.6	<1.6	<1.6	<1.8	<1.8	<2.6			
20 ppb FC0501 07			18.3	17.0	19.0	17.6	19.0	12.7		14-26	passed, except TCP

QA/QC and the Triad Approach

Executing the QA/QC program

- Close communication between the analyst(s) and the on site technical project manager
- Decision strategies should address corrective actions and/or communications strategies for QC variances
- Decision strategies should also address adaptation of QA/QC during field execution as necessary

QA/QC and the Triad Approach

Executing the QA/QC program

Examples of adapting QA/QC during project:

- Accepting failure of continuing calibration check for analytes not present at site
- Increasing number of spikes or duplicates to assess site specific matrix effects
- Real-time re-sampling at a specific location to differentiate analytical, sampling and CSM uncertainty
- Others

QA/QC and the Triad Approach

How is QA/QC is different in a Triad project?

QA/QC is as important in a Triad project as it is in a conventional project.

How is QA/QC is NOT different in a Triad project?

QA/QC has the same objectives for a Triad project as with a conventional project: **managing uncertainty in the data set and therefore in project decisions**

Triad projects do the same QA/QC as conventional projects and then some!!!

QA/QC and the Triad Approach

How is QA/QC is different in a Triad project?

Field analyst is more involved with sampling and can alert field project manager to potential sampling and analytical problems in real-time or near real-time. **Leads to very complete data sets.**

Communications of all data to decision makers is rapid, allows **real-time or near real-time adaptations of QA/QC procedures** as needed.

High through put analyses allow **additional QC data collection.**

Multiple lines of data/evidence **converging to the same conceptual site model increase acceptance.**

QA/QC and the Triad Approach

Summary

QA/QC in a Triad project is required to meet the same objects as QA/QC in a conventional project

Data verification and validation often occur in real-time or near real-time

QA/QC in a Triad project are part of the process of managing data and decision uncertainty, just the same as in conventional projects

The convergence, or lack there of, of multiple lines of data to a consistent conceptual site model is a form of QA unique to Triad projects and leads to higher confidence in project decisions

QA/QC and the Triad Approach

Summary

Quality Assurance: an integrated system of management activities involving planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer.

Quality Control: the overall system of technical activities that measure the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Source: US EPA 2000, "*Guidance for the Data Quality Objectives Process (EPA QA/G-4)*"

QA/QC and the Triad Approach

Summary

QA/QC, the DQO process
and the Triad process
all have the same objectives:

Supporting sound
project decisions

Proper QA/QC planning and
execution in a Triad project
help ensure project uncertainty
is identified and managed.

QA/QC and the Triad Approach

References

- Crumbling, et al, 2004, "The Maturing of the Triad Approach: Avoiding Misconceptions", Remediation, Autumn, 2004, 81-96

- Sampling, Characterization and Analysis team page
  www.itrcweb.org
- U.S. EPA Web page, good Triad resource
  cluin.org
- Multi-agency Web site on Triad
  www.triadcentral.org

EPA Method 8330B: Data Quality Impact on the Characterization of Energetic Residues on Military Training Ranges

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ABSTRACT

In the past, very little guidance has been available for site characterization activities addressing the concentration and mass of energetic residues in military training range soils. As a consequence the characterization of energetic residues depends heavily on sampling and analysis plans adopted by different branches of the government. Experiences gained through more than 25 training range studies conducted by ERDC-CRREL and others under the SERDP (ER-1155 and ER-1481) and Corps of Engineers Distributed Source Program led to modifications of EPA Method 8330 posted as Method 8330B (http://www.epa.gov/epaoswer/hazwaste/test/new-meth.htm#8330B) in which techniques are described that allow scientifically defendable project data quality objectives to be achieved.

Energetic residues are heterogeneously distributed over military training ranges as particles of various sizes, shapes and compositions. Most energetic residues are deposited on the surface, and the highest concentrations exist at firing positions, near targets, and where demolition activities are performed. In the case of impact and demolition ranges the greatest quantities of residues are from rounds that fail to detonate as designed. To address the compositional and distributional heterogeneity associated with the distribution of particles and to obtain representative mean energetic residue soil concentrations, the sampling strategy must strive for the acquisition of samples that contain the constituents of concern in the same proportion to the bulk matrix as exists within the decision unit (sampled area, population, exposure unit). This objective has been frequently achieved with samples of mass greater than 1 kg composed of 30 or more increments that have been collected starting at a randomly selected position followed by evenly spaced locations throughout the sampling area. To ensure that the subsample taken for analysis of energetic residues is representative of the sample, the field sample must be processed thoroughly. This objective has routinely been accomplished when the entire sample was air-dried, sieved, and the less than 2-mm portion mechanically pulverized prior to splitting or sub-sampling. This procedure is especially critical for firing point samples due to the polymeric composition of the particles.

This presentation will summarize the sampling and sample processing protocols recommend in Method 8330B, highlighting their impacts on data quality and risk assessment through the application of Pro UCL.

NEMC 2008

EPA Method 8330B: Data Quality Impact on the Characterization of Energetic Residues on Military Training Ranges

Live-fire Test of 155-mm Howitzer

Titan Booster Segment Disposal

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- Defence R&D Canada - Valcartier
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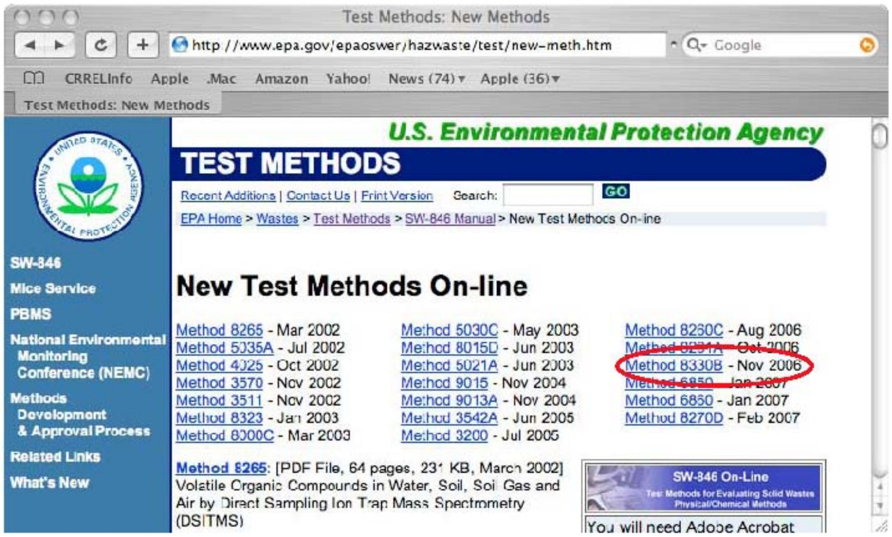
- EnviroStat
  Charles Ramsey

* Retired

Presentation Outline

- Method 8330B – Data quality
- Multi-increment sampling – Case study

  Discrete vs. MI samples –
  Upper confidence limit (UCL) of the mean



U.S. Environmental Protection Agency

TEST METHODS

New Test Methods On-line

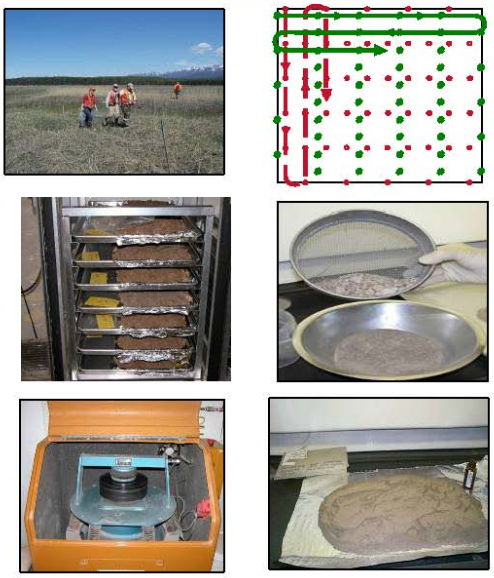
Method 8265 - Mar 2002
Method 5035A - Jul 2002
Method 4025 - Oct 2002
Method 3570 - Nov 2002
Method 3511 - Nov 2002
Method 8323 - Jan 2003
Method 8000C - Mar 2003
Method 5030C - May 2003
Method 8015D - Jun 2003
Method 5021A - Jun 2003
Method 9015 - Nov 2004
Method 9013A - Nov 2004
Method 3542A - Jun 2005
Method 3200 - Jul 2005
Method 8260C - Aug 2006
Method [illegible] - Oct 2006
Method 8330B - Nov 2006
Method 6850 - Jan 2007
Method 6850 - Jan 2007
Method 8270D - Feb 2007

Method 8265: [PDF File, 64 pages, 231 KB, March 2002] Volatile Organic Compounds in Water, Soil, Soil Gas and Air by Direct Sampling Ion Trap Mass Spectrometry (DSITMS)

You will need Adobe Acrobat

http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8330b.pdf

Method 8330B: Sampling and sample processing



Stratification of training range

Sampling strategy and design

Whole sample air drying

Whole sample sieving

Whole sample pulverization

Subsampling

Major changes to SW-846 Method 8330

- Determine analyte concentrations in the less than 2-mm size fraction in entire sample by using a #10 sieve to remove the oversize material.
- Machine grind (puck mill) soils from training ranges with high explosives for 60 s
- Machine grind (puck mill) soils from firing points and demolition areas for five 60-s cycles
- Build 10-g analytical subsamples by combining at least 30 increments of the ground field sample.
- Extract samples with 20 mL of acetonitrile on a platform shaker or cooled sonic bath.

Method 8330B addresses: Residues at Firing Points

Howitzers

Mortars

Light Anti-Tank Weapons

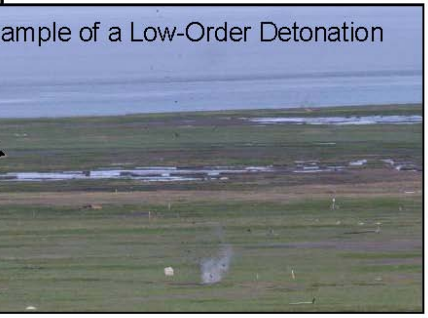
Burning of Excess Propellant

40-mm Grenades

Method 8330B addresses: Residues on Impact and Demolition Ranges: High Order, Low Order Detonations, and Duds

Example of a High-Order Detonation

High Order Detonation
- Round detonates as designed
- Metal fragments very small
- Residues deposited in sub millimeter particles

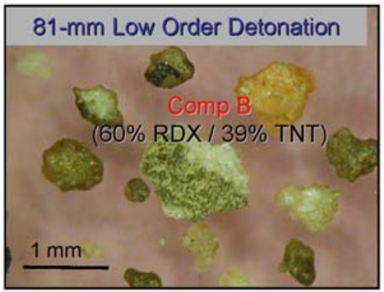


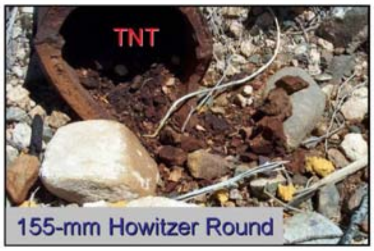
Example of a Low-Order Detonation

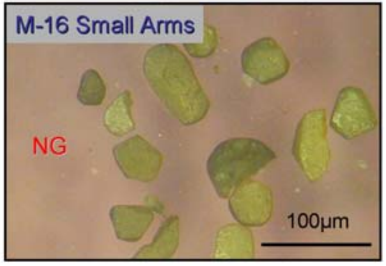
Low Order Detonation
- Round only partially detonates
- Large metal pieces remain
- Residues deposited in millimeter to centimeter particles and chunks

Propellant and High Explosive residues are deposited as particles


Fiber from105-mm Howitzer


81-mm Low Order Detonation


155-mm Howitzer Round


M-16 Small Arms

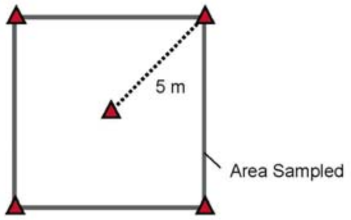
What Do We Want to Know?

- Is mass of energetic residue in area of concern sufficient to present an unacceptable risk to ground water and surface water resources? (estimated from mean concentration in source zone)
- Is mean concentration present in the exposure unit above some risk criteria for target organisms on range?

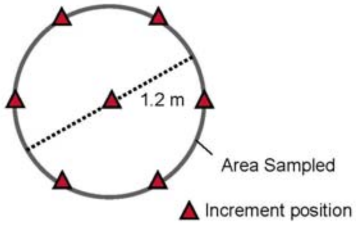
Sampling Designs

***Box & Wheel**

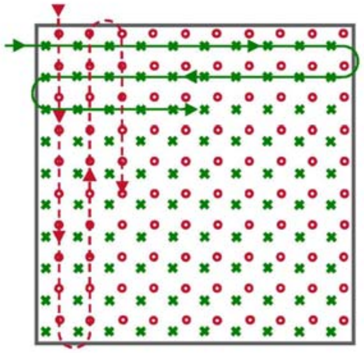
5-increment box sampling design



7-increment wheel sampling design



Multi-increment sampling design
Method 8330B



* <u>Not recommended in Method 8330B</u>

Concerns: Field Splitting and Laboratory Subsampling

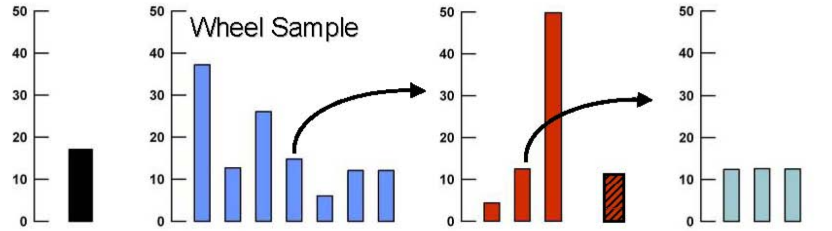
*Field splitting of wheel sample into seven portions after mixing in bowl.

*Triplicate >10-g subsamples removed in the laboratory from a moist unprocessed field sample.

* <u>Not recommended in Method 8330B</u>

Demo Range Sample

RDX (mg/kg)



Total Sample
(Mass = 702 g)

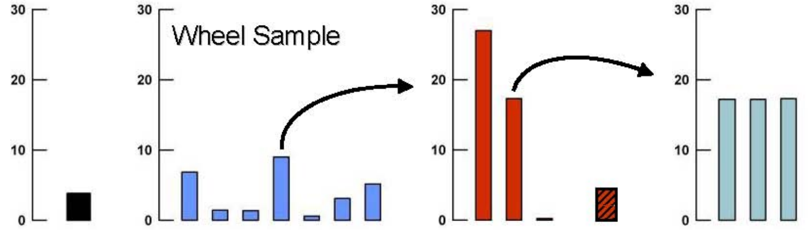
Split in Field
(7, ~100-g portions)
RSD = 62%

Laboratory
Sub-samples
(3, 10-g; 1, 61-g portion)
RSD = 105%

Analytical
Replicates
(3 analyses)
RSD = 0.7%

Firing Point Fox Sample from Ft. Richardson

NG (mg/kg)



Split in Field
(7, ~80-g portions)
RSD = 81%

Laboratory
Sub-samples
(3, 10-g; 1, 38-g portion)
RSD = 100%

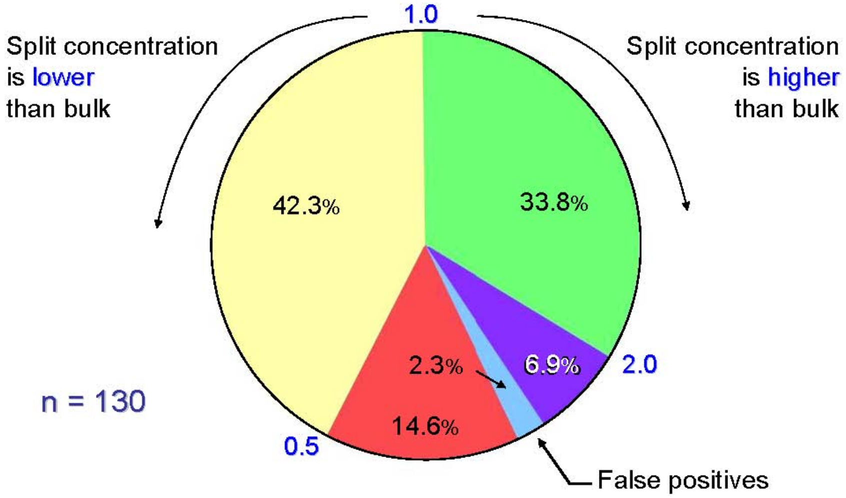
Analytical
Replicates
(3 analyses)
RSD = 0.3%

Among 20 sets of field splits of box and wheel samples **Median RSD = 43%**

Among 31 sets of triplicates **Median RSD = 62%**

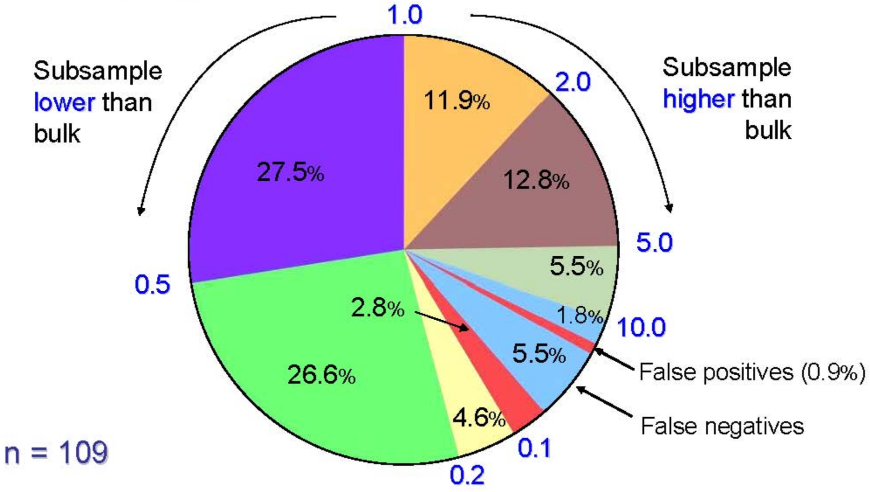
Split Sample Concentration Relative to Bulk Sample Concentration

Split sample BIAS : Wheel of fortune or misfortune?



Subsample Concentration Relative to Bulk Sample Concentration

Subsampling BIAS : Wheel of fortune or misfortune?



Multi-increment Bulk Sample and Subsample Extractions: Method 8330B

Comparison between Bulk and Average Subsample Concentration

(After 8330B Processing)

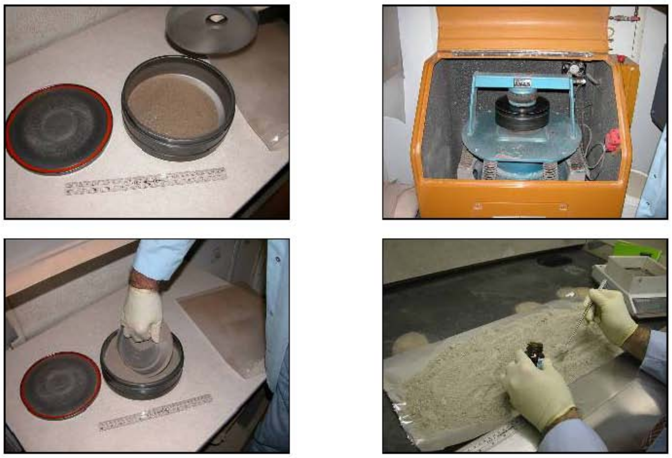
Location	Sample	Soil wt (g)	Acetone (mL)	Concentration (mg/kg)			
				HMX	RDX	TNT	2,4-DNT
	Bulk	1766	3540	2.02	11.9		4.81
FRA Demo MI-9	R1	10.0	20.0	1.98	11.7		4.58
	R2	10.0	20.0	2.00	11.6		4.92
	R3	10.0	20.0	1.98	11.8		5.22
(Demolition Range)			Ave	1.99	11.7		4.91
			Std Dev	0.009	0.090		0.320
			%RSD	0.48%	0.77%		6.53%
			RPD (Bulk vs. Rep Ave)	1.5%	1.7%		2.1%
	Bulk	1278	2560	2.76	14.3	1.56	
FRA LO# 3 MI-5	R1	10.0	20.0	2.72	14.1	1.60	
	R2	10.0	20.0	2.72	14.1	1.60	
(Impact Range)	R3	10.0	20.0	2.60	13.9	1.63	
			Ave	2.68	14.0	1.61	
			Std Dev	0.069	0.125	0.016	
			%RSD	2.59%	0.89%	1.00%	
			RPD (Bulk vs. Rep Ave)	3.1%	2.0%	3.2%	

Comparison between Bulk and Average Subsample Concentration

(After 8330B Processing)

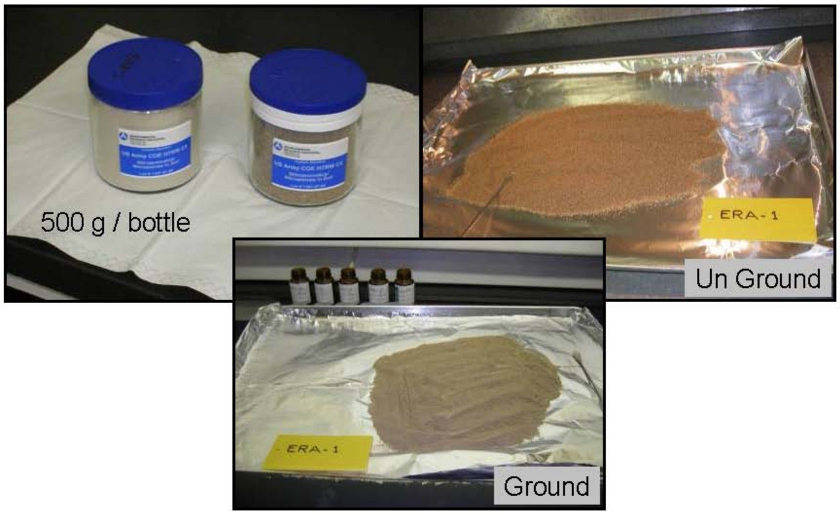
Location	Sample	Soil wt (g)	Acetone (mL)	Concentration (mg/kg)	
				2,4-DNT	NG
Ft. Richardson	**Bulk**	1196	2400		**4.21**
FP Fox	**R1**	10.0	20.0		4.00
MI-10	**R2**	10.0	20.0		5.04
	R3	10.0	20.0		4.06
(Firing Point)			Ave		**4.37**
			Std Dev		0.584
			%RSD		13.4%
			RPD (Bulk vs. Rep Ave)		**3.7%**
CFB Petawawa	**Bulk**	1935	3880	**0.964**	**2.97**
FP Juliet Tower	**R1**	10.0	20.0	0.88	2.38
140 MI-5	**R2**	10.0	20.0	1.09	2.84
	R3	10.0	20.0	1.17	3.36
(Firing Point)			Ave	**1.05**	**2.86**
			Std Dev	0.152	0.490
			%RSD	14.5%	17.1%
			RPD (Bulk vs. Rep Ave)	**8.5%**	**3.8%**

Particle Size Reduction by Machine Grinding: Are there losses ?



Minimize fundamental error due to compositional heterogeneity

Environmental Resource Associates (ERA) Performance Evaluation (PE) Material – US Army COE HTRW CX



Comparison of Mean Recoveries

Analyte	Certified Value (mg/kg)	Mean Recoveries		
		Historical	90 sec*	90 sec & 4x60 sec*
4AmDNT	0.946	72.3 ± 13.0%	91.4 ± 3.1%	85.1 ± 3.1%
2AmDNT	0.650	81.9 ± 12.9%	102 ± 1.5%	97.9 ± 2.1%
DNB	1.010	92.7 ± 11.8%	97.6 ± 1.7%	95.3 ± 2.0%
2,4-DNT	0.645	92.2 ± 14.0%	95.2 ± 1.8%	93.4 ± 2.2%
2,6-DNT	1.320	90.7 ± 15.4%	97.5 ± 1.7%	94.9 ± 1.8%
HMX	0.620	84.5 ± 15.4%	96.1 ± 3.0%	91.8 ± 2.9%
NB	1.400	88.5 ± 15.0%	83.7 ± 1.8%	80.8 ± 1.5%
2-NT (o)	1.460	91.9 ± 12.5%	98.0 ± 1.5%	94.0 ± 1.4%
3-NT (m)	1.020	96.1 ± 13.7%	91.4 ± 2.5%	89.9 ± 2.0%
4-NT (p)	1.840	92.8 ± 15.1%	93.0 ± 2.5%	90.0 ± 1.6%
RDX	0.583	88.0 ± 14.2%	87.2 ± 3.1%	84.7 ± 3.4%
TNB	0.696	87.0 ± 14.5%	99.8 ± 2.0%	96.8 ± 2.5%
TNT	0.808	82.4 ± 10.8%	95.7 ± 2.5%	93.4 ± 2.4%
NG	1.000		96.3 ± 1.3%	90.1 ± 2.8%
PETN	1.000		102 ± 4.5%	100 ± 6.1%

* Ground in puck mill

Test America / CRREL Comparison

(Post Grinding QA)

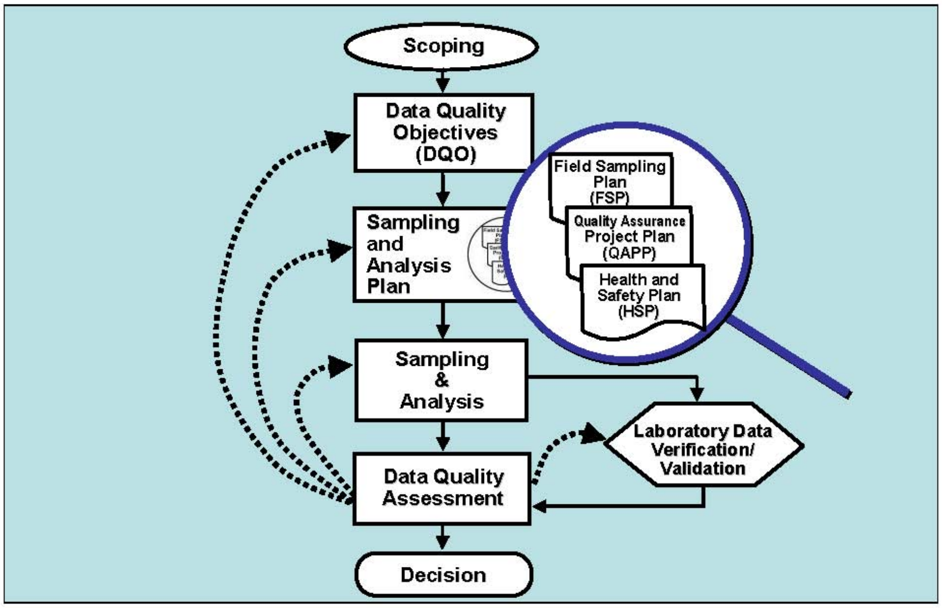
Sample	Compound	Concentration (mg/kg)		
		CRREL	TA*	TA
		HPLC-UV †	LC/MC	LC/MS/MS
LO#3 MI#5	HMX	2.19 ± 0.06	2.65	2.85
	RDX	13.0 ± 0.36	13.4	13.2
	TNT	1.14 ± 0.04	1.10	1.25
LO#3 MI#10	HMX	6.67 ± 0.09	7.7	8.39
	RDX	50.6 ± 0.20	49.4	49.7
	TNT	25.5 ± 0.12	27.7	26.0
FP Fox MI#5	NG	62.8 ± 2.16	57.3	51.5
FP Fox MI#10	NG	4.99 ± 0.16	4.42	3.99

* TA: Test America-Denver, CO

† CRREL Analyses: n = 3

Subsamples 10.0 g

Case Studies: The Decision Process



Scoping

Data Quality Objectives (DQO)

Sampling and Analysis Plan

Field Sampling Plan (FSP)

Quality Assurance Project Plan (QAPP)

Health and Safety Plan (HSP)

Sampling & Analysis

Laboratory Data Verification/ Validation

Data Quality Assessment

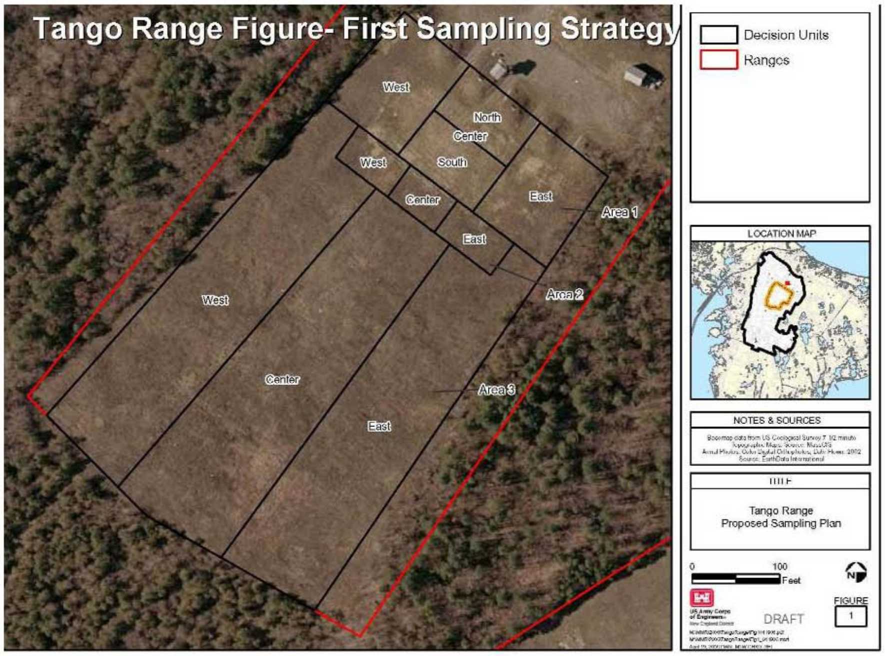
Decision

U.S. Army Corps
of Engineers

Lessons Learned During the Implementation of the CRREL Multi-Increment Sampling (MIS) Approach and Analysis by SW-846 Method 8330B

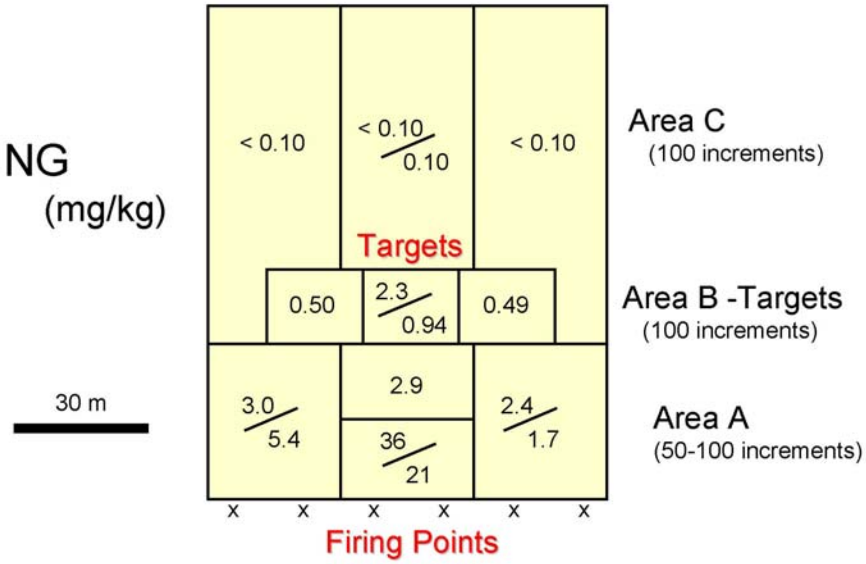
Mark R. Koenig
Senior QA Project Chemist
U.S. Army Corps of Engineers
New England District

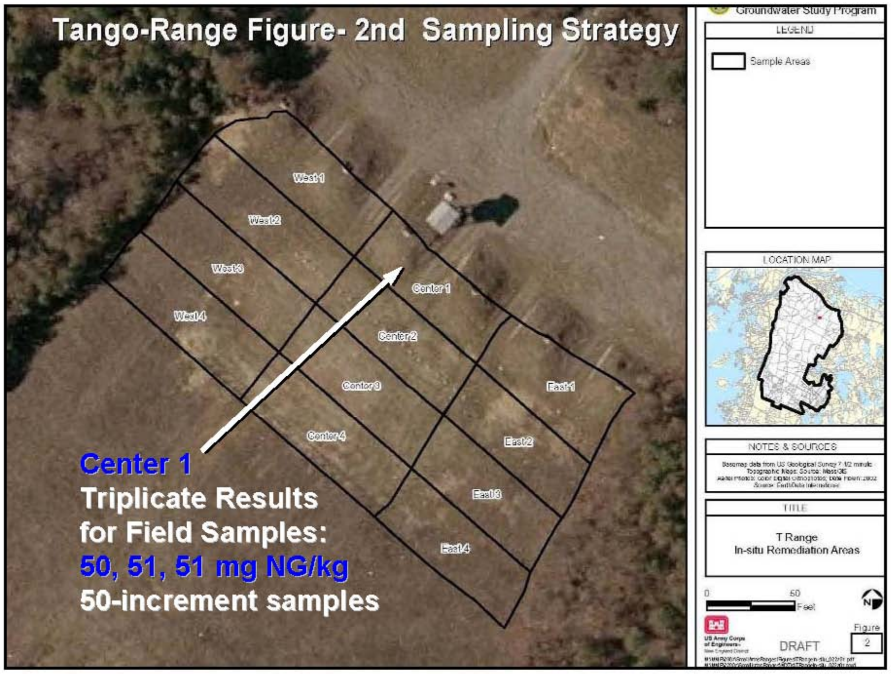
Source:
http://www.testamericainc.com/News/Events/WebinarMethod8330B.html



Tango Range Figure- First Sampling Strategy

Machine Gun Range





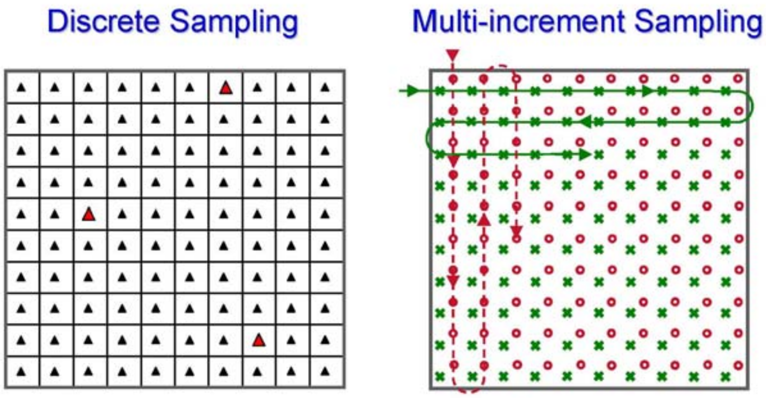
Tango-Range Figure- 2nd Sampling Strategy

Center 1
Triplicate Results
for Field Samples:
50, 51, 51 mg NG/kg
50-increment samples

Sampling Experiment

105-mm Howitzer Firing Point
Donnelly Training Area, AK

Field Sampling Experiment: Estimating mean concentrations



▲ Collection point for 100 discrete samples

▲ Typically only a few discrete samples are collected

– – → Path of travel

o ✖ Increment collection point for two separate MI samples

The CRREL Multi-Increment Sampling Tool

Features

- Fixed diameter plug
- Variable depth
- Stratified sampling
- Easy to clean

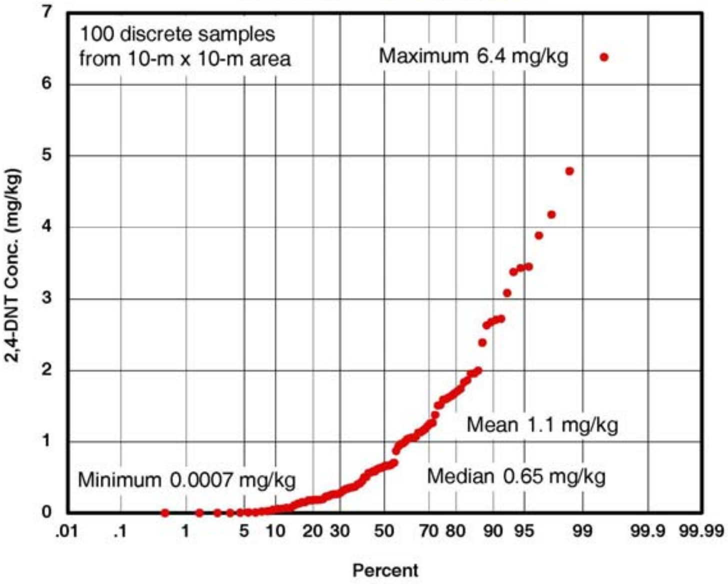
Available From:
GPL Laboratories, LLLP
7210A Corporate Court
Frederick, MD 21771
301-694-5310
<http://www.gplab.com>

Sampling Objective: What is the mean concentration of 2,4-DNT in a 10-m X 10-m area at a 105-mm Howitzer Firing Point?

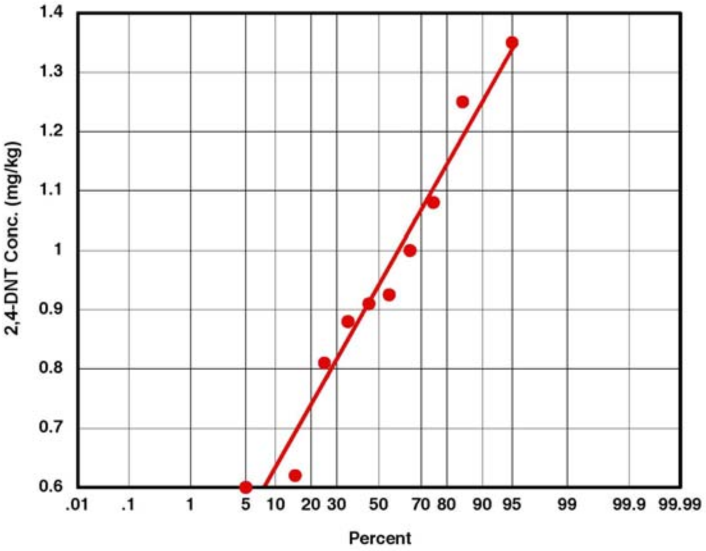
Comparison: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grid. 30-increment samples collected throughout entire 10-m X 10-m grid.

Results:	Discrete	Multi-increment
Number of Samples:	100	10
Minimum:	0.0007 mg/kg	0.60 mg/kg
Maximum	6.4 mg/kg	1.35 mg/kg
Mean:	1.1 mg/kg	0.94 mg/kg
Standard Deviation:	1.2 mg/kg	0.24 mg/kg
Median:	0.65 mg/kg	0.92 mg/kg
Distribution:	Skewed	Normal

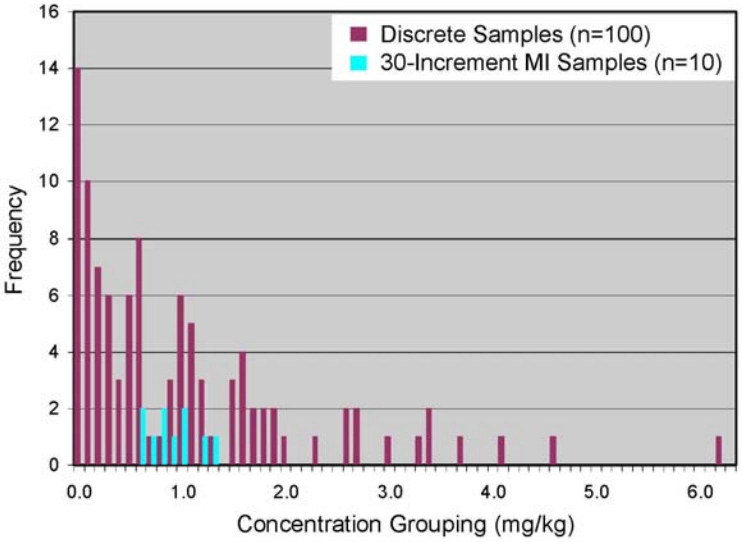
Normal Probability Plot:
100 Discrete Samples



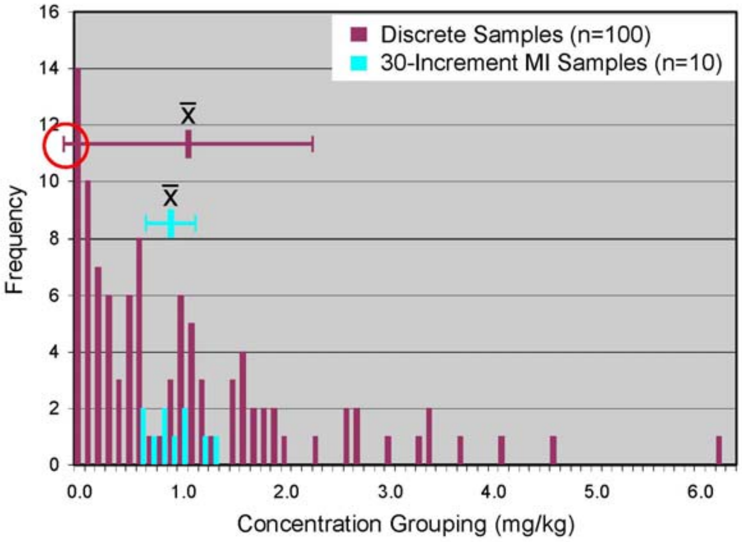
Normal Probability Plot:
Ten 30-Increment Samples



Distribution of 2,4-DNT Concentrations



Distribution of 2,4-DNT Concentrations



95% UCL – Mean 2,4-DNT Concentration (mg/kg)
10 x 10-m area – Firing point Mark

100 Discretes (1 x 1-m sub grids)

– Mean	1.1
– Median	0.65
– Min	0.0007
– Max	6.4
– 95% UCL w/ ProUCL	1.3

10 Multi-increment Samples (30-incr.)

– Mean	0.94
– Median	0.92
– Min	0.60
– Max	1.35
– 95% UCL w/ ProUCL	1.1

Grand mean concentration
0.94 mg 2,4-DNT/kg
(28.1 kg of surface soil)

FP Mark – Sampling Statistics:
2,4-DNT Concentration (mg/kg)

Using subsets of randomly selected values from both sampling strategies

10 Multi-increment Samples

Measured Concentration:

– 95% UCL w/ ProUCL 1.1

ProUCL Trials –

Number of Samples	95% UCL w/ ProUCL (5 trials)
n = 4 (30 incr.)	1.3, 1.1, 1.1, 1.4, 1.1

100 Discrete Samples

Measured Concentration:

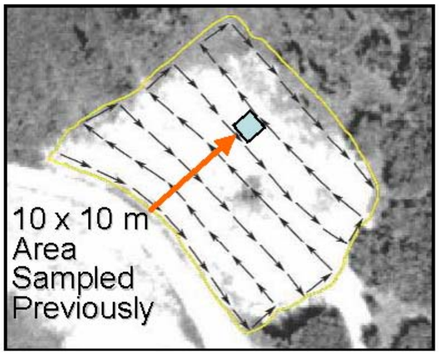
– 95% UCL w/ ProUCL 1.3

ProUCL Trials –

Number of Samples	95% UCL w/ ProUCL (5 trials)
n = 7	1.6, 3.6, 5.4, 0.72, 1.1
n = 15	2.6, 2.8, 2.5, 2.4, 2.4
n = 30	1.6, 1.4, 1.1, 1.5, 1.5

Grand mean concentration: 0.94 mg/kg

Illustration of systematic random sampling method used for collecting multi-increment samples from entire area at FP Mark. An increment was collected at each arrowhead.



Results (90 x 120 m):

NG Concentration (mg/kg)

50-Increment	0.49, 0.70, 0.62, 0.43, 0.73 $\bar{X}$ = 0.59 ± 0.13	 95% UCL – 0.73
200-Increment	0.58, 0.76, 0.59, 0.40, 0.46 $\bar{X}$ = 0.56 ± 0.14	 95% UCL – 0.71

Questions and Discussion

- Method 8330B
- Multi-increment Sampling
  - Cost Benefits / Risk

Fully Exploiting the Potential of Field Measurements: XRF Example

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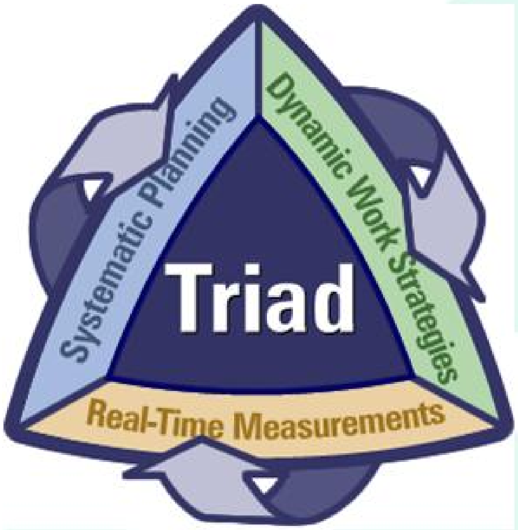
ABSTRACT

There is a wide variety of field instrumentation that can provide real-time pollutant data to support real-time decision-making for contaminated site cleanup. Most regulators and practitioners are aware that these tools are available. However, regulatory acceptance of their results can be difficult to obtain. Field portable X-ray fluorescence (XRF) instrumentation is now commonly used for many applications within the environmental industry. But XRF is seldom applied to its fullest potential. This presentation will review a spring 2008 XRF project. This project used a dynamic strategy that employed decision trees and pre-programmed spreadsheets to manage data uncertainty to the degree needed to make confident decisions.

Fully Exploiting the Potential of Field Measurements: an XRF Triad Project



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NEMC Conference Aug 12, 2008

What is the Triad Approach?

- A technical framework of best practices for cleaning up contaminated sites
- Goals:
  - Reduce project lifecycle time & costs
  - Increase transparency & scientific confidence in project decisions
- This talk's focus:
  - Exploit real-time tools to control aspects of data quality that are typically unaddressed

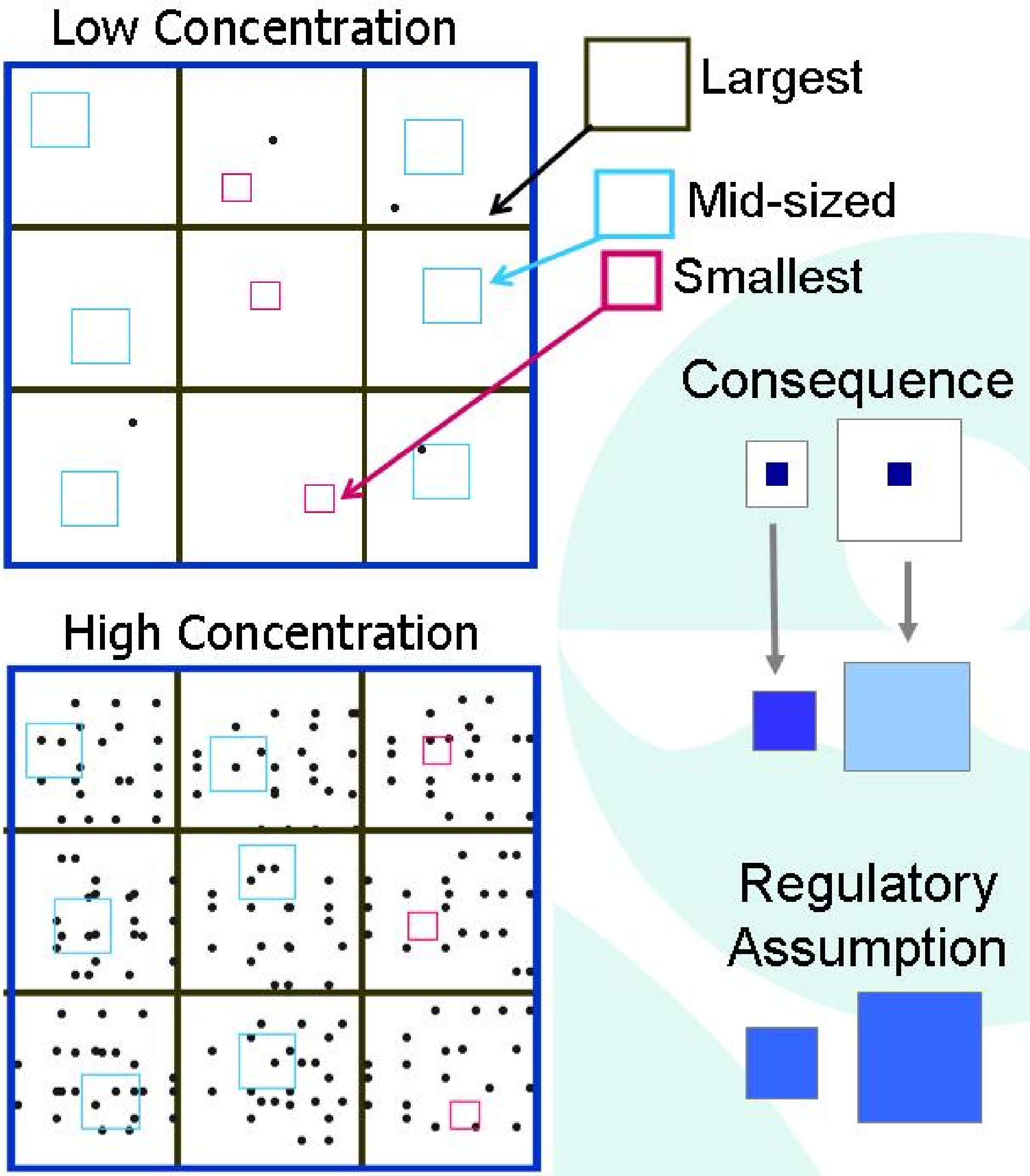
Factors that Complicate Data Quality for Soils

Contaminants Bind Best to Smaller Soil Particles: Causes Within-Sample Variability

Soil Grain Size Fractions (from largest to smallest)	Pb Concentration in Fraction (ppm)
Greater than 3/8”	**10**
Between 3/8” & 4-mesh	**50**
Between 4- & 10-mesh	**108**
Between 10- & 50-mesh	**165**
Between 50- & 200-mesh	**836**
Less than 200-mesh	**1,970**
Bulk Average Concentration	**927**

Firing range data, adapted from ITRC (2003)

Interaction between Concentration & Sample Mass



Low Concentration

Largest

Mid-sized

Smallest

Consequence

High Concentration

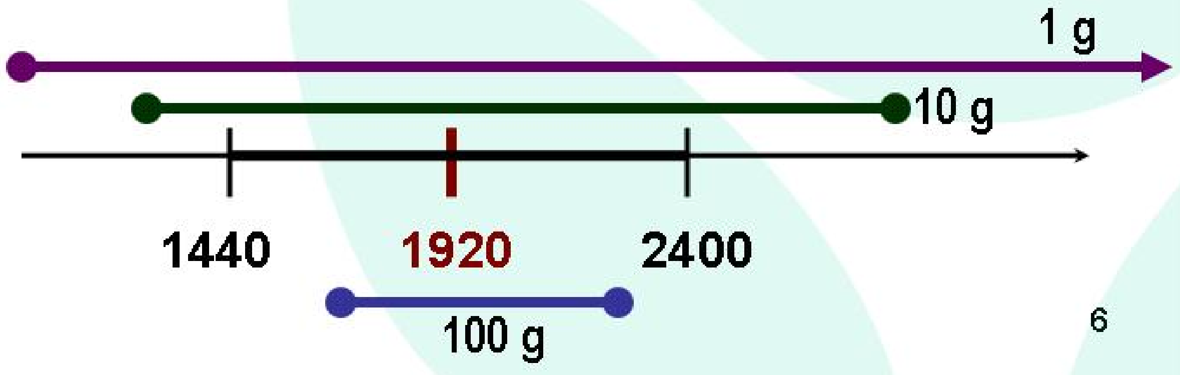
Regulatory Assumption

Relationship of Subsample Mass to Data Uncertainty

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

Subsample mass taken from a large partially homogenized soil **sample**	Range of results for 20 replicate **subsamples** (ppb)	How many **subsamples** to average to get a result w/in 25% of true **sample** mean? [1440 - 2400 ppb]
1 g	**1010 – 8000**	**39**
20 individual subsamples analyzed & averaged to get sample result		

Adapted from DOE (1978) americium-241 study



Sample heterogeneity creates data uncertainty, not because of the analytical method, but because of **sample handling**

This is why the definition of "definitive data" in the "DQOs for Superfund" 1993 guidance (p. 43) includes:

"For the data to be definitive, either analytical or total measurement error [variability] must be determined."

How Can This Be Done Cost-Effectively?

Real-time, inexpensive analytics with good QC & a well-planned dynamic, adaptive sampling design

XRF project illustrates control of data error in real-time

XRF Pb data from bagged soil samples (~300 gram)

Decision Goals

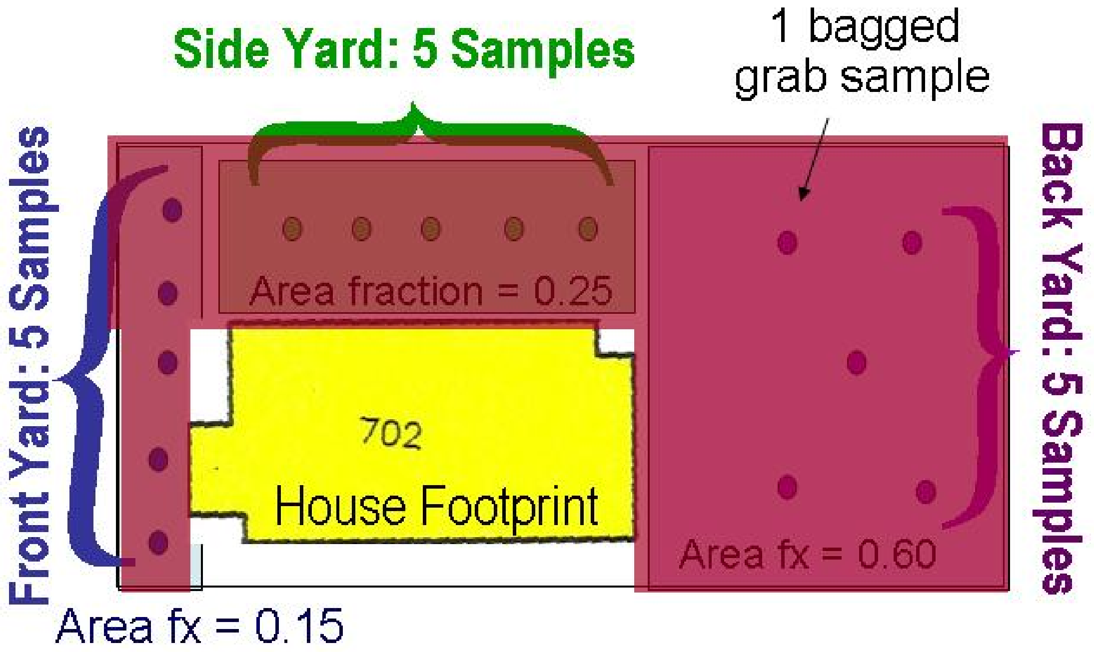
- Determine mean (95% UCL) for exposure unit (entire yard)
- Location of high Pb in yard helps indicate Pb source, so…

Data Collection Design

- A yard is divided into 3 sections
  - ► Front
  - ► Side
  - ► Back
- Section → 5 subsections
  - ► 1 grab soil sample (~300 g) per subsection into a plastic bag (i.e., 5 samples per yard section)

Illustrative Sampling Design & Results

Action Level (entire yard) = 500 ppm



Front yard average (at 95% statistical confidence) = 700 +/-150 (**550 – 850** ppm Pb)

Side yard average = 500 +/-100 (**400 – 600** ppm)

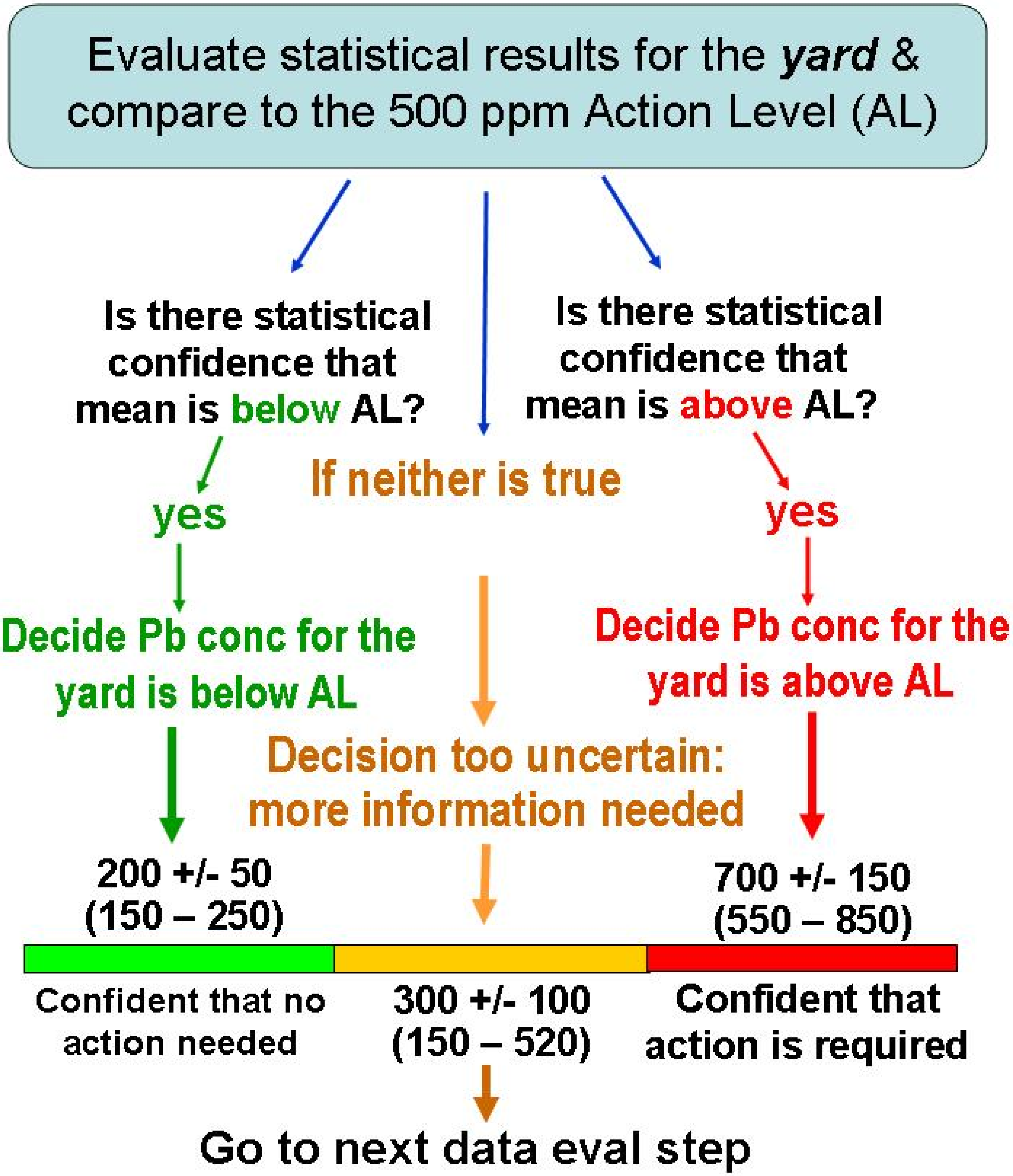
Back yard average = 300 +/-50 (**250 – 350** ppm)

Area-weighted total yard average determined statistically as 410 +/- 25 (385 – 435 ppm Pb)

XRF Bag Analysis

- 4 30-sec XRF readings on bag
  - (2 on front & 2 on back)
- Results entered real-time into pre-programmed spreadsheet
- Spreadsheet immediately calculates average & statistical uncertainty for
  - each bag
  - each yard section, and
  - the entire yard.
- Determine & control the largest source of data variability **IF** it interferes w/ confident decisions

Decision Tree



Evaluate statistical results for the *yard* & compare to the 500 ppm Action Level (AL)

Is there statistical confidence that mean is below AL?

yes

Decide Pb conc for the yard is below AL

200 +/- 50
(150 – 250)

If neither is true

Decision too uncertain: more information needed

Is there statistical confidence that mean is above AL?

yes

Decide Pb conc for the yard is above AL

700 +/- 150
(550 – 850)

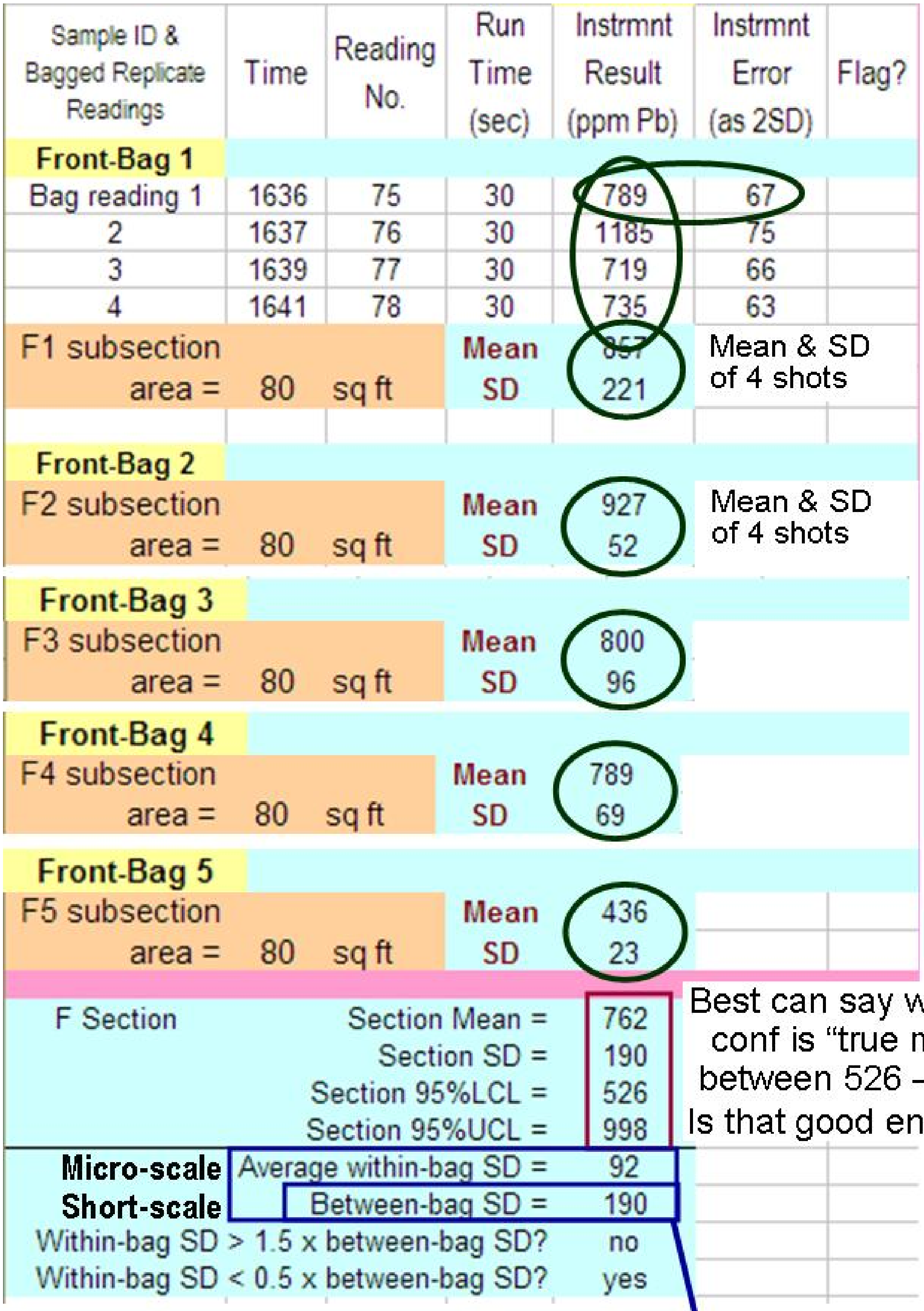
🟩🟨🟥

Confident that no action needed

300 +/- 100
(150 – 520)

Confident that action is required

Go to next data eval step



Sample ID & Bagged Replicate Readings	Time	Reading No.	Run Time (sec)	Instrmnt Result (ppm Pb)	Instrmnt Error (as 2SD)	Flag?
Front-Bag 1						
Bag reading 1	1636	75	30	789	67	
2	1637	76	30	1185	75	
3	1639	77	30	719	66	
4	1641	78	30	735	63	
F1 subsection area =	80	sq ft	**Mean** **SD**	857 221	Mean & SD of 4 shots	
Front-Bag 2						
F2 subsection area =	80	sq ft	**Mean** **SD**	927 52	Mean & SD of 4 shots	
Front-Bag 3						
F3 subsection area =	80	sq ft	**Mean** **SD**	800 96		
Front-Bag 4						
F4 subsection area =	80	sq ft	**Mean** **SD**	789 69		
Front-Bag 5						
F5 subsection area =	80	sq ft	**Mean** **SD**	436 23		
F Section			Section Mean =	762		
			Section SD =	190		
			Section 95%LCL =	526		
			Section 95%UCL =	998		
Micro-scale			Average within-bag SD =	92		
Short-scale			Between-bag SD =	190		
Within-bag SD > 1.5 x between-bag SD?				no		
Within-bag SD < 0.5 x between-bag SD?				yes		

Best can say w/ 95% conf is "true mean between 526 – 998"
Is that good enough?

If need to reduce data uncertainty, 2 options:
increase # shots/bag or increase # bags/section

Progressive Data Uncertainty Mgt for Exposure Area

Unit	Value (ppm)	CV	± (@ 95% confidence)
1 XRF Reading, from a Front yard (FY) bag (instrument-reported error)	**750**	**0.041** XRF only	**62** (688 – 812)
1 Bag sample (4 XRF readings on same bag)	**789**	**0.087** +micro-scale	**109** (680 – 898)
<u>Immature</u> CSM, FY section (10 bag samples)	**771**	**0.30** +short-scale	**167** (604 – 938)
<u>Mature</u> CSM, FY section (7 bag samples)	**900**	**0.012** CSM ↓	**97** (803 – 997)
Combine w/ Side & Back sections → mature CSM, entire yard (area-wt'd) (26 samples)	**199**	**0.49** + long-scale over yard	**37** (162 – 236) stratification & ↑**n** → ↓CI

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Continuous Profiling of Subsurface Pollutants

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ABSTRACT

Two sensing technologies have been developed for the rapid *in situ* profiling and speciation of subsurface pollutants at hazardous waste sites. The first technology is comprised of a thermal extraction cone penetrometer (TECP) attached to a heated transfer line (HTL) and coupled to a photoionization detector (PID) and gas chromatograph/mass spectrometer (GC/MS). The TECP was able to efficiently extract semi-volatile organics (SVOC's) at rates between 70-90% when soil temperatures reached 300°C and soil moisture content was <15%. If the moisture content should exceed 15% then a membrane inlet probe (MIP) can be used in place of the TECP. Although extraction efficiencies are decreased due to the temperature limitation of the membrane, the MIP can be used to profile soil-to-water or water-to-sediment interfaces in a continuum at depths of up to 28m. Soil analysis using the TECP or the MIP does not require the soil to be brought to the subsurface or into a collection chamber, a requirement when using traditional CP sample collectors. The agreement between PID signal levels and GC/MS results for total PAH was remarkable. Correlation coefficients of 0.92 and 0.99 were obtained between the PID and field GC/MS data for discrete and composite samples, respectively. In addition, no false positives or false negatives were found. The design of a new *online* freeze-trap enabled volatile organic compounds to be recovered from contaminated soil at an average rate of 90%. Analysis rates as fast as five minutes were used to extract volatile organic compounds (VOC's) and PAH simultaneously from the soil, a marked contrast to the much longer methods used by commercial laboratories for the separate analysis of these compounds. Overall, the effectiveness of conceptual site models (CSM) will be greatly improved since the PID can be depended upon to provide the exact location of pollutants in "real-time" while the GC/MS can be used to accurately determine what contaminants are present and their relative amounts.

INTRODUCTION

It has been estimated by the U.S. Environmental Protection Agency (EPA) that from now until 2033, the number of hazardous waste sites in need of cleanup will reach approximately 294,000 in the United States alone *(1)*. This figure of 294,000 only represents sites requiring cleanup and does not include sites where remediation is currently ongoing, a process that can take years or even decades. Sites grouped under the Superfund program, the Resource Conservation and Recovery Act, and those that contain underground storage tanks account for 736, 3,800, and 125,000 sites, respectively. The largest market segment, 150,000 sites, is under the control of individual states and includes those in state mandated programs, voluntary cleanup programs and Brownfield programs. Overall, the total cost for cleanup of all 294,000 sites is predicted to range from $170-$250 billion.

Our goal is to accelerate the site investigation process and, at the same time, reduce the overall cost of cleanup by developing CSM's that are information rich in geology, hydrology and chemical data. Toward this end, we continue to advance dynamic site investigations, consistent with EPA's TRIAD process, and have developed two different probes capable of extracting organic pollutants from subsurface soil and groundwater. The TECP probe incorporates a flexible, 280 °C, HTL and a 400°C sampling probe. Studies have shown that for SVOC's, extraction efficiencies of 70-90% are achievable with the direct inlet probe because soil temperatures can reach 300 ^{0}C *(2,3,4)*. However, the TECP cannot be used when moisture content exceeds 15% as the wall coating within the HTL becomes deactivated.

To overcome this problem, a second probe was developed whereby the HTL is combined with the MIP and coupled with a PID and GC/MS. The Teflon membrane facilitates the transport of organics while excluding water from entering the membrane and damaging the HTL. In contrast to the TECP, soil only reaches 120 ^{0}C with the membrane inlet probe and much lower extraction efficiencies are obtained. Data will be presented from a coal tar site in which PAHs are profiled continuously by PID as the probe is advanced into the subsurface. PID response is compared against GC/MS results at the same exact location, with the overall correlation coefficient > 0.92 (5,6). When the HTL is connected directly to an online freeze trap in series with the GC column, correlation coefficients increase. Results showed that low molecular weight, low boiling organics such as benzene, naphthalene and their alkylated analogs were much more efficiently captured that what was obtainable using the external freeze-trap.

EXPERIMENTAL

Our probes are connected on one end to a 300 ^{0}C flexible, HTL and, on the other end, to a heated six-port valve as illustrated in Figure 1. As the probe is advanced into the subsurface at a velocity of 0.75 ft/s, organic vapors are swept from the collection port through the transfer line into a valve that is connected to a PID for rapid subsurface profiling (flow path 2). When the valve is switched from the PID to an external freeze-trap (flow path 1), organics are trapped inside an empty glass sleeve, which is brought to a thermal desorption (TD) GC/MS instrument for on-site analysis.

Ion Signature Technology (North Smithfield, RI) quantitative deconvolution data analysis software was used to analyze all the data generated in Tables 1-4. Deconvolution refers to data analysis software that uses powerful mathematical algorithms to extract component spectra from the sample matrix spectrum or instrument noise. Good deconvolution algorithms are able to handle the accumulative ion signals that occur at a given scan at a specific m/z value when compounds coelute *(7,8,9,10,11)*. Thus, unambiguous compound identification did not pose a problem, even for runs as fast as five minutes with highly complex matrices.

RESULTS AND DISCUSSION

The TECP was field tested at a former manufactured gas plant (MGP) site by pushing it 10m into the ground and conducting a series of analyses on different soil samples. The results for one sample are displayed in Table 1where the soil was solvent-, TD-, and TECP extracted. All the priority PAH identified by the EPA were successfully extracted using the TECP with % recoveries as high as 86% for fluoranthene. The average % recovery obtained using the TECP was 59%. The same soil sample was analyzed in a closed cell TD system where there is no loss of organics to the environment during heating. As can be seen, the results between the TECP and TD were in remarkable agreement with the average % recovery obtained using TD equal to

60%. The average TECP vs. TD relative percent difference (RPD) for all PAH in the sample was only 8%, with only one above 21%. This is well within EPA'S criteria for accuracy which states that when measured concentration levels are >5 times the quantitation limit (QL), RPD <60%, and when <5 times the QL, RPD <100%. These results are made all the more impressive considering the fact that the moisture content in the soil sample was 16%.

Similar to the TECP, the HTL-MIP was also field tested at a different MGP site. The below surface sample depths for two Borings, their corresponding PID values, and the total PAH values as measured in the field and by off-site laboratories are shown in Table 2. Prior to each new boring, the probe was pushed ~0.2 in. below surface and the PID signal recorded and used as the baseline. This value was then subtracted from each subsequent PID reading when the probe was continuously advanced into the subsurface. The absence of organics at specific depths is indicated by the negative values shown for Boring 1. In contrast, the magnitude of the adjusted positive values indicates the presence and relative amounts of PAH at specific locations. A total of 29 discrete samples from five different Borings were analyzed and a correlation coefficient of 0.92 was obtained between the PID and field GC/MS data. This correlation coefficient increased to a remarkable 0.99 for field GC/MS and 0.97 for laboratory GC/MS when the PID response was compared against the eight samples where laboratory data was available. Importantly, no false positives (positive PID signal with no PAH detected by GC/MS) or false negatives (negative PID signal with PAH detected by GC/MS) were produced.

The results for MIP and methylene chloride extracted coal tar samples are shown in Table 3. The three samples tested contained 5%, 10% and 100% coal tar. In contrast to the 60-min laboratory analysis time required for forensic environmental analyses, a much faster 12-min analysis was used for field analyses. The overall precision (% RSD) was 46%, with PAH at 44% and alkylated PAH at 49%. These results were within the 50% benchmark set by the EPA for comparison of soil samples. Comparing the average RPD between the MIP and solvent extracted samples resulted in values of 133, 135, and 147%, respectively. It can be seen that there was an inverse relationship between PAH concentration and measurement accuracy. The average MIP % recovery was 20 ± 13% for the 5% and 10% coal tar samples only. These results can be attributed to limitations in the applied membrane temperature of 130°C and the 5-min collection time.

Lastly, Table 4 displays the results when the HTL-MIP was connected to an *online* freeze-trap cooled to -45°C and a GC/MS in a new sample cell design to rapidly detect and quantify VOCs in contaminated soils. This closed system ensured the maximum recovery of any organic vapors trapped and importantly, minimized the possibility of contaminants entering the system and being detected by the GC/MS. To match sample collection and analysis speeds, a 5-min GC/MS analysis was performed using the Ion Signature deconvolution algorithms to quantify target compounds. The average precision, % RPD, for the probe extracted samples was 36%, well within EPA's criteria for precision. Percent recoveries ranged from 22% to 266% with the average percent recovery value an impressive 90%. A reason for the percent recoveries exceeding 100% could be due to the much colder freeze-trap temperature of -45°C coupled with the collection time of 5 min. Thus, the organics preconcentrate for too long within the freeze-trap and the results are percent recoveries >100%. Further studies will have to be done to determine the optimum collection time. The average RPD for all compounds was 44% and this decreased to 34% when the alkylated naphthalenes were excluded. Again, these values are well within the EPA criteria for accuracy. Importantly, the *online* freeze-trap will result in an increase in correlation coefficients between PID signals and GC/MS results since the PID response is representative of the amount of contaminants contained in the subsurface, which includes both VOC's and SVOC's.

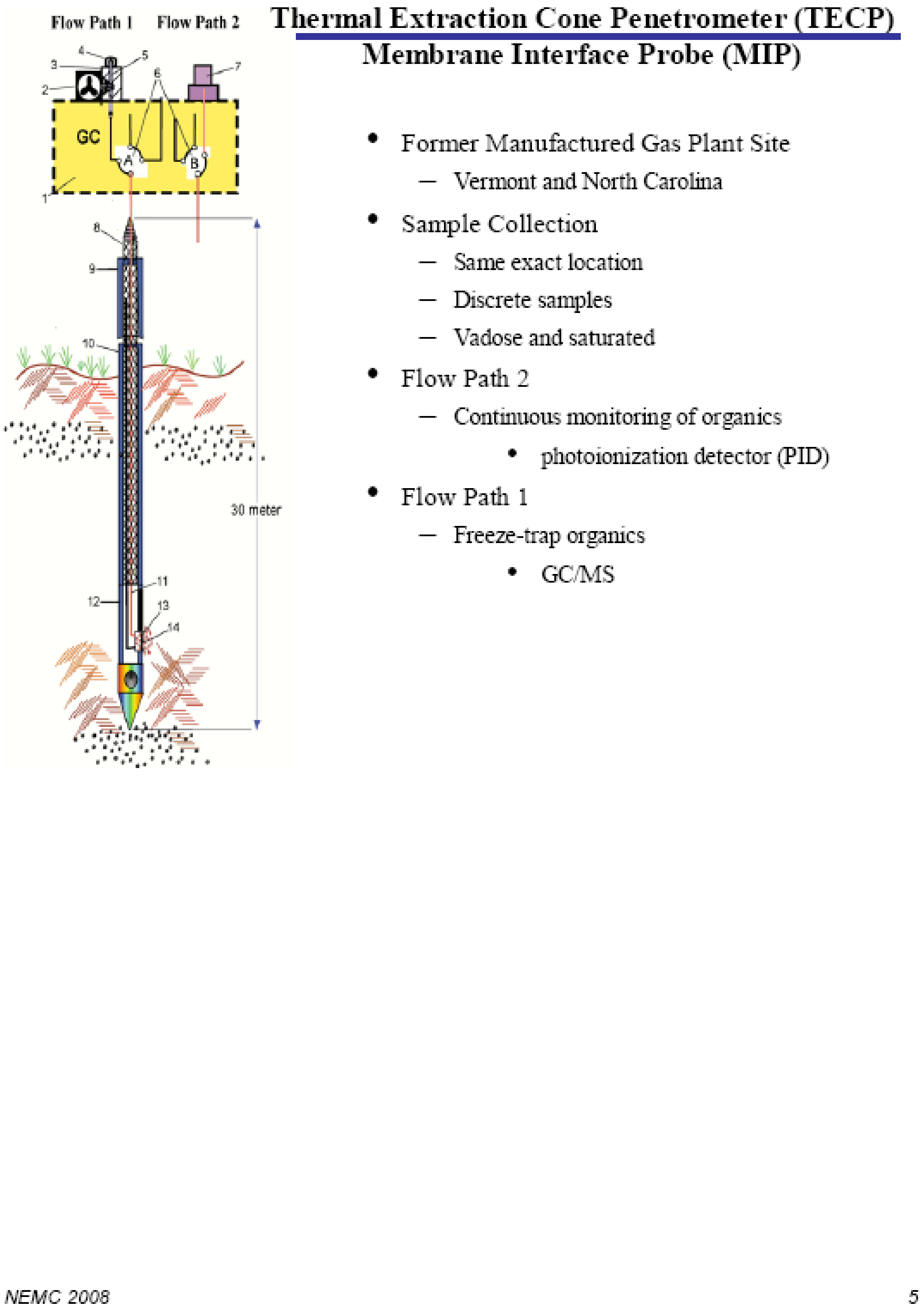
CONCLUSION

Combining the HTL-TECP/MIP, PID, and GC/MS served to maximize the efficiency of the site investigation process for a number of reasons. Firstly, the reliability and dependability of the PID ensured that that the site investigation will be completed in one visit as all of the confirmation samples selected will contain PAH concentrations. Secondly, no re-mobilization results in reductions in equipment and labor expenses and eliminates time wasted in setting up and re-calibrating the analytical instrumentation for sample collection. Thirdly, the technology described here, does not require any dilution of samples prior to analysis resulting in a more comprehensive and accurate site evaluation. Importantly, probe collected samples are ready for analysis, which is a marked time-savings over solvent extraction.

The heated transfer line, the TECP/MIP, and detectors proved to be rugged and ready for field use. Depending on the conditions encountered at the site, the TECP can be used when moisture content within the subsurface <15% and switched over to the MIP when moisture content >15%. Percent recoveries using the MIP were not as high as those obtained with the TECP due to the temperature limitations associated with the Teflon membrane. An advantage, however, is that the MIP can be used to profile soil-to-water or water-to-sediment interfaces in a continuum with PAH and their alkylated analogs being extracted at depths of up to 28m. The HTL, when maintained at a constant 280°C, displayed little or no signs of carryover. The PID was shown to be an excellent profiling tool and provided continuous evidence as to PAH presence/absence that resulted in the identification of soil channels containing coal tar from source material.

Combining the PID with the GC/MS can provide the detail necessary for development of effective CSM's to lead investigators into driving the TECP/MIP into dense nonaqueous phase liquid plumes. This task can prove to be an incredibly difficult proposition using current technologies. Field and laboratory data were shown to be statistically equivalent with analysis rates as fast as five minutes able to capture VOC's and SVOC's simultaneously. Off-site laboratories typically use separate methods to analysis VOC's and SVOC's thereby adding to the overall cost of the site investigation in addition to longer turnaround times. The combination of data from direct sensing, in situ, and traditionally collected samples should enable a more accurate assessment of the risk posed to human health and the environment when assessing land usage proposals.

Figure 1. Collection and analysis of soil samples using the TECP/MIP.



Thermal Extraction Cone Penetrometer (TECP)
Membrane Interface Probe (MIP)

- Former Manufactured Gas Plant Site
  - Vermont and North Carolina
- Sample Collection
  - Same exact location
  - Discrete samples
  - Vadose and saturated
- Flow Path 2
  - Continuous monitoring of organics
    - photoionization detector (PID)
- Flow Path 1
  - Freeze-trap organics
    - GC/MS

Table 1. PAH recoveries from coal tar contaminated site.

	Solvent	TD (closed cell)		TECP		RPD
PAHs	ppm	ppm	% Recov, R_{max}	ppm	% Recov, R	$100(R_{max}-R)/0.5(R_{max}+R)$
Naphthalene	1267	500	39	406	32	21
Acenaphthylene	351	248	71	224	64	10
Acenaphthene	297	227	77	230	77	-1
Fluorene	441	317	72	287	65	10
Phenanthrene	865	652	75	657	76	-1
Anthracene	866	653	75	618	71	5
Fluoranthene	567	507	89	488	86	4
Pyrene	1070	882	82	840	78	5
Chrysene	536	374	70	349	65	7
Benzo(a)anthracene	535	372	70	360	67	3
Benzo(b&k)fluoranthene	284	132	47	152	54	-14
Benzo(a)pyrene	427	242	57	262	61	-8
Indeno(1,2,3-cd)pyrene	186	56	30	63	34	-12
Dibenz(a,h)anthracene	187	57	30	65	35	-13
Benzo(g,h,i)perylene	132	29	22	28	21	4

Notes: 1) Soil Moisture Content = 16%.
2) Temperature of Probe = 450°C.
3) Temperature of Soil = 300°C.
4) Linear velocity of carrier gas (nitrogen) through the HTL = 1.8 m/s.

Table 2. MIP GC/MS vs PID and Lab GC/MS for Total PAH, mg/kg

Location	Depth, ft	PID	Field (% RSD)	Lab (% RPD)	Depth, ft	Field vs. Lab, % Rec.
Boring 1	2	-58,383				
	2.6	-38,847				
	3.1	-38,847				
	3.6	-38,847				
	4.2	-19,311				
	5.3	-19,311				
	5.35	136,977	3	190	4 to 5	2
	9.25	234,657	8	112	8 to 9	7
	15.1	1,250,530	70	1,010	15 to 16	7
	17.4	1,973,362	96			
Boring 4	4.35	14,054,640	1,303			
	4.85	15,715,202	2,074			
	Ave, n = 2	14,884,921	1,688	28,789	4 to 5	6
	5.35	7,588,217	224			
	6	3,974,054	448			
	8.45	5,634,616	361			
	9.05	4,462,454	427			
	10.05	5,712,760	246			
	11.05	2,626,068	117			
	12.05	4,247,558	178			
	Ave, n = 5	*4,536,691*	*266 (45)*	1,494 (2)	8.4 to 12	18
	13.05	2,626,068	141			
	14.15	2,665,140	129			
	14.85	516,178	101			
	Ave, n = 3	*1,935,795*	*124 (17)*	268 (6)	13 to 14.9	46

Notes: 1) NA, samples not analyzed.
2) % RSD, precision is based on the average of discrete samples measured over the distance specified.
3) % RPD, precision is based on the analysis of blind duplicates sent to lab (n=2).
4) % Rec, accuracy = (Field/Lab) * 100.

Table 3. MIP (Field), Methylene Chloride (Lab) Extracted Coal Tar Samples, mg/kg.

	Soil 1 (5% coal tar)				Soil 2 (10% coal tar)				Soil 3 (100% coal tar)			
Compounds	**Lab**	**Field (n = 3) Ave. (% RSD)**	**% Rec.**	**RPD**	**Lab**	**Field (n = 3) Ave. (% RSD)**	**% Rec.**	**RPD**	**Lab**	**Field (n = 3) Ave. (% RSD)**	**% Rec.**	**RPD**
Naphthalene	297	45 (6)	15	147	274	77 (57)	28	112	27,055	7,661 (21)	28	112
Acenaphthylene	57	20 (30)	35	97	83	11 (46)	13	153	4,440	437 (22)	10	164
Acenaphthene	32	13 (79)	41	86	38	8 (41)	21	130	1,264	152 (18)	12	157
Fluorene	94	42 (71)	45	76	118	26 (27)	22	128	3,942	322 (15)	8	170
Phenanthrene	252	70 (56)	28	113	339	67 (44)	20	134	8,236	391 (43)	5	182
Anthracene	75	13 (73)	17	141	80	13 (29)	16	146	2,525	92 (56)	4	186
Fluoranthene	62	3 (78)	5	184	103	7 (37)	7	174	2,361	53 (54)	2	191
Pyrene	150	3 (61)	2	193	192	8 (38)	4	184	3,484	62 (50)	2	193
Total non-alkylated PAH	*1,019*	*209 (57)*	*20*	*132*	*1,227*	*217 (40)*	*18*	*140*	*53,307*	*9,170 (35)*	*17*	*141*
C_1-naphthalenes	375	113 (32)	30	107	715	236 (45)	33	101	24,122	8,384 (25)	35	97
C_2-naphthalenes	623	149 (54)	24	123	882	175 (45)	20	134	15,215	2,004 (28)	13	153
C_1-fluorenes	105	45 (80)	43	80	152	34 (35)	22	127	5,687	255 (38)	4	183
C_2-fluorenes	35	4 (42)	11	159	62	12 (41)	19	135	2,202	93 (58)	4	184
C_1-phenanthrenes	301	22 (37)	7	173	409	43 (34)	10	162	15,692	359 (64)	2	191
C_2-phenanthrenes	65	0.4 (95)	1	198	71	8 (35)	11	159	6,262	103 (76)	2	194
C_1-fluoranthenes	168	ND			254	2 (56)	1	197	11,865	38 (59)	0.3	199
Total alkylated PAH	*1,672*	*333 (57)*	*20*	*134*	*2,545*	*510 (42)*	*20*	*133*	*81,045*	*11,236 (50)*	*14*	*151*
Total PAH	*2,691*	*542 (57)*	*20*	*133*	*3,772*	*727 (41)*	*19*	*135*	*134,352*	*20,406 (42)*	*15*	*147*

Notes: 1) MIP operating conditions: flow rate = 36 mL/min, probe = 130°C, collection time = 5 min, freeze-trap = -18°C
2) % Rec, recovery = (Field/Lab * 100).
3) RPD, accuracy = 100 ((Lab-Field)/0.5(lab + field)).
4) ND, non-detect.

Table 4. MIP (Probe), Methylene Chloride (Lab) Extracted Fuel Oil Samples, mg/kg.

	Fuel Oil Contaminated Soil Samples			
Compounds	**Lab (% RSD)**	**Probe (% RPD)**	**% Rec.**	**RPD**
Benzene	14 (41)	13 (73)	93	7
Toluene	357 (19)	251 (7)	70	35
Ethylbenzene & m,p-xylene & o-xylene	1,395 (20)	2,143 (16)	154	-42
Isopropylbenzene	112 (18)	97 (23)	87	14
n-Propylbenzene	359 (17)	468 (22)	130	-26
1-Methyl-3-Ethylbenzene	1,043 (21)	2,777 (23)	266	-91
1,2,4-Trimethylbenzene	2,257 (19)	2,456 (23)	109	-8
tert-Butylbenzene	318 (15)	543 (25)	171	-52
n-Butylbenzene	760 (13)	812 (27)	107	-7
1-Methyl-4-n-Propylbenzene & 1-Methyl-3-n-Propylbenzene	1,552 (14)	1,446 (25)	93	7
1,3-Dimethyl-5-Ethylbenzene & 1,4-Dimethyl-2-Ethylbenzene	1,864 (12)	1,598 (24)	86	15
1,2-Dimethyl-3-Ethylbenzene	885 (10)	723 (22)	82	20
1,2,4,5-Tetramethylbenzene	1,381 (17)	1,219 (34)	88	12
n-Pentylbenzene	1,843 (12)	1,651 (28)	90	11
Naphthalene	859 (34)	1,003 (44)	117	-15
1,3,5-Triethylbenzene	741 (29)	586 (48)	79	24
Biphenyl	370(31)	264 (51)	71	33
Acenaphthylene	106 (4)	54 (59)	51	65
Acenaphthene	182 (4)	74 (53)	41	84
Dibenzothiophene	54 (2)	17 (2)	31	104
C1-naphthalenes	3,158 (1)	1,155 (49)	37	93
C2-naphthalenes	5,928 (1)	2,971 (49)	50	66
C3-naphthalenes	3,763 (0)	1,446 (55)	38	89
C4-naphthalenes	1,983 (7)	441 (77)	22	127

Notes: 1) MIP operating conditions: flow rate = 6 mL/min, probe = 130°C, collection time = 5 min, freeze-trap = -45°C.
2) % RSD, precision is based on the average of three different samples.
3) % RPD, precision is based on the analysis of two different samples.
4) % Rec, recovery = (Probe/Lab * 100).
5) RPD, accuracy = 100 ((Lab-Probe)/0.5(lab + Probe)).

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Continuous Profiling of Subsurface Pollutants

2008 National Environmental Monitoring Conference

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Redevelopment of Hazardous Waste Sites


Before: Abandoned Chemical Plant

Brownfields Redevelopment:
Newark, NJ


After: Entertainment Complex

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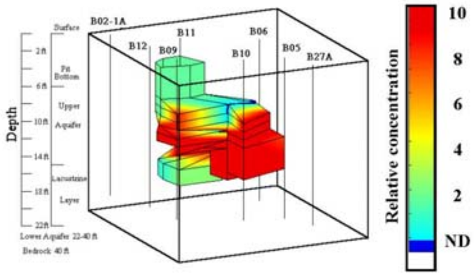
Tufts University
Department of Chemistry

Site Investigation and Cleanup

- Expensive and time-consuming!
- Small and large sites need the same systematic planning, adaptive sampling and analysis program as well as scientific, and engineering assessment.
- Data volume must increase to make determinations related to contaminant location, its components, and migration pathways.



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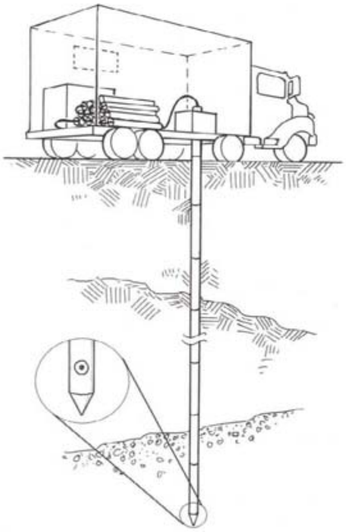
What is Decision Uncertainty?



How does sampling and analysis uncertainty influence decision uncertainty?

- How Many Soil Borings?
- How Many Wells?

- Where Do I Put Them?
- At What Depth Do I Collect Samples?

- What Role Does Soil Heterogeneity Play in the Sample Collection, Analysis and Decision Making Process?

The Solution: Continuous rapid profiling of the subsurface

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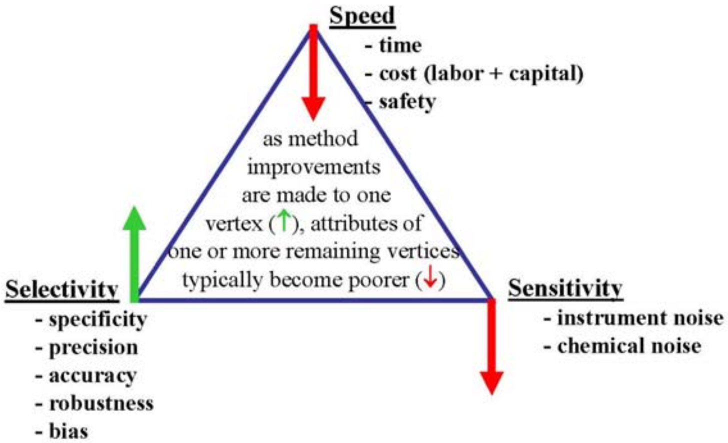
The Analytical Challenge



Speed
- time
- cost (labor + capital)
- safety

as method improvements are made to one vertex (↑), attributes of one or more remaining vertices typically become poorer (↓)

Selectivity
- specificity
- precision
- accuracy
- robustness
- bias

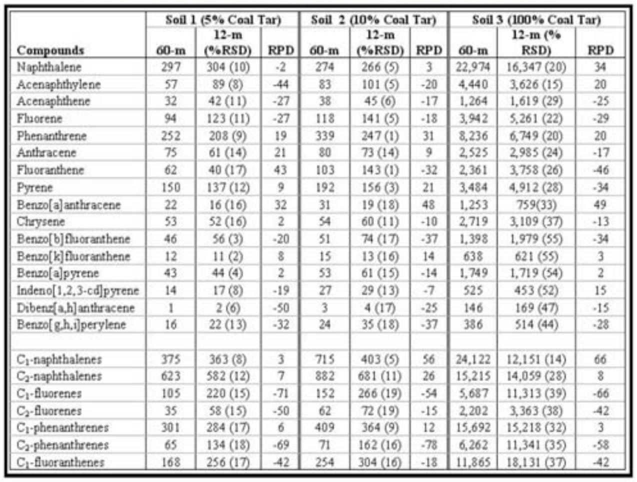
Sensitivity
- instrument noise
- chemical noise

Ion Signature Technology Deconvolution Software for Mass Spectrometry

Liquid Extracted Coal Tar

Modified EPA Method SW-846, 8270C

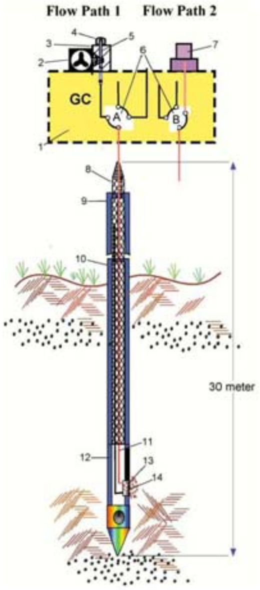
Forensic and Fast GC/MS Analyses, mg/kg



	Soil 1 (5% Coal Tar)			Soil 2 (10% Coal Tar)			Soil 3 (100% Coal Tar)		
Compounds	60-m	12-m (%RSD)	RPD	60-m	12-m (%RSD)	RPD	60-m	12-m (% RSD)	RPD
Naphthalene	297	304 (10)	-2	274	266 (5)	3	22,974	16,347 (20)	34
Acenaphthylene	57	89 (8)	-44	83	101 (5)	-20	4,440	3,626 (15)	20
Acenaphthene	32	42 (11)	-27	38	45 (6)	-17	1,264	1,619 (29)	-25
Fluorene	94	123 (11)	-27	118	141 (5)	-18	3,942	5,261 (22)	-29
Phenanthrene	252	208 (9)	19	339	247 (1)	31	8,236	6,749 (20)	20
Anthracene	75	61 (14)	21	80	73 (14)	9	2,525	2,985 (24)	-17
Fluoranthene	62	40 (17)	43	103	143 (1)	-32	2,361	3,758 (26)	-46
Pyrene	150	137 (12)	9	192	156 (3)	21	3,484	4,912 (28)	-34
Benzo[a]anthracene	22	16 (16)	32	31	19 (18)	48	1,253	759(33)	49
Chrysene	53	52 (16)	2	54	60 (11)	-10	2,719	3,109 (37)	-13
Benzo[b]fluoranthene	46	56 (3)	-20	51	74 (17)	-37	1,398	1,979 (55)	-34
Benzo[k]fluoranthene	12	11 (2)	8	15	13 (16)	14	638	621 (55)	3
Benzo[a]pyrene	43	44 (4)	2	53	61 (15)	-14	1,749	1,719 (54)	2
Indeno[1,2,3-cd]pyrene	14	17 (8)	-19	27	29 (13)	-7	525	453 (52)	15
Dibenz[a,h]anthracene	1	2 (6)	-50	3	4 (17)	-25	146	169 (47)	-15
Benzo[g,h,i]perylene	16	22 (13)	-32	24	35 (18)	-37	386	514 (44)	-28
C_1-naphthalenes	375	363 (8)	3	715	403 (5)	56	24,122	12,151 (14)	66
C_2-naphthalenes	623	582 (12)	7	882	681 (11)	26	15,215	14,059 (28)	8
C_1-fluorenes	105	220 (15)	-71	152	266 (19)	-54	5,687	11,313 (39)	-66
C_2-fluorenes	35	58 (15)	-50	62	72 (19)	-15	2,202	3,363 (38)	-42
C_1-phenanthrenes	301	284 (17)	6	409	364 (9)	12	15,692	15,218 (32)	3
C_2-phenanthrenes	65	134 (18)	-69	71	162 (16)	-78	6,262	11,341 (35)	-58
C_1-fluoranthenes	168	256 (17)	-42	254	304 (16)	-18	11,865	18,131 (37)	-42

Thermal Extraction Cone Penetrometer (TECP)

- Sample Collection
  - Exact location
  - Discrete samples
  - Vadose and saturated zones
- Flow Path 2
  - Continuous monitoring of organics
    - Photoionization detector (PID)
- Flow Path 1
  - Freeze-trap organics
    - GC/MS
- **Membrane Interface Probe (MIP)**



TECP vs Closed System: Thermal Desorption GC/MS

	TECP (T_{pipe} = 450 °C; $t_{soil\,1}$ = 280 °C; $T_{tr.line}$ = 300 °C; Re_m = 6,000; ω = 1.2 m/s; V_o = 30 L/d = 15; backyard soil)						Closed Cell ($t_{soil\,1}$ = 300 °C; $T_{tr.line}$ = 300 °C Re_m = 5,700; ω_g = 0.6 m/s; V_o = 32; backyard soil)	
	50-ppm	25-ppm	15-ppm	5-ppm	Ave Rec	% RSD	15 ppm	% Diff
naphthalene	52	69	58	45	56	18	65	14
acenaphthylene	53	60	65	50	57	12	63	10
acenaphthene	48	76	80	77	70	21	78	10
fluorene	60	52	70	59	60	12	75	20
phenanthrene	76	65	67	70	70	7	83	16
anthracene	65	60	59	62	62	4	78	21
fluoranthene	65	70	68	57	65	9	80	19
pyrene	64	75	70	78	72	8	83	13
benzo(a)anthracene	65	53	62	51	58	12	67	14
chrysene	47	57	41	61	52	18	61	16
benzo(b)fluoranthene	49	47	49	43	47	6	55	15
benzo(k)fluoranthene	40	48	56	44	47	15	54	13
benzo(a)pyrene	52	51	63	51	54	11	65	17
indeno(1,2,3-ed)pyrene	33	26	27	30	29	11	37	22
dibenz(a,b) anthracene	32	25	30	29	29	10	37	22
benzo(g,h,i)perylene	17	21	23	20	20	12	23	12

Note: % difference is between the average TECP recovery and closed chamber recovery

PAH Recovery from Coal Tar Contaminated Site

(wet = 16%; τ = 13 min; T_{probe} = 450°C; T_{soil} = 300°C; Re_m = 6000; w_g = 1.8 m/sec)

	Soxhlet	TD (closed cell)		TECP		RPD
PAHs	ppm	ppm	% Recov, R_{max}	ppm	% Recov, R	$100(R_{max}-R)/0.5(R_{max}+R)$
Naphthalene	1267	500	39	406	32	21
Acenaphthylene	351	248	71	224	64	10
Acenaphthene	297	227	77	230	77	-1
Fluorene	441	317	72	287	65	10
Phenanthrene	865	652	75	657	76	-1
Anthracene	866	653	75	618	71	5
Fluoranthene	567	507	89	488	86	4
Pyrene	1070	882	82	840	78	5
Chrysene	536	374	70	349	65	7
Benzo(a)anthracene	535	372	70	360	67	3
Benzo(b&k)fluoranthene	284	132	47	152	54	-14
Benzo(a)pyrene	427	242	57	262	61	-8
Indeno(1,2,3-cd)pyrene	186	56	30	63	34	-12
Dibenz(a,h)anthracene	187	57	30	65	35	-13
Benzo(g,h,i)perylene	132	29	22	28	21	4

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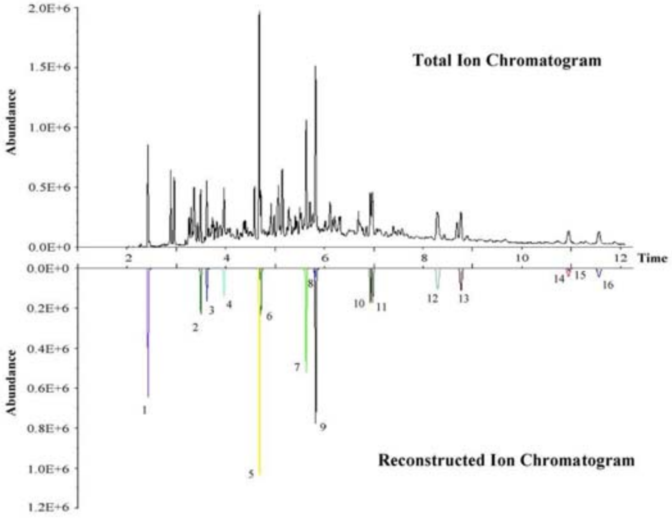
GC/MS Analysis of Sample Collected by TECP



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TECP-MIP GC/MS vs PID and Lab GC/MS for Total PAH, mg/kg

Location	Depth, ft	PID	Field (% RSD)	Lab (% RPD)	Depth, ft	Field vs Lab, % Rec.
Boring 1	2.1	-38,847				
	4.1	-19,311				
	5.3	-19,311				
	5.35	136,977	3	190	4 to 5	2
	9.25	234,657	8	112	8 to 9	7
	15.1	1,250,530	70	1,010	15 to 16	7
	17.4	1,973,362	96			
Boring 4	4.35	14,054,640	1,303			
	4.85	15,715,202	2,074			
	Ave, n = 2	14,884,921	1,688 (32)	28,789	4 to 5	6
	5.35	7,588,217	224			
	6	3,974,054	448			
	8.45	5,634,616	361			
	9.05	4,462,454	427			
	10.05	5,712,760	246			
	11.05	2,626,068	117			
	12.05	4,247,558	178			
	Ave, n = 5	*4,536,691*	*266 (45)*	1,494 (2)	8.4 to 12	18
	13.05	2,626,068	141			
	14.15	2,665,140	129			
	14.85	516,178	101			
	Ave, n = 3	*1,935,795*	*124 (17)*	268 (6)	13 to 14.9	46

Correlation coefficients between PID and field/lab GC/MS data:

1) **Discrete samples:** **0.92, field, n= 29.**
2) **Composite samples:** **0.99, field, n= 8**
0.97, lab, n=8

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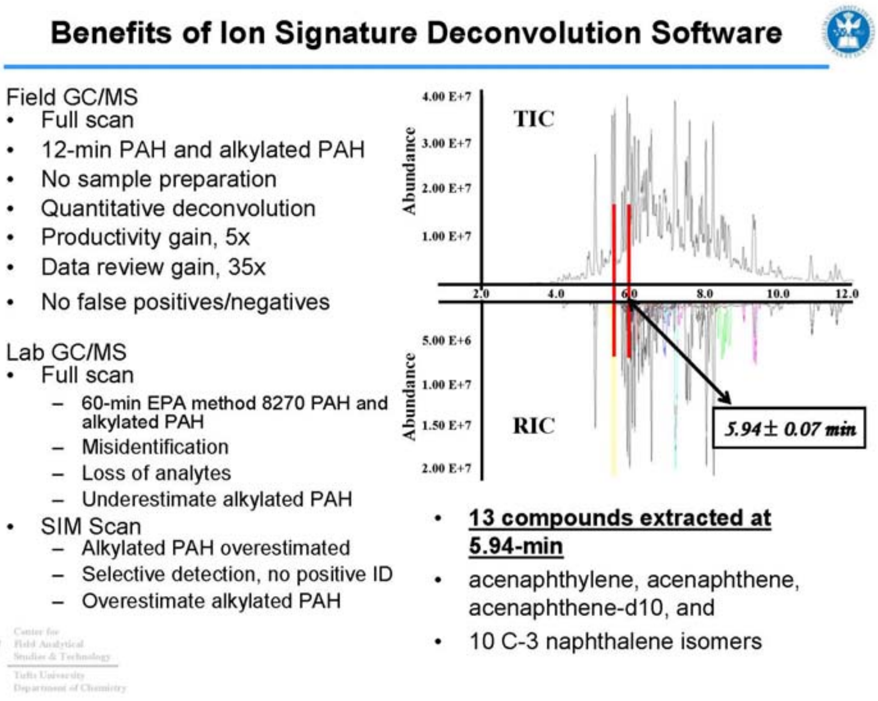

Benefits of Ion Signature Deconvolution Software

Field GC/MS
- Full scan
- 12-min PAH and alkylated PAH
- No sample preparation
- Quantitative deconvolution
- Productivity gain, 5x
- Data review gain, 35x
- No false positives/negatives

Lab GC/MS
- Full scan
  - 60-min EPA method 8270 PAH and alkylated PAH
  - Misidentification
  - Loss of analytes
  - Underestimate alkylated PAH
- SIM Scan
  - Alkylated PAH overestimated
  - Selective detection, no positive ID
  - Overestimate alkylated PAH

- **13 compounds extracted at 5.94-min**
- acenaphthylene, acenaphthene, acenaphthene-d10, and
- 10 C-3 naphthalene isomers

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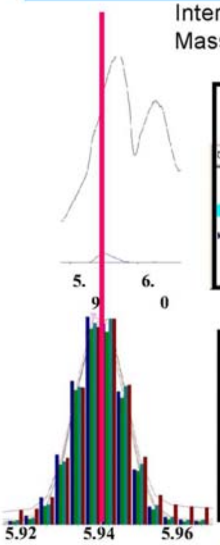
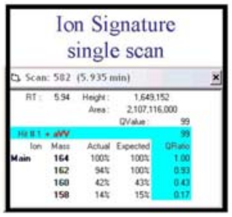
Ion Signature Technologies

Internal Standard: Acenaphthene-d10
Mass spectrum buried In high concentration chemical noise



Ion Signature
single scan

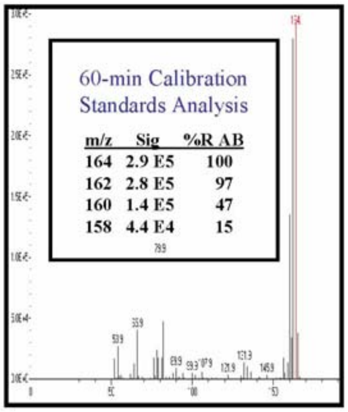


Scan: 582 (5.935 min)

RT:	5.94	Height:	1,649,152	
		Area:	2,107,116,000	
		QValue:		99
Hit # 1 + aVV				99
Ion	Mass	Actual	Expected	QRatio
Main	164	100%	100%	1.00
	162	94%	100%	0.93
	160	42%	43%	0.43
	158	14%	15%	0.17

Ion Signature
14 scan average

m/z	%RAB
164	100
162	94
160	42
158	14



60-min Calibration
Standards Analysis

m/z	Sig	%R AB
164	2.9 E5	100
162	2.8 E5	97
160	1.4 E5	47
158	4.4 E4	15

After deconvolution, qualifier ions are normalized to the quant ion, repetitive histograms show match at every scan across the peak

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TECP-MIP (Field) Methylene Chloride (Lab) Extracted Coal Tar Samples, mg/kg

	Soil 1 (5% coal tar)				Soil 2 (10% coal tar)				Soil 3 (100% coal tar)			
Compounds	**LAB**	**FIELD (n = 3) Ave. (% RSD)**	**% R**	**RPD**	**LAB**	**FIELD (n = 3) Ave. (% RSD)**	**% R**	**RPD**	**LAB**	**FIELD (n = 3) Ave. (% RSD)**	**% R**	**RPD**
Naphthalene	297	45 (6)	15	147	274	77 (57)	28	112	27,055	7,661 (21)	28	112
Acenaphthylene	57	20 (30)	35	97	83	11 (46)	13	153	4,440	437 (22)	10	164
Acenaphthene	32	13 (79)	41	86	38	8 (41)	21	130	1,264	152 (18)	12	157
Fluorene	94	42 (71)	45	76	118	26 (27)	22	128	3,942	322 (15)	8	170
Phenanthrene	252	70 (56)	28	113	339	67 (44)	20	134	8,236	391 (43)	5	182
Anthracene	75	13 (73)	17	141	80	13 (29)	16	146	2,525	92 (56)	4	186
Fluoranthene	62	3 (78)	5	184	103	7 (37)	7	174	2,361	53 (54)	2	191
Pyrene	150	3 (61)	2	193	192	8 (38)	4	184	3,484	62 (50)	2	193
Total non-alkylated PAH	*1,019*	*209 (57)*	*20*	*132*	*1,227*	*217 (40)*	*18*	*140*	*53,307*	*9,170 (35)*	*17*	*141*
C_1-naphthalenes	375	113 (32)	30	107	715	236 (45)	33	101	24,122	8,384 (25)	35	97
C_2-naphthalenes	623	149 (54)	24	123	882	175 (45)	20	134	15,215	2,004 (28)	13	153
C_1-fluorenes	105	45 (80)	43	80	152	34 (35)	22	127	5,687	255 (38)	4	183
C_2-fluorenes	35	4 (42)	11	159	62	12 (41)	19	135	2,202	93 (58)	4	184
C_1-phenanthrenes	301	22 (37)	7	173	409	43 (34)	10	162	15,692	359 (64)	2	191
C_2-phenanthrenes	65	0.4 (95)	1	198	71	8 (35)	11	159	6,262	103 (76)	2	194
C_1-fluoranthenes	168	ND			254	2 (56)	1	197	11,865	38 (59)	0.3	199
Total alkylated PAH	*1,672*	*333 (57)*	*20*	*134*	*2,545*	*510 (42)*	*20*	*133*	*81,045*	*11,236 (50)*	*14*	*151*
Total PAH	*2,691*	*542 (57)*	*20*	*133*	*3,772*	*727 (41)*	*19*	*135*	*134,352*	*20,406 (42)*	*15*	*147*

% R, recovery = (Probe/Lab * 100).
RPD, accuracy = 100 ((Lab - Probe) / 0.5 (Lab + Probe).
ND, non-detect.

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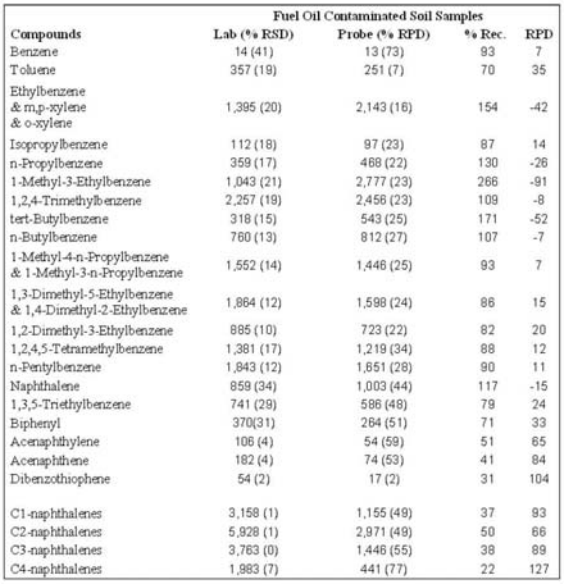
MIP (Probe), Methylene Chloride (Lab) Extracted Fuel Oil Samples, mg/kg



	Fuel Oil Contaminated Soil Samples			
Compounds	Lab (% RSD)	Probe (% RPD)	% Rec.	RPD
Benzene	14 (41)	13 (73)	93	7
Toluene	357 (19)	251 (7)	70	35
Ethylbenzene & m,p-xylene & o-xylene	1,395 (20)	2,143 (16)	154	-42
Isopropylbenzene	112 (18)	97 (23)	87	14
n-Propylbenzene	359 (17)	468 (22)	130	-26
1-Methyl-3-Ethylbenzene	1,043 (21)	2,777 (23)	266	-91
1,2,4-Trimethylbenzene	2,257 (19)	2,456 (23)	109	-8
tert-Butylbenzene	318 (15)	543 (25)	171	-52
n-Butylbenzene	760 (13)	812 (27)	107	-7
1-Methyl-4-n-Propylbenzene & 1-Methyl-3-n-Propylbenzene	1,552 (14)	1,446 (25)	93	7
1,3-Dimethyl-5-Ethylbenzene & 1,4-Dimethyl-2-Ethylbenzene	1,864 (12)	1,598 (24)	86	15
1,2-Dimethyl-3-Ethylbenzene	885 (10)	723 (22)	82	20
1,2,4,5-Tetramethylbenzene	1,381 (17)	1,219 (34)	88	12
n-Pentylbenzene	1,843 (12)	1,651 (28)	90	11
Naphthalene	859 (34)	1,003 (44)	117	-15
1,3,5-Triethylbenzene	741 (29)	586 (48)	79	24
Biphenyl	370(31)	264 (51)	71	33
Acenaphthylene	106 (4)	54 (59)	51	65
Acenaphthene	182 (4)	74 (53)	41	84
Dibenzothiophene	54 (2)	17 (2)	31	104
C1-naphthalenes	3,158 (1)	1,155 (49)	37	93
C2-naphthalenes	5,928 (1)	2,971 (49)	50	66
C3-naphthalenes	3,763 (0)	1,446 (55)	38	89
C4-naphthalenes	1,983 (7)	441 (77)	22	127

Conclusions

- Combination of TECP-MIP to PID and GC/MS maximizes efficiency of the site investigation process
- Reliable PID allows one visit for site investigation
  - All confirmation samples will contain PAHs
- No re-mobilization
  - Reduction in equipment and labor expenses
  - Eliminates time wasted
- No sample preparation
- Rugged, ready for field use

Funding Sources and Partners

- The U.S. Environmental Protection Agency (ORD and Regions)
- The U.S. Department of Defense (Army and Air Force)
- State Departments of Environmental Protection
  - Florida
  - Massachusetts
  - New Jersey
  - North Carolina
  - Illinois
  - Tennessee
  - Vermont
- The Electric Power Research Institute
- Agilent Technologies
- Ion Signature Technology

Polychlorinated Biphenyls (PCBs) and Obsolete US Government Ships

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ABSTRACT

The presence of Polychlorinated Biphenyls (PCBs) is an ongoing issue for obsolete ships designated for disposal as artificial reefs or by scrapping, particularly those ships built prior to 1978 phase-out of PCBs.

PCBs can be found in shipboard materials such as capacitors, hydraulic fluids, electrical cabling, paints and coatings, insulation, rubber products and gaskets. PCB-containing materials may be found throughout a ship and are not always easily identifiable or readily accessible. The type, amount, location and concentration of shipboard PCB-containing materials are highly variable. PCB-containing materials are also likely to vary from ship to ship and even ships in the same class can contain differing types, concentrations and amounts of PCB-containing materials. While these materials may be found throughout a ship, several areas on ships may have an increased likelihood of containing PCB-containing materials: areas or rooms subject to high heat or fire situations such as boiler rooms, engine rooms, electrical/radio rooms, weapons storage areas or areas with hydraulic equipment.

Sampling shipboard PCB-containing materials can present unique challenges. Working conditions onboard these ships are often far from ideal. While collecting samples is not technically difficult, it is destructive to equipment on the ship and can be physically demanding. In addition to the risks of working on and around a water environment, all sampling and health and safety equipment and supplies must be hand carried and it is nearly impossible to conduct a shipboard sampling event without encountering less than ideal temperatures, limited or blocked access to the ship or parts of the ship, no electricity, standing water, rotting or missing decks and/or missing ladders, treads and/or rails.

INTRODUCTION

The US Government has approximately 100 – 120 obsolete ships needing disposal. Disposal options for these ships include scrapping, artificial reefing and the US Navy's target practice program "SINKEX".

A major issue concerning the proper disposal of obsolete ships is the presence of PCBs either in liquid form (electrical equipment, hydraulic fluids) or non-liquid form (electrical cable, paint). PCB-containing materials cannot be readily identified. Collecting and analyzing samples is one path to determine regulatory status, alternately, the vessel owner can assume that shipboard materials are regulated and dispose of them without testing. Collecting samples from an obsolete ship presents a unique set of challenges often not encountered in environmental sampling scenarios.

PCBS AND OBSOLETE US GOVERNMENT SHIPS

The Ships

The US Government has approximately 100 – 120 obsolete ships needing disposal. Disposal options for these ships include scrapping, artificial reefing and the US Navy's target practice program "SINKEX".

The US Maritime Administration (MARAD) possesses the bulk of these ships as part of their Nation Defense Reserve Fleets (NDRF) or Ready Reserve Fleets (RRF). The NDRFs are located in Beaumont, TX, Suisun Bay, CA and Fort Eustis, VA. The ships in the NDRF are non-combatant ships such as tankers, troop transports, oilers and other support ships. The US Navy and other Federal agencies transfer non-combatant ships to MARAD for disposal. The US Navy disposes of combatant vessels such as battleships, destroyers and aircraft carriers.

Many of these ships were built between the 1940s and 1970s and are rapidly deteriorating. Many have exfoliating paint and rusting and leaking hulls or tanks and have been stripped or cannabilized of essential equipment and parts such as gauges and navigation and radio equipment. None of the ships designated for disposal can operate or function under their own power. Except for possibly the combatant ships, virtually none of these ships can or will be put back into service.

PCBs in Shipboard Materials

Many of the ships built between the 1940s and 1970s were constructed using materials containing regulated levels of PCBs (≥ 50 ppm). Since the PCBs were more than likely added at the time of manufacture, it is unlikely that the shipbuilders, MARAD or the Navy knew of the use of PCBs in shipboard materials. The US Navy maintains that the military specifications or "milspecs" for these shipboard materials never required the use of PCBs but did require they have the properties that PCBs would have added to a product – fire and heat resistance, elasticity and longevity.

PCBs can be found in a variety of shipboard materials and can be present as a result of a spill of liquids containing PCBs. These materials may be found throughout a ship and the type, amount, location and concentration can be highly variable. In addition, these materials are not easily identifiable or readily accessible. They are also likely to vary from ship to ship and even ships in the same class can contain differing types, concentrations and amounts of PCB-containing materials. The following materials are known or suspected to contain PCBs:

Materials and items that could contain solid PCBs

- Cable insulation
- Rubber and felt gaskets
- Thermal insulation material including fiberglass, felt, foam, and cork
- Voltage regulators, switches, reclosers, bushings, and electromagnets

- Electronic equipment, switchboards, and consoles
- Adhesives and tapes
- Oil-based paint
- Caulking
- Rubber isolation mounts
- Foundation mounts
- Pipe hangers
- Plastics

Materials and items that could contain liquid PCBs

- Oil used in electrical equipment and motors, anchor windlasses, hydraulic systems, and leaks and spills from such items

Materials and items that could contain either liquid or solid PCBs

- Transformers, capacitors, and electronic equipment with capacitors and transformers inside
- Fluorescent light ballasts
- Surface contamination of machinery and other solid surfaces due to spills

While these materials may be found throughout a ship, several areas on ships may have an increased likelihood of containing PCB-containing materials: areas or rooms subject to high heat or fire situations such as boiler rooms, engine rooms, electrical/radio rooms, weapons storage areas or areas with hydraulic equipment.

Collecting Samples Onboard the Ship

Sampling shipboard PCB-containing materials can present unique challenges. Carrying out a successful the sampling event requires extensive forethought and planning.

Become Familiar with the Ship

When planning a shipboard sampling event become as familiar with the ship or ships as possible. An internet search is probably the most convenient method to research a ship. There are several web sites that keep track of the status and history of obsolete US Government ships:

- Dictionary of American Fighting Ships - http://www.history.navy.mil/danfs/index.html
- Dictionary of American Naval Ships - http://www.hazegray.org/danfs/
- Naval Vessel Register - http://www.nvr.navy.mil/index.htm

In addition, a number of veterans/Merchant Marines groups and veterans/Merchant Marines who served these ships may maintain web sites dedicated to the ship's history and status.

Also, request the ship's owners or custodians locate and submit copies of the deck plans for the ship. If deck plans for the specific ship cannot be found, request the deck plans for a ship from the same class (often referred to as a "sister" ship). Deck plans are the maritime equivalent of blue prints for buildings. Ideally these plans should include a longitudinal cross section view and deck by deck views. Since these plans are similar in size to building blueprints, consider having reduced photocopies made in order to carry a copy during the sampling event.

In addition to the deck plans, request a site walk on the ship prior to the sampling event with an escort who is familiar with the ship and knows where any hazards such as missing or rotting decks or blocked passageways are located. This will aid in becoming familiar with the vessel. Request that an escort be made available for the sampling event, also.

Prior to the site walk and prior to the sampling event, schedule a pre-boarding meeting with the sampling team and the vessel owner/custodian and the escort to review ship conditions and deck plans. During this meeting obtain permission to photograph the vessel during the site walk and the sampling event. Also review the facility's emergency procedures and evacuation routes. The facility may also have an internal safety training that all team members will need to review and acknowledge receipt.

During the site walk, take note of the following:

- Assess the difficulty of accessing the ship since all equipment and supplies will be hand carried onboard and throughout the ship.
- Verify with the ship's owner/custodian that the vessel is completely powered down including shore power connections as electrical cables are often selected or targeted for sampling.
- Obtain permission to photograph the exterior and interior of the ship.
- Note the identification system for decks, compartments, bulkheads, passageways, door and hatches. They are often assigned a unique ID based on deck, frame number, starboard, port or center location and use. For Example: 1-150-5-L translates to Main Deck (1), Frame (150), Starboard side (5) and Living (L). Frames can be thought as the "ribs" of a ship. The higher the Frame numbers the closer to the stern. Odd numbers are assigned to Starboard (right side) and even numbers to Port (left side). The higher the number, the compartment will be located closer to the outside hull of the ship. Zero indicates the centerline of the ship.
- Identify areas where it may not be safe access such as blocked passages, low overheads and rotting or missing decks and ladders.
- Identify and mark possible sampling locations if using a targeted sampling scheme.
- If the sampling event will span several days, locate an equipment staging area such as a salon or mess hall

Identify Shipboard Materials for Sampling and Possible Locations

Prior to the sampling event, determine how many samples are desired and how they will be selected. Samples can be selected using either a random, unbiased sampling event or a targeted event aimed at particular shipboard materials. If a random sampling event is desired, plot the sampling locations on the deck plans prior to the sampling event.

Include enough sample locations that if some locations are inaccessible, a replacement location can be selected. If a targeted sampling event is desired, develop a list of target materials and target compartments or locations.

Consult with the laboratory of choice to determine the amounts of each media needed for analysis and laboratory QA/QC requirements.

Develop an Equipment List

When developing a list of equipment to take onboard, keep in mind that all equipment will have to hand carried and there will be no power, little natural light and possibly inadequate ventilation. When choosing sampling equipment and supplies, the goal should be minimization – carry as little as possible. Disposable equipment is preferred over reusable as carrying decontamination fluids and supplies would be difficult. Some equipment such bolt cutters or hack saws is not disposable but may be difficult to decontaminate in between samples on site. To resolve the decontamination issue, use hack saws with replaceable blades and change blades in between samples or instruct the laboratory remove the cut ends of the sample prior to homogenizing the sample for extraction and analysis.

Below is a list of suggested equipment.

Table 1 - Suggested List of Shipboard Sampling Equipment

Sample Collection Equipment	Personnel Protective Equipment	Documentation	Sample Handling	Waste Collection
Razor scrapers w/ disposable blades or Paint scrapers with disposable blades	Flashlights and Batteries (or other lighting source)*	Sample Identification Tags	Packing Tape	Waste containers for hazardous and non-hazardous wastes
Bolt cutters or hack saws with disposable blades	Latex/Nitrile Gloves	Field Log Book (Bound)	Chain-of-Custody Forms	Labels/Marks
Screwdrivers	Portable First Aid Kit	Camera, Film/Digital Media, Spare Batteries	Shipping Labels	Trash bags
Utility knives w/ disposable blades	Hard hat	Vessel Deck Plans	Bills of Lading	
Tape measure (100 foot)	Leather Gloves	Sharpies and/or indelible ink pens	Coolers	
Duct or Masking Tape	Safety shoes or boots	Spray Adhesive	Ice or ice packs	
Sample containers – wide mouth glass, pre-cleaned, Teflon-lined lids, 250 ml or 500 ml, or manila envelopes (for samples)	Signaling devices	Paint Crayons/Spray Paint	Custody Seals	
Templates or ruler	Personal Floatation Devices (PFDs)**	Calculator (if using a random sampling plan)	Plastic bags (Ziplocs ™)	
Heavy Duty Aluminum foil or weighing (glassine) paper	Safety glasses with side shields or goggles			
	Head lamp for hard hat			

* Each person should carry redundant lights in case of failure.
** If required by ship owner/custodian

Collecting the Samples

The most important factor is collecting samples from these ships is the overall health and safety of the sampling team members. No sample is worth putting a member of the sampling team in a threatening situation.

Working conditions onboard these ships are often far from ideal. It is nearly impossible to conduct a shipboard sampling event without encountering less than ideal temperatures, limited or blocked access to the ship or parts of the ship, no electricity, standing water, rotting or missing decks and/or missing ladders, treads and/or rails. The most effective way to avoid or overcome the majority of the challenges is to become familiar with the ship, have a knowledgeable escort and a set of deck plans.

In addition to the risks of working on and around a water environment, all sampling and health and safety equipment and supplies must be hand carried onboard and throughout the ship. Limit equipment to bare necessities and multi-purpose tools/equipment as much as possible. Identify a central staging area either during a pre-sampling site walk or as soon the ship is boarded. Stage as much equipment and supplies as possible to reduce the amount to be carried.

Once onboard the ship, it is not advisable to allow team members to separate. It is easy to become disoriented and lost. Once below deck the only available light will be from flashlights or lanterns. If possible, make sure each team member has their own copy of the deck plans and they are aware of where they are at all times. If it is necessary to move ahead of the sampling team, send a pair of team members as a "scout" team and limit how far ahead they can go.

While collecting samples is not technically difficult, it is destructive to equipment on the ship and can be physically demanding. Ships are typically not designed to freely move from one end to the other unimpeded. They are designed with the ability seal off compartments or entire sections of the ship using water or air tight doors and still remain operational. There will be climbing up and down ladders and over bulkheads and ducking under low overheads. Once sampling moves below the main and upper decks, there will be little to no natural light. Also, the interior atmosphere, while probably not oxygen deficient, will be stale and may be unpleasant to some team members. Temperature will vary throughout the vessel depending on location and the time of year. It is advisable to dress in warm, light, easily removable layers such as silk, cotton or fleece. If possible, schedule the sampling event for the spring or fall. Summer and winter can produce temperature extremes and in the winter, icy conditions which can add to challenges of sampling a ship.

The sampling itself involves sawing, cutting, scraping and gouging and will often require reaching overhead or crawling underneath or behind a piece of equipment. When sampling paints and coatings, the samples will require scraping to bare metal. To reduce the scraping effort, look for paint that is already exfoliating or peeling in the same vicinity as the selected location. When sampling gaskets, look for gaskets that already extruding from flanges or loosening from a water or air tight door or hatch. Once a sample has been collected, mark the location so if the sampling team needs to return to collect additional sample, it can be located quickly and with certainty. In addition, it will let other sampling team know that some one has been their before them and gives them an option to collect a “duplicate” sample.

When planning the sampling event, build in time for frequent breaks as the sampling team will need rest and fresh air and if working during the summer or winter, the team may need to either cool off or get warm.

CONCLUSION

Collecting samples for PCB analysis from obsolete ships can be done safely and successfully with detailed forethought and planning.

ACKNOWLEDGEMENTS

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San Francisco, CA

U.S. Navy

U.S. Maritime Administration

ESCO Marine/Resolve Marine Group, Brownsville, TX

ReefMakers, Inc., Morristown, NJ

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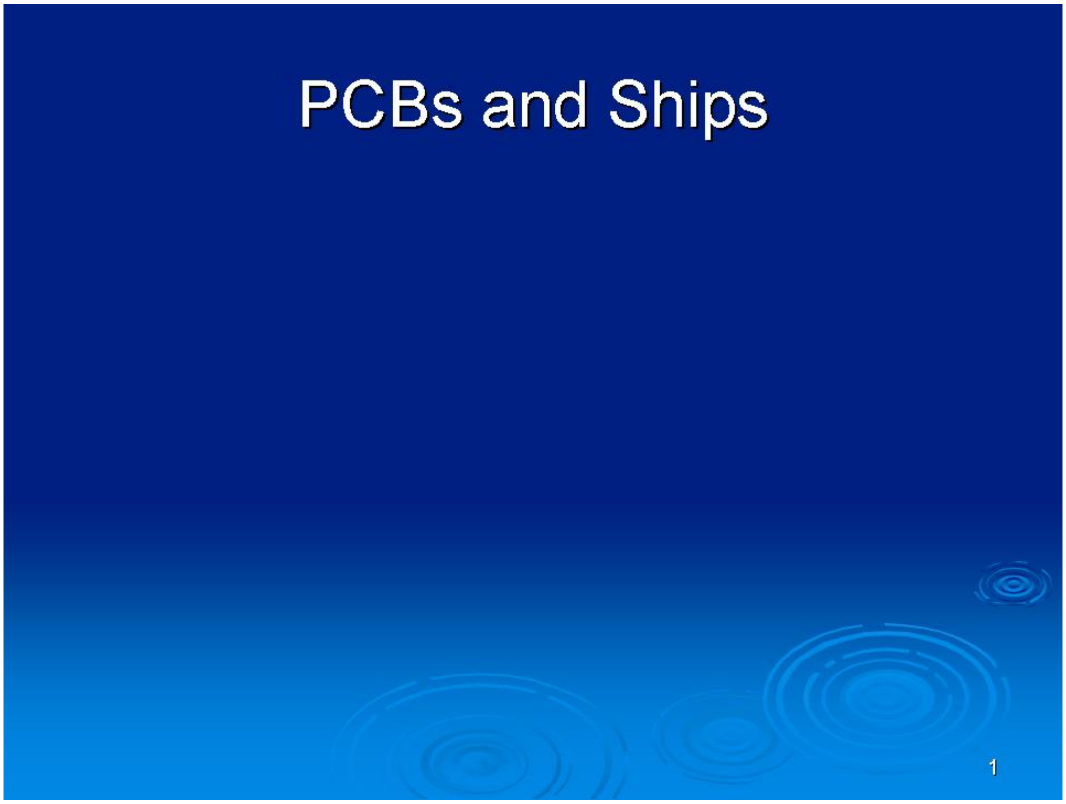
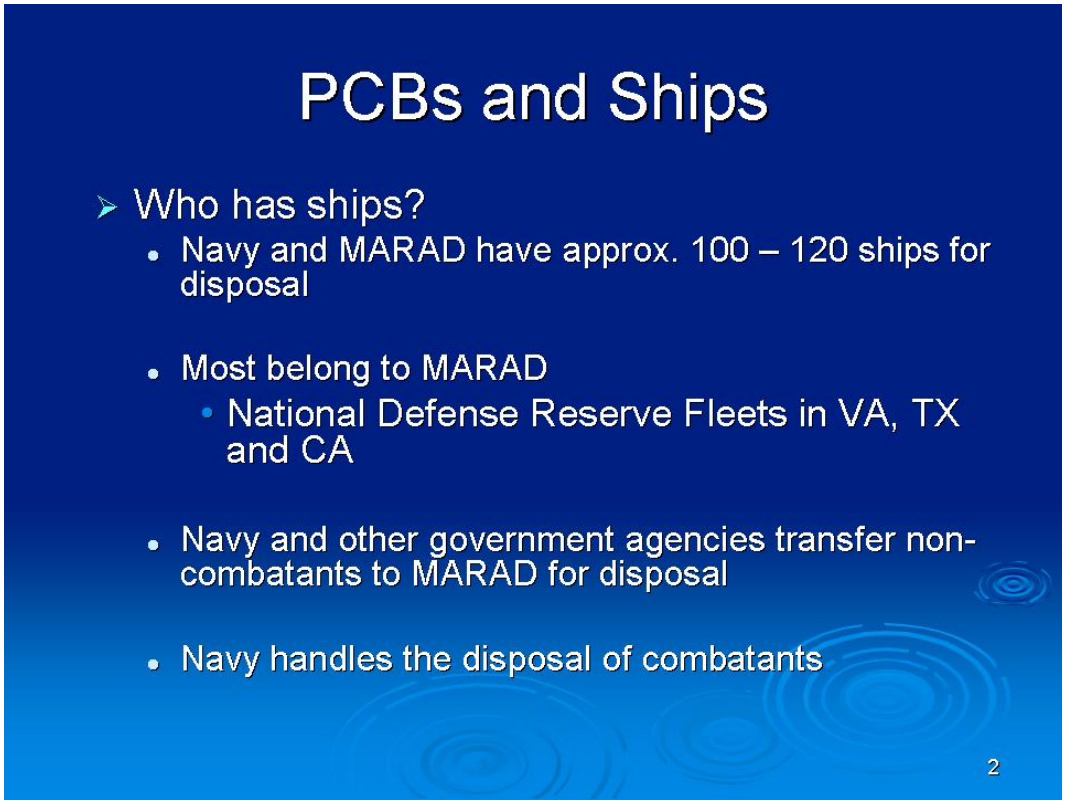
1. U.S. Environmental Protection Agency, U.S. Maritime Administration, 2006. *National Guidance: Best Management Practices for Preparing Vessels Intended to Create Artificial Reefs*. Office of Water.

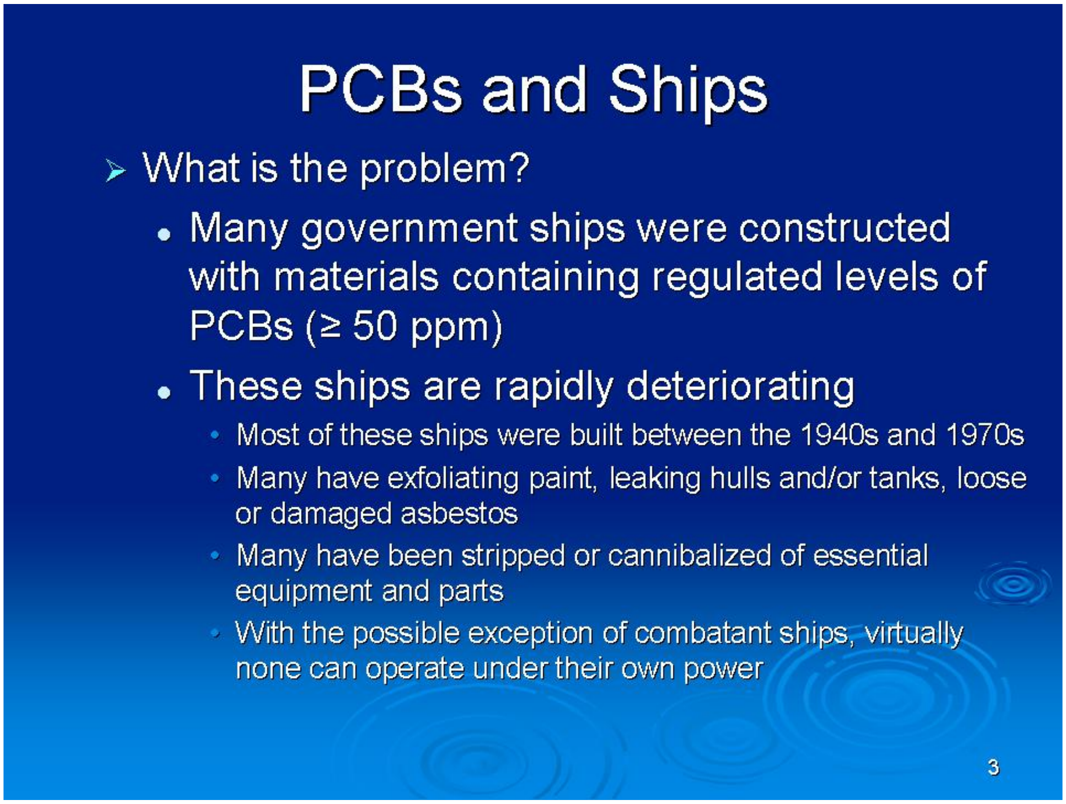


PCBs and Ships



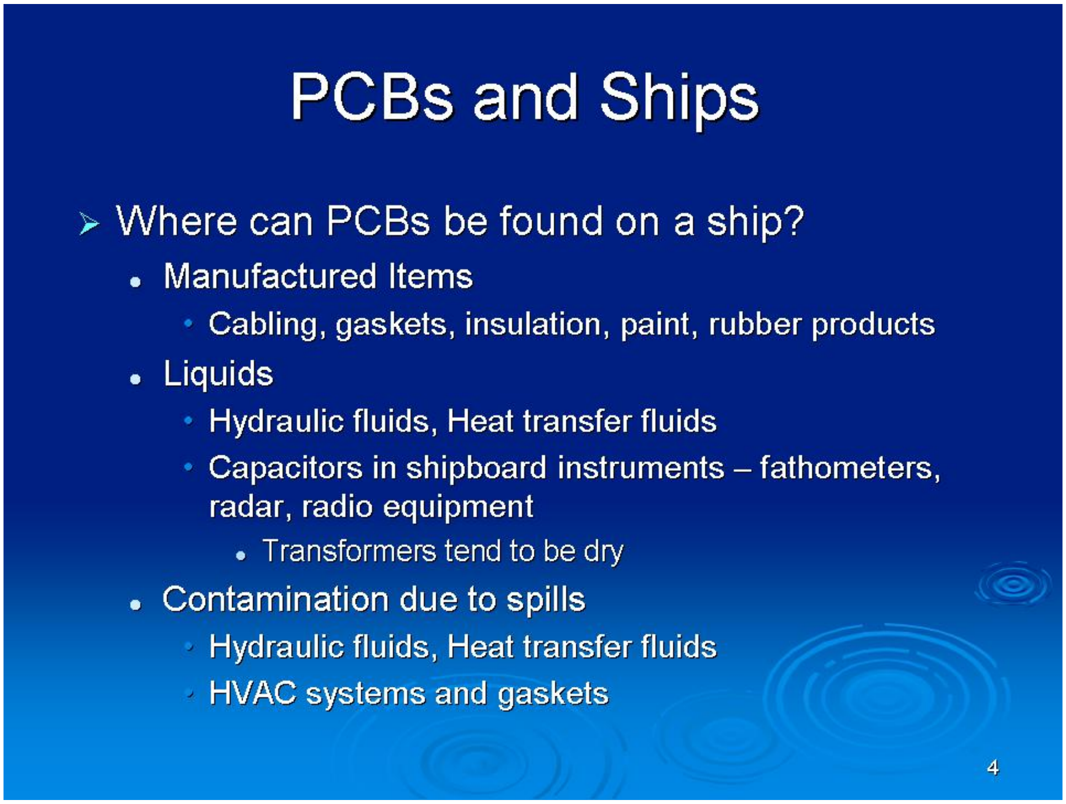
PCBs and Ships

- Who has ships?
  - Navy and MARAD have approx. 100 – 120 ships for disposal
  - Most belong to MARAD
    - National Defense Reserve Fleets in VA, TX and CA
  - Navy and other government agencies transfer non-combatants to MARAD for disposal
  - Navy handles the disposal of combatants



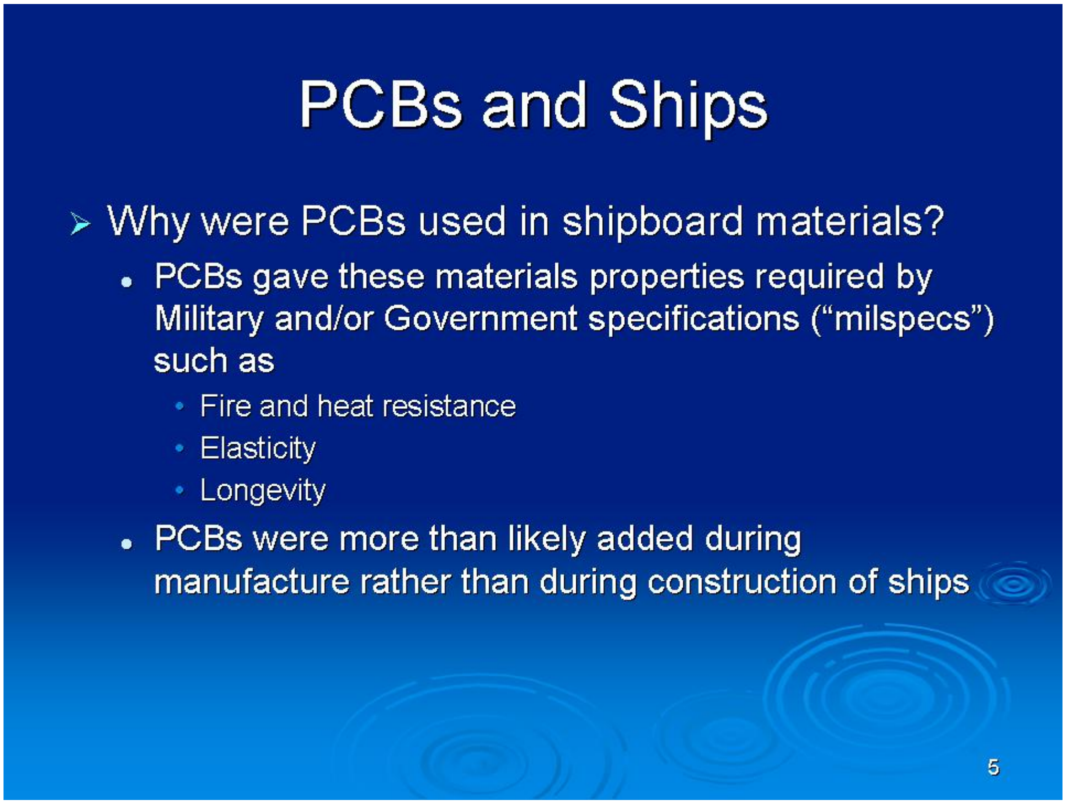
PCBs and Ships

- What is the problem?
  - Many government ships were constructed with materials containing regulated levels of PCBs (≥ 50 ppm)
  - These ships are rapidly deteriorating
    - Most of these ships were built between the 1940s and 1970s
    - Many have exfoliating paint, leaking hulls and/or tanks, loose or damaged asbestos
    - Many have been stripped or cannibalized of essential equipment and parts
    - With the possible exception of combatant ships, virtually none can operate under their own power



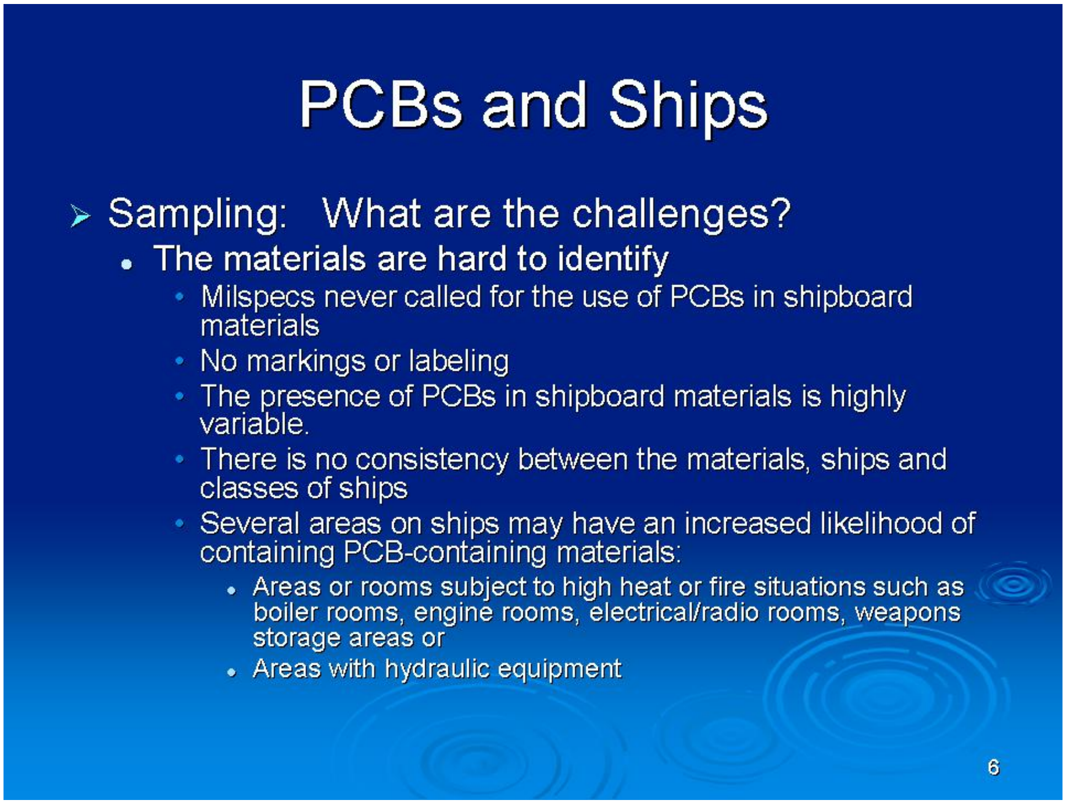
PCBs and Ships

- Where can PCBs be found on a ship?
  - Manufactured Items
    - Cabling, gaskets, insulation, paint, rubber products
  - Liquids
    - Hydraulic fluids, Heat transfer fluids
    - Capacitors in shipboard instruments – fathometers, radar, radio equipment
      - Transformers tend to be dry
  - Contamination due to spills
    - Hydraulic fluids, Heat transfer fluids
    - HVAC systems and gaskets



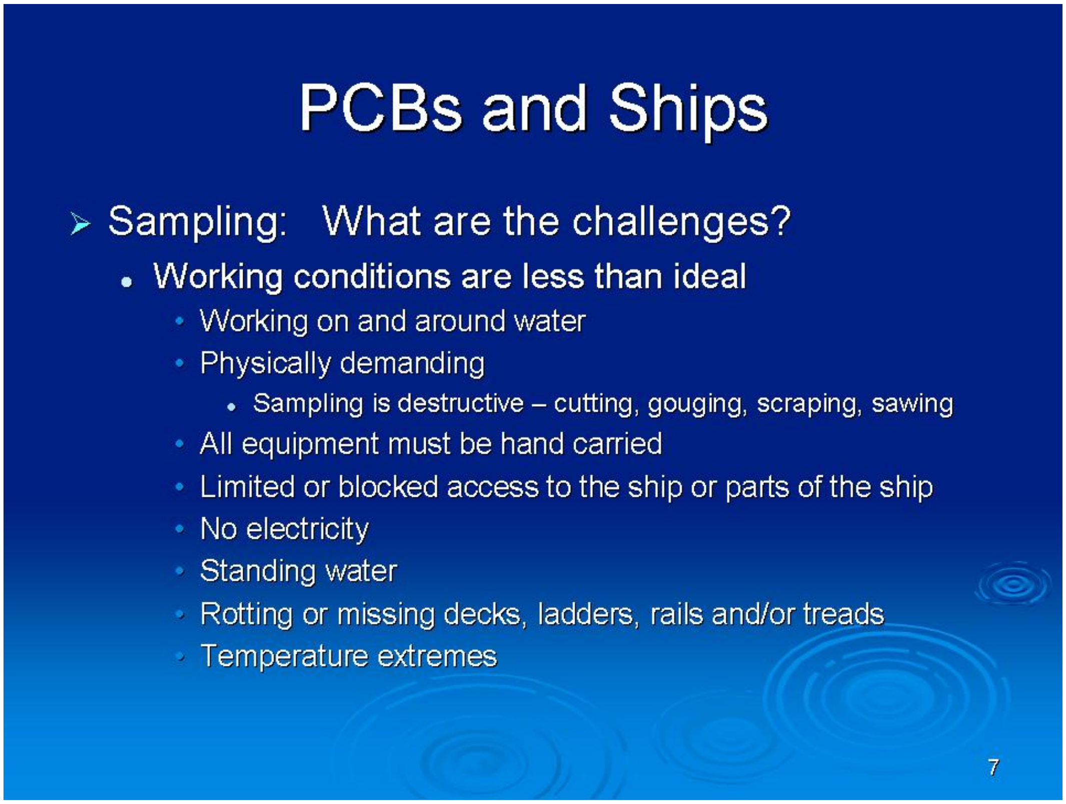
PCBs and Ships

- Why were PCBs used in shipboard materials?
  - PCBs gave these materials properties required by Military and/or Government specifications (“milspecs”) such as
    - Fire and heat resistance
    - Elasticity
    - Longevity
  - PCBs were more than likely added during manufacture rather than during construction of ships



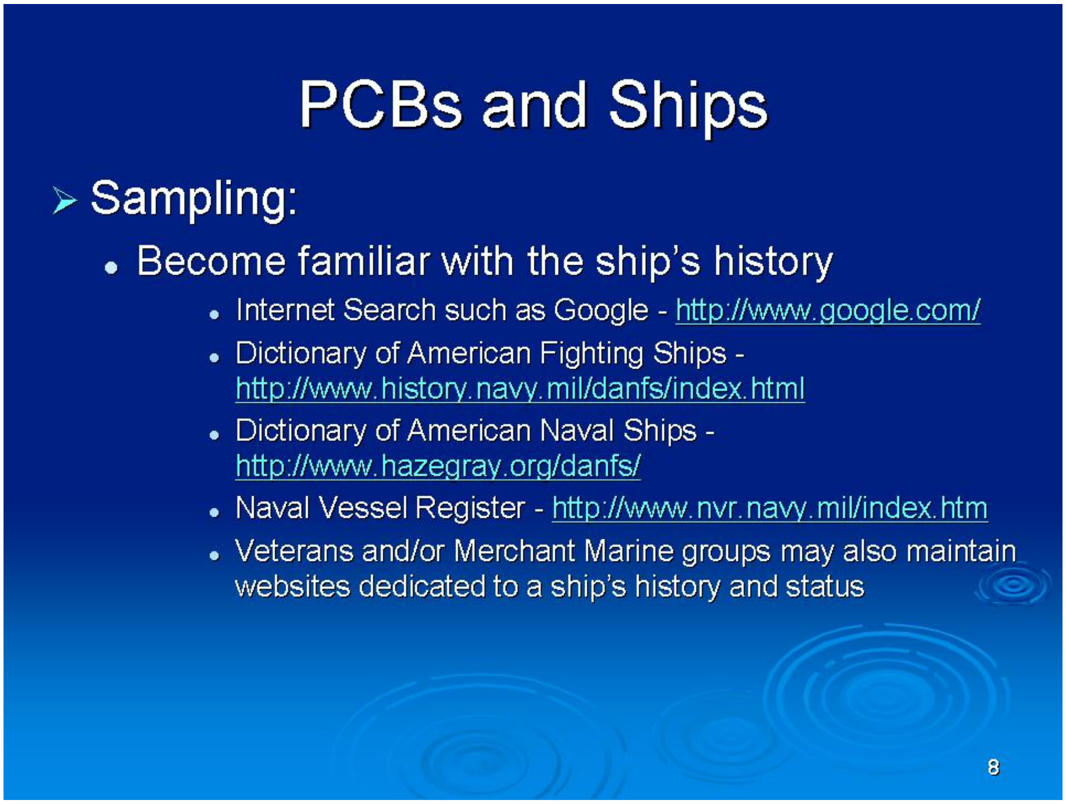
PCBs and Ships

- Sampling: What are the challenges?
  - The materials are hard to identify
    - Milspecs never called for the use of PCBs in shipboard materials
    - No markings or labeling
    - The presence of PCBs in shipboard materials is highly variable.
    - There is no consistency between the materials, ships and classes of ships
    - Several areas on ships may have an increased likelihood of containing PCB-containing materials:
      - Areas or rooms subject to high heat or fire situations such as boiler rooms, engine rooms, electrical/radio rooms, weapons storage areas or
      - Areas with hydraulic equipment



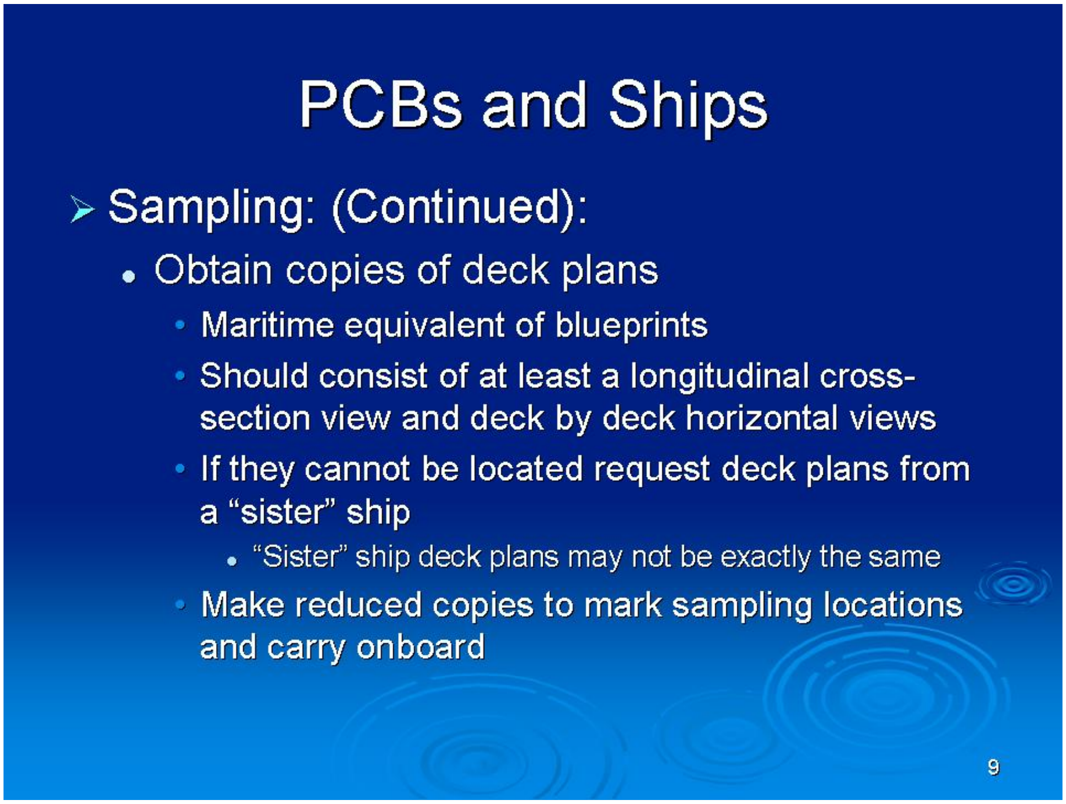
PCBs and Ships

- Sampling: What are the challenges?
  - Working conditions are less than ideal
    - Working on and around water
    - Physically demanding
      - Sampling is destructive – cutting, gouging, scraping, sawing
    - All equipment must be hand carried
    - Limited or blocked access to the ship or parts of the ship
    - No electricity
    - Standing water
    - Rotting or missing decks, ladders, rails and/or treads
    - Temperature extremes



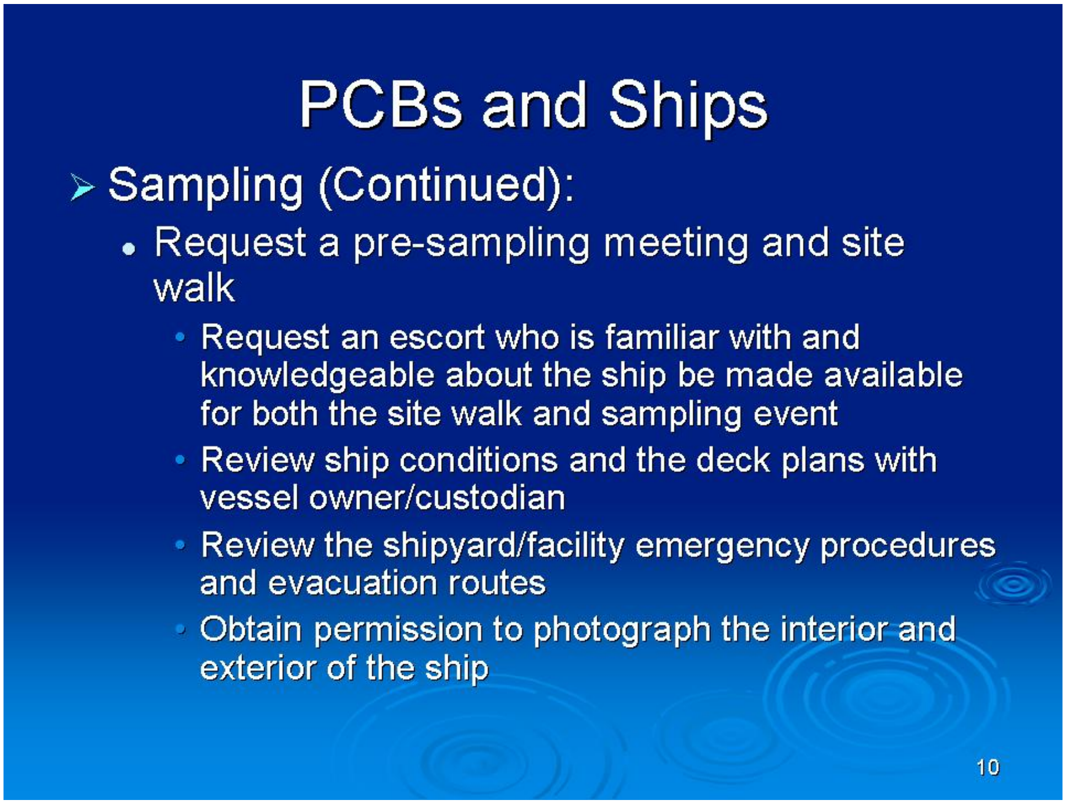
PCBs and Ships

- Sampling:
  - Become familiar with the ship's history
    - Internet Search such as Google - http://www.google.com/
    - Dictionary of American Fighting Ships - http://www.history.navy.mil/danfs/index.html
    - Dictionary of American Naval Ships - http://www.hazegray.org/danfs/
    - Naval Vessel Register - http://www.nvr.navy.mil/index.htm
    - Veterans and/or Merchant Marine groups may also maintain websites dedicated to a ship's history and status



PCBs and Ships

- Sampling: (Continued):
  - Obtain copies of deck plans
    - Maritime equivalent of blueprints
    - Should consist of at least a longitudinal cross-section view and deck by deck horizontal views
    - If they cannot be located request deck plans from a “sister” ship
      - “Sister” ship deck plans may not be exactly the same
    - Make reduced copies to mark sampling locations and carry onboard



PCBs and Ships

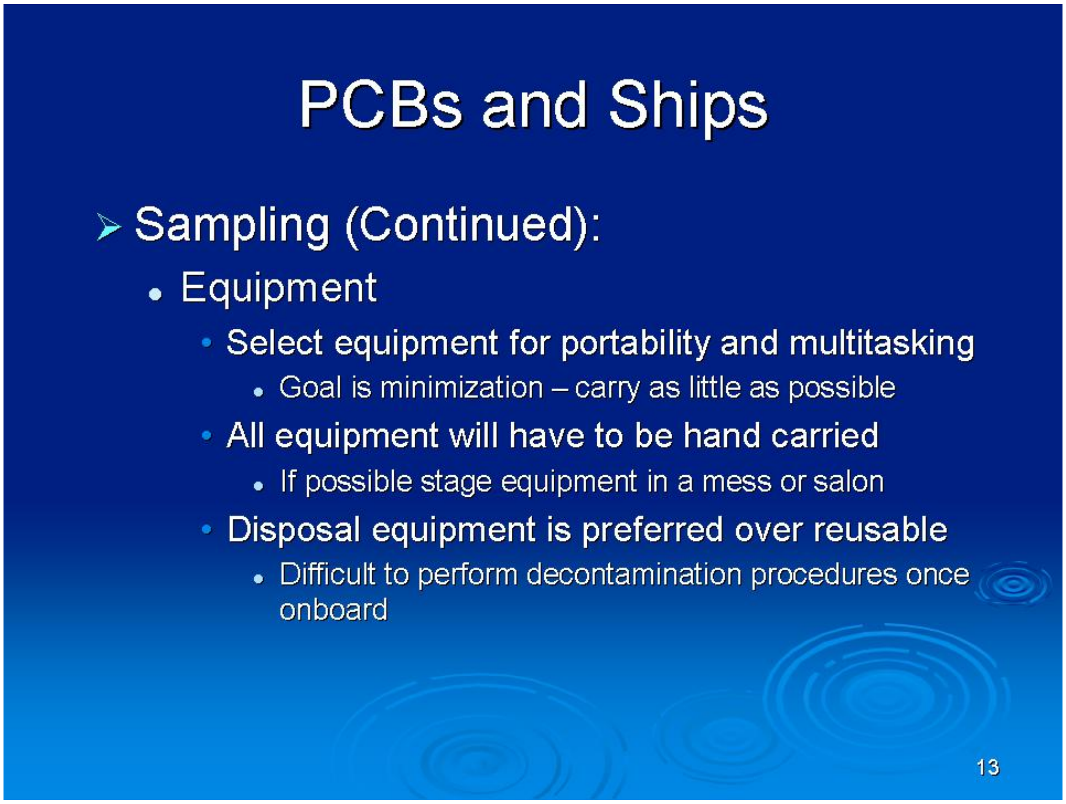
- Sampling (Continued):
  - Request a pre-sampling meeting and site walk
    - Request an escort who is familiar with and knowledgeable about the ship be made available for both the site walk and sampling event
    - Review ship conditions and the deck plans with vessel owner/custodian
    - Review the shipyard/facility emergency procedures and evacuation routes
    - Obtain permission to photograph the interior and exterior of the ship

PCBs and Ships

- Sampling (Continued):
  - During the site walk:
    - Where and how to board the ship
    - If the sampling will span several days, locate a possible staging area for equipment and supplies
      - A mess or salon will work well
    - Verify the ship is completely powered down including shore power
    - Take photographs
    - Take note of how the decks, compartments, bulkheads, passageways, doors and hatches are identified
      - Compare with deck plans
    - Identify possible safety hazards to avoid
    - Identify and mark possible sampling locations

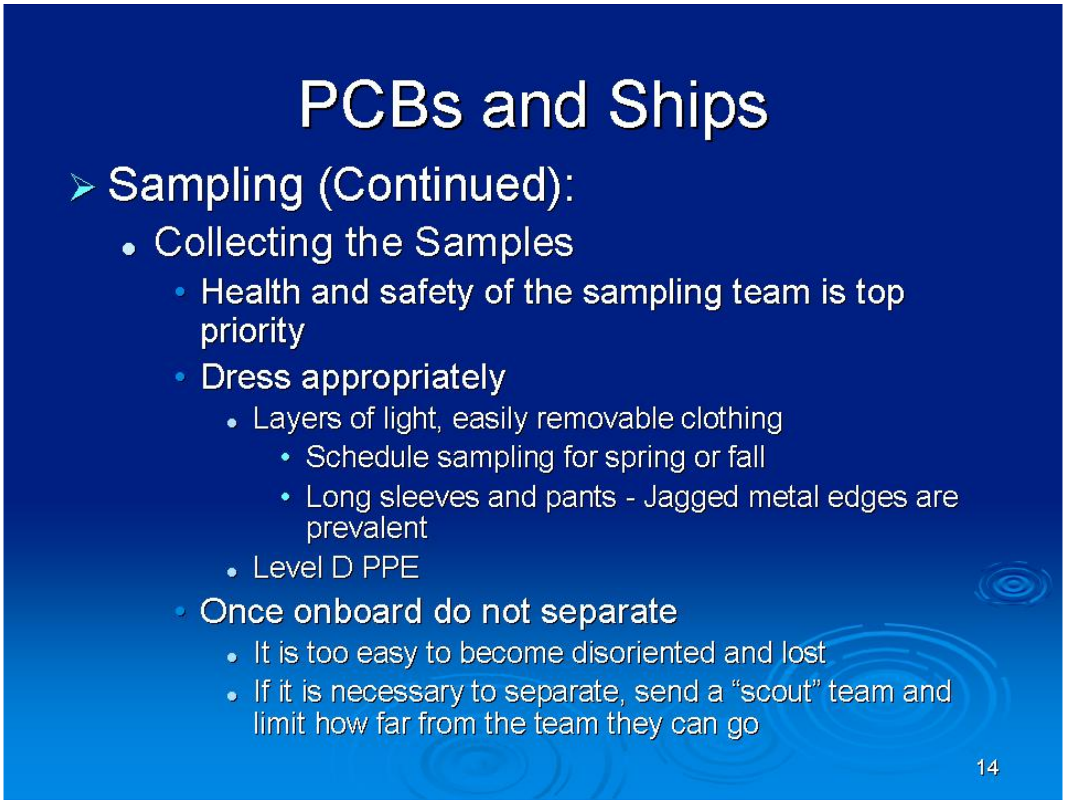
PCBs and Ships

- Sampling (Continued):
  - Materials and Locations
    - Determine the number of samples needed or desired
    - Random sampling vs. targeted sampling
      - Random Sampling
        - Pre-determine the sampling locations and plot on the deck plans
        - Select enough samples to cover required QA/QC
        - Select enough samples to have backups should an original location be inaccessible or not found
      - Targeted Sampling
        - Develop a list of materials and locations
        - Identify and mark possible locations and materials during site walk
    - Sample Size
      - Consult with the laboratory of choice



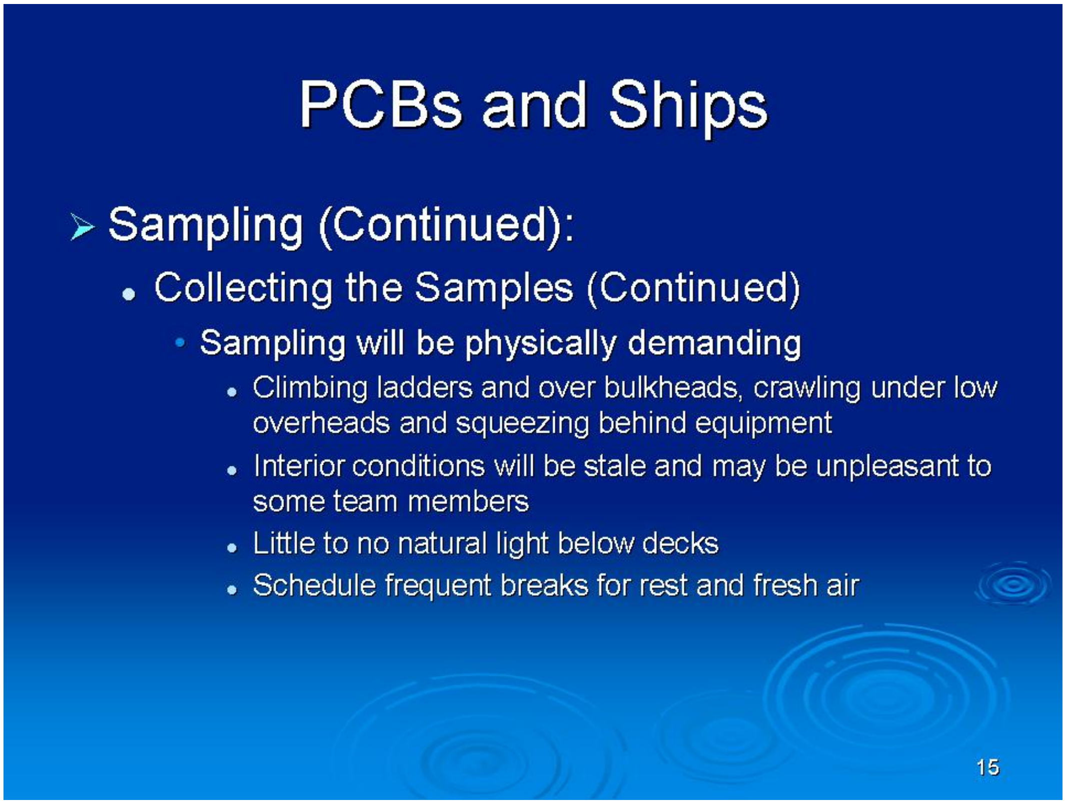
PCBs and Ships

- Sampling (Continued):
  - Equipment
    - Select equipment for portability and multitasking
      - Goal is minimization – carry as little as possible
    - All equipment will have to be hand carried
      - If possible stage equipment in a mess or salon
    - Disposal equipment is preferred over reusable
      - Difficult to perform decontamination procedures once onboard



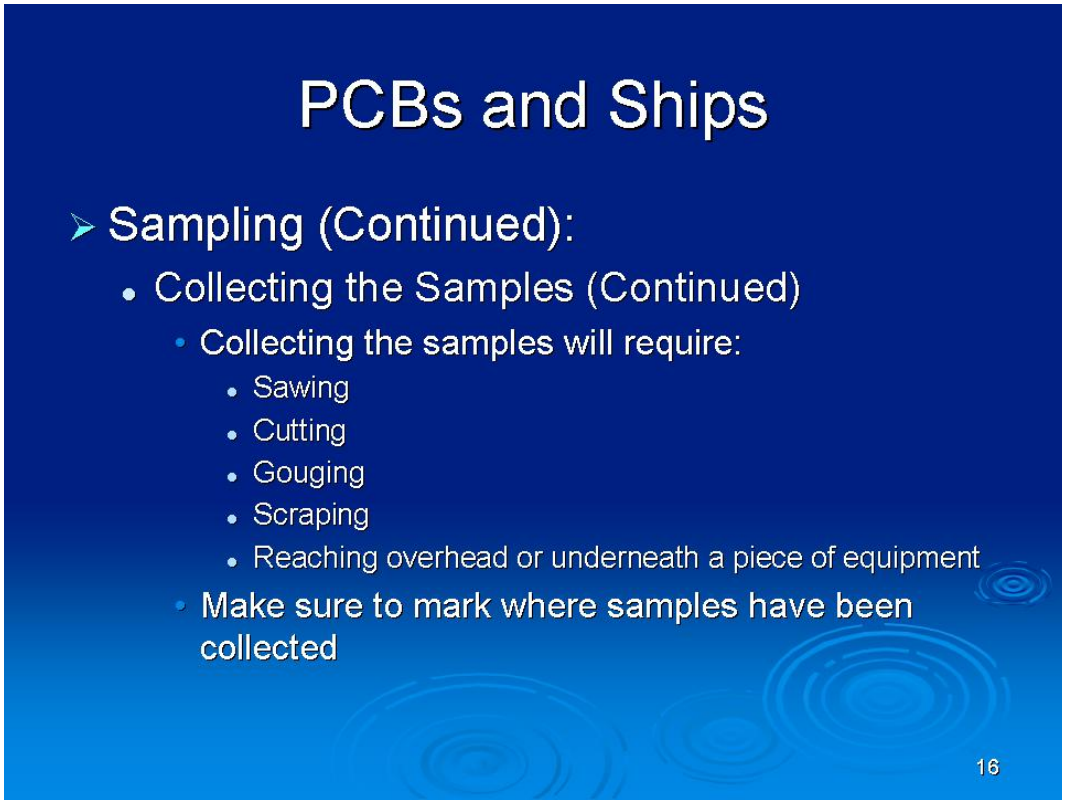
PCBs and Ships

- Sampling (Continued):
  - Collecting the Samples
    - Health and safety of the sampling team is top priority
    - Dress appropriately
      - Layers of light, easily removable clothing
        - Schedule sampling for spring or fall
        - Long sleeves and pants - Jagged metal edges are prevalent
      - Level D PPE
    - Once onboard do not separate
      - It is too easy to become disoriented and lost
      - If it is necessary to separate, send a “scout” team and limit how far from the team they can go



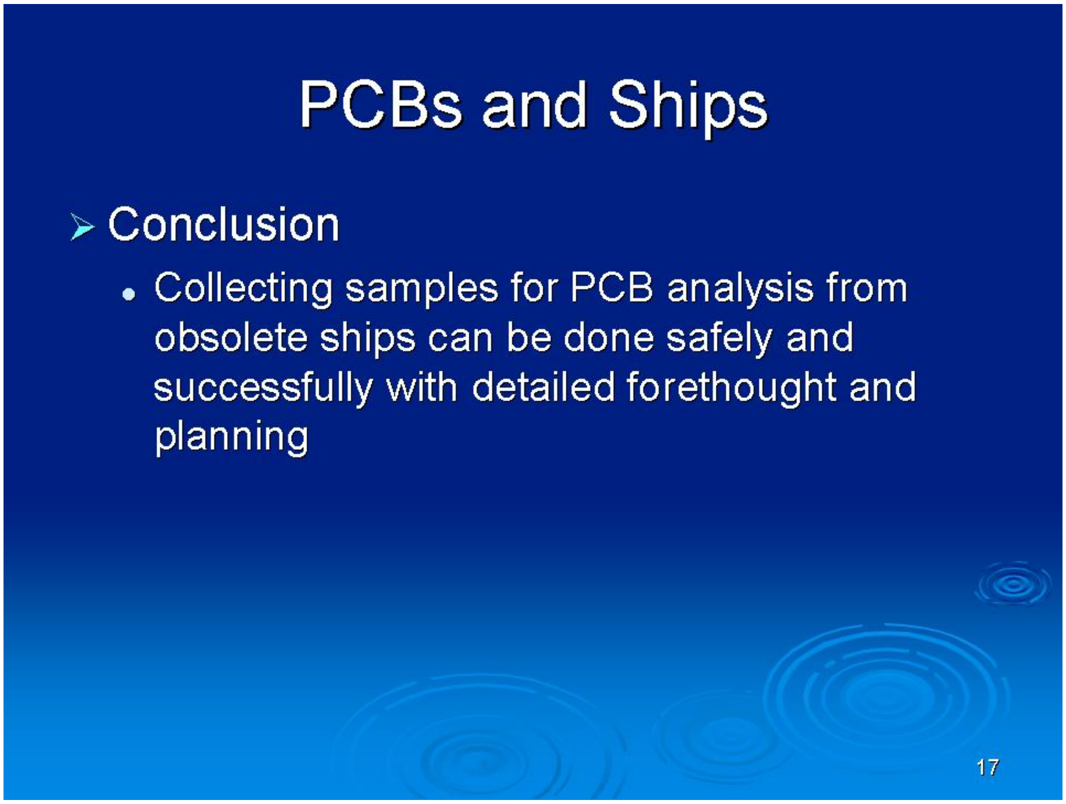
PCBs and Ships

- Sampling (Continued):
  - Collecting the Samples (Continued)
    - Sampling will be physically demanding
      - Climbing ladders and over bulkheads, crawling under low overheads and squeezing behind equipment
      - Interior conditions will be stale and may be unpleasant to some team members
      - Little to no natural light below decks
      - Schedule frequent breaks for rest and fresh air



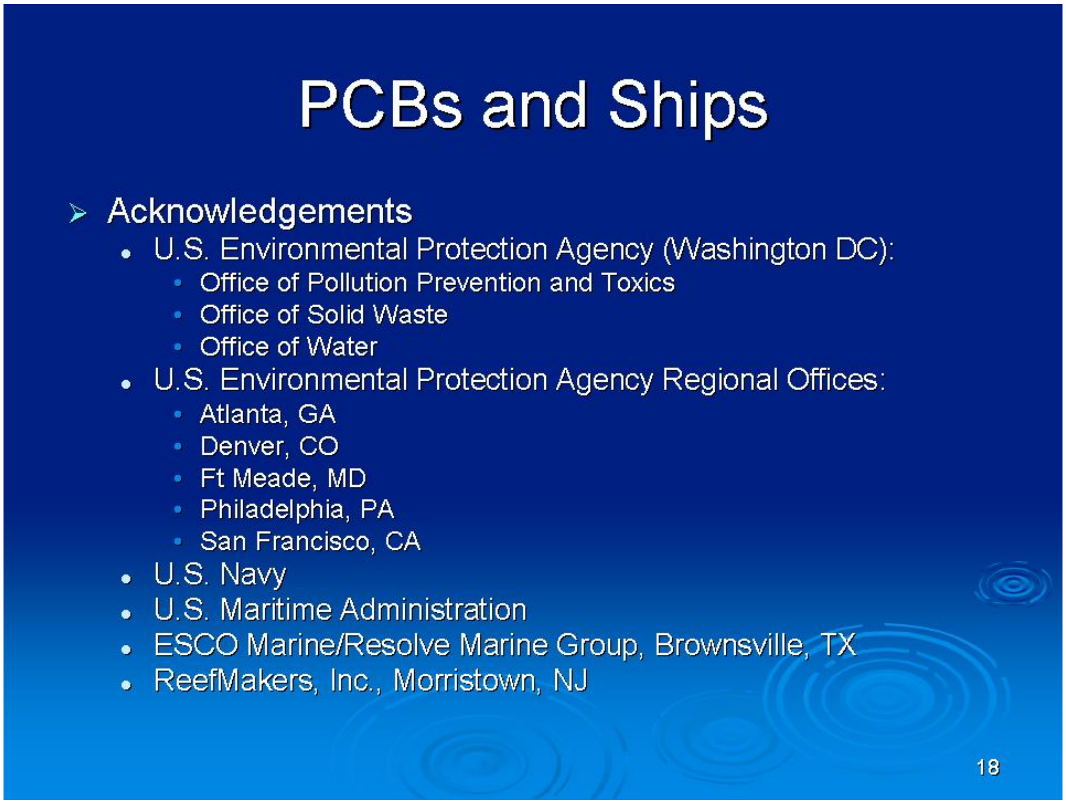
PCBs and Ships

- Sampling (Continued):
  - Collecting the Samples (Continued)
    - Collecting the samples will require:
      - Sawing
      - Cutting
      - Gouging
      - Scraping
      - Reaching overhead or underneath a piece of equipment
    - Make sure to mark where samples have been collected



PCBs and Ships

- Conclusion
  - Collecting samples for PCB analysis from obsolete ships can be done safely and successfully with detailed forethought and planning



PCBs and Ships

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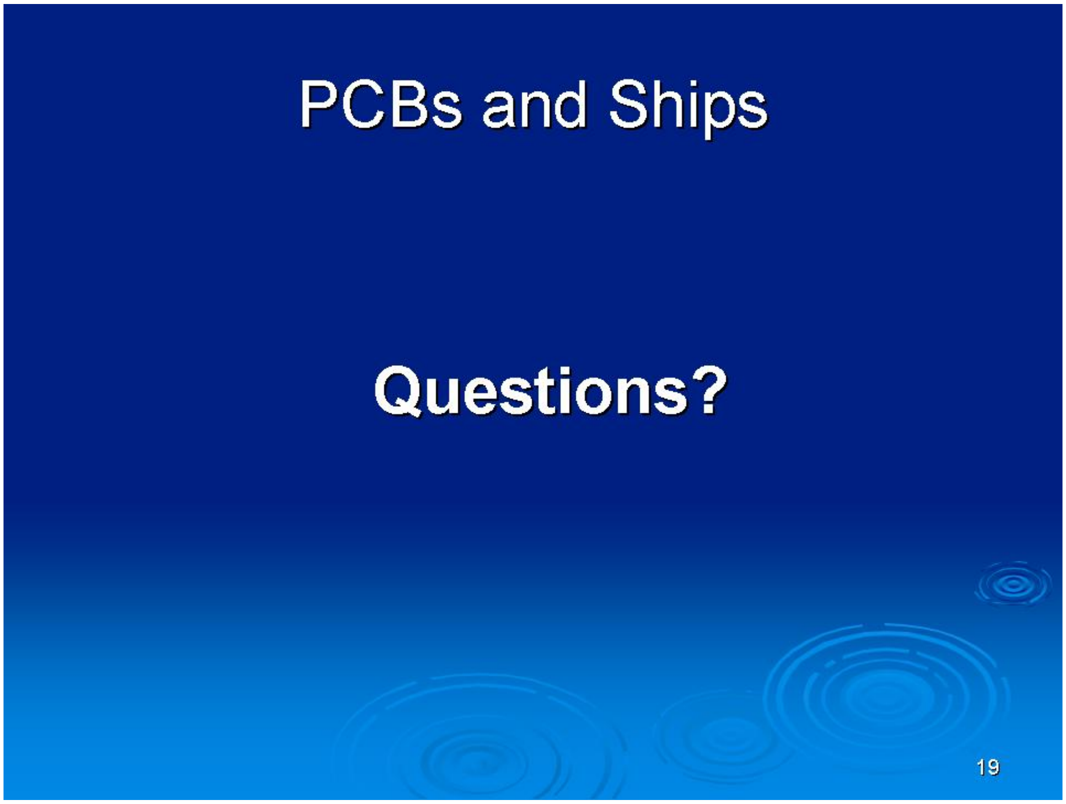
    - Ft Meade, MD
    - Philadelphia, PA
    - San Francisco, CA
  - U.S. Navy
  - U.S. Maritime Administration
  - ESCO Marine/Resolve Marine Group, Brownsville, TX
  - ReefMakers, Inc., Morristown, NJ



PCBs and Ships

Questions?

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METALS SPECIATION

Speciated Reference Materials: The Need and The Solution

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ABSTRACT

Knowledge of the speciated form of metals such as As, Cr and Hg in environmental and/or biological samples is critical to understanding the risk posed to public health and the environment. Analyses of environmental and/or biological samples requires the use of specie-specific methods that can be performed by academic, government and commercial laboratories; the reliability of these tests is enhanced by the use of reference materials of known specie concentration that approximate the conditions of the actual samples. This paper presents the issues with specie-specific analyses in a regulatory context and makes the case for the development of additional reference materials containing certified values of known metal species.

INTRODUCTION

Data on element species provides critical information that is not available from the results of total trace element determinations. Regulations based on total trace element determination can be supplemented or replaced by ones employing more meaningful concepts using the information of speciation that will permit evaluation of issues that include:

- Trace element speciation
- Toxicity of element species
- Species as environmental pollutants and workplace hazards
- Trace element species in human health and nutrition

The toxicity of what is often referred to as "toxic trace elements" really depends on their speciation and concentration. Examples include:

- Cr(III) is an essential nutrient; Cr(VI) is carcinogenic
- Inorganic As(III) compounds are carcinogenic; arsenobetaine is non-toxic
- Inorganic tin compounds are essential for plants and animals; tributyltin (TBT) is an endocrine disrupter

From the website of the European Virtual Institute for Speciation Analysis (EVISA), we have

"It is therefore essential that toxicological studies should always consider the species rather than the elemental constituent in order to create meaningful data. With respect to risk assessment and legislation it becomes more and more clear that failure to consider properly chemical speciation of elements other than carbon can lead to poor use of our resources. Laws and regulations based on simple elemental analysis may wrongly condemn environmental media or products as toxic and prevent the use of important resources."

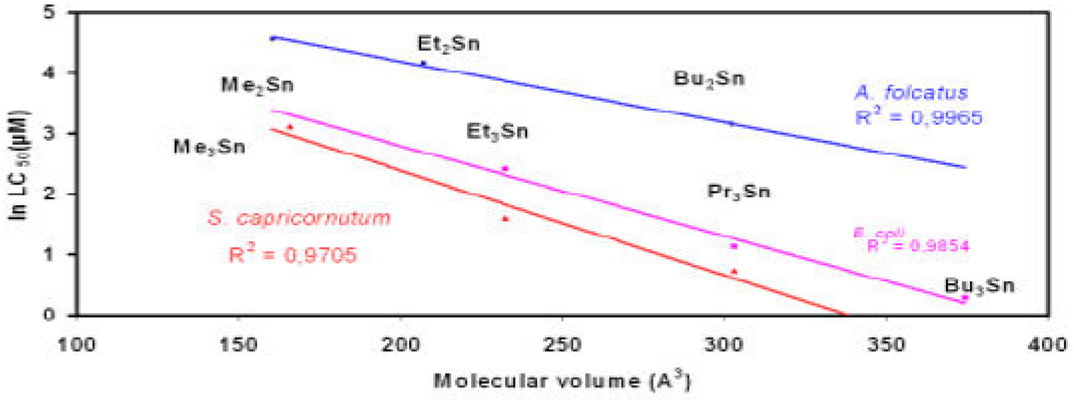
www.speciation.net

For example, the following Table shows the differences in the toxicity of various As species:

Chemical Specie	**DL50 (mg/kg)**
Arsenite [As(III)]	14
Arsenate [As(V)]	20
Arsine	3
MMA	700-1800
DMA	700-2600
Arsenocholine	> 10,000
Arsenobutane	> 10,000

From EVISA Website, www.speciation.net

and the following figure shows similar information for Sn species:



From EVISA Website, www.speciation.net

Among the justifications for use of speciation data in lieu of total metal concentrations are:

- Toxicity differences
- Mobility differences
- Bioavailability differences

The uses of speciated metals information can address the bioavailability of nutrient species in food production, reduced human exposure to toxic substances and prevent or intervene in human health issues such as cancer and autism

Potential Users of speciated reference materials include the following:

- CDC
- EPA/USGS
- USDA
- FDA
- State and Local government agencies
- Commercial laboratories

The integrity of any speciated measurement would be enhanced by the concurrent analysis of a reference material that mimics the concentration level and matrix conditions of the sample.

DEVELOPMENT OF SPECIATION STANDARDS

There are a series of "drivers" that impact the need for future speciation standards, First, academic research must help create new speciation analytical methods and then assist with the transfer of these new technologies to the commercial laboratory community. Academia must help to educate the regulatory community, which needs a greater understanding of the impact of speciation on environmental and biological assessments. This can help to incorporate some of these new analytical methodologies into government methods compendiums/regulatory guidance documents regarding methods of analysis, and eventually lead to the incorporation of speciation end-points in State and Federal regulations and permits.

The only specie that Federal and State agencies regulate using direct analytical measurement is Cr(VI); all other State regulations and permits infer the amount of a speciated metal from a measured "total" concentration. The lengthy cycle of regulations/permit evaluations often discourages the rapid adoption of state-of-the-art technologies.

For speciated analyses to be generally available, there must be a mechanism to certify these speciation methods by State and/or NELAC laboratory certification programs. There should not be any issues with NELAC and State lab. cert. programs offering certification for speciation methods; however, most accrediting authorities do not now have the expertise or experience to recognize the importance of speciation measurements and how to conduct effective and detailed laboratory assessments of speciation methods. Commercial laboratories and State accrediting authorities have (or can acquire) this capability. To prove that this can be done, the New Jersey Department of Environmental Protection, Office of Quality Assurance, has certified laboratories to date for the speciation for As, Cr and Hg.

To assist with this task, the availability of SRMs to appropriately QA speciation measurements is highly desired. Some categories of Future Speciated Standards include:

Biological
- Tissue
- Biofluids
- Solids (e.g., hair, fingernails)

and

Environmental
- Soils and wastes
- Sediments
- Sludges
- Air and Dust
- Water
- Others (including food)

These new SRMS should address the following issues:

- Health, environmental and/or toxicological concerns
- Impact upon regulatory standards @ Federal or state levels
- Uniqueness of:
    - Analyte
    - Species
- Capability of commercial lab. community to run speciation analytical methods
- Concentration Level(s)
- Better representativeness of critical conditions for proposed reference materials than other existing reference materials

CANDIDATE SRMS

EVISA has compiled a list of commercially available materials where one or more specie has a speciated reference value. The amended list is shown below:

	Aqueous	Blood	Hair	Sediment	Soil	Tissue
As						
Cr					Under Development	
Hg						
Se						
Sn						

Some overlap in matrix type is not necessarily a bad thing if the specie(s) and/or concentration levels differ from existing reference materials. The following are brief summaries of some potential SRMs:

As in Seaweed/Biota
Speciation of arsenic is important from both the toxicological mechanistic and regulatory perspectives. There are as many as three orders of magnitude differences between among the toxicity of different species or arsenic, many of which can be found in the diet. Like chromium, some of the arsenic species are not thought to be toxic at all or have a very limited toxicity. This is especially true for the dietary species of arsenic. Arsenic in seaweed would serve as a possible surrogate for dietary arsenic from seafood as well as a potentially different food based matrix for other vegetarian based foods containing arsenic such as rice mushrooms and carrots. Levels of arsenic species in seafood such as oyster tissue, or other shellfish is also important, but may be addressable via additional analyses of existing NIST SRM's such as Lake Superior Fish Tissue (1946) and Mussel Tissue (2976).

Seaweed should be relatively easy to acquire and the extraction protocols should be adaptable from extraction protocols already used for marine tissue. Processing for SRM evaluation could be accomplished by USGS or perhaps USDA. It is likely that once the seaweed is removed from its native environmental and freeze dried, arsenic species should then be stable. This material could be used by laboratories performing both regulatory-based assay and biomonitoring-based assays

Hg in Human Hair
Hg in human hair will principally of interest to laboratories doing biomonitoring. Hair is one of the principal sinks for mercury and has seen a renaissance of interest because of its possible link to thermerisol and autism. It is likely to be used as a biomarker for mercury contamination in any study looking at human exposure to mercury.

There are multiple published methods for the specie intact extraction and analysis of mercury from hair. Some available environmental methods used for extraction and analysis of mercury in soils may be adapted to this media as well. The acquisition of sample should be relatively easy, but processing would be a potential concern. The stability of Hg species within the sample matrix is unknown, but should be stable because its conversion should have taken place before being deposited in the hair. Mercury in hair in not part of current Federal biomonitoring programs, so the development of a relevant SRM would anticipate future needs in this area.

Hg in Sediment
Mercury's primary pathway to human exposure is through consumption of fish. Since mercury both bioaccumulates and biomagnifies through the food chain, the higher up the food chain the fish resides the higher the mercury concentration is libel to be. The first step in this pathway is the sediment near where fish reside

Mercury speciation as methyl-mercury in available in certified reference materials from the Canadian Research Council (DOLT-4: Dogfish Liver and DORM-3: Fish Protein). Sediment provides a useful alternative for environmental applications because it is a dry solid that can be used as a surrogate for soils, wastes and potentially even sludge. It is likely to be used primarily by the regulatory community and those responsible for environmental monitoring of various types of solid wastes.

The State of New Jersey has an abundance of freshwater sources known to contain lots of mercury contaminated sediments. The biological processes have converted some of the inorganic form to the monomethyl form and once processed they should remain stable. The concentration in the sediments is generally high enough to represent a contaminated sight and can be diluted to represent more pristine environments. Unfortunately, there are no completely uncontaminated (mercury free) sites left, but there are many locations where varying Hg concentrations can be found. Mercury is not currently regulated based on individual species, so creating this SRM could help to drive changes in future environmental regulations. There are several analytical methods available for both extraction and quantitation of mercury species that would be directly applicable to this proposed SRM.

Sn in the Marine Environment

Antifouling agents containing tin have been used in paints for ships. Various organotin compounds accumulate in sediments, with their concentrations and toxicities varying widely. For example, tributyltin is extremely toxic for molluscs such as mussels and oysters, leading to its restriction in marine paints. Despite the ban, sediments act as sink for such materials, making the amount of certain organotins in sediments a major concern. Potential SRM's could exists either on the tissue side (Sn in barnicles for example) or on the regulatory side (Sn in sediment). There is also the possibility that existing material NIST may be converted to an application for Sn in the marine environment. Like the current situation for mercury, there are no current regulatory statutes related to Sn species and no current speciation methods either acceptable or proposed by/to the EPA for Sn speciation, but the availability of a Sn reference material could drive regulatory changes.

A summary of potential SRMs and issues related to their development is shown below:

PRIORITIZATION OF FUTURE METAL SPECIATION SRM

Element	Matrix	Scientific Need	Regulatory Need	Ease of Acquisition/ Processing	Exclusivity	Commercial Lab. Capability
As	Seaweed/ Biota	3	3	3	2	3
Hg	Sediment	3	3	2	2/3	2
Sn	Sediment	2	2/3	2	3	2
Hg	Hair	3	1	1	2/3	1
Cr	Dust	2	2	2	3	3
Cr	Urine	2	1	2	3	1

3: Strong scientific/regulatory Needs, Ease of Sample Collection/Processing, No Other Speciated QA Materials Available, Commercial Lab. Community Can Easily Run Methods

2: Moderate/Limited scientific/regulatory Needs, Some Issues w/Sample Collection/Processing, Limited Availability of other Speciated QA Materials, Lab. Community Will Struggle to Run Methods

1: Questionable scientific/regulatory Needs, Difficulty w/Sample Collection/Processing, Other Speciated QA Materials Available, Commercial Lab. Community Will Have Great Difficulty Running Methods

NEXT STEPS

- Continue to compile a list of potential SRMs
- Gather input from other potential users such as the CDC and FDA
- Gain consensus from EPA, States and academic advisors on priorities
- Ask NIST, in collaboration with USGS, to develop a long-range plan to create an inventory of speciated SRMs

ACKNOWLEDMENTS

The author wishes to thank Drs. Brian Buckley, Clay Davis and Steve Long for their contributions.

REFERENCES

1. *European Virtual Institute for Speciation Analysis (EVISA),* www.*speciation*.net

SPECIATED REFERENCE MATERIALS - THE NEED AND THE SOLUTION

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WHY SPECIATION?

☒**Elemental forms differ in their**
  - Distribution
  - Mobility
  - Environmental Availability

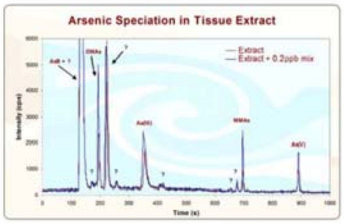
☒**Speciation information enables an understanding of**
  - Toxicity
  - Risk
  - Biological Activity

☒**Examples**
  - As: **inorganic-toxic**; arsenobetaine-innocuous
  - Cr: Cr(III)-nutrient; **Cr(VI)-carcinogen**
  - Sn: inorganic-innocuous; **TBT-toxic**

As SPECIE TOXICITY

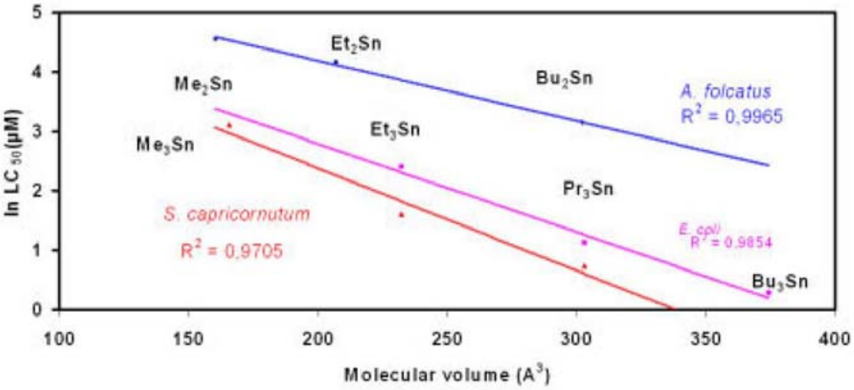
Chemical Specie	DL50 (mg/kg)
Arsenite [As(III)]	14
Arsenate [As(V)]	20
Arsine (AsH_3)	3
MMA	700-1,800
DMA	700-2,600
Arsenocholine	> 10,000
Arsenobutane	> 10,000

From EVISA Website,
www.speciation.net



With the Permission of Applied
Speciation and Consulting, LLC

Sn SPECIE TOXICITY



From EVISA Website,
www.speciation.net

SOME BENEFITS OF SPECIE-SPECIFIC DATA

☒Bioavailability of nutrient species can guide food production

☒Reduced human exposure to toxic substances

☒Prevention/Intervention related to human health issues such as:
- Cancer
- Autism

WHAT (CAN) DRIVE SPECIATION?

⌘ Academic research that develops new speciation analytical methods

⌘ Technology transfer to the commercial laboratory community

⌘ Greater understanding of the impact of speciation on environmental and biological assessments

⌘ **Evaluation of analytical methods for speciation that are found in government methods compendiums/regulatory guidance documents**

⌘ **Incorporation of speciation end-points in State and Federal regulations and permits**

⌘ **Certification of speciation methods by State/NELAC lab. cert. programs**

⌘ **Availability of SRMs to appropriately QA speciation measurements**

SPECIATION ANALYTICAL METHODOLOGIES

- EPA SW-846 has several analytical methods that include speciated metals
  - As (in development)
    - 3110
    - 6870
  - Cr
    - 3060A
    - 7196A
    - 7199
    - **6800 (can speciate other elements)**
  - Hg
    - 3200
- ROHS/WEEE Compliance Testing
  - EU statement that Method 6800 is the only valid method for generating speciated metals data

SPECIATION AND REGULATION

- The only specie that Federal and State agencies regulate using direct analytical measurement is Cr(VI)
- Other State regulations and permits infer the amount of a speciated metal from a measured “total” concentration.
- The lengthy cycle of regulations/permit evaluations discourages adoption of state-of-the-art technologies

SPECIATION & LAB. CERT.

- There should be no issue with NELAC and State lab. cert. programs offering certification for speciation methods
- The problem is, most accrediting authorities do not have the expertise or experience to:
  - to recognize the importance of speciation measurements
  - conduct effective and detailed lab. assessments
- Commercial labs. & accrediting authorities have (or can acquire) this capability; the NJDEP has certified laboratories for speciation for As, Cr, and Hg speciation

Cr(VI) in SOIL

- NJ (and other States) are responsible for managing COPR remediations
- Clean-ups based upon measurement of Cr(VI) in soil; historically, analyses are done by USEPA Methods 3060A and 7196A; some recent data by Method 7199
- Much of the NJ data includes QA outside method limits; there is concern about the validity of some of the results
- Consortium of collected COPR-contaminated soil and, via intercomparison studies, created NIST SRM 2701
- Cr(VI) certified by NIST as 551 ± 34 mg/kg by Method 6800
- Data by 7196A/7199 ~70% of the certified value
- Plans to develop a lower [Cr(VI)] SRM underway

Cr(VI) in SOIL

- Commercial lab. community capable of adopting & applying former research methods like Method 6800
- Different speciation methods may generate different results for the same sample; impact on remediation decision-making??
- Use of SRMs like NIST SRM 2701 are an essential component to any QA plan to effectively evaluate the efficacy of Cr(VI) in soil data

AVAILABILITY OF SPECIATION REFERENCE MATERIALS

	Aqueous	Blood	Hair	Sediment	Soil	Tissue
As	√					√
Cr	√				**Under Development**	
Hg		√	√	√		√
Se						√
Sn				√		√

We Need a Wider Variety of Appropriate SRMs to Support Speciated Measurements

CRITERIA FOR NEW SRM DEVELOPMENT

- Addresses analytical concerns involving important health, environmental and/or toxicological concerns
- Impact upon regulatory standards @ Federal or state levels
- Uniqueness of:
  - Analyte
  - Matrix
  - Species
- Ability of commercial lab. community to run speciation methods
- Concentration Level(s)
  - More representative of critical conditions than existing material

Some overlap in matrix type is not a bad if specie(s) and/or concentration levels differ from existing RMs

SOME POTENTIAL NEW SRMS

- **As in Seaweed, Biota or Food**
- Cr in Dust
- Cr in Urine
- **Hg in Sediment**
- Hg in Human Hair
- Sn in the Marine Environment

As IN SEAWEED, BIOTA AND/OR FOOD

- ⌘ Toxicity of As species differ by > 3 orders of magnitude
- ⌘ Useful for environmental as well as biomonitoring applications
- ⌘ As is seaweed could be a surrogate for dietary As from seafood as well as food matrices types such as rice, mushrooms and carrots; useful for food safety assays
- ⌘ Source of potential SRM should be easy to acquire
- ⌘ Once extracted and freeze-dried, As specie distribution would be expected to be stable

Hg IN SEDIMENT

- ⌘ Hg bioaccumulates and biomagnifies through the food chain; the 1st step is to analyze it in sediment, near where fish reside
- ⌘ RMs with higher total MeHg values are available as fish protein (DOLT-4) and dogfish liver (DORM-3)
- ⌘ Sediment is a useful surrogate for soils, wastes and sludges
- ⌘ Many potential sites to obtain useful sediment samples
- ⌘ Analytical methods are fairly well established

FUTURE PLANS

- ⌘ Continue to compile a list of potential SRMs
- ⌘ Gather input from other potential users such as the CDC and FDA
- ⌘ Gain consensus from EPA, States and academic advisors on priorities
- ⌘ Ask NIST, in collaboration with USGS, to develop a long-range plan to create an inventory of speciated SRMs

Arsenic Speciation in Groundwater Samples from Iowa's Private Well Waters

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ABSTRACT

The University Hygienic Laboratory (UHL), Iowa's environmental and public health laboratory, is monitoring Iowa's natural water system for various inorganic and organic pollutants, including arsenic. Arsenic is a highly regulated trace element due to its potential harmful effects to both ecosystems and human health. However, it is difficult to assess the toxicity of arsenic without mentioning speciation. Understanding the distribution of arsenic species in environmental samples, such as water from private wells, is essential in selecting appropriate approaches for treatment or eliminations of arsenic in drinking water. We have developed and validated a High Performance Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS) system for the determination of arsenic speciation. In the hyphenated system, HPLC is utilized for the separation of different arsenic species in the samples, and its effluent is directly injected into ICP-MS. The ICP-MS serves as an element specific detector for the HPLC. We determined method detection limits (MDL) for arsenite (As-III) and arsenate (As-V), the most common forms of arsenic in water, as 35 and 45 ng/L, respectively.

Nearly 200 water samples were collected throughout Iowa as part of the Statewide Rural Well Water Survey (SWRL) Phase 2 as well as a study in an individual county. Arsenic speciation analysis was performed on more than 70 water samples from these private wells with the highest (total) arsenic concentration of 181.4 μg/L. In our study we noted that water chemistry or sample matrix affects the measurement. However, the stability study we performed associated with the method indicates that with an appropriate sampling approach and pretreatment, the arsenic species in the water samples are stable for more than a month. Geographic information system (GIS) maps were generated to show total arsenic concentrations and arsenic species distribution within the state. The results confirm that 1) Groundwater arsenic contamination continues to be an environmental problem in the state of Iowa, especially in the north central part of the state. 2) Speciation determination is necessary to better assess arsenic contamination since both As-III and As-V are found in the majority of the samples analyzed.

Future work includes additional speciation method development and validation for other metals of environmental interest. These studies will extend the laboratory's analytical capabilities and capacity to provide routine speciation testing for Iowa and beyond.

Arsenic Speciation in Groundwater Samples from Iowa's Private Well Waters

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Brian Wels, Ph.D.
Steve Bernholtz
Don Simmons, Ph.D.

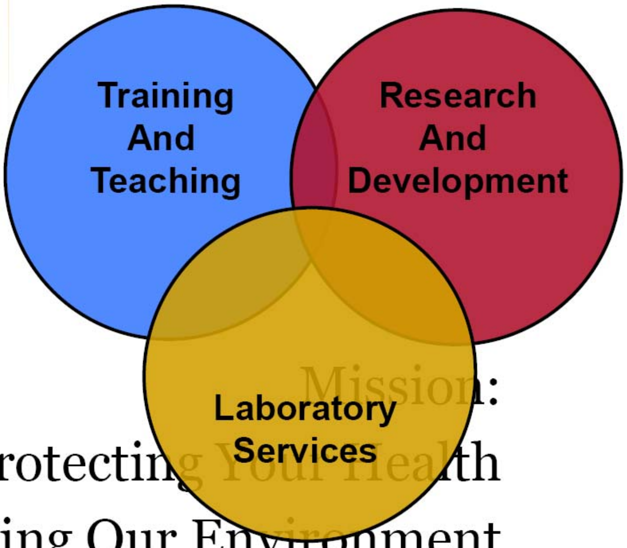
National Environmental Monitoring Conference
Washington, D.C.
August 11th, 2008

1904
2004
UNIVERSITY HYGIENIC LABORATORY
100 Years

University Hygienic Laboratory

Iowa's Environmental and Public Health Laboratory

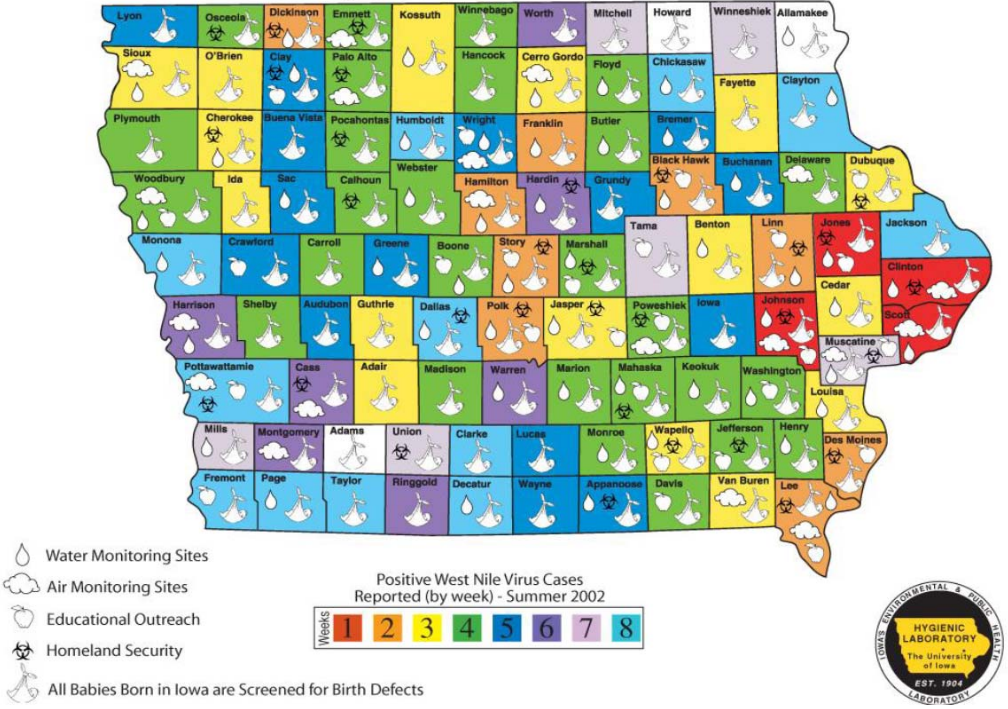
Imagine the Possibilities



Mission:
Protecting Your Health
Preserving Our Environment

The University of Iowa Hygienic Laboratory

Ensuring the Health of All Iowans



Outline

- Introduction
- Method
  - Instrumentation
  - Sample collection and pretreatment
- Results and discussion
  - Analytical merit
  - Arsenic speciation in Iowa's ground waters
- Conclusion and future work

Arsenic (As), facts about

- A highly toxic metalloid, group 1 carcinogen (species dependent).
- MCL:
  - EPA USEPA recently decreased the drinking water standard for arsenic (*total*) to 10 µg/L from 50 µg/L due to its human toxicity [2001].
- Arsenic in Iowa's drinking water sources: IDNR 2003 Survey.

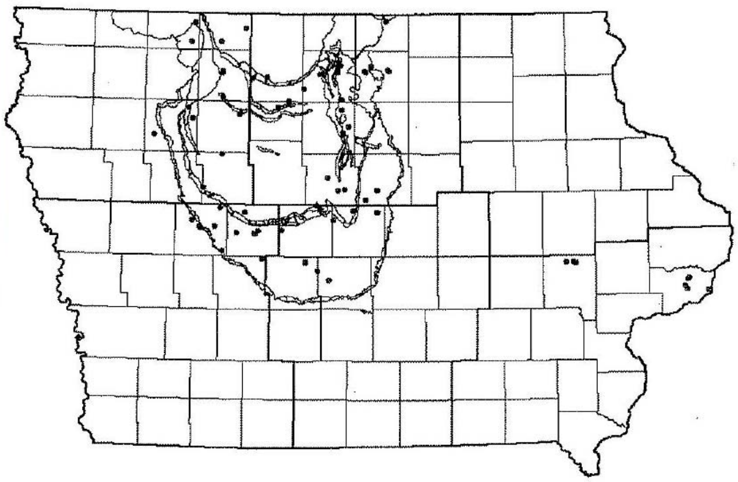
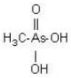
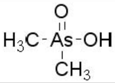
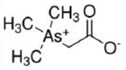


Figure 1: Iowa's public water supply sites with arsenic above 10 µg/L in raw groundwater. [IDNR, 2003].

Call for arsenic speciation

- Different toxicity.

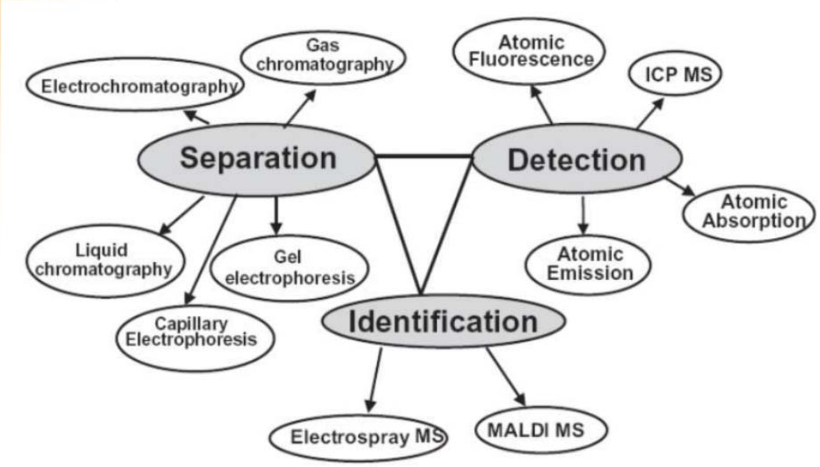
Species	Arsine	Arsenite (As-III)	Arsenate (As-V)	Monomethylarsonic Acid (MMA)	Dimethylarsenic Acid (DMA)	Arsenobetaine (AsB)
Mol. Structure	AsH_3	$H_2AsO_3^-$	AsO_4^{3-}	 $\mathrm{H_3C{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{As}}{-}OH}$	 $\mathrm{H_3C{-}\underset{\underset{CH_3}{\vert}}{\overset{\overset{O}{\Vert}}{As}}{-}OH}$	
LD50 (mg/Kg)	3	14	20	700-1800	700-2600	>10,000

- Assess treatment needs.
  - As-V - Reverse osmosis or distillation
  - As-III - Distillation or chlorination followed by RO

Elemental speciation

- Definition (IUPAC) of ***speciation***: the methods for and results of establishing the physio-chemical form of metal(loid)s – including oxidation states, coordination numbers, ligands, and individual concentrations.

Speciation analysis



Separation

Electrochromatography

Gas chromatography

Liquid chromatography

Gel electrophoresis

Capillary Electrophoresis

Detection

Atomic Fluorescence

ICP MS

Atomic Absorption

Atomic Emission

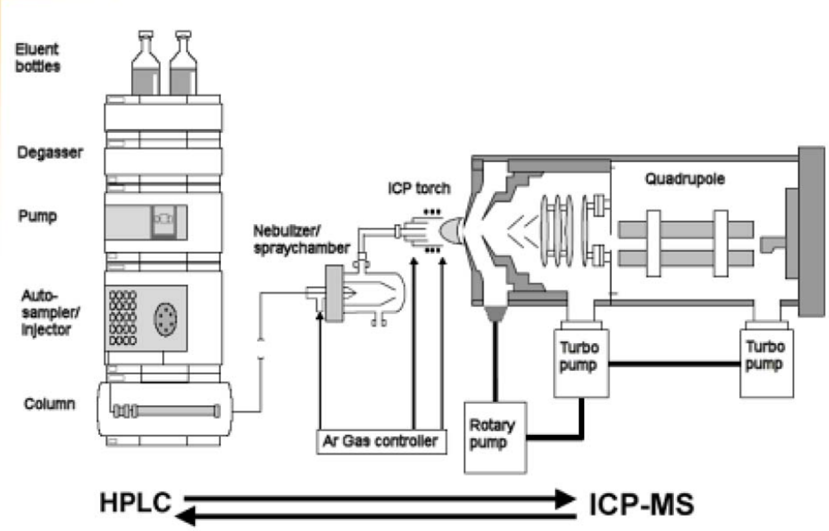
Identification

Electrospray MS

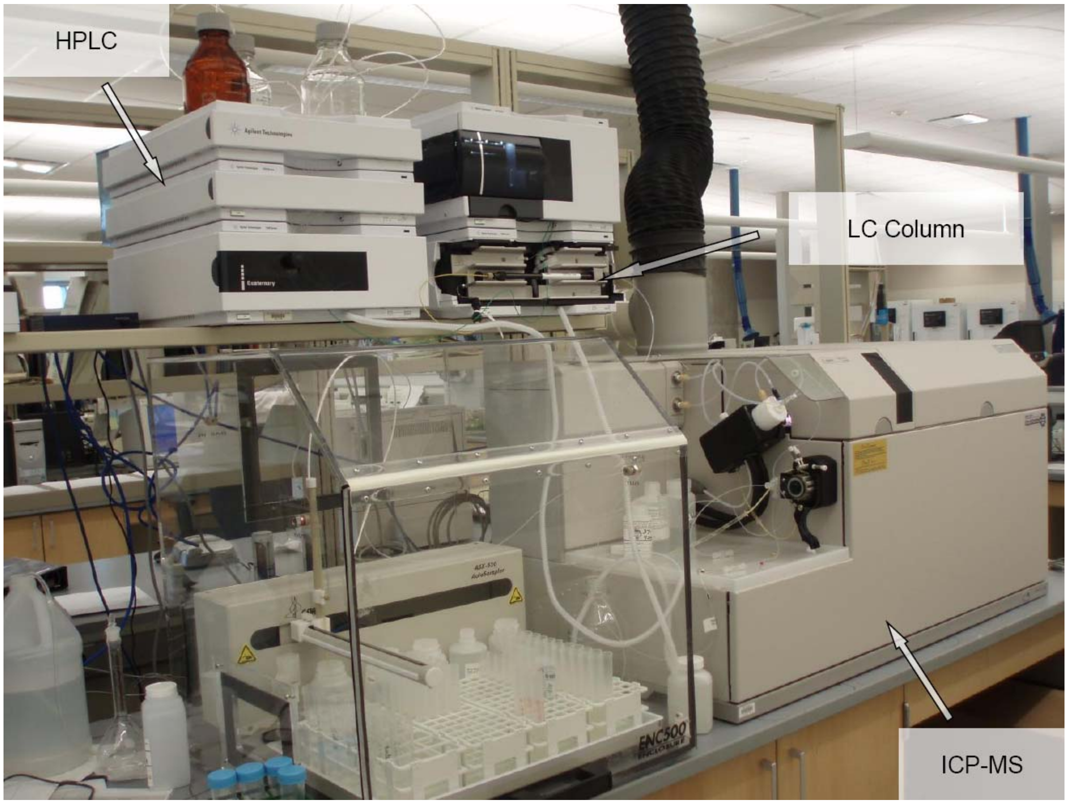
MALDI MS

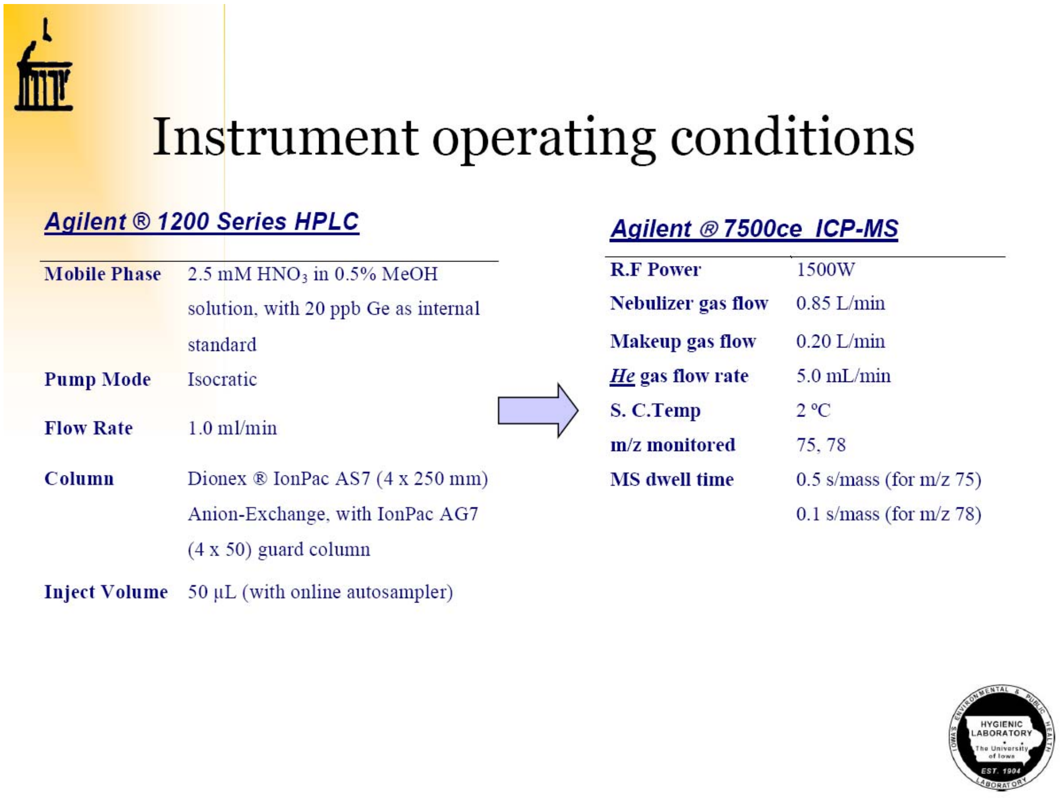
Source: *Szpunar, J., and R. Lobinski, Hyphenated techniques in speciation analysis, RSC, 2004.*

HPLC-ICP-MS coupling



bi-directional communication allows for system integration





Instrument operating conditions

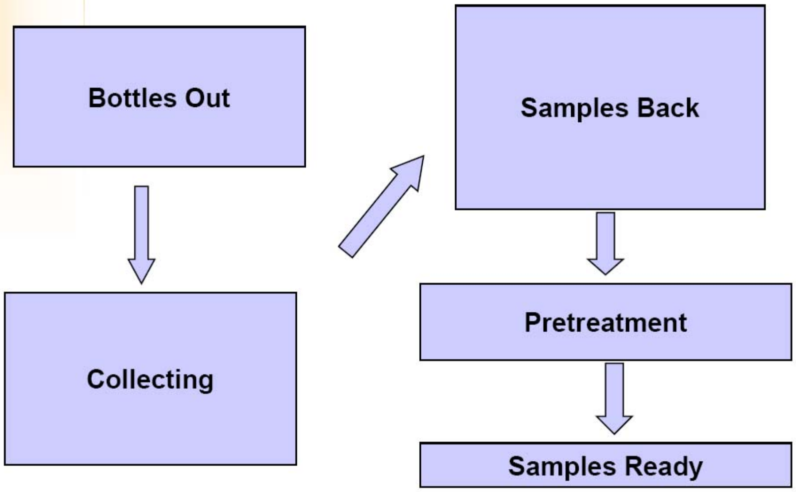
Agilent ® 1200 Series HPLC

Mobile Phase	2.5 mM HNO_3 in 0.5% MeOH solution, with 20 ppb Ge as internal standard
Pump Mode	Isocratic
Flow Rate	1.0 ml/min
Column	Dionex ® IonPac AS7 (4 x 250 mm) Anion-Exchange, with IonPac AG7 (4 x 50) guard column
Inject Volume	50 µL (with online autosampler)

Agilent ® 7500ce ICP-MS

R.F Power	1500W
Nebulizer gas flow	0.85 L/min
Makeup gas flow	0.20 L/min
He gas flow rate	5.0 mL/min
S. C.Temp	2 ºC
m/z monitored	75, 78
MS dwell time	0.5 s/mass (for m/z 75) 0.1 s/mass (for m/z 78)

Sample collection and pretreatment



Bottles Out

Collecting

Samples Back

Pretreatment

Samples Ready

Analytical merit – *satisfactory separation*

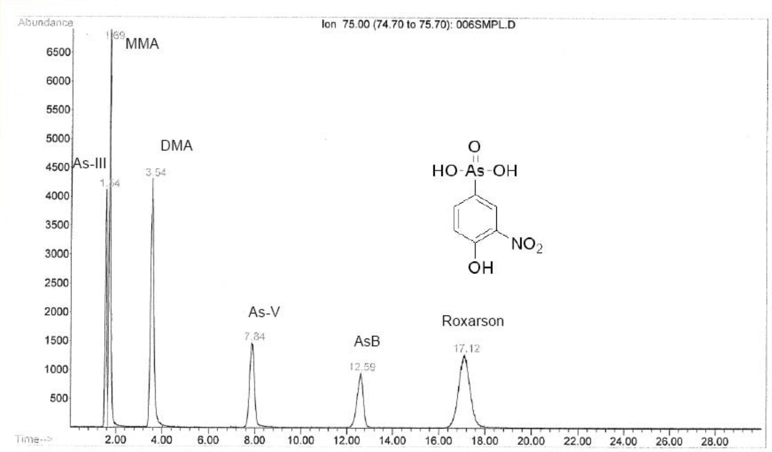


Figure 2: HPLC chromatograph (m/z 75) of a mixture solution of six arsenic standards

Analytical merit – *superior sensitivity*

As Species	MDL (ng/L)
As-III	35
As-V	**45**

$MDL = t_{\nu,\alpha} \times s$

QA/QC

- Both accuracy and precision are achieved for quantitative speciation analysis through in-house QA/QC procedures:
  - Duplicate measurements
  - Recovery of matrix spikes

*** *and* ***

  - $As_{total} = As_{III} + As_{V}$ (luckily, it holds true for most of cases in Iowa’s ground water samples)

Stability study

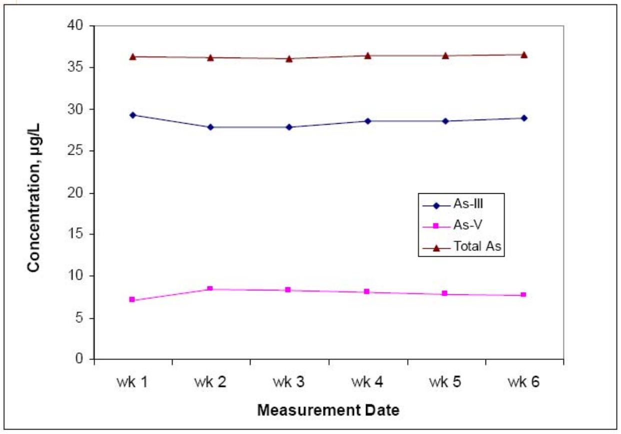


Figure 3: Repeat measurements of one groundwater sample over the time period of six weeks.

Chromatography examples

Sample ID	Date of Sampling	Sampling Site	As-III (ppb)	As-V (ppb)
ASP-39	9/17/2007	Mason City	0.46	14.13
ASP-55	11/20/2007	Thornton	166.84	14.53
ASP-58	11/28/2007	Clear Lake	14.1	6.83

```
File       : D:\DATA\AS092407.B\010SMPL.D
Operator   : YC
Acquired   : 24 Sep 2007  15:11     using AcqMethod
Instrument :    ICP-MS
Sample Name: ASP-39
Misc Info  :
Vial Number: 1
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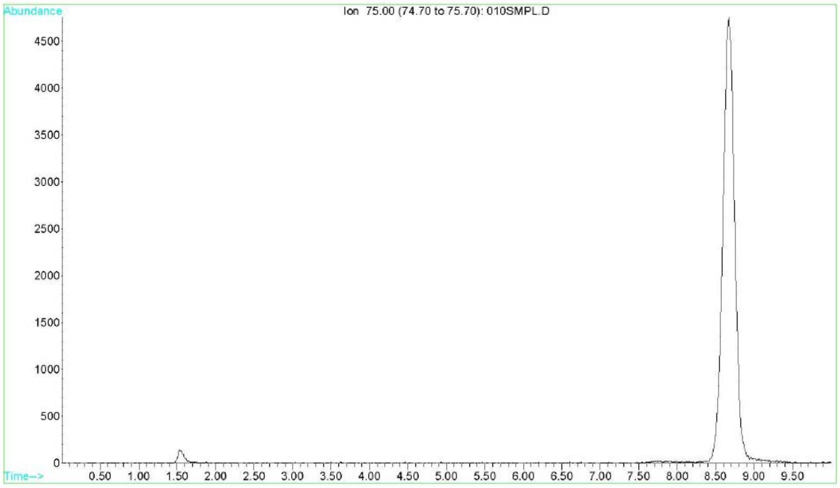

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Operator   : YC
Acquired   : 26 Nov 2007  14:17     using AcqMethod
Instrument :    ICP-MS
Sample Name: ASP-55
Misc Info  :
Vial Number: 1
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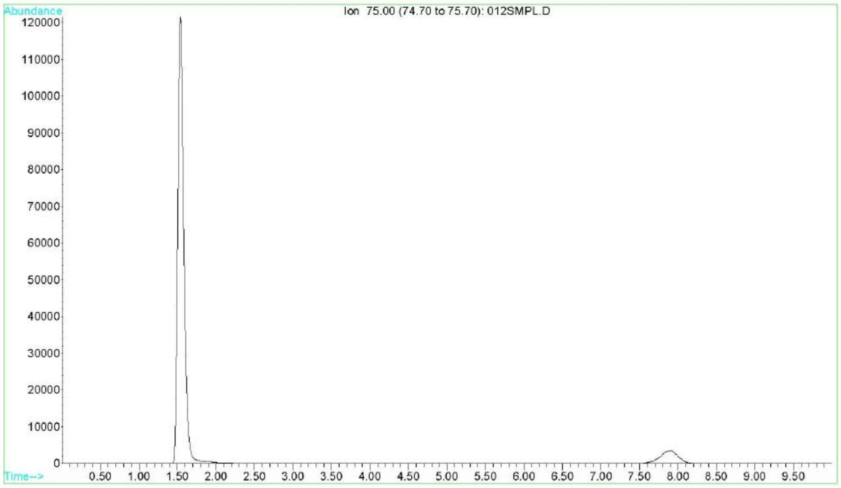

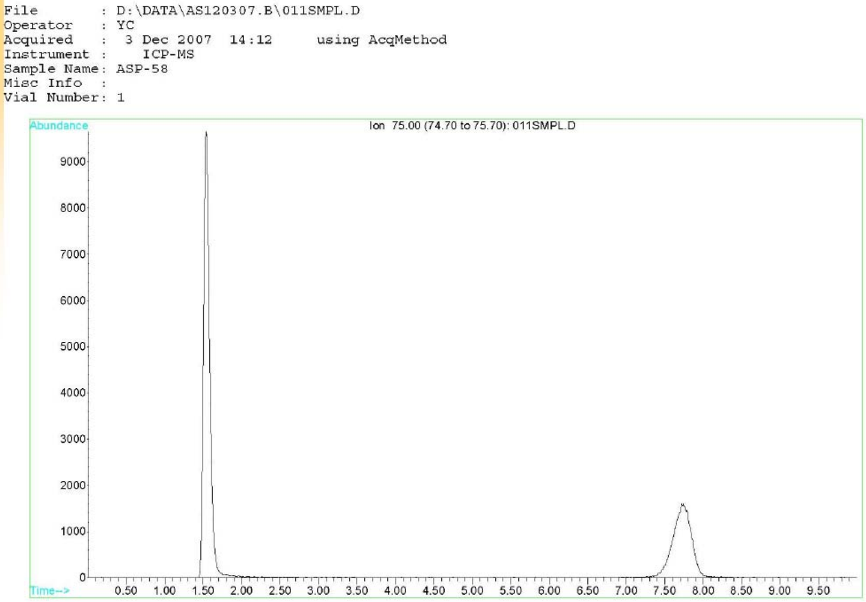

```
File        : D:\DATA\AS120307.B\011SMPL.D
Operator    : YC
Acquired    :  3 Dec 2007  14:12     using AcqMethod
Instrument  :    ICP-MS
Sample Name: ASP-58
Misc Info   :
Vial Number: 1
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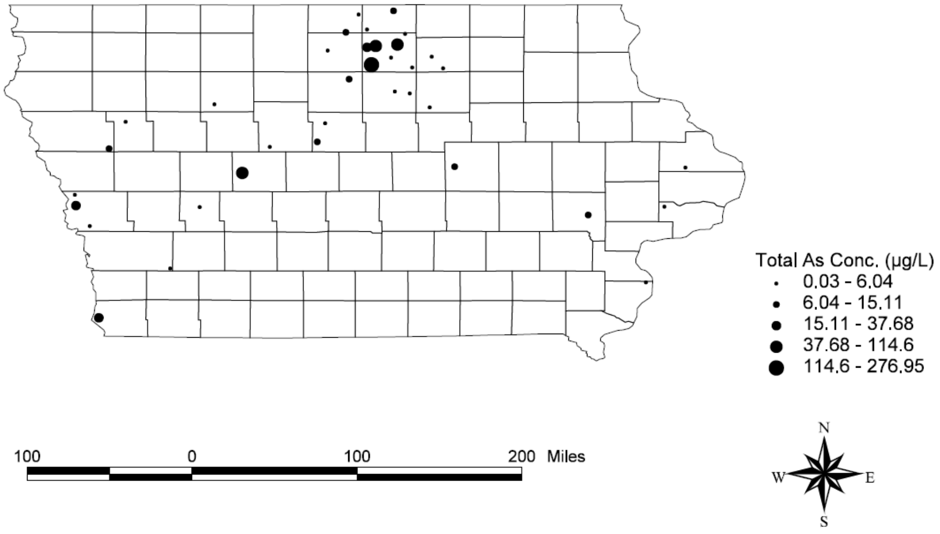
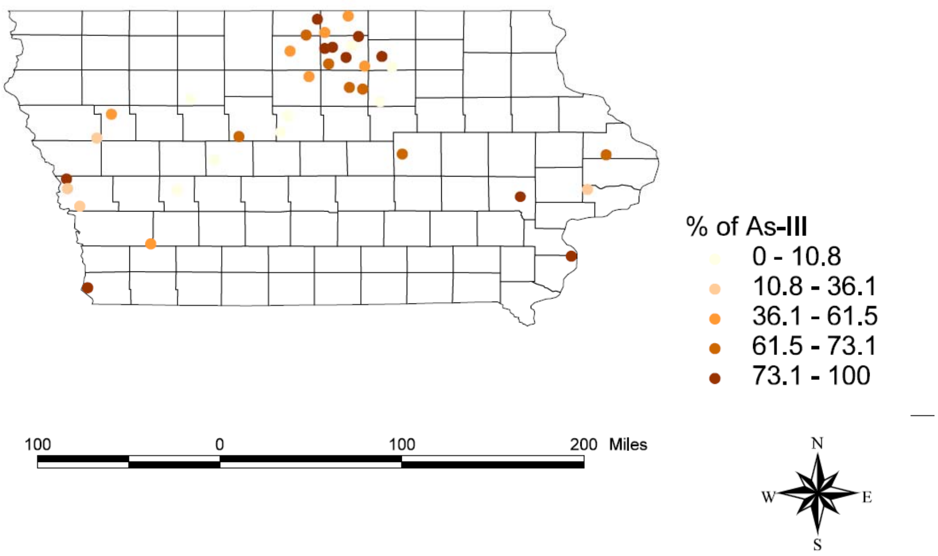
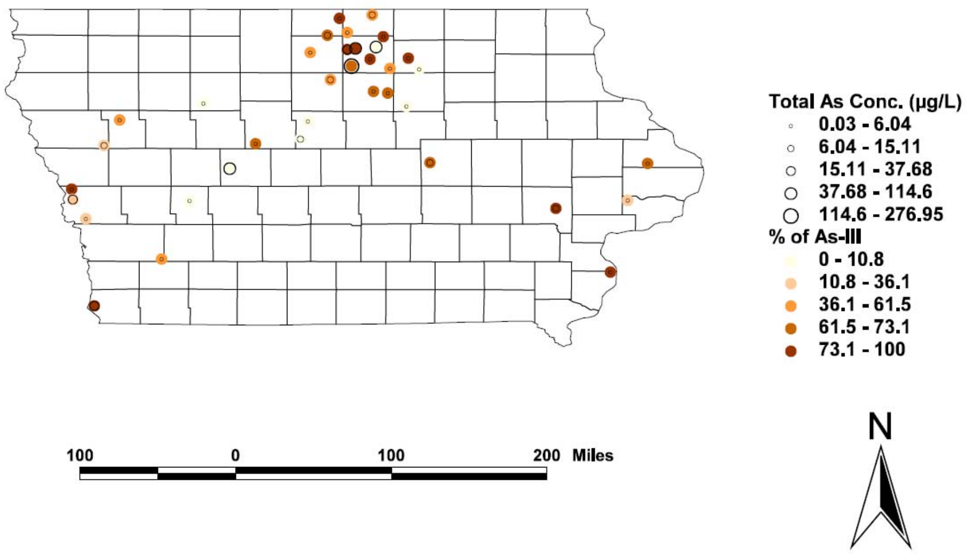
Total Arsenic Concentration



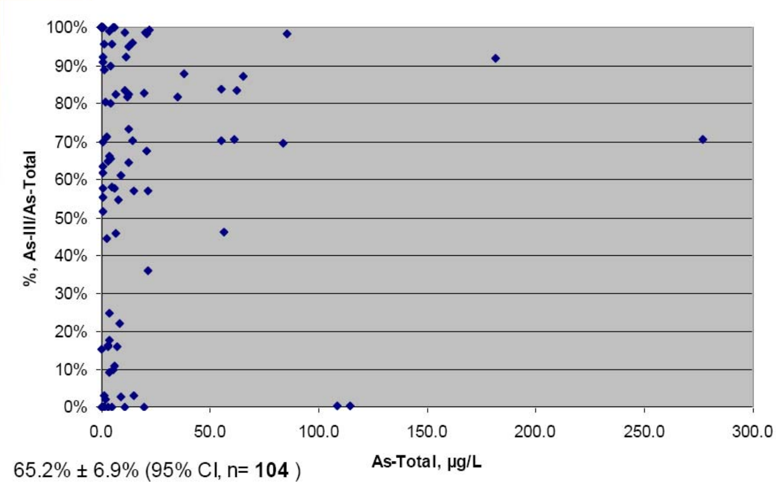
Percentage of Arsenite (As-III) in Total Arsenic



Arsenic Speciation Data



Arsenic speciation data - *continue*



65.2% ± 6.9% (95% CI, n= **104**)

Localized data – Cerro Gordo County

After a Reverse Osmosis Filter System

City	**Address**	**Date of Measurement**	**Conc. (µg/L)**	
			As III	**As V**
Mason City	*** Address -4***	6/19/2008	0.1	n.d.
Mason City	*** Address -3***	6/19/2008	0.12	n.d.
Mason City	*** Address -2***	6/26/2008	n.d.	0.03
Mason City	*** Address -1***	6/26/2008	1.13	5.89
Mason City	*** Address -1***	6/26/2008	0.24	108.1
Clear Lake	*** Address -V***	7/1/2008	56.93	8.34
Clear Lake	*** Address -IV***	7/10/2008	83.83	1.51
Clear Lake	*** Address -III***	7/10/2008	0.19	0.14
Clear Lake	*** Address -II***	7/16/2008	5.43	3.45
Clear Lake	*** Address -I***	7/16/2008	0.02	19.77

Conclusion

- Groundwater arsenic contamination continues to be an environmental problem in the state of Iowa, especially in the north central part of the state.
- *Speciation analysis* is necessary to better assess arsenic contamination.

Future work

- Further validation, including proficiency testing (?), of the UHL AS-SPEC test;
  - Current report trailers: *This data was generated using a procedure under development and should be considered for research purposes only and not used for compliance purposes.*
- Continuous monitoring private drinking water wells of arsenic speciation, for Iowa and beyond, and potential bio-monitoring;
- Method development and validation for other metals of environmental interest.

Acknowledgements

- The University of Iowa Center for Health Effects of Environmental Contamination (CHEEC)
- US FDA
- Colleagues at UHL
- Cerro Gordo County Department of Public Health

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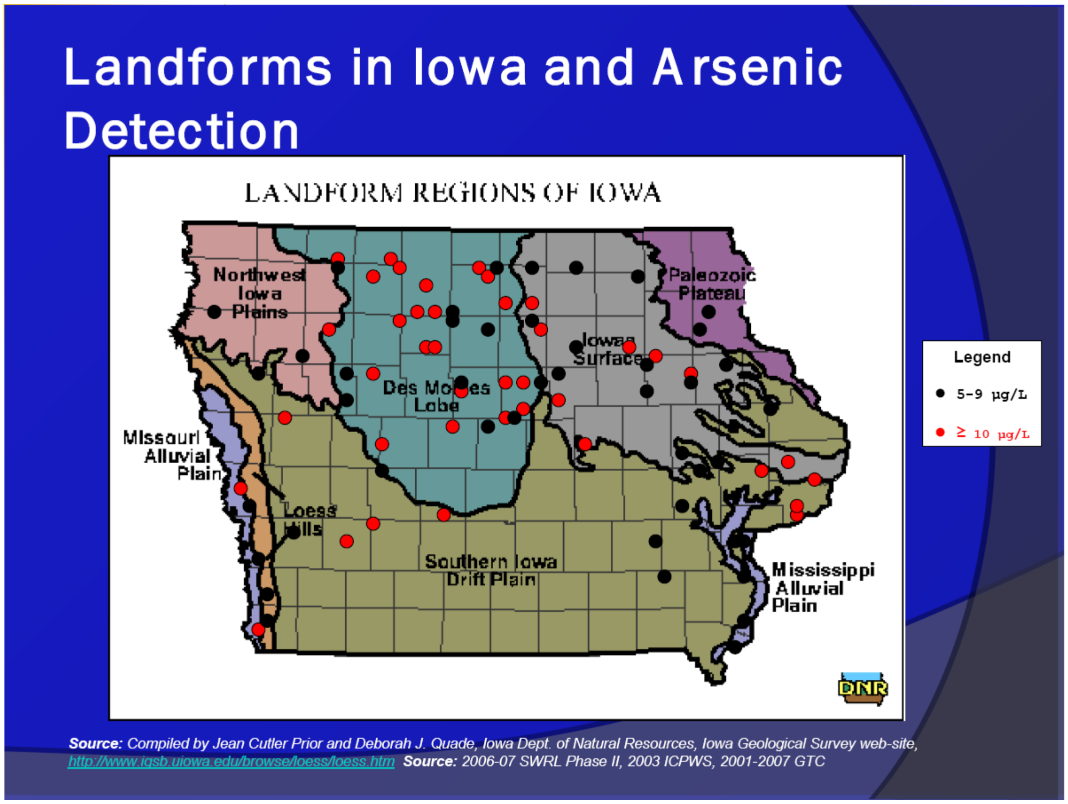

Landforms in Iowa and Arsenic Detection

Source: *Compiled by Jean Cutler Prior and Deborah J. Quade, Iowa Dept. of Natural Resources, Iowa Geological Survey web-site,* *http://www.igsb.uiowa.edu/browse/loess/loess.htm* **Source:** *2006-07 SWRL Phase II, 2003 ICPWS, 2001-2007 GTC*

New and Improved Methodology for the Analysis of Hexavalent Chromium in Soil and Water

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281-484-5000
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ABSTRACT

Hexavalent Chromium is currently measured using two different methodologies, USEPA 218.6 for Water matrix and SW846 7199 for Soil matrix. This new and improved methodology overcomes shortcomings of the current methodology and provides flexibility in the analysis for either matrix.

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New and Improved methodology for the analysis of Hexavalent Chromium (Cr^{+6}) in Soil and Water

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Houston TX
Johnson Mathew, Env. Scientist
USEPA – Region 6 Laboratory
Houston TX

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Outline

- **Method SW846 7199 – review**
- **USEPA Method 218.6 – review**
- **Chemistries of Eluant, Reagent and Columns for this analysis**
- **Suggested improvement**
- **Data to support improvement**
- **Summary**

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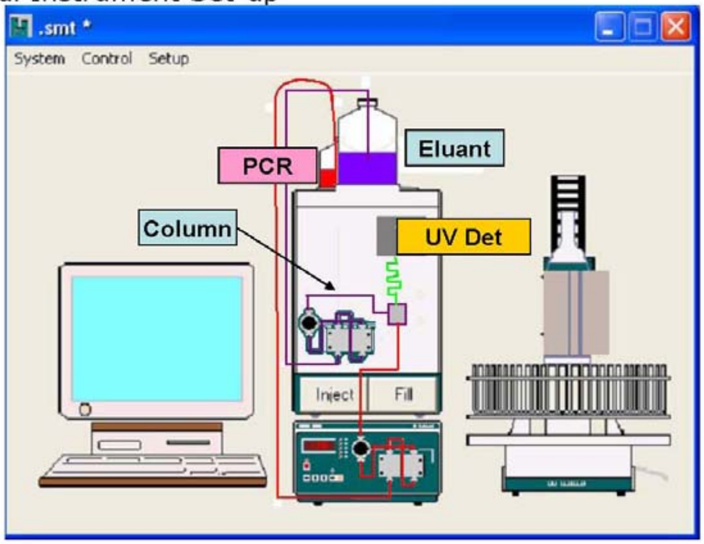
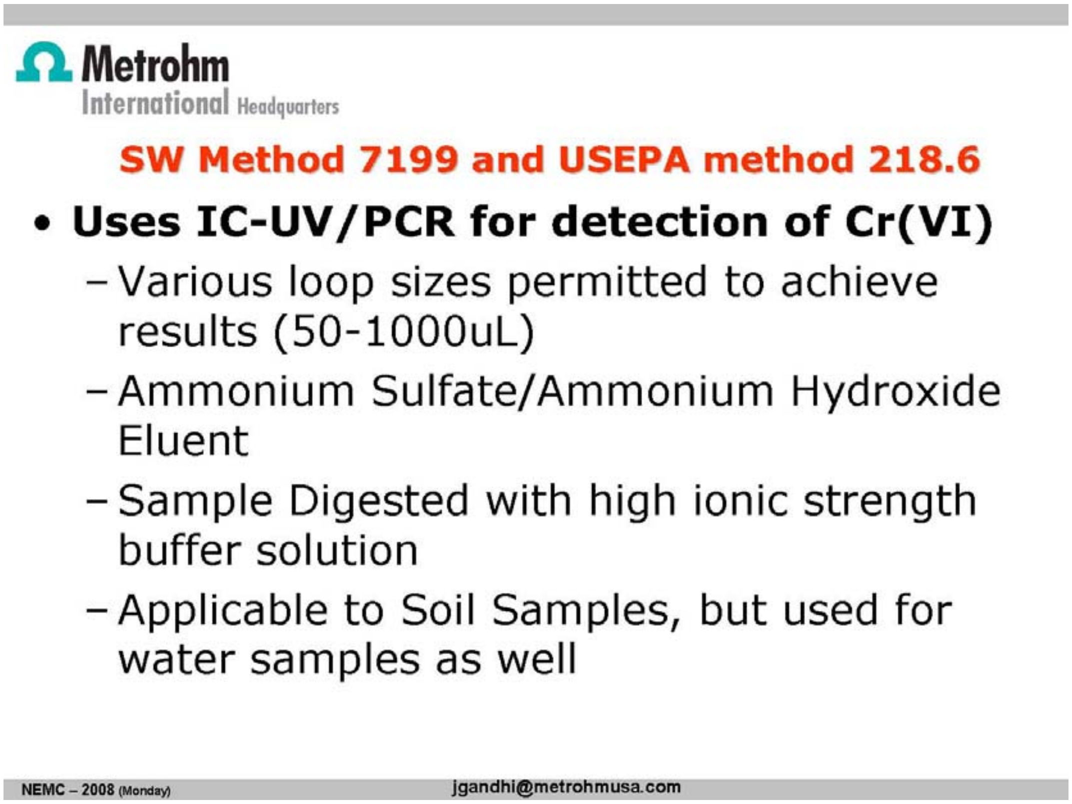
Typical Instrument Set-up



SW 846 method 7199
Or
US EPA method 218.6

Chromium (VI) by UV/PCR



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SW Method 7199 and USEPA method 218.6

- **Uses IC-UV/PCR for detection of Cr(VI)**
  - Various loop sizes permitted to achieve results (50-1000uL)
  - Ammonium Sulfate/Ammonium Hydroxide Eluent
  - Sample Digested with high ionic strength buffer solution
  - Applicable to Soil Samples, but used for water samples as well

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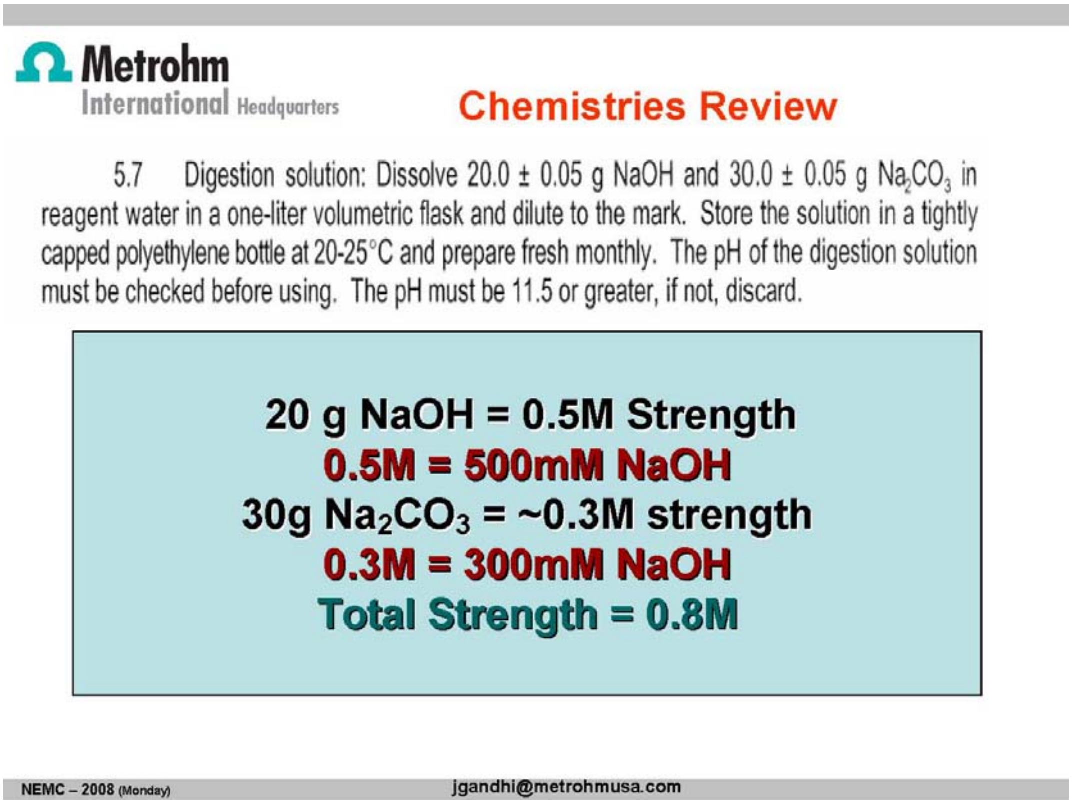

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Chemistries Review

5.7 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

20 g NaOH = 0.5M Strength
0.5M = 500mM NaOH
30g Na_2CO_3 = ~0.3M strength
0.3M = 300mM NaOH
Total Strength = 0.8M

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Eluant:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4 Flow Rate = 1.5 mL/min
Post-Column Reagent:	2mM Diphenylcarbohydrazide 10% v/v CH_3OH 1 N H_2SO_4 Flow rate = 0.5 mL/min

Eluent = 0.25M + 0.1M = 0.35M Strength
PCR Reagent = 0.5M (1N) H_2SO_4

Neutralizing 0.5M Acid @ 0.5mls with
1.1M Base (0.35M+0.8M digestion) @ 0.8 or 1.0mls/min

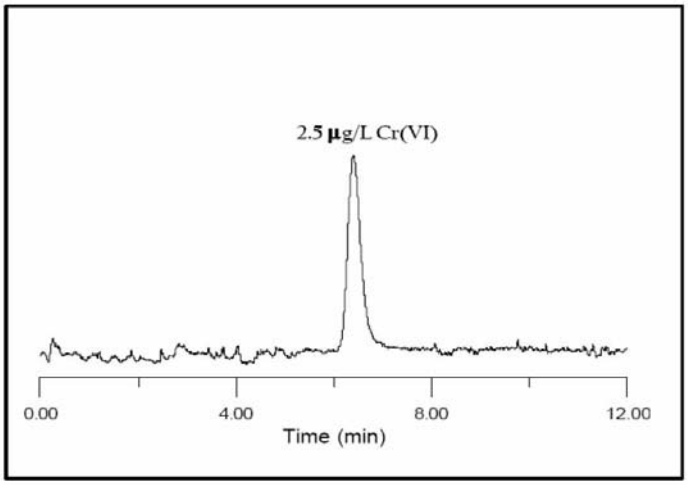
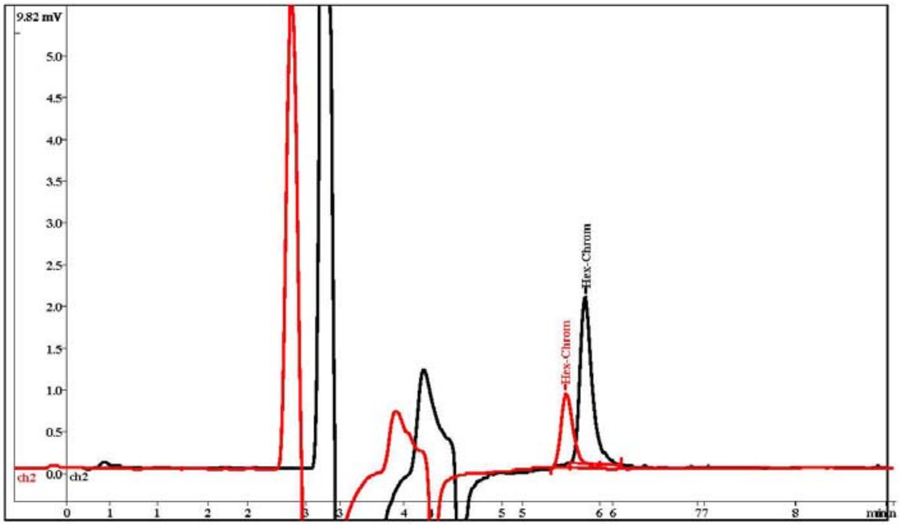


Figure 6: Chromatogram of 2.5 µg/L Cr(VI) fortified in a simulated wastewater effluent sample using a 100 mV analog output. The synthetic sample contained 100 mg/L chloride, 100 mg/L sulfate, 100 mg/L carbonate and 50 mg/L nitrate.

Then, What is the problem??



2ppb in Drinking Water with No Buffer

2ppb in Drinking Water with Buffer Solution

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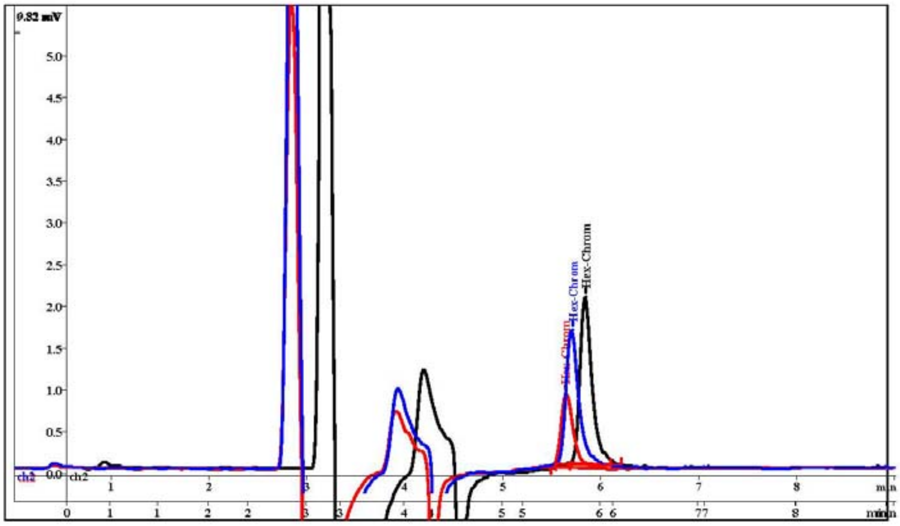

2ppb in Drinking Water with No Buffer

2ppb in Drinking Water with Buffer Solution

2ppb in Drinking Water with 1/200X diluted Buffer Solution

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Solution for the problem

(jointly developed with USEPA – Region 6 Lab)

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Experimental Conditions (modified)

Chromatographic Conditions

Analytical Column: Metrosep A Supp 10- 250 or
Metrosep ASUPP16-250
Eluent: 10mm Lithium Hydroxide / 7.8mm Lithium Sulfate
Flow rate: 0.8ml/min
Post Column Reagent: 2.0mM 1,5-Diphenylcarbohydrazide (DPC)
10% HPLC-grade Methanol
0.5M 98% Sulfuric Acid
Flow rate: 0.4ml/min
Buffer Solution: 1mM Lithium Hydroxide / 7.8mM Lithium Sulfate (pH 9.5)
Detection Wavelength: 530nm
Sample Volume: 2000µl

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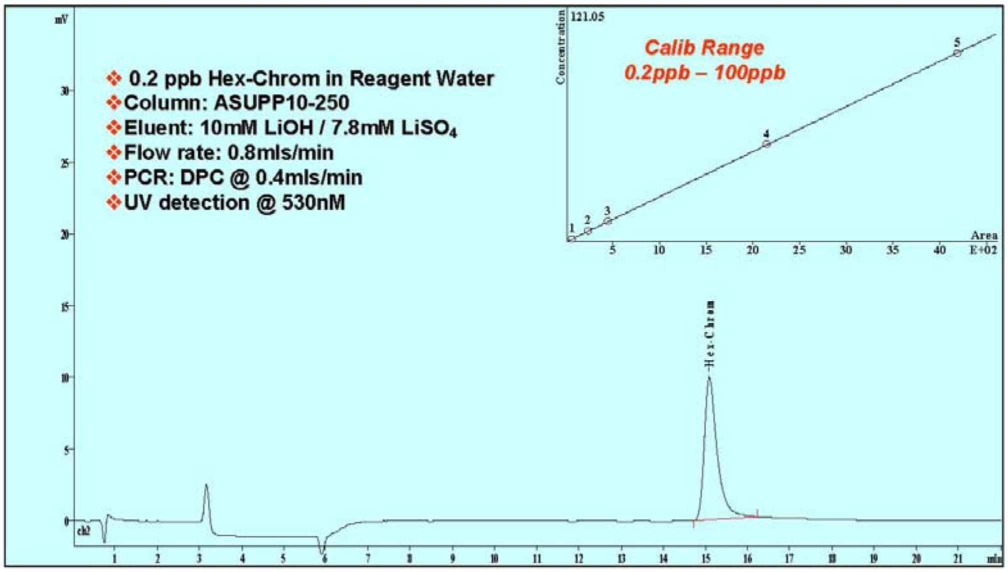
Chromatogram (Cr^{+6})



- 0.2 ppb Hex-Chrom in Reagent Water
- Column: ASUPP10-250
- Eluent: 10mM LiOH / 7.8mM $LiSO_4$
- Flow rate: 0.8mls/min
- PCR: DPC @ 0.4mls/min
- UV detection @ 530nM

Calib Range
0.2ppb – 100ppb

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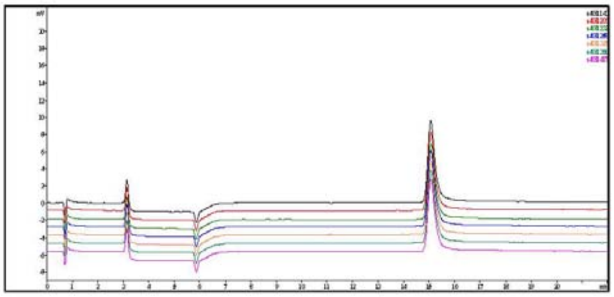
Stacked Calibration Standard – 0.2ppb (7replicates)



Sample ID	Hex-Chrom ug/L
0.2ppb Std	0.190
0.2ppb Std	0.185
0.2ppb Std	0.186
0.2ppb Std	0.190
0.2ppb Std	0.185
0.2ppb Std	0.187
0.2ppb Std	0.218
Average	0.191
Std.Dev	0.012
%RSD	6.190
Calculated MDL	0.037

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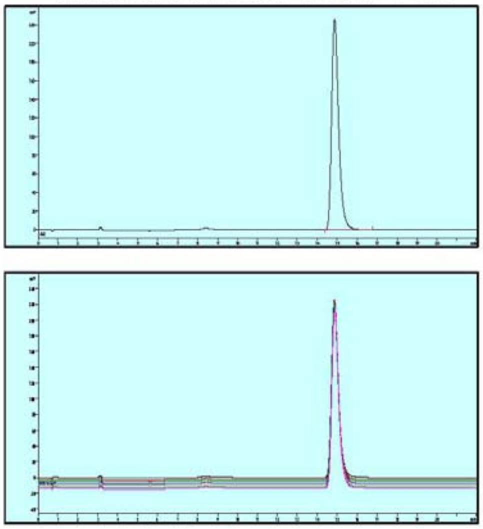
Soil Sample extracted with modified buffer (pH 9.5)



Sample ID	Hex-Chrom mg/Kg
NIST SRM Soil Sample extract (1/500 dilution)	516.80
NIST SRM Soil Sample extract (1/500 dilution)	514.83
NIST SRM Soil Sample extract (1/500 dilution)	515.77
NIST SRM Soil Sample extract (1/500 dilution)	515.76
NIST SRM Soil Sample extract (1/500 dilution)	514.89
NIST SRM Soil Sample extract (1/500 dilution)	514.82
NIST SRM Soil Sample extract (1/500 dilution)	515.29
Average	515.45
Std.Dev	0.723
%RSD	0.140
Calculated MDL (at 1/500 dilution level)	2.272

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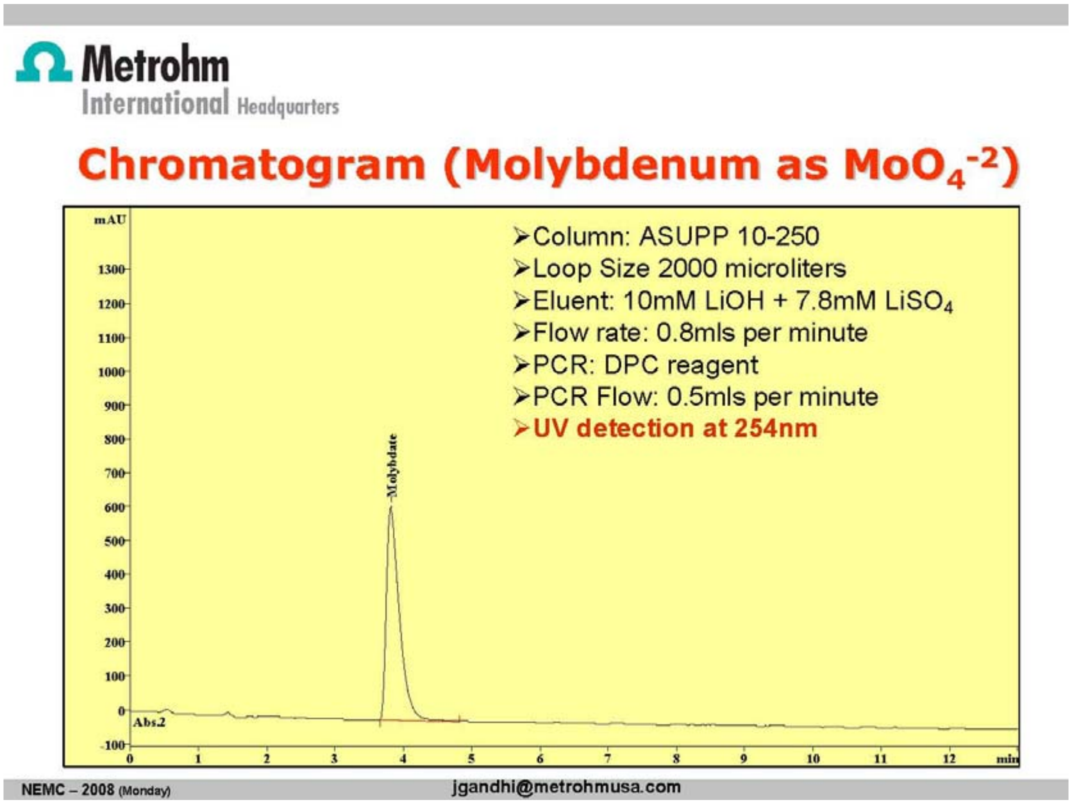
Hex Chrom Data

- Similar data for 0.5, 1.0, 5.0ppb in Reagent Water, Waste Water(s), Soil Samples were produced
- NIST SRM Soil Sample was used for soil sample reference sample

Interferences???
Or
Other emerging analytes



Chromatogram (Molybdenum as MoO_4^{-2})

- ➢Column: ASUPP 10-250
- ➢Loop Size 2000 microliters
- ➢Eluent: 10mM LiOH + 7.8mM $LiSO_4$
- ➢Flow rate: 0.8mls per minute
- ➢PCR: DPC reagent
- ➢PCR Flow: 0.5mls per minute
- ➢**UV detection at 254nm**

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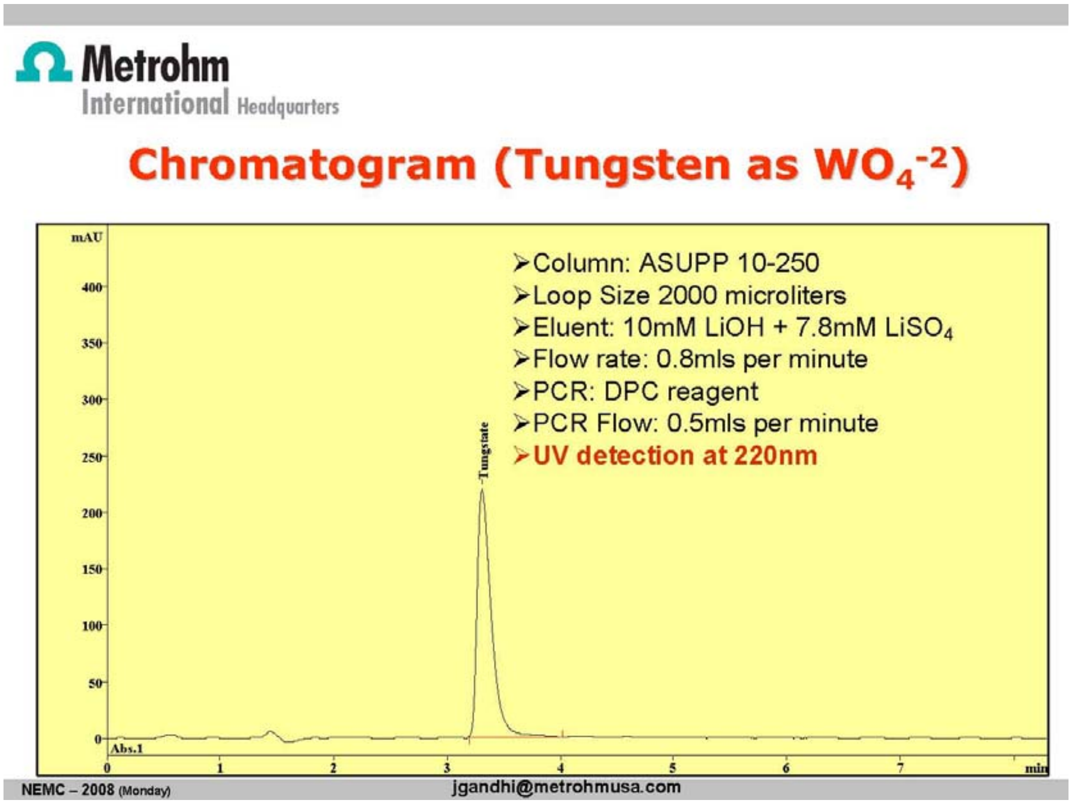

Chromatogram (Tungsten as WO_4^{-2})

- ➢Column: ASUPP 10-250
- ➢Loop Size 2000 microliters
- ➢Eluent: 10mM LiOH + 7.8mM $LiSO_4$
- ➢Flow rate: 0.8mls per minute
- ➢PCR: DPC reagent
- ➢PCR Flow: 0.5mls per minute
- ➢**UV detection at 220nm**

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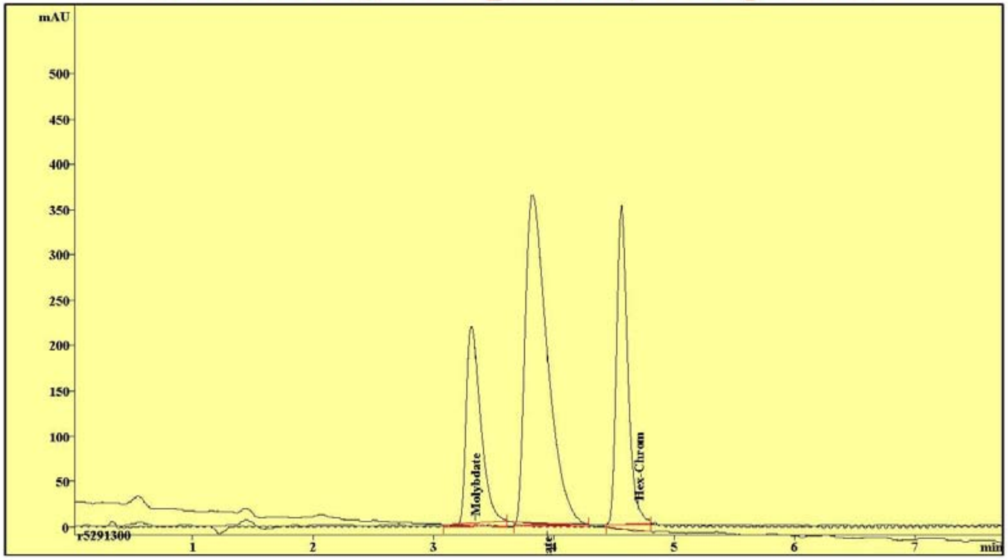
Chromatate, Tungstate, Molybdate



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Summary

- Currently there is confusion in the market place and problem with the Chromium-6 analysis by EPA methodologies
- Simple change in chemistries of eluent will resolve the issue of the analysis
- This presentation has demonstrated flexibility of the method that can be adopted for water and soil matrix alike
- Also this method is directly adoptable for emerging contaminants like Tungstate

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Acknowledgements

- Mr. Rick McMillin – USEPA Region 6, Houston TX
- Dr. Melvin Ritter – USEPA Region 6, Houston TX
- Dr. Stuart Nagourney – NJ DEP (for providing NIST SRM)
- Metrohm Competency Center, Herisau – Switzerland
- Metrohm-Peak Customers for providing samples

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Environmental Human Health Monitoring of Toxic Metals and Some of Their Species in Urine and Blood Using US EPA Method 6800

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Scott Faber; Children's Institute Pittsburgh.

ABSTRACT

In order to obtain a more complete picture of human exposure to chemicals it has become increasingly important to monitor biological fluids. Recently it has been shown that Autistic children may potentially be diagnosed by their blood and serum levels of transition metals. These data will be used to illustrate the importance of environmental health monitoring. One particular advantage of this protocol for biological monitoring is that it provides a measure of the internal dose received by an individual in the context of his or her lifestyle from all routes of exposure. During this study a simple, rapid and accurate quantification method for simultaneous determination of 27 elements of toxicological and nutritional interest (Sb, B, Ba, Cd, Cr, Cu, Fe, Pb, Mg, Hg, Mo, Ni, K, Se, Ag, Sr, Tl, V, Zn, Rb, Br, Sn, Ti, U, Li, Zr and Te among other elements) in urine and blood has been developed using isotope dilution inductively coupled plasma-mass spectrometry (ID-ICP-MS). The method is sensitive and rapid enough to screen urine and specimens from subjects suspected to be exposed to a number of important elements and elemental species or to evaluate environmental and/or other occupational exposure to theses elements. Toxicity of some metal-speciated forms is much greater than their elemental forms. To address this problem, a new multi-elemental speciation method will be developed based on EPA Method 6800 for simultaneous routine analysis of those species using MALDI-TOF-ID-MS and ESI-TOF-ID-MS and other Mass Spectrometric analysis. Sample preparation of urine and blood is simplified and instrumental measurements are reduced in error contribution. Direct mathematical concentrations are obtained without calibration curves and are more accurate than traditional methods.

Environmental Human Health Monitoring of Toxic Metals and Some of Their Species in Urine and Blood using US EPA Method 6800

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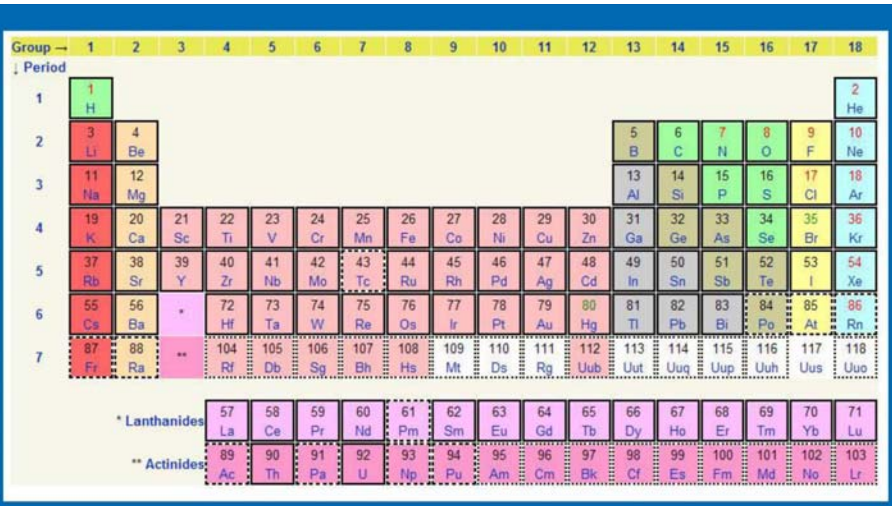
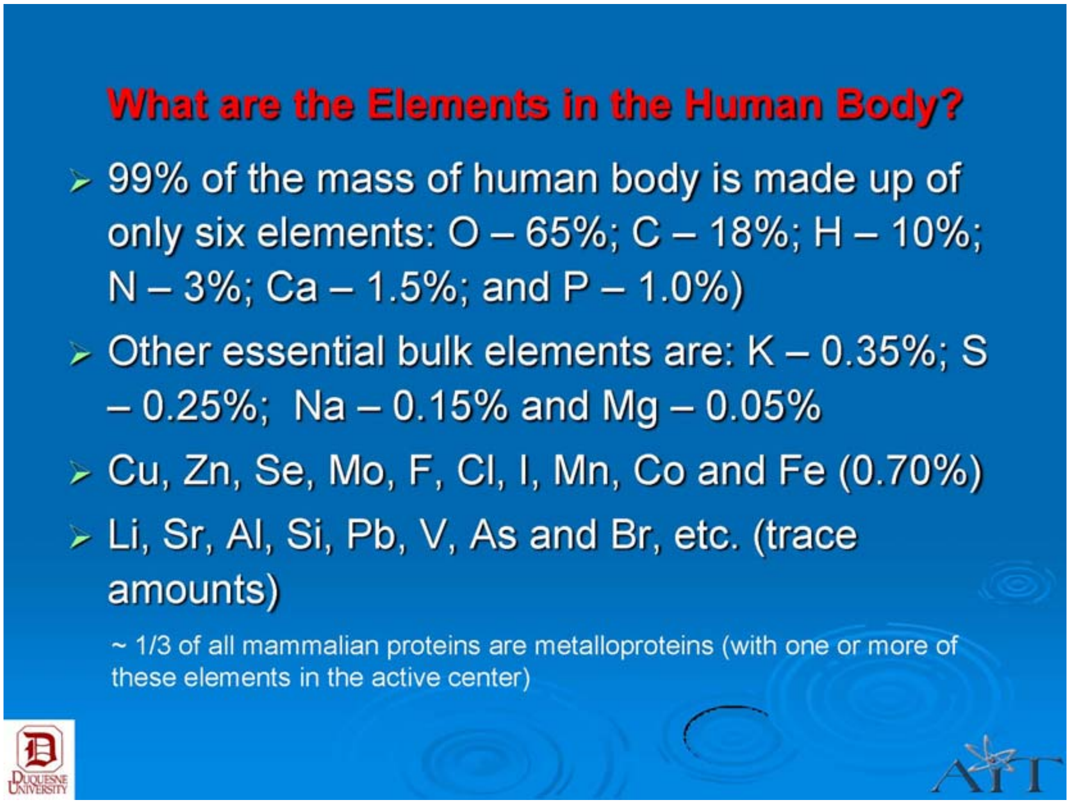
Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA
*Applied Isotope Technologies, Inc., Sunnyvale, CA 94087



Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

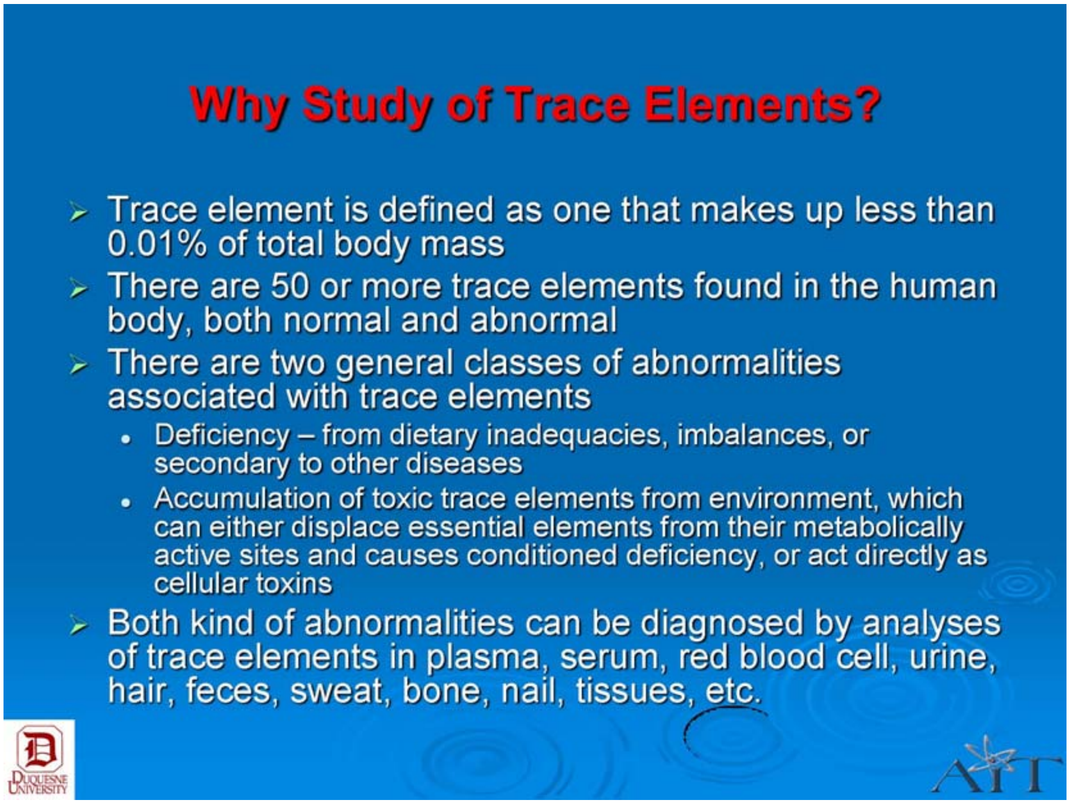
- Of the first 20 elements of the periodic table
  - 12 are bases of organic molecules, electrolytes, or structures
  - 3 are noble gases
  - 2 (B and F) have functions for living organisms, and
  - 3 (Li, Be and Al) are functionless
- Of the next 14 elements
  - 11 are essential trace elements
- Only two essential elements, Mo and I, have atomic numbers greater than 34



What are the Elements in the Human Body?

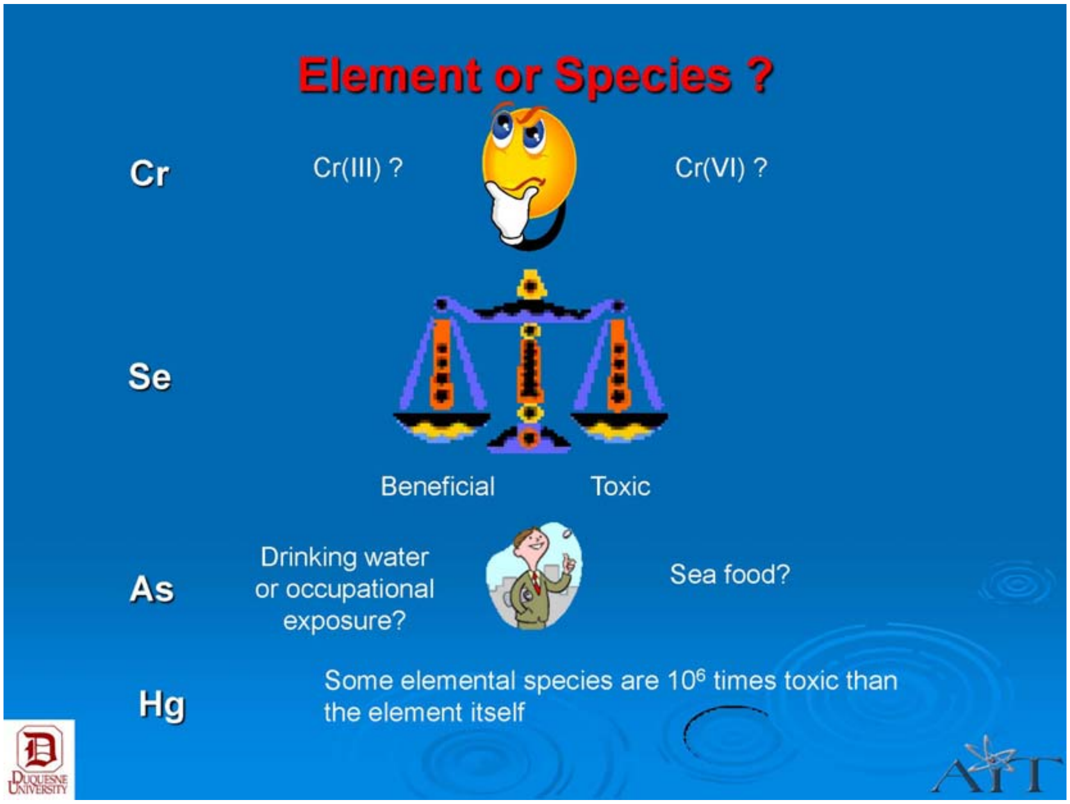
- 99% of the mass of human body is made up of only six elements: O – 65%; C – 18%; H – 10%; N – 3%; Ca – 1.5%; and P – 1.0%)
- Other essential bulk elements are: K – 0.35%; S – 0.25%; Na – 0.15% and Mg – 0.05%
- Cu, Zn, Se, Mo, F, Cl, I, Mn, Co and Fe (0.70%)
- Li, Sr, Al, Si, Pb, V, As and Br, etc. (trace amounts)

~ 1/3 of all mammalian proteins are metalloproteins (with one or more of these elements in the active center)



Why Study of Trace Elements?

- Trace element is defined as one that makes up less than 0.01% of total body mass
- There are 50 or more trace elements found in the human body, both normal and abnormal
- There are two general classes of abnormalities associated with trace elements
  - Deficiency – from dietary inadequacies, imbalances, or secondary to other diseases
  - Accumulation of toxic trace elements from environment, which can either displace essential elements from their metabolically active sites and causes conditioned deficiency, or act directly as cellular toxins
- Both kind of abnormalities can be diagnosed by analyses of trace elements in plasma, serum, red blood cell, urine, hair, feces, sweat, bone, nail, tissues, etc.



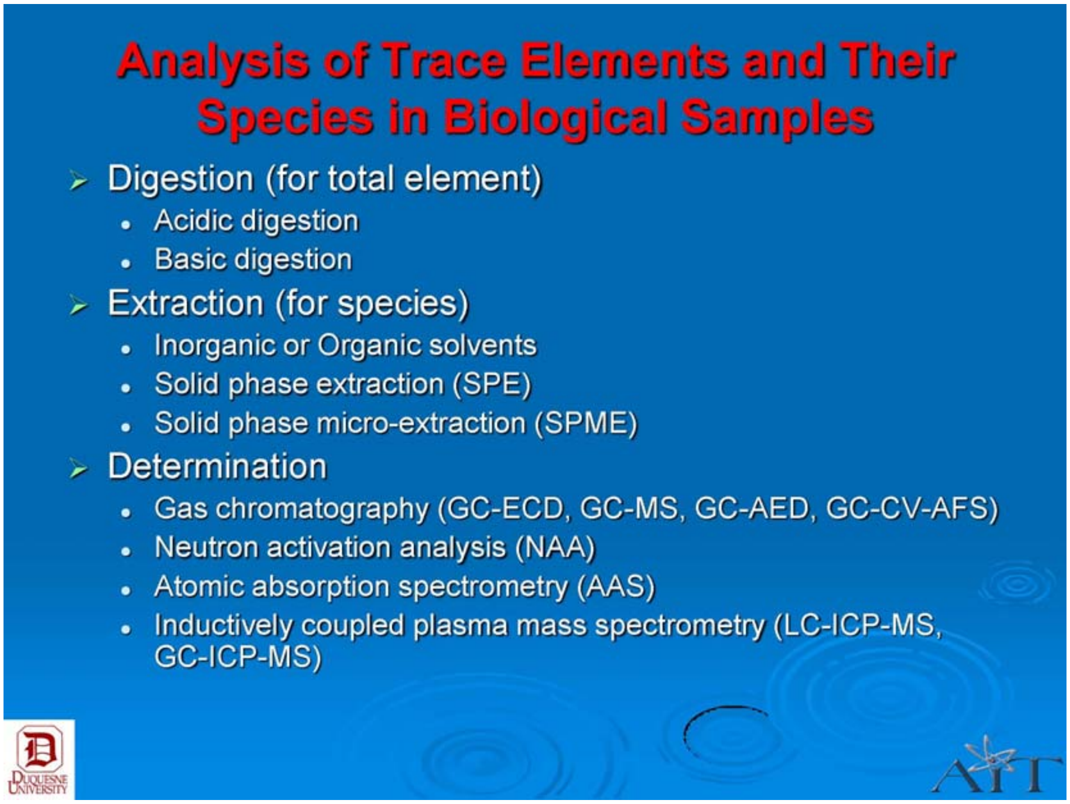
Element or Species ?

Cr Cr(III) ? Cr(VI) ?

Se Beneficial Toxic

As Drinking water or occupational exposure? Sea food?

Hg Some elemental species are 10^6 times toxic than the element itself



Analysis of Trace Elements and Their Species in Biological Samples

- Digestion (for total element)
  - Acidic digestion
  - Basic digestion
- Extraction (for species)
  - Inorganic or Organic solvents
  - 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)

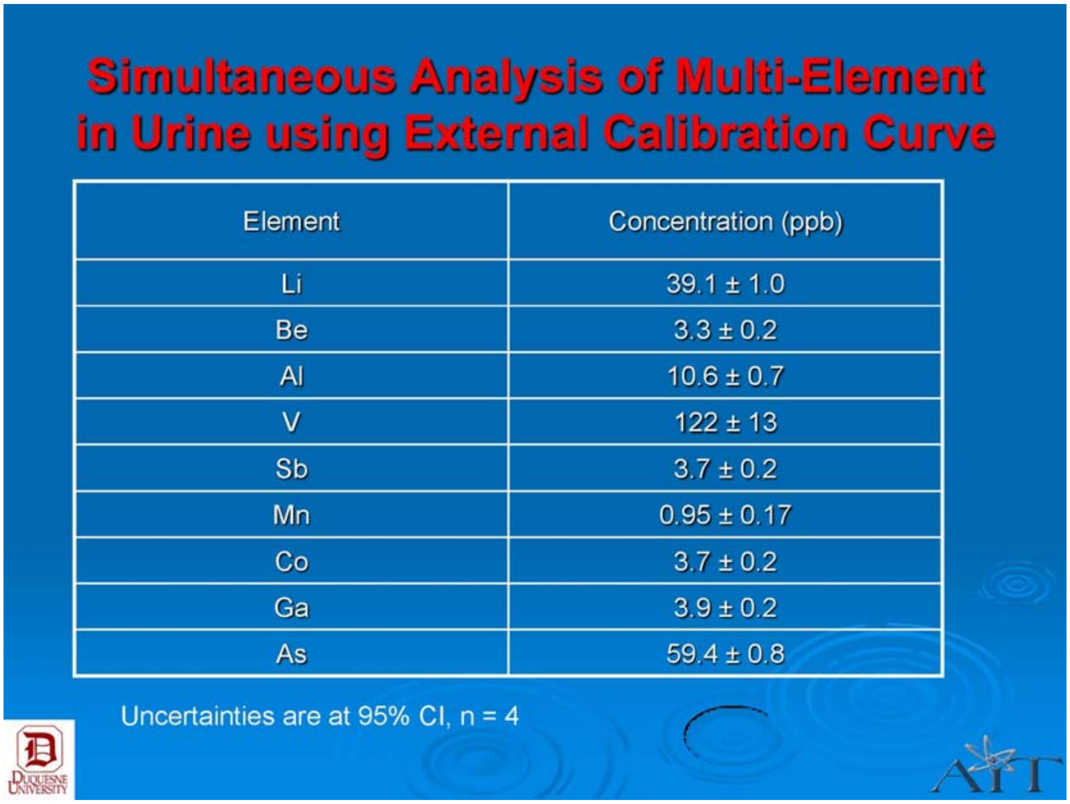
Comparison of External Calibration and IDMS for Total Elemental Analysis in Urine

- External Calibration Method:
    - 1 mL of Urine was diluted with 9 mL of 1% HNO_3 (v/v)
    - Analyzed with ICP-MS in spectrum mode and results were calculated by external calibration method
- IDMS (Method 6800)
    - 1 mL of urine was spiked with a known amount of multi-element isotopic spike whose concentrations are also known
    - Equilibrate for 0.5 h
    - Diluted with 9 mL of 1% HNO_3 (v/v)
    - Analyzed with ICP-MS in spectrum mode and concentrations of different elements in urine were calculated using the IDMS software

Comparison of External Calibration and IDMS for Multi-Element Analysis in Urine

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

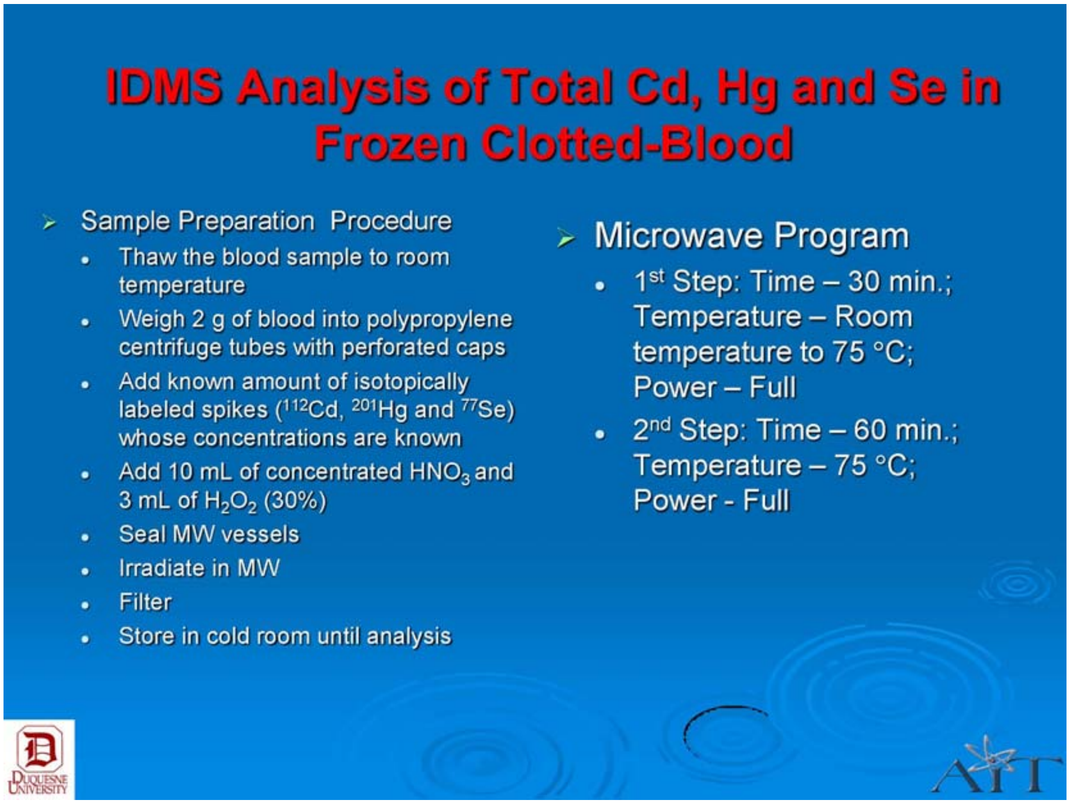
Uncertainties are at 95% CI, n = 4



Simultaneous Analysis of Multi-Element in Urine using External Calibration Curve

Element	Concentration (ppb)
Li	39.1 ± 1.0
Be	3.3 ± 0.2
Al	10.6 ± 0.7
V	122 ± 13
Sb	3.7 ± 0.2
Mn	0.95 ± 0.17
Co	3.7 ± 0.2
Ga	3.9 ± 0.2
As	59.4 ± 0.8

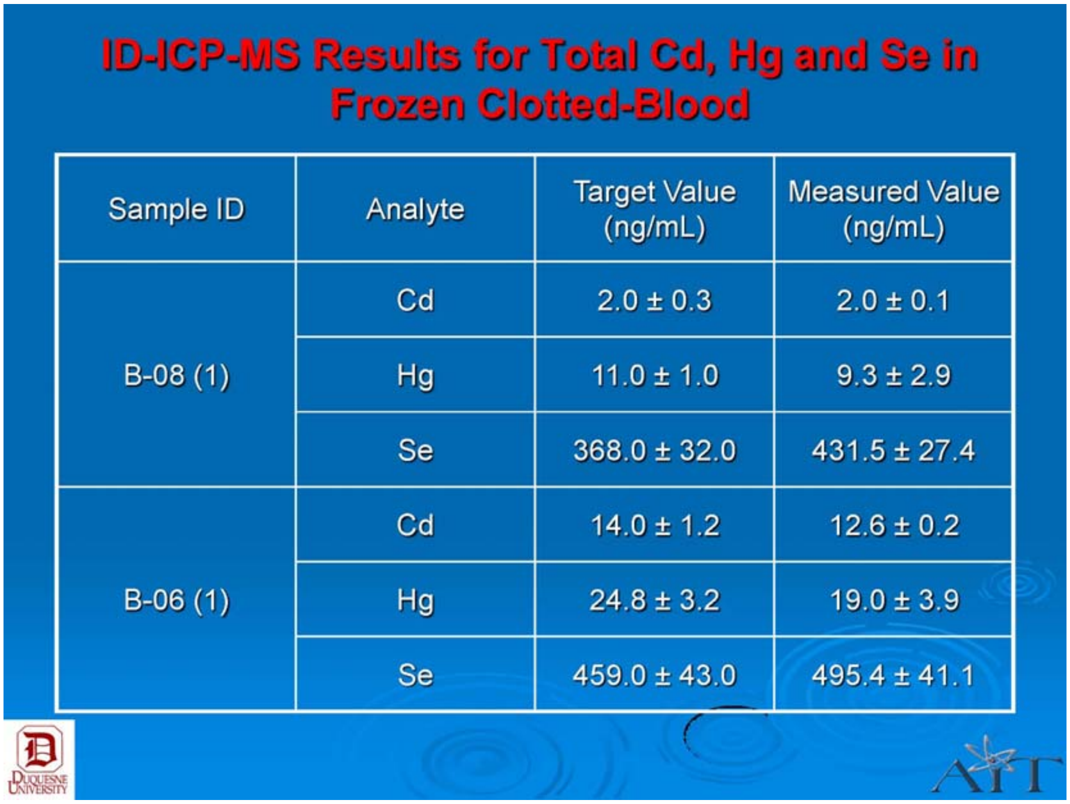
Uncertainties are at 95% CI, n = 4



IDMS Analysis of Total Cd, Hg and Se in Frozen Clotted-Blood

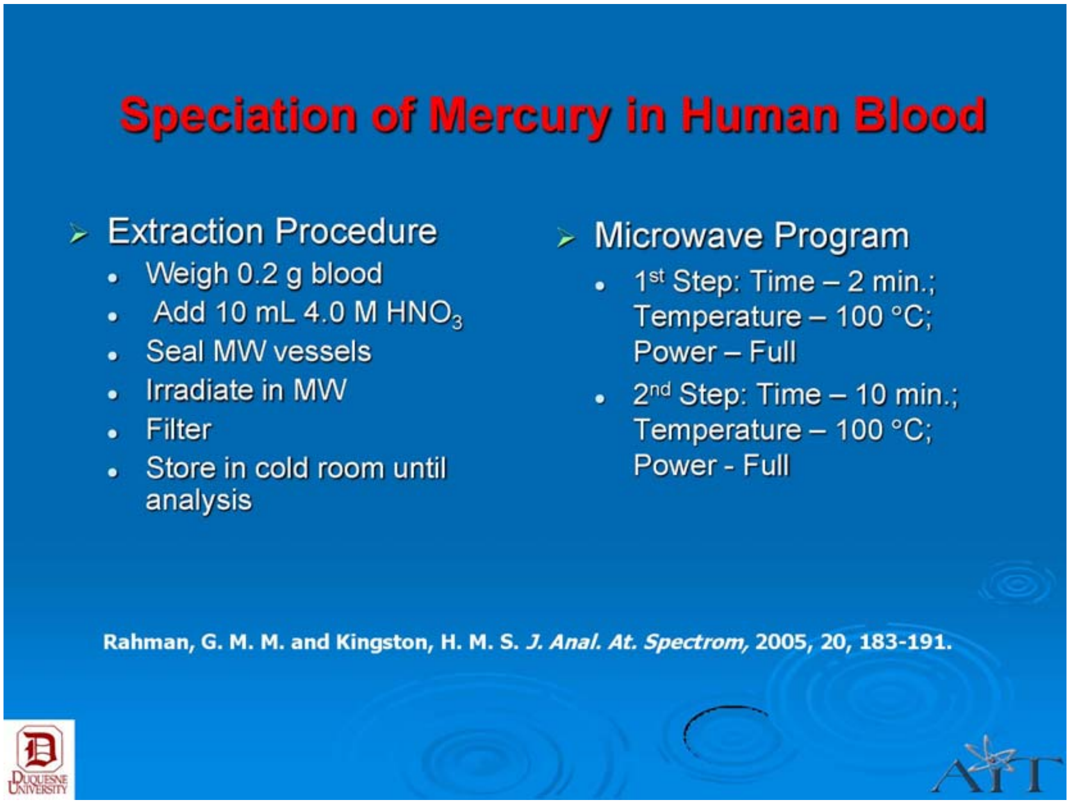
- Sample Preparation Procedure
  - Thaw the blood sample to room temperature
  - Weigh 2 g of blood into polypropylene centrifuge tubes with perforated caps
  - Add known amount of isotopically labeled spikes (^{112}Cd, ^{201}Hg and ^{77}Se) whose concentrations are known
  - Add 10 mL of concentrated HNO_3 and 3 mL of H_2O_2 (30%)
  - Seal MW vessels
  - Irradiate in MW
  - Filter
  - Store in cold room until analysis

- Microwave Program
  - 1st Step: Time – 30 min.; Temperature – Room temperature to 75 °C; Power – Full
  - 2nd Step: Time – 60 min.; Temperature – 75 °C; Power - Full



ID-ICP-MS Results for Total Cd, Hg and Se in Frozen Clotted-Blood

Sample ID	Analyte	Target Value (ng/mL)	Measured Value (ng/mL)
B-08 (1)	Cd	2.0 ± 0.3	2.0 ± 0.1
	Hg	11.0 ± 1.0	9.3 ± 2.9
	Se	368.0 ± 32.0	431.5 ± 27.4
B-06 (1)	Cd	14.0 ± 1.2	12.6 ± 0.2
	Hg	24.8 ± 3.2	19.0 ± 3.9
	Se	459.0 ± 43.0	495.4 ± 41.1

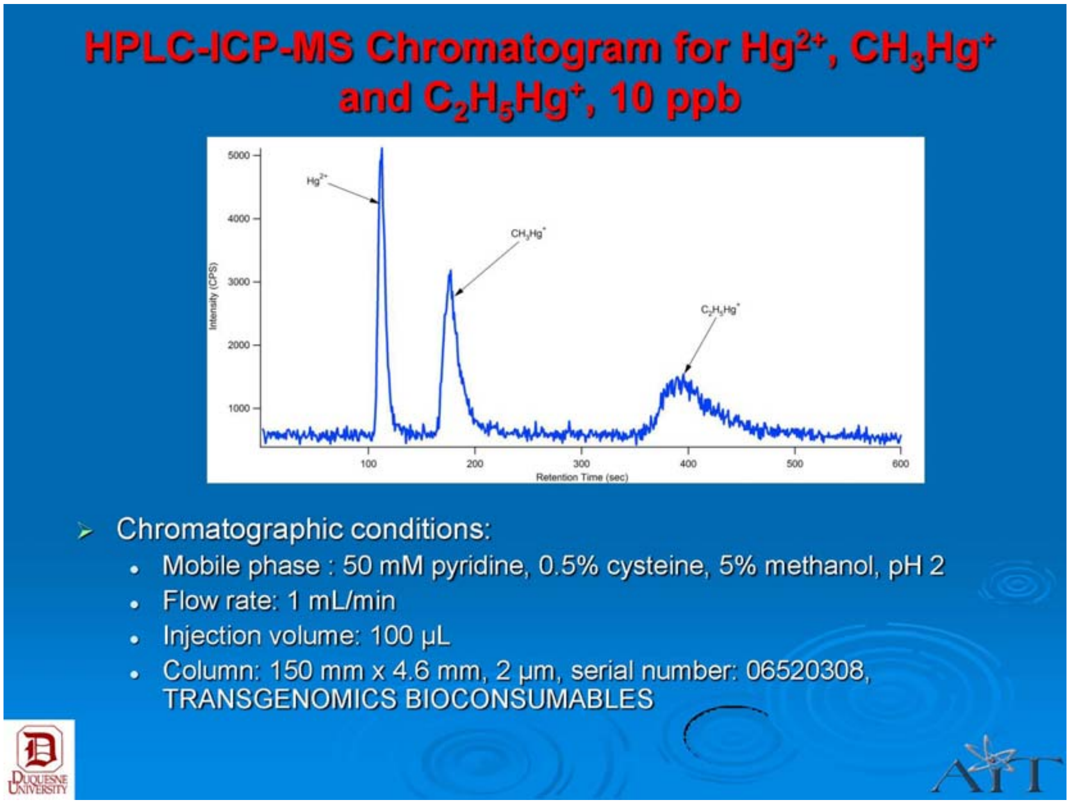


Speciation of Mercury in Human Blood

- Extraction Procedure
  - Weigh 0.2 g blood
  - Add 10 mL 4.0 M HNO_3
  - Seal MW vessels
  - Irradiate in MW
  - Filter
  - Store in cold room until analysis

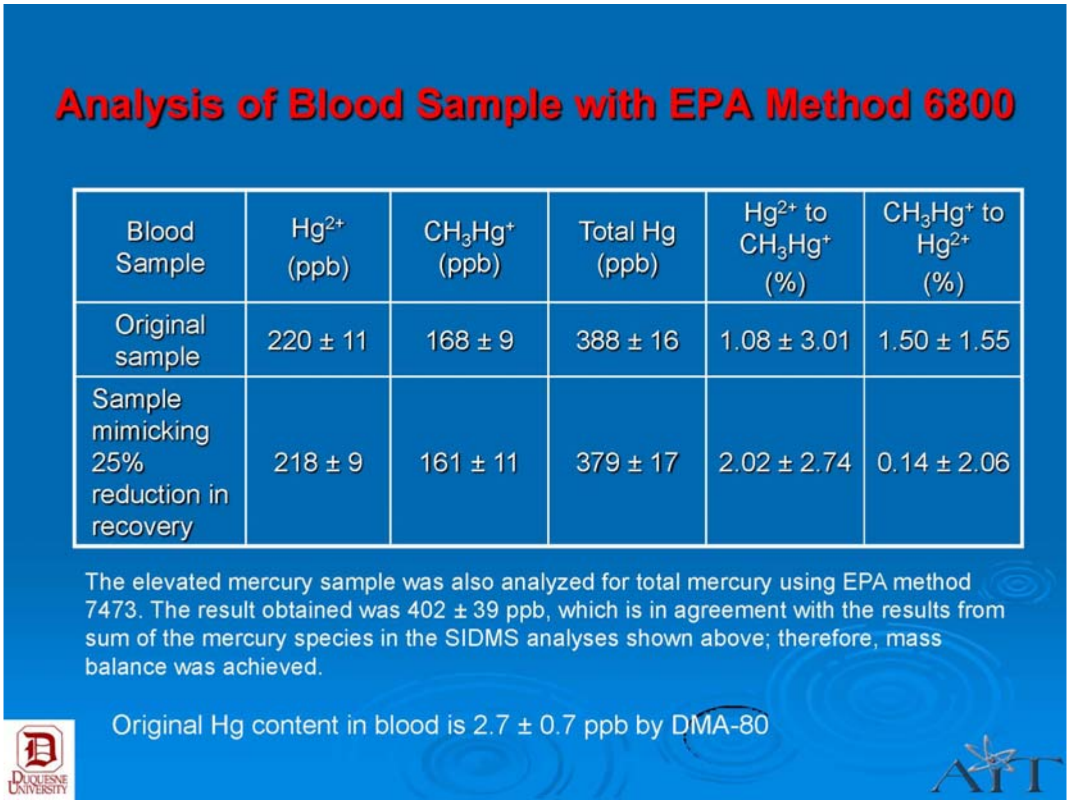
- Microwave Program
  - 1st Step: Time – 2 min.; Temperature – 100 °C; Power – Full
  - 2nd Step: Time – 10 min.; Temperature – 100 °C; Power - Full

Rahman, G. M. M. and Kingston, H. M. S. *J. Anal. At. Spectrom*, 2005, 20, 183-191.



HPLC-ICP-MS Chromatogram for Hg^{2+}, CH_3Hg^+ and $C_2H_5Hg^+$, 10 ppb

- Chromatographic conditions:
  - Mobile phase : 50 mM pyridine, 0.5% cysteine, 5% methanol, pH 2
  - Flow rate: 1 mL/min
  - Injection volume: 100 µL
  - Column: 150 mm x 4.6 mm, 2 µm, serial number: 06520308, TRANSGENOMICS BIOCONSUMABLES



Analysis of Blood Sample with EPA Method 6800

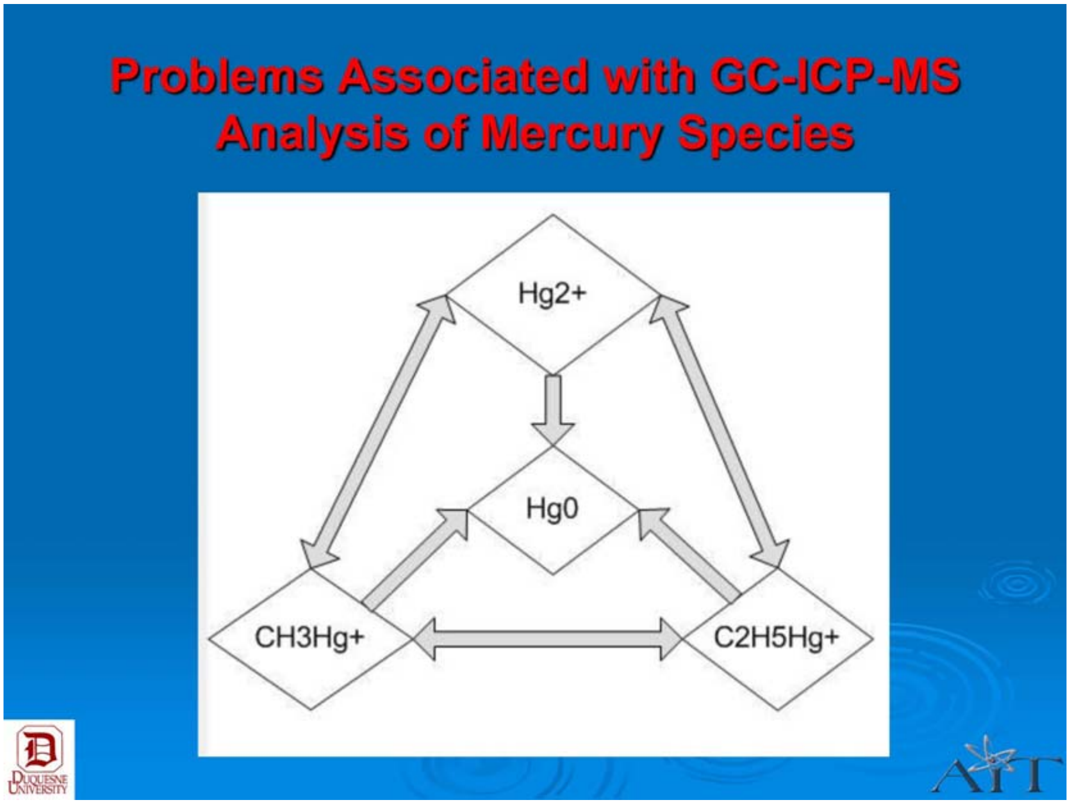
Blood Sample	Hg^{2+} (ppb)	CH_3Hg^+ (ppb)	Total Hg (ppb)	Hg^{2+} to CH_3Hg^+ (%)	CH_3Hg^+ to Hg^{2+} (%)
Original sample	220 ± 11	168 ± 9	388 ± 16	1.08 ± 3.01	1.50 ± 1.55
Sample mimicking 25% reduction in recovery	218 ± 9	161 ± 11	379 ± 17	2.02 ± 2.74	0.14 ± 2.06

The elevated mercury sample was also analyzed for total mercury using EPA method 7473. The result obtained was 402 ± 39 ppb, which is in agreement with the results from sum of the mercury species in the SIDMS analyses shown above; therefore, mass balance was achieved.

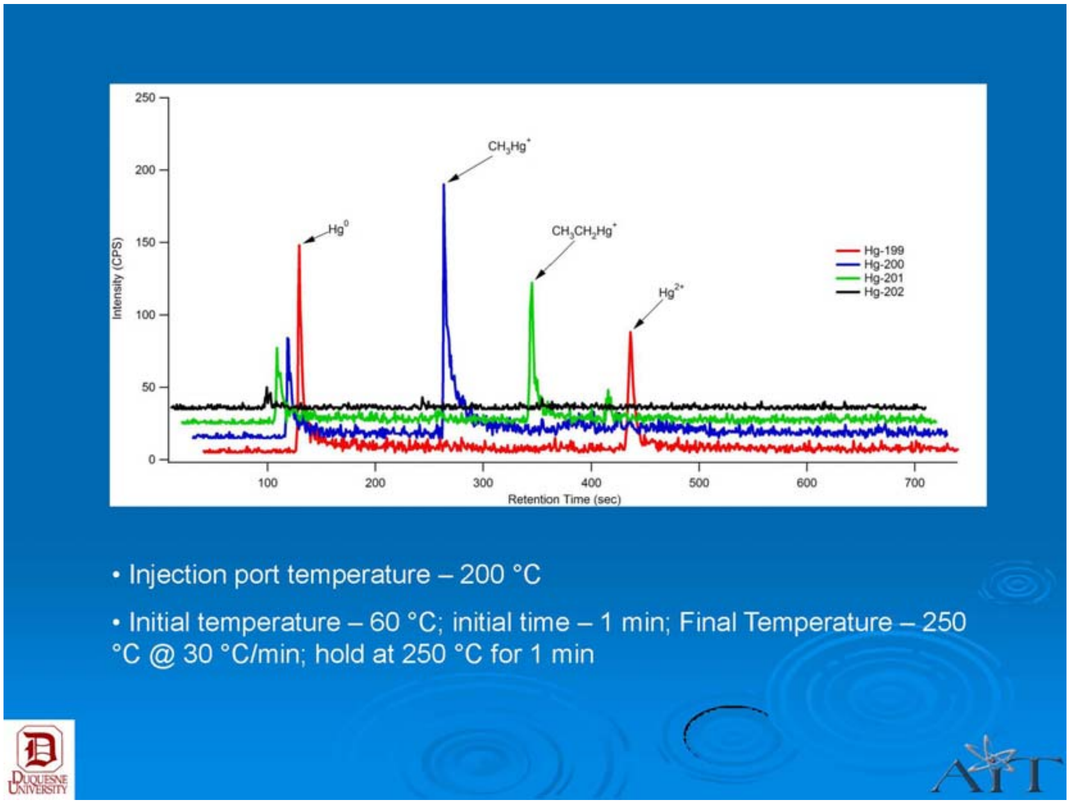
Original Hg content in blood is 2.7 ± 0.7 ppb by DMA-80

Mercury Speciation by GC-ICP-MS

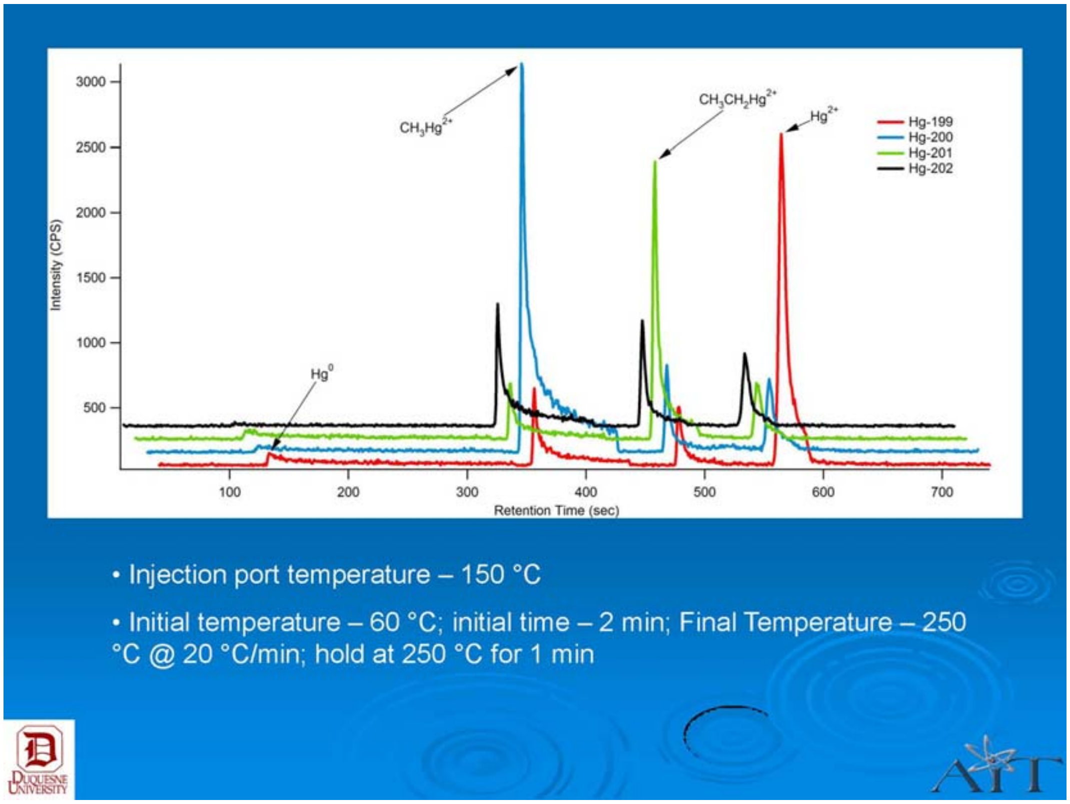
- GC – HP 5890
- ICP-MS – HP 4500
- Transfer line assembly – Hyphenated Solutions, L.L.L.P.



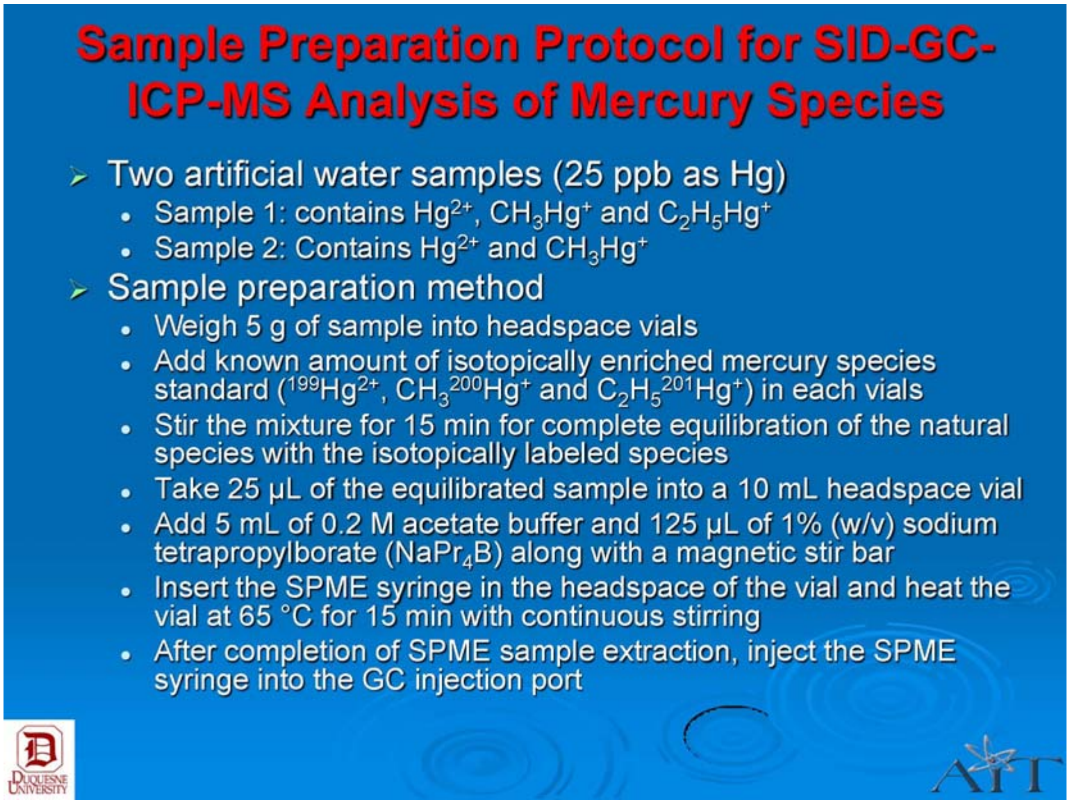
Problems Associated with GC-ICP-MS Analysis of Mercury Species



- Injection port temperature – 200 °C
- Initial temperature – 60 °C; initial time – 1 min; Final Temperature – 250 °C @ 30 °C/min; hold at 250 °C for 1 min

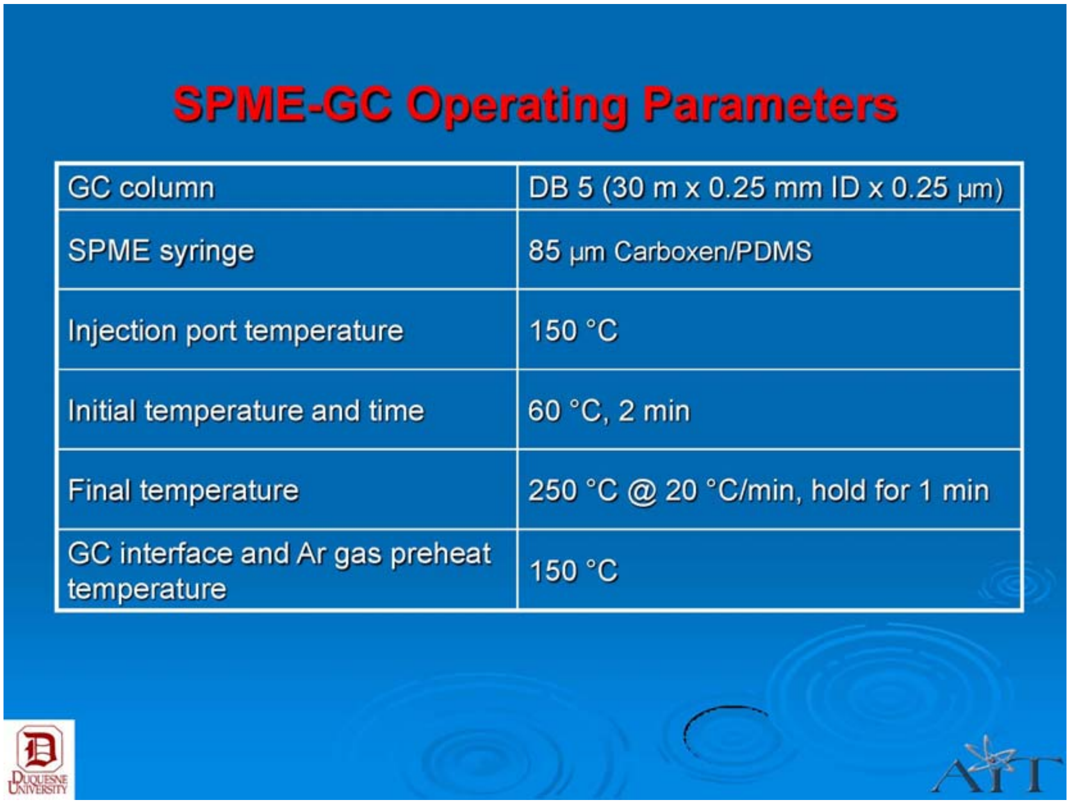


- Injection port temperature – 150 °C
- Initial temperature – 60 °C; initial time – 2 min; Final Temperature – 250 °C @ 20 °C/min; hold at 250 °C for 1 min



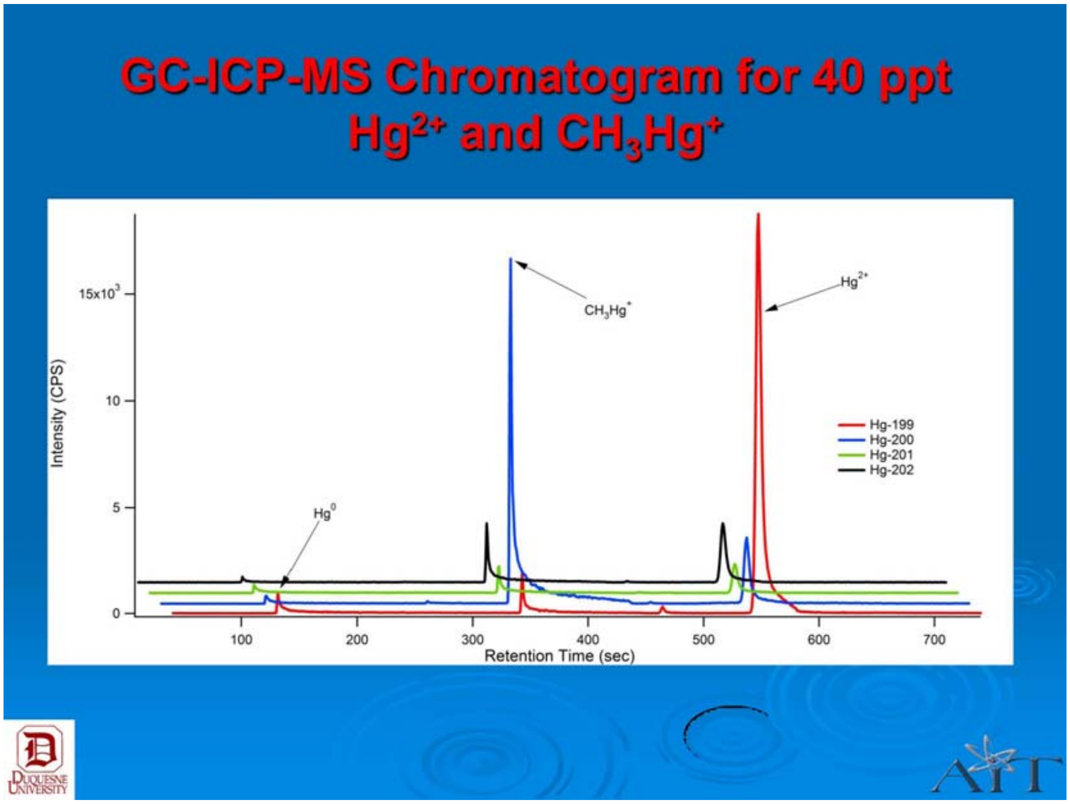
Sample Preparation Protocol for SID-GC-ICP-MS Analysis of Mercury Species

- Two artificial water samples (25 ppb as Hg)
  - Sample 1: contains Hg^{2+}, CH_3Hg^+ and $C_2H_5Hg^+$
  - Sample 2: Contains Hg^{2+} and CH_3Hg^+
- Sample preparation method
  - Weigh 5 g of sample into headspace vials
  - Add known amount of isotopically enriched mercury species standard ($^{199}Hg^{2+}$, $CH_3{}^{200}Hg^+$ and $C_2H_5{}^{201}Hg^+$) in each vials
  - Stir the mixture for 15 min for complete equilibration of the natural species with the isotopically labeled species
  - Take 25 µL of the equilibrated sample into a 10 mL headspace vial
  - Add 5 mL of 0.2 M acetate buffer and 125 µL of 1% (w/v) sodium tetrapropylborate ($NaPr_4B$) along with a magnetic stir bar
  - Insert the SPME syringe in the headspace of the vial and heat the vial at 65 °C for 15 min with continuous stirring
  - After completion of SPME sample extraction, inject the SPME syringe into the GC injection port

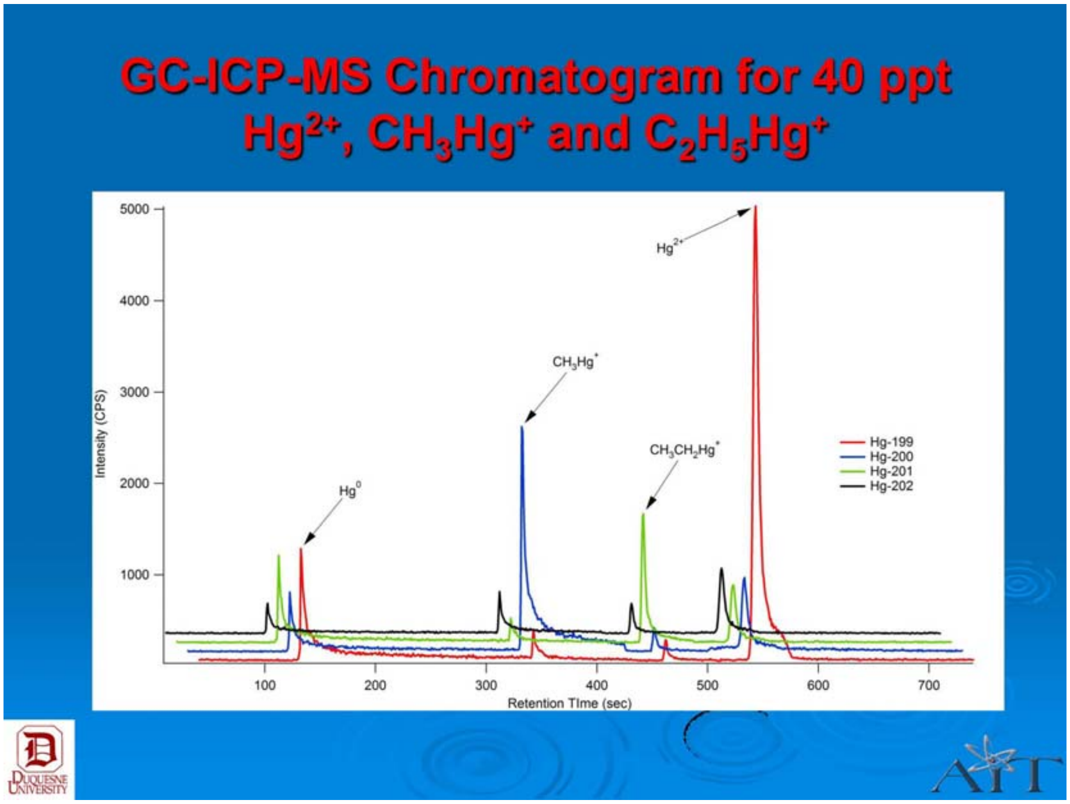


SPME-GC Operating Parameters

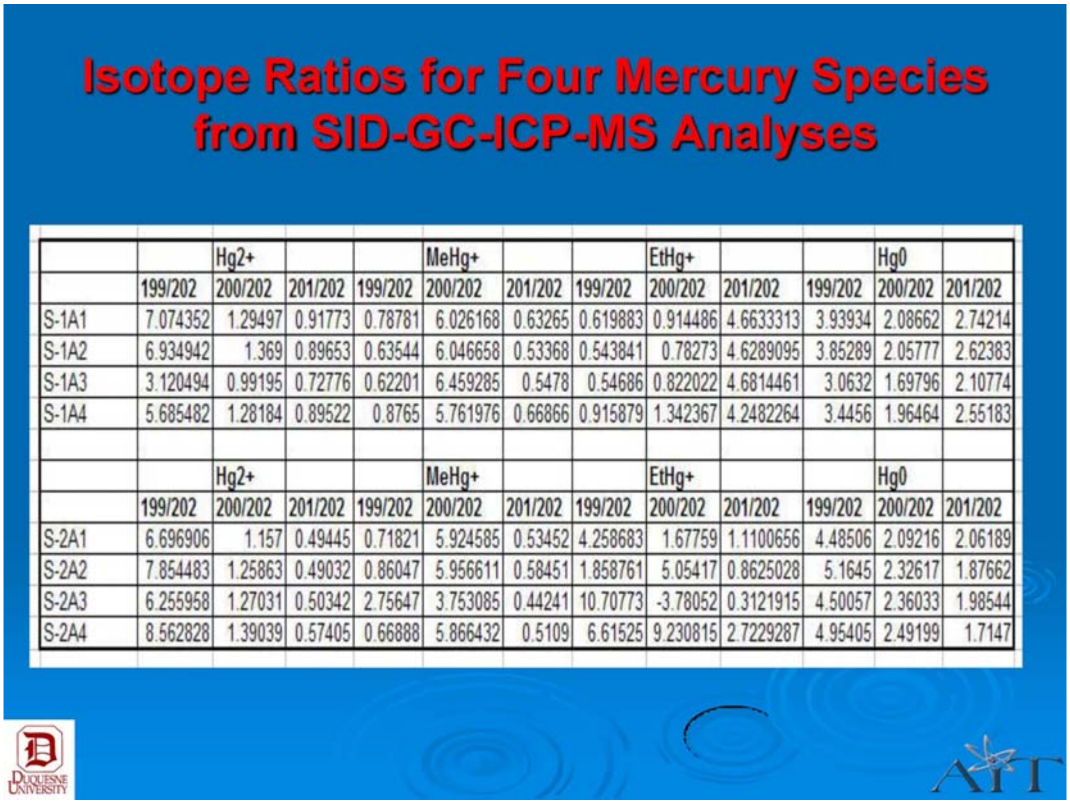
GC column	DB 5 (30 m x 0.25 mm ID x 0.25 µm)
SPME syringe	85 µm Carboxen/PDMS
Injection port temperature	150 °C
Initial temperature and time	60 °C, 2 min
Final temperature	250 °C @ 20 °C/min, hold for 1 min
GC interface and Ar gas preheat temperature	150 °C



GC-ICP-MS Chromatogram for 40 ppt Hg^{2+} and CH_3Hg^+



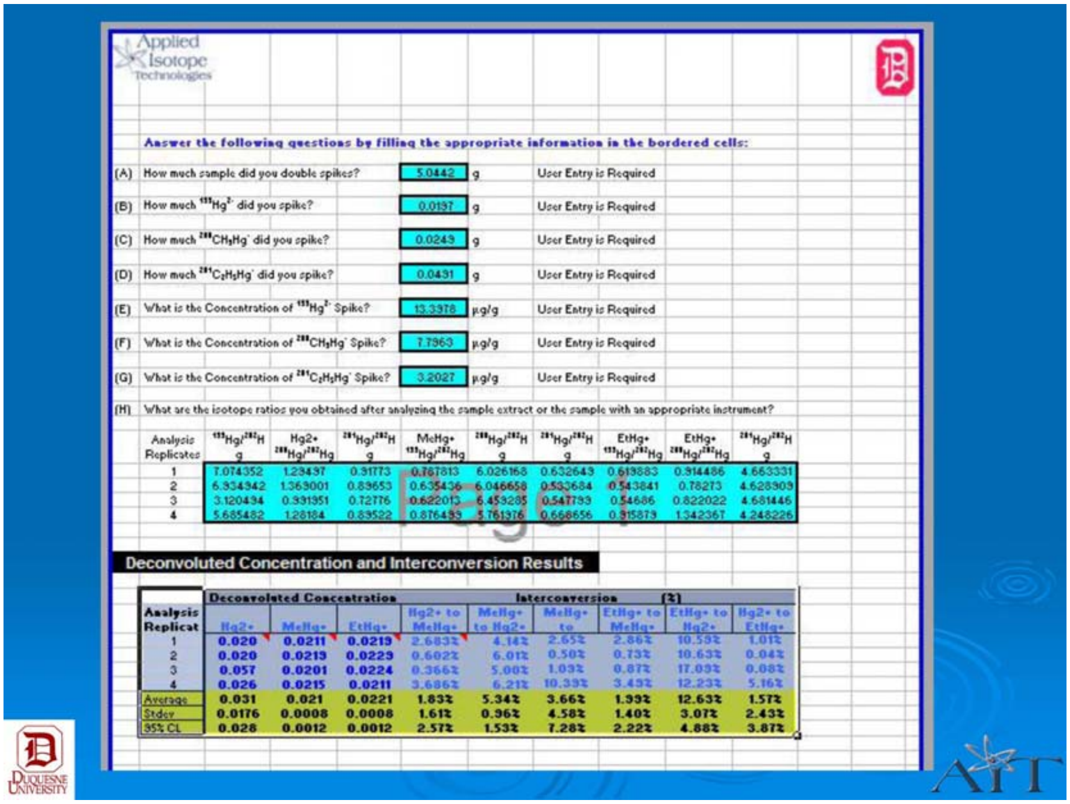
GC-ICP-MS Chromatogram for 40 ppt Hg^{2+}, CH_3Hg^+ and $C_2H_5Hg^+$



Isotope Ratios for Four Mercury Species from SID-GC-ICP-MS Analyses

		Hg2+			MeHg+			EtHg+			Hg0	
	199/202	200/202	201/202	199/202	200/202	201/202	199/202	200/202	201/202	199/202	200/202	201/202
S-1A1	7.074352	1.29497	0.91773	0.78781	6.026168	0.63265	0.619883	0.914486	4.6633313	3.93934	2.08662	2.74214
S-1A2	6.934942	1.369	0.89653	0.63544	6.046658	0.53368	0.543841	0.78273	4.6289095	3.85289	2.05777	2.62383
S-1A3	3.120494	0.99195	0.72776	0.62201	6.459285	0.5478	0.54686	0.822022	4.6814461	3.0632	1.69796	2.10774
S-1A4	5.685482	1.28184	0.89522	0.8765	5.761976	0.66866	0.915879	1.342367	4.2482264	3.4456	1.96464	2.55183

		Hg2+			MeHg+			EtHg+			Hg0	
	199/202	200/202	201/202	199/202	200/202	201/202	199/202	200/202	201/202	199/202	200/202	201/202
S-2A1	6.696906	1.157	0.49445	0.71821	5.924585	0.53452	4.258683	1.67759	1.1100656	4.48506	2.09216	2.06189
S-2A2	7.854483	1.25863	0.49032	0.86047	5.956611	0.58451	1.858761	5.05417	0.8625028	5.1645	2.32617	1.87662
S-2A3	6.255958	1.27031	0.50342	2.75647	3.753085	0.44241	10.70773	-3.78052	0.3121915	4.50057	2.36033	1.98544
S-2A4	8.562828	1.39039	0.57405	0.66888	5.866432	0.5109	6.61525	9.230815	2.7229287	4.95405	2.49199	1.7147



Applied Isotope Technologies

Answer the following questions by filling the appropriate information in the bordered cells:

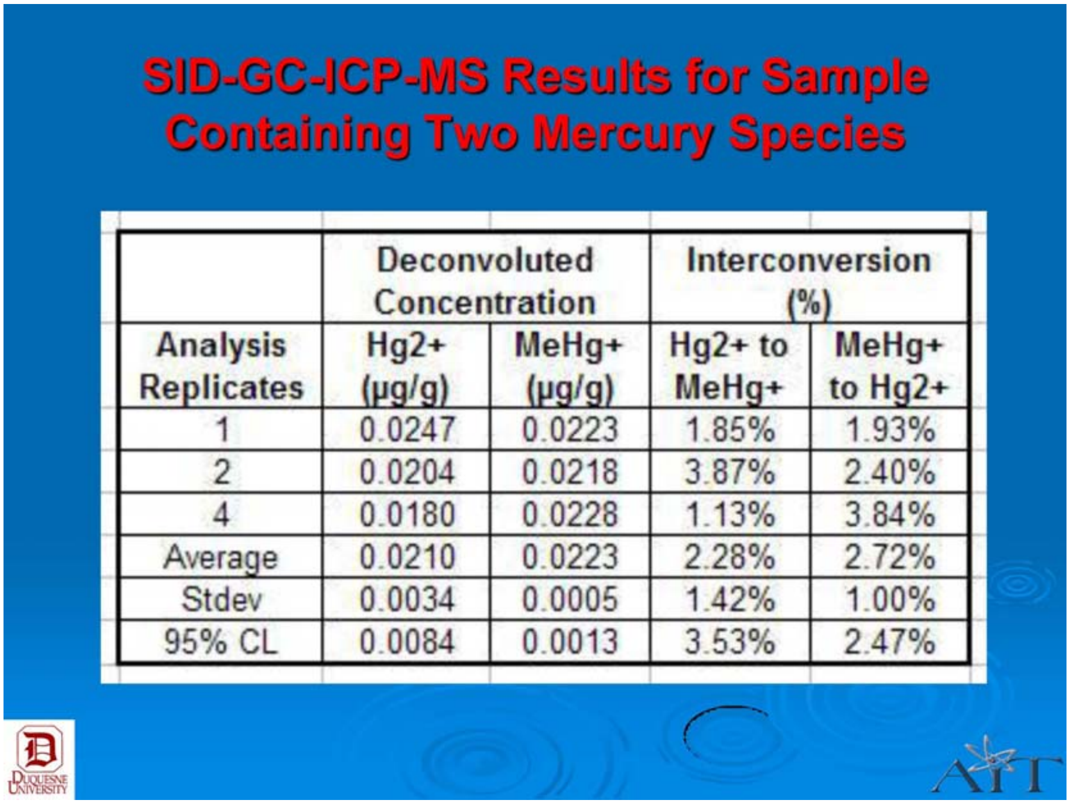
(A)	How much sample did you double spikes?	5.0442	g	User Entry is Required
(B)	How much $^{199}Hg^{2+}$ did you spike?	0.0197	g	User Entry is Required
(C)	How much $^{200}CH_3Hg^+$ did you spike?	0.0243	g	User Entry is Required
(D)	How much $^{201}C_2H_5Hg^+$ did you spike?	0.0431	g	User Entry is Required
(E)	What is the Concentration of $^{199}Hg^{2+}$ Spike?	13.3978	µg/g	User Entry is Required
(F)	What is the Concentration of $^{200}CH_3Hg^+$ Spike?	7.7963	µg/g	User Entry is Required
(G)	What is the Concentration of $^{201}C_2H_5Hg^+$ Spike?	3.2027	µg/g	User Entry is Required

(H) What are the isotope ratios you obtained after analyzing the sample extract or the sample with an appropriate instrument?

Analysis Replicates	$^{199}Hg/^{202}Hg$	Hg2+ $^{200}Hg/^{202}Hg$	$^{201}Hg/^{202}Hg$	MeHg+ $^{199}Hg/^{202}Hg$	$^{200}Hg/^{202}Hg$	$^{201}Hg/^{202}Hg$	EtHg+ $^{199}Hg/^{202}Hg$	EtHg+ $^{200}Hg/^{202}Hg$	$^{201}Hg/^{202}Hg$
1	7.074352	1.29497	0.91773	0.787813	6.026168	0.632649	0.619883	0.914486	4.663331
2	6.934942	1.369001	0.89653	0.635436	6.046658	0.533684	0.543841	0.78273	4.628909
3	3.120494	0.991951	0.72776	0.622013	6.459285	0.547799	0.54686	0.822022	4.681446
4	5.685482	1.28184	0.89522	0.876499	5.761976	0.668656	0.915879	1.342367	4.248226

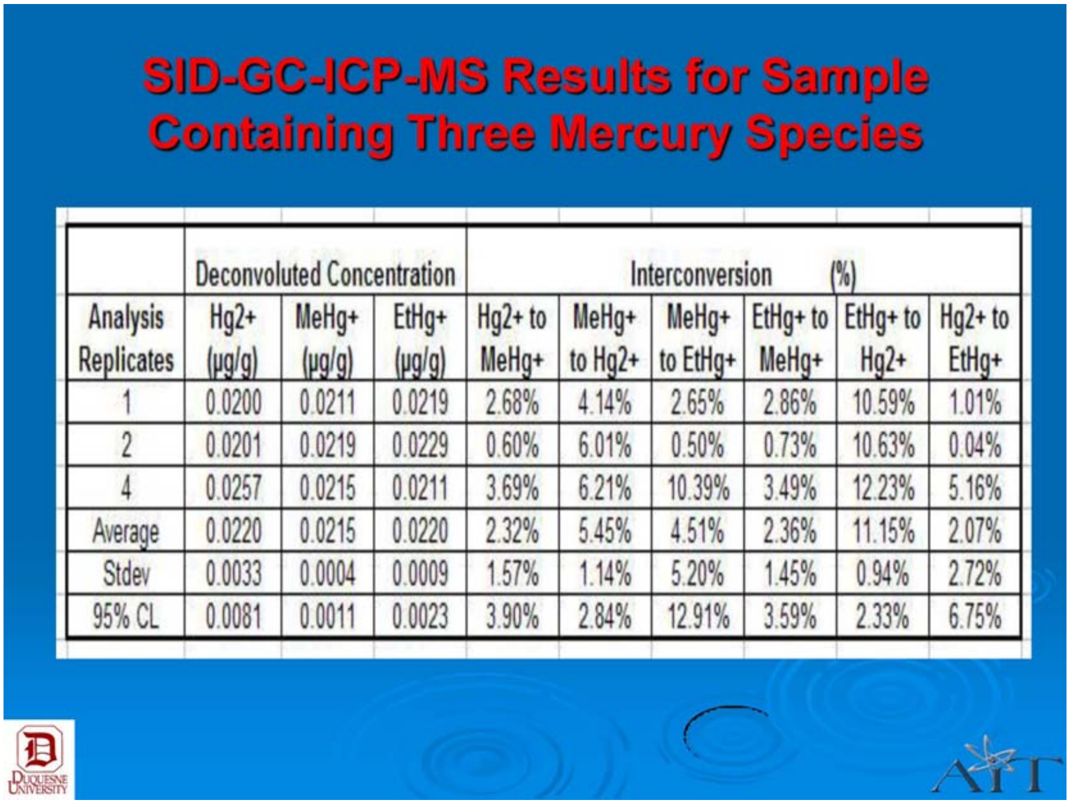
Deconvoluted Concentration and Interconversion Results

	Deconvoluted Concentration			Interconversion (%)					
Analysis Replicat	Hg2+	MeHg+	EtHg+	Hg2+ to MeHg+	MeHg+ to Hg2+	MeHg+ to	EtHg+ to MeHg+	EtHg+ to Hg2+	Hg2+ to EtHg+
1	0.020	0.0211	0.0219	2.683%	4.14%	2.65%	2.86%	10.59%	1.01%
2	0.020	0.0219	0.0229	0.602%	6.01%	0.50%	0.73%	10.63%	0.04%
3	0.057	0.0201	0.0224	0.366%	5.00%	1.03%	0.87%	17.03%	0.08%
4	0.026	0.0215	0.0211	3.686%	6.21%	10.39%	3.43%	12.23%	5.16%
Average	0.031	0.021	0.0221	1.83%	5.34%	3.66%	1.93%	12.63%	1.57%
Stdev	0.0176	0.0008	0.0008	1.61%	0.96%	4.58%	1.40%	3.07%	2.43%
95% CL	0.028	0.0012	0.0012	2.57%	1.53%	7.28%	2.22%	4.88%	3.87%



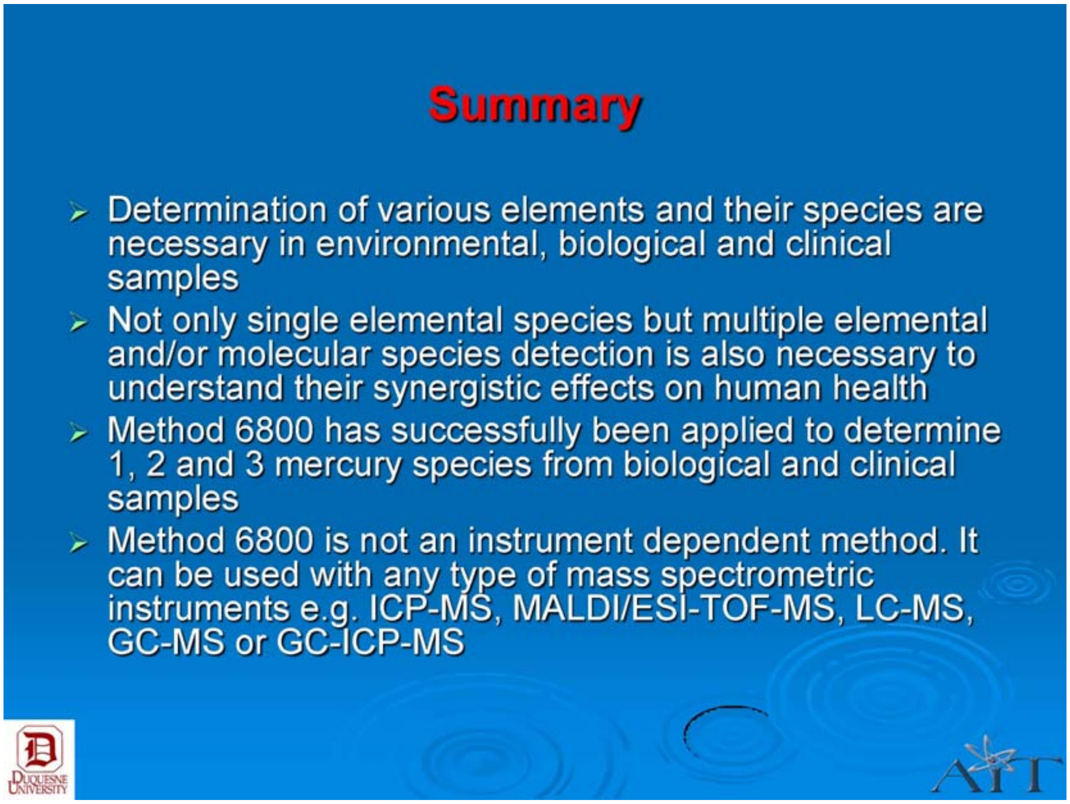
SID-GC-ICP-MS Results for Sample Containing Two Mercury Species

	Deconvoluted Concentration		Interconversion (%)	
Analysis Replicates	Hg2+ (µg/g)	MeHg+ (µg/g)	Hg2+ to MeHg+	MeHg+ to Hg2+
1	0.0247	0.0223	1.85%	1.93%
2	0.0204	0.0218	3.87%	2.40%
4	0.0180	0.0228	1.13%	3.84%
Average	0.0210	0.0223	2.28%	2.72%
Stdev	0.0034	0.0005	1.42%	1.00%
95% CL	0.0084	0.0013	3.53%	2.47%



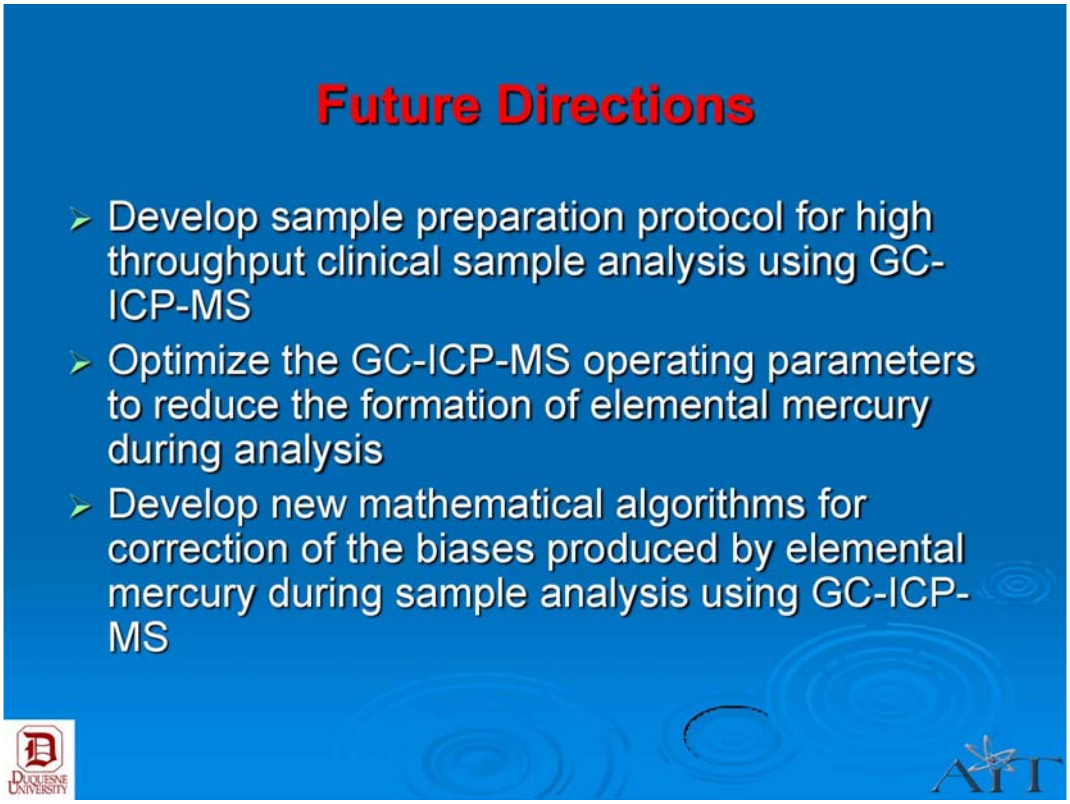
SID-GC-ICP-MS Results for Sample Containing Three Mercury Species

	Deconvoluted Concentration			Interconversion (%)					
Analysis Replicates	Hg2+ (µg/g)	MeHg+ (µg/g)	EtHg+ (µg/g)	Hg2+ to MeHg+	MeHg+ to Hg2+	MeHg+ to EtHg+	EtHg+ to MeHg+	EtHg+ to Hg2+	Hg2+ to EtHg+
1	0.0200	0.0211	0.0219	2.68%	4.14%	2.65%	2.86%	10.59%	1.01%
2	0.0201	0.0219	0.0229	0.60%	6.01%	0.50%	0.73%	10.63%	0.04%
4	0.0257	0.0215	0.0211	3.69%	6.21%	10.39%	3.49%	12.23%	5.16%
Average	0.0220	0.0215	0.0220	2.32%	5.45%	4.51%	2.36%	11.15%	2.07%
Stdev	0.0033	0.0004	0.0009	1.57%	1.14%	5.20%	1.45%	0.94%	2.72%
95% CL	0.0081	0.0011	0.0023	3.90%	2.84%	12.91%	3.59%	2.33%	6.75%



Summary

- Determination of various elements and their species are necessary in environmental, biological and clinical samples
- Not only single elemental species but multiple elemental and/or molecular species detection is also necessary to understand their synergistic effects on human health
- Method 6800 has successfully been applied to determine 1, 2 and 3 mercury species from biological and clinical samples
- Method 6800 is not an instrument dependent method. It can be used with any type of mass spectrometric instruments e.g. ICP-MS, MALDI/ESI-TOF-MS, LC-MS, GC-MS or GC-ICP-MS



Future Directions

- Develop sample preparation protocol for high throughput clinical sample analysis using GC-ICP-MS
- Optimize the GC-ICP-MS operating parameters to reduce the formation of elemental mercury during analysis
- Develop new mathematical algorithms for correction of the biases produced by elemental mercury during sample analysis using GC-ICP-MS

Acknowledgments

- Kingston Research Group
- Sample Provider
    - Stanford University Blood Bank
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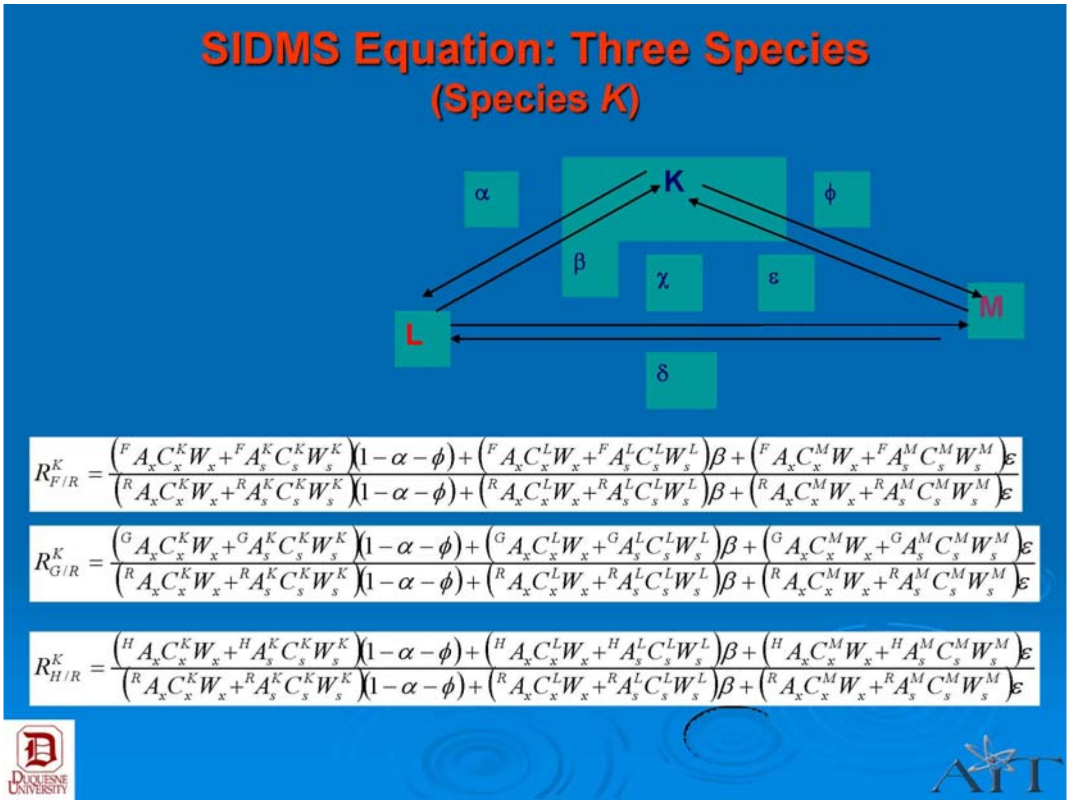
- Instrumentation Support
    - Agilent Technologies
    - Milestone Inc.
    - Metrohm-Peak, LLC
    - Hyphenated Solutions, LLLP
- Sponsor
    - Applied Isotope Technologies, Inc (AIT)
    - Pittsburgh Life Sciences Greenhouse
    - Department of Chemistry & Biochemistry, Duquesne University, Pittsburgh, PA 15282



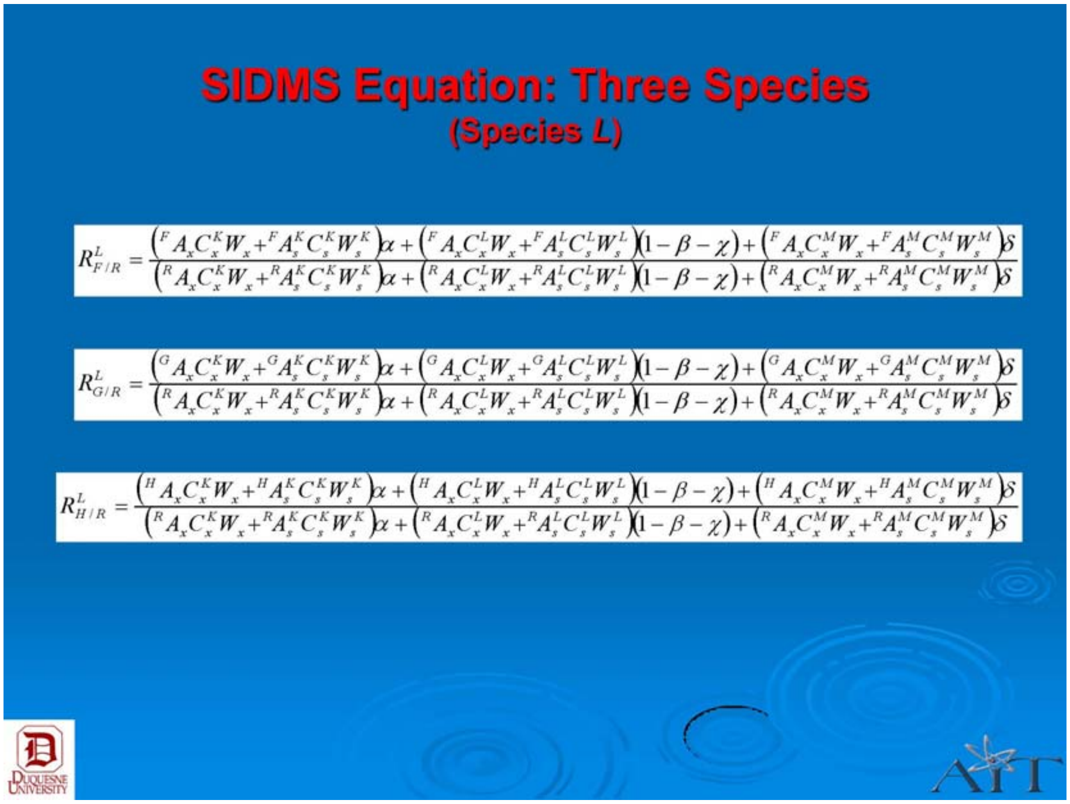
SIDMS Equation: Three Species

(Species *K*)

$$R^K_{F/R} = \frac{\left({}^F A_x C^K_x W_x + {}^F A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^F A_x C^L_x W_x + {}^F A^L_s C^L_s W^L_s\right)\beta + \left({}^F A_x C^M_x W_x + {}^F A^M_s C^M_s W^M_s\right)\varepsilon}{\left({}^R A_x C^K_x W_x + {}^R A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^R A_x C^L_x W_x + {}^R A^L_s C^L_s W^L_s\right)\beta + \left({}^R A_x C^M_x W_x + {}^R A^M_s C^M_s W^M_s\right)\varepsilon}$$

$$R^K_{G/R} = \frac{\left({}^G A_x C^K_x W_x + {}^G A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^G A_x C^L_x W_x + {}^G A^L_s C^L_s W^L_s\right)\beta + \left({}^G A_x C^M_x W_x + {}^G A^M_s C^M_s W^M_s\right)\varepsilon}{\left({}^R A_x C^K_x W_x + {}^R A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^R A_x C^L_x W_x + {}^R A^L_s C^L_s W^L_s\right)\beta + \left({}^R A_x C^M_x W_x + {}^R A^M_s C^M_s W^M_s\right)\varepsilon}$$

$$R^K_{H/R} = \frac{\left({}^H A_x C^K_x W_x + {}^H A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^H A_x C^L_x W_x + {}^H A^L_s C^L_s W^L_s\right)\beta + \left({}^H A_x C^M_x W_x + {}^H A^M_s C^M_s W^M_s\right)\varepsilon}{\left({}^R A_x C^K_x W_x + {}^R A^K_s C^K_s W^K_s\right)(1-\alpha-\phi) + \left({}^R A_x C^L_x W_x + {}^R A^L_s C^L_s W^L_s\right)\beta + \left({}^R A_x C^M_x W_x + {}^R A^M_s C^M_s W^M_s\right)\varepsilon}$$



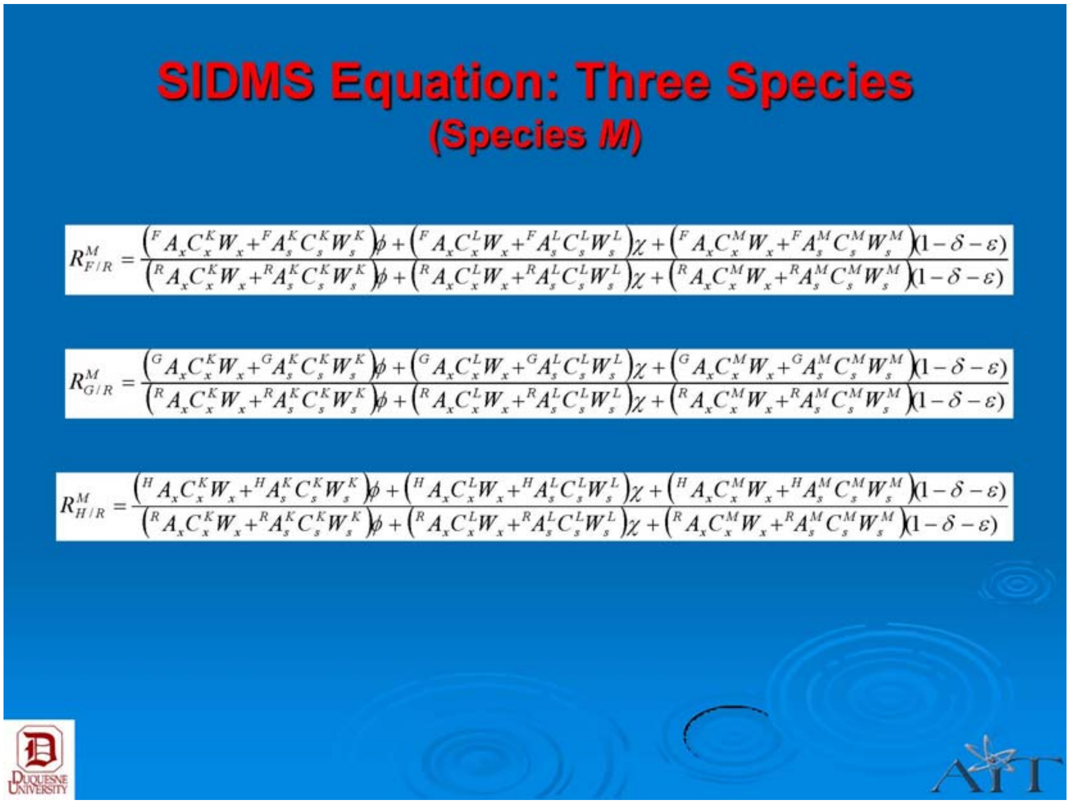
SIDMS Equation: Three Species

(Species *L*)

$$R^{L}_{F/R} = \frac{\left({}^{F}A_x C^{K}_x W_x + {}^{F}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{F}A_x C^{L}_x W_x + {}^{F}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{F}A_x C^{M}_x W_x + {}^{F}A^{M}_s C^{M}_s W^{M}_s\right)\delta}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)\delta}$$

$$R^{L}_{G/R} = \frac{\left({}^{G}A_x C^{K}_x W_x + {}^{G}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{G}A_x C^{L}_x W_x + {}^{G}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{G}A_x C^{M}_x W_x + {}^{G}A^{M}_s C^{M}_s W^{M}_s\right)\delta}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)\delta}$$

$$R^{L}_{H/R} = \frac{\left({}^{H}A_x C^{K}_x W_x + {}^{H}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{H}A_x C^{L}_x W_x + {}^{H}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{H}A_x C^{M}_x W_x + {}^{H}A^{M}_s C^{M}_s W^{M}_s\right)\delta}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\alpha + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)(1-\beta-\chi) + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)\delta}$$



SIDMS Equation: Three Species

(Species *M*)

$$R^{M}_{F/R} = \frac{\left({}^{F}A_x C^{K}_x W_x + {}^{F}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{F}A_x C^{L}_x W_x + {}^{F}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{F}A_x C^{M}_x W_x + {}^{F}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}$$

$$R^{M}_{G/R} = \frac{\left({}^{G}A_x C^{K}_x W_x + {}^{G}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{G}A_x C^{L}_x W_x + {}^{G}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{G}A_x C^{M}_x W_x + {}^{G}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}$$

$$R^{M}_{H/R} = \frac{\left({}^{H}A_x C^{K}_x W_x + {}^{H}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{H}A_x C^{L}_x W_x + {}^{H}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{H}A_x C^{M}_x W_x + {}^{H}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}{\left({}^{R}A_x C^{K}_x W_x + {}^{R}A^{K}_s C^{K}_s W^{K}_s\right)\phi + \left({}^{R}A_x C^{L}_x W_x + {}^{R}A^{L}_s C^{L}_s W^{L}_s\right)\chi + \left({}^{R}A_x C^{M}_x W_x + {}^{R}A^{M}_s C^{M}_s W^{M}_s\right)(1-\delta-\varepsilon)}$$

Optimization of Microwave-Assisted Extraction Methods for Arsenic Speciation in Fish Tissue and Analysis by IC-ICP-MS

Laura H. Reyes, G. M. Mizanur Rahman, Bryan M. Seybert, Jorge Guzman-Mar, H. M. Skip Kingston, Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA; kingston@duq.edu; reyesl@duq.edu

ABSTRACT

Marine organisms can bioaccumulate high arsenic concentrations and transform species. Typical concentrations of total arsenic in marine organisms are in the range of 1 to 100 mg kg-1 (fresh weight). However, the determination of total arsenic is not sufficient to assess the risks associated with consumption of arsenic-containing seafood since the toxicity of arsenic is known to be dependent on its chemical forms. Inorganic arsenic (As (III) and As (V)) are more toxic than monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Arsenobetaine and arsenocholine are considered non-toxic to living organisms. Arsenobetaine has been identified to be the major arsenical species of fish, while As (III) and As (V) constitute a minor amount of the total content.

To perform arsenic speciation analyses, extraction methods must be capable of quantitatively extracting arsenic from the sample without altering the individual arsenic species under the extraction conditions used. Methanol-water mixtures and tetramethyl ammonium hydroxide (TMAH) are often used for arsenic species extraction from fish tissue samples using agitation, ultrasonic-assisted extraction and microwave-assisted extraction.

The primary aim of this study was to compare different extraction methods that are used in the literature, and develop an effective and simple microwave-assisted extraction procedure for arsenic species from fish tissue samples. Identification and quantification of the major arsenic species present in fish tissue samples after extraction was carried out by IC-ICP-MS and the developed method was used for the analysis of a set of commonly consumed fish types.

Determination of Arsenic and Selenium Species in Fish by Microwave-Assisted Enzymatic Extraction and Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry

Laura H. Reyes, Jorge Guzmán-Mar, G. M. Mizanur Rahman, Bryan M. Seybert, H. M. "Skip" Kingston

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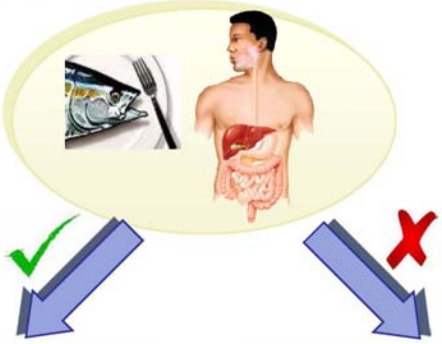
Advantages and disadvantages of fish in our diet[1]

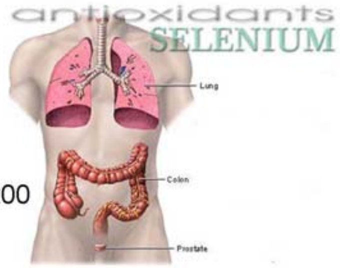


(1) Dietary fish provides a rich source of the essential element selenium
(2) Fish provides a low-fat and high protein source of food
(3) It is a source of omega-3 fatty acids that are important for optimal brain and nervous system development
(4) Fish provides other minerals and vitamins

(1) Heavy metals such as arsenic or mercury can accumulate and biomagnify in marine organisms
(2) Marine organisms are known to accumulate arsenic in the range of 1-100 mg/kg

[1] Verger P., Houdart S., Marette S., Roosen J., Blanchemanche S., "Impact of a risk-benefit advisory on fish consumption and dietary exposure to methylmercury in France", *Regulatory Toxicology and Pharmacology* 48 (2007) 259–269.

Importance of selenium[1]



- Selenium is an essential trace element for human nutrition. The recommended intake is between of 50-200 mg/day.
- Selenium functions as an essential part of antioxidant enzymes such as glutathione peroxidase which protects cells against oxidative damage.
- Numerous studies in animal models and more recent studies in humans have demonstrated the cancer chemopreventive effects of selenium.
- Selenium is involved in the detoxification of several heavy metals (e.g. arsenic, mercury, cadmium, lead, tin).

[1] H. Goenaga-Infante, et al., Current mass spectrometry strategies for selenium speciation in dietary sources of high-selenium, *Anal. Bioanal. Chem.* (2005) **382**: 957–967.

Selenium speciation in fish[1]

- Marine foods are rich in selenium, but some studies have indicated a low bioavailability of selenium from fish and seafood.
- In foods derived from animal sources, selenium is presented as selenoproteins containing selenomethionine (SeMet) and selenocysteine (SeCys).
- Trimethylselenonium ion ($TMSe^+$) was found in tuna and mussel tissues.

Selenium species in fish

Se-Methionine (SeMet)

Se-Cysteine (SeCys)

Trimethylselenonium ion ($TMSe^+$)

[1] P. Moreno, et al. Fractionation studies of selenium compounds from oysters, and their determination by high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, (2001) **16**, 1044 – 1050.

Importance of arsenic speciation in fish[1]

- Diverse toxicity in arsenic species.
- Both As(III) and As(V) have been classified as carcinogens.
- Methylated forms, MMA and DMA, have been identified as cancer promoters.
- AsBet and AsCho, both highly methylated substitutes, are nontoxic to humans.

Arsenic species in fish and selfish

Arsenite [As(III)]	Arsenate [As(V)]
Monomethylarsonic acid (MMA)	Dimethylarsinic acid (DMA)
Arsenobetaine (AsBet)	Arsenocholine (AsCho)
Trimethylarsine oxide (TMAO)	Tetramethylarsonium ion (TMAs)

[1] S. Hirata, Determination of Arsenic Species in Marine Samples by HPLC-ICP-MS, *Analytical Sciences*, 22 (2006), 39-43.

Importance of arsenic speciation in fish[1]

- The majority of arsenic in marine organisms is organoarsenic species metabolized from inorganic arsenic present in seawater or accumulated organoarsenic from food chain.
- AsBet often contributes 50-90% of the total arsenic in fish.
- Minor species, such as AsCho, trimethylarsonium propionate, DMA and tetramethylarsonium ion have been found in fish.

[1] S. Hirata, Determination of Arsenic Species in Marine Samples by HPLC-ICP-MS, *Analytical Sciences*, 22 (2006), 39-43.

Simultaneous extraction of As and Se species from fish

- Arsenic species are xenobiotics. They are not involved in fish or mammalian metabolism.
- Selenium species are incorporated in amino acids, peptides, proteins and/or metabolites.
- Arsenic and selenium species subsequently required different mechanisms of extraction for quantitative recovery.

Objectives

1. Evaluate and compare various extraction procedures in the literature for the determination of arsenic **or** selenium species and apply these methods for simultaneous determination of arsenic **and** selenium species in fish.
2. Optimize a Microwave Assisted Enzymatic Extraction (MAEE) procedure using *Pronase E* and *Lipase* for the determination of arsenic and selenium species.
3. Validate MAEE procedure using BCR-627 (tuna fish tissue) and DOLT-3 (dogfish liver) to determine arsenic and selenium species.
4. Apply the validated MAEE to determine arsenic and selenium species in fish samples.

Experimental conditions:
IC-ICP-MS parameters

IC parameters

Column: Metrosep Anion Dual 3 column 100 x 4.0 mm, 6 µm and guard column 1.7 × 3.5 mm, 0.2µm (Metrohm Peak, LLC.)
Mobile phase: A: 5 mM NH_4NO_3, and B: 50 mM NH_4NO_3, 2% (v/v) MeOH, pH 8.7
Elution: Gradient
Flow rate: 1 mL/min
Volume injection: 100 µL

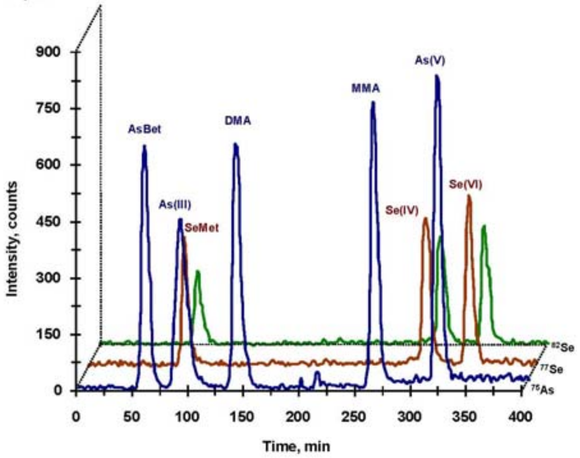
ICP-MS conditions

Monitoring isotopes: ^{75}As[a,b], ^{77}Se[a,b] and ^{82}Se[a,b]
Acquisition mode: Spectrum[a] and Time Resolved Analysis[b]
Integration time: 0.30[a] and 0.20[b] sec per mass
Analysis mode: Spectrum[a] and Time Resolved Analysis[b]
Total Analysis time: 34.45[a] and 720[b] sec

[a]total analysis and [b]speciation analysis

Experimental conditions:

IC-ICP-MS chromatogram for the mixture of five As standards (2 µg/L) and three Se standards (8 µg/L)



LOD values of As and Se species[1]	
Arsenic species	**LOD, µg/L**
AsBet	0.12 ± 0.03
As(III)	0.08 ± 0.02
DMA	0.08 ± 0.02
MMA	0.07 ± 0.02
As(V)	0.09 ± 0.03
Selenium species	**LOD (Se), µg/L**
SeMet	1.1 ± 0.03
Se(IV)	0.7 ± 0.02
Se(VI)	0.7 ± 0.02

[1] The detection limits (DOL) under optimum conditions were calculated as 3σ of the baseline noise based on peak height .

Chromatographic conditions:

Mobile phase: A: 5 mM NH_4NO_3, 2% methanol, pH 8.7 and B: 50 mM NH_4NO_3, 2% methanol, pH 8.7
Elution: gradient
Gradient program: **1:** 0 min, 0% B, **2:** 2 min, 0% B, **3:** 7 min, 100% B, **4:** 9 min, 100% B, **5:** 9.5 min, 0% B, and **6:** 12 min, 0% B

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4. Apply the validated MAEE to determine arsenic and selenium species in fish samples.

Comparison of extraction procedures for arsenic and selenium determination in DOLT-3 CRM (Dog fish liver)

Extractant reagent	Extraction conditions	Total As (mg/kg)*	As extraction (%)
Methanol:water (80:20)	MAE at 80 °C during 3 min.	6.4 ± 0.1	63 ± 1
8.25 % (w/w) TMAH in water	MAE at 50 °C during 30 min.	9.0 ± 0.3	88 ± 3
Trypsin	2.5:1 ratio sample : enzyme in 0.1M NH_4HCO_3, pH 8. Water bath at 37 °C during 20 h.	7.4 ± 0.3	73 ± 3
Trypsin	2.5:1 ratio sample: enzyme in 0.1M NH_4HCO_3, pH 8. MAE at 37°C during 40 min.	7.0 ± 0.1	69 ± 1
Protease XIV	10:1 ratio of sample to enzyme in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	7.8 ± 0.1	77 ± 1
Pronase E	10:1 ratio of sample to enzyme in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	7.6 ± 0.1	74 ± 1
Pronase E and Lipase	10:1 ratio of sample to *Pronase E* in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	7.4 ± 0.2	72 ± 2
Pronase E and Lipase	10:1 ratio of sample to *Pronase E* in 50 mM phosphate buffer, pH 7.5. MAE at 37 °C during 1h.	8.6 ± 0.2	84 ± 2

*Arsenic Certified value 10.2 ± 0.5 mg/kg

Comparison of extraction procedures for arsenic and selenium determination in DOLT-3 CRM (Dog fish liver)

Extractant reagent	Extraction conditions	Total Se (mg/kg)[1]	Se extraction (%)
Methanol : water (80:20)	MAE at 80 °C during 3 min.	0.9 ± 0.1	13 ± 1
8.25 % (w/w) TMAH in water	MAE at 50 °C during 30 min.	7.6 ± 0.2	107 ± 3
Trypsin	2.5:1 ratio sample: enzyme in 0.1M NH_4HCO_3, pH 8. Water bath at 37 °C during 20 h.	5.0 ± 0.1	70 ± 2
Trypsin	2.5:1 ratio sample: enzyme in 0.1M NH_4HCO_3, pH 8. MAE at 37°C during 40 min.	4.7 ± 0.2	67 ± 3
Protease XIV	10:1 ratio of sample to enzyme in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	5.6 ± 0.2	79 ± 3
Pronase E	10:1 ratio of sample to enzyme in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	5.0 ± 0.2	71 ± 3
Pronase E and Lipase	10:1 ratio of sample to *Pronase E* in 50 mM phosphate buffer, pH 7.5. Water bath extraction at 37 °C during 20 h.	5.4 ± 0.3	77 ± 4
Pronase E and Lipase	10:1 ratio of sample to *Pronase E* in 50 mM phosphate buffer, pH 7.5. MAE at 37 °C during 1h.	6.4 ± 0.2	91 ± 3

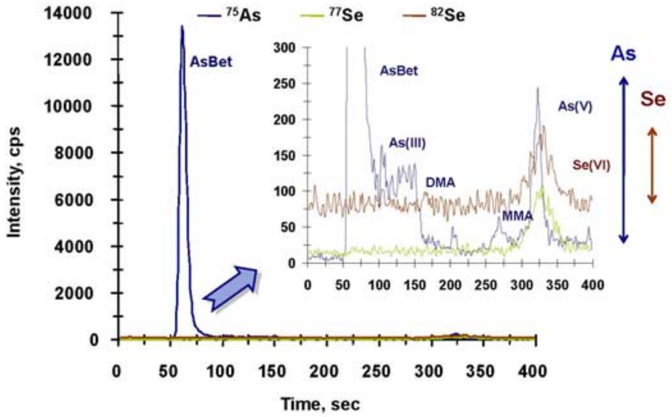
[1] **Selenium Certified Value 7.06 ± 0.48 mg/kg**

Microwave assisted extraction (8.25 % TMAH)

Interconversion of species was promoted using TMAH agent:

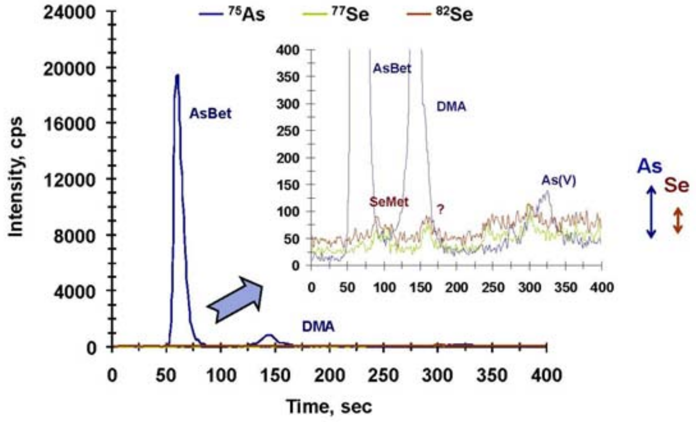
1) As species were converted to As(V).

2) SeMet was converted to Se(IV).



CRM	As extraction recovery (%)	Se extraction recovery (%)
DOLT-3	88 ± 3	107 ± 3

Microwave assisted enzymatic extraction procedure (Pronase E and Lipase)



CRM	As extraction recovery (%)	Se extraction recovery (%)
DOLT-3	84 ± 2	91 ± 3

Objectives

1. Evaluate and compare various extraction procedures in the literature for the determination of arsenic **or** selenium species and apply these methods for simultaneous determination of arsenic **and** selenium species in fish.
2. Optimize a Microwave Assisted Enzymatic Extraction (MAEE) procedure using *Pronase E* and *Lipase* for the determination of arsenic and selenium species.
3. Validate MAEE procedure using BCR-627 (tuna fish tissue) and DOLT-3 (dogfish liver) to determine arsenic and selenium species.
4. Apply the validated MAEE to determine arsenic and selenium species in fish samples.

Reaction mechanism of Protease (*Pronase E*) and Lipase during MAEE procedure[1]

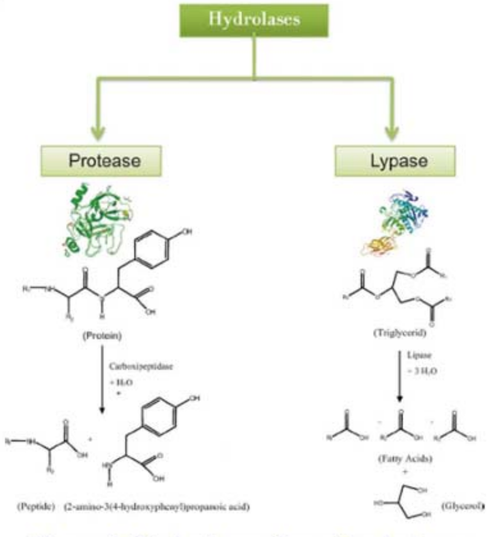


Figure 1. Typical reaction of hydrolases

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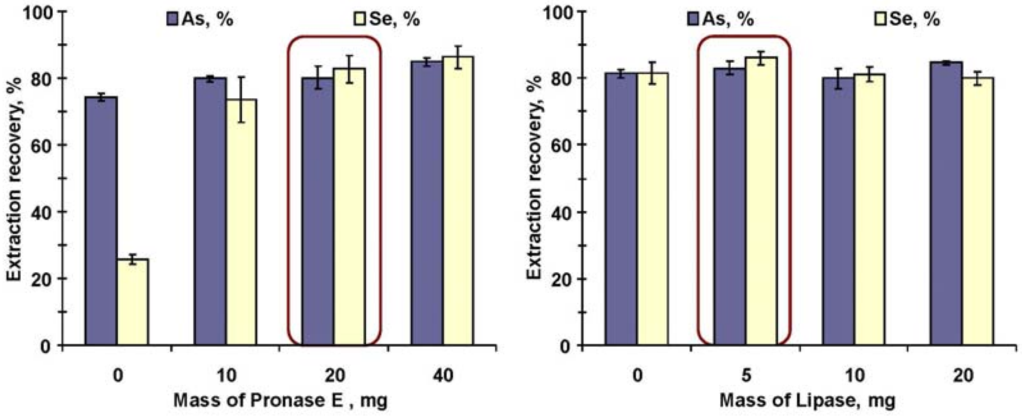
[1] G. Vale, et al., Ultrasonic-assisted enzymatic digestion (USAED) for total elemental determination and elemental speciation: A tutorial, *Talanta*, **75** (2008) 872–884

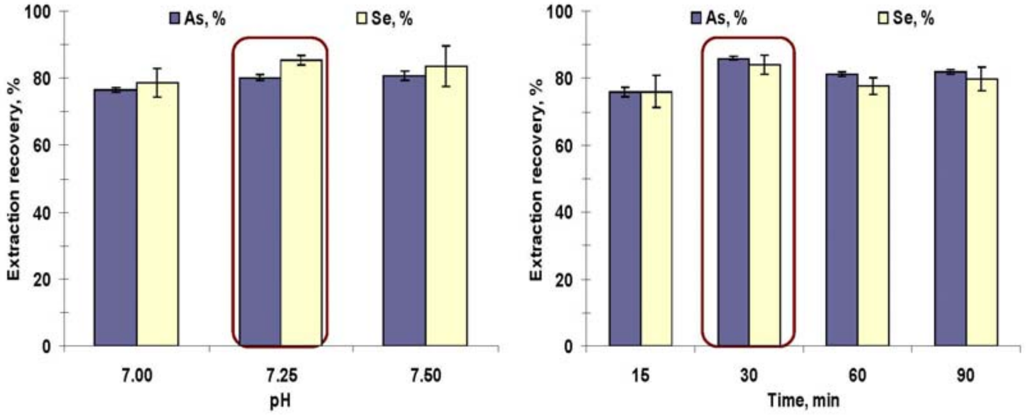
Optimization of *Pronase E* and *Lipase* for the extraction of arsenic and selenium in DOLT-3



a) *Pronase E*

b) *Lipase*

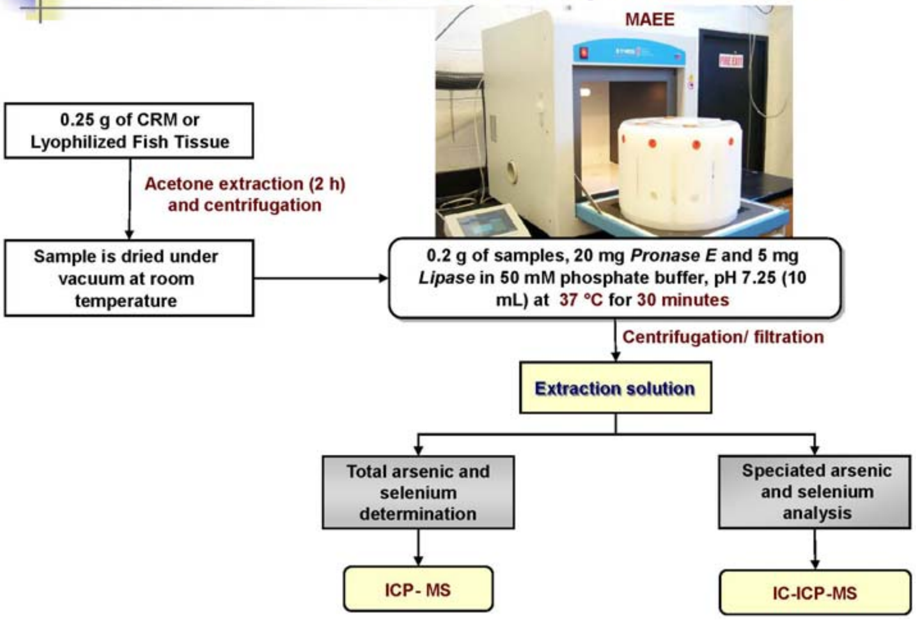
Effect of pH and irradiation time on arsenic and selenium extraction from DOLT-3



c) pH

d) Irradiation time

Microwave assisted enzymatic extraction protocol for the determination of arsenic and selenium species in fish tissue



0.25 g of CRM or Lyophilized Fish Tissue

Acetone extraction (2 h) and centrifugation

Sample is dried under vacuum at room temperature

0.2 g of samples, 20 mg *Pronase E* and 5 mg *Lipase* in 50 mM phosphate buffer, pH 7.25 (10 mL) at 37 °C for 30 minutes

Centrifugation/ filtration

Extraction solution

Total arsenic and selenium determination

Speciated arsenic and selenium analysis

ICP- MS

IC-ICP-MS

Objectives

1. Evaluate and compare various extraction procedures in the literature for the determination of arsenic **or** selenium species and apply these methods for simultaneous determination of arsenic **and** selenium species in fish.
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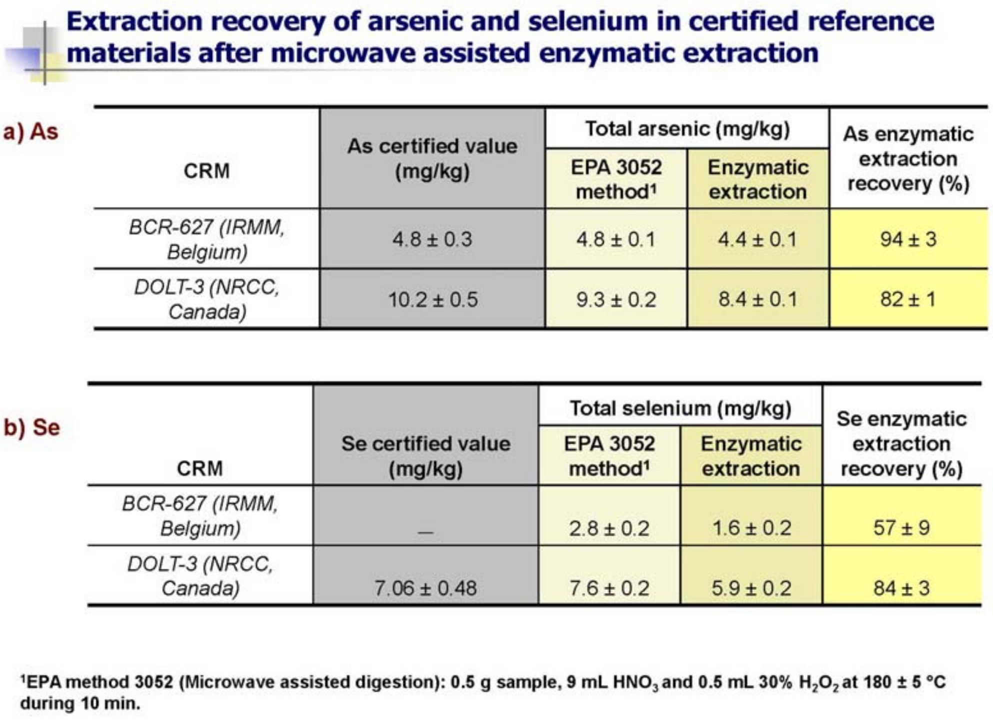


Extraction recovery of arsenic and selenium in certified reference materials after microwave assisted enzymatic extraction

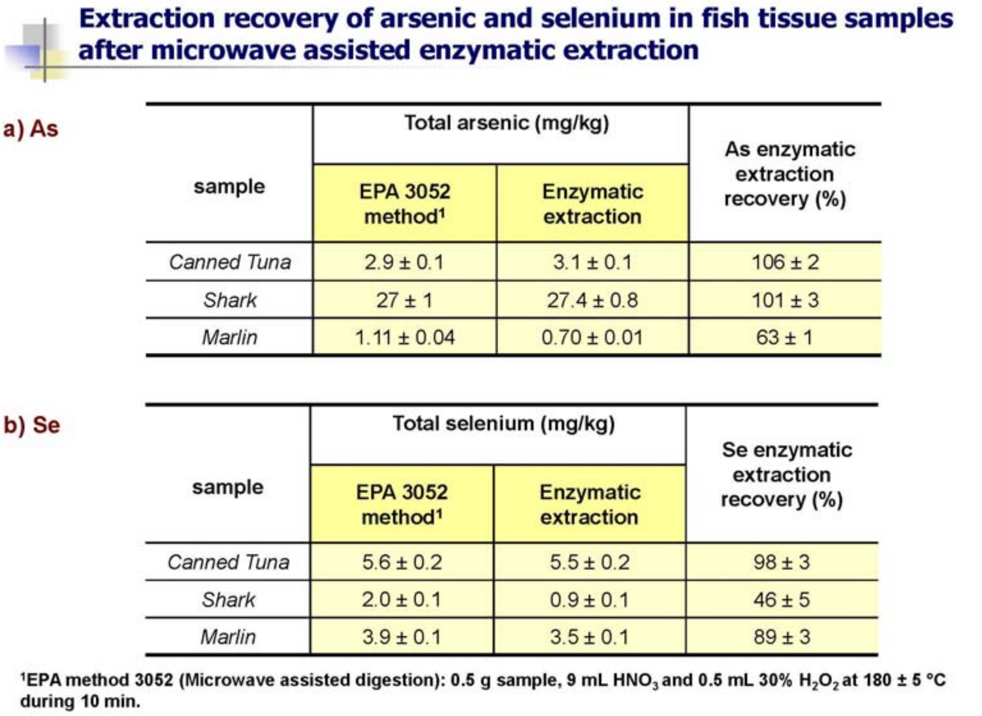
a) As

CRM	As certified value (mg/kg)	Total arsenic (mg/kg)		As enzymatic extraction recovery (%)
		EPA 3052 method[1]	Enzymatic extraction	
BCR-627 (IRMM, Belgium)	4.8 ± 0.3	4.8 ± 0.1	4.4 ± 0.1	94 ± 3
DOLT-3 (NRCC, Canada)	10.2 ± 0.5	9.3 ± 0.2	8.4 ± 0.1	82 ± 1

b) Se

CRM	Se certified value (mg/kg)	Total selenium (mg/kg)		Se enzymatic extraction recovery (%)
		EPA 3052 method[1]	Enzymatic extraction	
BCR-627 (IRMM, Belgium)	–	2.8 ± 0.2	1.6 ± 0.2	57 ± 9
DOLT-3 (NRCC, Canada)	7.06 ± 0.48	7.6 ± 0.2	5.9 ± 0.2	84 ± 3

[1] **EPA method 3052 (Microwave assisted digestion): 0.5 g sample, 9 mL HNO_3 and 0.5 mL 30% H_2O_2 at 180 ± 5 °C during 10 min.**



Extraction recovery of arsenic and selenium in fish tissue samples after microwave assisted enzymatic extraction

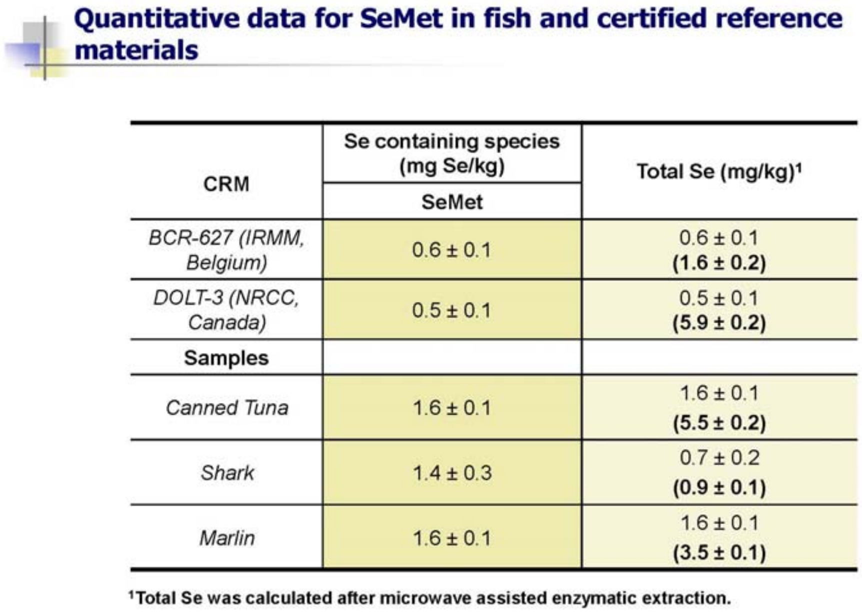
a) As

sample	Total arsenic (mg/kg)		As enzymatic extraction recovery (%)
	EPA 3052 method[1]	Enzymatic extraction	
Canned Tuna	2.9 ± 0.1	3.1 ± 0.1	106 ± 2
Shark	27 ± 1	27.4 ± 0.8	101 ± 3
Marlin	1.11 ± 0.04	0.70 ± 0.01	63 ± 1

b) Se

sample	Total selenium (mg/kg)		Se enzymatic extraction recovery (%)
	EPA 3052 method[1]	Enzymatic extraction	
Canned Tuna	5.6 ± 0.2	5.5 ± 0.2	98 ± 3
Shark	2.0 ± 0.1	0.9 ± 0.1	46 ± 5
Marlin	3.9 ± 0.1	3.5 ± 0.1	89 ± 3

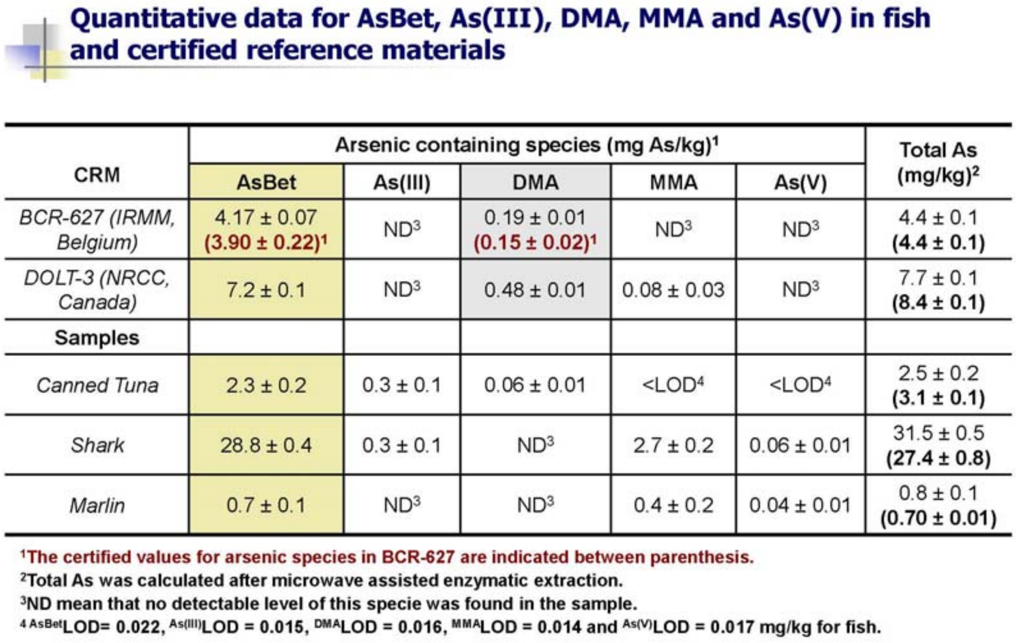
[1] **EPA method 3052 (Microwave assisted digestion): 0.5 g sample, 9 mL HNO_3 and 0.5 mL 30% H_2O_2 at 180 ± 5 °C during 10 min.**



Quantitative data for SeMet in fish and certified reference materials

CRM	Se containing species (mg Se/kg)	Total Se (mg/kg)[1]
	SeMet	
BCR-627 (IRMM, Belgium)	0.6 ± 0.1	0.6 ± 0.1 **(1.6 ± 0.2)**
DOLT-3 (NRCC, Canada)	0.5 ± 0.1	0.5 ± 0.1 **(5.9 ± 0.2)**
Samples		
Canned Tuna	1.6 ± 0.1	1.6 ± 0.1 **(5.5 ± 0.2)**
Shark	1.4 ± 0.3	0.7 ± 0.2 **(0.9 ± 0.1)**
Marlin	1.6 ± 0.1	1.6 ± 0.1 **(3.5 ± 0.1)**

[1] Total Se was calculated after microwave assisted enzymatic extraction.



Quantitative data for AsBet, As(III), DMA, MMA and As(V) in fish and certified reference materials

CRM	Arsenic containing species (mg As/kg)[1]					Total As (mg/kg)[2]
	AsBet	As(III)	DMA	MMA	As(V)	
BCR-627 (IRMM, Belgium)	4.17 ± 0.07 **(3.90 ± 0.22)[1]**	ND[3]	0.19 ± 0.01 **(0.15 ± 0.02)[1]**	ND[3]	ND[3]	4.4 ± 0.1 **(4.4 ± 0.1)**
DOLT-3 (NRCC, Canada)	7.2 ± 0.1	ND[3]	0.48 ± 0.01	0.08 ± 0.03	ND[3]	7.7 ± 0.1 **(8.4 ± 0.1)**
Samples						
Canned Tuna	2.3 ± 0.2	0.3 ± 0.1	0.06 ± 0.01	<LOD[4]	<LOD[4]	2.5 ± 0.2 **(3.1 ± 0.1)**
Shark	28.8 ± 0.4	0.3 ± 0.1	ND[3]	2.7 ± 0.2	0.06 ± 0.01	31.5 ± 0.5 **(27.4 ± 0.8)**
Marlin	0.7 ± 0.1	ND[3]	ND[3]	0.4 ± 0.2	0.04 ± 0.01	0.8 ± 0.1 **(0.70 ± 0.01)**

[1] The certified values for arsenic species in BCR-627 are indicated between parenthesis.

[2] Total As was calculated after microwave assisted enzymatic extraction.

[3] ND mean that no detectable level of this specie was found in the sample.

[4] ^{AsBet}LOD= 0.022, $^{As(III)}$LOD = 0.015, ^{DMA}LOD = 0.016, ^{MMA}LOD = 0.014 and $^{As(V)}$LOD = 0.017 mg/kg for fish.

Conclusions

1. **A closed vessel microwave-assisted enzymatic extraction method was used for the determination arsenic and selenium species in fish. The extraction procedure was faster and easier (30 min at 37 °C) compared to the conventional enzymatic procedures (20 h at 37 °C).**
2. **The optimized IC-ICP-MS procedure provides lower detection limits and reproducibility sufficient for investigation of species patterns of As(III), As(V), MMA, DMA, AsBet, Se(IV), Se(VI) and SeMet in fish.**
3. **This procedure was successfully validated by the analysis of two certified reference materials, BCR-627 (total As, AsBet and DMA) and DOLT-3 (total As and Se).**
4. **The total selenium concentration found in the analyzed fish was ~2.0 - 5.6 mg/kg. Although SeMet was the only Se-compound identified in fish, SeMet content in the extract was accounted for 29-78 % of the extracted selenium.**
5. **The total arsenic concentration found in the analyzed fish was ~1.1 - 27 mg/kg. AsBet was found the major species in fish samples (0.7 - 27 mg/kg).**

Future work

- **Study of other selenium species in fish extract using complementary chromatographic techniques such as SEC.**
- **Application of Speciated Isotope Dilution Mass Spectrometry (SIDMS):**
  - ✓ Accurate quantification independent of extraction recovery or species interconversion.

Acknowledges

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Department of Chemistry and Biochemistry
Kingston Research Group
Gregory M. Zinn

Applied Isotope Technologies Inc.

Speciation of Organometallic Contaminants in Environmental Matrices, Comparing the Metal's Colors to Its Weight

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ABSTRACT

Developing effective tools for metals environmental monitoring necessitates characterization of the chemical species of the metal. Arsenic, for example, comes in many chemical forms, some very toxic and related to a dinking water source, others much less toxic and traced to dietary sources. Chromium is both a micronutrient and a lung carcinogen depending on its oxidation state. The chemical form of the metal is often more important then the total amount of a metal in a sample collected. As more is understood about each metal's toxicity, more will have to be done on characterizing the chemical species of the metal within both the biological sample and its environmental source.

The science of organometallic speciation has begun to make significant improvements by utilizing mass spectrometric instruments. More and more methods are being developed for identification and quantization of different organometallic species in all environmental samples to characterize the fate and transport of a metal from environmental contaminant to biological sample. The use of speciated stable isotope labels and new SRMs such as 2701 and 2669 will make methods development significantly easier in the future and have been used both to measure the success of a new extraction protocol and the identification of interconversion pathways.

We have developed three different speciation methods for both environmental and biological samples. Mercury, chromium and arsenic all present significant human health risks and all can be traced to one type of environmental contaminant pathway or another. The chromatographic separation with ICPMS detection has been demonstrated as more effective at measuring Cr in a new standard and is used to measure extraction efficiency for new extraction protocols. This presentation will focus on microwave extraction methods developed for Cr, the use of stable isotope labels and a comparison to colormetric methods.

Speciation of Organometallic Contaminants in Environmental Matrices, Comparing The Metal's Colors to Its Weight

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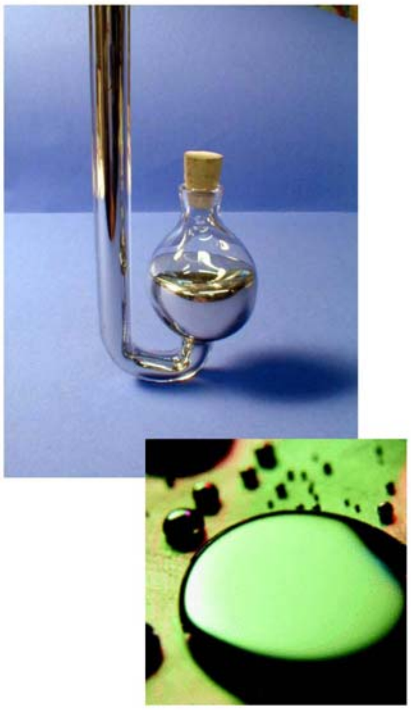
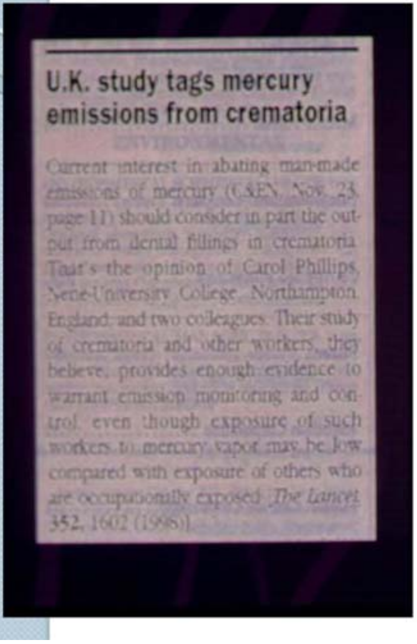
Stu Nagourney, Ruimin Xie, Steve Spayd, Robert Stiles

Mercury



Metals with isotopic labels

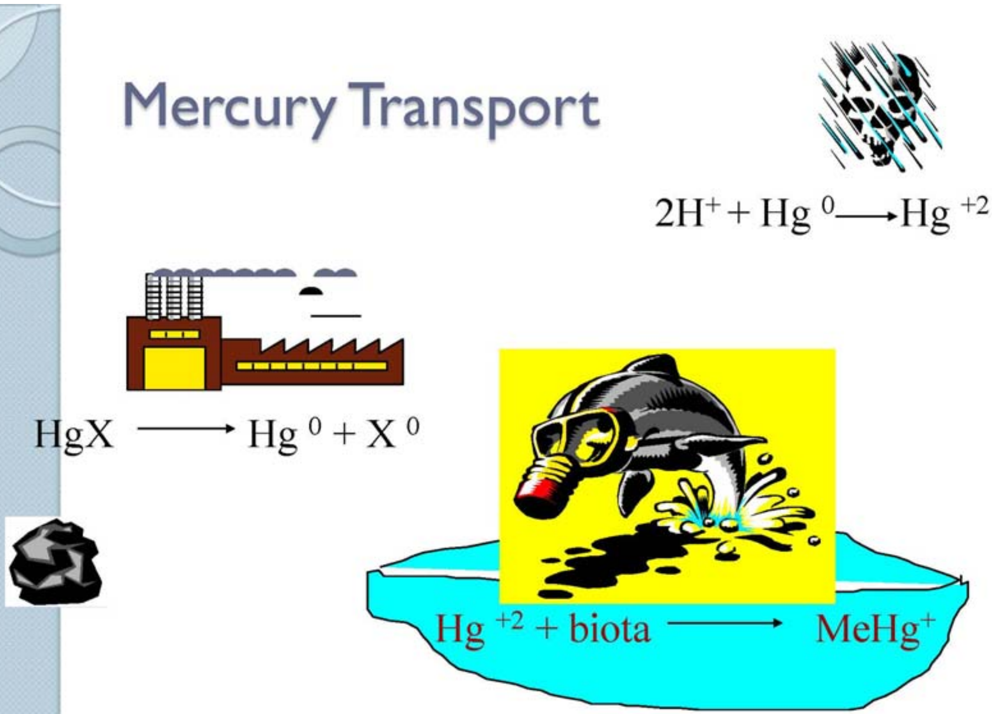


U.K. study tags mercury emissions from crematoria

Current interest in abating man-made emissions of mercury (C&EN, Nov. 23, page 11) should consider in part the output from dental fillings in crematoria. That's the opinion of Carol Phillips, Nene-University College, Northampton, England, and two colleagues. Their study of crematoria and other workers, they believe, provides enough evidence to warrant emission monitoring and control even though exposure of such workers to mercury vapor may be low compared with exposure of others who are occupationally exposed. *The Lancet* 352, 1602 (1998)]

MERCURY RISING

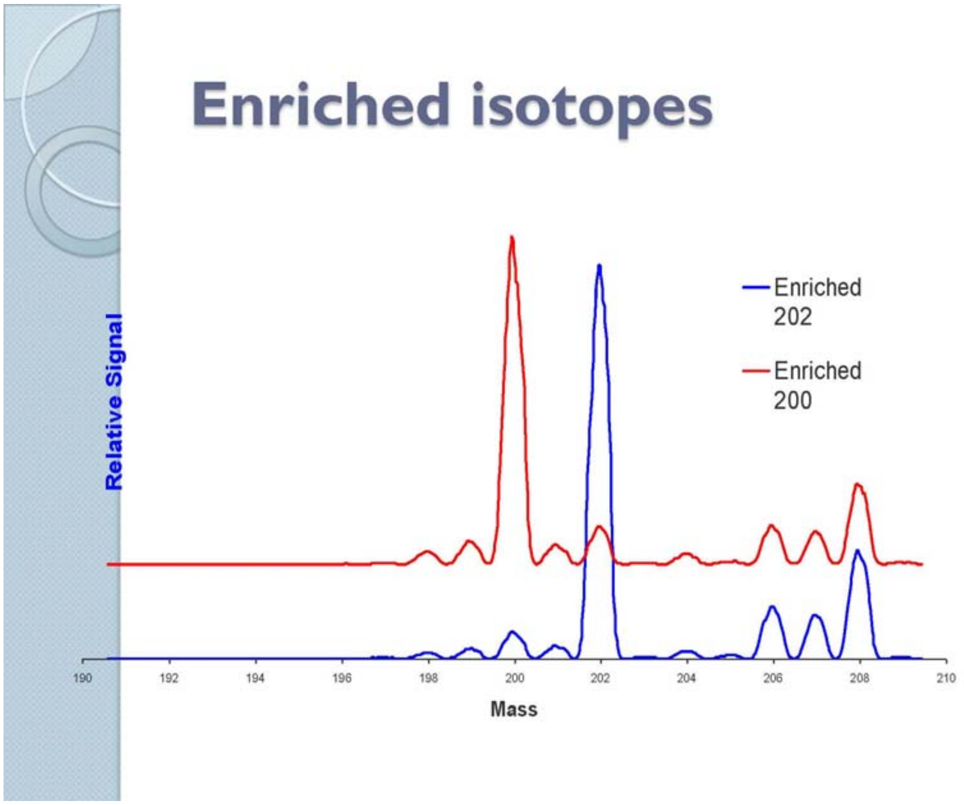
Mercury Transport



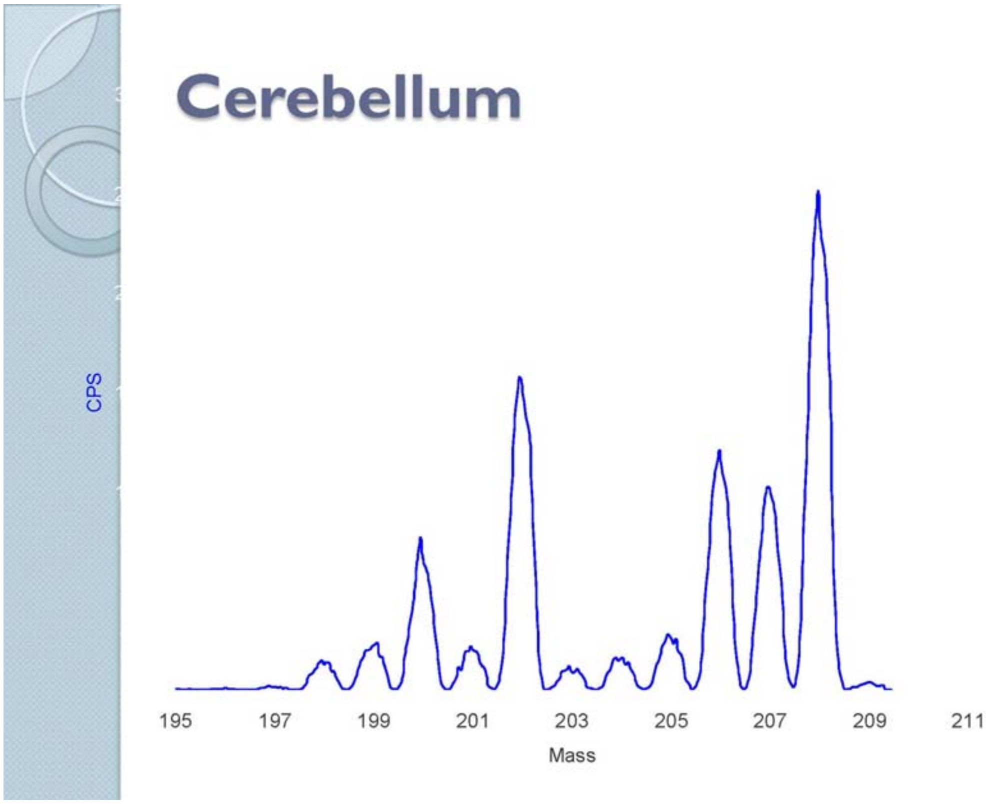
$2H^+ + Hg^0 \longrightarrow Hg^{+2}$

$HgX \longrightarrow Hg^0 + X^0$

$Hg^{+2} + \text{biota} \longrightarrow MeHg^+$

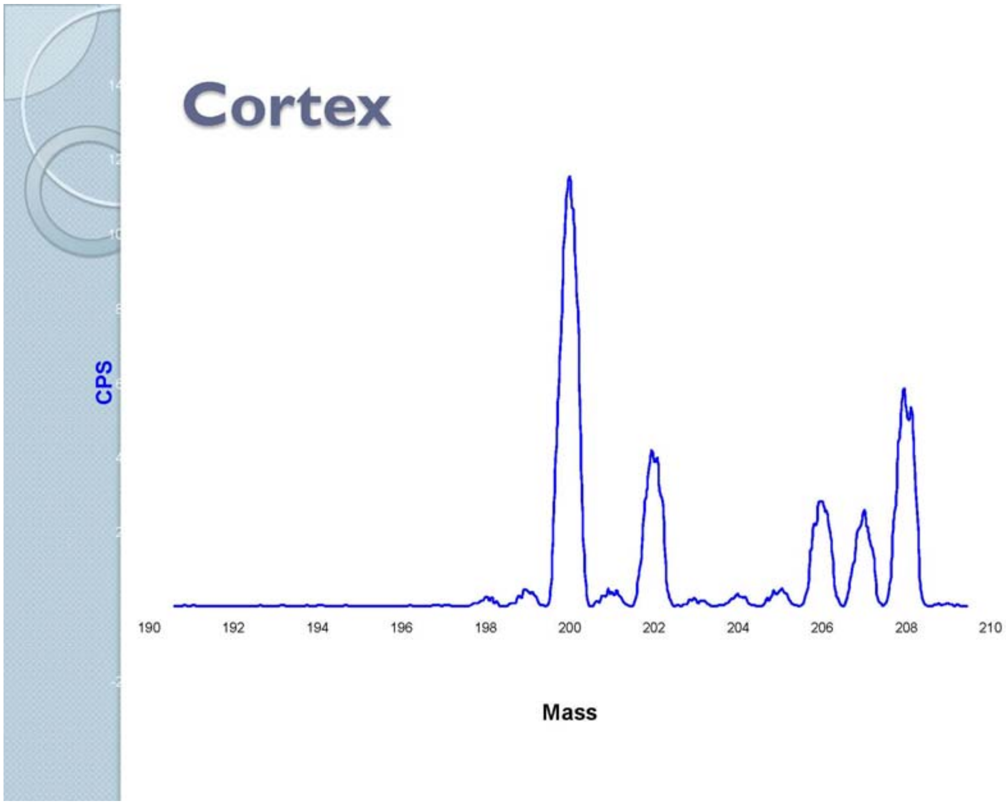


Enriched isotopes

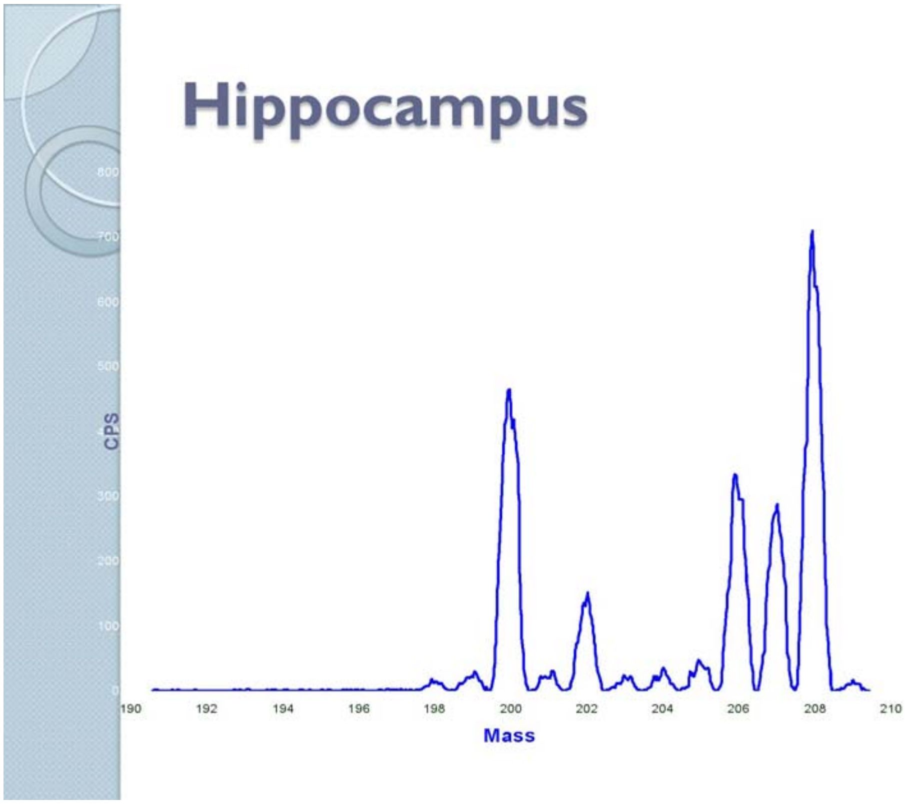


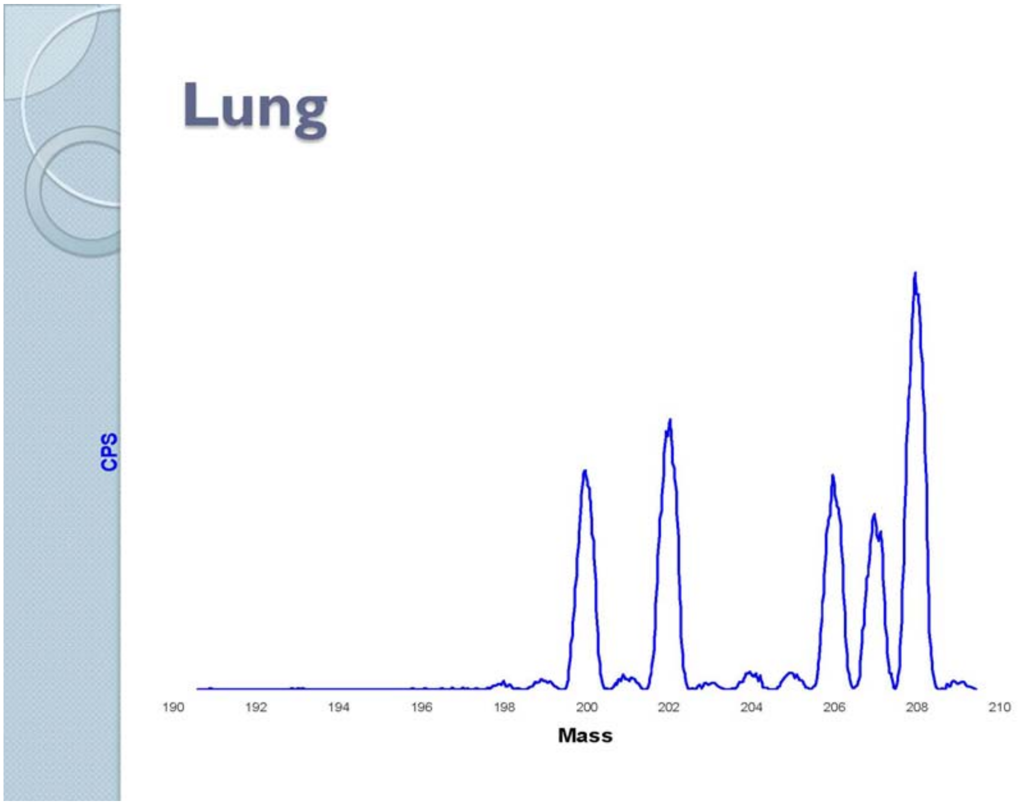
Cerebellum

Cortex

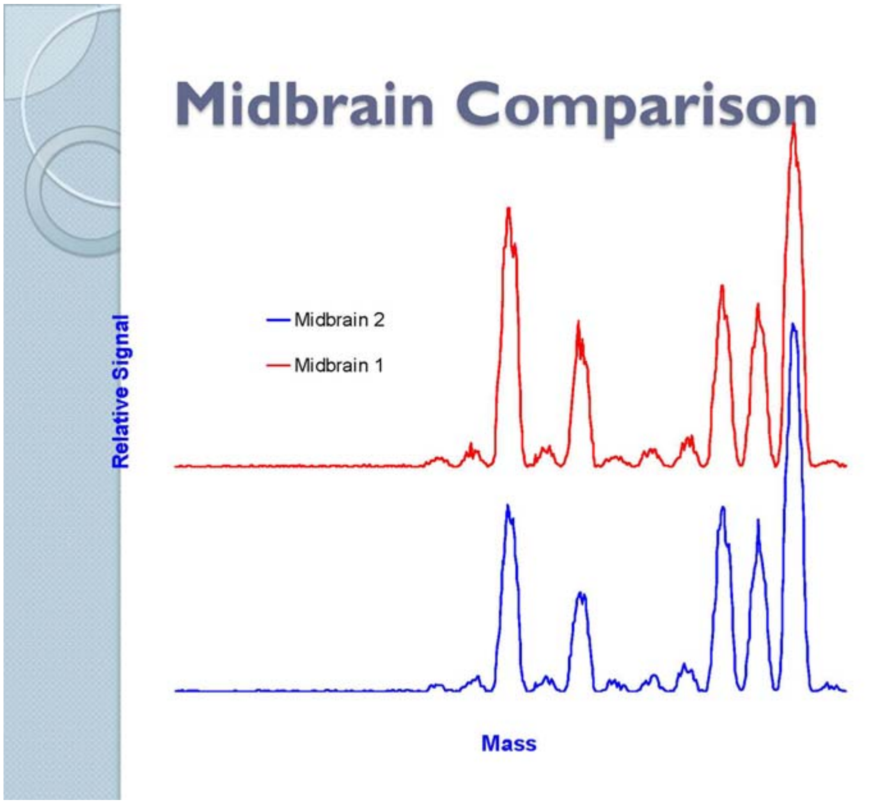


Hippocampus



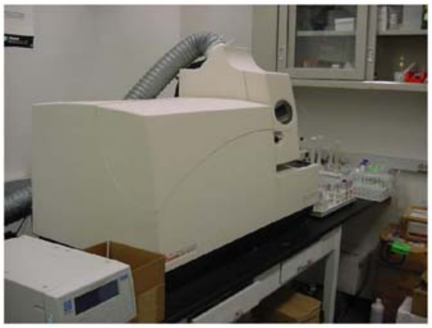


Lung

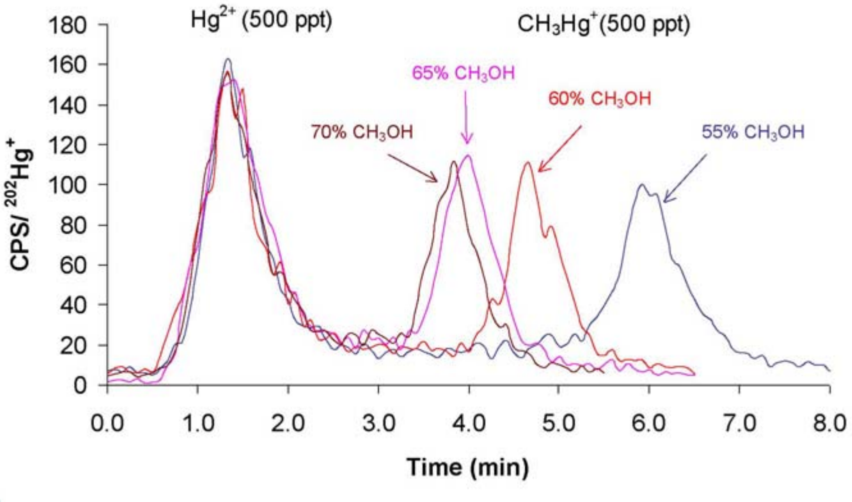


Midbrain Comparison

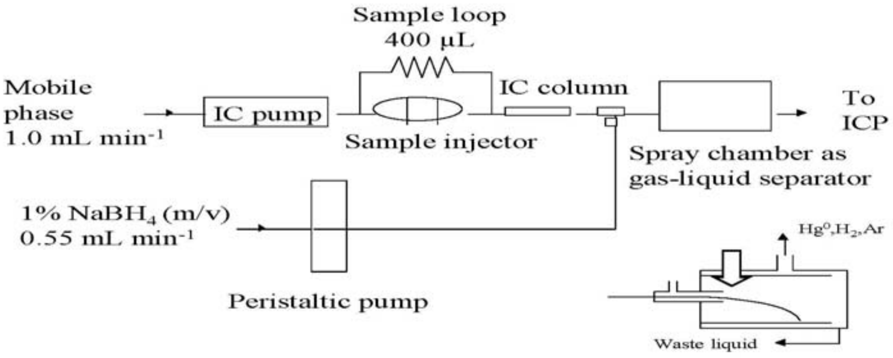
Ion Chromatography-Inductively Coupled Plasma Mass Spectrometer



The effect of MeOH in the mobile phase on the separation of Hg^{2+} and CH_3Hg^+ for CV



Schematic diagram of the IC-CV-ICP-MS system



Tu, Q. Johnson Jr., W. and **Buckley, B.**, *J. Anal. Atomic Spectrometry*, **18**: 696-701, 2003.

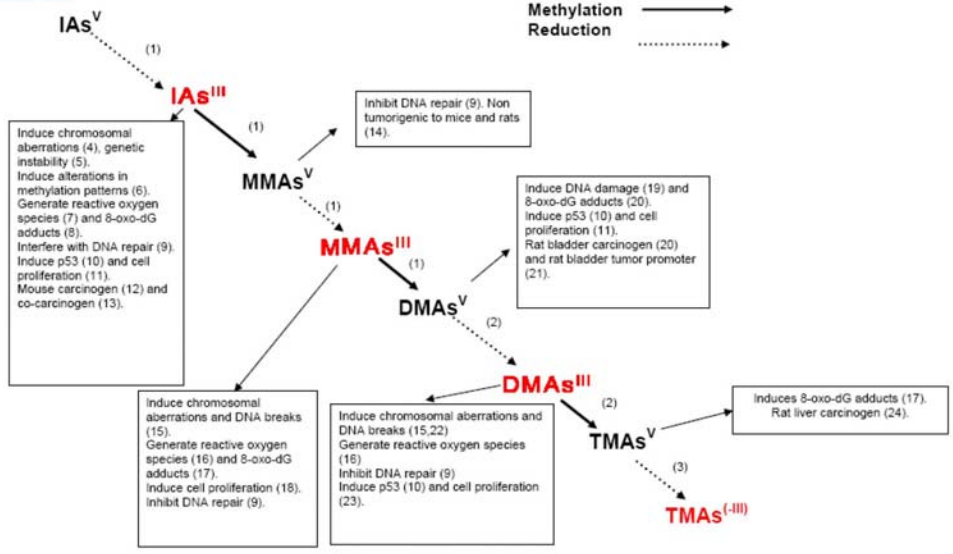
Analytical Figures of Merit

	Detection Limit [a,b] (pg mL^{-1} as Hg)		RSD (peak area) n=6
	IC-CV-ICPMS	IC-ICPMS	IC-CV-ICPMS
Hg^{2+}	35	3000	5.9 %
CH_3Hg^+	73	15000	7.8%

Arsenic uses (CCA)

Shalat, S., Solo Gabriele, H., Fleming, L. E., **Buckley, B.** , Black, K., Jimenez, M., Shibata, T., Durbin M., Graygo, J., Stephan, W., Van De Bogart, G., A Pilot Study of Children's Exposure to CCA-Treated Wood from Playground Equipment *Science of the Total Environ*. 367, 80-88, 2006

Arsenic in our body



Induce chromosomal aberrations (4), genetic instability (5).
Induce alterations in methylation patterns (6).
Generate reactive oxygen species (7) and 8-oxo-dG adducts (8).
Interfere with DNA repair (9).
Induce p53 (10) and cell proliferation (11).
Mouse carcinogen (12) and co-carcinogen (13).

Inhibit DNA repair (9). Non tumorigenic to mice and rats (14).

Induce DNA damage (19) and 8-oxo-dG adducts (20).
Induce p53 (10) and cell proliferation (11).
Rat bladder carcinogen (20) and rat bladder tumor promoter (21).

Induce chromosomal aberrations and DNA breaks (15).
Generate reactive oxygen species (16) and 8-oxo-dG adducts (17).
Induce cell proliferation (18).
Inhibit DNA repair (9).

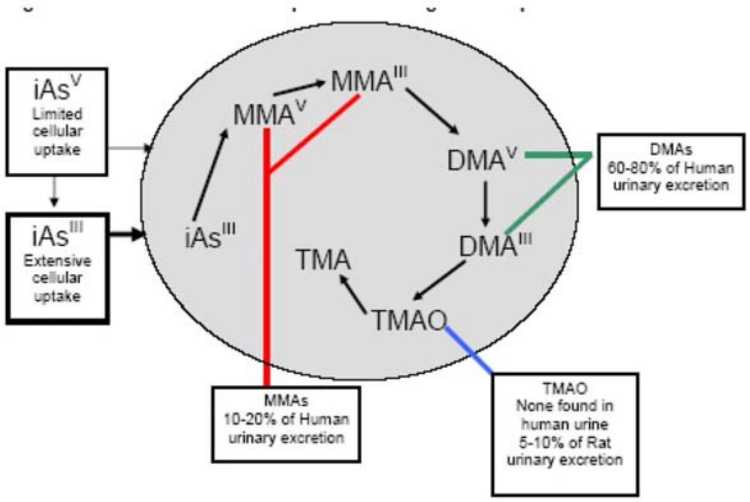
Induce chromosomal aberrations and DNA breaks (15,22)
Generate reactive oxygen species (16)
Inhibit DNA repair (9)
Induce p53 (10) and cell proliferation (23).

Induces 8-oxo-dG adducts (17).
Rat liver carcinogen (24).

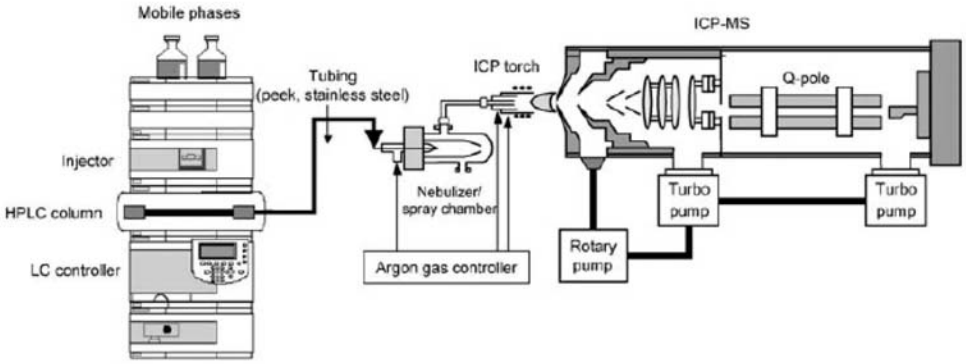
In-vitro LC50 (mM) values

Reference	Cell line	iAs^{V}	iAs^{III}	MMA^{V}	MMA^{III}	DMA^{V}	DMA^{III}	TMAO
Petrick, *et al.*, 2000	Chang human hepatocytes	1.6	0.068	8.2	0.006	9.1	NT	NT
Cohen *et al.*, 2002a	Rat epithelial bladder (MYP3)	0.0053	0.0004	1.7	0.0008	1.1	0.0005	4.5
	Human epithelial urinary bladder (1T1)	0.031	0.0048	1.7	0.0001	0.5	0.0008	1.7

Methylated forms from inorganic exposure

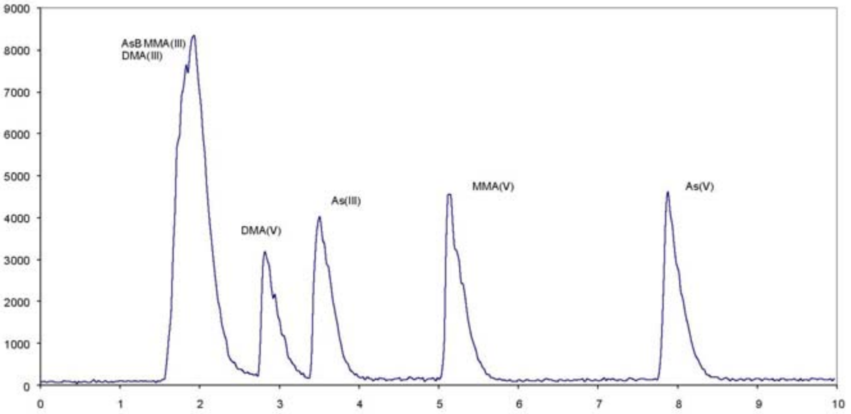


Further need for speciation by HPLC-ICP-MS

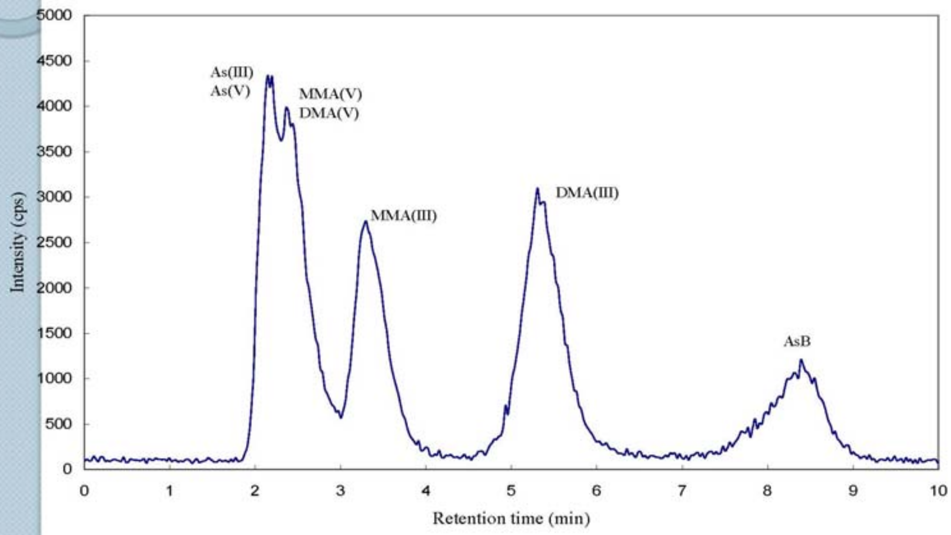


Not just the water related compounds

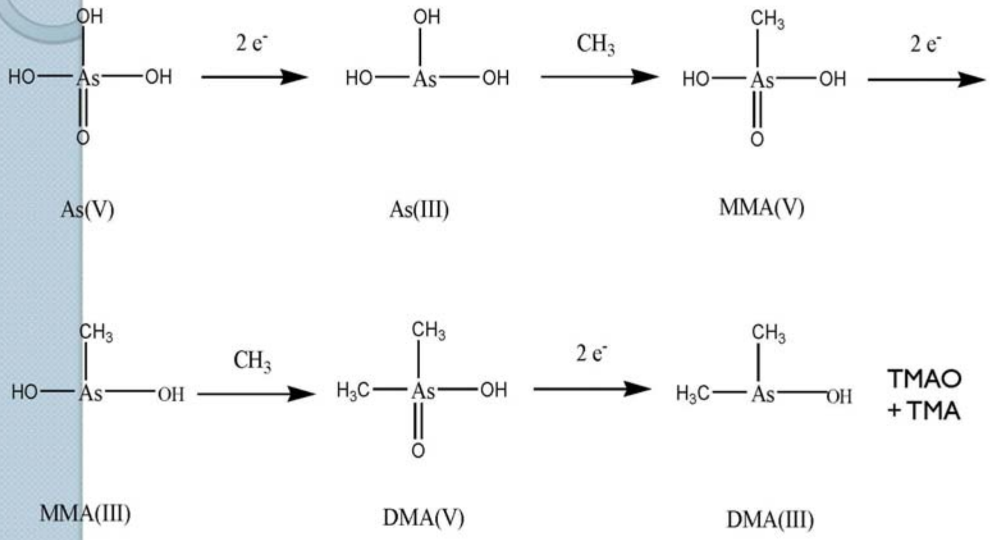
As separation of "charged" species



As separation of "non-charged" species



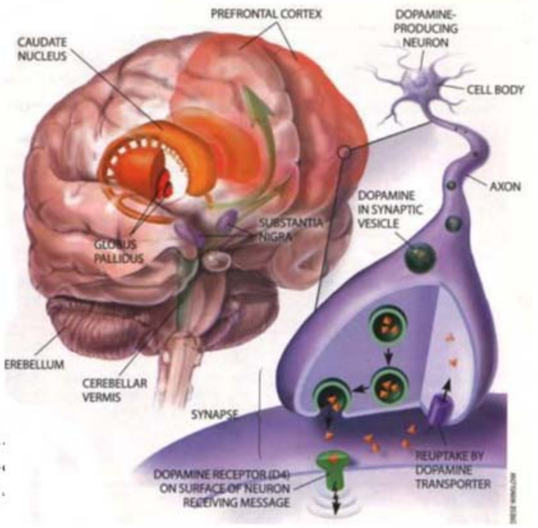
Metabolism/ Detoxification of Inorganic Arsenic in the Human Body

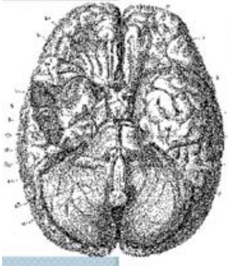


Detection limits and repeatability

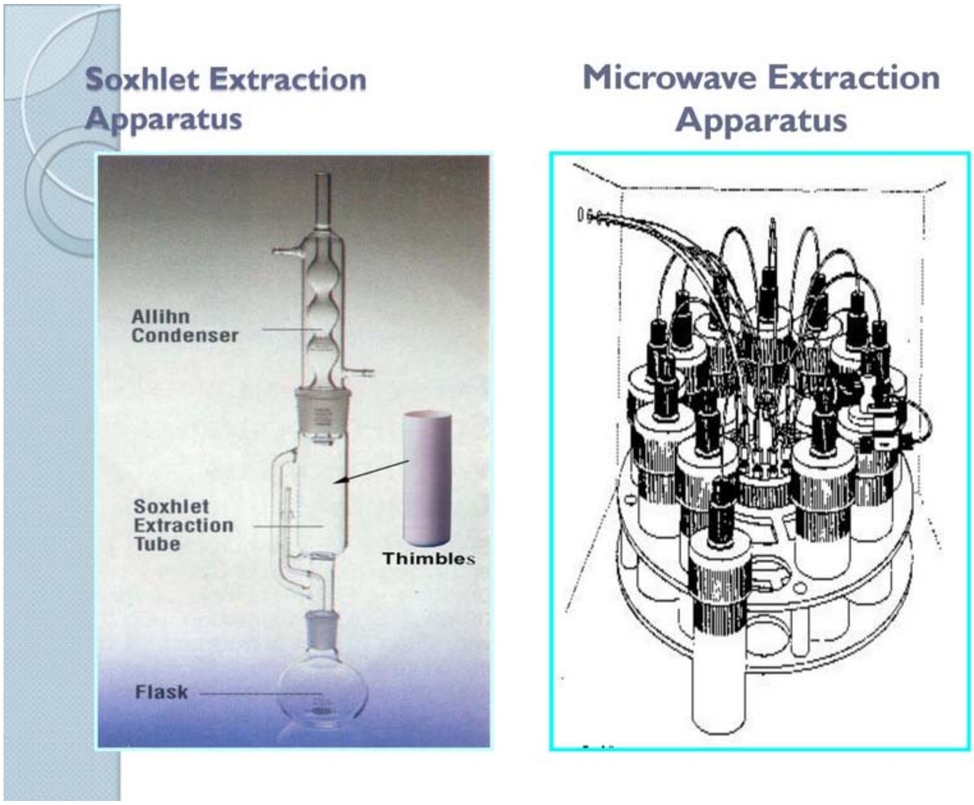
	As(III)[a]	As(V)	MMA(V)	DMA(V)	MMA(III)	DMA(III)	***AsB***
Detection limit (ng mL^{-1})	0.11	0.25	0.18	0.17	0.61	0.44	0.75
Repeatability (%RSD)	1.9	2.7	2.1	1.9	3.3	2.1	2.8

Neurological studies with tissue



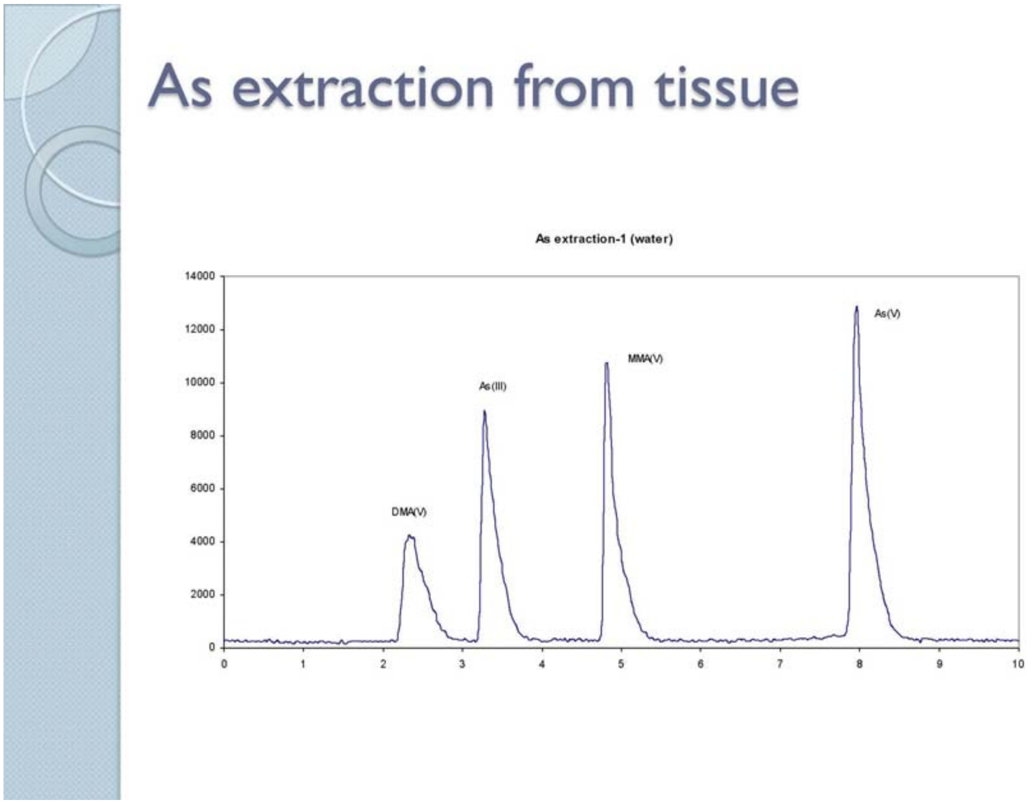


Arsenic and Intellectual Function
Bangladeshi Children at Risk

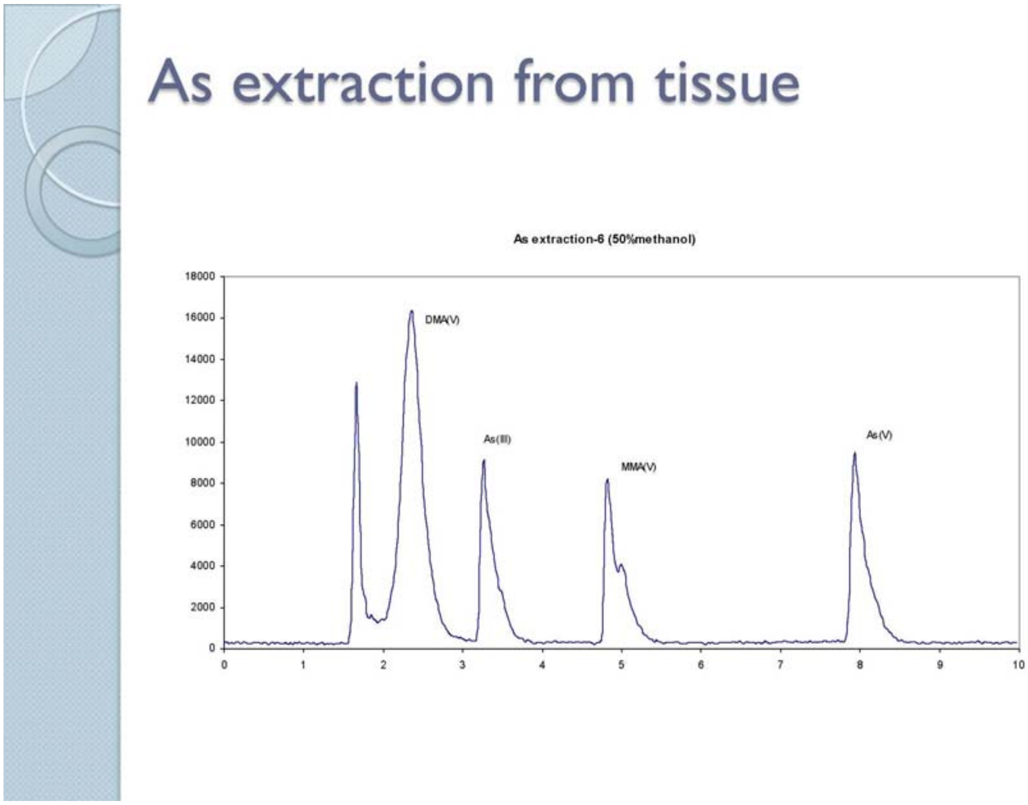


Soxhlet Extraction Apparatus

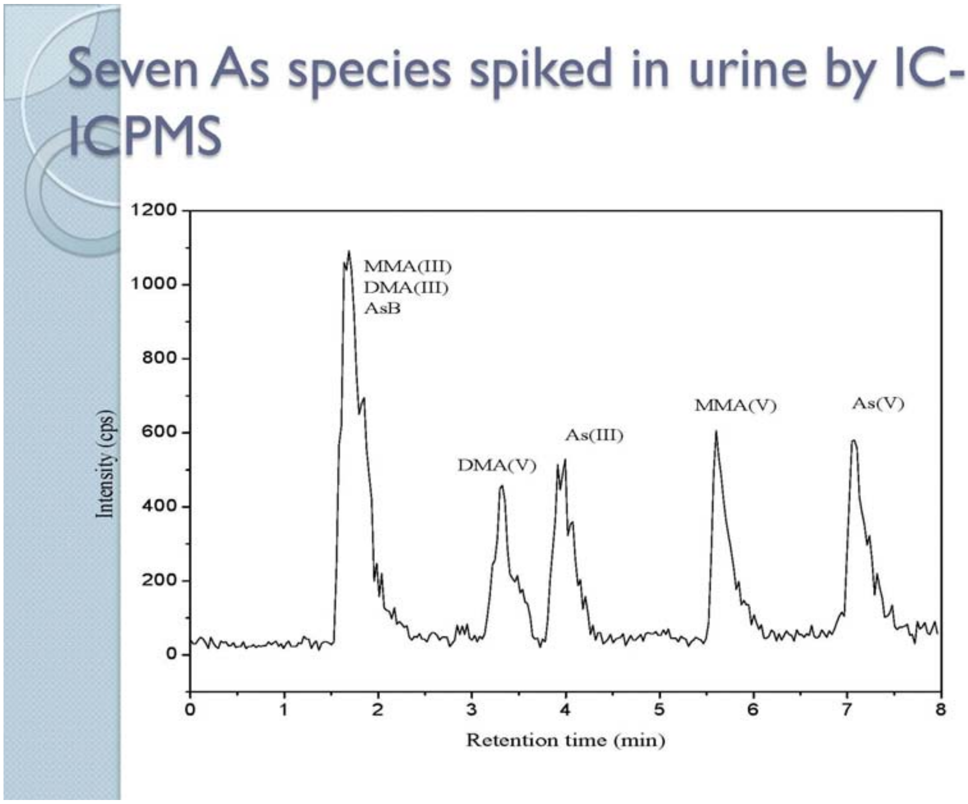
Microwave Extraction Apparatus



As extraction from tissue



As extraction from tissue



Seven As species spiked in urine by IC-ICPMS

As species of NIST SRM and urine samples by IC-ICP-MS

	As(V)	As(III)	MMA(V)	DMA(V)	MMA(III)	DMA(III)	AsB	Sum	*Reference value total arsenic*
NIST 2670a (elevated value)	166	50.8	2.1	N.D.	N.D.	1.4	0.9	221.5	220
Spiked urine (10.0 each)	11.0	9.3	9.6	9.1	9.7	10.8	10.0	69.7	70.0
Urine 101	3.9	20.7	4.5	1.9	8.4	1.9	N.D.	41.3	45.8
Urine 102	N.D.	N.D.	2.2	N.D.	3.1	0.8	N.D.	6.1	10.8
Urine 103	N.D.	N.D.	3.8	N.D.	N.D.	9.4	82.9	96.1	101.9

As species of NIST SRM and urine samples by IC-ICP-MS

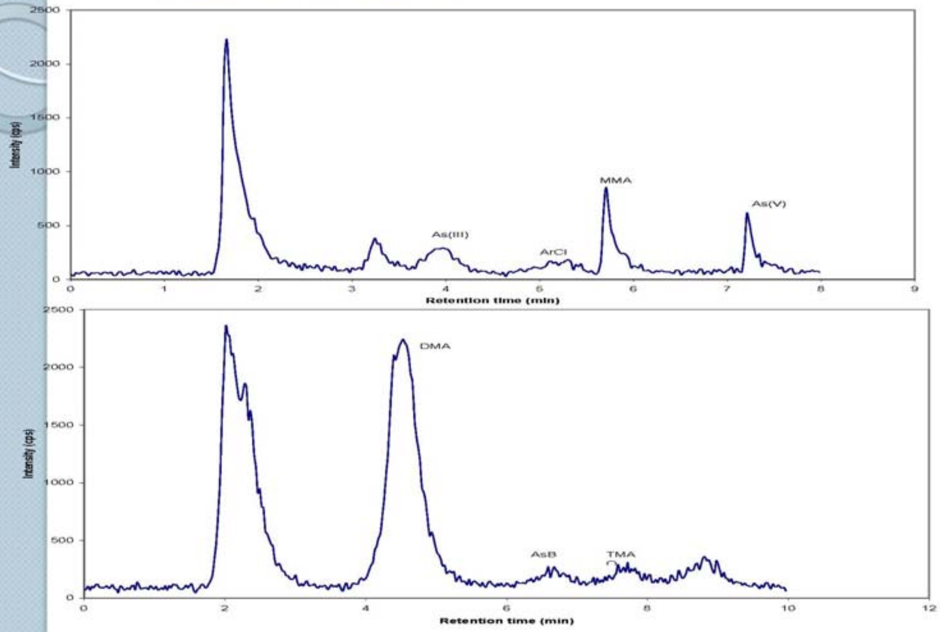
	As(V)	As(III)	MMA(V)	DMA(V)	MMA(III)	DMA(III)	AsB	Sum	*Reference value total arsenic*
NIST 2670a (elevated value)	166	50.8	2.1	N.D.	N.D.	1.4	0.9	221.5	220
Spiked urine (10.0 each)	11.0	9.3	9.6	9.1	9.7	10.8	10.0	69.7	70.0
Urine 101	3.9	20.7	4.5	1.9	8.4	1.9	N.D.	41.3	45.8
Urine 102	N.D.	N.D.	2.2	N.D.	3.1	0.8	N.D.	6.1	10.8
Urine 103	N.D.	N.D.	3.8	N.D.	N.D.	9.4	82.9	96.1	101.9

As species of NIST SRM and urine samples by IC-ICP-MS

	As(V)	As(III)	MMA(V)	DMA(V)	MMA(III)	DMA(III)	AsB	Sum	***Reference value total arsenic***
NIST 2670a (elevated value)	166	50.8	2.1	N.D.	N.D.	1.4	0.9	221.5	220
Spiked urine (10.0 each)	11.0	9.3	9.6	9.1	9.7	10.8	10.0	69.7	70.0
Urine 101	3.9	20.7	4.5	1.9	8.4	1.9	N.D.	41.3	45.8
Urine 102	N.D.	N.D.	2.2	N.D.	3.1	0.8	N.D.	6.1	10.8
Urine 103	N.D.	N.D.	3.8	N.D.	N.D.	9.4	82.9	96.1	101.9

As Speciation in Urine Application

2669 level II

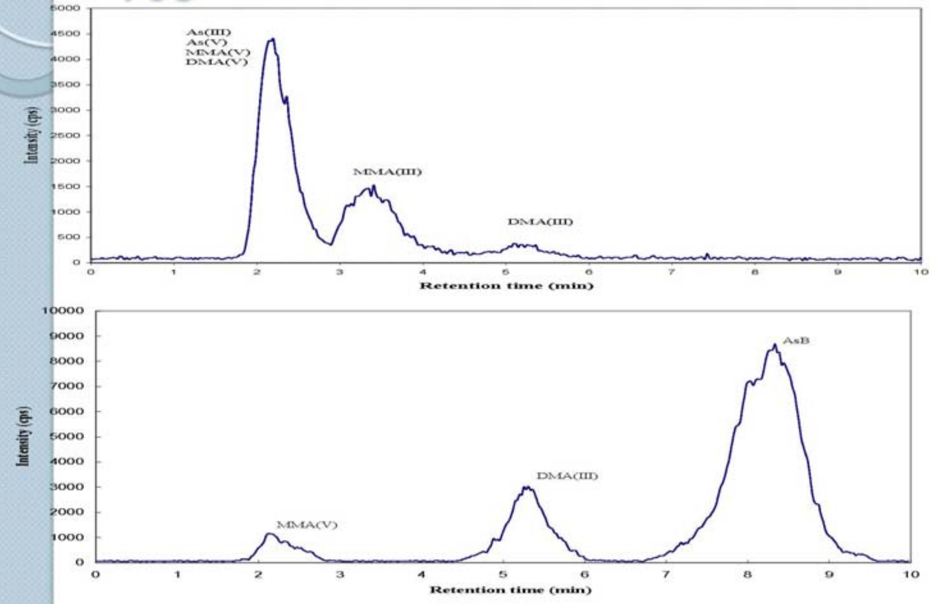


As speciation of NIST SRM 2669 using IC-ICP-MS

	As(V)	As(III)	MMA	DMA	TMAO	***AsB***
SRM 2669 (level I)	2.68 ± 0.20	N.D.	1.65 ± 0.14	3.42 ± 0.35	N.D.	34.3 ± 0.7
SRM 2669 (level II)	6.89 ± 0.43	4.99 ± 0.33	6.87 ± 0.30	25.2 ± 0.6	2.15 ± 0.17	3.37 ± 0.13

Sometimes you miss your target

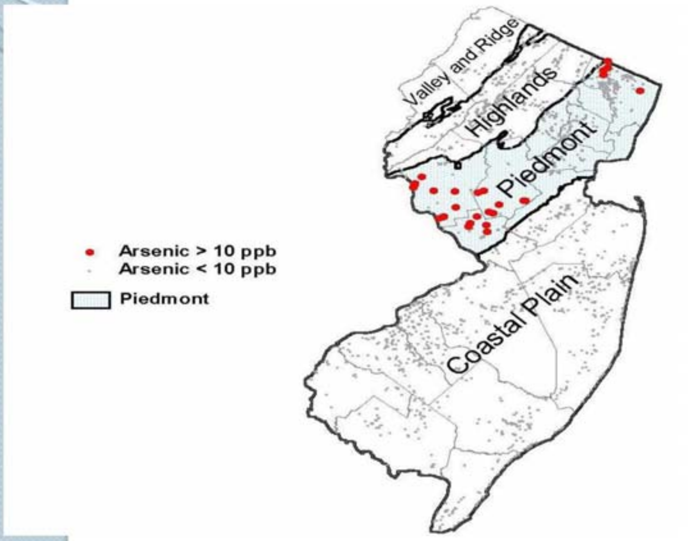
Subject Sample Number 101 and 103



Analysis of Urine Sample

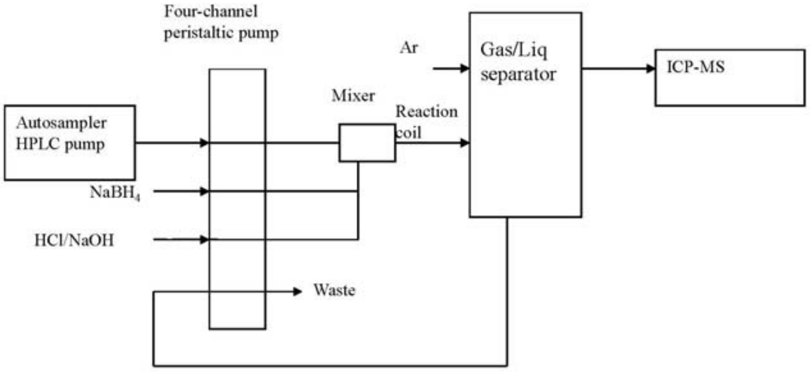
	As(V)	As(III)	MMA(V)	DMA(V)	MMA(III)	DMA(III)	AsB	Sum	Total arsenic (ICP-MS)
Urine sample 101	3.9	20.7	4.5	1.9	8.4	1.9	N.D.	41.3	45.8
Urine sample 102	N.D.	N.D.	2.2	N.D.	3.1	0.8	N.D.	6.1	7.8
Urine sample 103	N.D.	N.D.	3.8	N.D.	N.D.	9.4	82.9	96.1	101.9

Arsenic in NJ



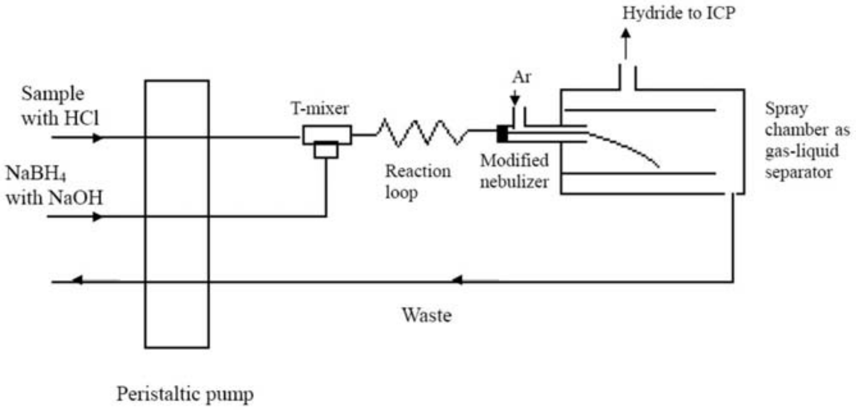
- Arsenic in drinking water wells in the Piedmont region

HG system as a speciation tool

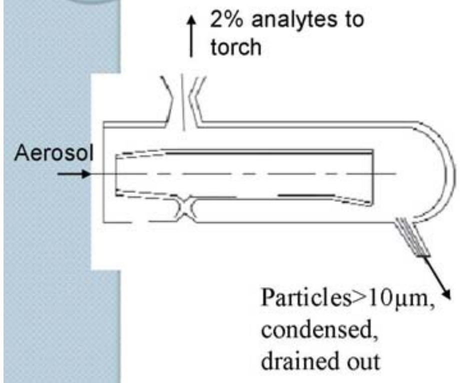


Xie, R., Johnson, W., Spayd, S., Hall, G. and **Buckley, B.**, Determination Of Total Toxic Arsenic Species In Human Urine Using Hydride Generation Inductively Coupled Plasma Mass Spectrometry, *J. Anal. Atomic Spec.*, **22,** 553 – 560, 2007

Schematic diagram of HG-ICP-MS system



Spray chamber

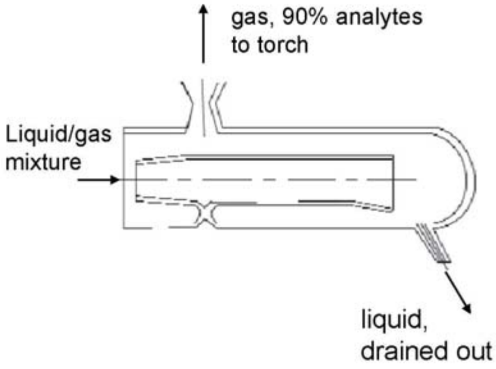


2% analytes to torch

Aerosol

Particles>10μm, condensed, drained out

Traditional function



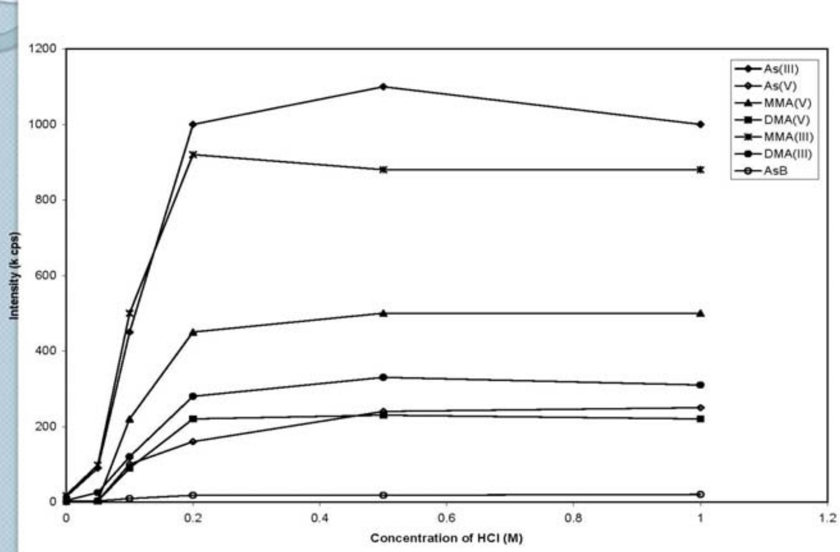
gas, 90% analytes to torch

Liquid/gas mixture

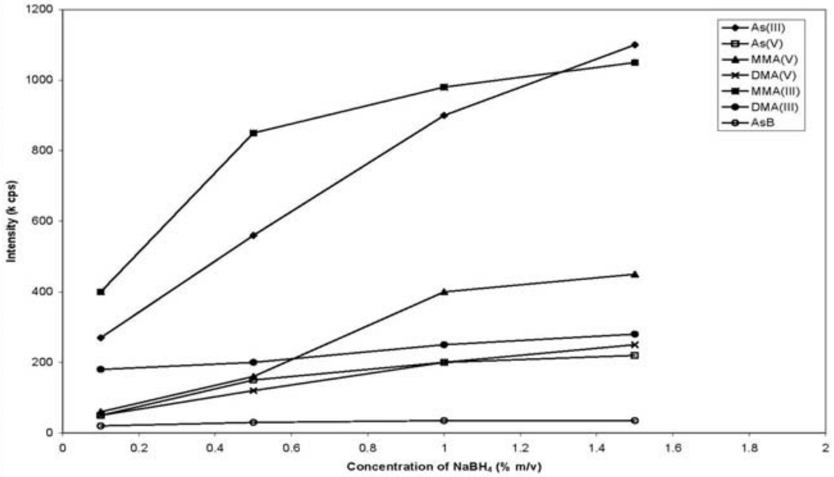
liquid, drained out

Liquid/gas separater in HG

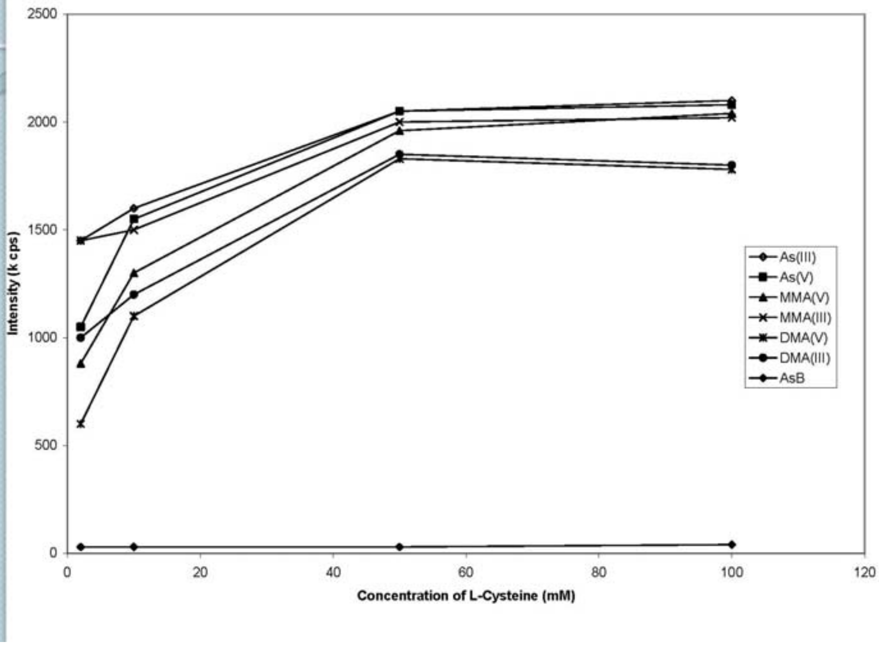
Effect of HCl on HG-ICP-MS signal



Effect of NaBH$_4$ on HG-ICP-MS signal



Effect of L-Cysteine on HG-ICP-MS signal

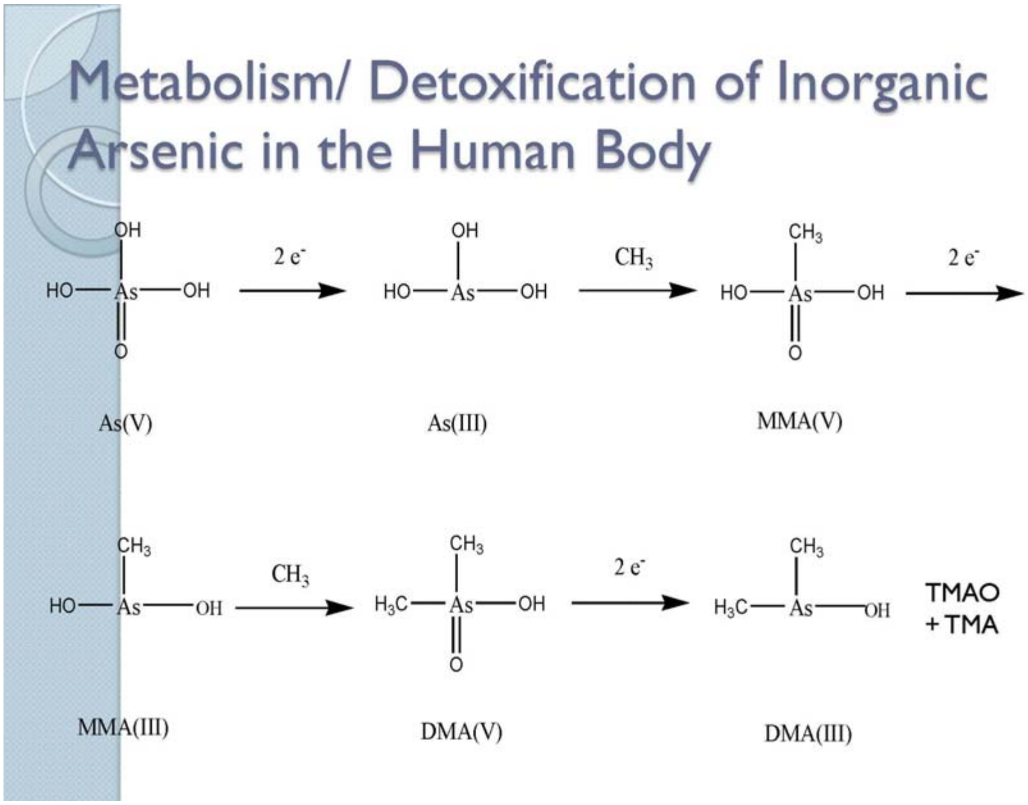


% recovery As species in water by HG-ICP-MS

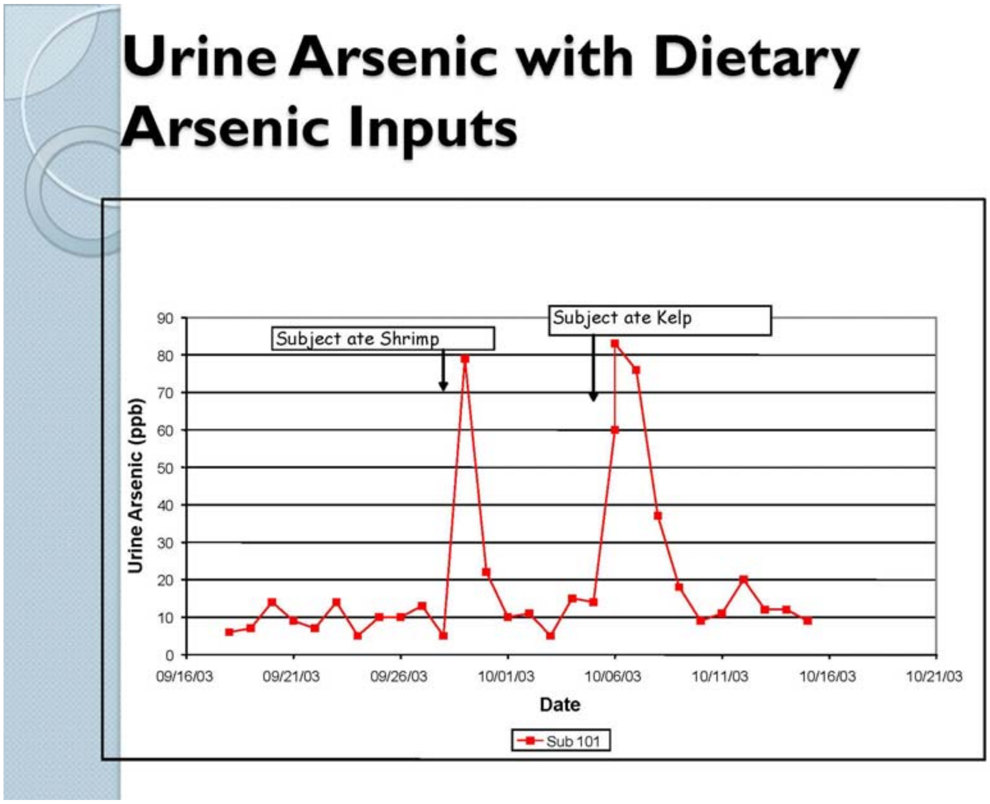
	As(III)	As(V)	MMA(V)	MMA(III)	DMA(V)	DMA(III)	***AsB***
Recovery (%)	102.5	101.2	92.4	91.3	84.5	86.5	4.8
Repeatability (%RSD)	2.0	1.5	0.4	0.5	1.3	1.2	4.7

Total toxic arsenic species in NIST urine SRM (2670a) by HG-ICPMS

sample	*HG-ICPMS*	*ICPMS*	**Reference value**
NIST 2670a (elevated value)	*213.2*	*220.6*	**220.0**

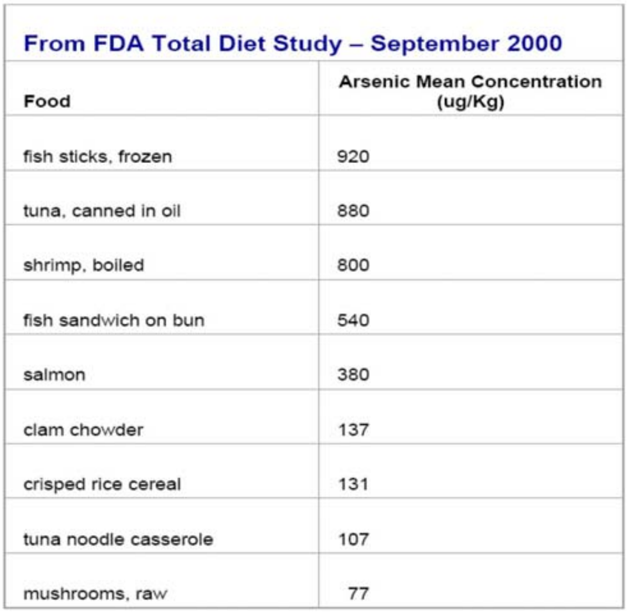


Metabolism/ Detoxification of Inorganic Arsenic in the Human Body



Urine Arsenic with Dietary Arsenic Inputs

Arsenic in food



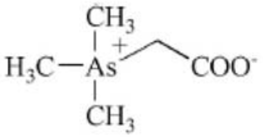
From FDA Total Diet Study – September 2000

Food	Arsenic Mean Concentration (ug/Kg)
fish sticks, frozen	920
tuna, canned in oil	880
shrimp, boiled	800
fish sandwich on bun	540
salmon	380
clam chowder	137
crisped rice cereal	131
tuna noodle casserole	107
mushrooms, raw	77

Arsenic leaves your plate

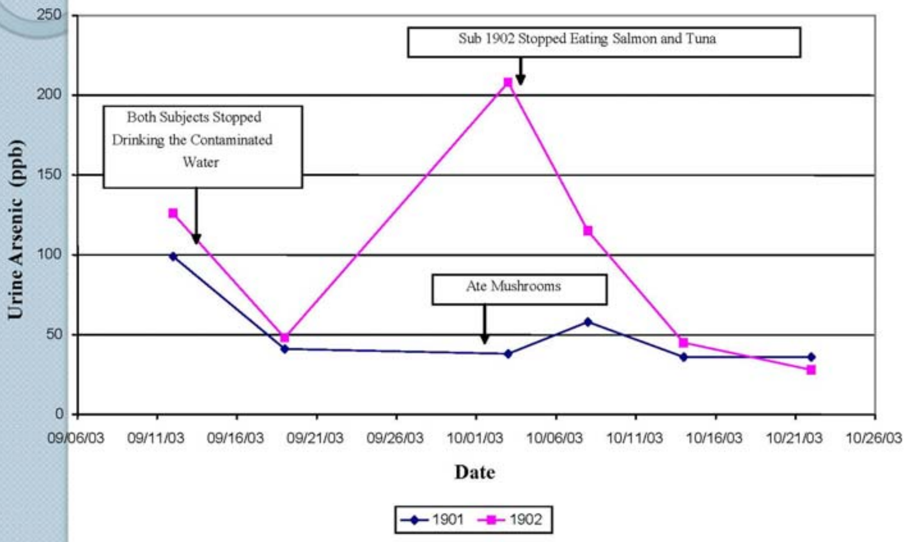
Arsenobetaine (AsB)

- > 90% As species in seafood are AsB
- AsB is non-toxic, it doesn't undergo metabolism in human body
- It can interfere with the analysis of other As species in urine



Trimethylarsonioacetate
(Arsenobetaine, AB)

Urine As from well water and diet 80 ppb in well



Arsenic Hydride Generation (HG)

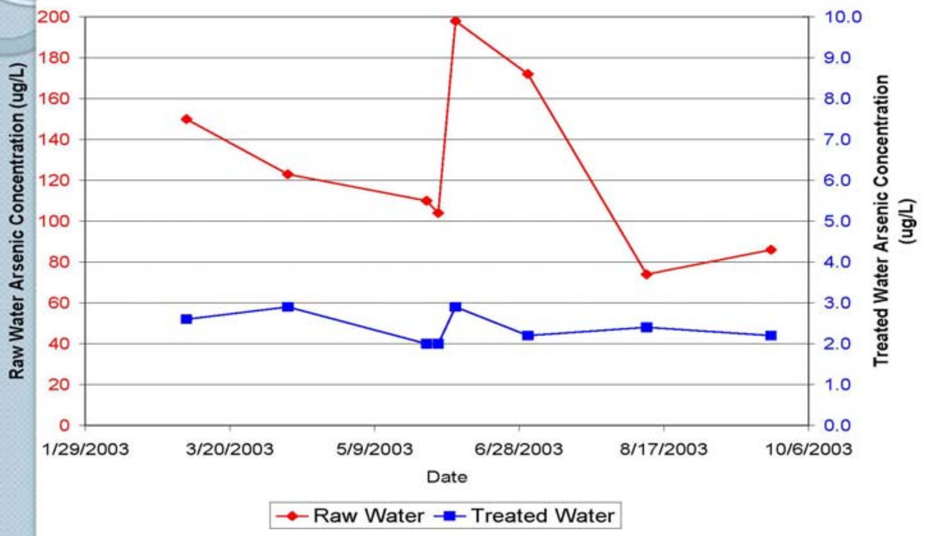
$$As(III)/As(V) + NaBH_4 \rightarrow AsH_3$$

$$MMA(III)/MMA(V) + NaBH_4 \rightarrow MeAsH_2$$

$$DMA(III)/DMA(V) + NaBH_4 \rightarrow Me_2AsH$$

AsB: no reaction

Treatment efficacy

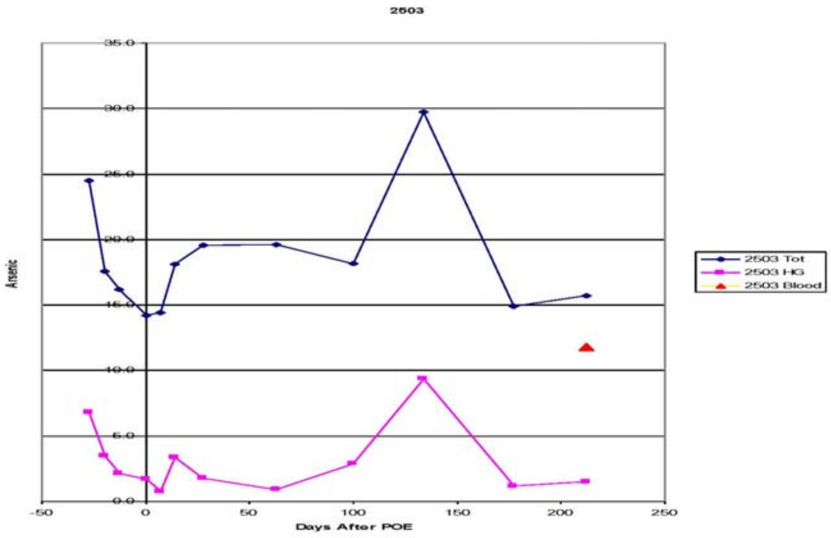


Q:As in diet vs. well water?

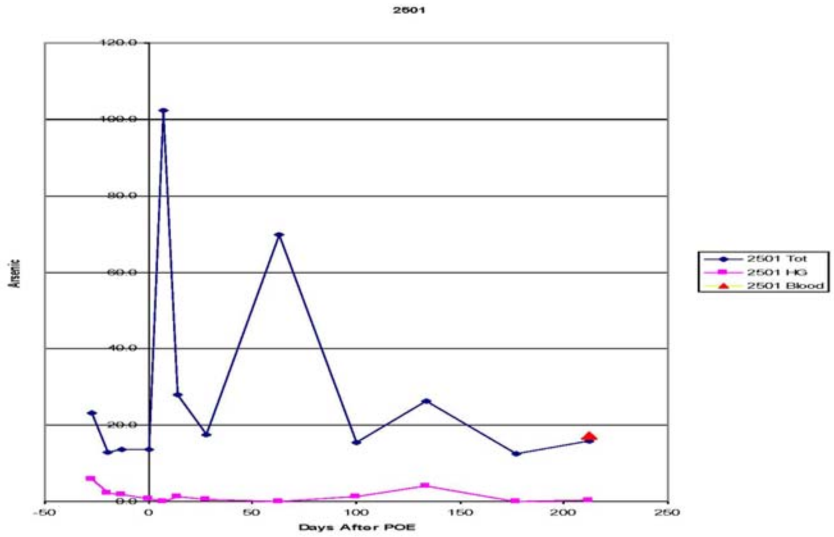
Need a less expensive

A:Hydride Generation

Total Arsenic vs. HG As (Dietary)

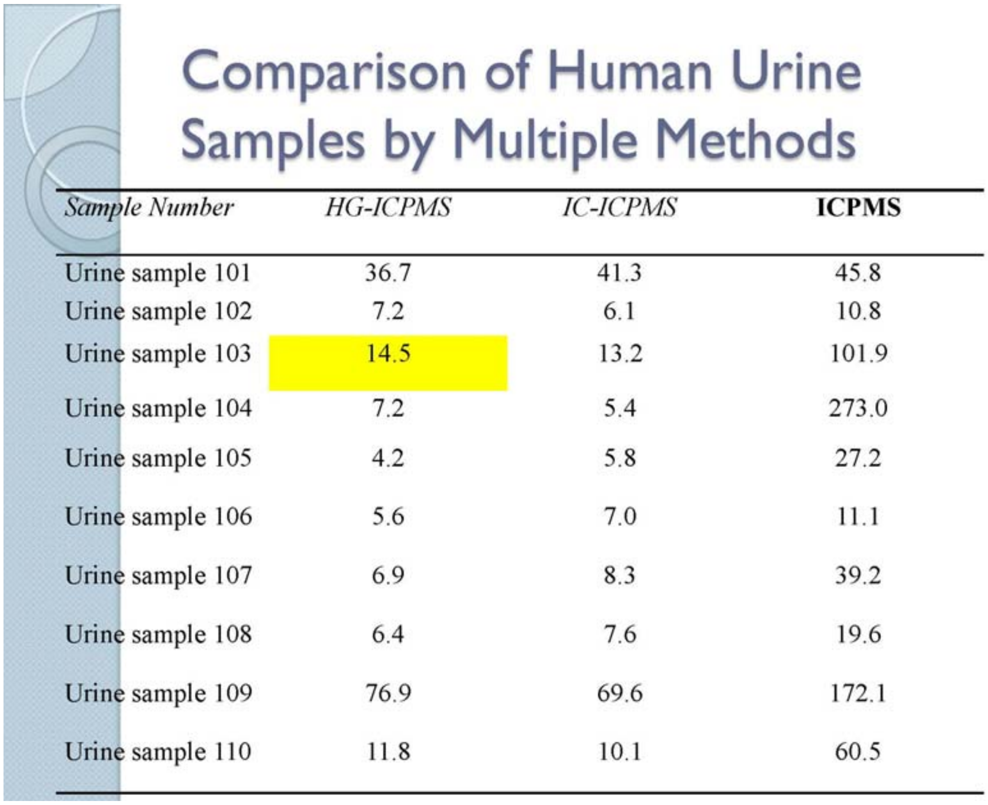


Temporal diet contribution



Comparison of Human Urine Samples by Multiple Methods

Sample Number	*HG-ICPMS*	*IC-ICPMS*	**ICPMS**
Urine sample 101	36.7	41.3	45.8
Urine sample 102	7.2	6.1	10.8
Urine sample 103	14.5	13.2	101.9
Urine sample 104	7.2	5.4	273.0
Urine sample 105	4.2	5.8	27.2
Urine sample 106	5.6	7.0	11.1
Urine sample 107	6.9	8.3	39.2
Urine sample 108	6.4	7.6	19.6
Urine sample 109	76.9	69.6	172.1
Urine sample 110	11.8	10.1	60.5



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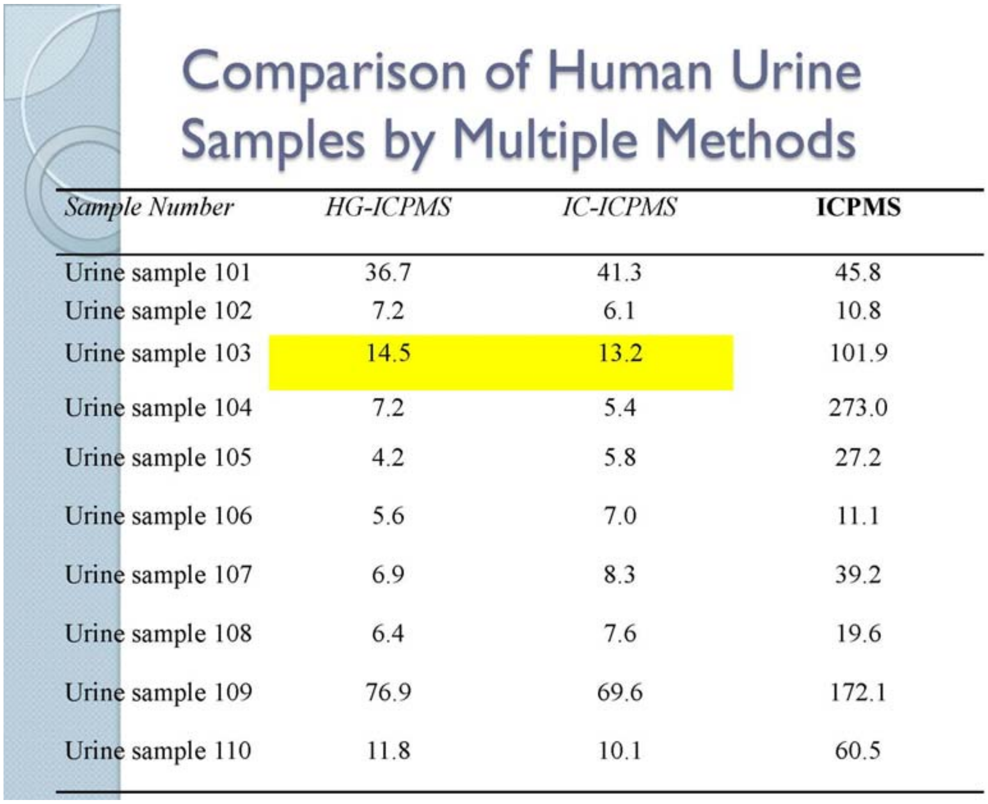

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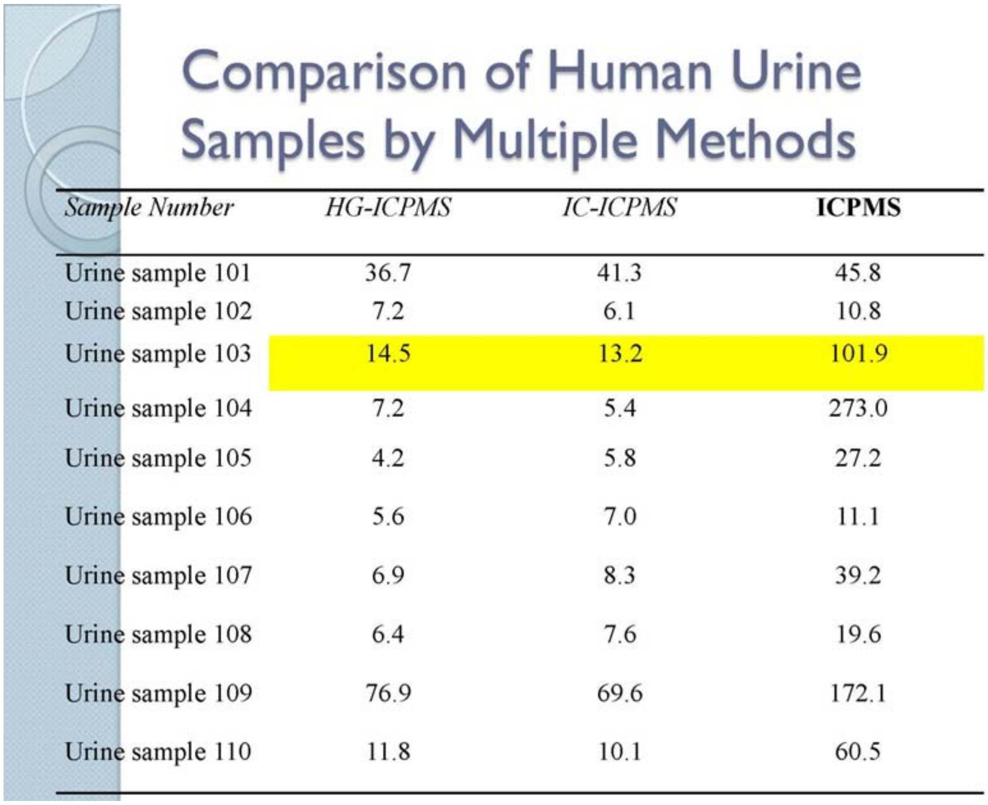

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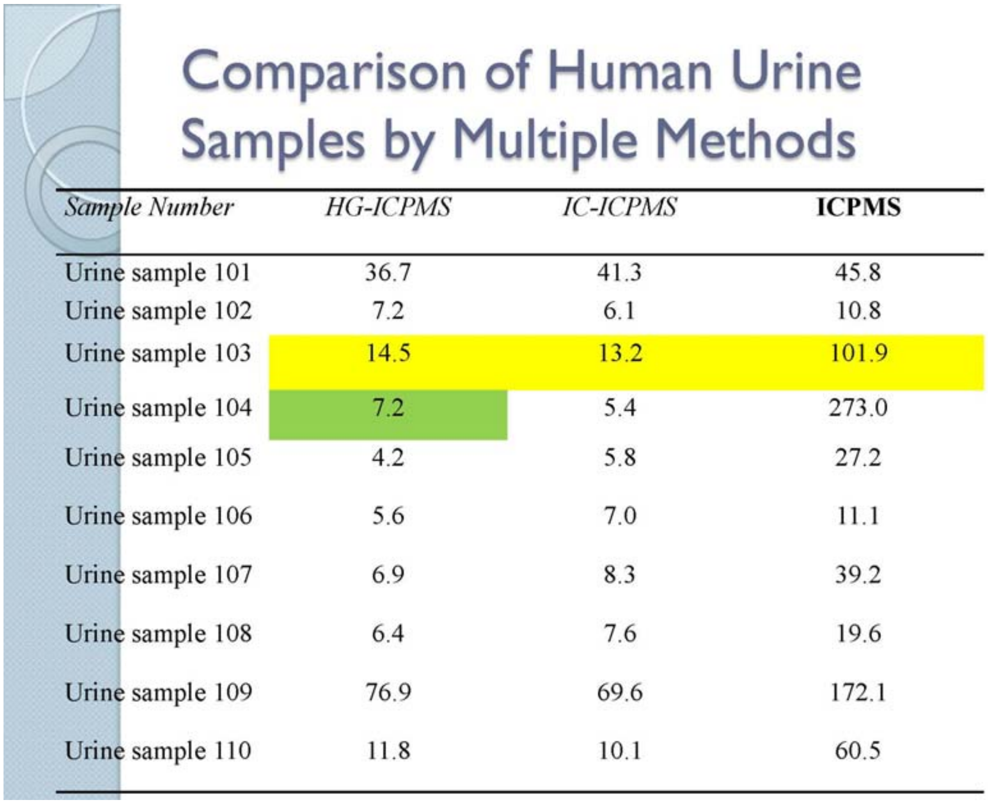

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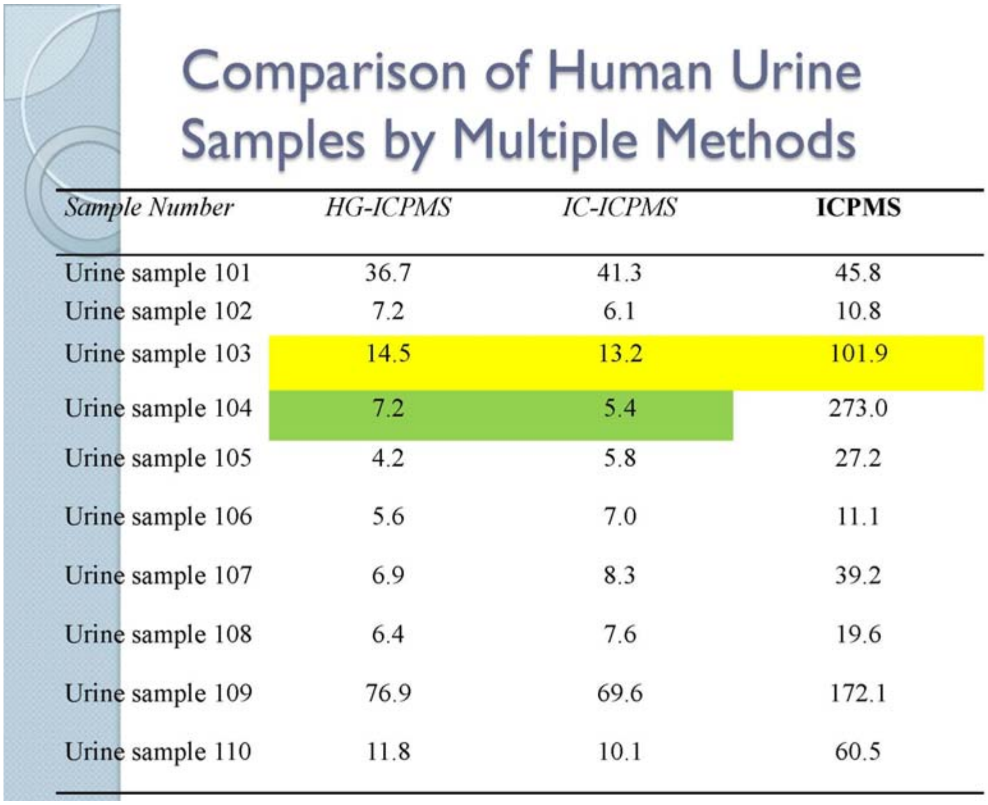

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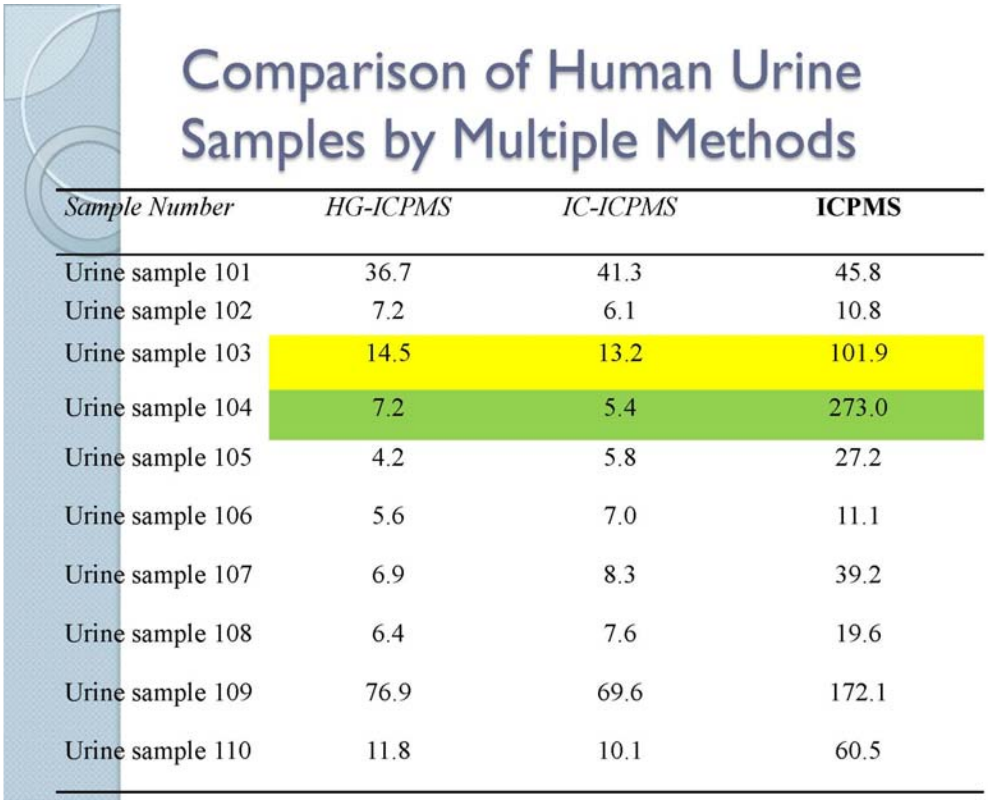

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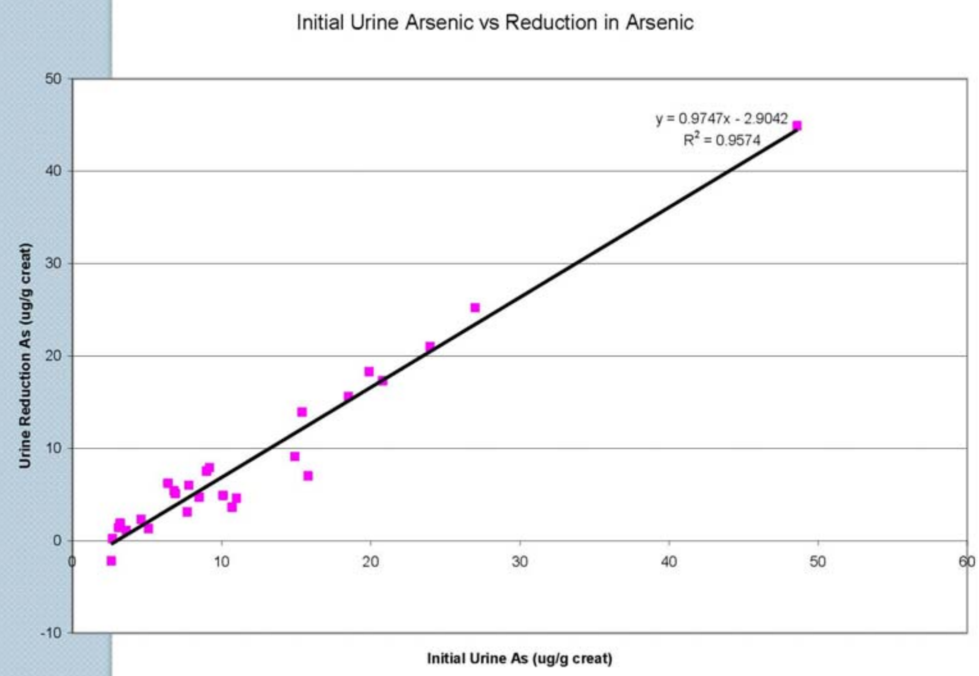
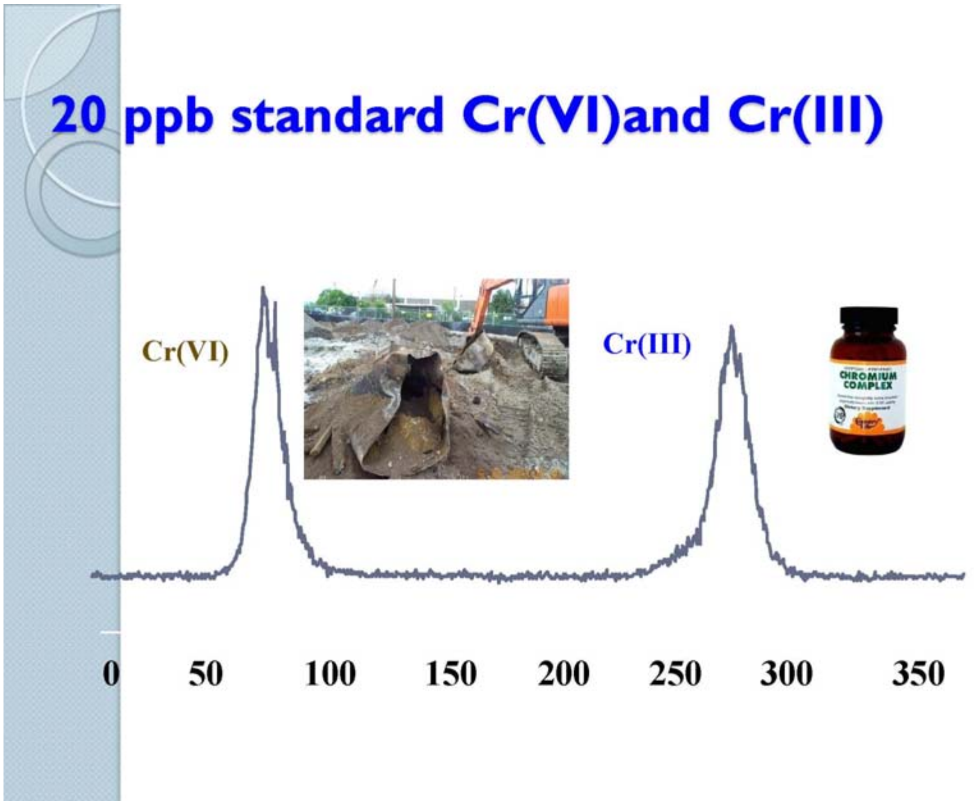
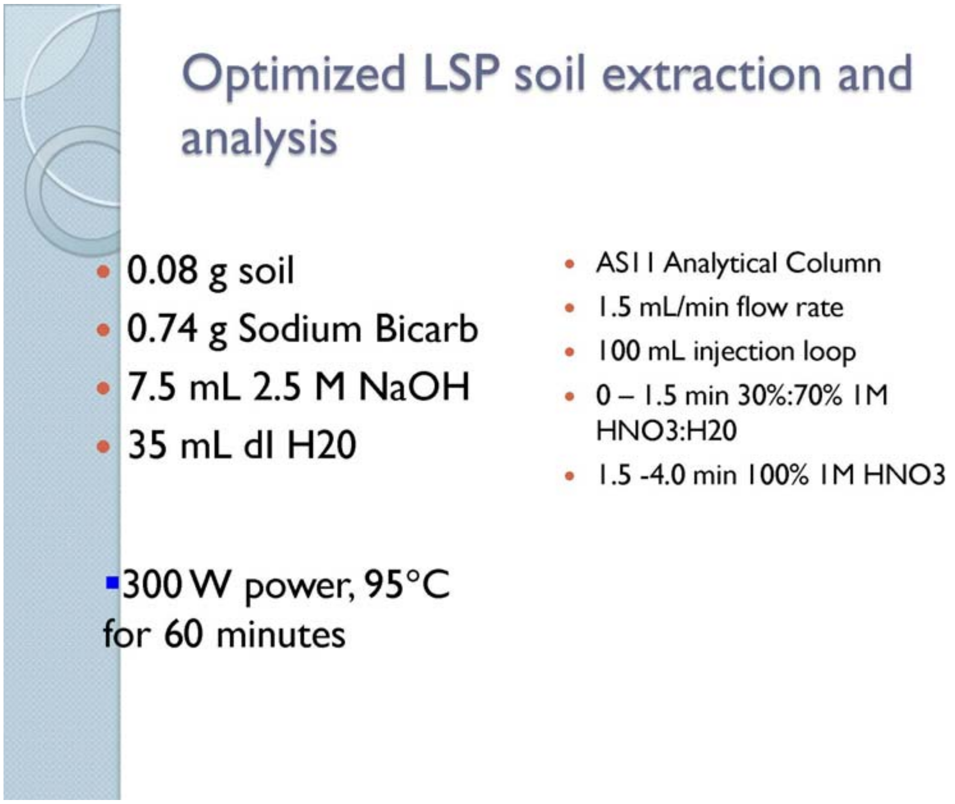


Moving on to chromium



20 ppb standard Cr(VI)and Cr(III)



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

- 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

- 300 W power, 95°C for 60 minutes

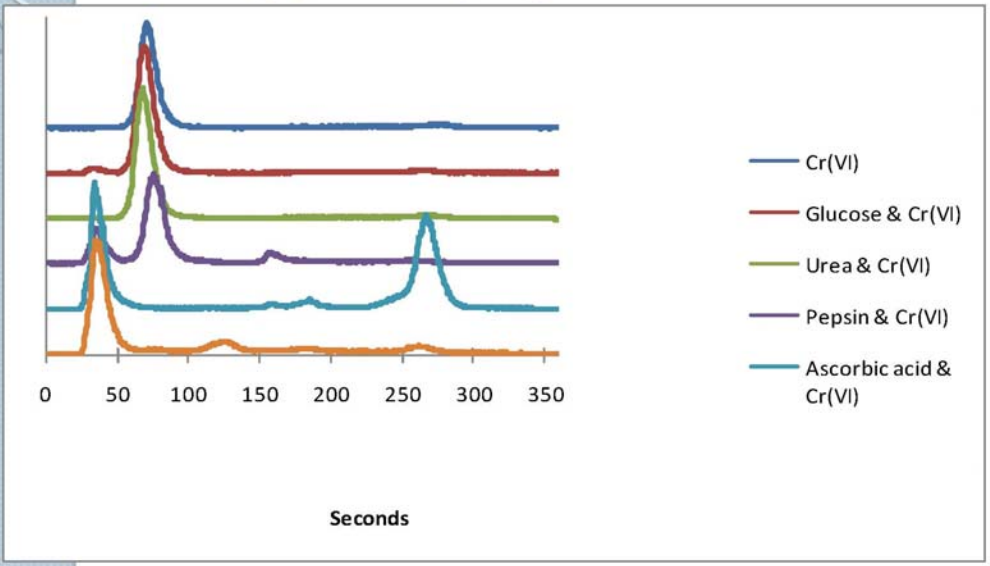
Liberty State Park Soil

	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%
%CV	108.4%	123.4%	55.2%	

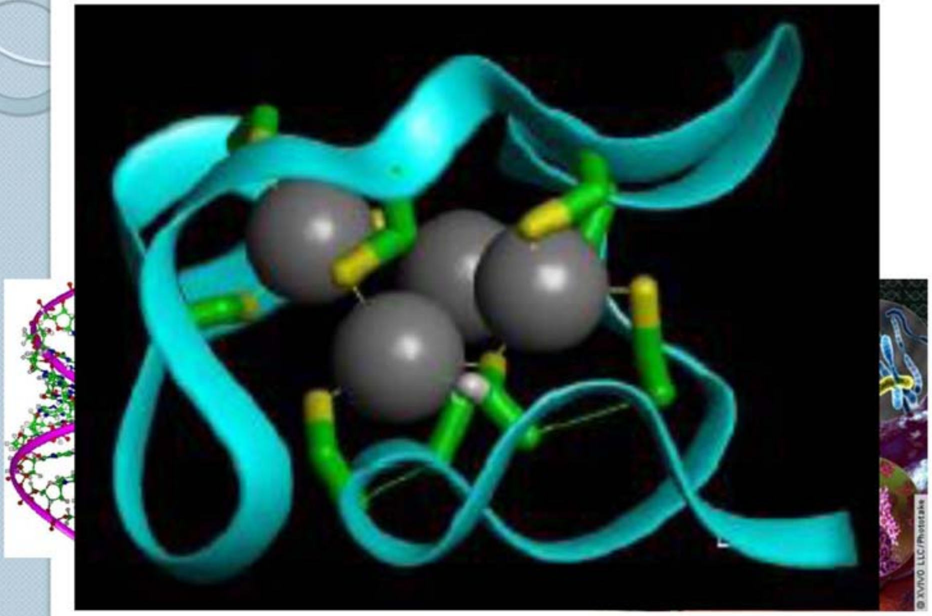
Optimized Method

Sample Name	Cr (III)	Cr (VI)	Total Cr	%CV	Recovery
Gateway	267	778	1045	17.6%	15.9%
Society Hill	499	57	556	50.6%	10.5%
PPG Garfield Ave	265	288	553	35.0%	18.7%

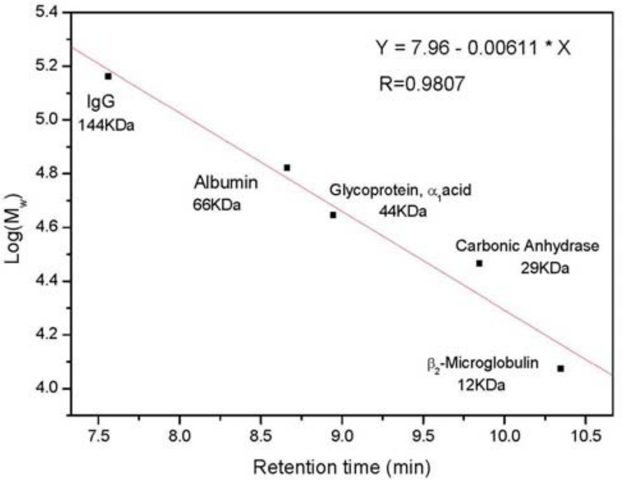
Gastric juice components spiked with 50 ppb Cr(VI)



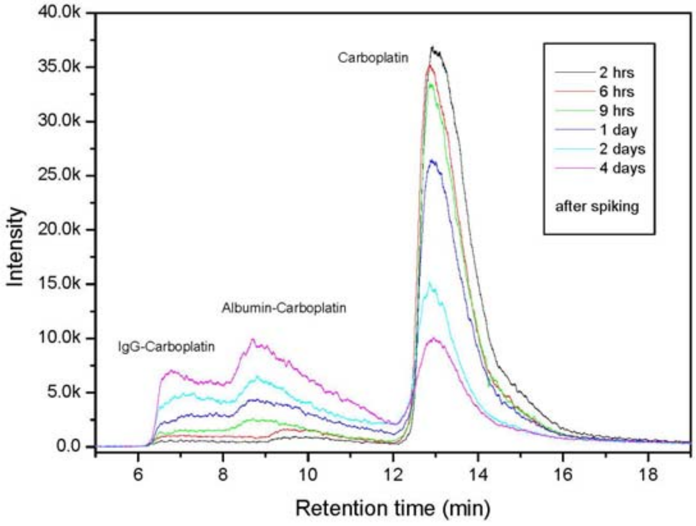
New Biomarkers



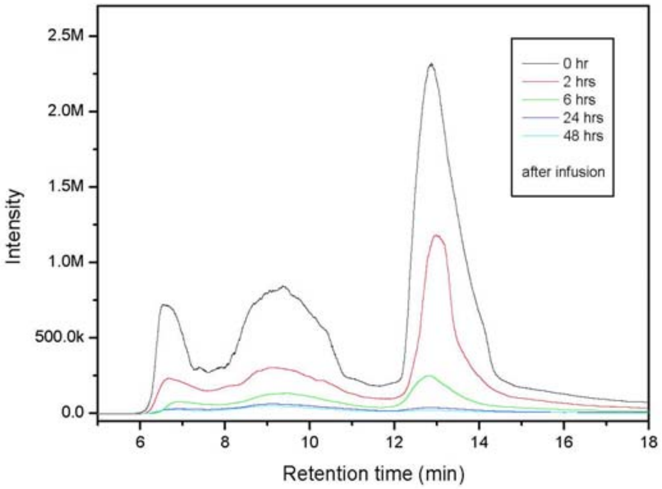
Calibration curve for G3000SW column



Speciation of Pt in blood plasma spiked with carboplatin



Speciation of Pt in blood plasma from patient under chemotherapy

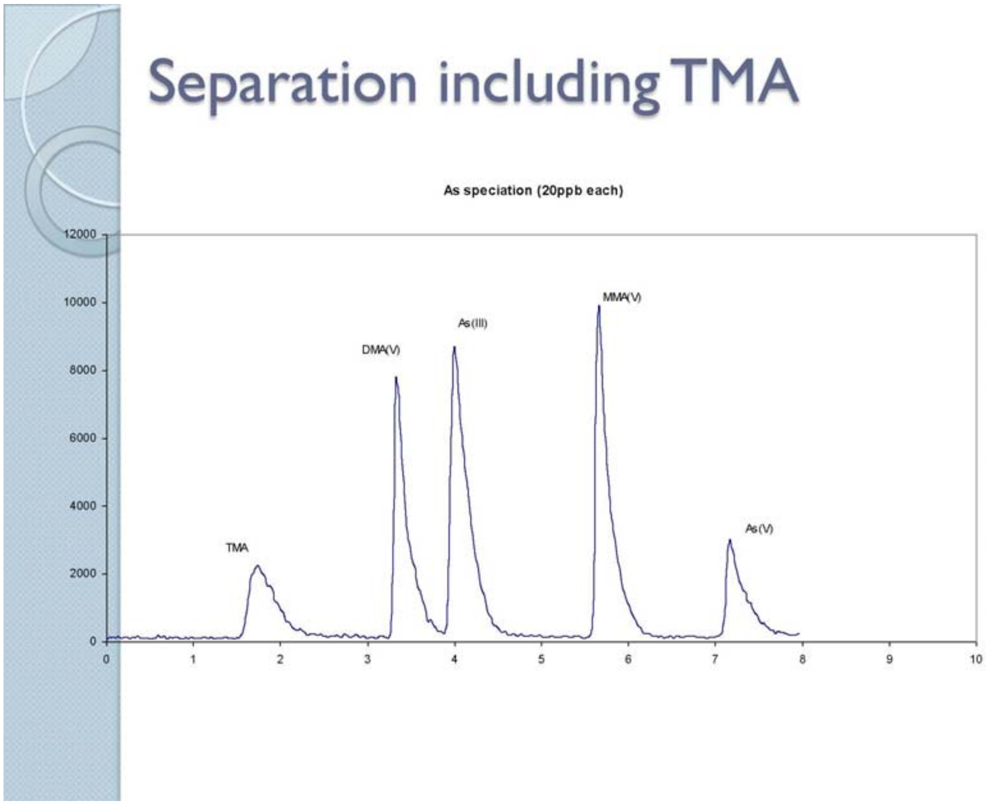


Acknowledgements

NJDEP
NIEHS

Thank you

Any Questions?



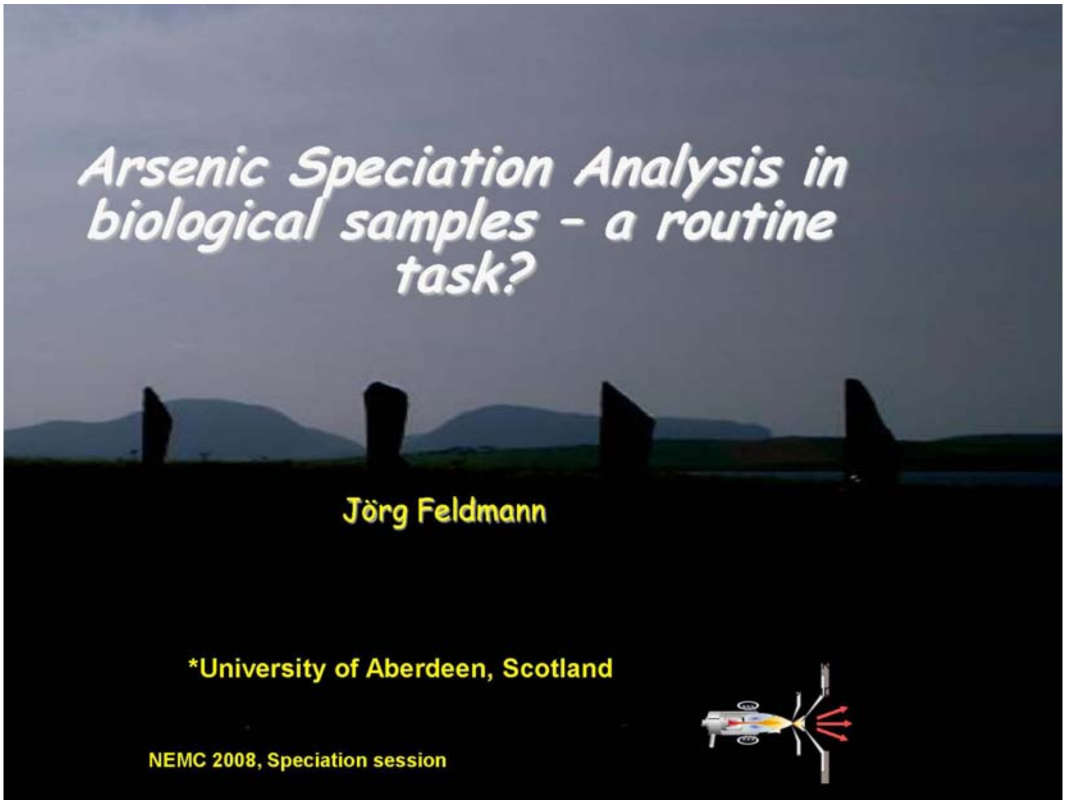
Separation including TMA

Arsenic Speciation Analysis in Biological Samples: A Routine Task?

Jorg Feldmann
University of Aberdeen
Meston Walk
Aberdeen, UK AB243UE
+44-1224-272911
j.feldmann@abdn.ac.uk

ABSTRACT

In order to determine the molecular structure of an arsenic containing compound in a complex matrix such as biological fluids or foodstuff, it is necessary to choose a methodology which comprises of very selective and sensitive detection and a sample preparation which allows quantitative and qualitative preconcentration of the trace amounts of analytes without changing the molecular structure. In this lecture, advantages and possibilities of HPLC-ICP-MS for arsenic speciation in routine applications and research will be shown, while limitations and pitfalls that can be encountered using such methods for complicated matrix samples will be pointed out as well. The use of complementary analytical methods such as HPLC-ES-MS and XANES/EXAFS, which can be used to unravel problems encountered with routine methods will be discussed.



Arsenic Speciation Analysis in biological samples – a routine task?

Jörg Feldmann

*University of Aberdeen, Scotland

NEMC 2008, Speciation session

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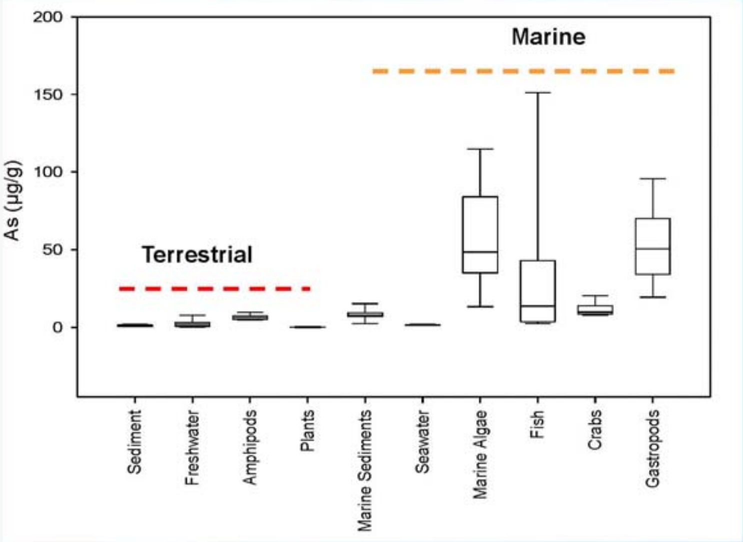
challenge 1 : large differences in concentration



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Challenge 2: large differences in As species diversity

- Marine biota
  - Arsenobetaine, choline
  - > 20 arsenosugars
  - DMA, MA
  - Inorganic arsenic
  - $Me_2As(=O)$-containing short-chain fatty acids
  - $Me_2As(=O)$-containing hydrocarbons
  - Thio-arsenosugars
  - Thio-forms of short chain fatty acids
  - …
- Terrestrial biota
  - Inorganic arsenic
  - DMA, MA
  - …
  - > arseno-peptides (As^{iii}-PCs, MA^{iii}-PCs, thio-DMA^{v}-GS)
  - Traces of arsenobetaine, arsenosugars

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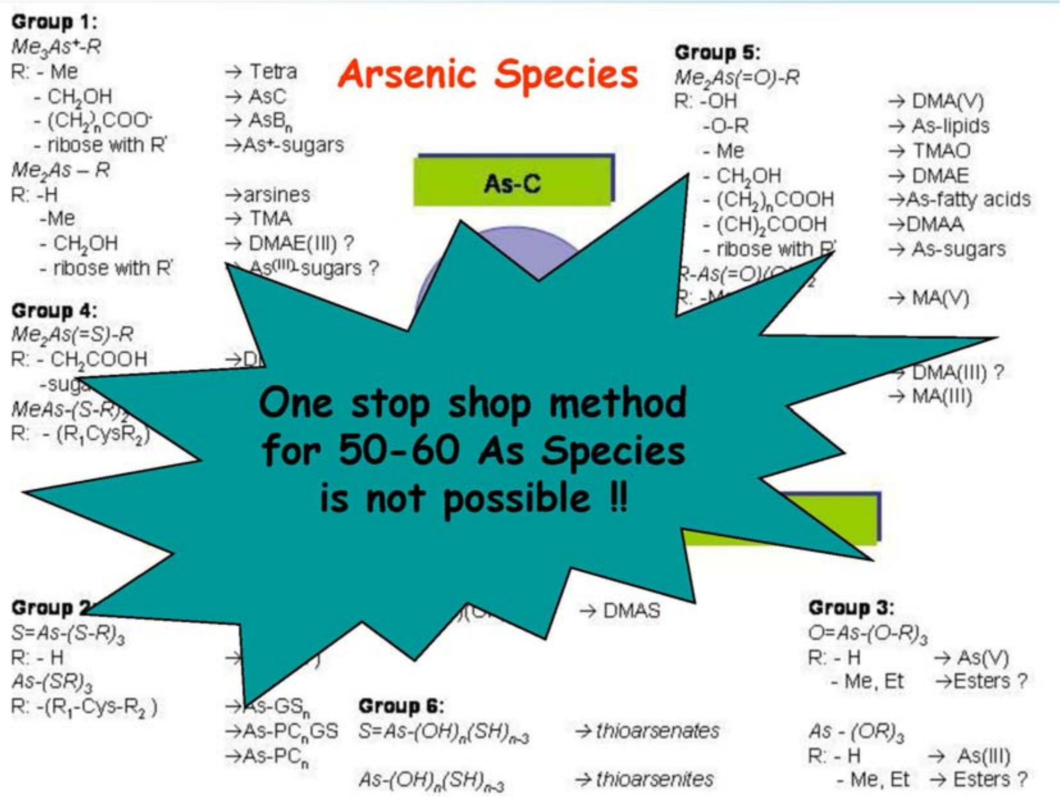


Arsenic Species

Group 1:
Me_3As^+-R
R: - Me → Tetra
- CH_2OH → AsC
- $(CH_2)_nCOO^-$ → AsB_n
- ribose with R' → As^+-sugars

Me_2As – R
R: -H → arsines
-Me → TMA
- CH_2OH → DMAE(III) ?
- ribose with R' → $As^{(III)}$-sugars ?

Group 4:
$Me_2As(=S)$-R
R: - CH_2COOH →D
-sug
MeAs-$(S\text{-}R)_2$
R: - (R_1CysR_2)

Group 5:
$Me_2As(=O)$-R
R: -OH → DMA(V)
-O-R → As-lipids
- Me → TMAO
- CH_2OH → DMAE
- $(CH_2)_nCOOH$ → As-fatty acids
- $(CH)_2COOH$ → DMAA
- ribose with R' → As-sugars
R-As(=O)(O
R: -M → MA(V)
→ DMA(III) ?
→ MA(III)

One stop shop method for 50-60 As Species is not possible !!

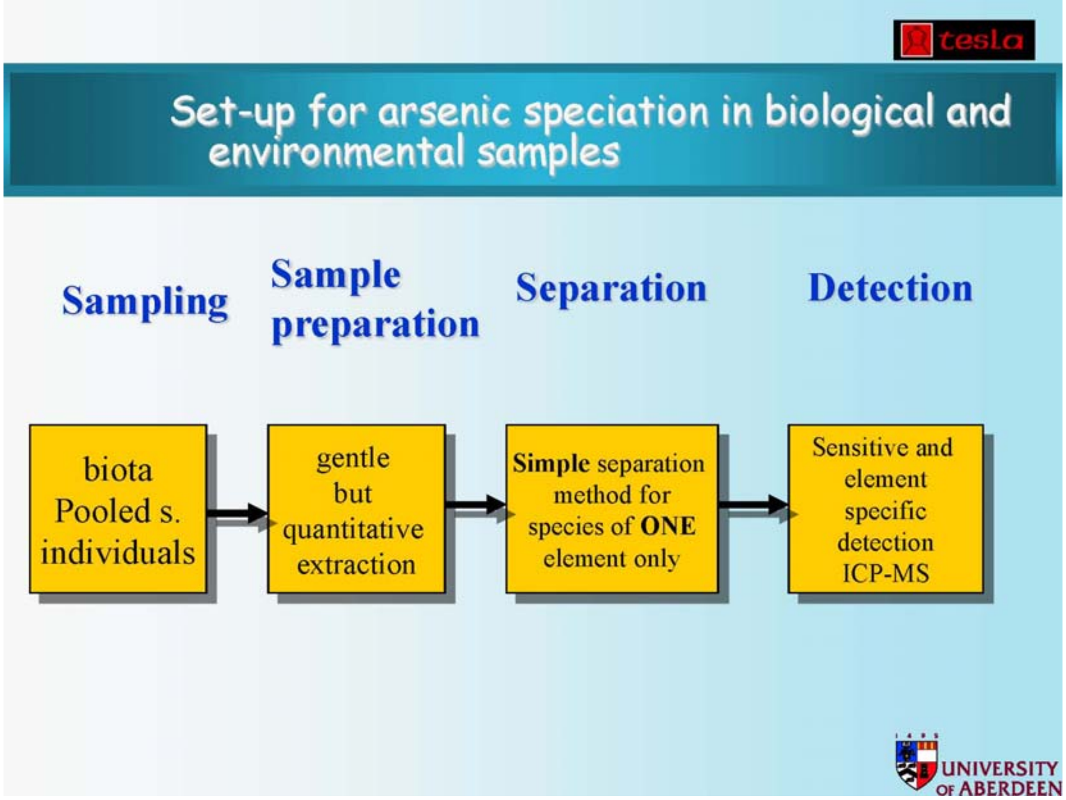
Group 2
S=As-$(S\text{-}R)_3$
R: - H →
As-$(SR)_3$
R: -$(R_1$-Cys-$R_2)$ → As-GS_n
→ As-PC_nGS
→ As-PC_n

→ DMAS

Group 6:
S=As-$(OH)_n(SH)_{n-3}$ → *thioarsenates*
As-$(OH)_n(SH)_{n-3}$ → *thioarsenites*

Group 3:
O=As-$(O\text{-}R)_3$
R: - H → As(V)
- Me, Et → Esters ?

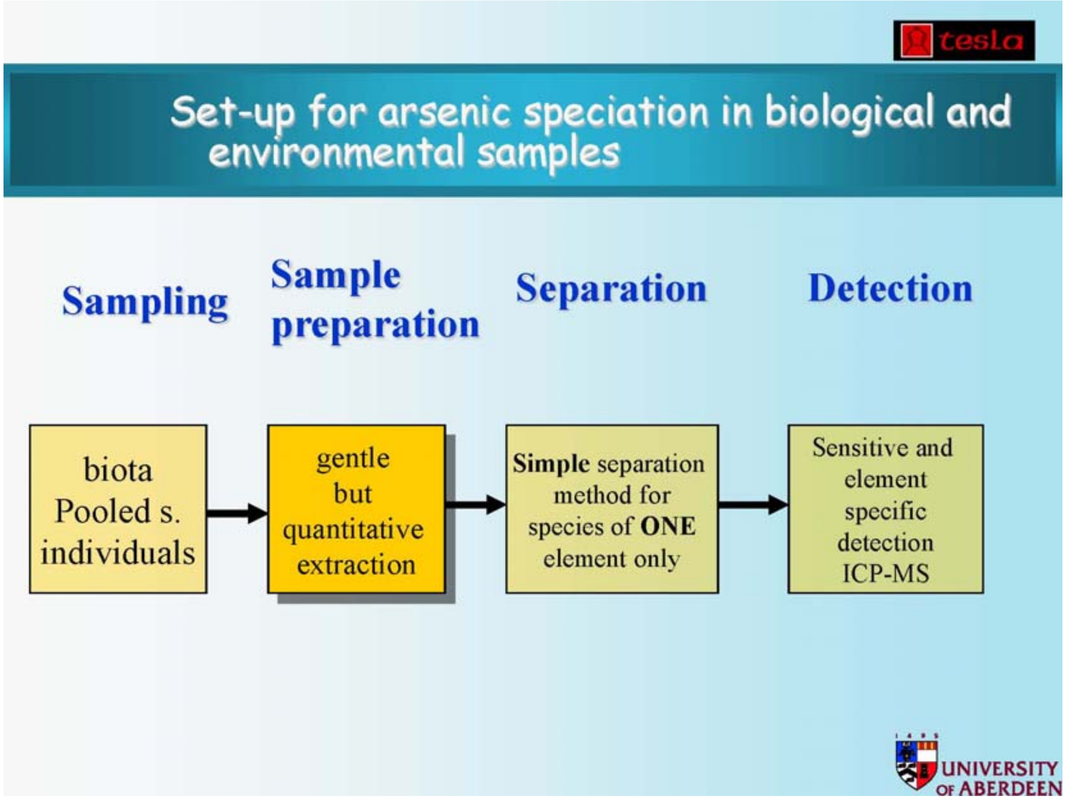
As - $(OR)_3$
R: - H → As(III)
- Me, Et → Esters ?



Set-up for arsenic speciation in biological and environmental samples

Sampling — **Sample preparation** — **Separation** — **Detection**

biota Pooled s. individuals → gentle but quantitative extraction → **Simple** separation method for species of **ONE** element only → Sensitive and element specific detection ICP-MS



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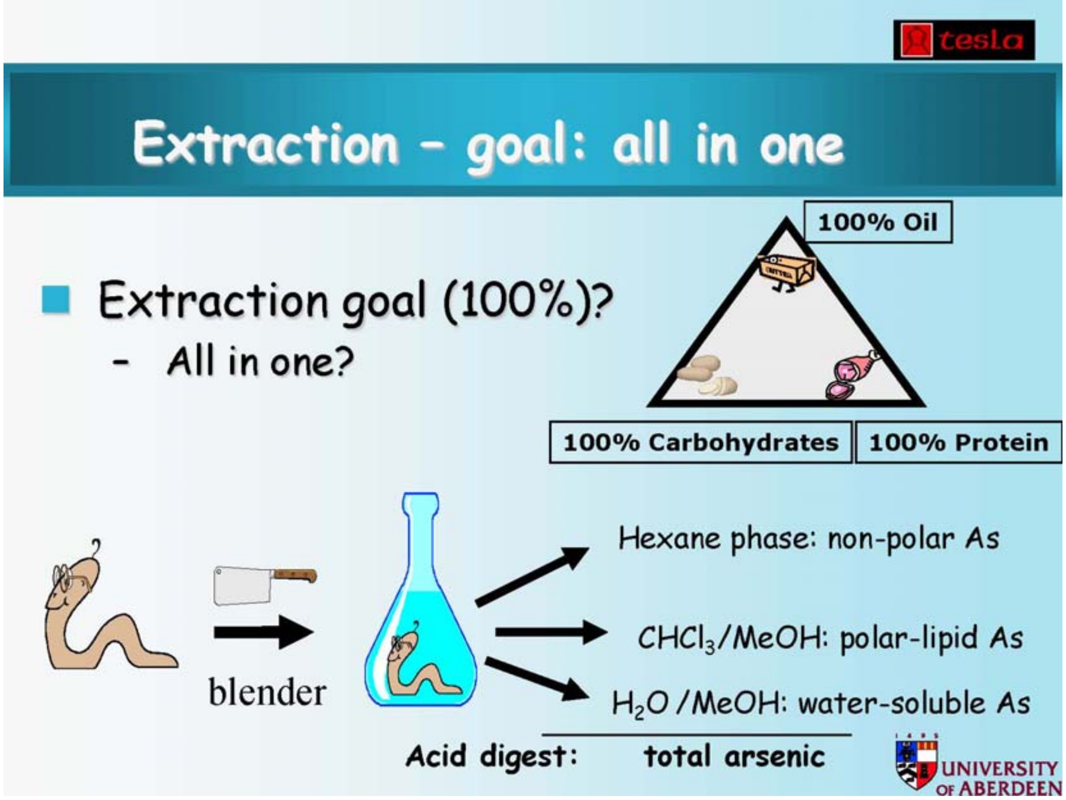


Extraction – goal: all in one

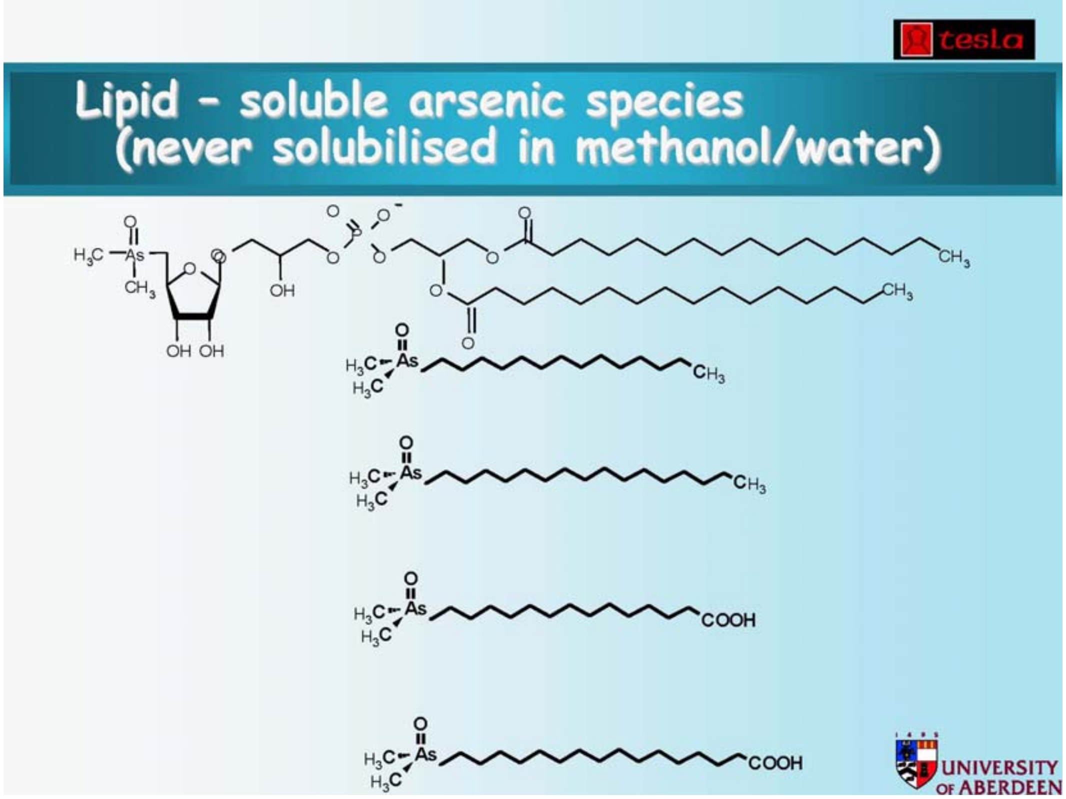
- Extraction goal (100%)?
  - All in one?

Hexane phase: non-polar As

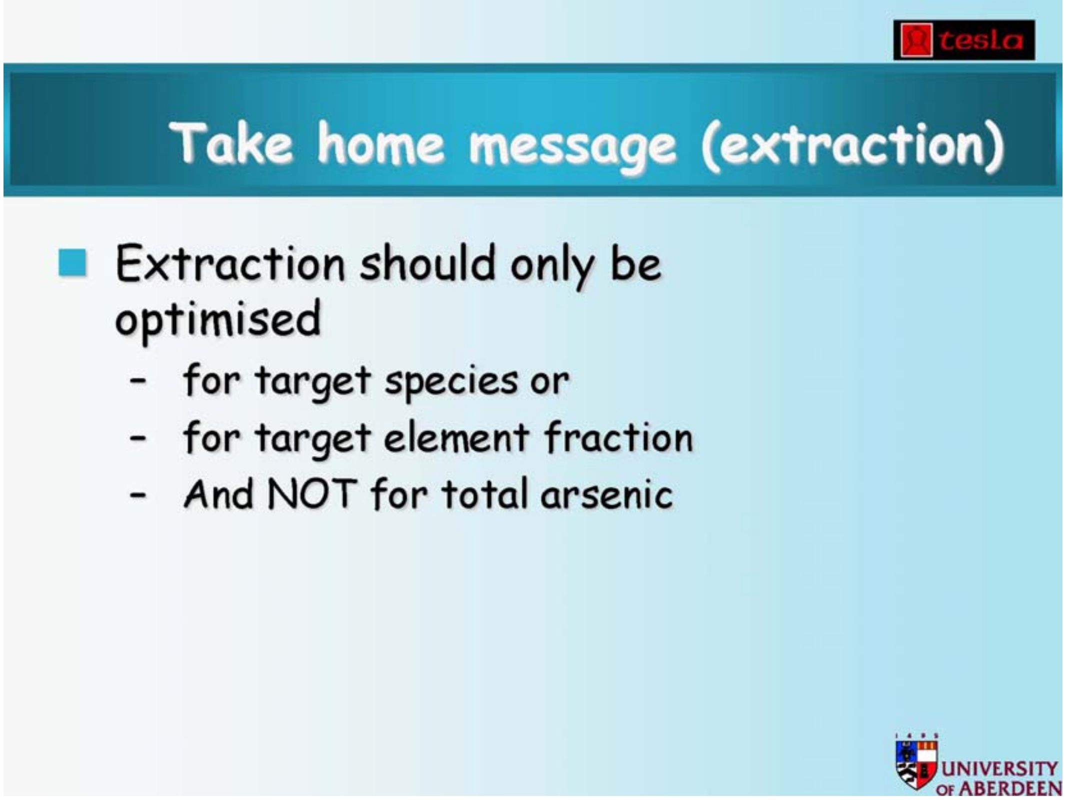
$CHCl_3$/MeOH: polar-lipid As

H_2O /MeOH: water-soluble As

Acid digest: **total arsenic**



Lipid – soluble arsenic species (never solubilised in methanol/water)



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Take home message (extraction)

- Extraction should only be optimised
  - for target species or
  - for target element fraction
  - And NOT for total arsenic

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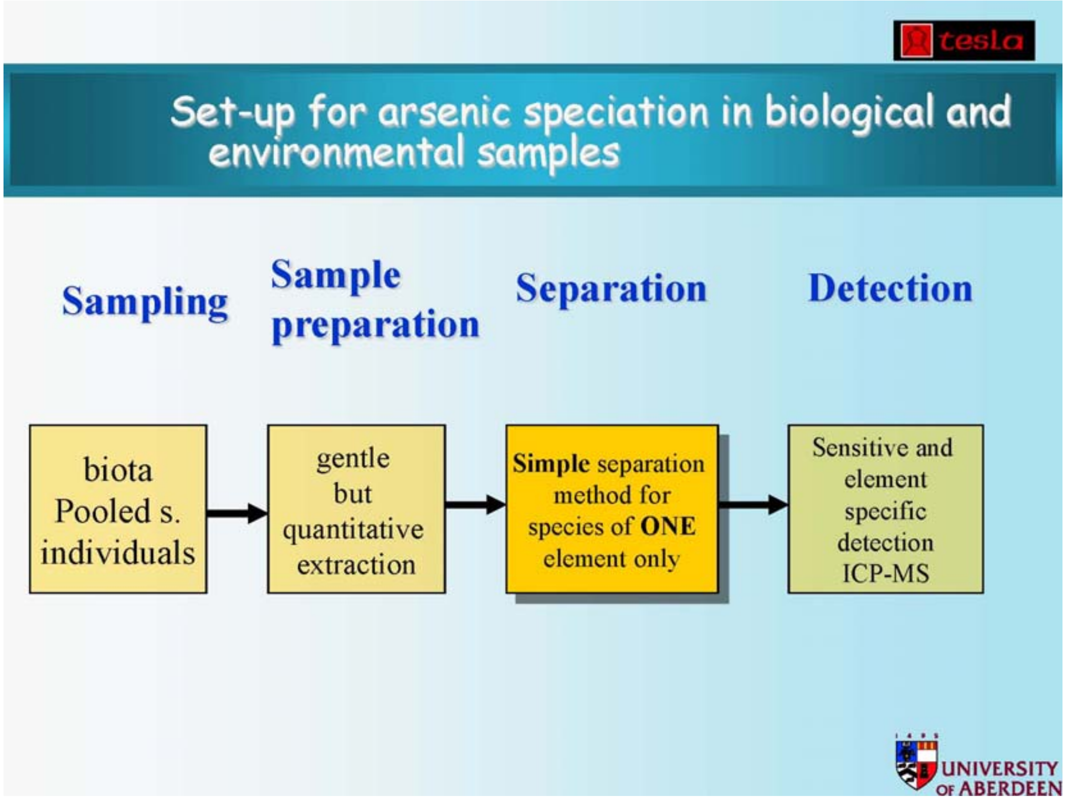

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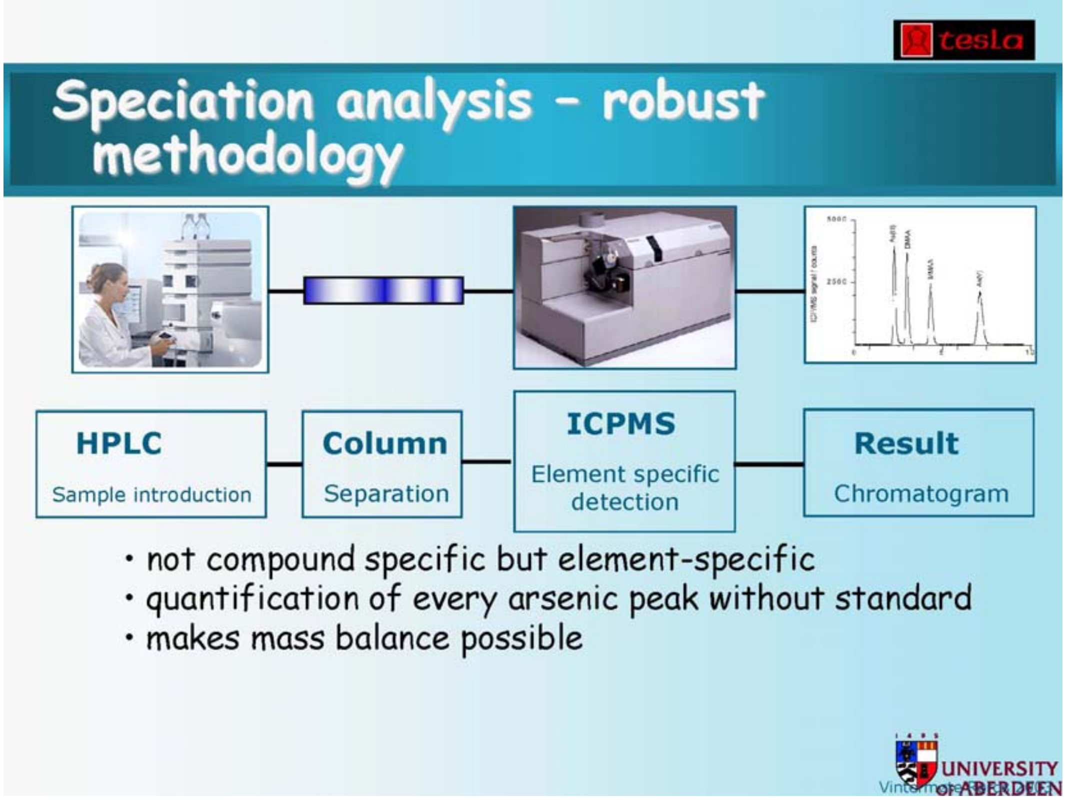


Speciation analysis – robust methodology

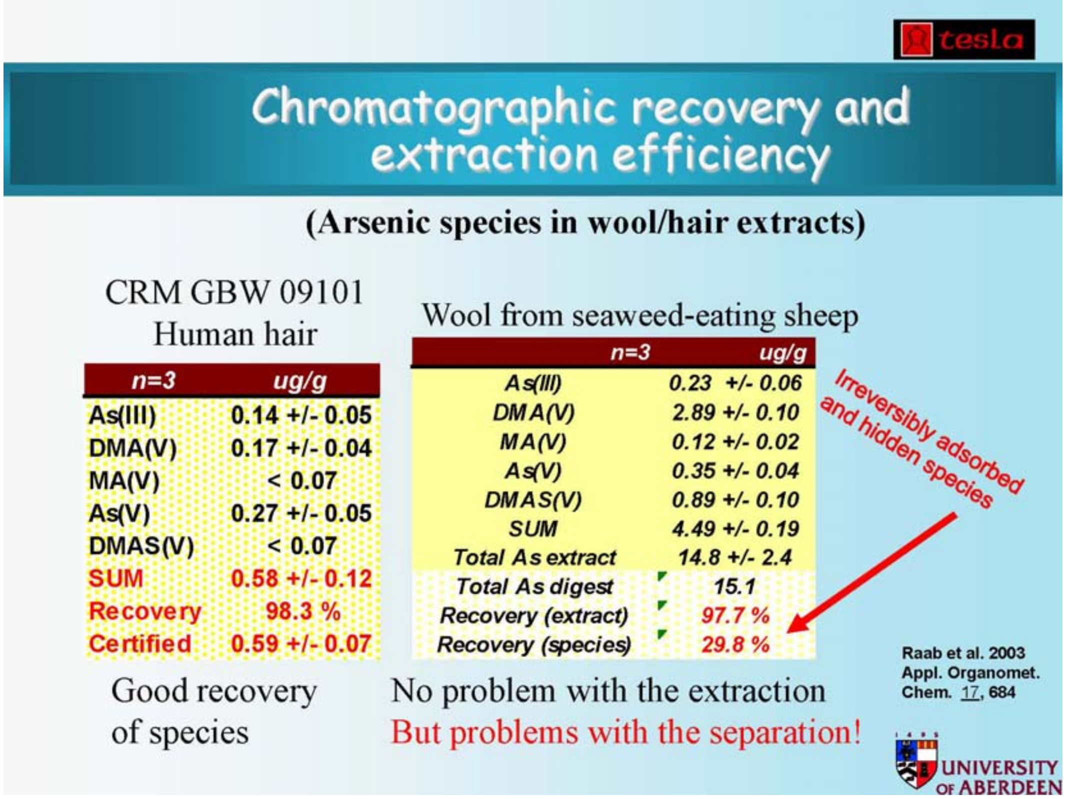
HPLC
Sample introduction

Column
Separation

ICPMS
Element specific detection

Result
Chromatogram

- not compound specific but element-specific
- quantification of every arsenic peak without standard
- makes mass balance possible



Chromatographic recovery and extraction efficiency

(Arsenic species in wool/hair extracts)

CRM GBW 09101
Human hair

n=3	ug/g
As(III)	0.14 +/- 0.05
DMA(V)	0.17 +/- 0.04
MA(V)	< 0.07
As(V)	0.27 +/- 0.05
DMAS(V)	< 0.07
SUM	0.58 +/- 0.12
Recovery	98.3 %
Certified	0.59 +/- 0.07

Good recovery of species

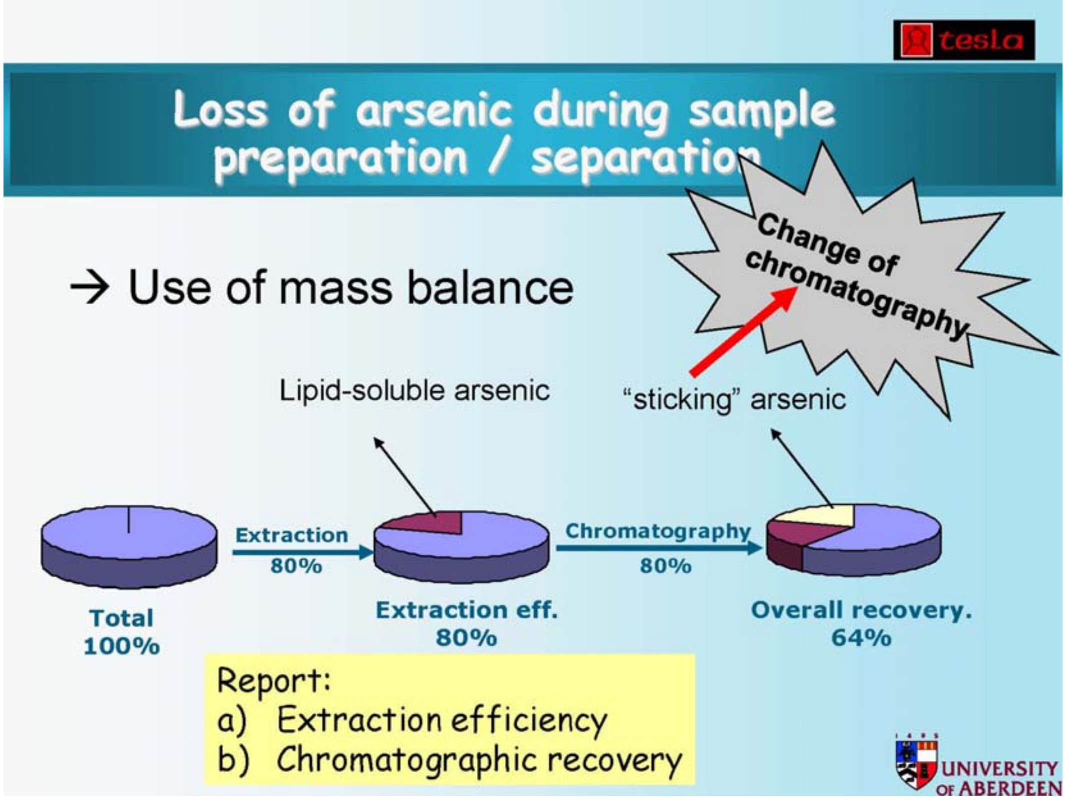
Wool from seaweed-eating sheep

n=3	ug/g
As(III)	0.23 +/- 0.06
DMA(V)	2.89 +/- 0.10
MA(V)	0.12 +/- 0.02
As(V)	0.35 +/- 0.04
DMAS(V)	0.89 +/- 0.10
SUM	4.49 +/- 0.19
Total As extract	14.8 +/- 2.4
Total As digest	15.1
Recovery (extract)	97.7 %
Recovery (species)	29.8 %

Irreversibly adsorbed and hidden species

No problem with the extraction
But problems with the separation!

Raab et al. 2003
Appl. Organomet. Chem. 17, 684



Loss of arsenic during sample preparation / separation

→ Use of mass balance

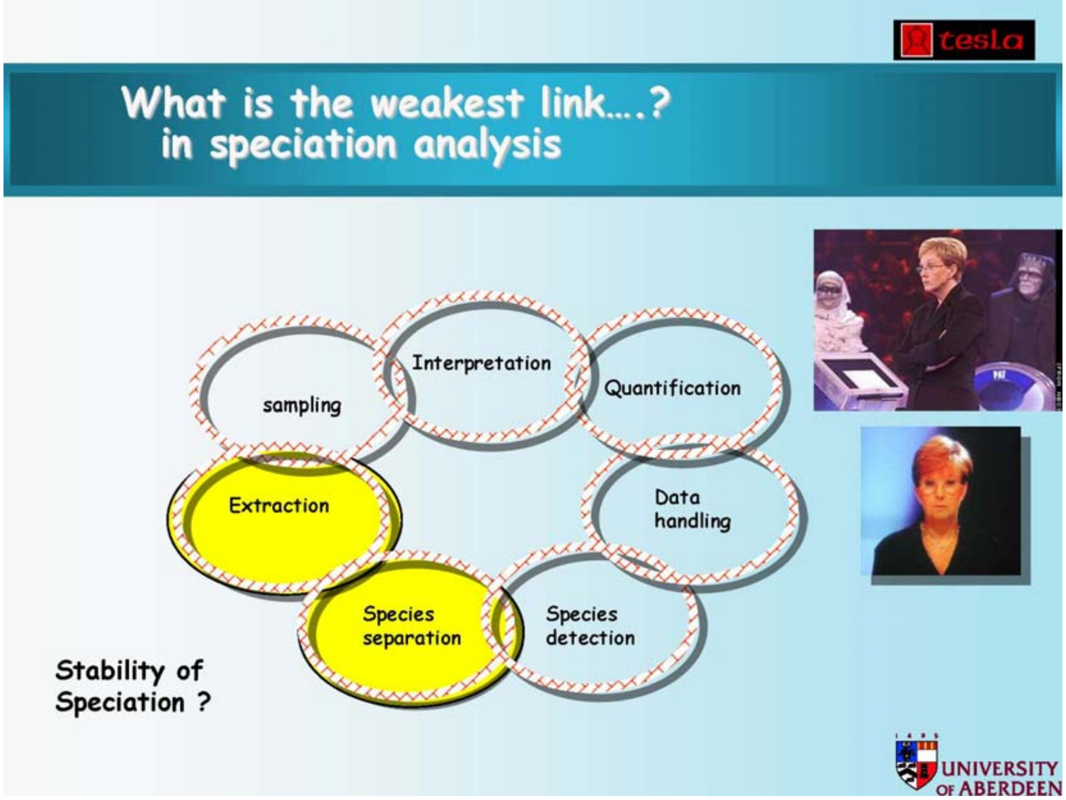
Report:

a) Extraction efficiency

b) Chromatographic recovery

Take home message (separation 1)

- chromatography can be optimised
  - for target arsenicals
  - needs checking for "all" arsenic species of one fraction.



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What is the weakest link….? in speciation analysis

sampling

Interpretation

Quantification

Extraction

Data handling

Species separation

Species detection

Stability of Speciation ?

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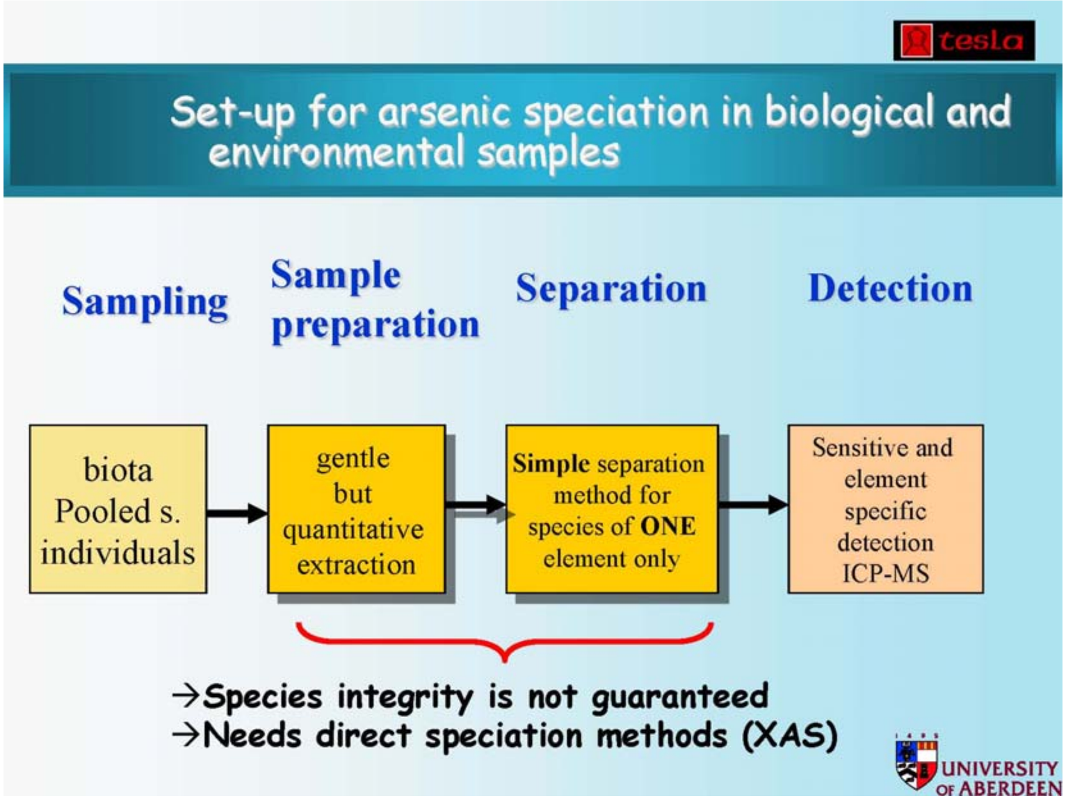

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Set-up for arsenic speciation in biological and environmental samples

Sampling → **Sample preparation** → **Separation** → **Detection**

biota Pooled s. individuals

gentle but quantitative extraction

Simple separation method for species of **ONE** element only

Sensitive and element specific detection ICP-MS

→Species integrity is not guaranteed

→Needs direct speciation methods (XAS)

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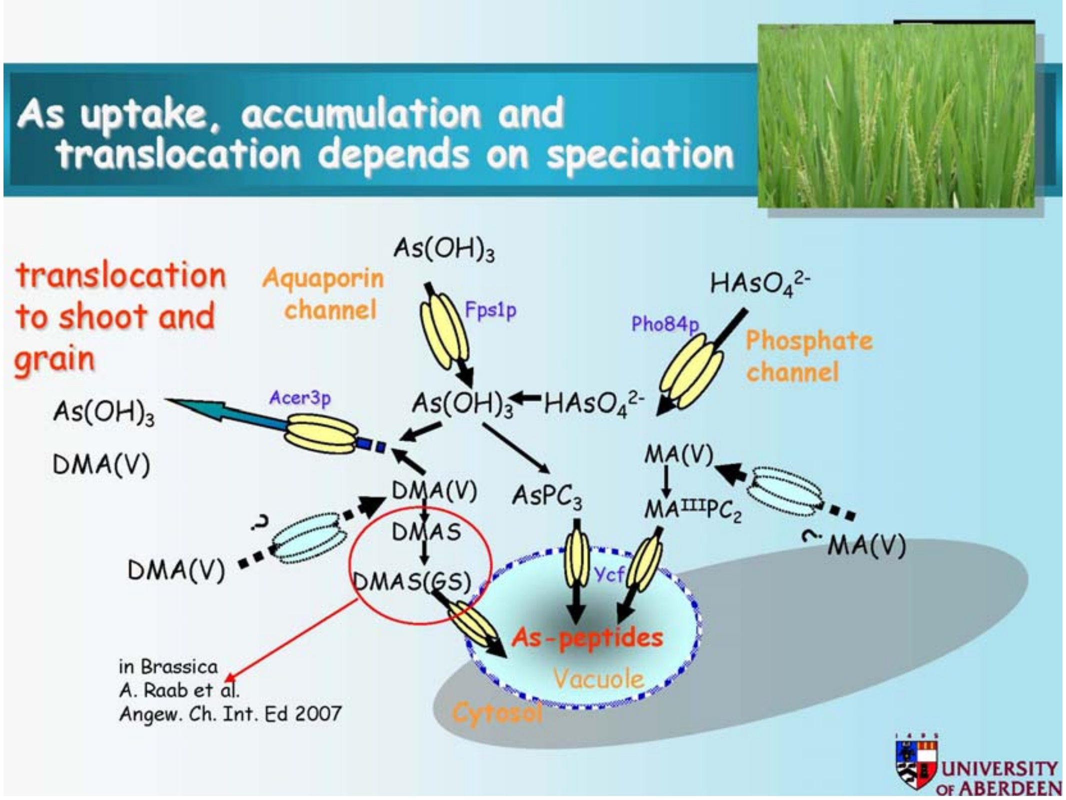

As uptake, accumulation and translocation depends on speciation

translocation to shoot and grain

As(OH)$_3$

DMA(V)

Aquaporin channel

Phosphate channel

in Brassica
A. Raab et al.
Angew. Ch. Int. Ed 2007

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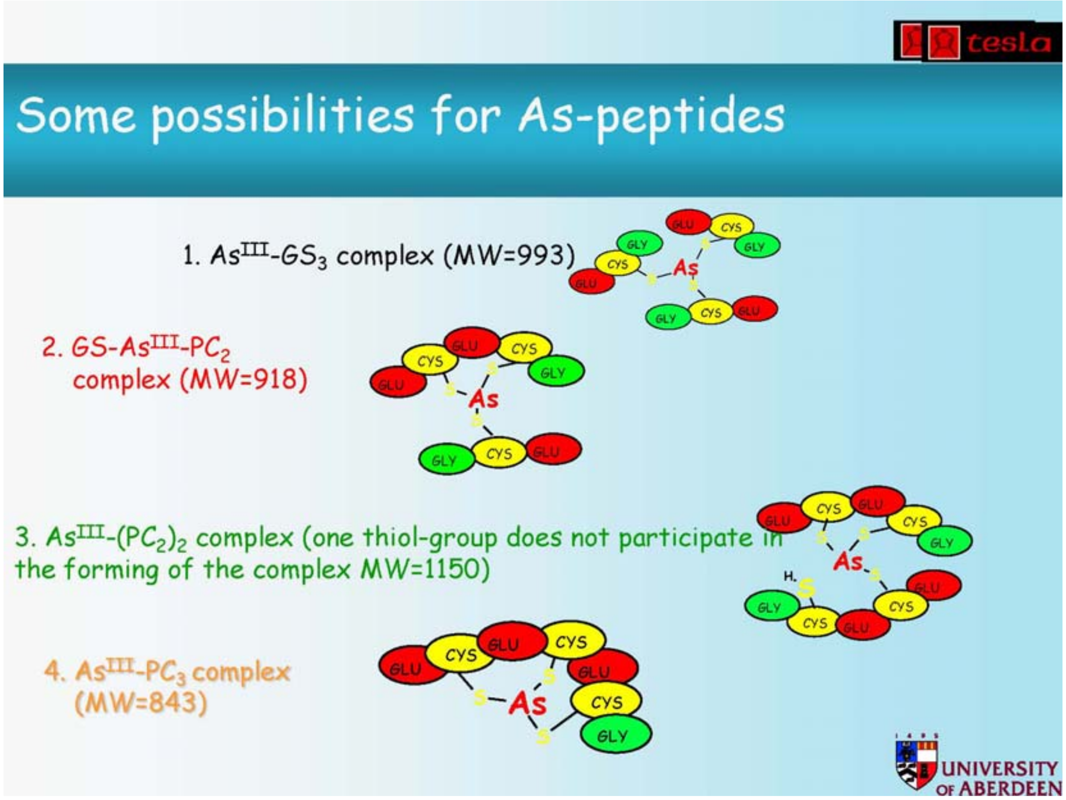

Some possibilities for As-peptides

1. As^{III}-GS$_3$ complex (MW=993)

2. GS-As^{III}-PC$_2$ complex (MW=918)

3. As^{III}-(PC$_2$)$_2$ complex (one thiol-group does not participate in the forming of the complex MW=1150)

4. As^{III}-PC$_3$ complex (MW=843)

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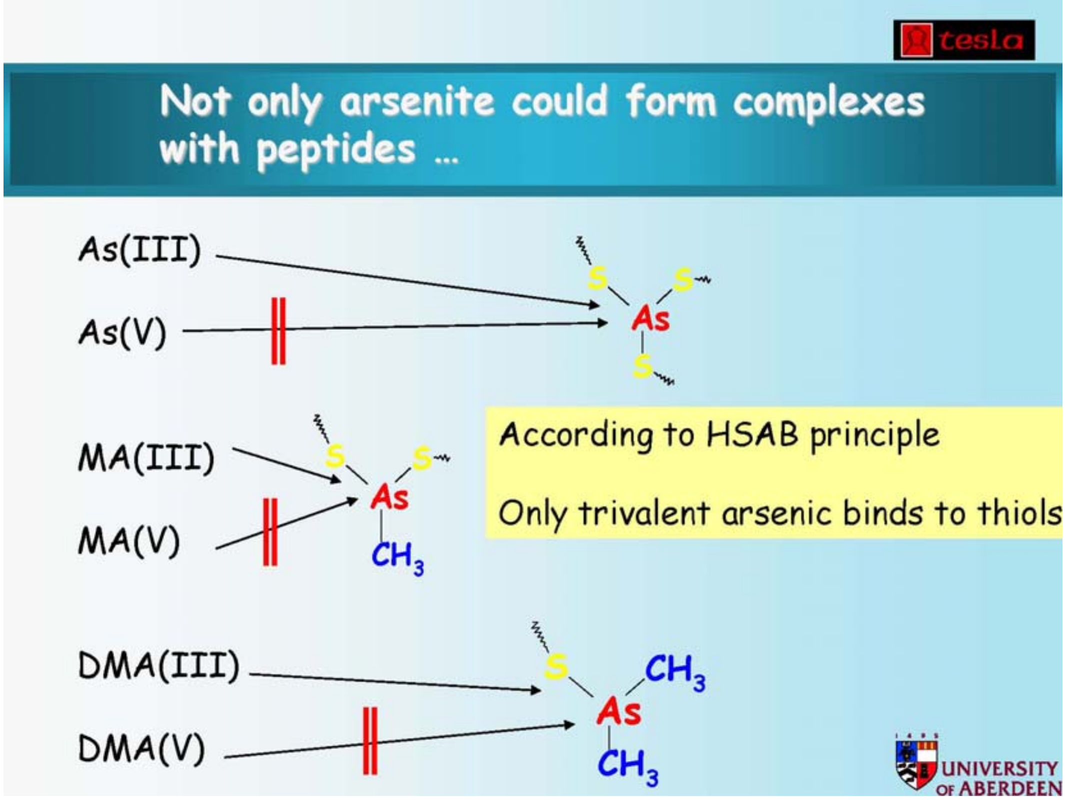
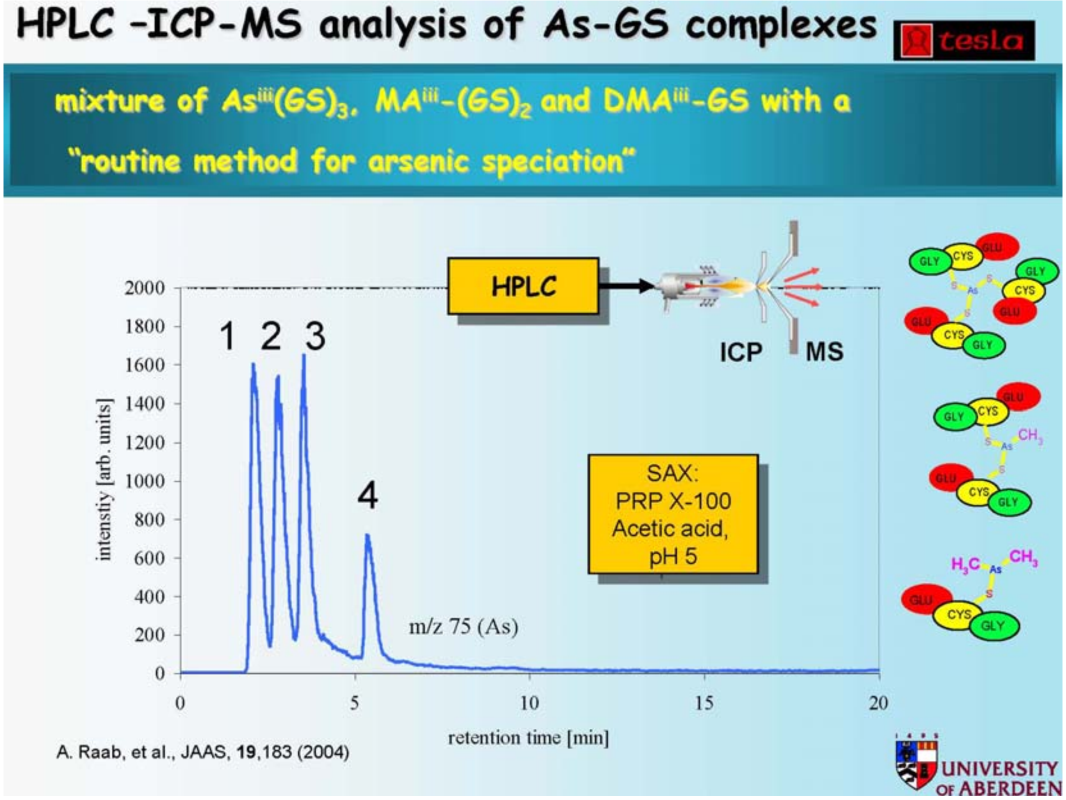


Not only arsenite could form complexes with peptides …

According to HSAB principle

Only trivalent arsenic binds to thiols



HPLC –ICP-MS analysis of As-GS complexes

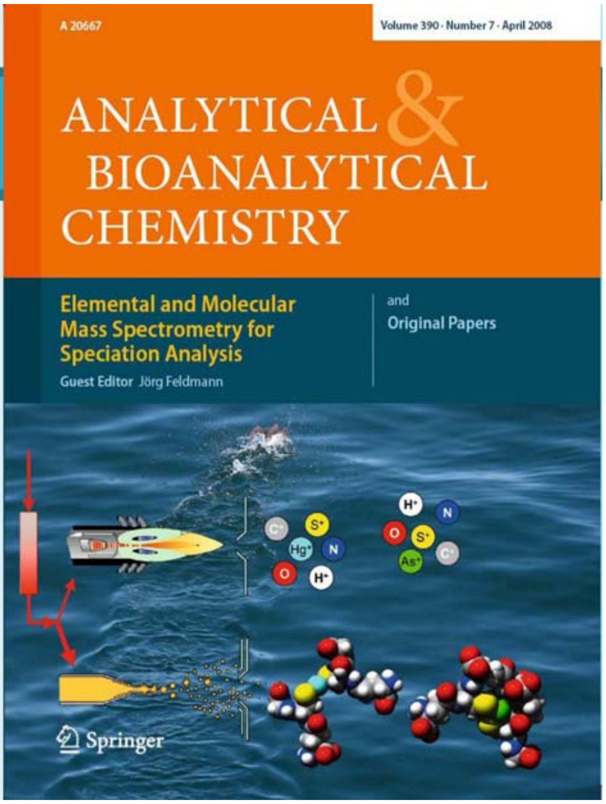
mixture of $As^{iii}(GS)_3$, MA^{iii}-$(GS)_2$ and DMA^{iii}-GS with a "routine method for arsenic speciation"

SAX:
PRP X-100
Acetic acid,
pH 5

A. Raab, et al., JAAS, **19**,183 (2004)

Analytical methodology

- Element-specific detection for HPLC by ICPMS
  - Identification of element containing species
  - Quantification w/o a species standard
- Simultaneous molecular detection by ES-MS
  - Molecular mass identification
  - Structure information



A 20667

Volume 390 · Number 7 · April 2008

ANALYTICAL & BIOANALYTICAL CHEMISTRY

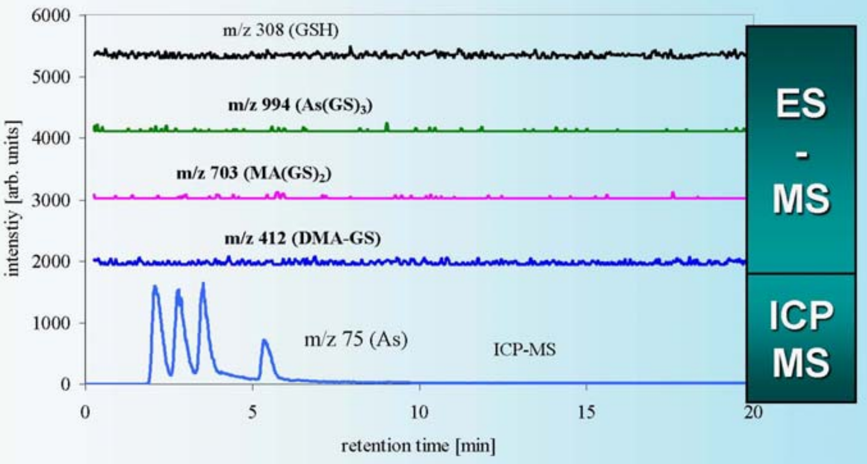
Elemental and Molecular Mass Spectrometry for Speciation Analysis

Guest Editor Jörg Feldmann

and Original Papers

Springer

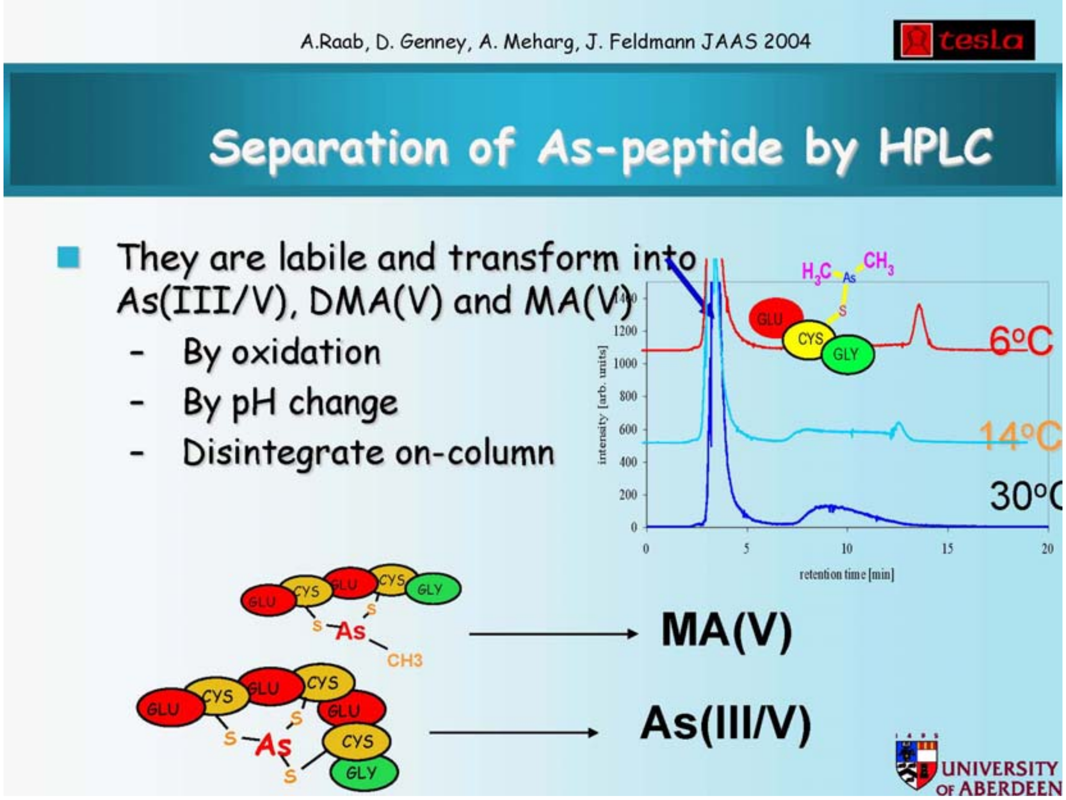
HPLC -ICP-MS / ES-MS of $As(GS)_3$, $MA(GS)_2$, DMA(GS)



Decomposition on column

A. Raab, et al.
JAAS, **19**,183 (2004)

UNIVERSITY OF ABERDEEN



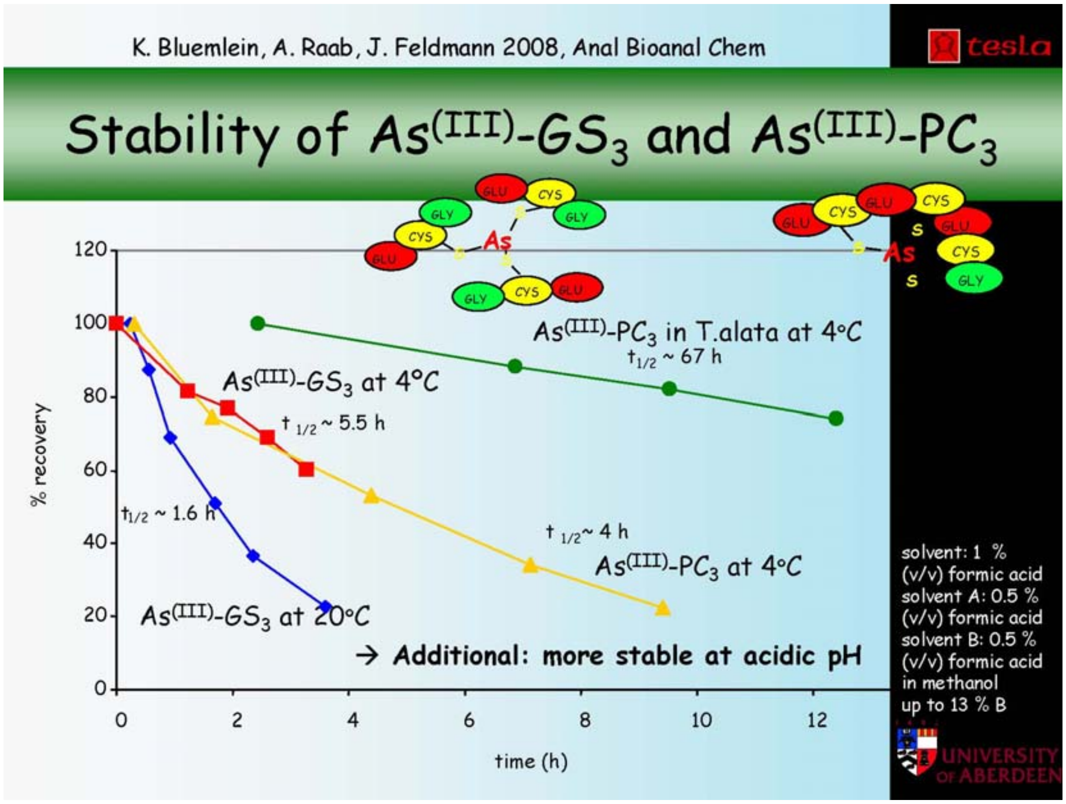
A.Raab, D. Genney, A. Meharg, J. Feldmann JAAS 2004

Separation of As-peptide by HPLC

- They are labile and transform into As(III/V), DMA(V) and MA(V)
  - By oxidation
  - By pH change
  - Disintegrate on-column

MA(V)

As(III/V)

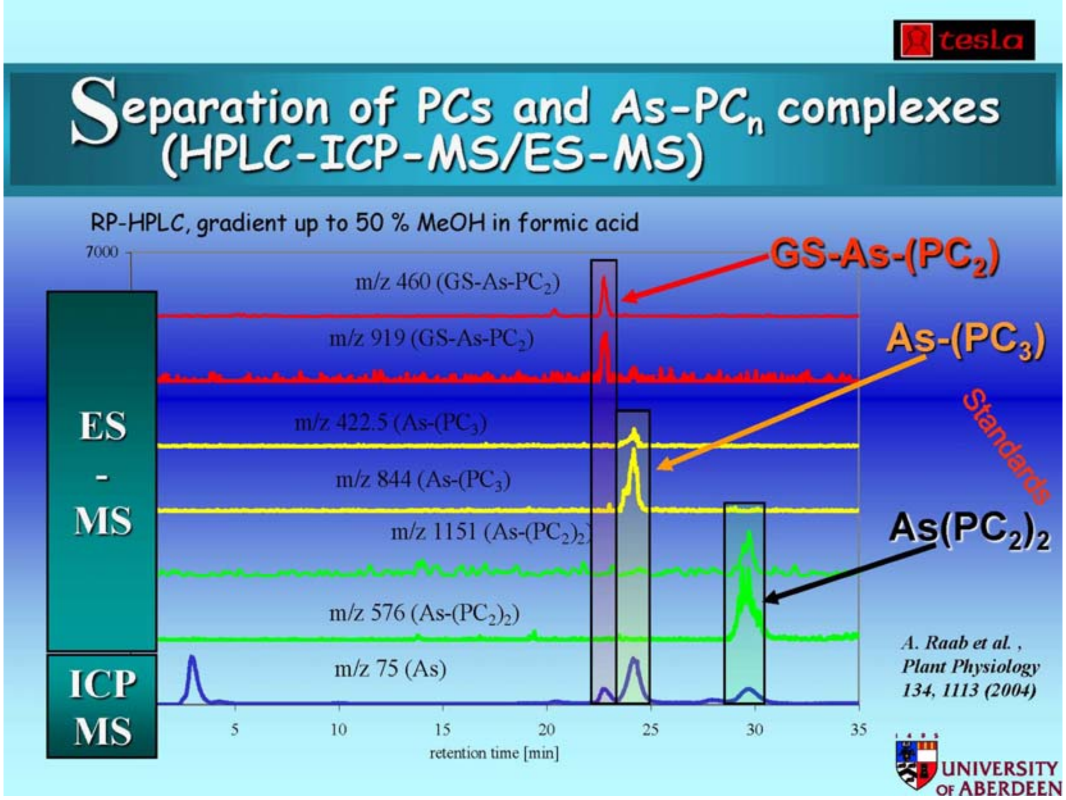


K. Bluemlein, A. Raab, J. Feldmann 2008, Anal Bioanal Chem

Stability of As$^{(III)}$-GS$_3$ and As$^{(III)}$-PC$_3$

→ **Additional: more stable at acidic pH**

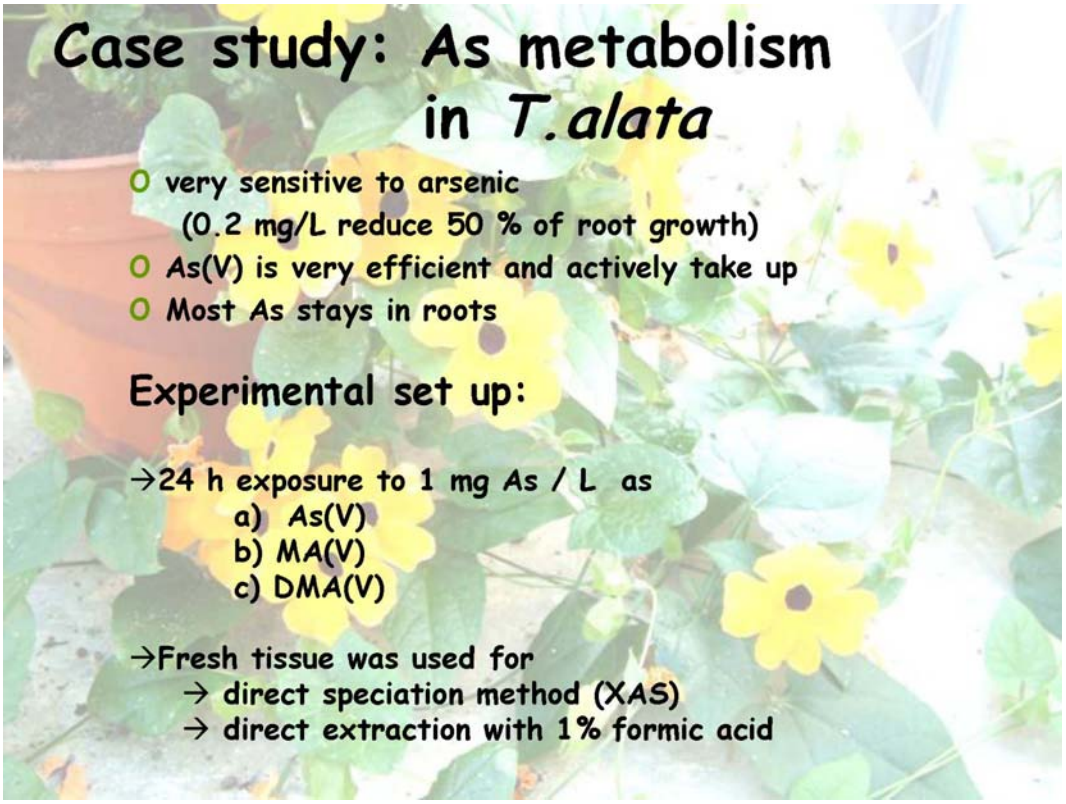
solvent: 1 % (v/v) formic acid
solvent A: 0.5 % (v/v) formic acid
solvent B: 0.5 % (v/v) formic acid in methanol
up to 13 % B



Separation of PCs and As-PC$_n$ complexes (HPLC-ICP-MS/ES-MS)

RP-HPLC, gradient up to 50 % MeOH in formic acid

A. Raab et al. , Plant Physiology 134, 1113 (2004)



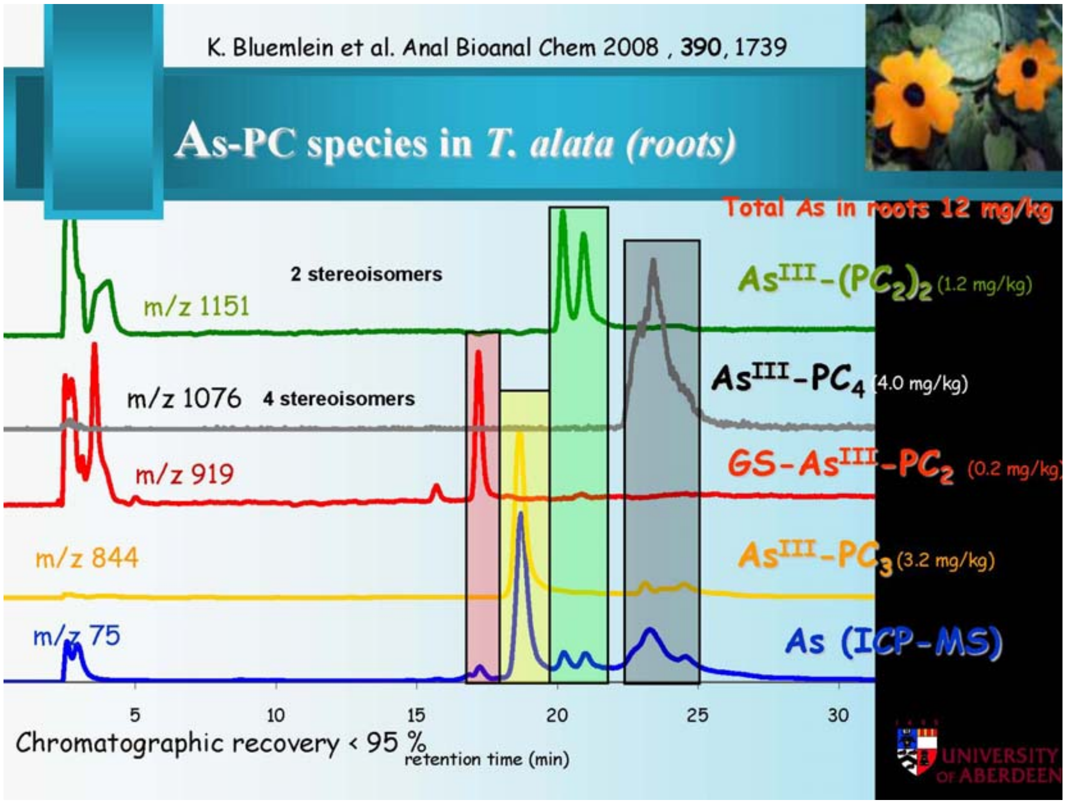
Case study: As metabolism in *T.alata*

- very sensitive to arsenic
  (0.2 mg/L reduce 50 % of root growth)
- As(V) is very efficient and actively take up
- Most As stays in roots

Experimental set up:

→24 h exposure to 1 mg As / L as
- a) As(V)
- b) MA(V)
- c) DMA(V)

→Fresh tissue was used for
- → direct speciation method (XAS)
- → direct extraction with 1% formic acid



K. Bluemlein et al. Anal Bioanal Chem 2008 , **390**, 1739

As-PC species in *T. alata (roots)*

Total As in roots 12 mg/kg

As^{III}-$(PC_2)_2$ (1.2 mg/kg)

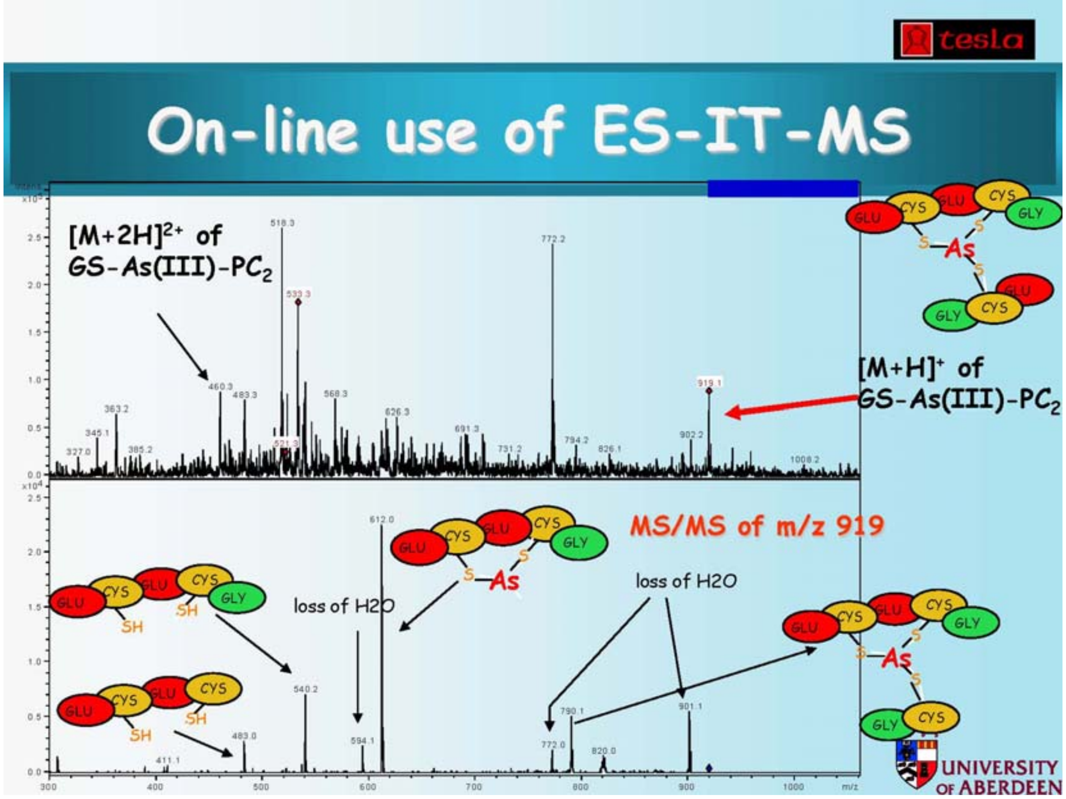
As^{III}-PC_4 (4.0 mg/kg)

GS-As^{III}-PC_2 (0.2 mg/kg)

As^{III}-PC_3 (3.2 mg/kg)

As (ICP-MS)

Chromatographic recovery < 95 %



On-line use of ES-IT-MS

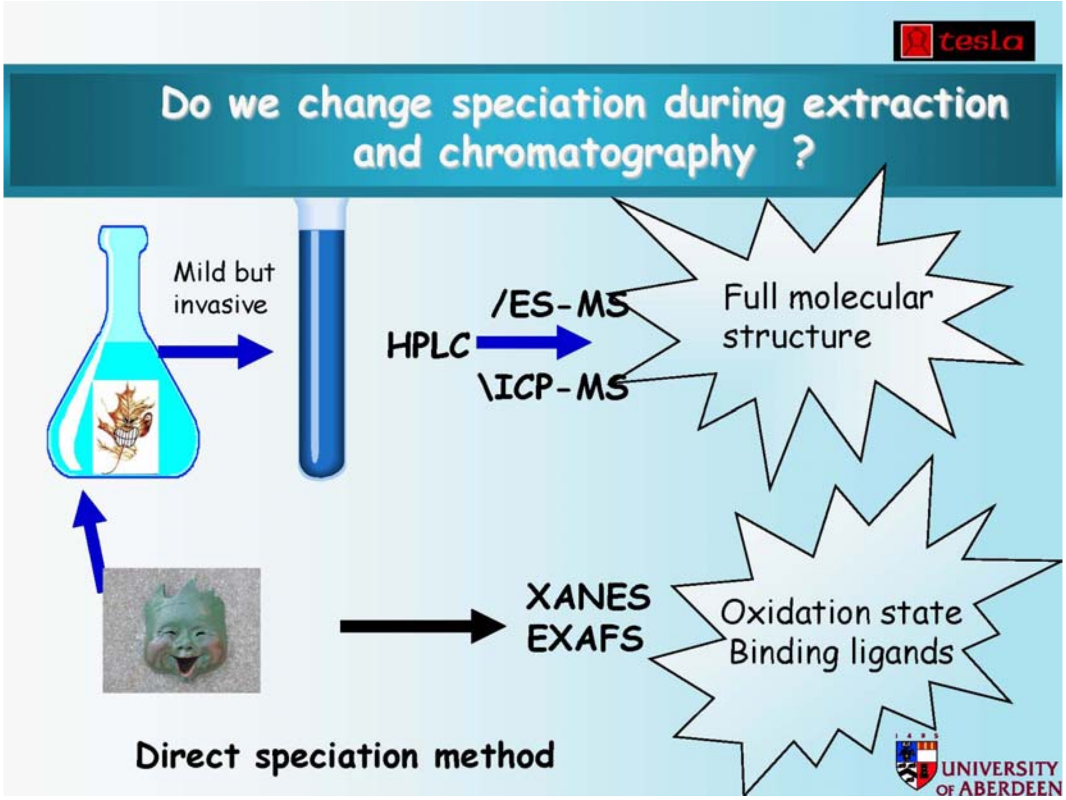
$[M+2H]^{2+}$ of GS-As(III)-PC_2

$[M+H]^{+}$ of GS-As(III)-PC_2

MS/MS of m/z 919

loss of H2O

loss of H2O



tesla

Do we change speciation during extraction and chromatography ?

Mild but invasive

HPLC /ES-MS \ICP-MS

Full molecular structure

XANES
EXAFS

Oxidation state
Binding ligands

Direct speciation method

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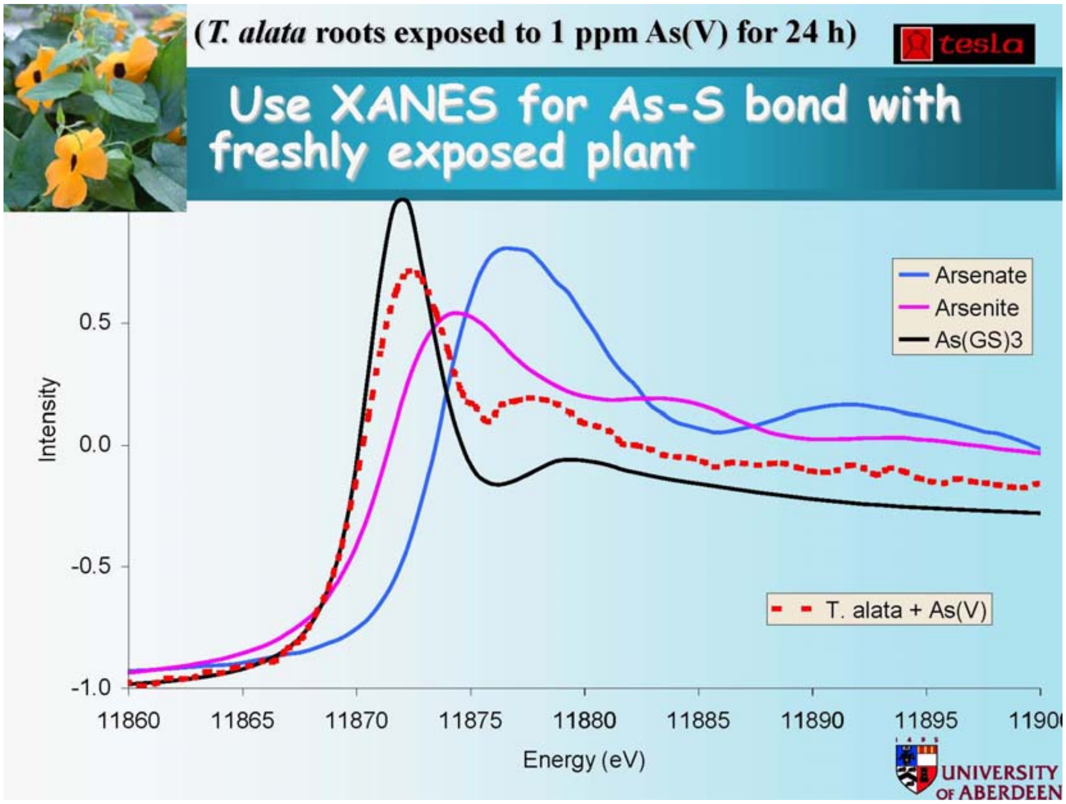

(*T. alata* roots exposed to 1 ppm As(V) for 24 h)

tesla

Use XANES for As-S bond with freshly exposed plant

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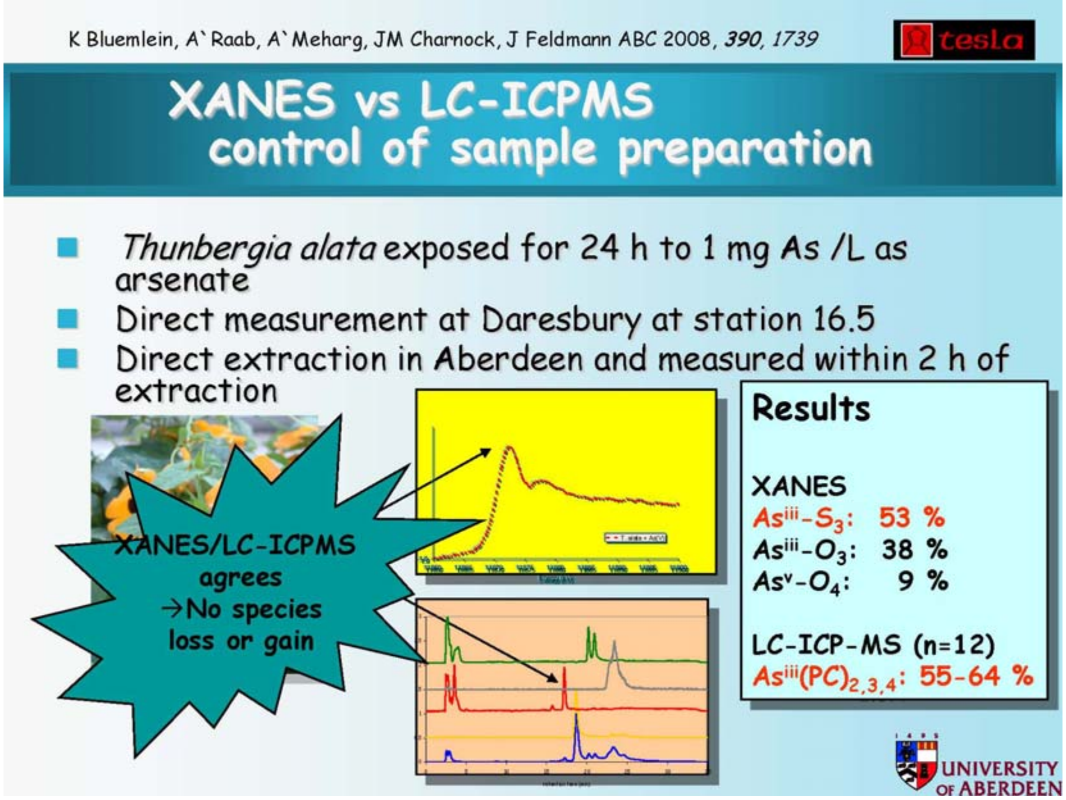


K Bluemlein, A`Raab, A`Meharg, JM Charnock, J Feldmann ABC 2008, ***390*, *1739***

XANES vs LC-ICPMS control of sample preparation

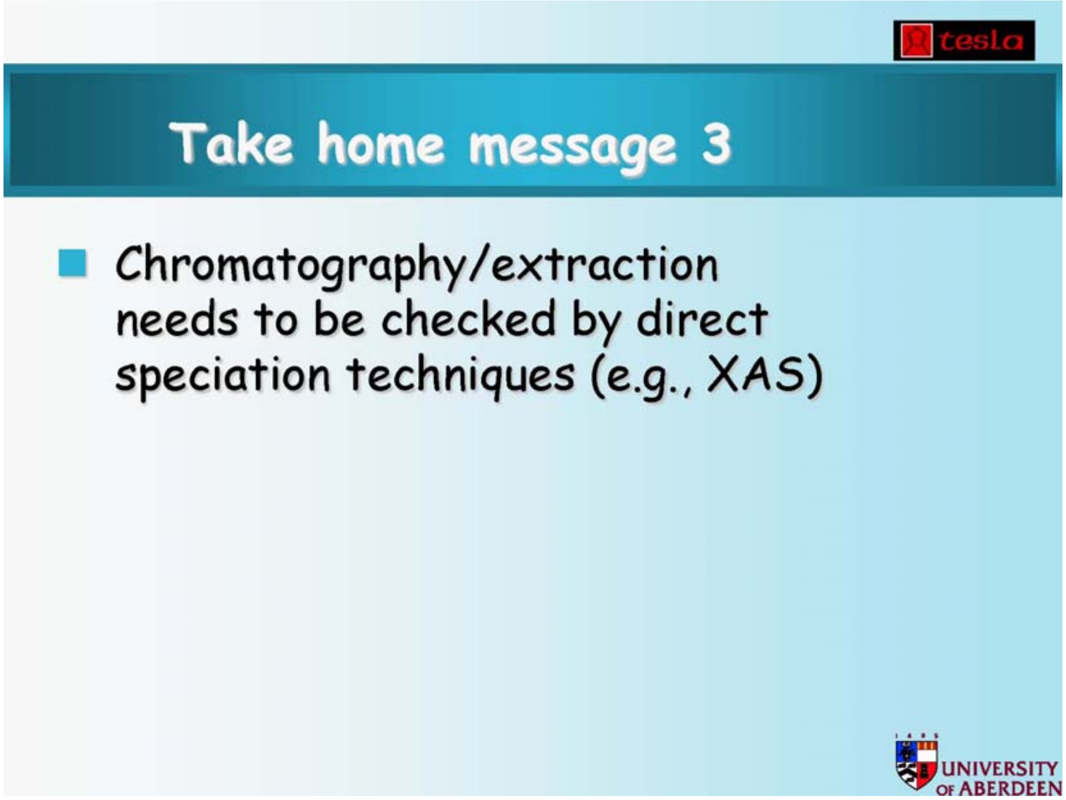
- *Thunbergia alata* exposed for 24 h to 1 mg As /L as arsenate
- Direct measurement at Daresbury at station 16.5
- Direct extraction in Aberdeen and measured within 2 h of extraction

XANES/LC-ICPMS agrees
→No species loss or gain

Results

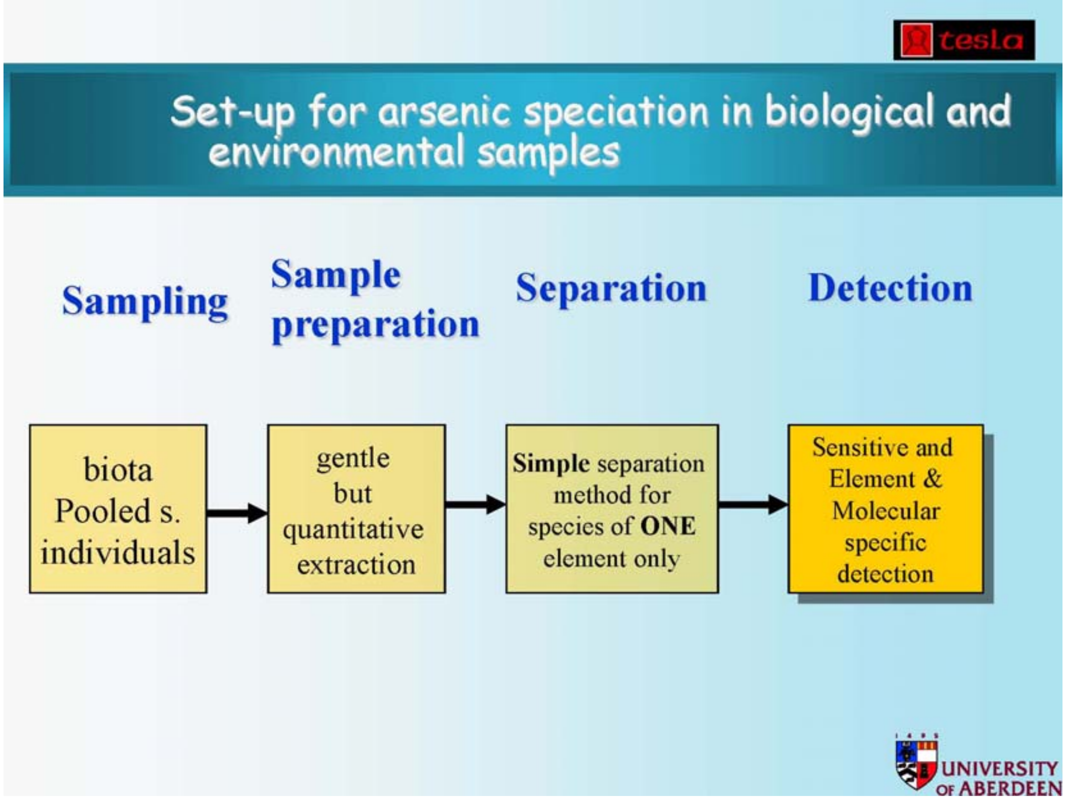
XANES
As^{iii}-S_3: 53 %
As^{iii}-O_3: 38 %
As^{v}-O_4: 9 %

LC-ICP-MS (n=12)
$As^{iii}(PC)_{2,3,4}$: 55-64 %



Take home message 3

- Chromatography/extraction needs to be checked by direct speciation techniques (e.g., XAS)



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Set-up for arsenic speciation in biological and environmental samples

Sampling → **Sample preparation** → **Separation** → **Detection**

- biota Pooled s. individuals
- gentle but quantitative extraction
- **Simple** separation method for species of **ONE** element only
- Sensitive and Element & Molecular specific detection

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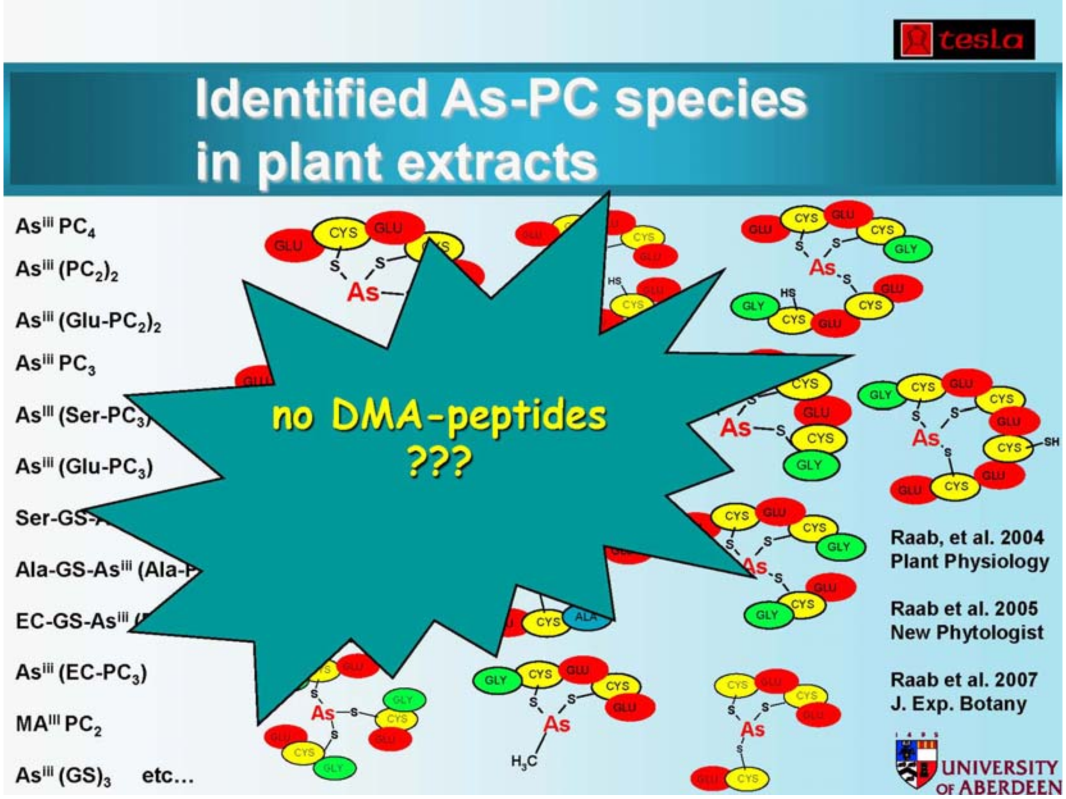

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Identified As-PC species in plant extracts

- As^{iii} PC_4
- As^{iii} $(PC_2)_2$
- As^{iii} $(Glu\text{-}PC_2)_2$
- As^{iii} PC_3
- As^{iii} $(Ser\text{-}PC_3)$
- As^{iii} $(Glu\text{-}PC_3)$
- Ser-GS-
- Ala-GS-As^{iii} (Ala-
- EC-GS-As^{iii}
- As^{iii} $(EC\text{-}PC_3)$
- MA^{III} PC_2
- As^{iii} $(GS)_3$ etc…

no DMA-peptides ???

Raab, et al. 2004 Plant Physiology

Raab et al. 2005 New Phytologist

Raab et al. 2007 J. Exp. Botany

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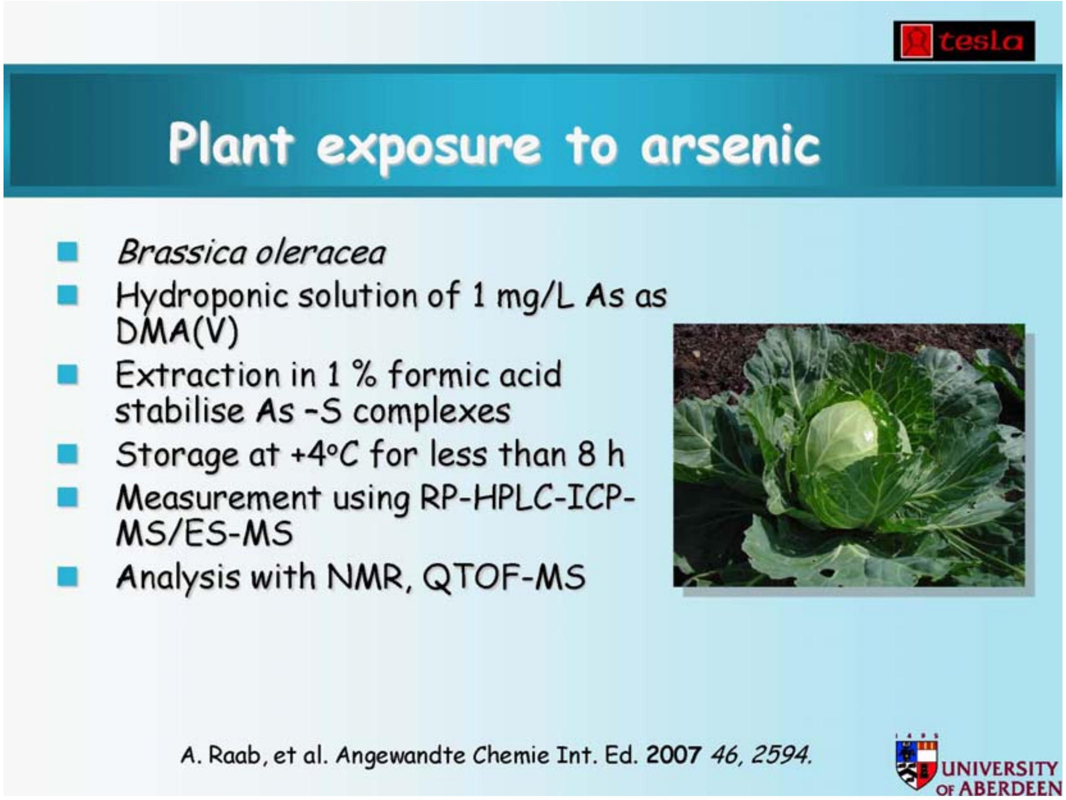


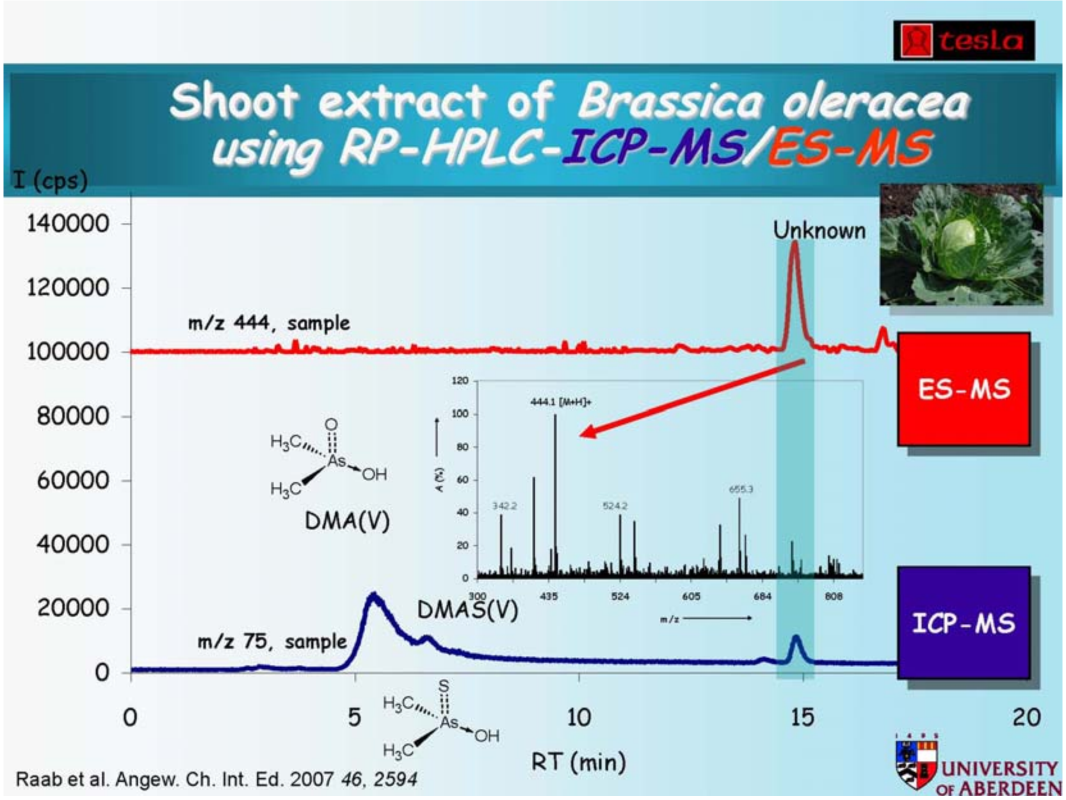
tesla

Plant exposure to arsenic

- *Brassica oleracea*
- Hydroponic solution of 1 mg/L As as DMA(V)
- Extraction in 1 % formic acid stabilise As -S complexes
- Storage at +4°C for less than 8 h
- Measurement using RP-HPLC-ICP-MS/ES-MS
- Analysis with NMR, QTOF-MS

A. Raab, et al. Angewandte Chemie Int. Ed. **2007** *46, 2594.*

UNIVERSITY OF ABERDEEN



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Shoot extract of *Brassica oleracea* using *RP-HPLC-ICP-MS/ES-MS*

Raab et al. Angew. Ch. Int. Ed. 2007 *46, 2594*

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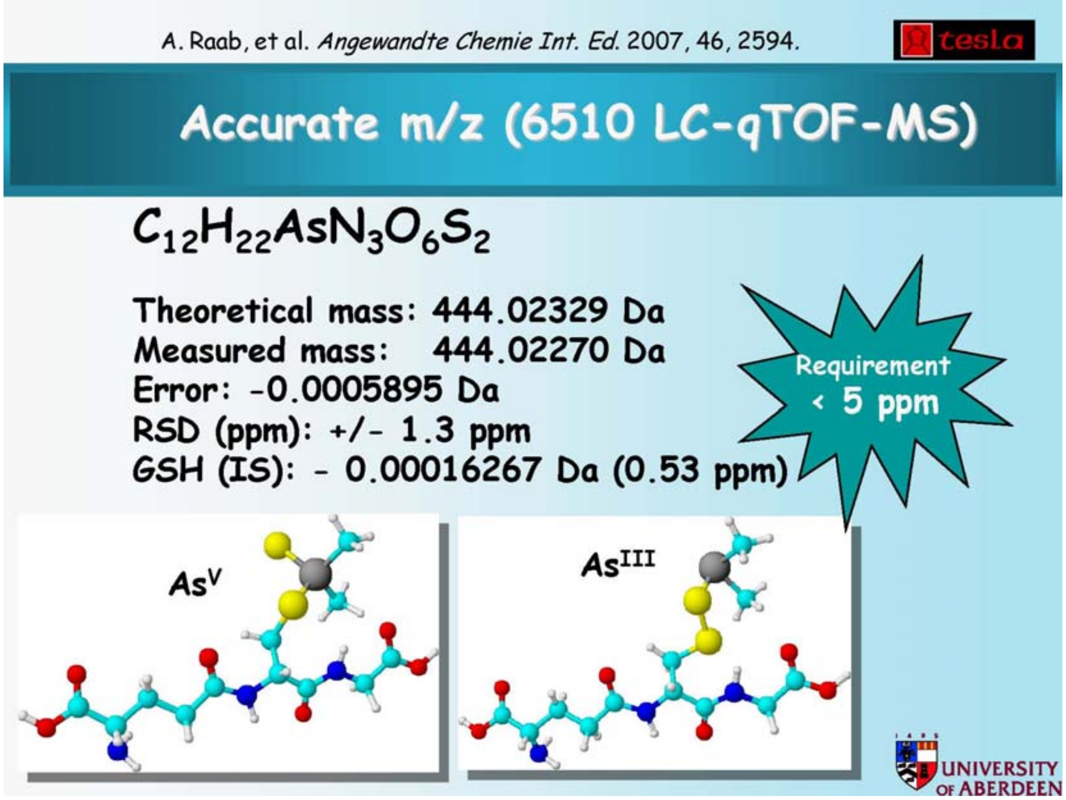


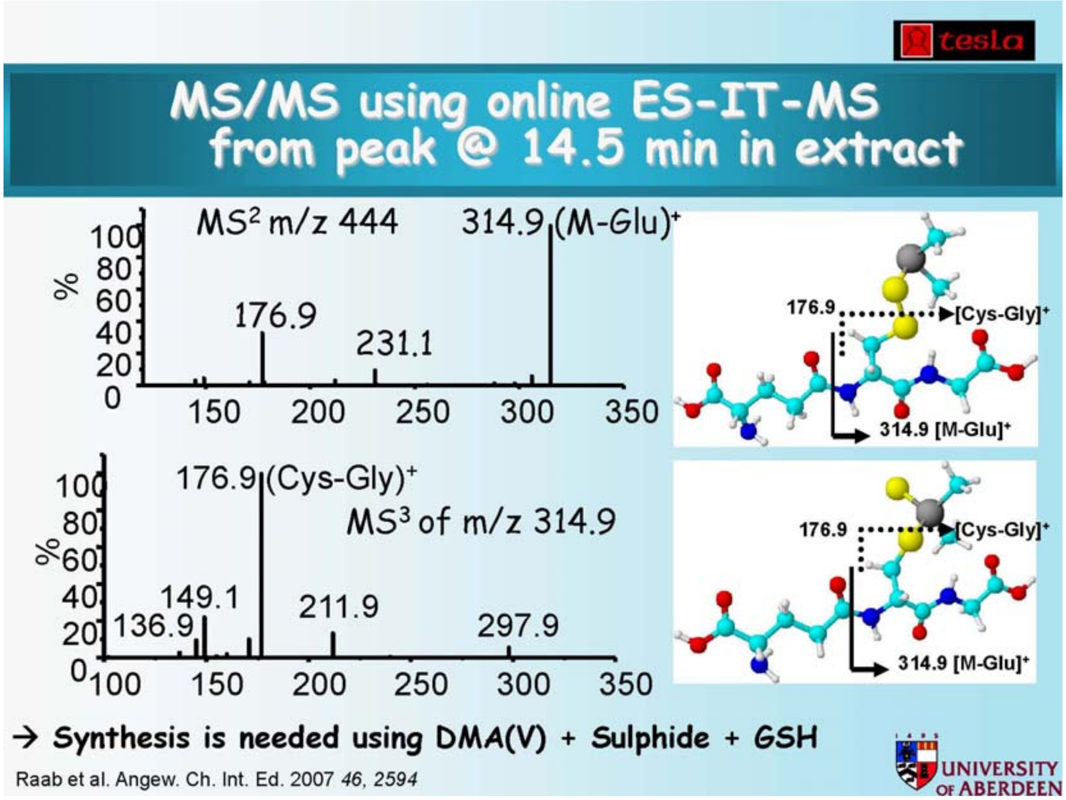
A. Raab, et al. *Angewandte Chemie Int. Ed.* 2007, 46, 2594.

Accurate m/z (6510 LC-qTOF-MS)

$C_{12}H_{22}AsN_3O_6S_2$

Theoretical mass: 444.02329 Da
Measured mass: 444.02270 Da
Error: -0.0005895 Da
RSD (ppm): +/- 1.3 ppm
GSH (IS): - 0.00016267 Da (0.53 ppm)

Requirement
< 5 ppm



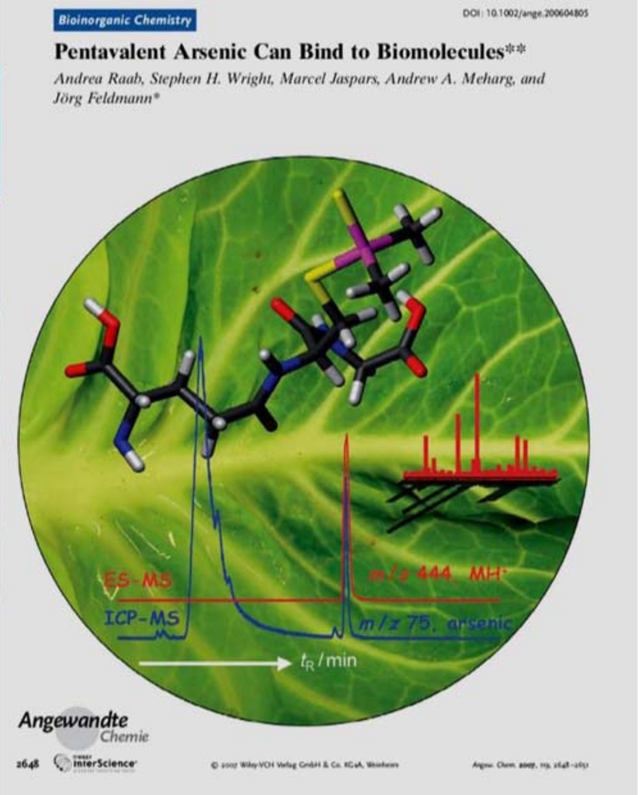
MS/MS using online ES-IT-MS from peak @ 14.5 min in extract

→ Synthesis is needed using DMA(V) + Sulphide + GSH

Raab et al. Angew. Ch. Int. Ed. 2007 *46, 2594*

¹H-NMR

	Chemical shift / ppm
DMA^{V}	1.97 ppm
$DMAS^{V}$	1.99 ppm
$DMAS^{V}$-GS	1.99 ppm
DMA^{III}-GS	1.34 ppm
DMA^{III}	1.36 ppm



Bioinorganic Chemistry

DOI: 10.1002/ange.200604805

Pentavalent Arsenic Can Bind to Biomolecules****

*Andrea Raab, Stephen H. Wright, Marcel Jaspars, Andrew A. Meharg, and Jörg Feldmann**

Angewandte Chemie

2648 Wiley InterScience

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Angew. Chem. 2007, 119, 2648–2651

tesla

Conclusion

- Arsenic speciation analysis is very complex
- “all species at once” is not possible
- Labile species can be disintegrated during extraction or chromatography
- Simultaneous MS is useful for molecular detection of new species
- MS methods need direct speciation methods such as XANES/EXAFS to validate analytical protocol

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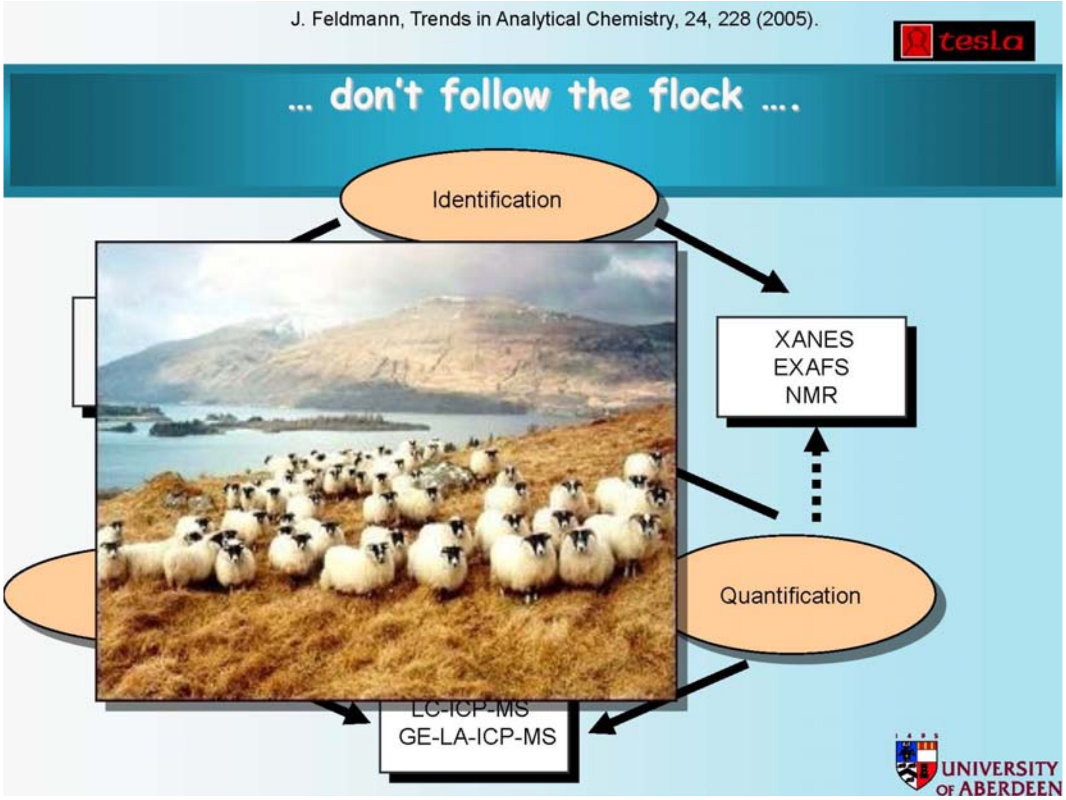


J. Feldmann, Trends in Analytical Chemistry, 24, 228 (2005).

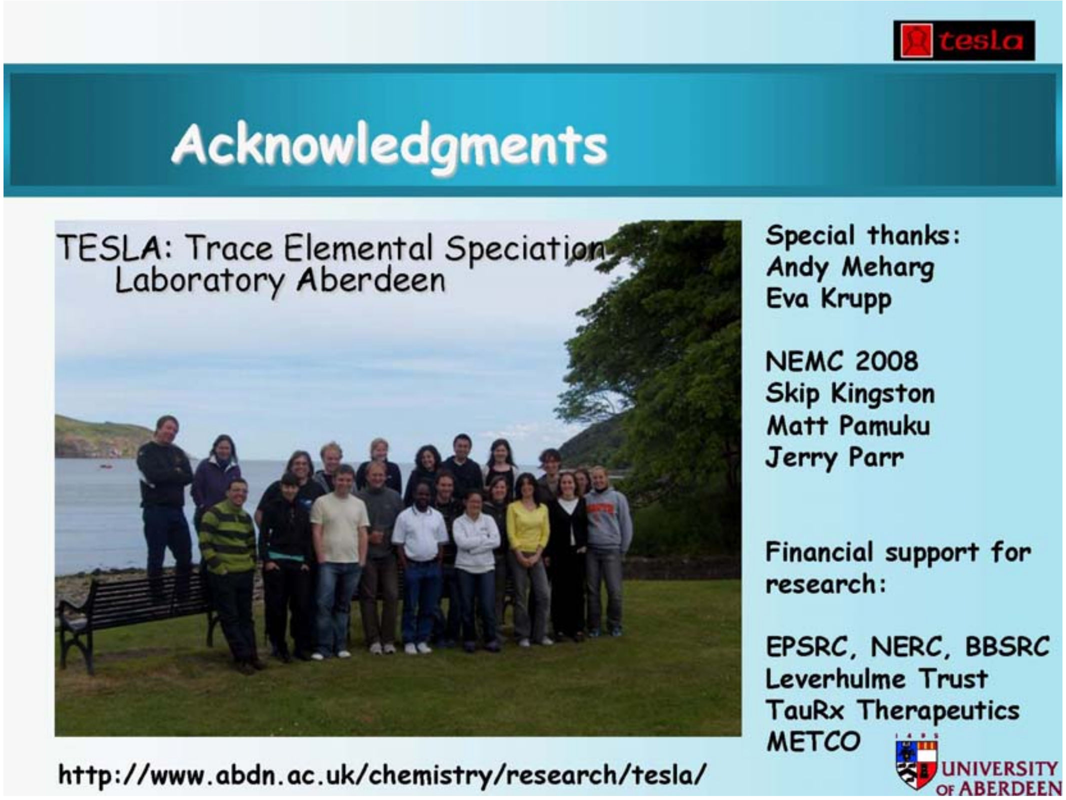
… don't follow the flock ….

Identification

XANES
EXAFS
NMR

Quantification

LC-ICP-MS
GE-LA-ICP-MS



Acknowledgments

TESLA: Trace Elemental Speciation Laboratory Aberdeen

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TauRx Therapeutics
METCO

http://www.abdn.ac.uk/chemistry/research/tesla/

Determination of Arsenic and Selenium Species in Rice and Baby Food Products by IC–ICP-MS After Microwave-Assisted Extraction

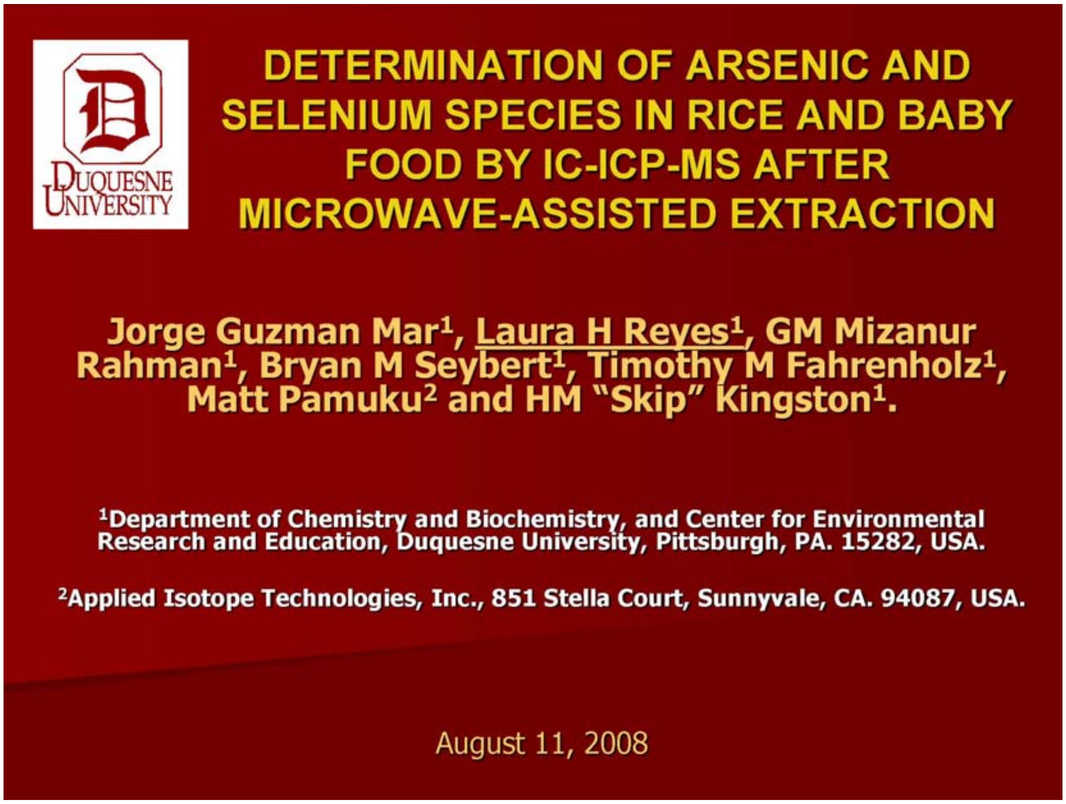
Jorge Guzman Mar, Laura H. Reyes, Mizanur Rahman, Timothy M. Fahrenholz, and H.M. Skip Kingston; Duquesne University Department of Chemistry and Biochemistry and Center for Environmental Research and Education, 600 Forbes Avenue; 335 Mellon Hall, Pittsburgh, PA 15282; 412-396-4106; kingston@duq.edu and guzmanmarj@duq.edu
Matt Pamuku; Applied Isotope Technologies, Inc., 851 Stella Court, Sunnyvale, CA 94087

ABSTRACT

The determination of arsenic and selenium in environmental and biological samples is important, mainly because of the ubiquitous nature of these elements and the toxic characteristics of some of their species. In this context, there is growing concern that the contents of arsenic and selenium in rice may represent a potential health hazard to the consumer. Rice is, in fact, widely cultivated in warm climates and is one of the major sources of food for a large fraction of the human population [1,2]. On the other hand, guidelines from the American Academy of Pediatrics suggest rice cereals as the first solid food for babies 4-6 months old. According to results from the FDA Total Diet Study, products such as rice cereal and mixed rice cereal products contribute as much as 31% of the total arsenic intake for infants [3,4]. Toxicity and impacts of arsenic and selenium contamination are increasing in foods, and the demand for an efficient, fast and reliable analytical method for determination of these species also increases. The aim of this study was to develop a microwave assisted extraction method for the determination of arsenic and selenium species in rice and baby food products. The procedure was validated by the analysis of arsenic and selenium in Certified Reference Material (SRM-1568a). Arsenic and selenium species were measured by Ion Chromatography coupled to Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS). The proposed method was applied to the determination of arsenic and selenium species in real samples of rice and baby food products.

---

[1] M. D'Amato, G. Forte and S. Caroli. J. AOAC Int. 87 (2004), 238.
[2] A.H. Ackerman, P.A. Creed, A.N. Parks, M.W. Fricke, C.A. Schwegel, C.A. Schwegel, J.T. Creed, D.T. Heitkemper and N.P. Vela. Environ. Sci. Technol. 39 (2005), 5241.
[3] N.P. Vela and D.T. Heitkemper. J. AOAC Int. 87 (2004), 244.
[4] W.R. Mindak and S.P. Dolan. J. Food Compos. Anal. 12 (1999), 111.



DETERMINATION OF ARSENIC AND SELENIUM SPECIES IN RICE AND BABY FOOD BY IC-ICP-MS AFTER MICROWAVE-ASSISTED EXTRACTION

Jorge Guzman Mar[1], Laura H Reyes[1], GM Mizanur Rahman[1], Bryan M Seybert[1], Timothy M Fahrenholz[1], Matt Pamuku[2] and HM "Skip" Kingston[1].

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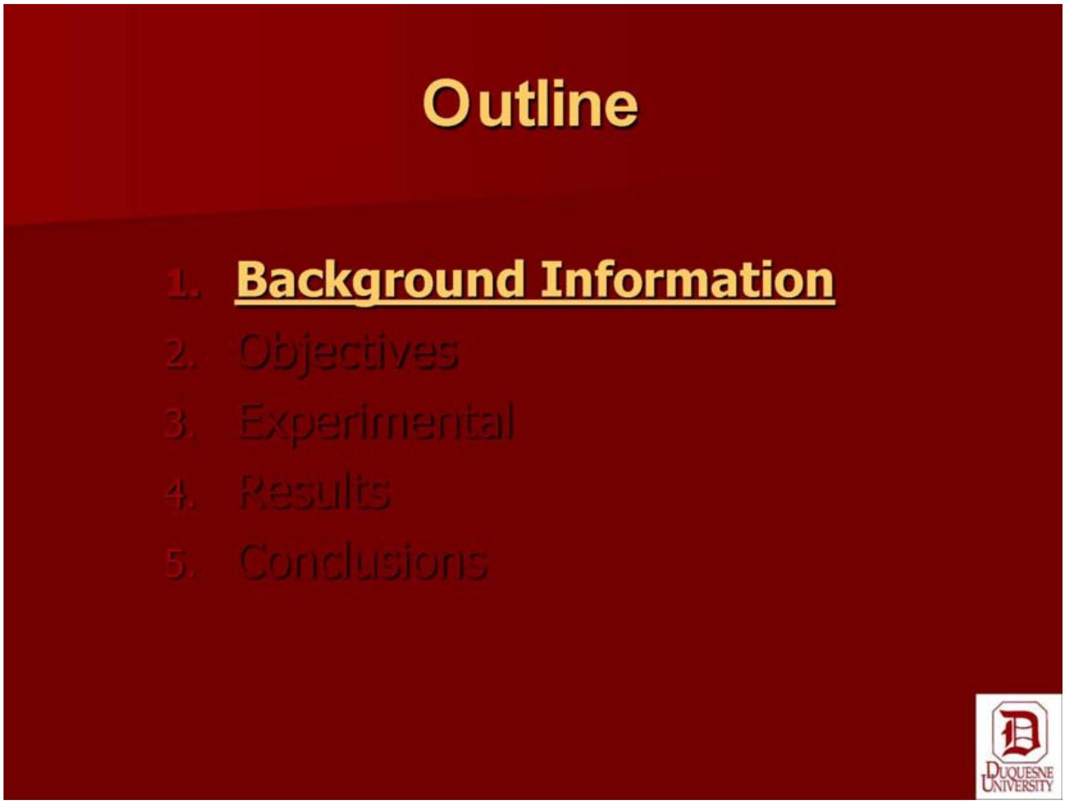
[2]Applied Isotope Technologies, Inc., 851 Stella Court, Sunnyvale, CA. 94087, USA.

August 11, 2008

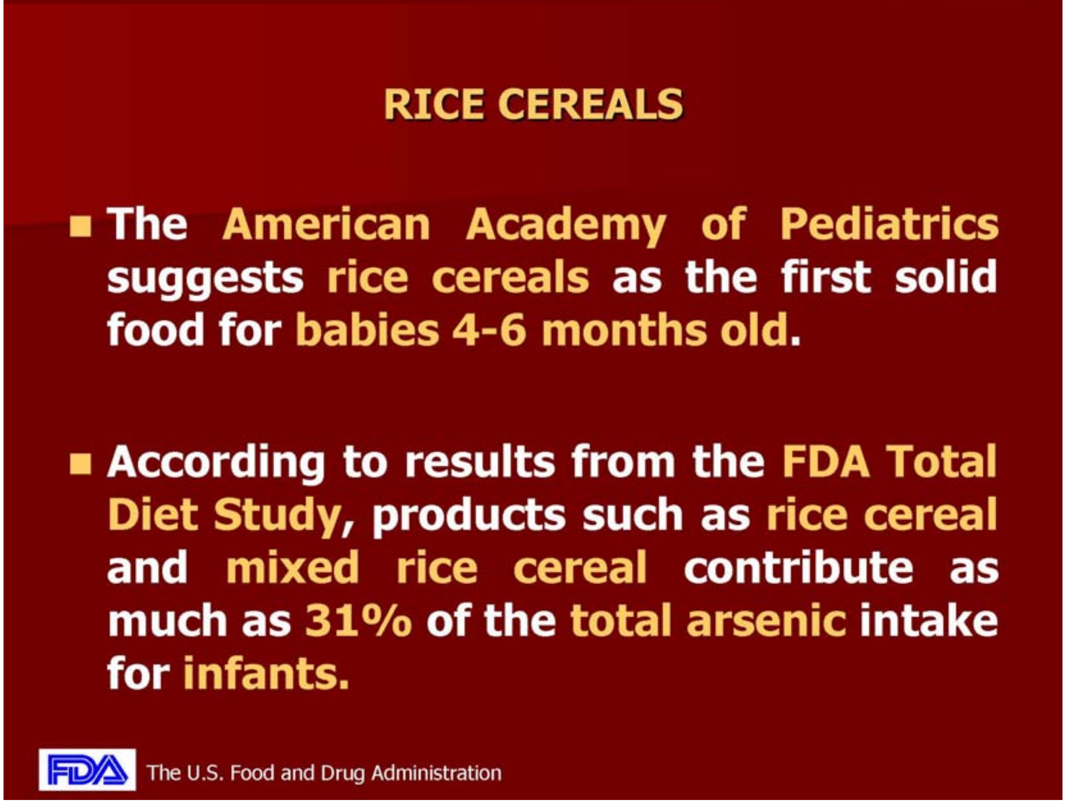


Outline

1. **Background Information**
2. Objectives
3. Experimental
4. Results
5. Conclusions

RICE (*Oryza sativa L.*)

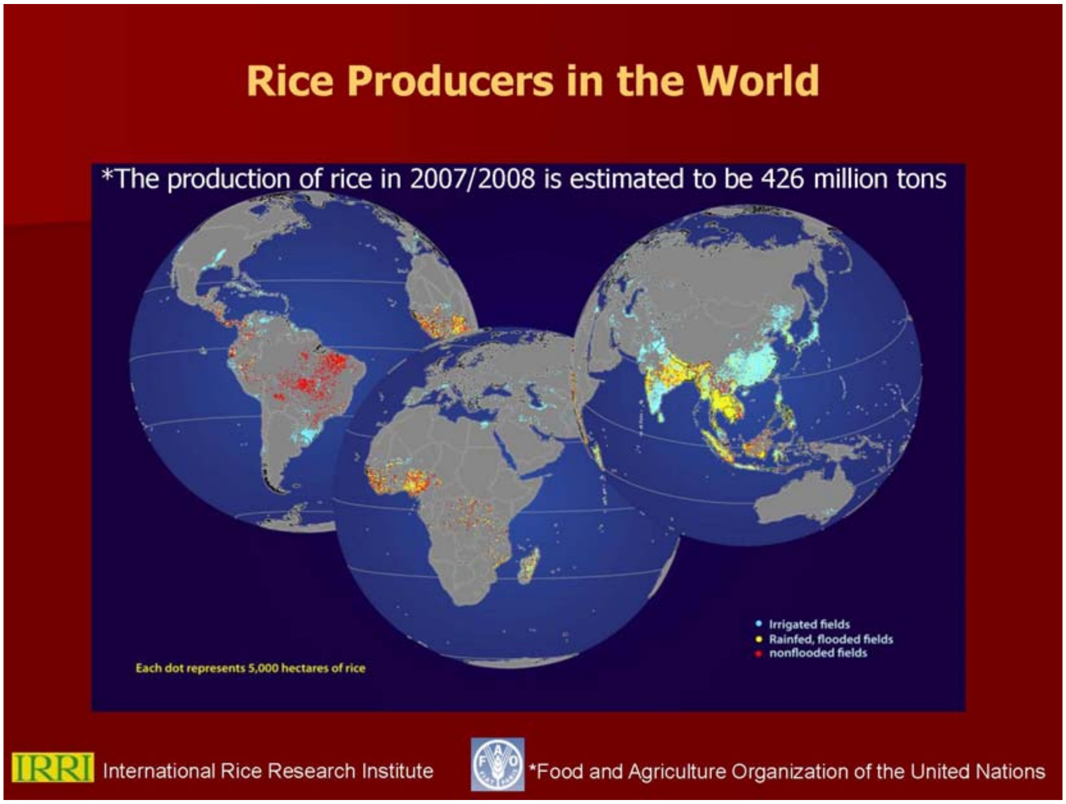
- One of the most important foodstuffs in the world.
- The staple diet in more than 39 countries (one billion people).
- A bio-accumulative plant for the most toxic arsenic species.



RICE CEREALS

- The American Academy of Pediatrics suggests rice cereals as the first solid food for babies 4-6 months old.
- According to results from the FDA Total Diet Study, products such as rice cereal and mixed rice cereal contribute as much as 31% of the total arsenic intake for infants.

FDA The U.S. Food and Drug Administration

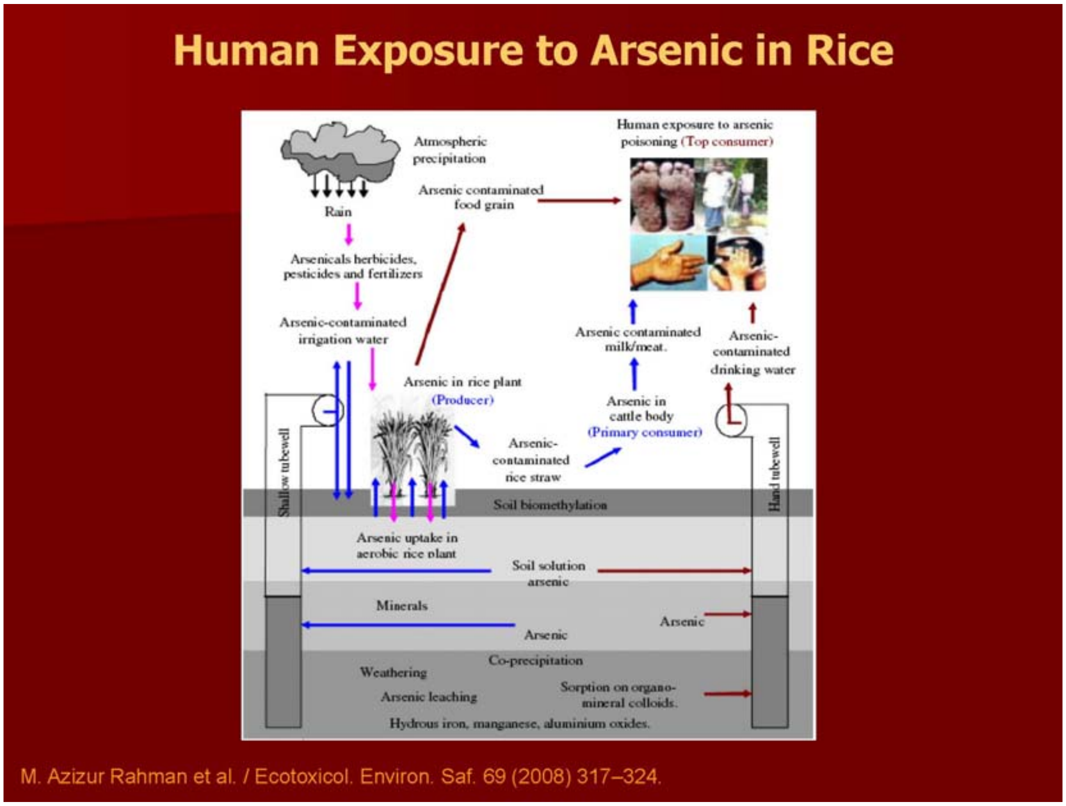


Rice Producers in the World

*The production of rice in 2007/2008 is estimated to be 426 million tons

IRRI International Rice Research Institute

*Food and Agriculture Organization of the United Nations

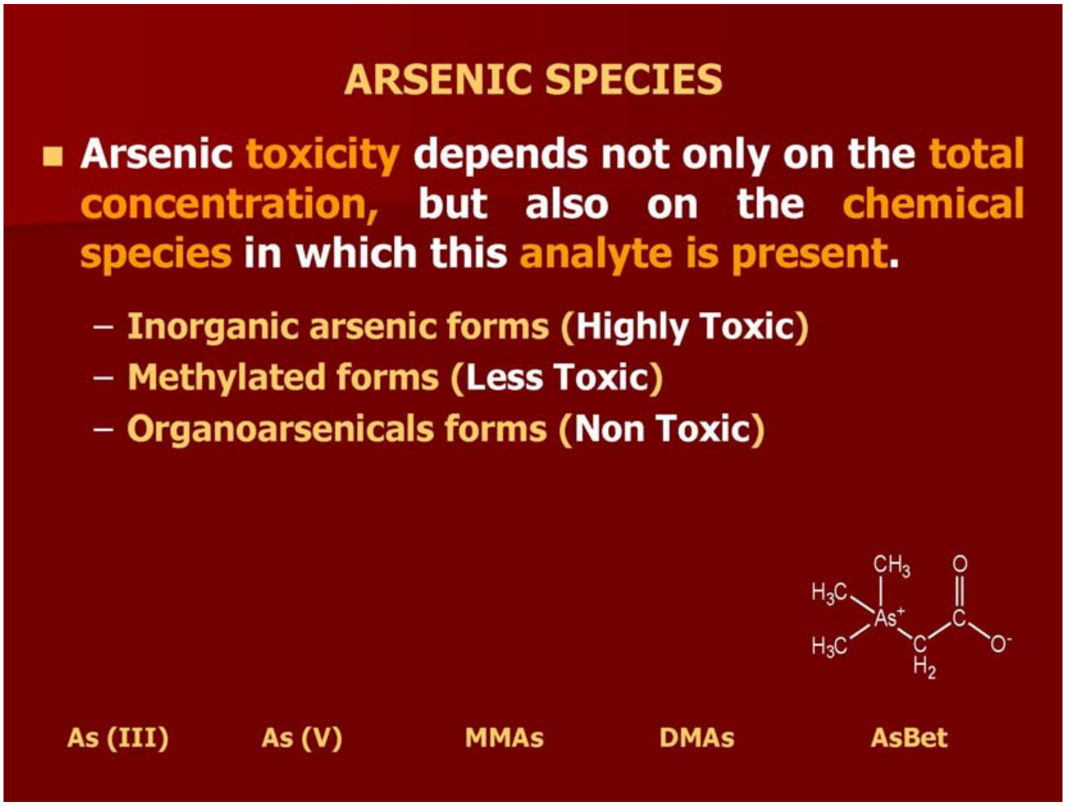


Human Exposure to Arsenic in Rice

M. Azizur Rahman et al. / Ecotoxicol. Environ. Saf. 69 (2008) 317–324.

ARSENIC SPECIES

- Human uptake of arsenic mainly occurs via the food chain (dietary sources and drinking water) and anthropogenic activities.
- The permissible level for total arsenic in drinking water is 10 μg/L.
- Food products do not have a definitive, maximum allowed value.
- The Food and Agriculture Organization (FAO) and World Health Organization (WHO) recommended a Provisional Tolerable Level Weekly Intake (PTWI) of no more than 15 μg inorganic Arsenic/kg body weight.



ARSENIC SPECIES

- Arsenic toxicity depends not only on the total concentration, but also on the chemical species in which this analyte is present.
  - Inorganic arsenic forms (Highly Toxic)
  - Methylated forms (Less Toxic)
  - Organoarsenicals forms (Non Toxic)

As (III) As (V) MMAs DMAs AsBet

SELENIUM SPECIES

- Selenium is an essential trace element for mammals, safe within in a very narrow concentration range. Outside this range, deficiency or toxicity occurs.
- Selenium is a key component for functional proteins (selenoproteins) of primary importance for human health.
- Selenoproteins (for example, glutathione peroxidases and thioredoxin reductases) play an important antioxidant and detoxificating function.

SELENIUM SPECIES

- Nutritional bioavailability and toxicity are dependent upon its chemical form (species) and concentration present in food and in dietary factors.
- Selenium Species:
  - Inorganic selenium forms (Toxic, ex. Se (IV) > Se (VI))
  - Seleno-amino acid (Non Toxic, ex. SeMet)
  - Selenoproteins forms (Non Toxic)

Se (IV)

Se (VI)

SeMet

As and Se: Intertwined Biochemistry

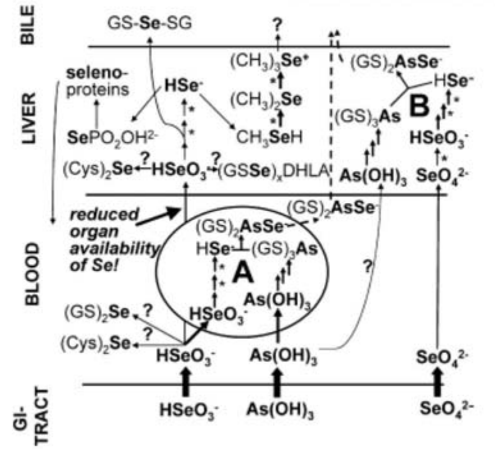


Fig. 7. Interaction between As^{III} and Se^{IV} in erythrocytes (A) and between As^{III} and Se^{VI} in the liver (B). Oval shape: erythrocyte; Cys: L-cysteine; GSH: L-glutathione; DHLA: dihydrolipoic acid. Asterisk indicates enzymatically mediated biotransformation.

– Arsenic is a xenobiotic; the body has no need for it.

– Selenium is an essential component of mediated biotransformations of xenobiotics (glutathione).

– The destinies of As and Se in the human body are often linked.

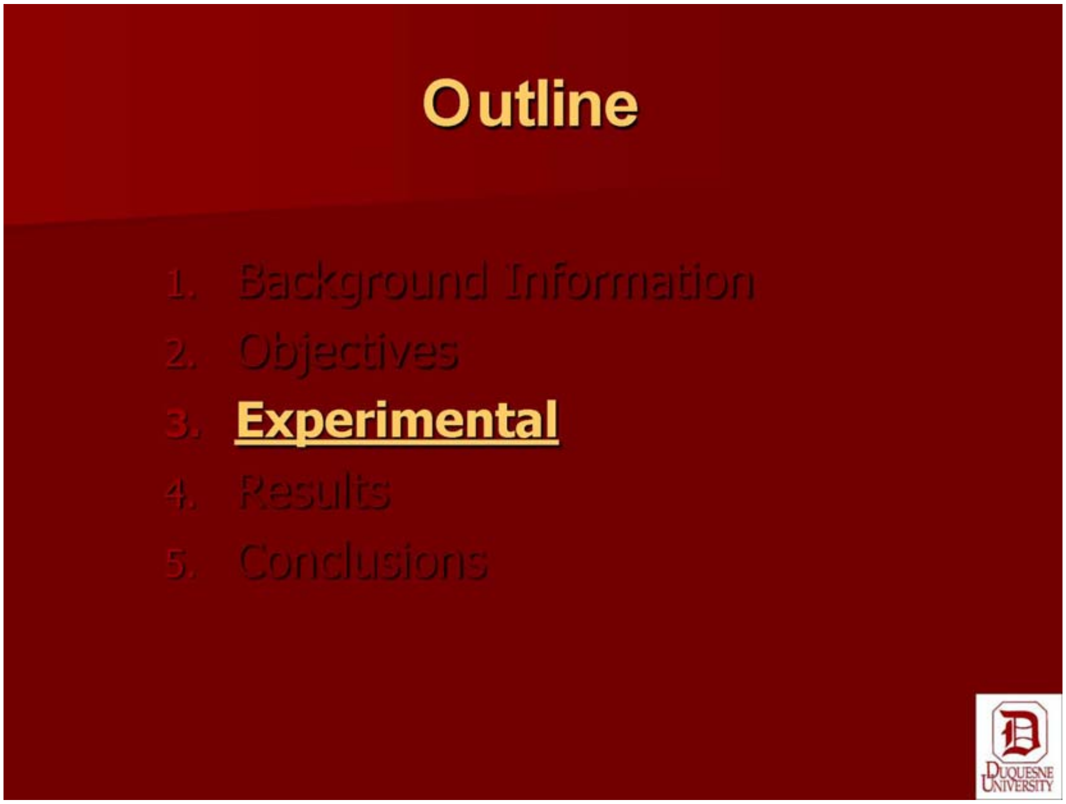
J. Gailer / Coord. Chem. Rev. 251 (2007) 234–254.

Outline

1. Background Information
2. **Objectives**
3. Experimental
4. Results
5. Conclusions

OBJECTIVES

- **Develop a Microwave-Assisted Extraction method for the determination of arsenic and selenium species in rice and baby food.**
- **Validate the extraction procedure by the analysis of rice flour (SRM®-1568a).**
- **Apply the proposed extraction method to determine arsenic and selenium species in rice and baby food.**



Outline

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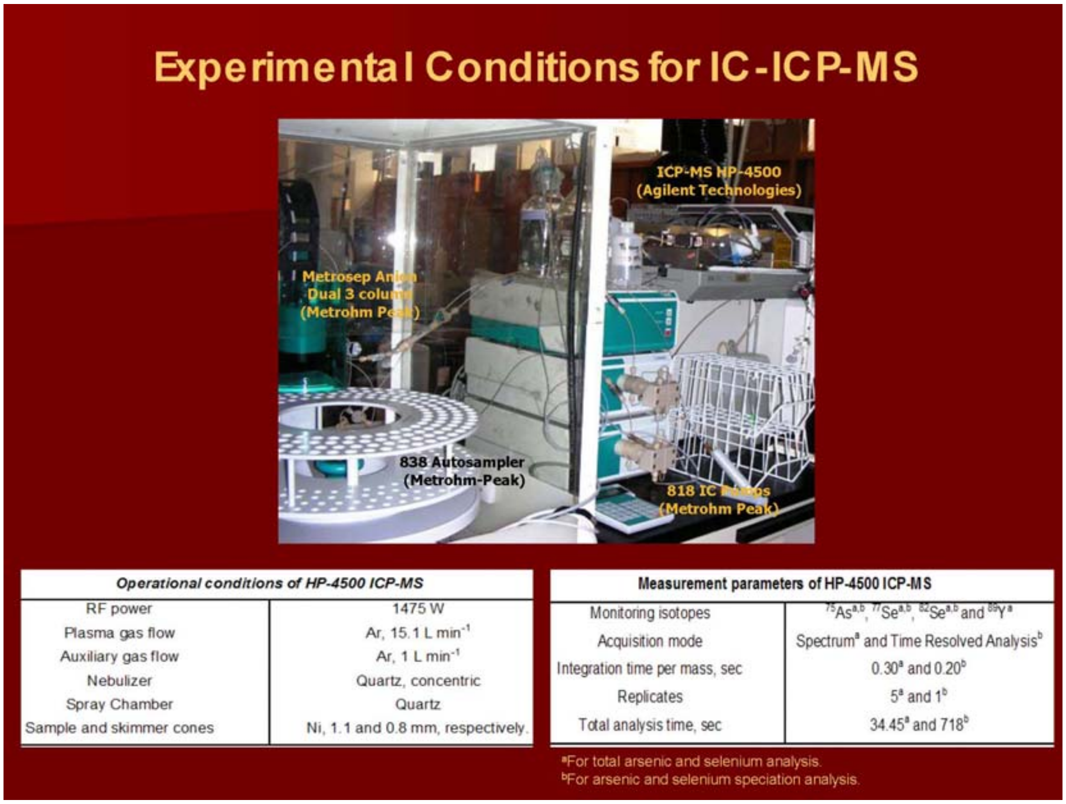


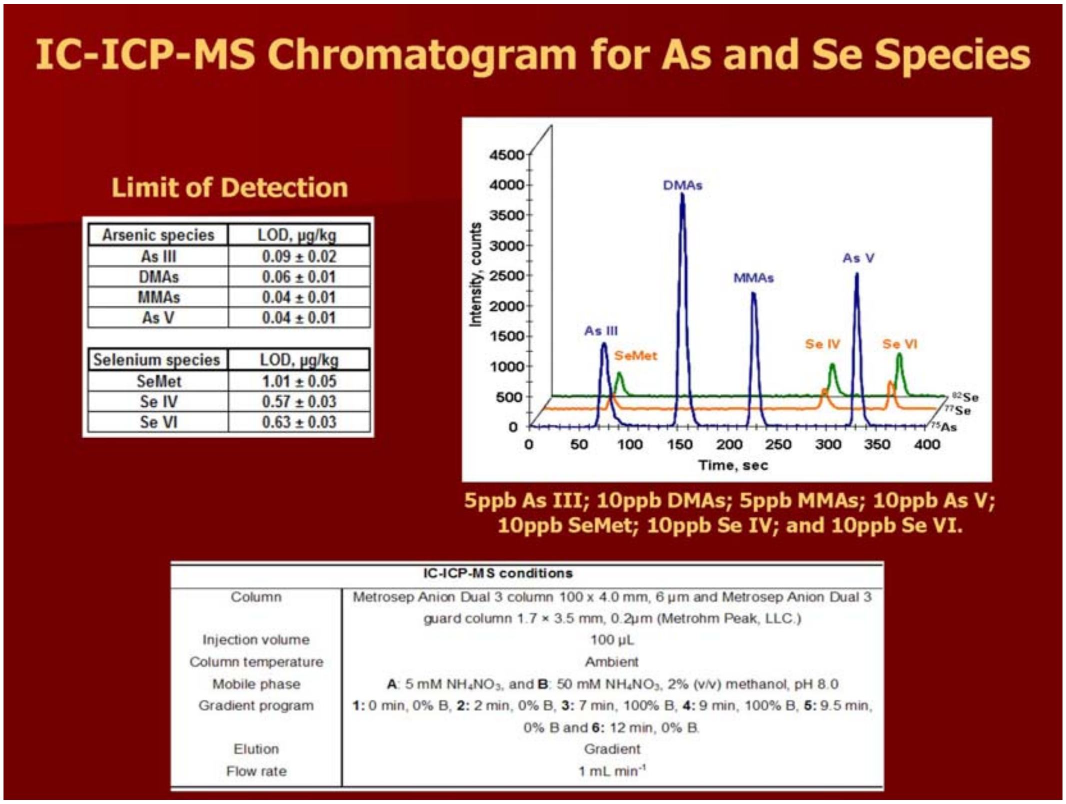
Experimental Conditions for IC-ICP-MS

Operational conditions of HP-4500 ICP-MS	
RF power	1475 W
Plasma gas flow	Ar, 15.1 L min^{-1}
Auxiliary gas flow	Ar, 1 L min^{-1}
Nebulizer	Quartz, concentric
Spray Chamber	Quartz
Sample and skimmer cones	Ni, 1.1 and 0.8 mm, respectively.

Measurement parameters of HP-4500 ICP-MS	
Monitoring isotopes	$^{75}As^{a,b}$, $^{77}Se^{a,b}$, $^{82}Se^{a,b}$ and $^{89}Y^{a}$
Acquisition mode	Spectrum[a] and Time Resolved Analysis[b]
Integration time per mass, sec	0.30[a] and 0.20[b]
Replicates	5[a] and 1[b]
Total analysis time, sec	34.45[a] and 718[b]

[a] For total arsenic and selenium analysis.

[b] For arsenic and selenium speciation analysis.



IC-ICP-MS Chromatogram for As and Se Species

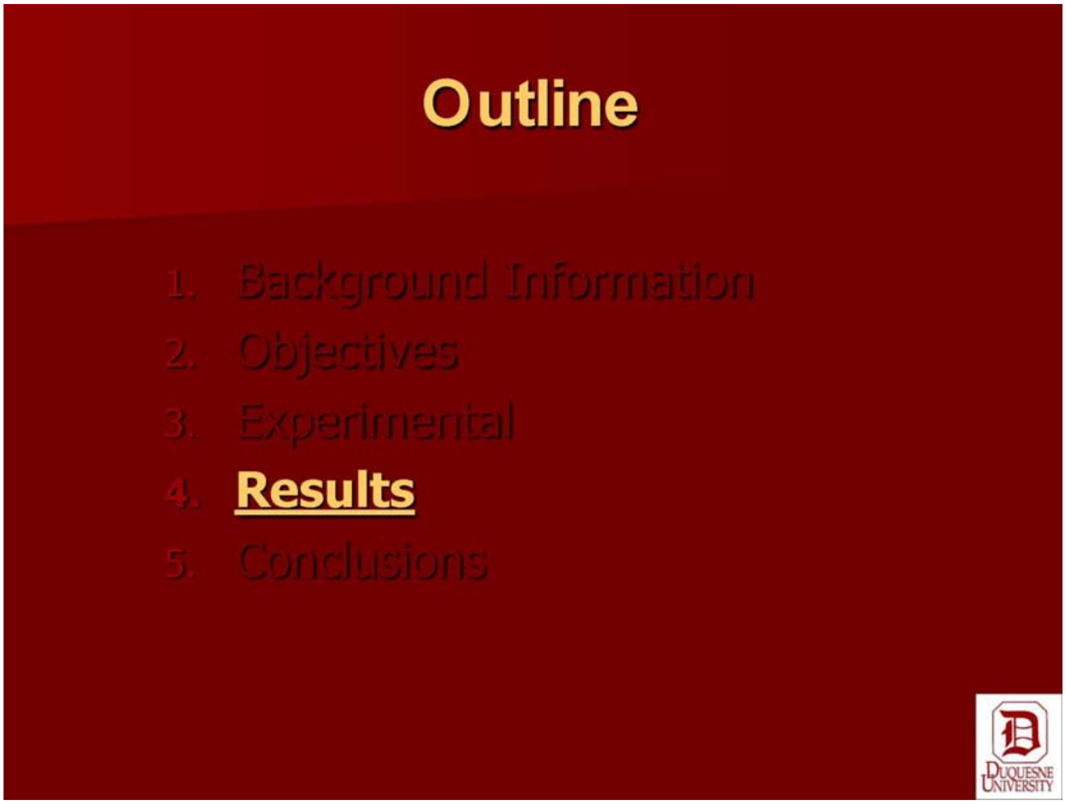
Limit of Detection

Arsenic species	LOD, µg/kg
As III	0.09 ± 0.02
DMAs	0.06 ± 0.01
MMAs	0.04 ± 0.01
As V	0.04 ± 0.01

Selenium species	LOD, µg/kg
SeMet	1.01 ± 0.05
Se IV	0.57 ± 0.03
Se VI	0.63 ± 0.03

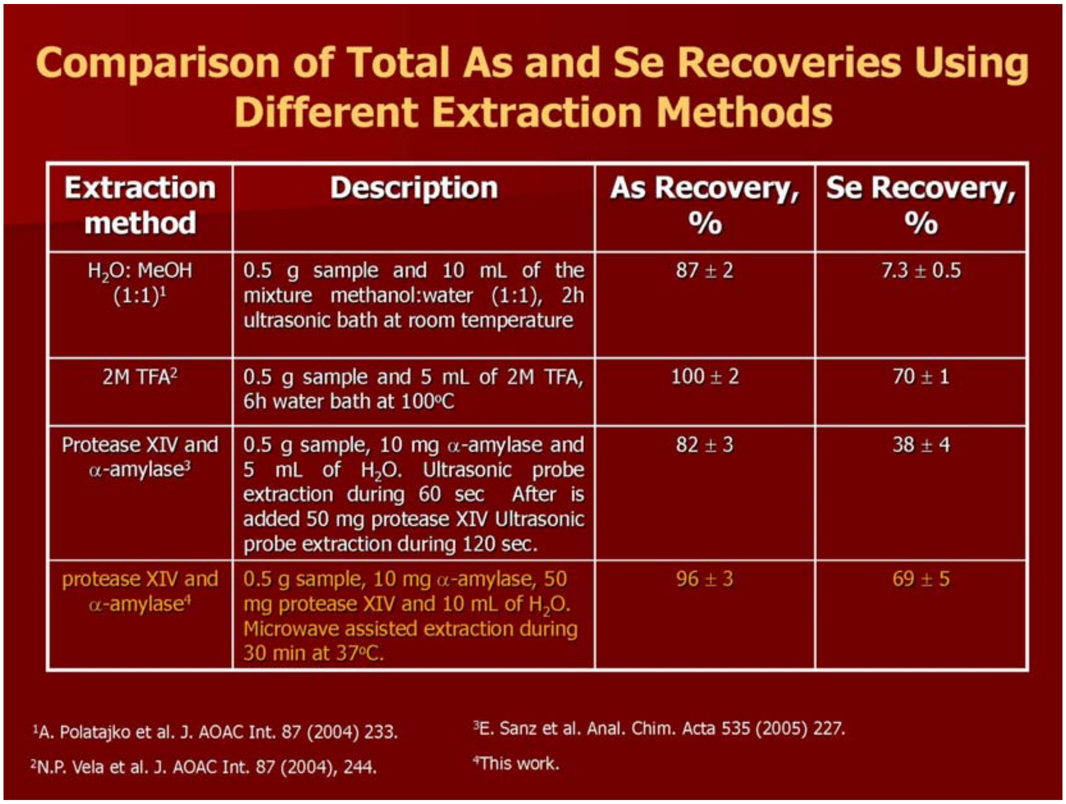
5ppb As III; 10ppb DMAs; 5ppb MMAs; 10ppb As V; 10ppb SeMet; 10ppb Se IV; and 10ppb Se VI.

IC-ICP-MS conditions	
Column	Metrosep Anion Dual 3 column 100 x 4.0 mm, 6 µm and Metrosep Anion Dual 3 guard column 1.7 × 3.5 mm, 0.2µm (Metrohm Peak, LLC.)
Injection volume	100 µL
Column temperature	Ambient
Mobile phase	**A**: 5 mM NH_4NO_3, and **B**: 50 mM NH_4NO_3, 2% (v/v) methanol, pH 8.0
Gradient program	**1:** 0 min, 0% B, **2:** 2 min, 0% B, **3:** 7 min, 100% B, **4:** 9 min, 100% B, **5:** 9.5 min, 0% B and **6:** 12 min, 0% B.
Elution	Gradient
Flow rate	1 mL min^{-1}



Outline

1. Background Information
2. Objectives
3. Experimental
4. **Results**
5. Conclusions



Comparison of Total As and Se Recoveries Using Different Extraction Methods

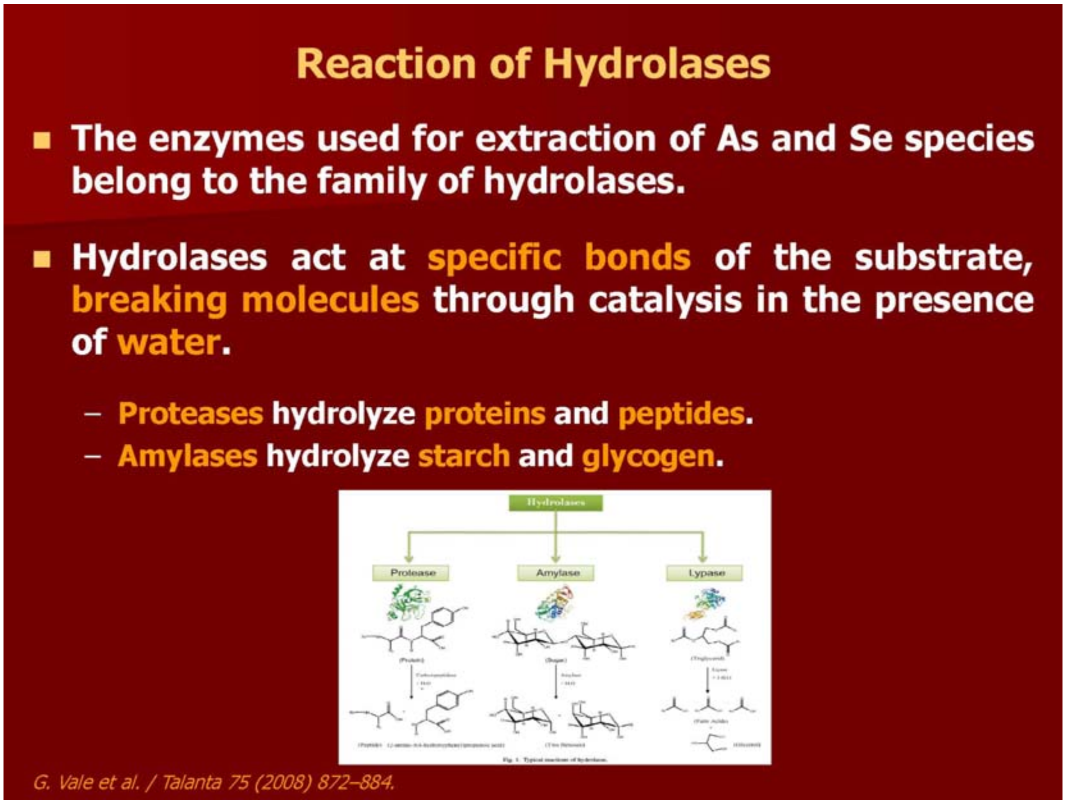
Extraction method	Description	As Recovery, %	Se Recovery, %
H_2O: MeOH (1:1)[1]	0.5 g sample and 10 mL of the mixture methanol:water (1:1), 2h ultrasonic bath at room temperature	87 ± 2	7.3 ± 0.5
2M TFA[2]	0.5 g sample and 5 mL of 2M TFA, 6h water bath at 100°C	100 ± 2	70 ± 1
Protease XIV and α-amylase[3]	0.5 g sample, 10 mg α-amylase and 5 mL of H_2O. Ultrasonic probe extraction during 60 sec After is added 50 mg protease XIV Ultrasonic probe extraction during 120 sec.	82 ± 3	38 ± 4
protease XIV and α-amylase[4]	0.5 g sample, 10 mg α-amylase, 50 mg protease XIV and 10 mL of H_2O. Microwave assisted extraction during 30 min at 37°C.	96 ± 3	69 ± 5

[1] A. Polatajko et al. J. AOAC Int. 87 (2004) 233.

[2] N.P. Vela et al. J. AOAC Int. 87 (2004), 244.

[3] E. Sanz et al. Anal. Chim. Acta 535 (2005) 227.

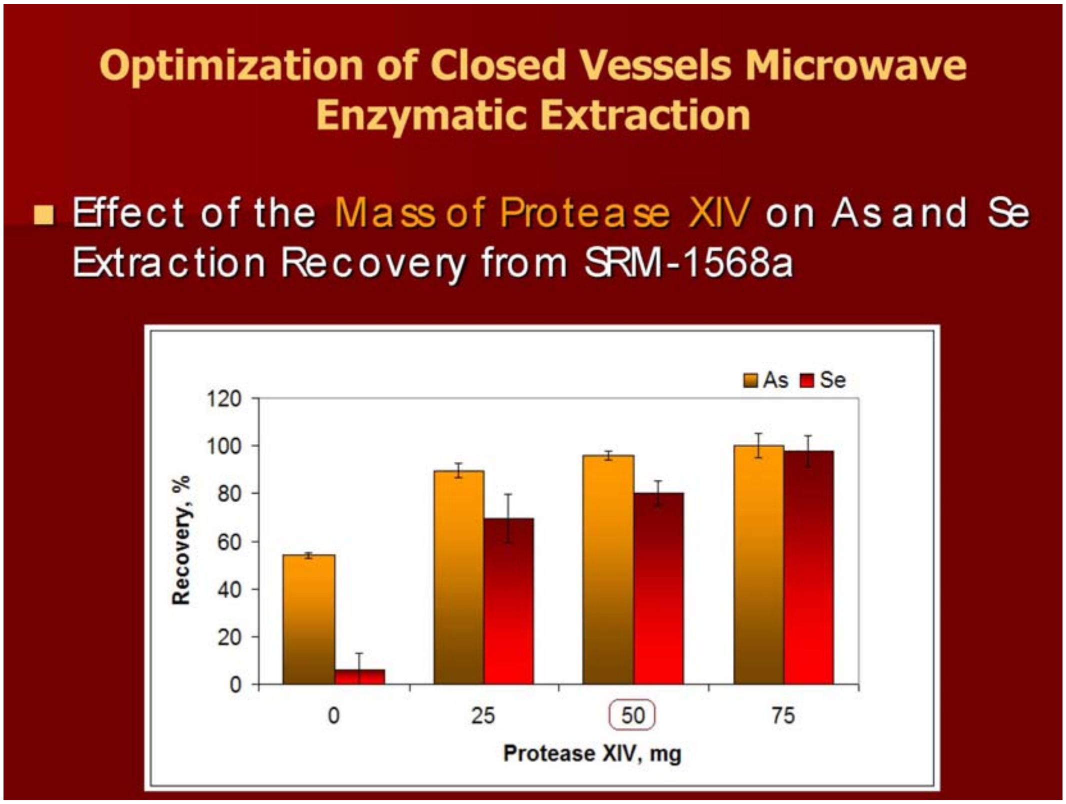
[4] This work.



Reaction of Hydrolases

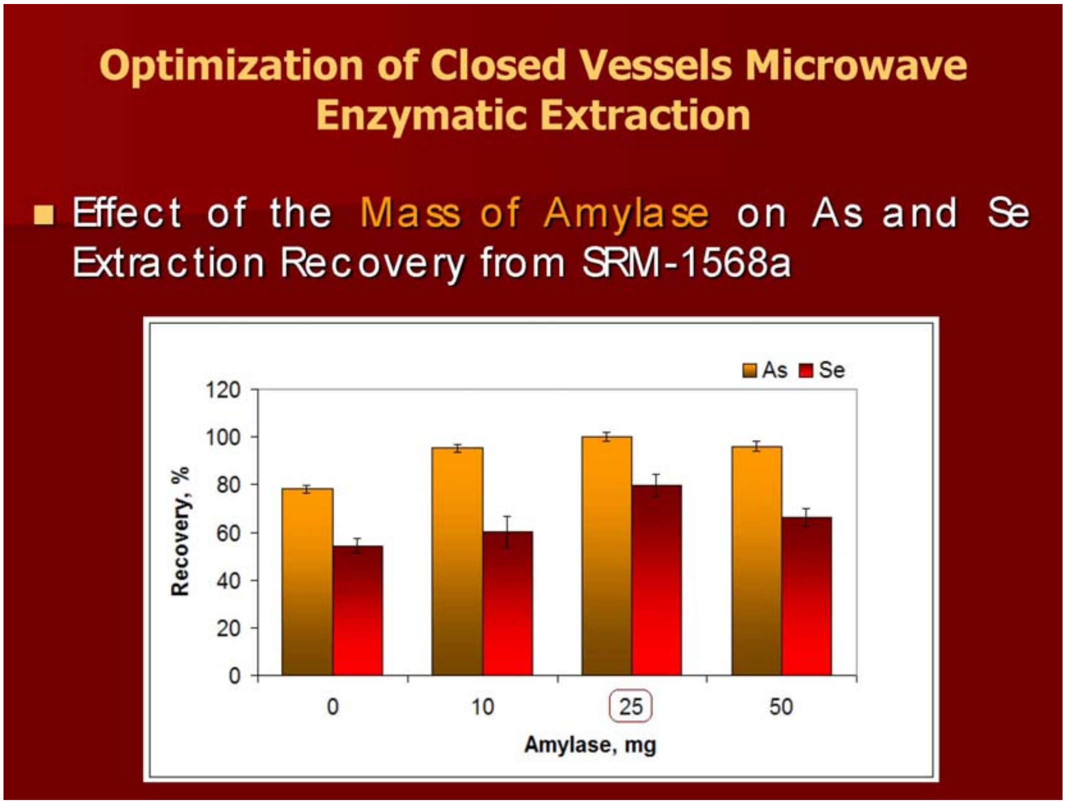
- The enzymes used for extraction of As and Se species belong to the family of hydrolases.
- Hydrolases act at specific bonds of the substrate, breaking molecules through catalysis in the presence of water.
  - Proteases hydrolyze proteins and peptides.
  - Amylases hydrolyze starch and glycogen.

G. Vale et al. / Talanta 75 (2008) 872–884.



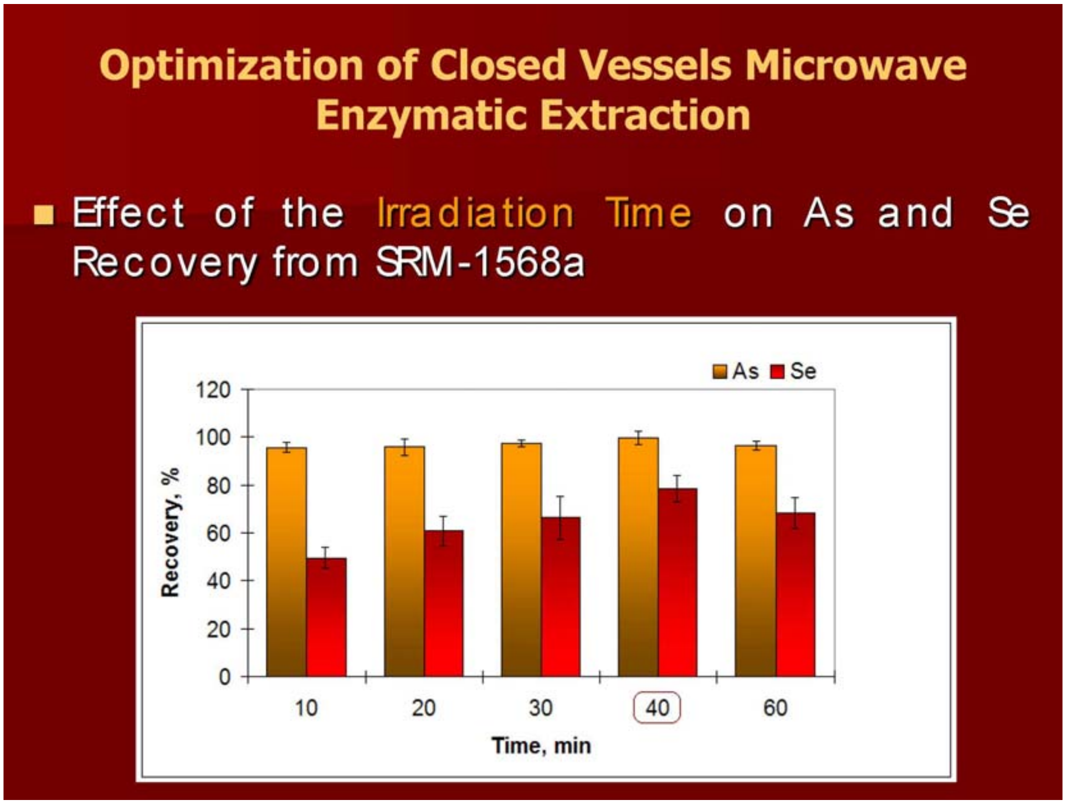
Optimization of Closed Vessels Microwave Enzymatic Extraction

- Effect of the Mass of Protease XIV on As and Se Extraction Recovery from SRM-1568a



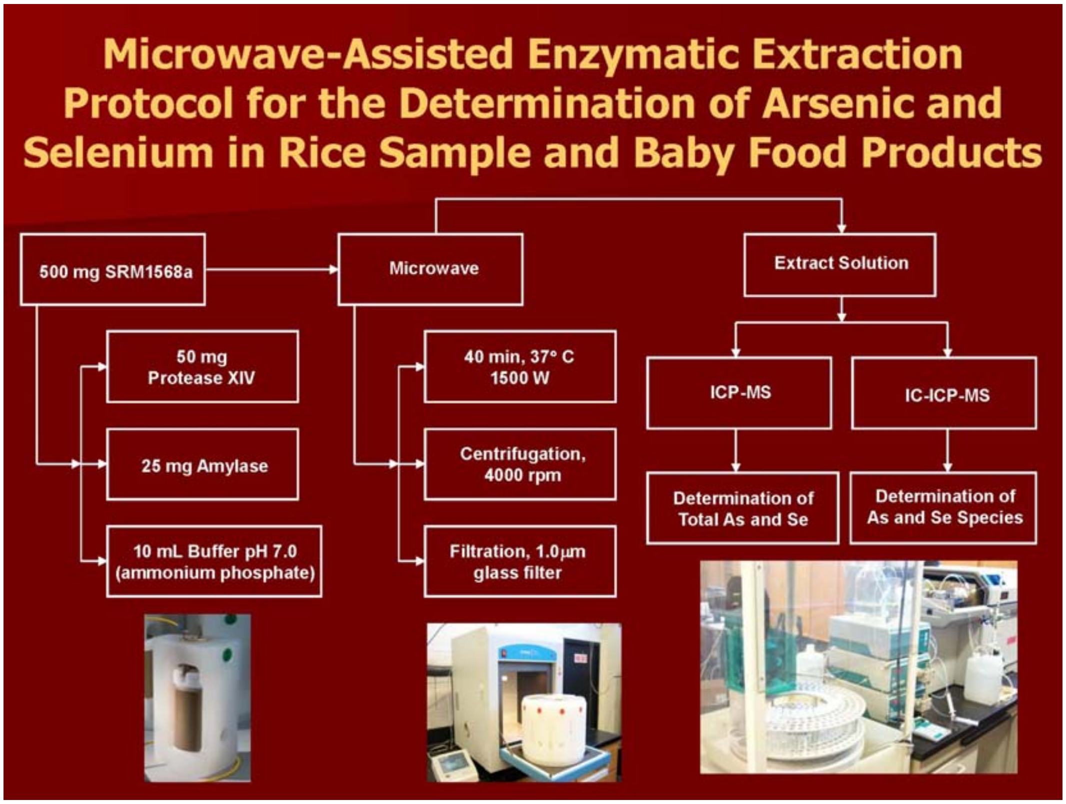
Optimization of Closed Vessels Microwave Enzymatic Extraction

- Effect of the Mass of Amylase on As and Se Extraction Recovery from SRM-1568a



Optimization of Closed Vessels Microwave Enzymatic Extraction

- Effect of the Irradiation Time on As and Se Recovery from SRM-1568a



Microwave-Assisted Enzymatic Extraction Protocol for the Determination of Arsenic and Selenium in Rice Sample and Baby Food Products

500 mg SRM1568a

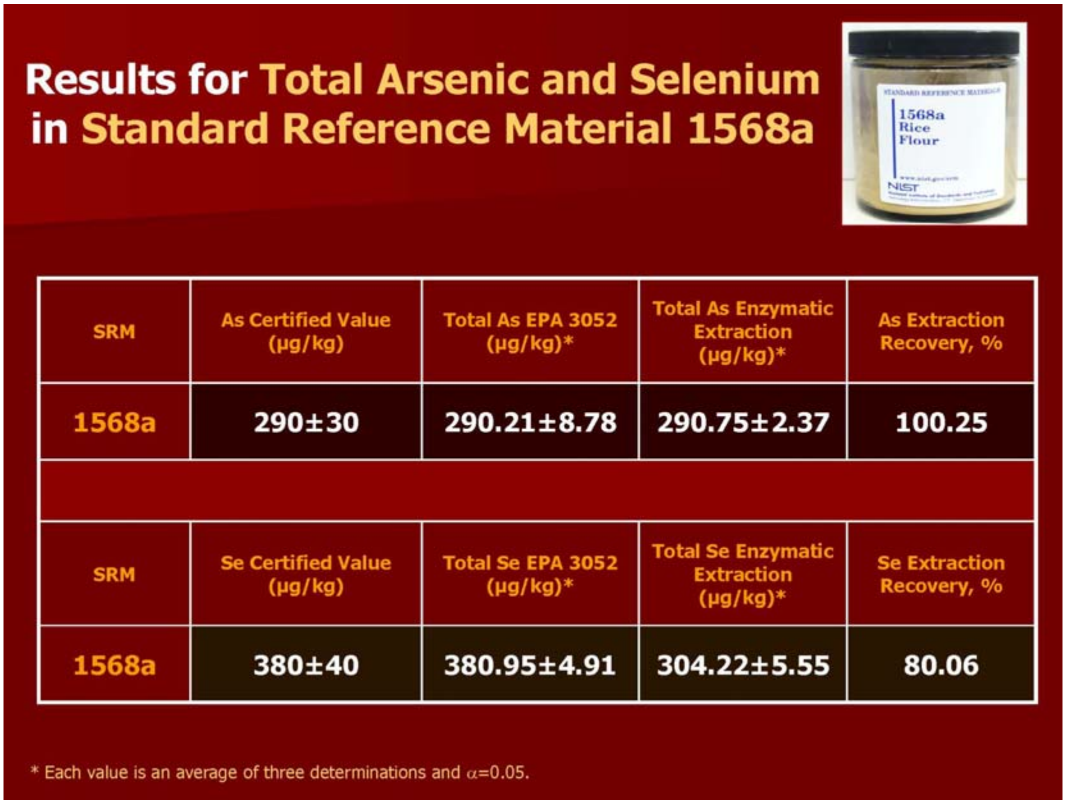
- 50 mg Protease XIV
- 25 mg Amylase
- 10 mL Buffer pH 7.0 (ammonium phosphate)

Microwave

- 40 min, 37° C 1500 W
- Centrifugation, 4000 rpm
- Filtration, 1.0µm glass filter

Extract Solution

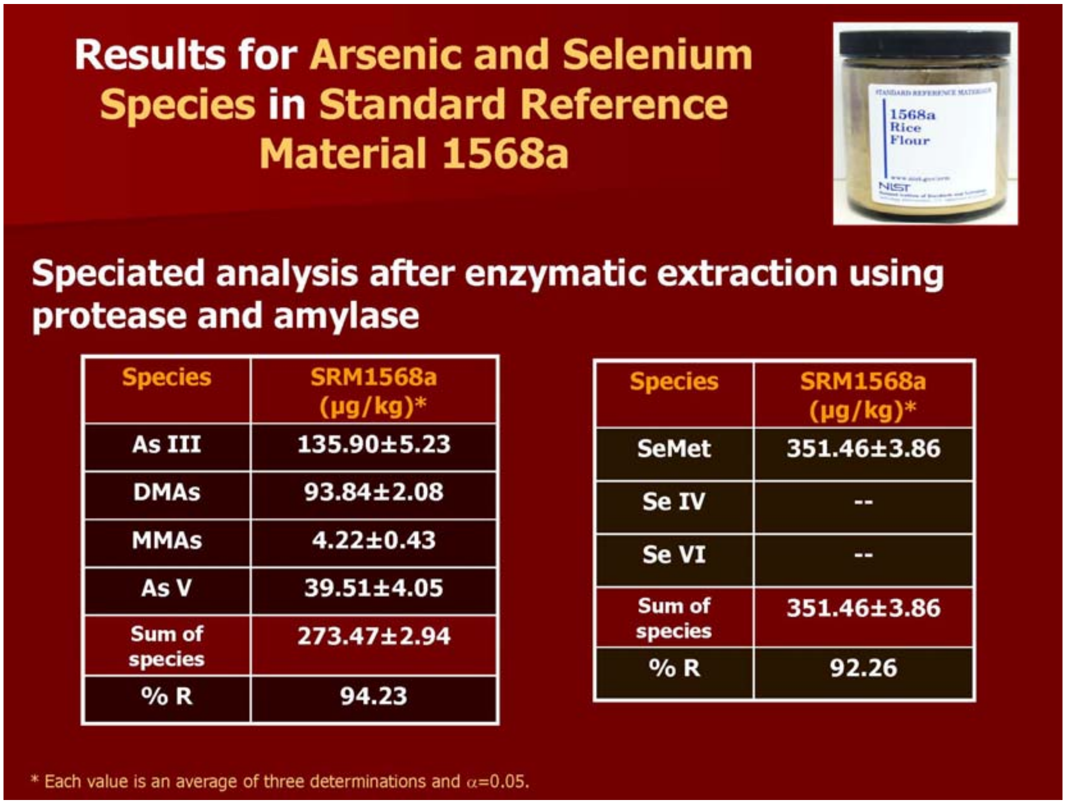
- ICP-MS → Determination of Total As and Se
- IC-ICP-MS → Determination of As and Se Species



Results for Total Arsenic and Selenium in Standard Reference Material 1568a

SRM	As Certified Value (µg/kg)	Total As EPA 3052 (µg/kg)*	Total As Enzymatic Extraction (µg/kg)*	As Extraction Recovery, %
1568a	290±30	290.21±8.78	290.75±2.37	100.25
SRM	Se Certified Value (µg/kg)	Total Se EPA 3052 (µg/kg)*	Total Se Enzymatic Extraction (µg/kg)*	Se Extraction Recovery, %
1568a	380±40	380.95±4.91	304.22±5.55	80.06

* Each value is an average of three determinations and α=0.05.



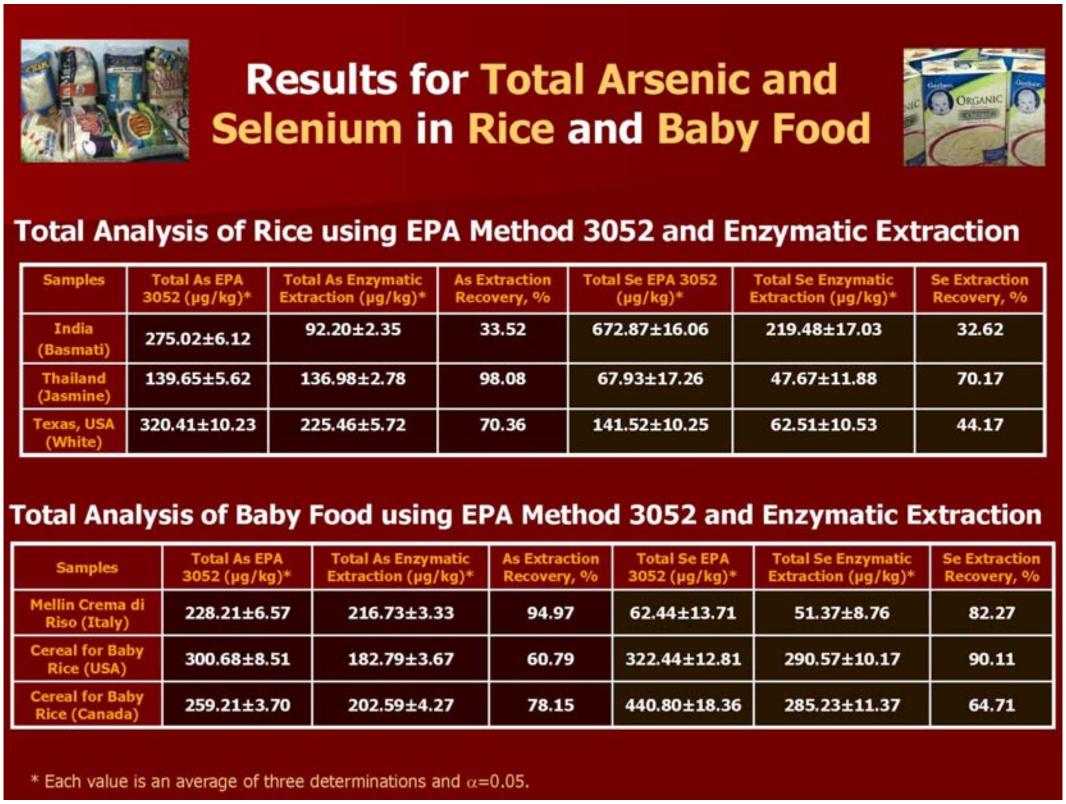
Results for Arsenic and Selenium Species in Standard Reference Material 1568a

Speciated analysis after enzymatic extraction using protease and amylase

Species	SRM1568a (µg/kg)*
As III	135.90±5.23
DMAs	93.84±2.08
MMAs	4.22±0.43
As V	39.51±4.05
Sum of species	273.47±2.94
% R	94.23

Species	SRM1568a (µg/kg)*
SeMet	351.46±3.86
Se IV	--
Se VI	--
Sum of species	351.46±3.86
% R	92.26

* Each value is an average of three determinations and α=0.05.



Results for Total Arsenic and Selenium in Rice and Baby Food

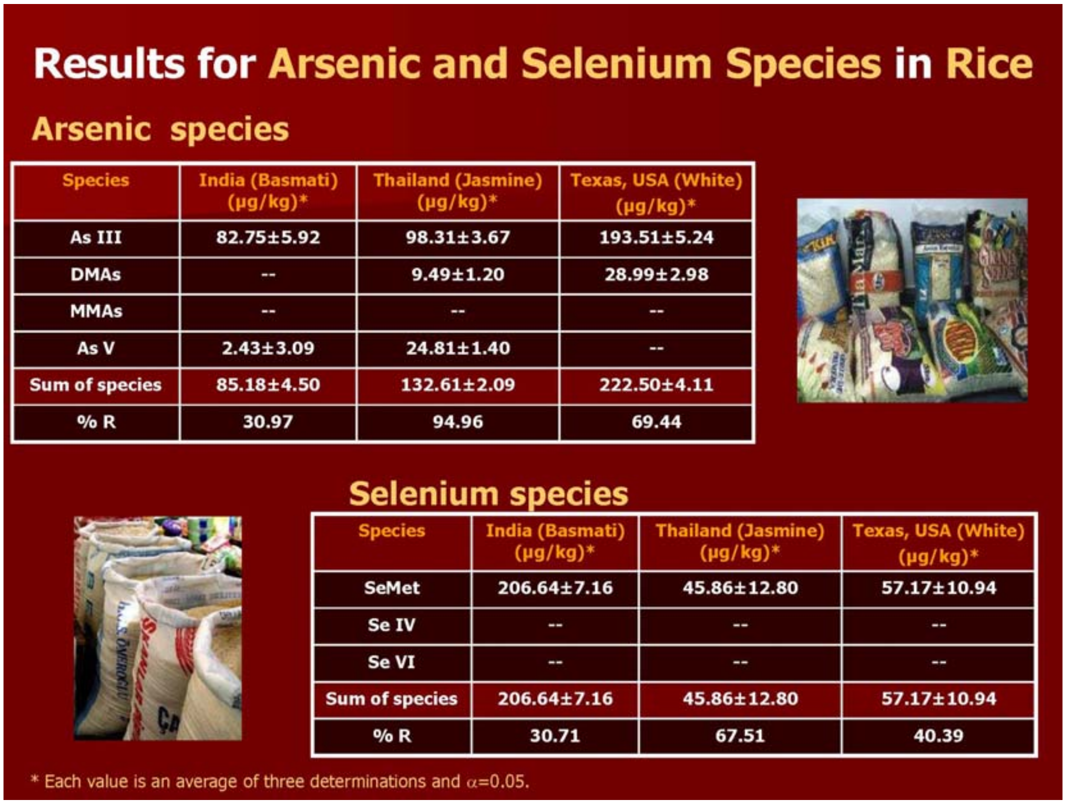
Total Analysis of Rice using EPA Method 3052 and Enzymatic Extraction

Samples	Total As EPA 3052 (µg/kg)*	Total As Enzymatic Extraction (µg/kg)*	As Extraction Recovery, %	Total Se EPA 3052 (µg/kg)*	Total Se Enzymatic Extraction (µg/kg)*	Se Extraction Recovery, %
India (Basmati)	275.02±6.12	92.20±2.35	33.52	672.87±16.06	219.48±17.03	32.62
Thailand (Jasmine)	139.65±5.62	136.98±2.78	98.08	67.93±17.26	47.67±11.88	70.17
Texas, USA (White)	320.41±10.23	225.46±5.72	70.36	141.52±10.25	62.51±10.53	44.17

Total Analysis of Baby Food using EPA Method 3052 and Enzymatic Extraction

Samples	Total As EPA 3052 (µg/kg)*	Total As Enzymatic Extraction (µg/kg)*	As Extraction Recovery, %	Total Se EPA 3052 (µg/kg)*	Total Se Enzymatic Extraction (µg/kg)*	Se Extraction Recovery, %
Mellin Crema di Riso (Italy)	228.21±6.57	216.73±3.33	94.97	62.44±13.71	51.37±8.76	82.27
Cereal for Baby Rice (USA)	300.68±8.51	182.79±3.67	60.79	322.44±12.81	290.57±10.17	90.11
Cereal for Baby Rice (Canada)	259.21±3.70	202.59±4.27	78.15	440.80±18.36	285.23±11.37	64.71

* Each value is an average of three determinations and α=0.05.



Results for Arsenic and Selenium Species in Rice

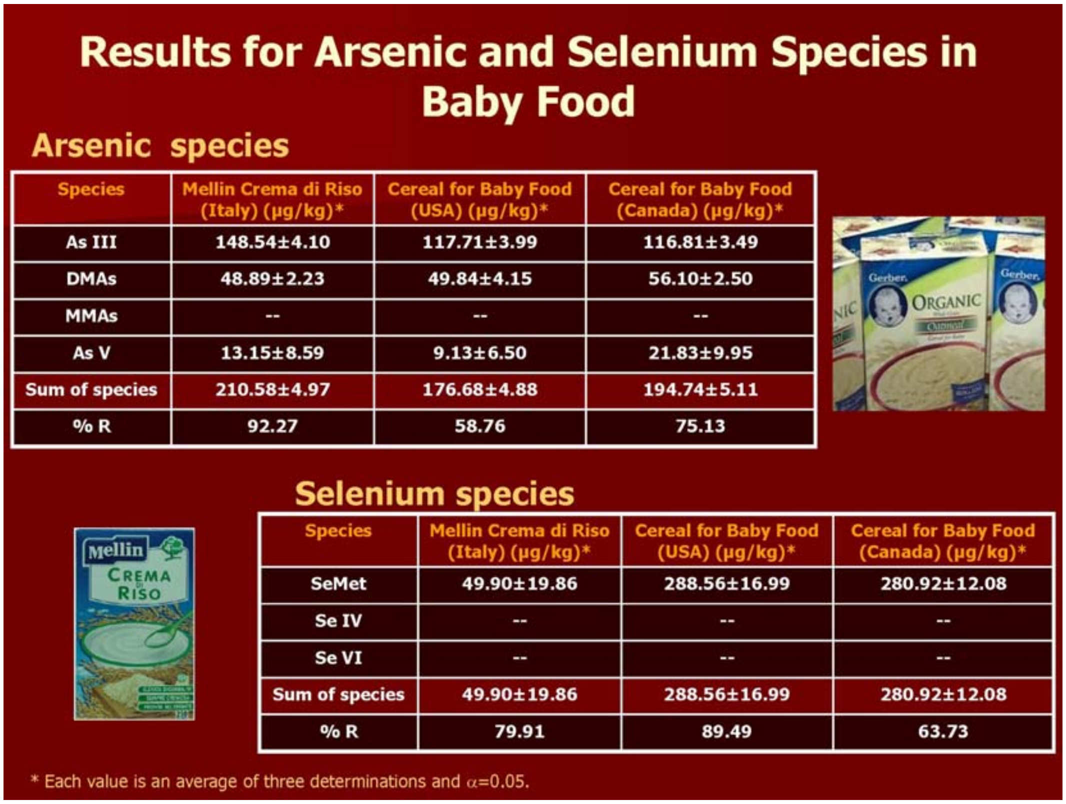
Arsenic species

Species	India (Basmati) (µg/kg)*	Thailand (Jasmine) (µg/kg)*	Texas, USA (White) (µg/kg)*
As III	82.75±5.92	98.31±3.67	193.51±5.24
DMAs	--	9.49±1.20	28.99±2.98
MMAs	--	--	--
As V	2.43±3.09	24.81±1.40	--
Sum of species	85.18±4.50	132.61±2.09	222.50±4.11
% R	30.97	94.96	69.44

Selenium species

Species	India (Basmati) (µg/kg)*	Thailand (Jasmine) (µg/kg)*	Texas, USA (White) (µg/kg)*
SeMet	206.64±7.16	45.86±12.80	57.17±10.94
Se IV	--	--	--
Se VI	--	--	--
Sum of species	206.64±7.16	45.86±12.80	57.17±10.94
% R	30.71	67.51	40.39

* Each value is an average of three determinations and α=0.05.



Results for Arsenic and Selenium Species in Baby Food

Arsenic species

Species	Mellin Crema di Riso (Italy) (µg/kg)*	Cereal for Baby Food (USA) (µg/kg)*	Cereal for Baby Food (Canada) (µg/kg)*
As III	148.54±4.10	117.71±3.99	116.81±3.49
DMAs	48.89±2.23	49.84±4.15	56.10±2.50
MMAs	--	--	--
As V	13.15±8.59	9.13±6.50	21.83±9.95
Sum of species	210.58±4.97	176.68±4.88	194.74±5.11
% R	92.27	58.76	75.13

Selenium species

Species	Mellin Crema di Riso (Italy) (µg/kg)*	Cereal for Baby Food (USA) (µg/kg)*	Cereal for Baby Food (Canada) (µg/kg)*
SeMet	49.90±19.86	288.56±16.99	280.92±12.08
Se IV	--	--	--
Se VI	--	--	--
Sum of species	49.90±19.86	288.56±16.99	280.92±12.08
% R	79.91	89.49	63.73

* Each value is an average of three determinations and α=0.05.

Calculated Real World Application

Baby Food	PTWI	Average Weight	Serving Size	1 Serving/Day for 1 Week (µg Ing As/kg body weight)
Italy (Mellin)	15 µg Ing As/kg body weight	Baby Age 6 months: 7.990 kg	¼ Cup (15g) per Day	2.12
USA (Gerber)				1.66
Canada (Nature's Goodness)				1.82

Outline

1. Background Information
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CONCLUSIONS

- Efficient Closed Vessel Microwave-Assisted Enzymatic Extraction method for sample preparation of As and Se Species in Rice and Baby Food was developed
- The accuracy of the method was validated by analyzing Standard Reference Material 1568a for Total Elemental extraction of As and Se (100% recovery for As and 80% recovery for Se)
- As III, DMAs, As V and SeMet were the predominant species of As and Se in Rice and Baby Food

Acknowledgements

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Kingston Research Group and Department of Chemistry and Biochemistry

Metrohm-Peak Ion Chromatography

MILESTONE Microwave Laboratory Systems

Applied Isotope Technologies

Commercialization of Metal Speciation Analyses – Status and Obstacles for Future Applications

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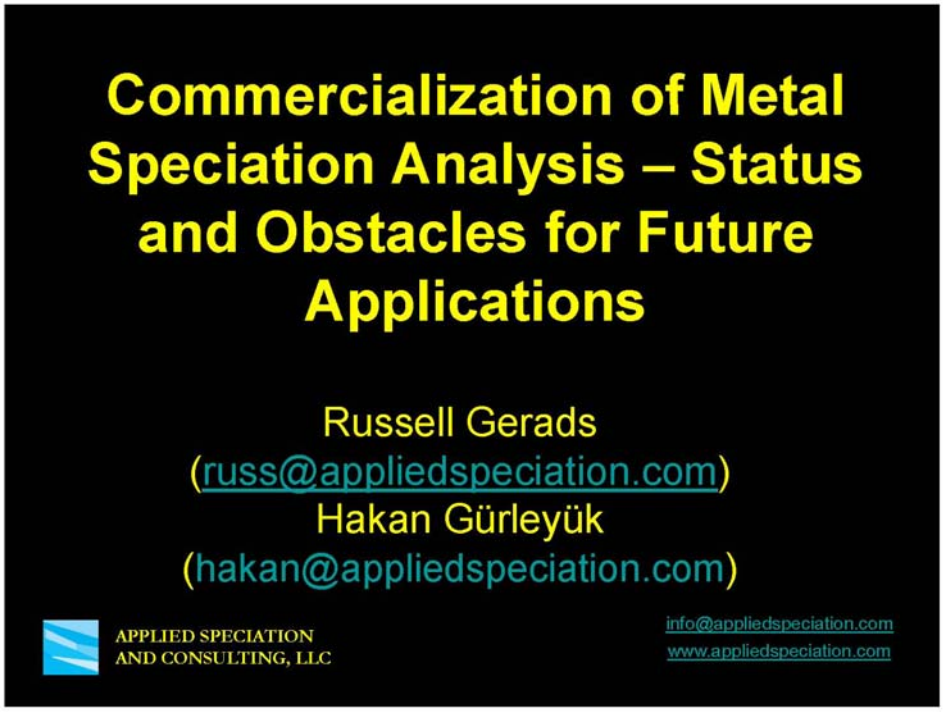
ABSTRACT

The advent and application of new technologies have born analytical tools allowing for the differentiation between valence states and molecular forms of metal molecules. The lack of universal method acceptance between scientists, regulatory authorities, and laboratories has produced a haphazard application of methodologies resulting in misinformation and disinformation. Information dissemination regarding method limitations and applicability is now predicated on the education and experience of the laboratory staff. The current obstacles and future of metal speciation analyses will be discussed with regards to commercialization and application for regulatory compliance.



Commercialization of Metal Speciation Analysis – Status and Obstacles for Future Applications

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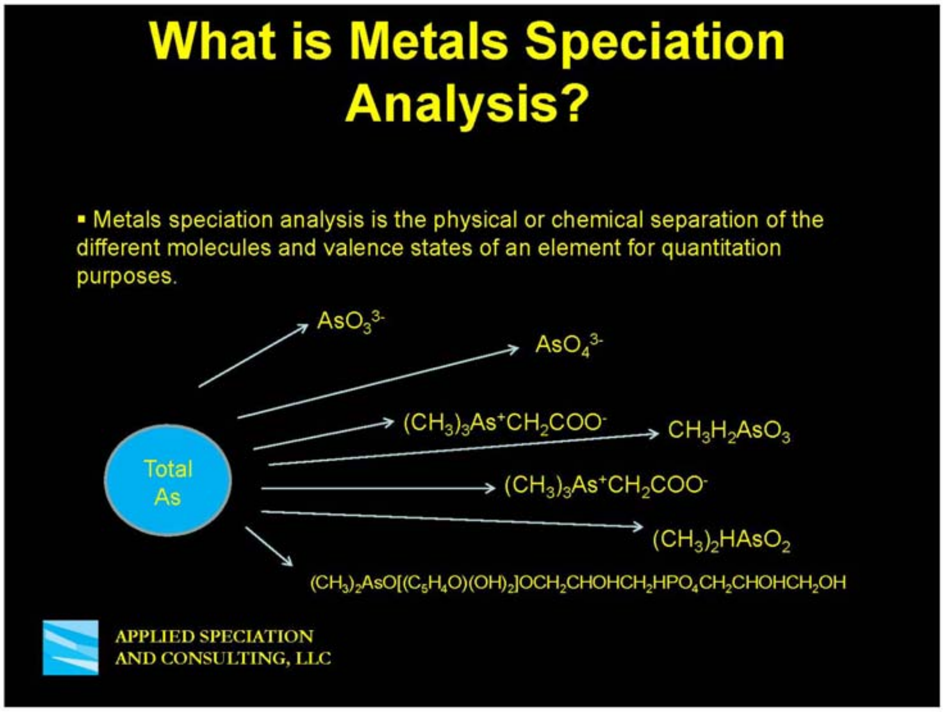

What is Metals Speciation Analysis?

- Metals speciation analysis is the physical or chemical separation of the different molecules and valence states of an element for quantitation purposes.

Total As

AsO_3^{3-}

AsO_4^{3-}

$(CH_3)_3As^+CH_2COO^-$

$CH_3H_2AsO_3$

$(CH_3)_3As^+CH_2COO^-$

$(CH_3)_2HAsO_2$

$(CH_3)_2AsO[(C_5H_4O)(OH)_2]OCH_2CHOHCH_2HPO_4CH_2CHOHCH_2OH$

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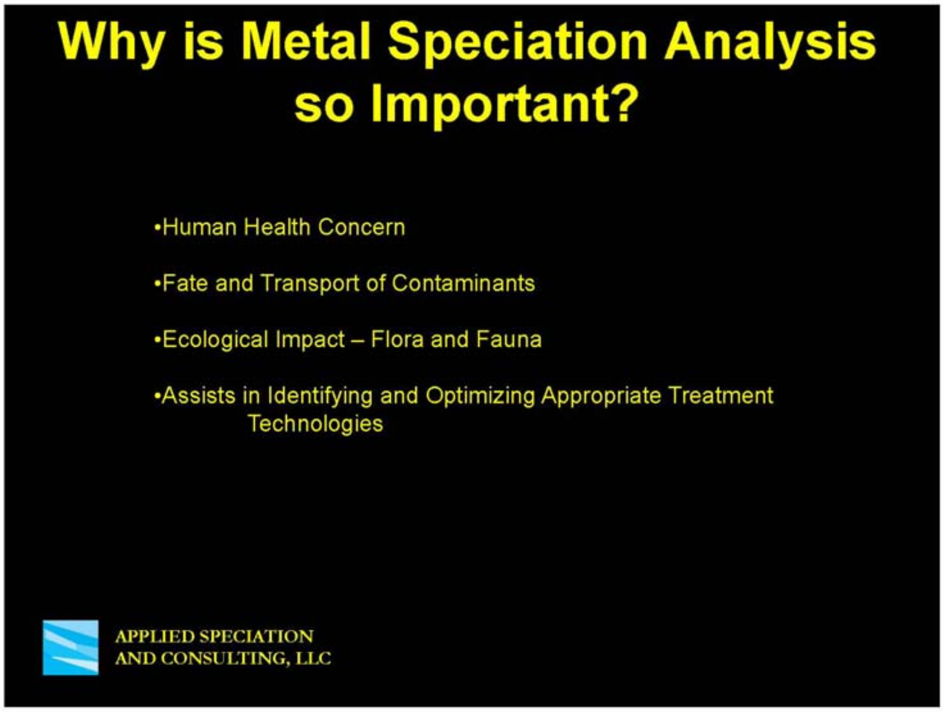

Why is Metal Speciation Analysis so Important?

- Human Health Concern
- Fate and Transport of Contaminants
- Ecological Impact – Flora and Fauna
- Assists in Identifying and Optimizing Appropriate Treatment Technologies

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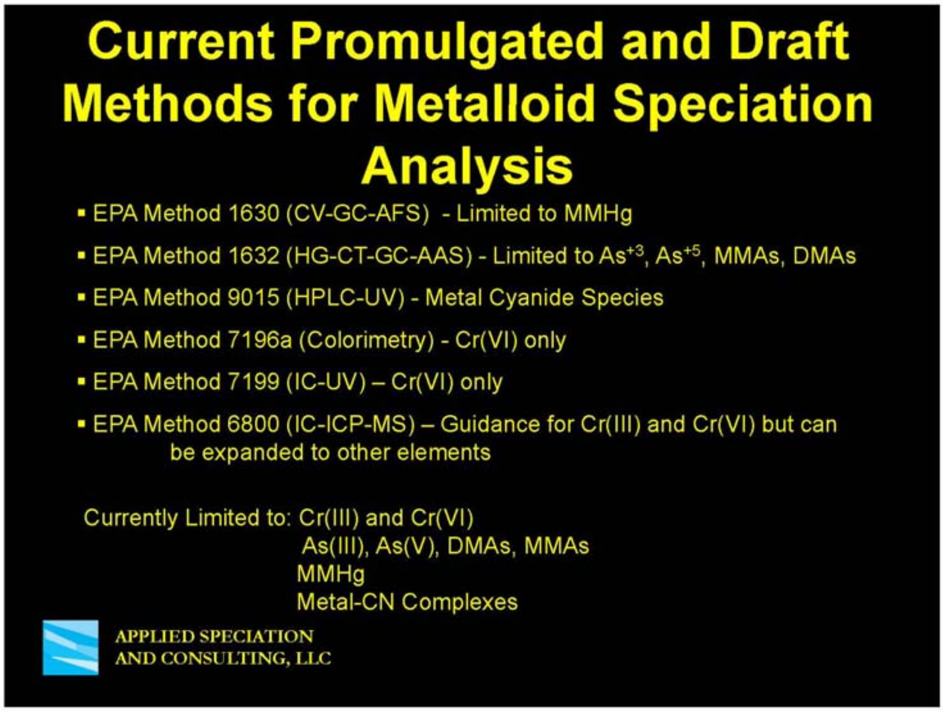

Current Promulgated and Draft Methods for Metalloid Speciation Analysis

- EPA Method 1630 (CV-GC-AFS) - Limited to MMHg
- EPA Method 1632 (HG-CT-GC-AAS) - Limited to As^{+3}, As^{+5}, MMAs, DMAs
- EPA Method 9015 (HPLC-UV) - Metal Cyanide Species
- EPA Method 7196a (Colorimetry) - Cr(VI) only
- EPA Method 7199 (IC-UV) – Cr(VI) only
- EPA Method 6800 (IC-ICP-MS) – Guidance for Cr(III) and Cr(VI) but can be expanded to other elements

Currently Limited to: Cr(III) and Cr(VI)
As(III), As(V), DMAs, MMAs
MMHg
Metal-CN Complexes

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What Other Elements Require Further Investigation?

- Expand on current list of Elements and matrices: Cr, As, Hg
  - Generate more robust methods and expand on known limitations for complex groundwater, tissues, and impacted soils
- Other Elements Requested by Industry but not supported:
  - As, Se, Hg (more matrices and species), Mn, Cu, Fe, V, Ni, Cd, Mo, Pb, Sn
- Other Inorganic Elements requested by industry but not supported (fully speciated for mass balance): I, Br, Cl, N, S

If the industry needs are not met by the commercial laboratory industry where do they go?

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Available Sources for Speciation Analytical Services

- Handful of North American laboratories with only a few applying hyphenated ICP methods
- Academic laboratories – Limited to the specialty of the professors' and students' projects. Also limited experience with real world sample matrices.
- European Specialty laboratories – Still remain relatively unregulated
- Academic laboratories across the world – Limited to the specialty of the professors' and students' projects. Unregulated quality control and assurance.

No unified scientific approach

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Issues due to nonstandardized scientific approach

- Method performance limited to experience of laboratory personnel
- Most laboratories only have one method for speciating a single element – limited method applicability
- Applied quality control and quality assurance measures are often limited or non-existent
- Lack of confidence by industry due to poor scientific approach of laboratory – decreases demand for service and funding for research
- Lack of standards and reference materials

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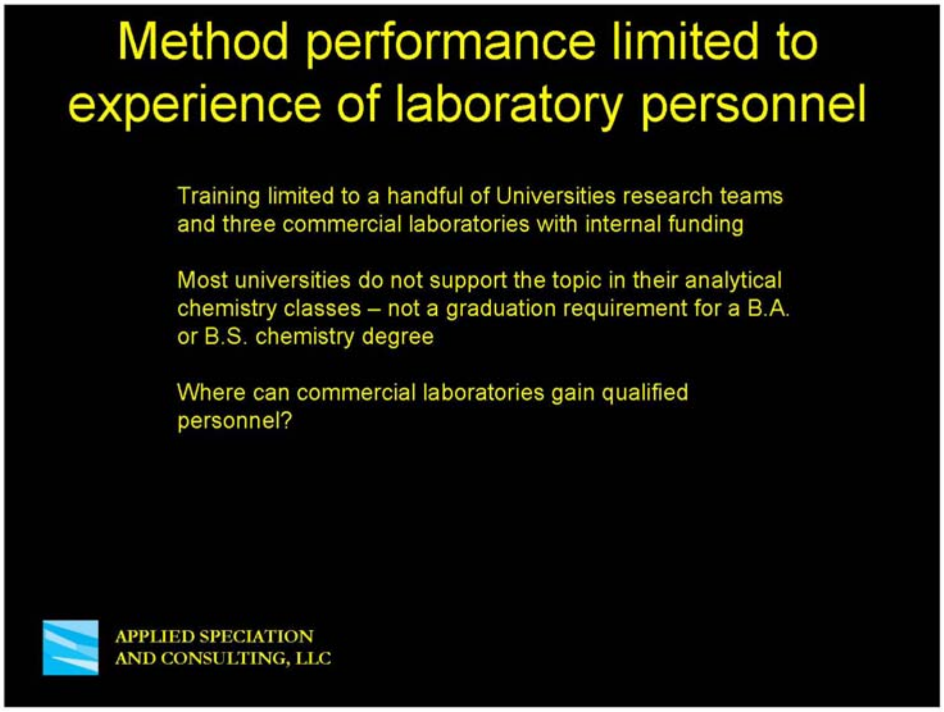

Method performance limited to experience of laboratory personnel

Training limited to a handful of Universities research teams and three commercial laboratories with internal funding

Most universities do not support the topic in their analytical chemistry classes – not a graduation requirement for a B.A. or B.S. chemistry degree

Where can commercial laboratories gain qualified personnel?

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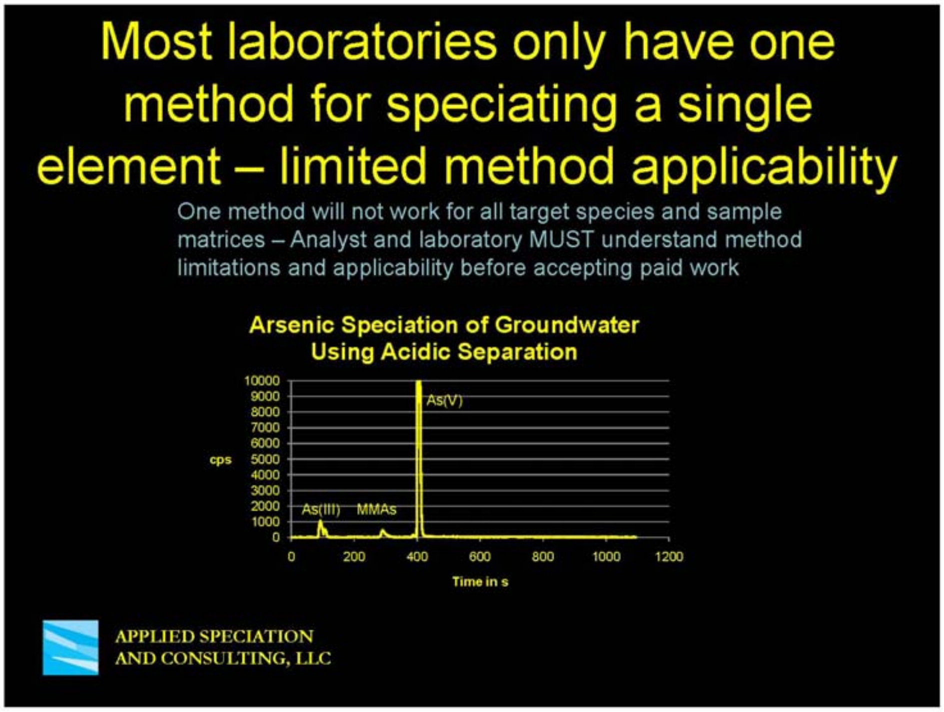

Most laboratories only have one method for speciating a single element – limited method applicability

One method will not work for all target species and sample matrices – Analyst and laboratory MUST understand method limitations and applicability before accepting paid work

Arsenic Speciation of Groundwater Using Acidic Separation

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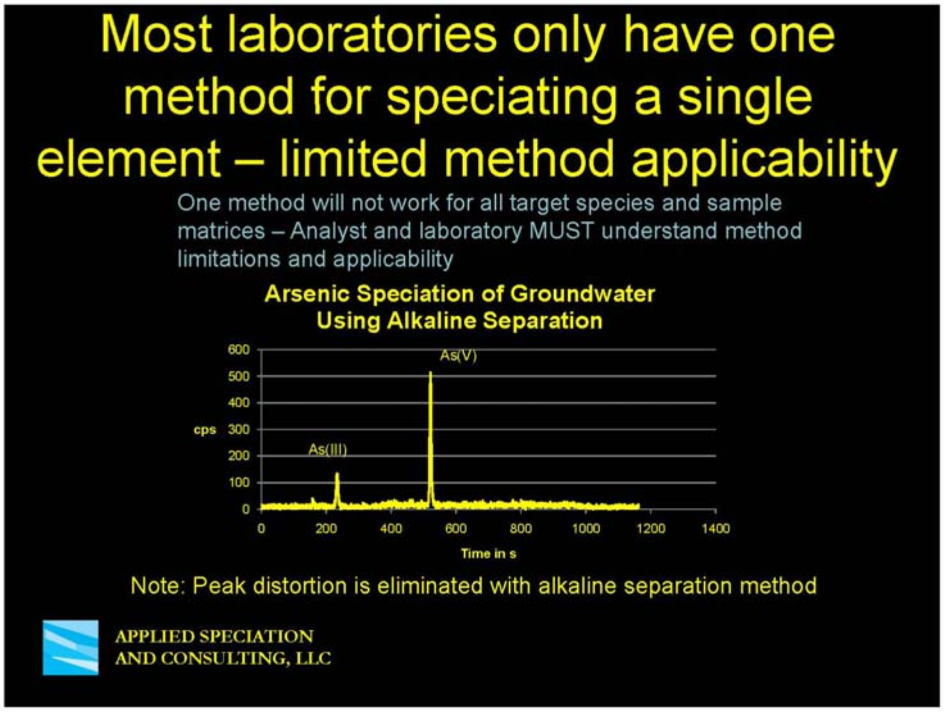

Most laboratories only have one method for speciating a single element – limited method applicability

One method will not work for all target species and sample matrices – Analyst and laboratory MUST understand method limitations and applicability

Arsenic Speciation of Groundwater Using Alkaline Separation

Note: Peak distortion is eliminated with alkaline separation method

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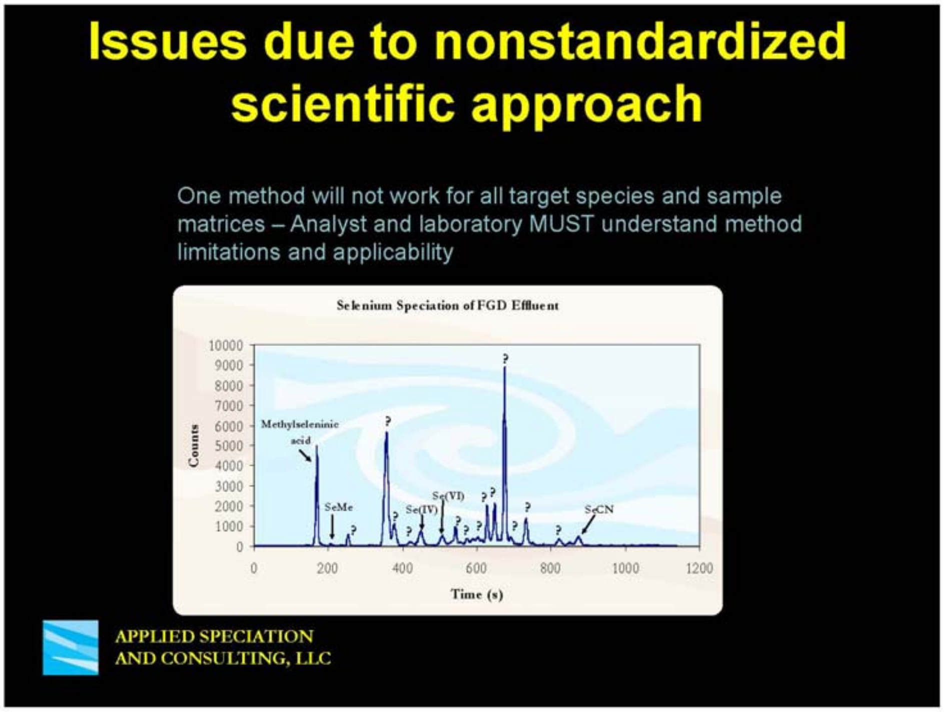

Issues due to nonstandardized scientific approach

One method will not work for all target species and sample matrices – Analyst and laboratory MUST understand method limitations and applicability

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Applied quality control and quality assurance measures are often limited or non-existent

Currently – QC limited to triplicate analysis or "batch QC"

Internal standards – similar to current EPA promulgated GC-MS methods to monitor RT, column loading, and signal depression/enhancement. Selection important!

MD/MS/MSD performed on EVERY DIFFERENT SAMPLE MATRIX – availability of "batch QC" limited to samples with the same matrix type

MS/MSD recovery failure may not be indicator of method failure

Mass balance – performed for EVERY sample

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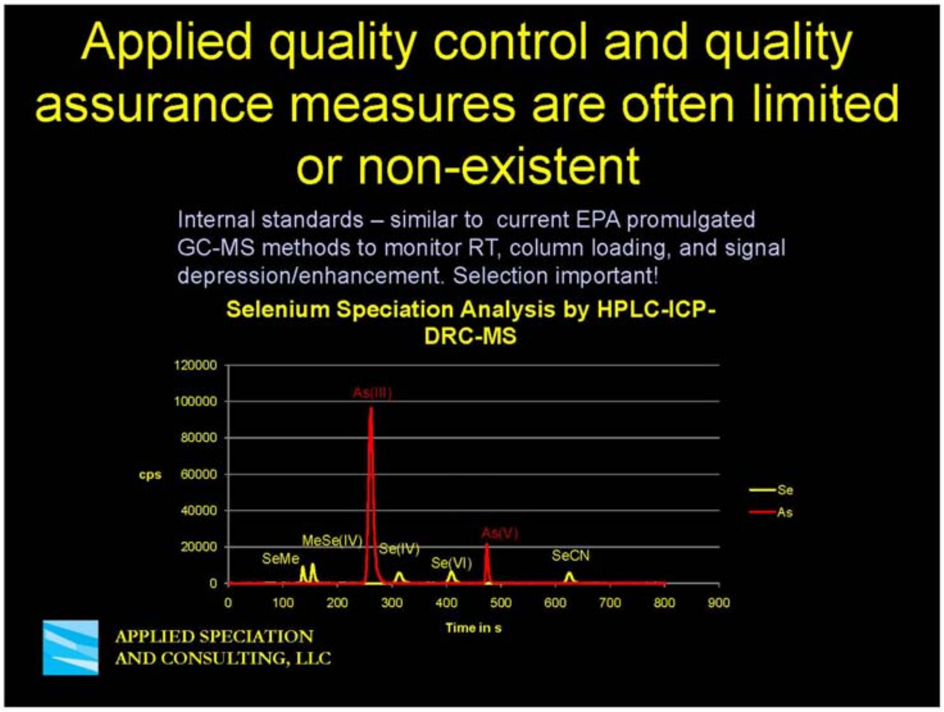

Applied quality control and quality assurance measures are often limited or non-existent

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Selenium Speciation Analysis by HPLC-ICP-DRC-MS

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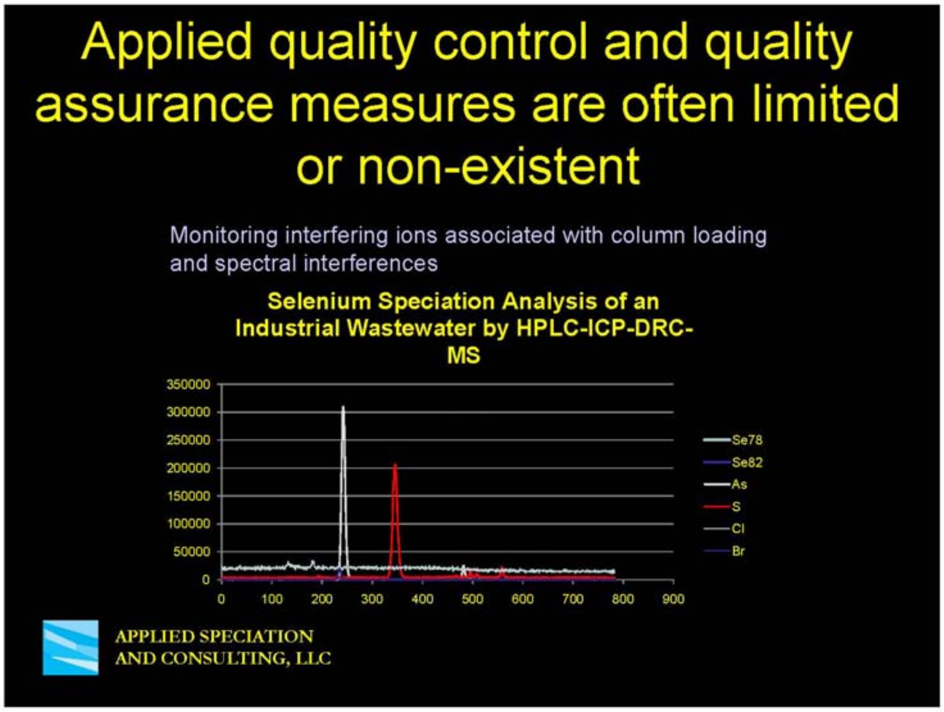

Applied quality control and quality assurance measures are often limited or non-existent

Monitoring interfering ions associated with column loading and spectral interferences

Selenium Speciation Analysis of an Industrial Wastewater by HPLC-ICP-DRC-MS

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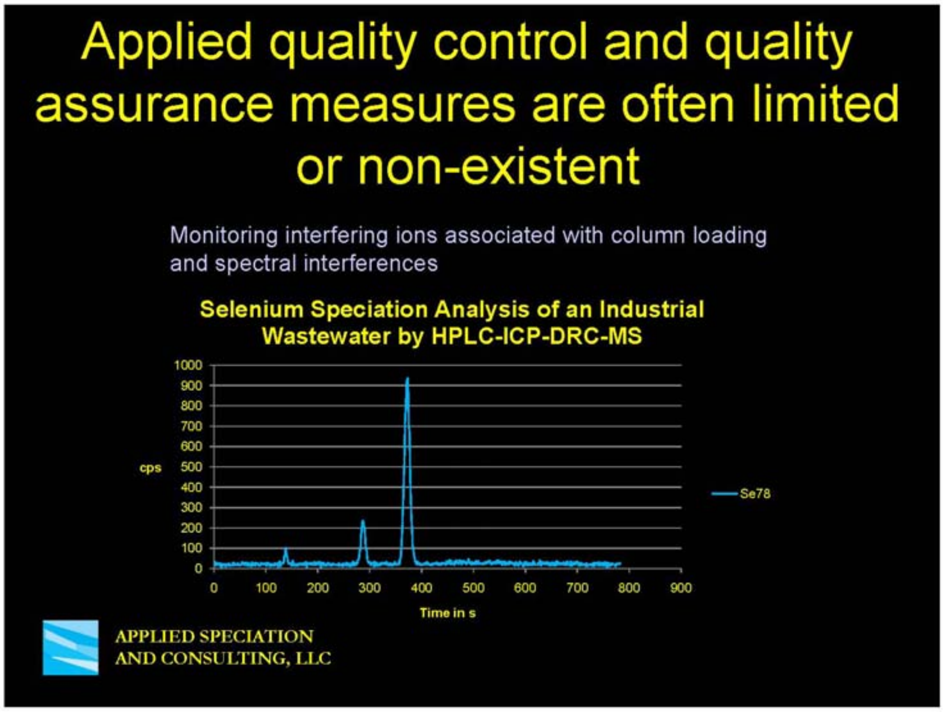

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Monitoring interfering ions associated with column loading and spectral interferences

Selenium Speciation Analysis of an Industrial Wastewater by HPLC-ICP-DRC-MS

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Applied quality control and quality assurance measures are often limited or non-existent

MS/MSD recovery failure may not be indicator of method failure

Analyte (µg/L)	Sample ID	Spike Conc	MS Result	Recovery	Spike Conc	MSD Result	Recovery	RPD
Se(IV)	Outfall	125.0	203.2	101.5	125.0	212.6	109.0	4.5
	Influent	500.0	782.0	147.0	500.0	791.0	148.8	1.1
Se(VI)	Outfall	125.0	132.2	99.2	125.0	141.5	106.6	6.8
	Influent	500.0	550.1	104.9	500.0	553.5	105.6	0.6
SeCN	Outfall	125.0	119.2	95.4	125.0	121.8	97.4	2.2
	Influent	500.0	247.0	49.4	500.0	238.0	47.6	3.7
Total Se	Outfall	125.0	252.5	100.0	125.0	250.0	98.1	1.0

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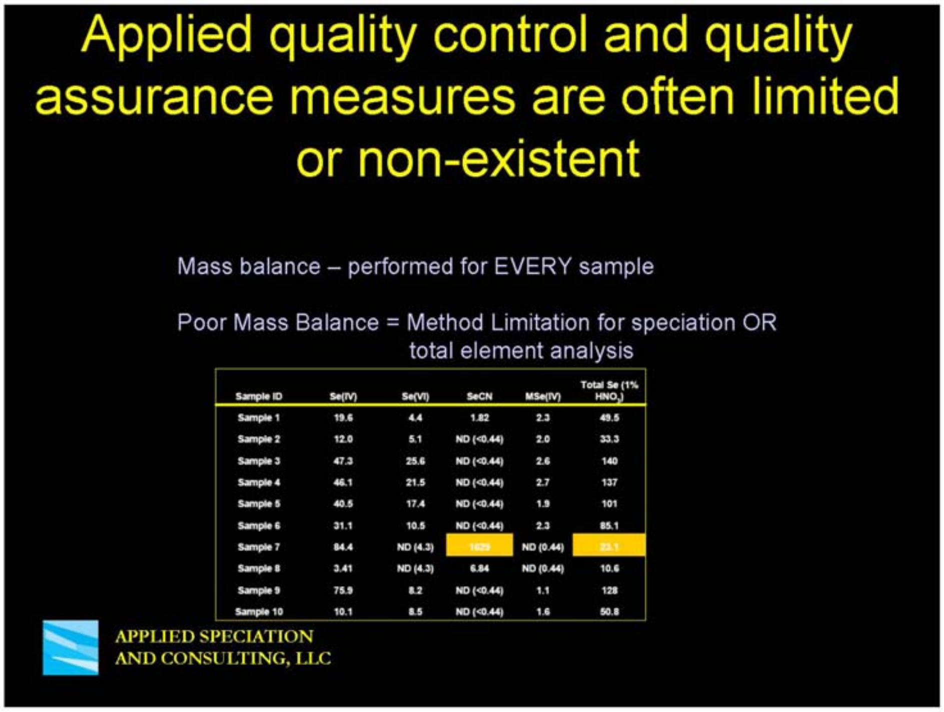

Applied quality control and quality assurance measures are often limited or non-existent

Mass balance – performed for EVERY sample

Poor Mass Balance = Method Limitation for speciation OR total element analysis

Sample ID	Se(IV)	Se(VI)	SeCN	MSe(IV)	Total Se (1% HNO_3)
Sample 1	19.6	4.4	1.82	2.3	49.5
Sample 2	12.0	5.1	ND (<0.44)	2.0	33.3
Sample 3	47.3	25.6	ND (<0.44)	2.6	140
Sample 4	46.1	21.5	ND (<0.44)	2.7	137
Sample 5	40.5	17.4	ND (<0.44)	1.9	101
Sample 6	31.1	10.5	ND (<0.44)	2.3	85.1
Sample 7	84.4	ND (4.3)	1629	ND (0.44)	23.1
Sample 8	3.41	ND (4.3)	6.84	ND (0.44)	10.6
Sample 9	75.9	8.2	ND (<0.44)	1.1	128
Sample 10	10.1	8.5	ND (<0.44)	1.6	50.8

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Lack of confidence by industry due to poor scientific approach of laboratory – decreases demand for service and funding for research

Due to the unregulated market for speciation analysis poor performance from one laboratory may impact the client or regulatory agency's acceptance of the field or a specific analytical platform.

Example: Selenium and Arsenic Speciation Analysis by Selective HG-AFS and IC-HG-AFS

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Lack of standards and reference materials

How are the speciation standards certified?

Gravimetrically…

Certified reference materials and standard reference materials:

Addressed by other presentations but what is the schedule and what sample matrices will be supported?

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How to regulate without promulgated methods?

- Provide scientific guidance
    - list of method recommendations
        - Separation techniques
        - Known method limitations
    - References - Books, journal articles, etc.
    - QC requirements to guide industry
- Make certification available – Done! However…
    - Method validation and verification must be performed prior to commercial application of method – guidance is already available from "Guidance for Industry Bioanalytical Method Validation" generated by the U.S. Department of Health and Human Services

- Provide education and training for appropriate personnel in regulatory agencies (not happening on a state basis)

- Problem for all remedial actions = FUNDING

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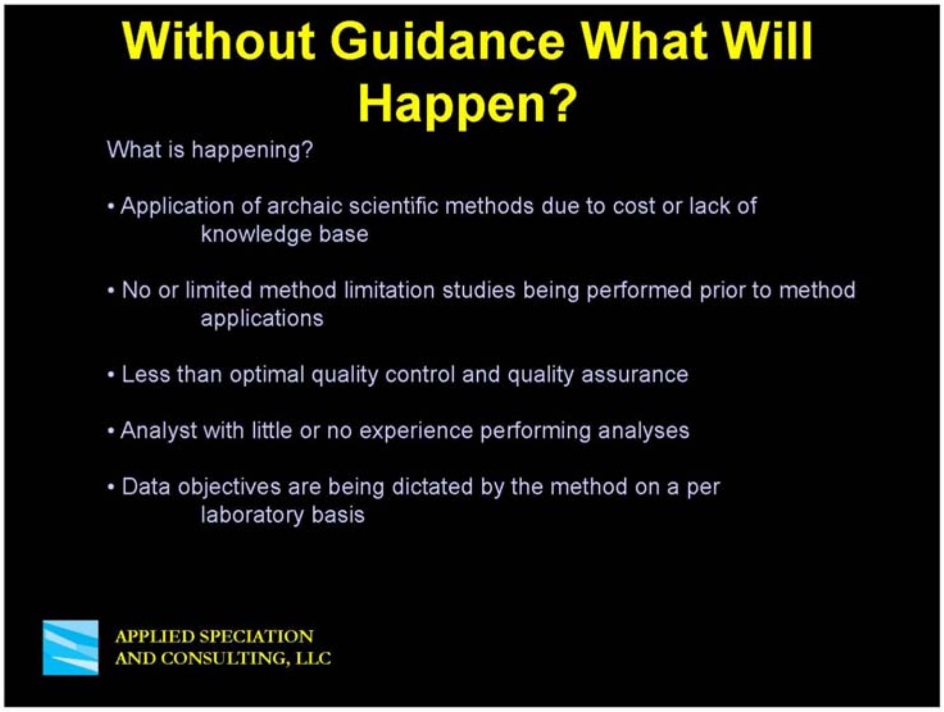

Without Guidance What Will Happen?

What is happening?

- Application of archaic scientific methods due to cost or lack of knowledge base
- No or limited method limitation studies being performed prior to method applications
- Less than optimal quality control and quality assurance
- Analyst with little or no experience performing analyses
- Data objectives are being dictated by the method on a per laboratory basis

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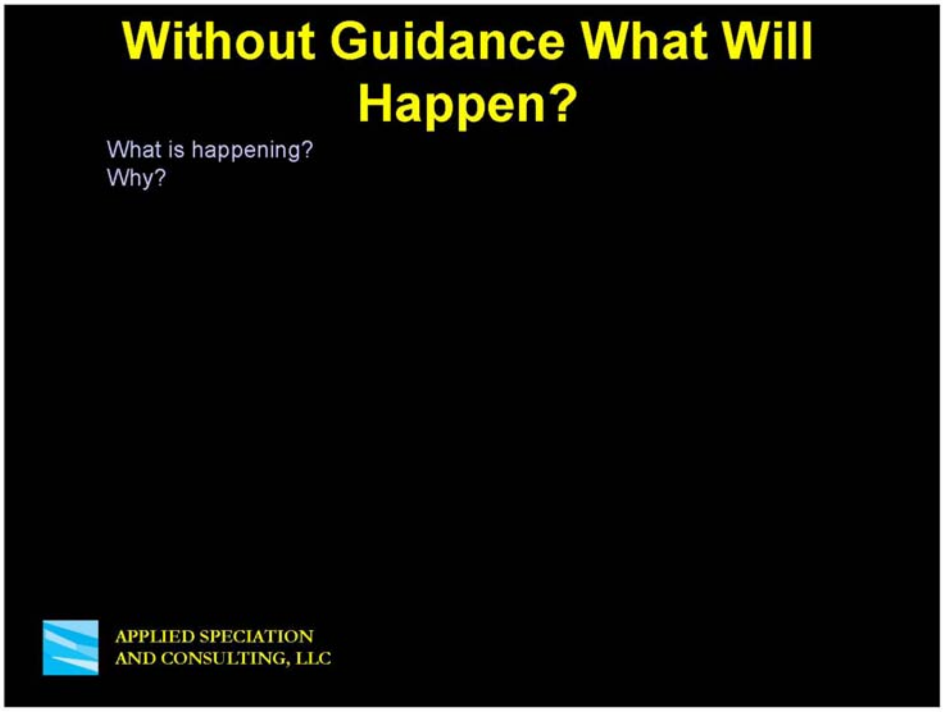

Without Guidance What Will Happen?

What is happening?
Why?

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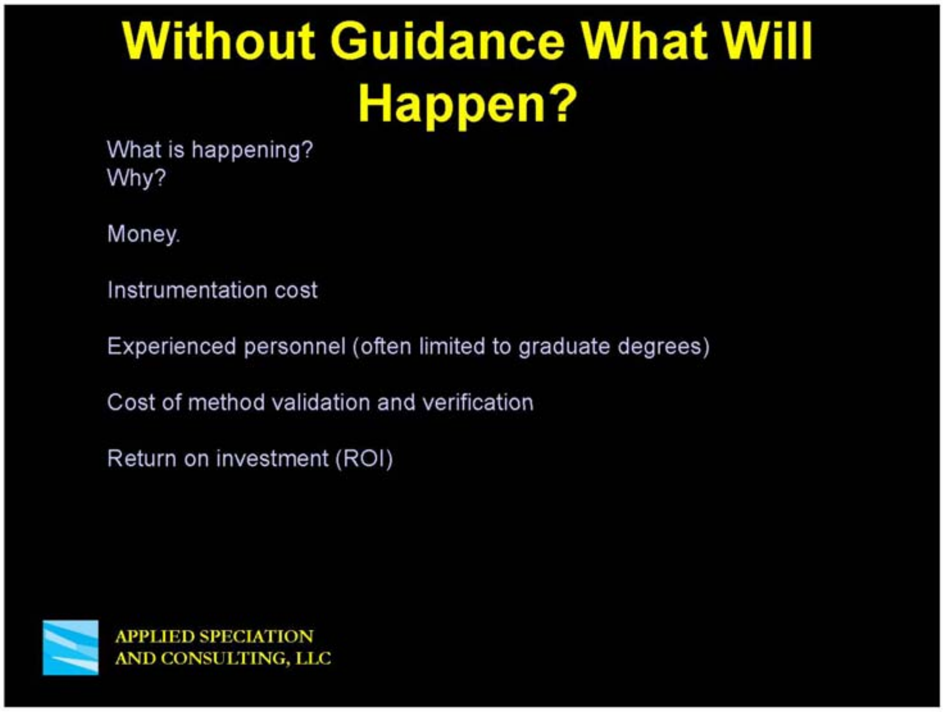

Without Guidance What Will Happen?

What is happening?
Why?

Money.

Instrumentation cost

Experienced personnel (often limited to graduate degrees)

Cost of method validation and verification

Return on investment (ROI)

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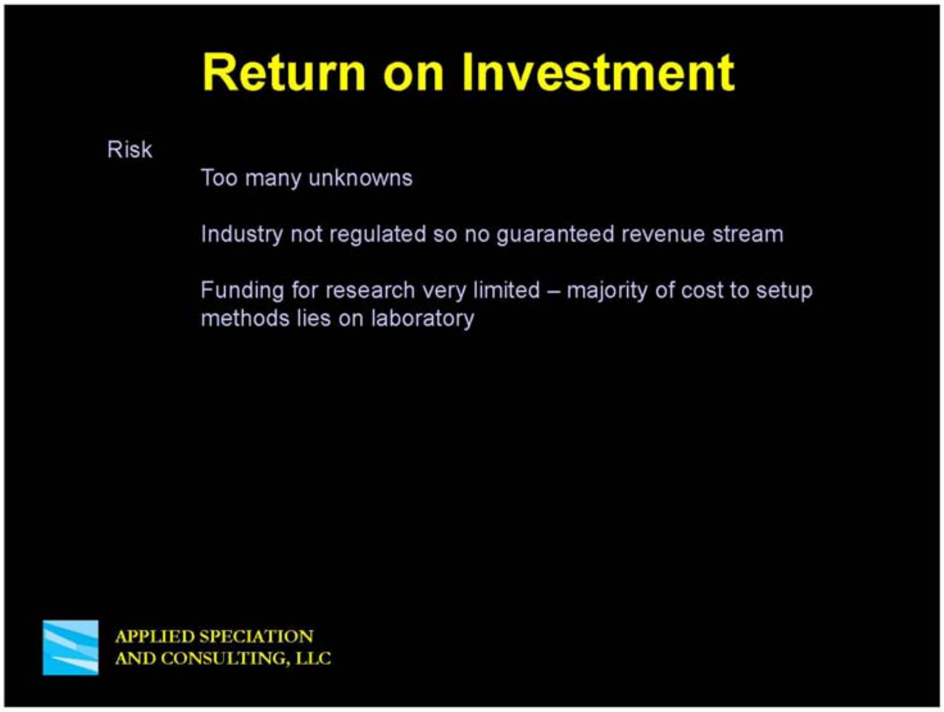

Return on Investment

Risk

- Too many unknowns
- Industry not regulated so no guaranteed revenue stream
- Funding for research very limited – majority of cost to setup methods lies on laboratory

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Current and Future Demand

Applicable Markets

- Environmental – monitoring and remediation
- Energy
- Petroleum
- Pharmaceutical
- Nutraceutical
- Academia
- Textile industry – purity and product development

The market exists but dissemination of information regarding applicability and availability is limited.

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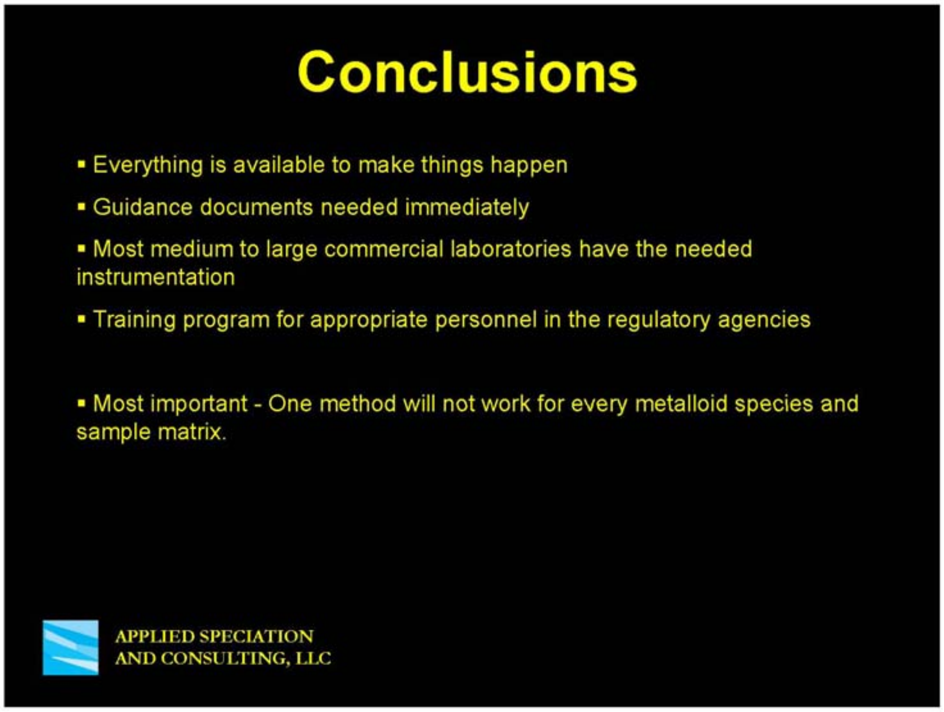

Conclusions

- Everything is available to make things happen
- Guidance documents needed immediately
- Most medium to large commercial laboratories have the needed instrumentation
- Training program for appropriate personnel in the regulatory agencies

- Most important - One method will not work for every metalloid species and sample matrix.

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Determination of Inorganic Mercury – Selenium – Glutathione Species by Nanospray: TOFMS Method 6800 IDMS Quantification Protocols

Timothy M. Fahrenholz, H.M. Skip Kingston, Mizanur Rahman, Laura Reyes, Jorge Guzman-Mar, Joshua Seither, Bryan Seybert, Matt Pamuku; Duquesne University Department of Chemistry and Biochemistry and Center for Environmental Research and Education, 308 Mellon Hall, Pittsburgh, PA 15282; 410-258-4108; fahrenholzt@yahoo.com

ABSTRACT

The evaluation of a person's ability to eliminate toxins such as inorganic mercury from the body is necessary for the purpose of determining the level of sensitivity the person has to these toxins and for assessing personal toxin effects. With respect to inorganic mercury, one of the means by which one can assess how well the body is detoxifying it is by analyzing, not only its total quantity and quantity of specific species in a biological sample, but also the complexes that form with it and the human xenobiotic immune system, as such an analysis would give insight into the mechanisms of mercury detoxification. A study by Gailer, et. al. in which rabbits were exposed to mercuric chloride and sodium selenite and had their plasma analyzed by X-ray absorption fine structure spectroscopy suggested that inorganic mercury, selenium, and glutathione form a non-toxic species as part of the inorganic mercury detoxification system (1). To expand upon this study, an analysis of these species made in vitro was done by nanospray time of flight mass spectrometry (nanoESI-TOF-MS). For quantification of the inorganic mercury in this complex, the sample was spiked with enriched 199Hg2+, and the determination of the inorganic mercury concentration was made by isotope dilution mass spectrometry (IDMS) following EPA Method 6800 protocols. The sample preparation was done in duplicate, and four analyses per sample preparation replicate were completed (N = 8). To test what would happen if the percentage recovery was less than 100%, the original spiked solutions were diluted so as to mimic a 25% reduction in recovery to assess robustness of the protocol, and the diluted solutions were also analyzed by IDMS just as the original solutions were.

In the analyses of both the original solutions and the ones mimicking a 25% reduction in recovery, the experimental results for the concentration of inorganic mercury were in agreement with the known values to within the 95% C.I. These results suggest that, by using nanospray-TOFMS combined with isotope dilution methods such as IDMS and SIDMS, one can qualitatively and quantitatively determine the mercury species concentrations even if the recovery is not constant; one can also determine which biomolecules the inorganic mercury is binding to and, thus, achieve a greater understanding of the roles these biomolecules play in environmental exposure and the related detoxification processes.

Determination of Inorganic Mercury – Selenium – Glutathione Species by Nanospray -TOFMS Method 6800

IDMS quantification protocols

Timothy Fahrenholz, Joshua Seither, G.M. Mizanur Rahman, Laura Reyes, H.M. Skip Kingston
Duquesne University

Introduction

☐ Mercury Toxicity

- Mercury is one of the most toxic elements known
- Different species of mercury have different levels of toxicity

Hg^{2+} targets primarily the kidney and is mainly eliminated through the urine (1).

$MeHg^{+}$ is a neurotoxin which can penetrate the blood brain barrier (1)

$EtHg^{+}$ is a component of the preservative Thimerosal. The toxicological information on it is limited (2)

1 Application of Speciated Isotope Dilution Mass Spectrometry in Evaluation of Different Literature Methods for the Speciation of Mercury in Hair Samples, G. M. Mizanur Rahman, H. M. Skip Kingston, Matt Pamuku, Pittcon 2006 Presentation

2 Dept. of Health and Human Services Agency for Toxic Substances and Disease Registry, website http://www.atsdr.cdc.gov/cabs/mercury/mercury_cabs.pdf

Selenium

- This element has a strong affinity for mercury and appears to play a significant role in mercury detoxification (3).
- Selenium also appears to play a role in the detoxification of As(III) (4).
- Additionally, selenium been associated with a decreased cancer risk (5).

3. Wantabe, C.; Modification of Mercury Toxicity by Selenium: Practical Importance?, Tohoku J. Exp. Med., 2002, 196, 71-77

4. Gailer, J.; Arsenic-selenium and mercury-selenium bonds in biology, Coordination Chemistry Reviews, 2007, 251, 234 – 254.

5. J. Nutr. 128: 1845-1854, 1998

Glutathione

- Glutathione (GSH) is among the strongest antioxidants in the body and, like selenium, appears to play a significant role in mercury detoxification (6).
- This important biomolecule also appears to be involved in the detoxification of other heavy metals as well, such as Cr (VI) (7) and cadmium (8).

6. Patrick, L.; Mercury Toxicity and Antioxidants: Part I: Role of Glutathione and alpha-Lipoic Acid in the Treatment of Mercury Toxicity, Alternative Medicine Review, 2002, vol. 7, no. 6., pp. 456-471.

7. Upreti, R.K.; Shrivastava, R.; Chaturvedi, U.C., Gut microflora & toxic metals: Chromium as a model, Indian J Med Res, 2004, 119, pp. 49-59.

8. Singhal, R.; Anderson, M.; Meister, A.; Glutathione, a first line of defense against cadmium toxicity, FASEB Journal, 1987, 1: 220 – 223.

Mammalian Detoxification

- Naganuma, et al. found that, when equamolar amounts of mercury (as mercuric chloride) and selenium (as sodium selenite) were combined with excess reduced glutathione, a water soluble black complex formed (9).
- This complex was administered to mice and found to have a very low toxicity level compared to mercuric chloride and sodium selenite (9).

(9) Naganuma, A.; Tabata, J.; Imura, N.; A Reaction Product from Mercuric Mercury, Selenite, and Reduced Glutathione, Research Communications in Pathology and Pharmacology, 38, 2, 1982.

Mammalian Detoxification

- Yoneda, et al. found that, when equamolar amounts of $HgCl_2$ and Na_2SeO_3 were combined with rat plasma in the presence of glutathione, a product consisting of several $(Hg\text{-}Se)_{100}$ subunits complexed with Selenoprotein P (a protein with ten selenocysteinyl residues) formed (10).

10. Yoneda, S.; Suzuki, K.; Equamolar Hg-Se Complex binds to Selenoprotein P, Biomedical and Biophysical Research Communications, 231, 7-11, 1997.

Bioanalytical Assessment

- Gailer, et al. produced the black mercury-selenium-glutathione complex described by Naganuma by combining equamolar amounts of $HgCl_2$ and Na_2SeO_3 with a five molar excess of reduced glutathione in pH 7.4 PBS buffer (11).
- This black complex was purified using size exclusion chromatography with ICP-AES for detection, shown below (11).

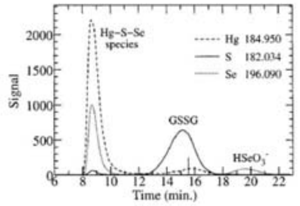


Figure 1. Simultaneous on-line mercury, selenium, and sulfur specific chromatogram of the mixture prepared by reacting mercuric chloride and sodium selenite with 5 molar equiv of GSH in buffered, aqueous solution on a Sephadex G-25 (SF) column (29.5 cm × 1.0 cm) at a flow rate of 1 mL/min. The mobile phase was PBS buffer (pH 7.4); the injection volume was 200 μL.

11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Denton, Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Bioanalytical Assessment

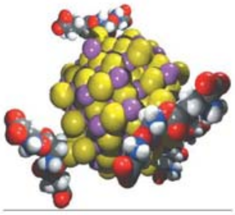
- Gailer et al. then analyzed the purified complex by ESI-MS (positive and negative mode) and MALDI-MS. No signals from the complex were detected using either of these two methods (11).

11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Postulated Structure

- Gailer et al. analyzed the purified black complex by X-ray absorption spectroscopy and came up with the postulated structure below with a Hg-Se core and glutathione residues attached on the exterior which renders the complex water soluble (11):

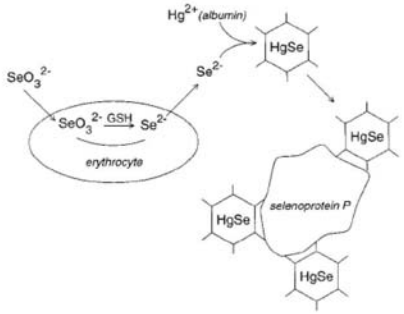
Proposed Structure: $HgSe_{100}$ core with 5 GSH → ~30,000 Da
Abbreviation - $(HgSe)_{100}(GSH)_5$



11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Denton, Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Postulated Mechanism

- Gailer, et al. also detected what appeared to be the same Hg-Se-Glutathione in vivo (rabbit plasma) as that produced in vitro. The authors suggested that this complex is the same as that which complexes with Selenoprotein P, as described by Yoneda, et al. (11)



11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Denton, Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Qualitative and Quantitative Metrology

- Isotopic Dilution Mass Spectrometry (IDMS) is a method that can be used to determine the concentration of a polyisotopic element or compound by spiking the sample with an isotopically enriched form of the analyte. The sample is analyzed by mass spectrometry, and the concentration is determined from an isotopic ratio.
- An important advantage of IDMS is that the isotopic ratio used in the calculation remains constant regardless of the intensity of the signal coming from the mass spectrometer.

Isotopic Dilution Mass Spectrometry

- IDMS equation

$$C_x = \left(\frac{C_s W_s}{W_x}\right)\left(\frac{A_s - R_m B_s}{R_m B_x - A_x}\right)$$

Ax = atom or molecule fraction of isotope A sample
Bx = atom or molecule fraction of isotope B sample
As = atom or molecule fraction of isotope A spike
Bs = atom or molecule fraction of isotope B spike
Cx = concentration of element or compound in the sample
Cs = concentration of element or compound in the spike
Wx = weight of the sample
Ws = weight of the spike
Rm = measured isotope ratio of isotope A to isotope B

Experiment with black complex that is formed from mercury-selenium-glutathione

- The black water soluble mercury-selenium-glutathione complex was prepared in our laboratory according to the method described by Gailer, et al (11).
  - Equamolar amounts of Na_2SeO_3 and $HgCl_2$ were dissolved in1M pH 7.4 PBS buffer in one container.
  - In a second container, five molar equivalents of glutathione (relative to the moles of Na_2SeO_3 and $HgCl_2$) were dissolved in 1M pH 7.4 PBS buffer.
  - The two solutions were combined, and a black liquid formed.
  - The final concentrations were as follows: Hg – 48,100 ppm, Se – 19,300 ppm, glutathione – 122,000 ppm.

11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Denton, Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Experiment with black mercury-selenium-glutathione complex

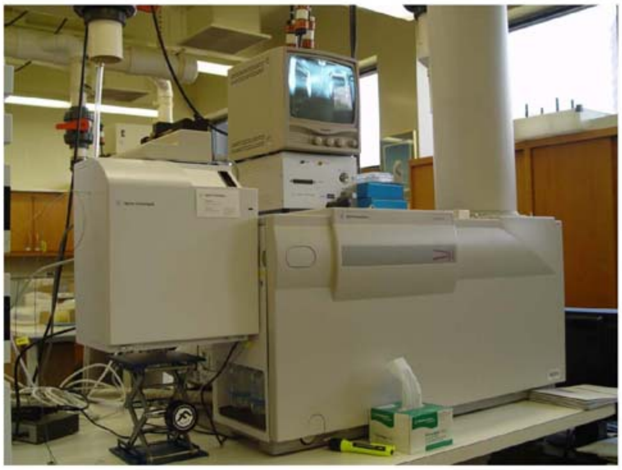
- The black complex:

Experiment with black mercury-selenium-glutathione complex

- An aliquot of the black complex solution was run through a Sephadex G25 size exclusion mobile phase with DD H_2O, and the black band which moved down the column was collected.
- An aliquot of the collected fraction with the black complex was diluted ~ 100x with DD H_2O. This solution was filtered through a Nalgene 300,000 Dalton cutoff filter unit, then analyzed by nanospray –TOFMS (positive mode).

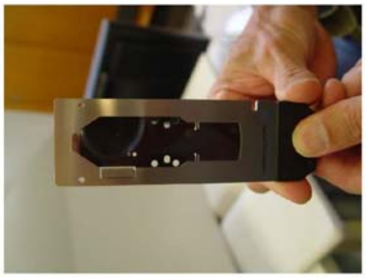
Experiment with black mercury-selenium-glutathione complex

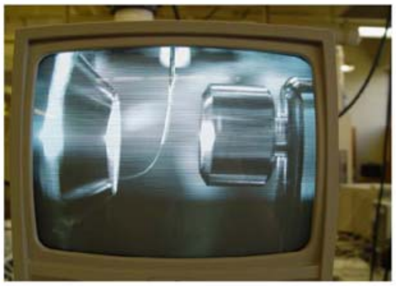
- Nanospray -TOFMS



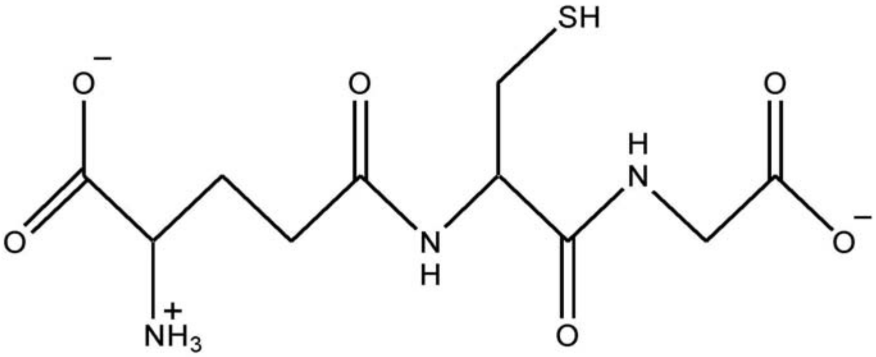
Experiment with black mercury-selenium-glutathione complex

- Nanospray -TOFMS
  - With respect to the chipcube TOF-MS, the sample is injected onto a chip with a plain capillary. The ions are introduced into the time of flight mass spectrometer (TOFMS) via nanospray ionization from the chipcube.

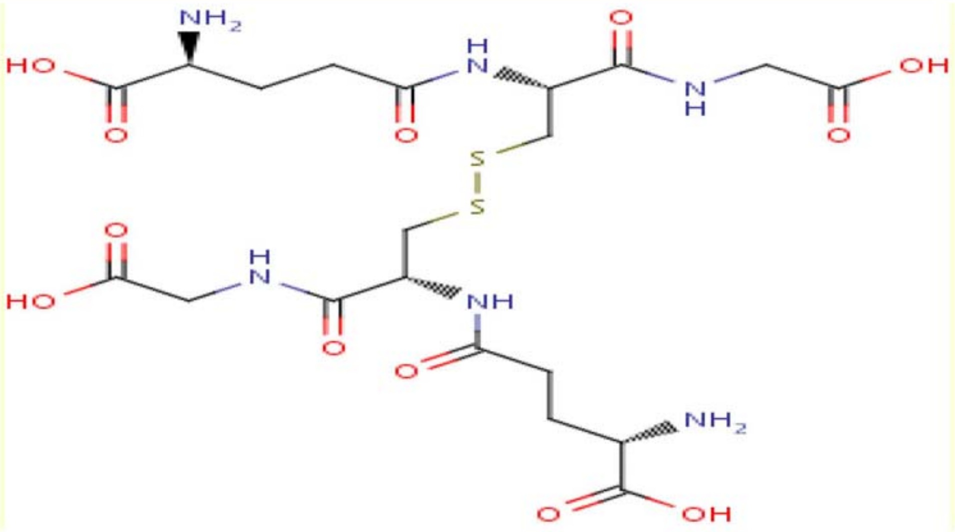




Glutathione, reduced (GSH)

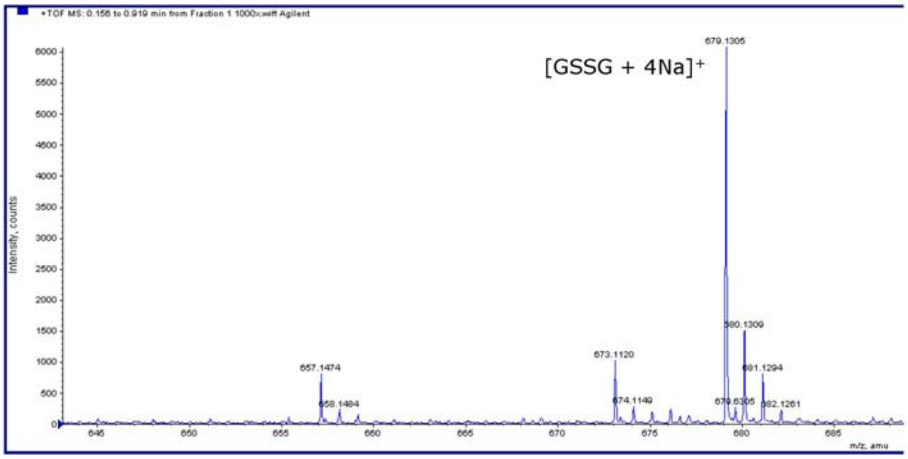


Glutathione, oxidized (GSSG)



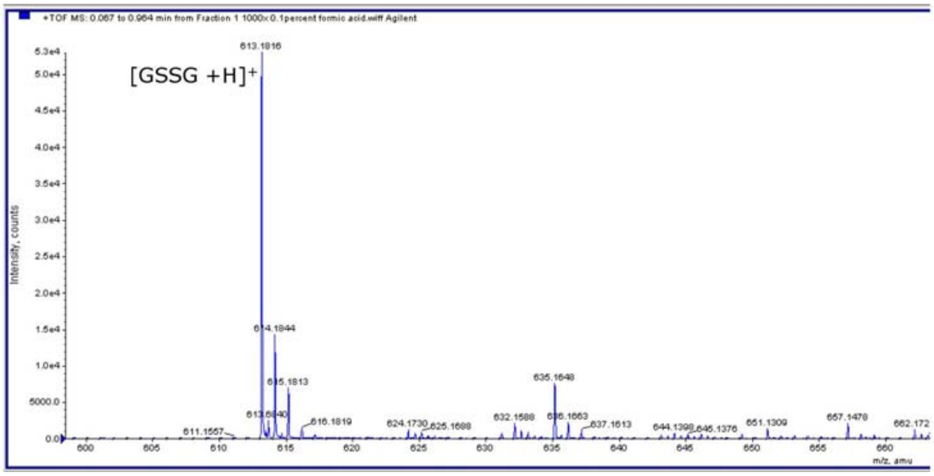
Experimental results with black mercury-selenium-glutathione complex

- Nanospray TOFMS analysis (positive mode) indicated the presence of oxidized glutathione with sodium adducts (the one with four Na's per oxidized glutathione - ~ 679 m/z - being predominant). No reduced glutathione (~308 m/z) was detected. Note upper range of this TOF instrument is ~ 11,000 m/z



Experiment results with black mercury-selenium-glutathione complex

- The dilution of the fraction from the G25 column was repeated with 0.1% Formic acid, and oxidized glutathione with no sodium adducts (~ 613 m/z) became the predominant glutathione species detected. No reduced glutathione was detected. Note: upper range of this TOF system is 11,000 m/z



Experiment with black mercury-selenium-glutathione complex

- The detection of oxidized glutathione was consistent with the results from Gailer, et al. (11). This result suggested that a redox reaction occurred in which reduced glutathione was consumed (4).
- The nondetection of the mercury-selenium-glutathione complex by mass spectrometry with a soft ionization method (nanospray) was also consistent with results from Gailer, et al. (11), who, as mentioned earlier, used ESI-MS and MALDI-MS.

4. Gailer, J.; Arsenic-selenium and mercury-selenium bonds in biology, Coordination Chemistry Reviews, 2007, 251, 234 – 254.

11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Denton, Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Experiment with black mercury-selenium-glutathione complex

- According to Gailer et al., a possible reason why mercury-selenium-glutathione species could not be detected by ESI-MS or MALDI-MS was because of the difficulty in ionizing the species (11).
- Additionally, given that the mass of the complex is estimated to be ~ 30,000 Daltons, the possibility exists that the signal from the complex was out of the m/z range of the instrument. With our instrument, the m/z limit is ~11,000; hence, only $(HgSe)_{100}(GSH)_5$ with charges of +5 or greater would be potentially detectable.

11. Gailer, J.; George, G.; Pickering, I.; Madden, S.; Prince, R.; Yu, E.; Bonner Denton, M.; Younis, H.; Aposhian, V.; Structural Basis of the Antagonism between Inorganic Mercury and Selenium in Mammals; Chem. Res. Toxicol., 2000, 13, 1135 – 1142.

Future work with the black mercury-selenium-glutathione complex

- An isotopically enriched form of the black mercury-selenium-glutathione complex will be made and used to analyze the complex by IDMS with SEC-ICPMS.
- As noted earlier, the black mercury-selenium-glutathione species appears to complex with Selenoprotein P (8). This complex with Selenoprotein P will be examined by SEC-ICPMS, Nanospray - TOFMS, and MALDI-TOFMS.

8. Yoneda, S.; Suzuki, K.; Equamolar Hg-Se Complex binds to Selenoprotein P, Biomedical and Biophysical Research Communications, 231, 7-11, 1997.

Future work with the black mercury-selenium-glutathione complex

- It is possible that the body's production of the mercury-selenium-glutathione species is one of the means by which it detoxifies mercury
- Individuals who have a deficiency in reduced glutathione and/or selenium may be less able to produce this species and are, therefore, more susceptible to environmental mercury toxins.
- Dr. S. Jill James et al. found that autistic children appear to have significantly lower levels of reduced glutathione, as well as decreased GSH/GSSG ratios, compared to normal children. These factors may contribute to increased vulnerability of autistic individuals to environmental toxins (12).

12. James, S. J.; Cutler, P.; Melnyk, S.; Hernigan, S.; Janak, L.; Gaylor, D. W.; Neubrander, J. A. Metabolic biomarkers of increased oxidative stress and methylationcapacity in children with autism, *American Journal of Clinical Nutrition*. 80 (6): 1611 – 1617.

Collaboration with Dr. Scott Faber

- Our research group will work with autism expert Scott Faber, M.D. from the Children's Institute in Pittsburgh to expand upon the work done by Dr. S. Jill James by looking for biomarkers which can be used for the early detection of autism.

- Research will also be conducted with Dr. Faber to assess the effectiveness of various treatments for autism is concerned. Biological samples such as blood, hair, and urine will be analyzed for toxic heavy metal species and other toxins.

Continuing on…

- Dr. Skip Kingston, in the next talk, will expand upon this relationship between exposure to environmental toxins and autism incidence. Below are titles from recent articles pertaining to this topic:

The Environment as an Etiologic Factor in Autism: A New Direction for Research

Metabolic biomarkers of increased oxidative stress and impaired methylation capacity in children with autism[1,2]

Mercury, Lead, and Zinc in Baby Teeth of Children with Autism Versus Controls

Acknowledgements

- Duquesne University
- Applied Isotope Technologies
- Heinz Foundation

Question and answer slides

Reasons for using SEC and Nanospray TOFMS

- In this experiment, it was hypothesized that, by running the black complex through a size exclusion column with water for desalting purposes and by analyzing with nanospray -TOFMS (more sensitive than ESI-TOFMS), the black complex could be detected. This did not occur.

Mechanism, expanded

From Gailer, et al. (4)

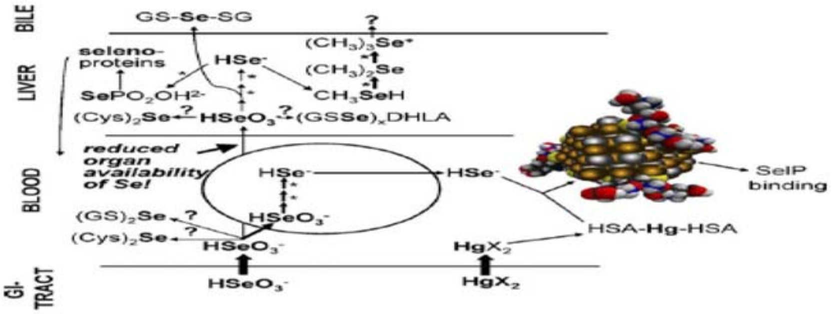


Fig. 8. Interaction between Hg^{2+} and Se^{IV} in the bloodstream. Oval shape: erythrocyte; Cys: L-cysteine; GSH: L-glutathione; DHLA: dihydrolipoic acid; SelP: selenoprotein, coloured species represents $(Hg–Se)_{100}(GS)_5$ species. Asterisk indicates enzymatically mediated biotransformation.

4. Gailer, J.; Arsenic-selenium and mercury-selenium bonds in biology,
Coordination Chemistry Reviews, 2007, 251, 234 – 254.

Oxidation of GSH

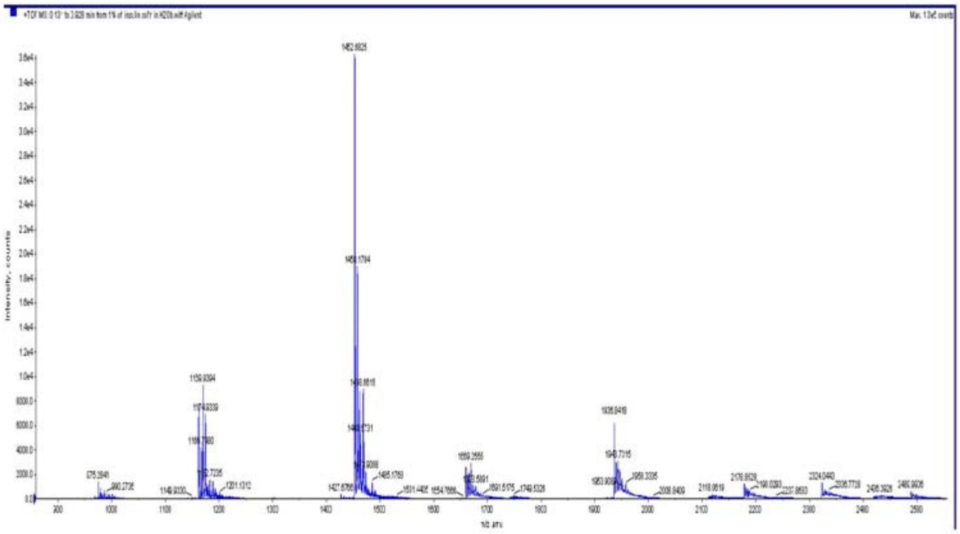
- Mechanism

$$4GSH + SeO_3^{2-} \longrightarrow GSSG + GS\text{-}Se\text{-}SG + 2OH^- + H_2O$$

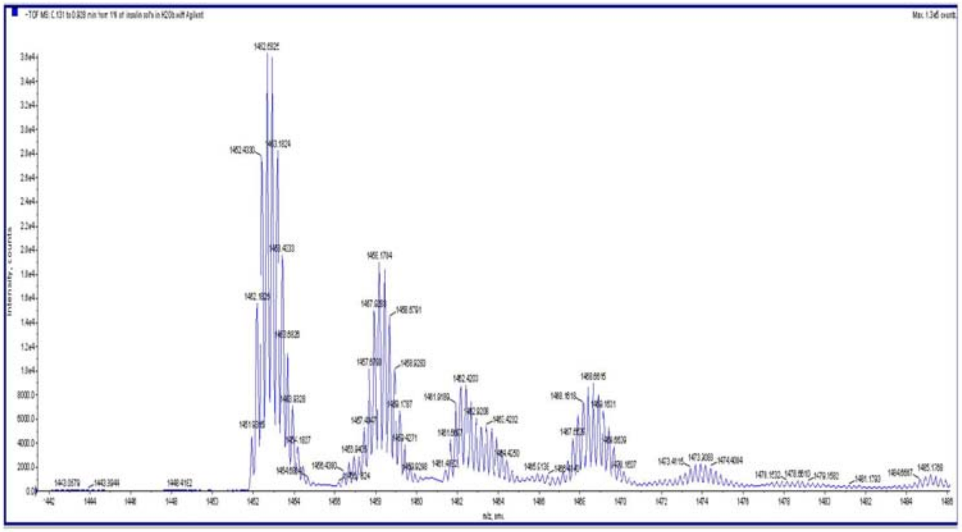
$$GS\text{-}Se\text{-}SG + 2OH^- + O_2 \longrightarrow GSSG + SeO_3^{2-} + H_2O$$

13. Sheng-Yun Cui, Hua Jin, Seung -Jin Kim, Avvaru Praveen Kumar, Yong-Ill Lee, Interaction of Glutathione and Sodium Selenite In vitro investigated by Electrospray Ionization Tandem Mass Spectrometry, J. Biochem. 2008, 143, 685-693.

Insulin (5808 Daltons) analyzed by Nanospray TOFMS



Insulin (5808 Daltons) analyzed by Nanospray TOFMS



State of the Art in Environmental Human Health and Speciated Measurement

H. M. Skip Kingston, G. M. Mizanur Rahman, Laura H. Reyes, Jorge G. Mar, Matt Pamuku, Timothy Fahrenholz, Gregory M. Zinn, Sara M. Kallop and Rebecca L. Wagner; Duquesne University Department of Chemistry and Biochemistry, and Center for Environmental Research and Education, 600 Forbes Avenue, Pittsburgh, PA 15282; 412-396-5564; kingston@duq.edu
Scott Faber; Children's Institute, Pittsburgh, PA

ABSTRACT

Only recently have we been able to make quantitative measurements of reactive elemental and molecular species in the environment and in ourselves with new protocols and mass spectrometry. We are now able to assess health significances that were previously not quantifiable in a reliable manner and these are leading to new medical diagnoses and a new ability to evaluate human health. New applications of these analyses are now permitting assessment of toxicological interactions of the immune system and are providing the ability to relate these to exposure, immune response and environmental and human health assessment with meaningful quantification. Examples of some of these new overarching capabilities are the subject of this discussion of the state of the art of measurement and assessment of chemical interactions.

A futuristic glimpse of the future capabilities and of what is on the horizon will be presented based on the shoulders of giants. In 2006, the Nobel Prize was awarded for the discovery of the epigenome and the realization that we express genes that reflect our environment and may pass these expression and suppression down thought three generations of offspring. In 2002, the Nobel Prize was awarded for the development of Electrospray Mass Spectrometry and the ability to measure intact molecules and even viruses as they fly ionized through a mass spectrometer. The ability to see the actual complex molecular world has enabled measurement science, the field of metrology with new tools and opportunities. Both of these Nobel Prizes will be combined as they provide the current state of human health measurements and its importance. For examples, speciated isotope dilution mass spectrometry analysis of toxic species in human blood, fluids and tissue using different analytical techniques, e.g. GC-MS, LC-ESI-MS, LC-APCI-MS, nano-LC-ESI-TOF-MS, MALDI-TOF-MS, GC-ICP-MS and LC-ICP-MS will be discussed and demonstrated as the state of the art of measurement and some projections for our current capabilities and observations will be made.

State-of-the-art in Environmental Human Health and Speciated Measurement

Dr. H. M. Skip Kingston

Duquesne University, Department of Chemistry and Biochemistry,
Center for Environmental Research and Education

With Contributions from:

Dr. Scott Faber (MD), Children's Institute

Dr. Mizan Rahman, Dr.Laura Reyes, Dr.Jorge Mar, Matt Pamuku (AIT)

Graduate Students: Timothy Fahrenholz & Greg Zinn, Becky Wagner
Duquesne University

August 11, 2008

US and International Laws are "Human Health and Environmental" Laws

- US Example RCRA (1976 – 1992 as amended):
  - Objectives and National Policy 42 USC 6902 sec. 1003
    - "waste … should be treated, stored, or disposed of so as to minimize the present and future threat to human health and the environment."
- EU Example Directive 2004:
  - The European Parliament and of the Council
    - "Relating to As, Cd, Hg, Ni and polycyclic aromatic hydrocarbons in ambient air"
    - Sec 11 "The effect of As, Cd, Hg, Ni and PAH on human health including via the food chain, and the environment as a whole…"
- EU Reduction of Hazardous Substances (RoHS)
  - Pb, Cd, Cr(VI), Hg and PBDEs …

State-of-the-Art in Speciation

- Books on state-of-the-art in speciation appeared in the 1990s and continue today they are hyphenated techniques mainly Chromatography and Mass Spectrometry
    - EU website for books on "state-of-the-art" in speciation
    - www.speciation.net/Public/Document/2005...
- These are mainly assessment and measurement techniques for popular species in popular matrices
- The field expanded as our understanding expanded
- What are these new understandings of what state-of-the-art means and what are the important new knowledge that makes speciation an important and compelling field?

focal point

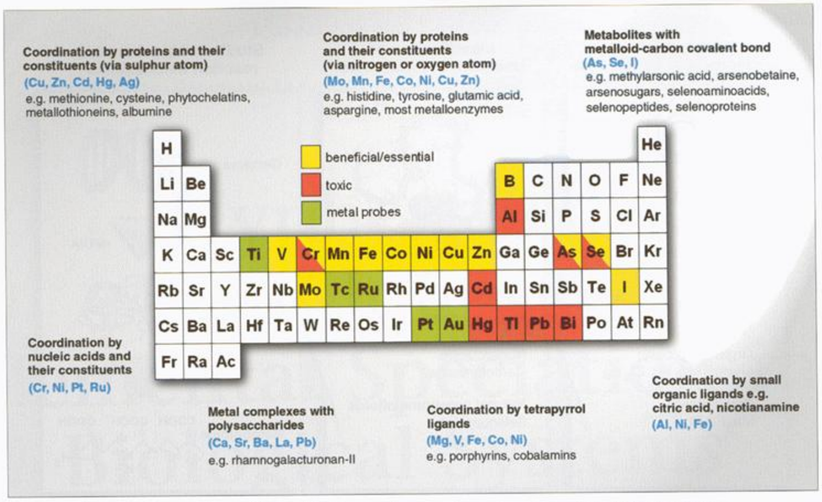


FIG. 2. *Trace elements of interest in medicine and biology: endogenous trace element species in biological systems.*

"Hyphenated Techniques for Species in Biological Systems" J. Szpunar, et.al, in Applied Spectroscoy, Vol. 57, No. 3, pgs. 102A-112A, 2003

We started with the identification of some species of interest

Example:
Hexavalent
Chromium

1 erin quicktime trailer blood Med rec Hex Cr

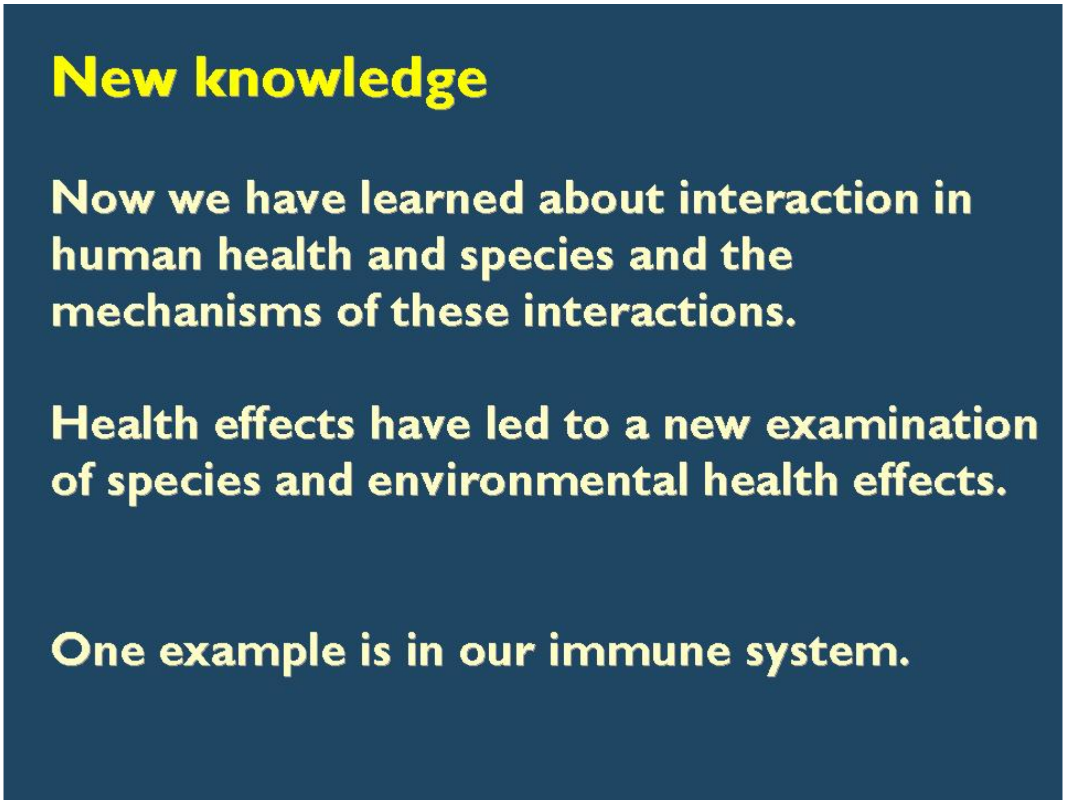
Species and Fields of Interest

Field of Interest	Species Examples
Plant and animal biochemistry, ecotoxicology, nutrition	***Organometalloid species*: arsenobetaine, arsenocholine, selenoamino acids** ***Metallothioneines*: Cd, Cu, Zn** ***Phytochelatins*: Cd, Cu, Zn, Co, As** ***Polysaccharides*: Pb, Sr, Ba, Ca, Mg** ***Macrocycles*: chlorophyll derivatives, cobalamines**
Environmental (aquatic and atmospheric chemistry	*Redox states*: As(III)/As(V), Cr(III)/Cr(VI), Se(IV)/Se(VI), Sb(III)/Sb(V), Fe(II)/Fe(III) *Alkylmetals*: $(CH_3)_nSn^{(3-n)+}$, $(C_4H_9)_nSn^{(3-n)+}$, $(C_6H_5)_nSn^{(3-n)+}$, CH_3Hg^+, $(CH_3)_2Hg$, $C_2H_5Hg^+$, $(C_2H_5)_2Hg$, $(CH_3)_n(C_2H_5)_mPb^{(4-m-n)+}$, CH_3Cd^+, $(CH_3)_2Cd$ Transformations of Roxarsone into As(III)/ As(V) Epigenetic changes of human DNA
Industrial chemistry	***Metalloporphyrins*: Ni, V, Fe, Ga** ***Catalytic mixtures*: Ni, Ru, Rh** ***Organomercury and organoarsenic*: shale oil, gasoline, natural gas condensate**
Clinical biochemistry	*Metalloenzymes*: Zn, Mo, Co *Metallodrugs*: Pt, Ru, Ti *Nucleic acids*: Cr, Ni, Pt, Ru *Transport proteins*: Al, Cu, Zn, Fe Epigenetic Expression and Silencing of human DNA

Modified from Ref. Hyphenated Techniques in Speciation Analysis; Szpunar, J.;Lobinski, R. Eds. The Royal Society of Chemistry: London, UK, pp 3, 2004

Human Health and Environmental Forensic Analysis Drivers

- Legal Requirements for Elemental Speciation Analysis Required in Addition to Elemental Analysis
  - Europe – 2004 and 2006 targeted – As, Cd, Cr(VI), Hg, Ni Pb, and others
  - Korea – species based
  - Japan – species based
  - New Jersey (Cr(VI), AlkylHg…
  - California …
  - Other Countries
- Species Determine
  - Chemistry
  - Toxicity
  - Remediation and environmental impact
  - Human Health
- Speciation Requirements
  - Speciation Analysis Methods
  - Speciated Reagents and Standards
  - Speciated Standards - SRMs, CRMs, RMs
- New Medical Understanding and Treatment in Human Health



New knowledge

Now we have learned about interaction in human health and species and the mechanisms of these interactions.

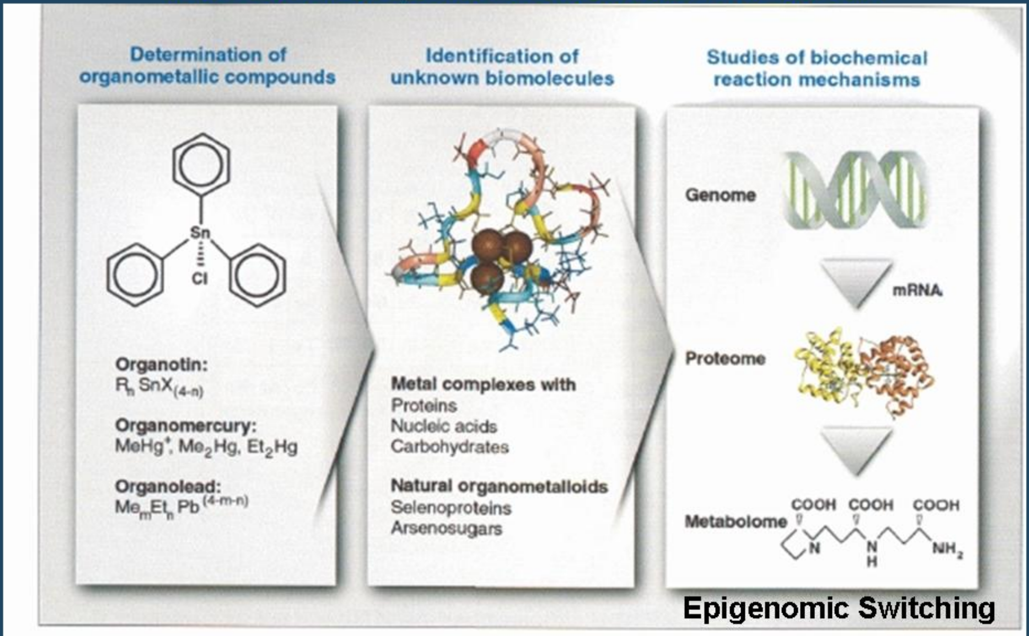
Health effects have led to a new examination of species and environmental health effects.

One example is in our immune system.

Contributions of Metal Species and Pesticides in human health degradation, and as factors in Autism have been identified

Metal Protein_2.wmv

Evolution of Species Definition and Effects



Epigenomic Switching

FIG. 1. Evolution of the concept of speciation analysis: from the determination of anthropogenic organometallic contaminants to-

"Hyphenated Techniques for Species in Biological Systems" J. Szpunar, et.al, in Applied Spectroscoy, Vol. 57, No. 3, pgs. 102A-112A, 2003

New Understanding of Species and Human Health

- We experienced the understanding that some species were Endocrine Disrupters
  - Species that interrupt normal hormone switches in the fish, mammalian and human body
- Genes and DNA are the same in each cell of an organism
  - Q: So what makes a skin cell different from an eye cell from a brain cell?
  - A: It depends on gene switching.

1 Ghost In Your Genes Gene on off light switch more

2 Ghost In Your Genes 2041 c-twins and changes around us

Recent Studies 2005-2008 – CDC, ATSDR & WHO

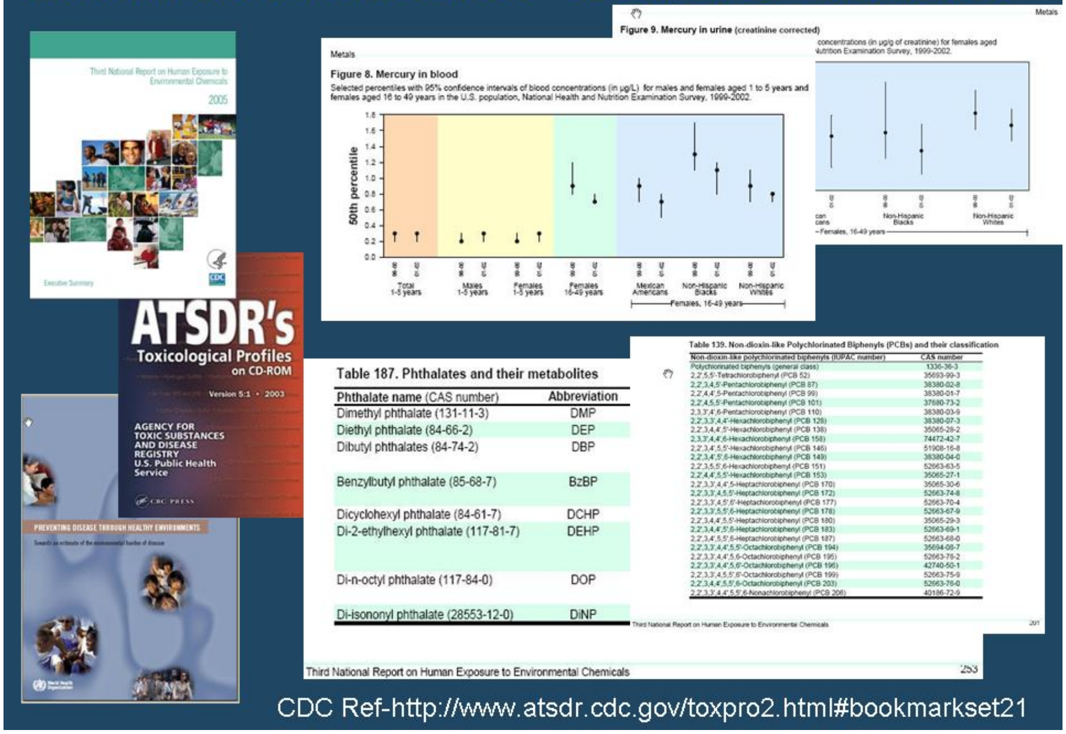


Figure 8. Mercury in blood

Selected percentiles with 95% confidence intervals of blood concentrations (in µg/L) for males and females aged 1 to 5 years and females aged 16 to 49 years in the U.S. population, National Health and Nutrition Examination Survey, 1999-2002.

Figure 9. Mercury in urine (creatinine corrected)

concentrations (in µg/g of creatinine) for females aged
Nutrition Examination Survey, 1999-2002.

Table 187. Phthalates and their metabolites

Phthalate name (CAS number)	Abbreviation
Dimethyl phthalate (131-11-3)	DMP
Diethyl phthalate (84-66-2)	DEP
Dibutyl phthalates (84-74-2)	DBP
Benzylbutyl phthalate (85-68-7)	BzBP
Dicyclohexyl phthalate (84-61-7)	DCHP
Di-2-ethylhexyl phthalate (117-81-7)	DEHP
Di-n-octyl phthalate (117-84-0)	DOP
Di-isononyl phthalate (28553-12-0)	DiNP

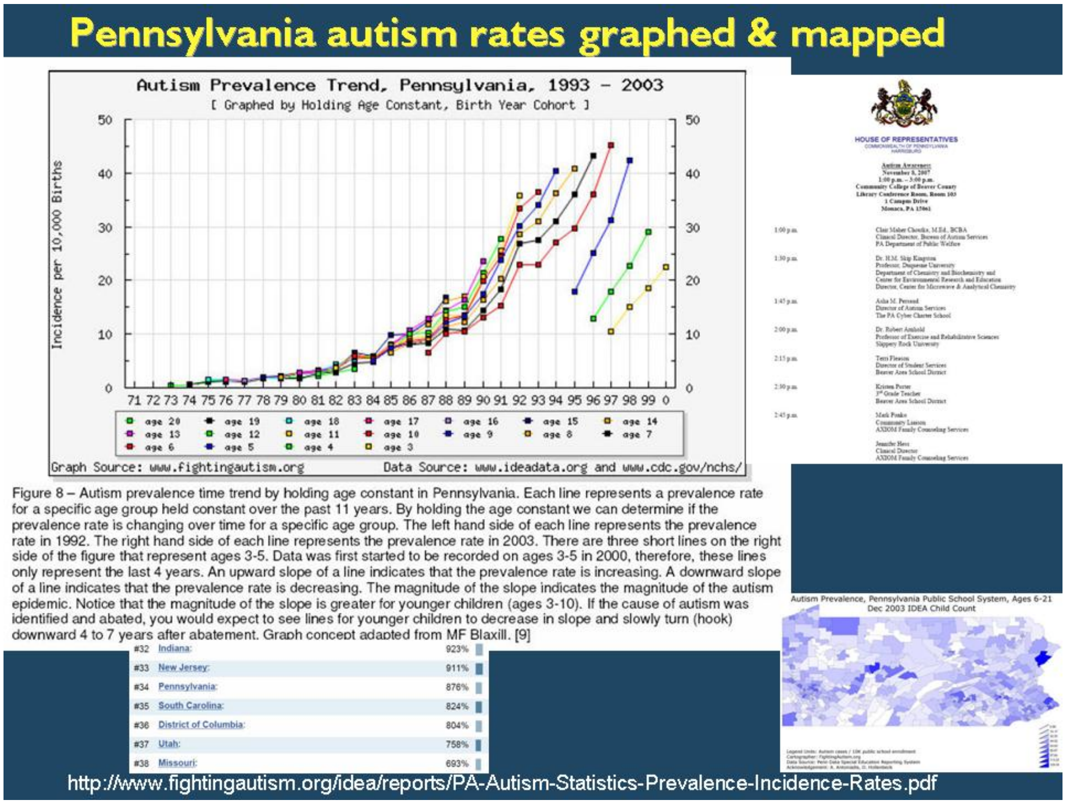
Third National Report on Human Exposure to Environmental Chemicals 253

Table 139. Non-dioxin-like Polychlorinated Biphenyls (PCBs) and their classification

Non-dioxin-like polychlorinated biphenyls (IUPAC number)	CAS number
Polychlorinated biphenyls (general class)	1336-36-3
2,2',5,5'-Tetrachlorobiphenyl (PCB 52)	35693-99-3
2,2',3,4,5'-Pentachlorobiphenyl (PCB 87)	38380-02-8
2,2',4,4',5-Pentachlorobiphenyl (PCB 99)	38380-01-7
2,2',4,5,5'-Pentachlorobiphenyl (PCB 101)	37680-73-2
2,3,3',4',6-Pentachlorobiphenyl (PCB 110)	38380-03-9
2,2',3,3',4,4'-Hexachlorobiphenyl (PCB 128)	38380-07-3
2,2',3,4,4',5'-Hexachlorobiphenyl (PCB 138)	35065-28-2
2,3,3',4,4',6-Hexachlorobiphenyl (PCB 158)	74472-42-7
2,2',3,4',5,5'-Hexachlorobiphenyl (PCB 146)	51908-16-8
2,2',3,4',5',6-Hexachlorobiphenyl (PCB 149)	38380-04-0
2,2',3,5,5',6-Hexachlorobiphenyl (PCB 151)	52663-63-5
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	35065-27-1
2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB 170)	35065-30-6
2,2',3,3',4,5,5'-Heptachlorobiphenyl (PCB 172)	52663-74-8
2,2',3,3',4,5',6'-Heptachlorobiphenyl (PCB 177)	52663-70-4
2,2',3,3',5,5',6-Heptachlorobiphenyl (PCB 178)	52663-67-9
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180)	35065-29-3
2,2',3,4,4',5',6-Heptachlorobiphenyl (PCB 183)	52663-69-1
2,2',3,4',5,5',6-Heptachlorobiphenyl (PCB 187)	52663-68-0
2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB 194)	35694-08-7
2,2',3,3',4,4',5,6-Octachlorobiphenyl (PCB 195)	52663-78-2
2,2',3,3',4,4',5,6'-Octachlorobiphenyl (PCB 196)	42740-50-1
2,2',3,3',4,5,5',6'-Octachlorobiphenyl (PCB 199)	52663-75-9
2,2',3,4,4',5,5',6-Octachlorobiphenyl (PCB 203)	52663-76-0
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB 206)	40186-72-9

Third National Report on Human Exposure to Environmental Chemicals 201

CDC Ref-http://www.atsdr.cdc.gov/toxpro2.html#bookmarkset21



Pennsylvania autism rates graphed & mapped

Autism Prevalence Trend, Pennsylvania, 1993 – 2003
[Graphed by Holding Age Constant, Birth Year Cohort]

Graph Source: www.fightingautism.org Data Source: www.ideadata.org and www.cdc.gov/nchs/

Figure 8 – Autism prevalence time trend by holding age constant in Pennsylvania. Each line represents a prevalence rate for a specific age group held constant over the past 11 years. By holding the age constant we can determine if the prevalence rate is changing over time for a specific age group. The left hand side of each line represents the prevalence rate in 1992. The right hand side of each line represents the prevalence rate in 2003. There are three short lines on the right side of the figure that represent ages 3-5. Data was first started to be recorded on ages 3-5 in 2000, therefore, these lines only represent the last 4 years. An upward slope of a line indicates that the prevalence rate is increasing. A downward slope of a line indicates that the prevalence rate is decreasing. The magnitude of the slope indicates the magnitude of the autism epidemic. Notice that the magnitude of the slope is greater for younger children (ages 3-10). If the cause of autism was identified and abated, you would expect to see lines for younger children to decrease in slope and slowly turn (hook) downward 4 to 7 years after abatement. Graph concept adapted from MF Blaxill. [9]

HOUSE OF REPRESENTATIVES
COMMONWEALTH OF PENNSYLVANIA
HARRISBURG

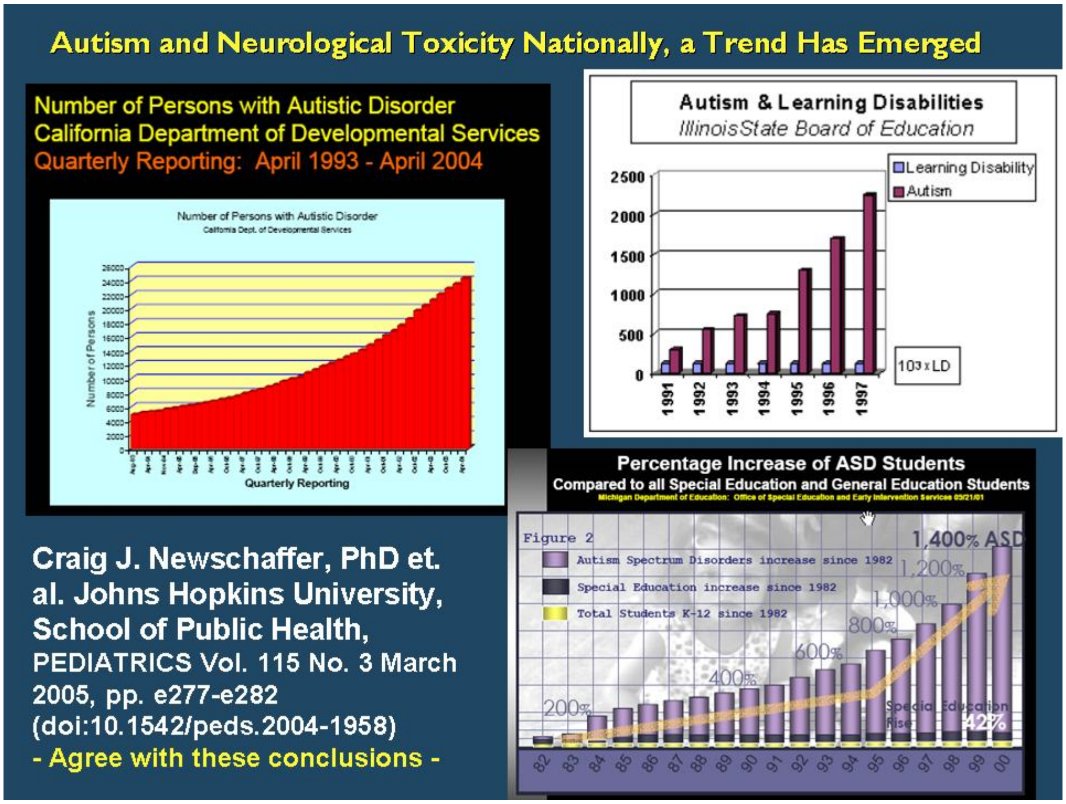
Autism Awareness
November 8, 2007
1:00 p.m. – 3:00 p.m.
Community College of Beaver County
Library Conference Room, Room 103
1 Campus Drive
Monaca, PA 15061

1:00 p.m.	Clair Maher Chowka, M.Ed., BCBA Clinical Director, Bureau of Autism Services PA Department of Public Welfare
1:30 p.m.	Dr. H.M. Skip Kingston Professor, Duquesne University Department of Chemistry and Biochemistry and Center for Environmental Research and Education Director, Center for Microwave & Analytical Chemistry
1:45 p.m.	Asha M. Persaud Director of Autism Services The PA Cyber Charter School
2:00 p.m.	Dr. Robert Arnhold Professor of Exercise and Rehabilitative Sciences Slippery Rock University
2:15 p.m.	Terri Fleeson Director of Student Services Beaver Area School District
2:30 p.m.	Kristen Porter 3rd Grade Teacher Beaver Area School District
2:45 p.m.	Mark Pinko Community Liaison AXIOM Family Counseling Services
	Jennifer Hess Clinical Director AXIOM Family Counseling Services

#32	Indiana:	923%
#33	New Jersey:	911%
#34	Pennsylvania:	876%
#35	South Carolina:	824%
#36	District of Columbia:	804%
#37	Utah:	758%
#38	Missouri:	693%

Autism Prevalence, Pennsylvania Public School System, Ages 6-21
Dec 2003 IDEA Child Count

http://www.fightingautism.org/idea/reports/PA-Autism-Statistics-Prevalence-Incidence-Rates.pdf



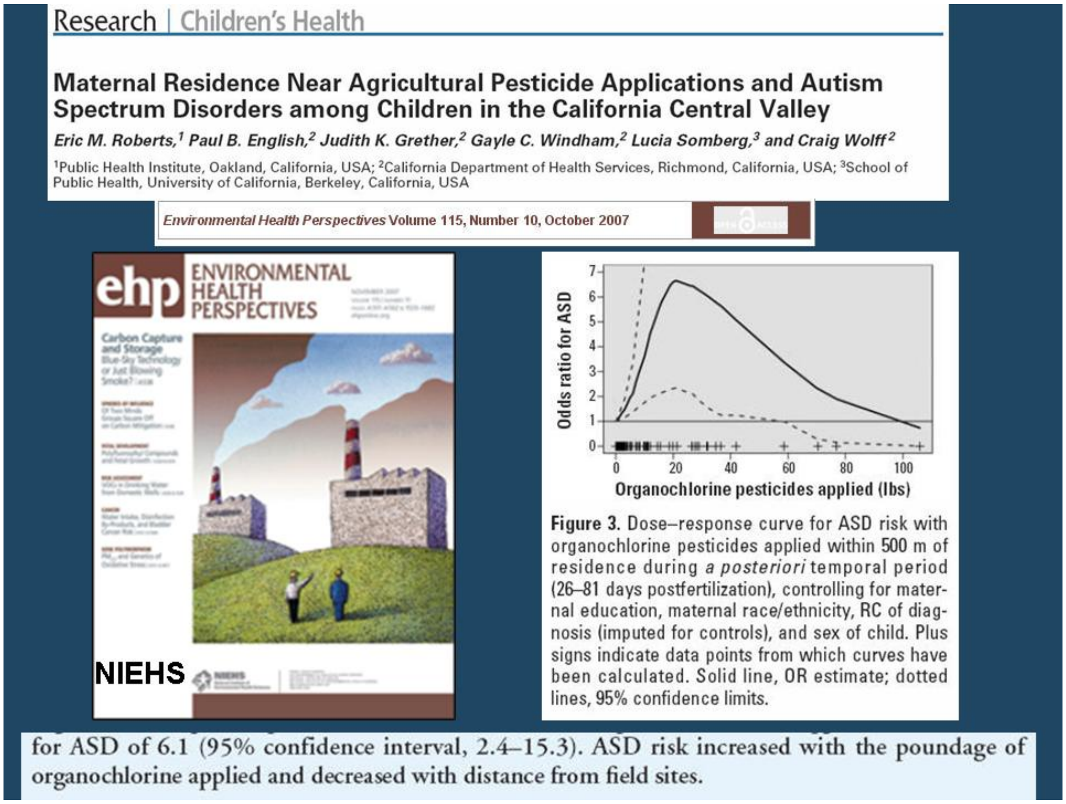
Autism and Neurological Toxicity Nationally, a Trend Has Emerged

Number of Persons with Autistic Disorder
California Department of Developmental Services
Quarterly Reporting: April 1993 - April 2004

Autism & Learning Disabilities
Illinois State Board of Education

Percentage Increase of ASD Students
Compared to all Special Education and General Education Students
Michigan Department of Education: Office of Special Education and Early Intervention Services 05/21/01

Craig J. Newschaffer, PhD et. al. Johns Hopkins University, School of Public Health,
PEDIATRICS Vol. 115 No. 3 March 2005, pp. e277-e282 (doi:10.1542/peds.2004-1958)
- Agree with these conclusions -



Research | Children's Health

Maternal Residence Near Agricultural Pesticide Applications and Autism Spectrum Disorders among Children in the California Central Valley

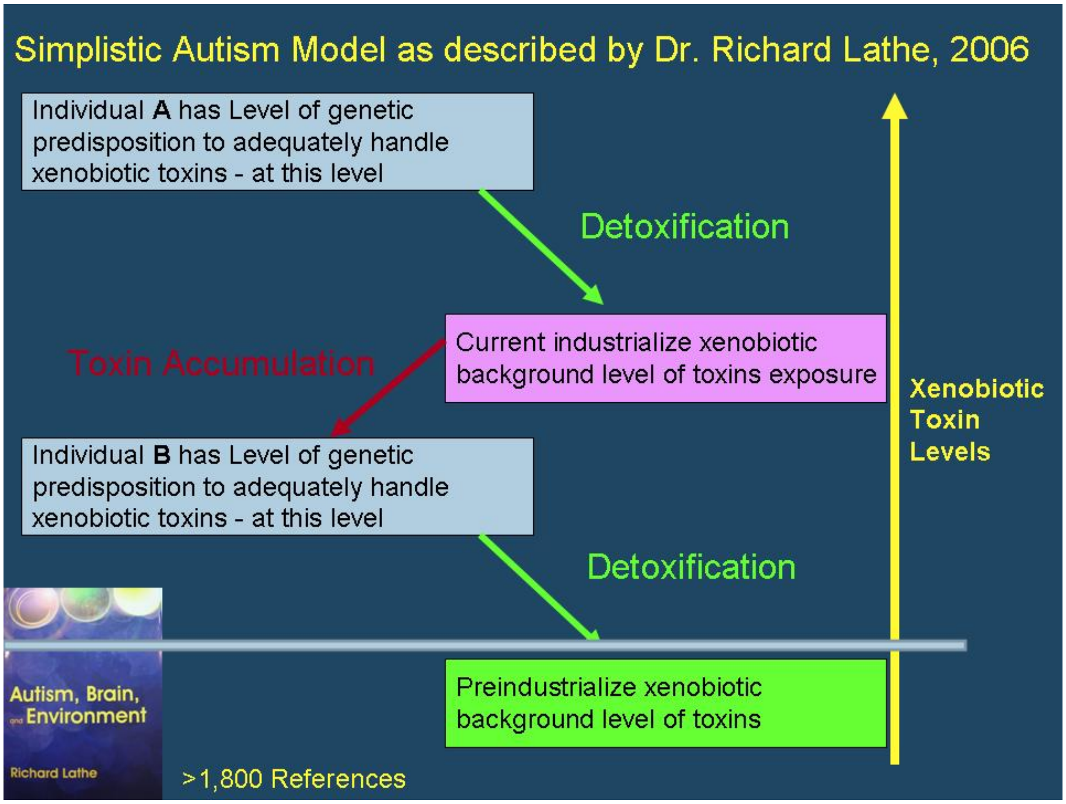
Eric M. Roberts,[1] Paul B. English,[2] Judith K. Grether,[2] Gayle C. Windham,[2] Lucia Somberg,[3] and Craig Wolff[2]

[1]Public Health Institute, Oakland, California, USA; [2]California Department of Health Services, Richmond, California, USA; [3]School of Public Health, University of California, Berkeley, California, USA

Environmental Health Perspectives Volume 115, Number 10, October 2007

Figure 3. Dose–response curve for ASD risk with organochlorine pesticides applied within 500 m of residence during *a posteriori* temporal period (26–81 days postfertilization), controlling for maternal education, maternal race/ethnicity, RC of diagnosis (imputed for controls), and sex of child. Plus signs indicate data points from which curves have been calculated. Solid line, OR estimate; dotted lines, 95% confidence limits.

for ASD of 6.1 (95% confidence interval, 2.4–15.3). ASD risk increased with the poundage of organochlorine applied and decreased with distance from field sites.



Simplistic Autism Model as described by Dr. Richard Lathe, 2006

Individual **A** has Level of genetic predisposition to adequately handle xenobiotic toxins - at this level

Detoxification

Current industrialize xenobiotic background level of toxins exposure

Toxin Accumulation

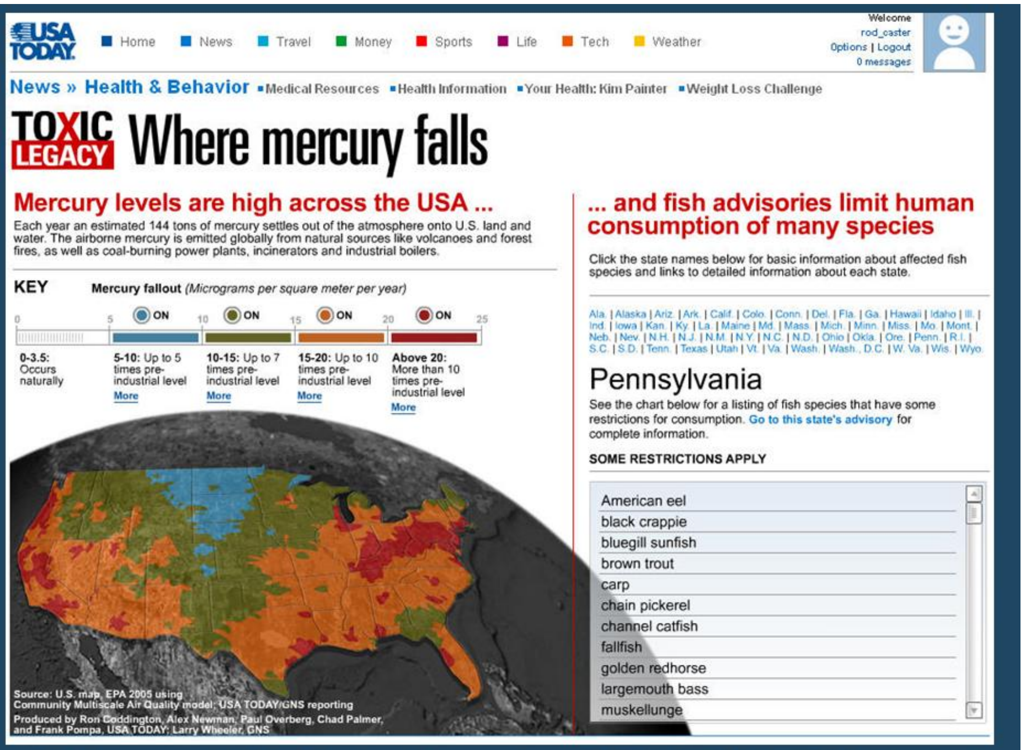
Individual **B** has Level of genetic predisposition to adequately handle xenobiotic toxins - at this level

Detoxification

Preindustrialize xenobiotic background level of toxins

Xenobiotic Toxin Levels

>1,800 References



Where mercury falls

Mercury levels are high across the USA ...

Each year an estimated 144 tons of mercury settles out of the atmosphere onto U.S. land and water. The airborne mercury is emitted globally from natural sources like volcanoes and forest fires, as well as coal-burning power plants, incinerators and industrial boilers.

KEY **Mercury fallout** *(Micrograms per square meter per year)*

Range	Description
0-3.5:	Occurs naturally
5-10:	Up to 5 times pre-industrial level More
10-15:	Up to 7 times pre-industrial level More
15-20:	Up to 10 times pre-industrial level More
Above 20:	More than 10 times pre-industrial level More

Source: U.S. map, EPA 2005 using Community Multiscale Air Quality model; USA TODAY/GNS reporting

Produced by Ron Coddington, Alex Newman, Paul Overberg, Chad Palmer, and Frank Pompa, USA TODAY; Larry Wheeler, GNS

... and fish advisories limit human consumption of many species

Click the state names below for basic information about affected fish species and links to detailed information about each state.

Ala. | Alaska | Ariz. | Ark. | Calif. | Colo. | Conn. | Del. | Fla. | Ga. | Hawaii | Idaho | Ill. | Ind. | Iowa | Kan. | Ky. | La. | Maine | Md. | Mass. | Mich. | Minn. | Miss. | Mo. | Mont. | Neb. | Nev. | N.H. | N.J. | N.M. | N.Y. | N.C. | N.D. | Ohio | Okla. | Ore. | Penn. | R.I. | S.C. | S.D. | Tenn. | Texas | Utah | Vt. | Va. | Wash. | Wash., D.C. | W. Va. | Wis. | Wyo.

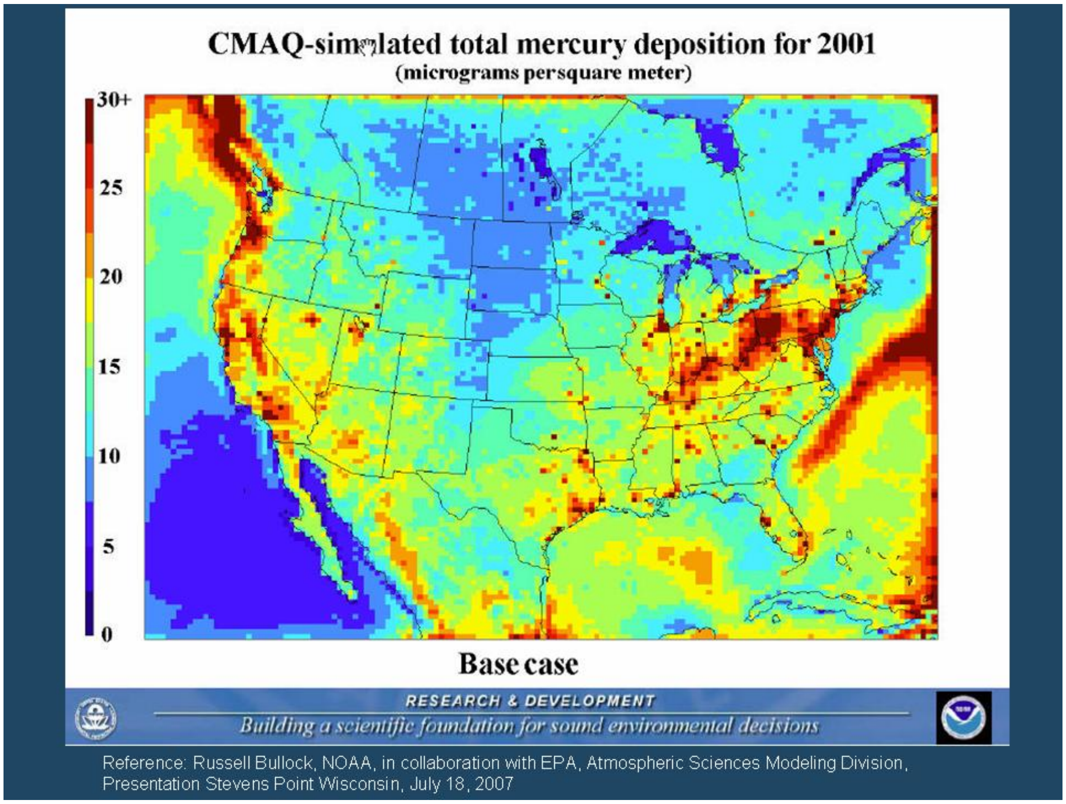
Pennsylvania

See the chart below for a listing of fish species that have some restrictions for consumption. Go to this state's advisory for complete information.

SOME RESTRICTIONS APPLY

- American eel
- black crappie
- bluegill sunfish
- brown trout
- carp
- chain pickerel
- channel catfish
- fallfish
- golden redhorse
- largemouth bass
- muskellunge

Reference: USA Today November 2007, NOAA/EPA Report

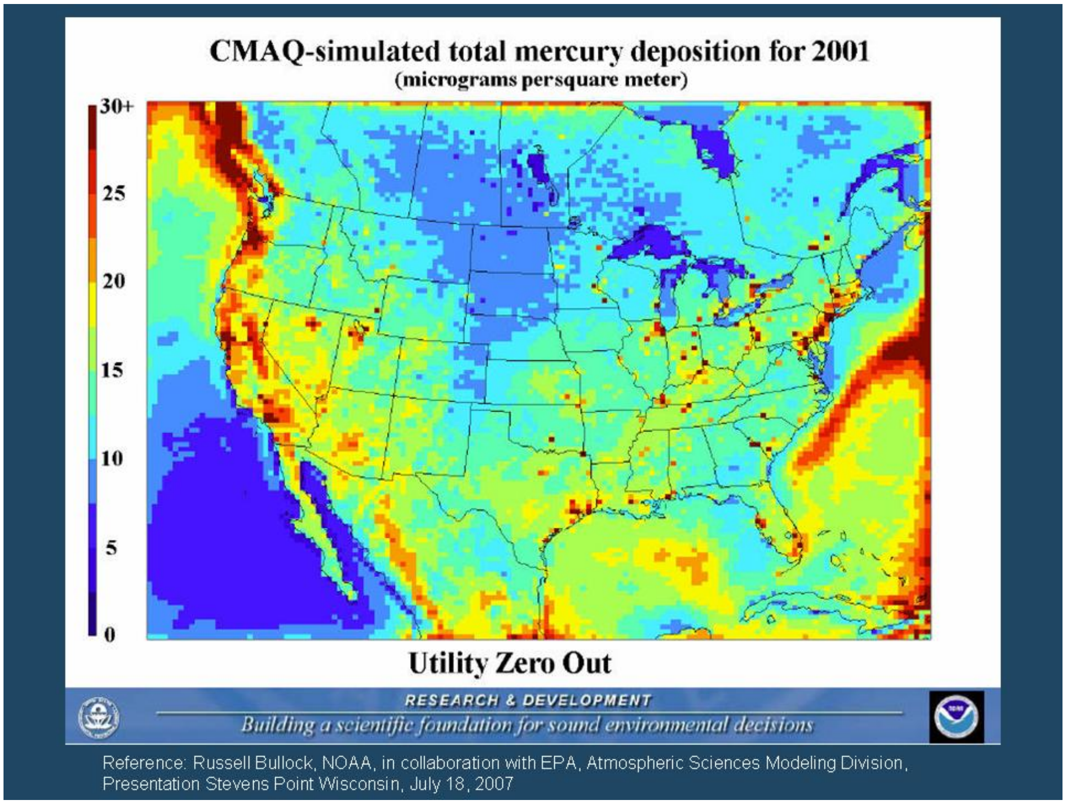


CMAQ-simulated total mercury deposition for 2001

(micrograms persquare meter)

Base case

Reference: Russell Bullock, NOAA, in collaboration with EPA, Atmospheric Sciences Modeling Division, Presentation Stevens Point Wisconsin, July 18, 2007



CMAQ-simulated total mercury deposition for 2001

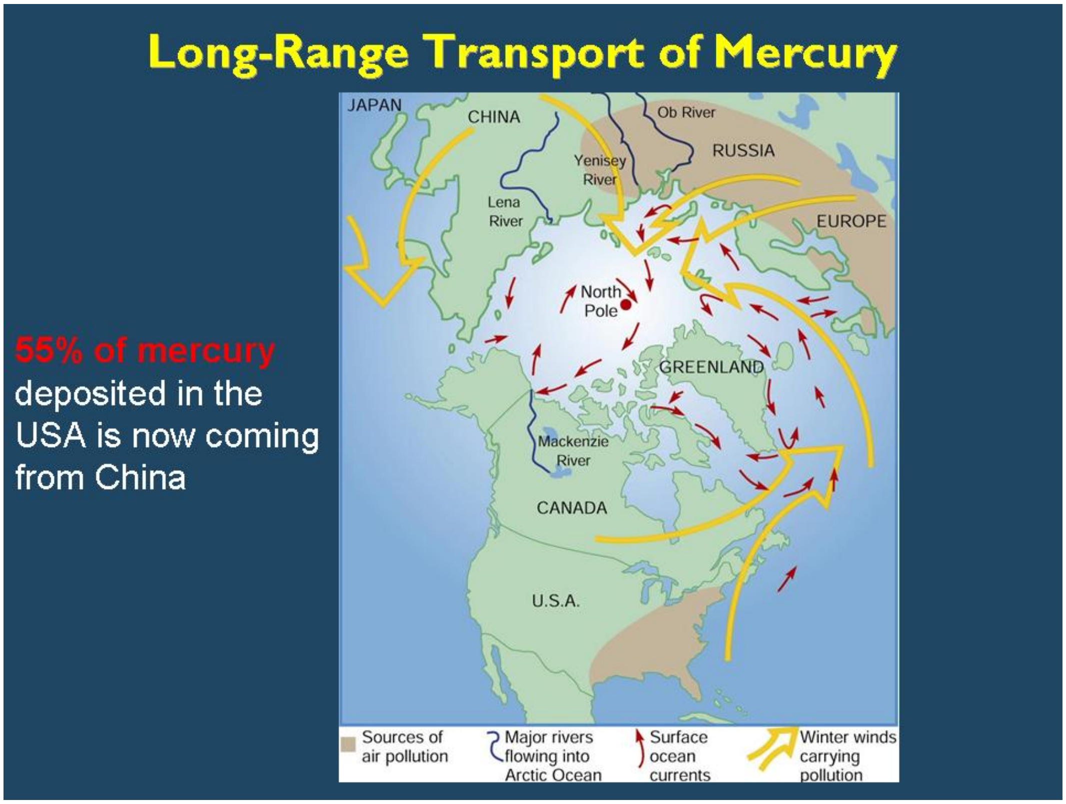
(micrograms persquare meter)

Utility Zero Out

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

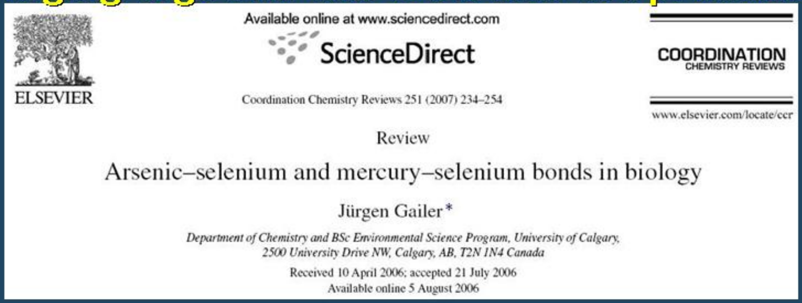
Reference: Russell Bullock, NOAA, in collaboration with EPA, Atmospheric Sciences Modeling Division, Presentation Stevens Point Wisconsin, July 18, 2007



Long-Range Transport of Mercury

55% of mercury deposited in the USA is now coming from China

Bringing together the tools and the problems



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COORDINATION CHEMISTRY REVIEWS

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Review

Arsenic–selenium and mercury–selenium bonds in biology

Jürgen Gailer*

Department of Chemistry and BSc Environmental Science Program, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4 Canada

Received 10 April 2006; accepted 21 July 2006

Available online 5 August 2006

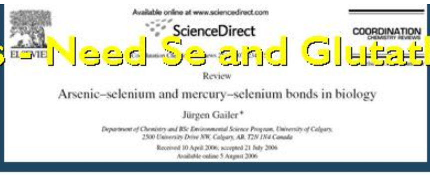
Many others now in the literature:

Mercury, Lead, and Zinc in Baby Teeth of Children with Autism Versus Controls, James B Adams et.al, J of Toxicology and Environmental Health, Part A, 70, 1046-1051, 2007

Metabolic biomarkers of increased oxidative stress and impaired methylation capacity in children with autism, s.Jill James, et.al., Am J Clin Nutr, 80, 16112004

The Environment as an Etiologic Factor in Autism: A New Direction for Research, Eric London et.al., Env. Health Perspectives 108, Supp 3 401, 2000.

Hg^{2+}, CH_3Hg^+ and As - Need Se and Glutathione



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COORDINATION CHEMISTRY REVIEWS

Review

Arsenic–selenium and mercury–selenium bonds in biology

Jürgen Gailer*

Received 10 April 2006; accepted 21 July 2006

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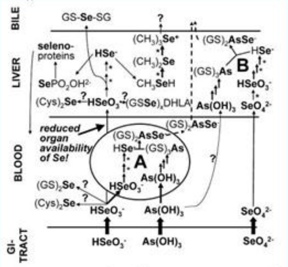


Fig. 7. Interaction between As^{III} and Se^{IV} in erythrocytes (A) and between As^{III} and Se^{VI} in the liver (B). Oval shape: erythrocyte; Cys: L-cysteine; GSH: L-glutathione; DHLA: dihydrolipoic acid. Asterisk indicates enzymatically mediated biotransformation.

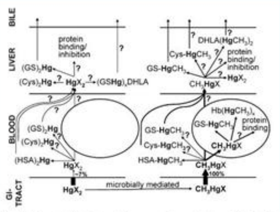


Fig. 4. Schematic illustration of the mammalian metabolism of Hg^{2+} and CH_3Hg^+. Oval shape: erythrocyte; Cys: L-cysteine; GSH: L-glutathione; HSA: human serum albumin; DHLA: dihydrolipoic acid; X = Cl^- or Cys.

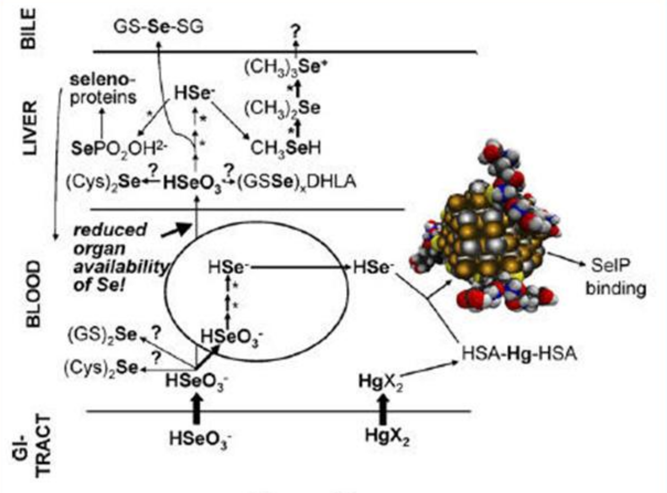
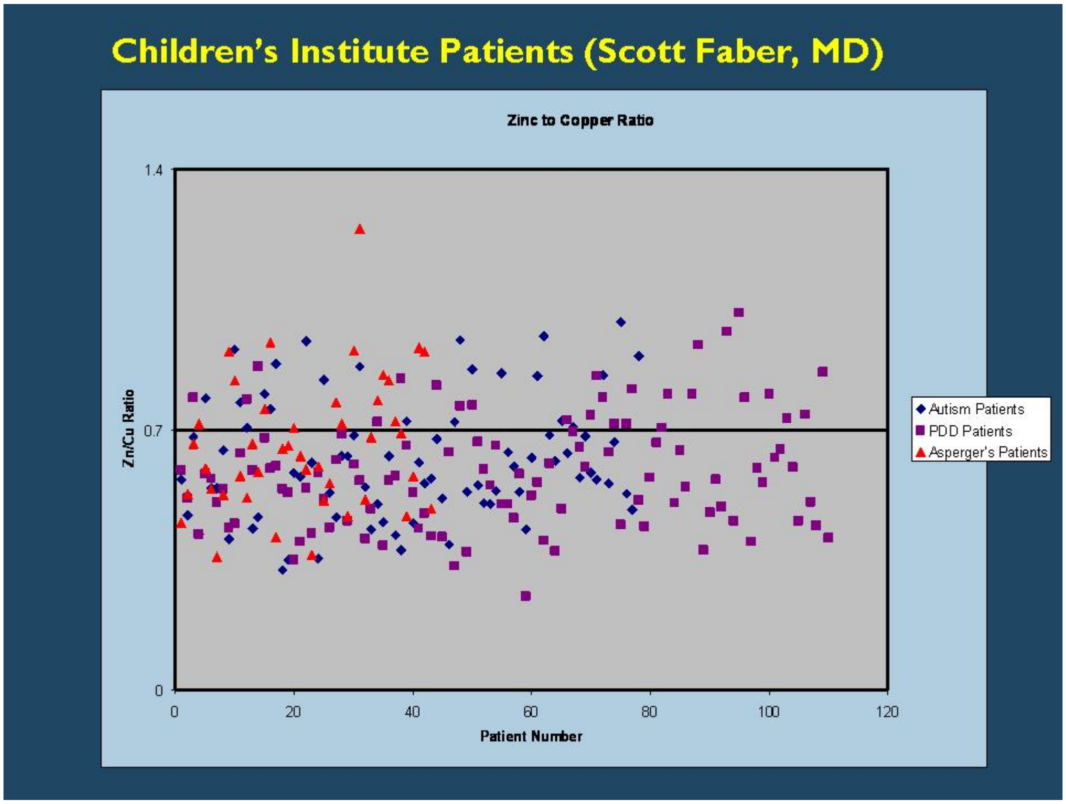
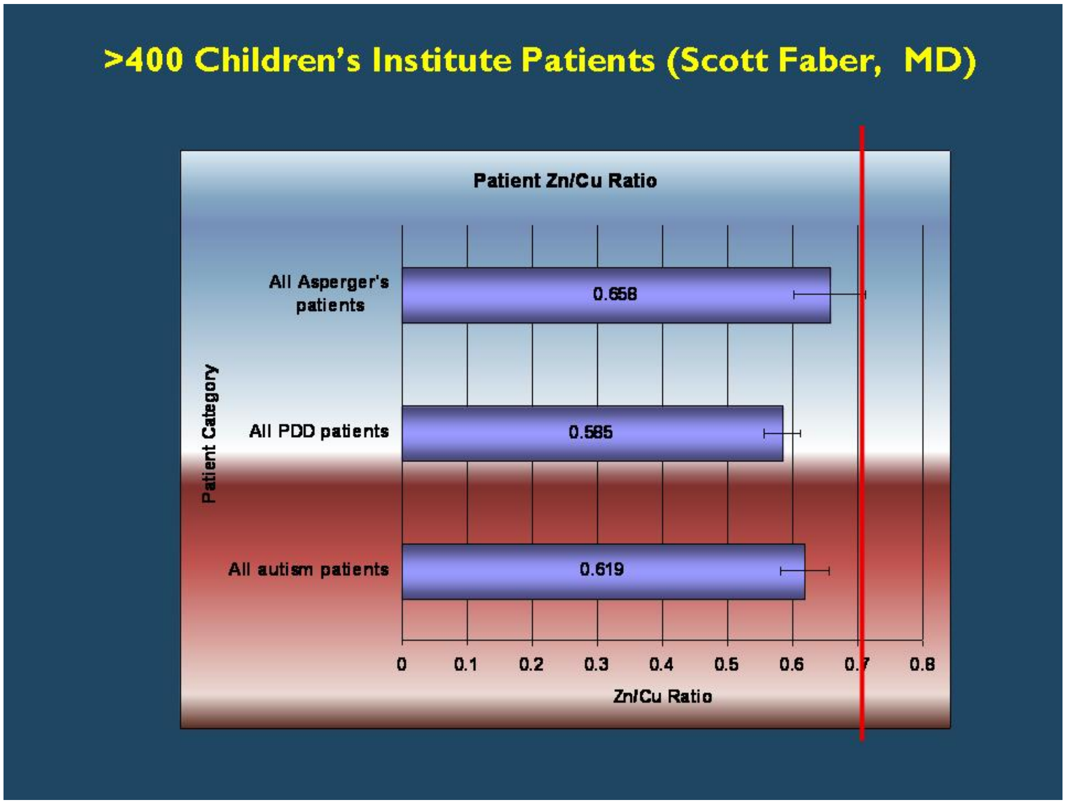


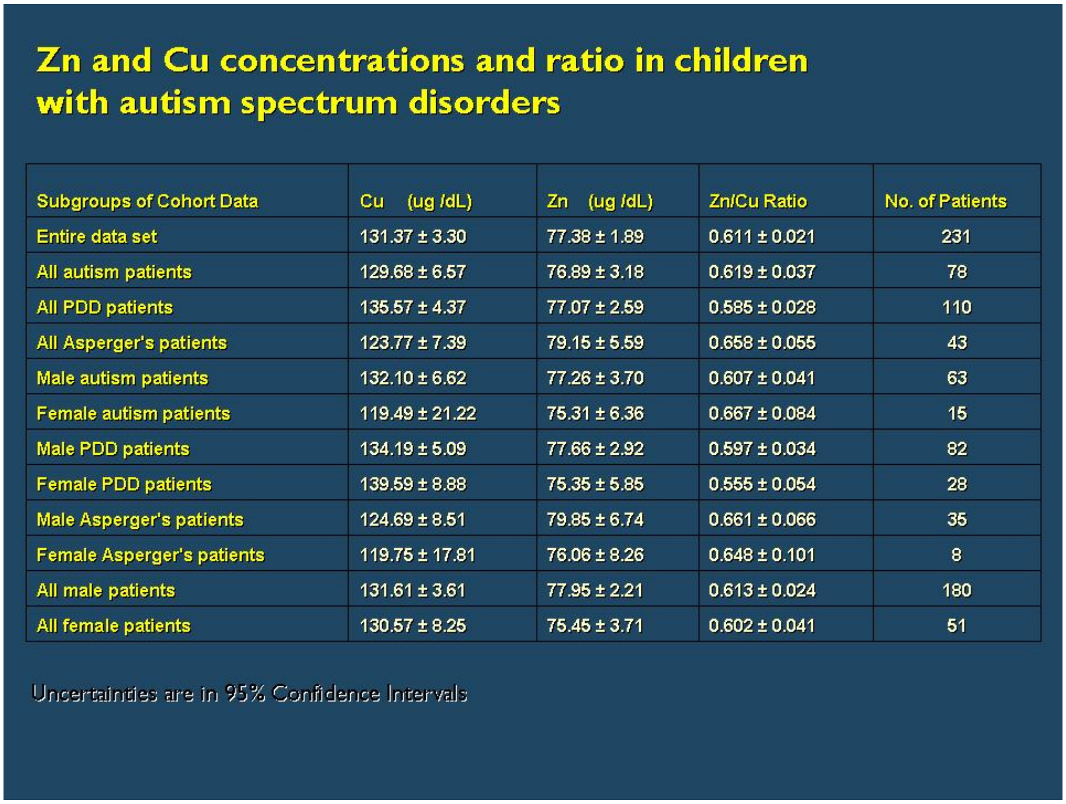
Fig. 8. Interaction between Hg^{2+} and Se^{IV} in the bloodstream. Oval shape: erythrocyte; Cys: L-cysteine; GSH: L-glutathione; DHLA: dihydrolipoic acid; SelP: selenoprotein, coloured species represents $(Hg–Se)_{100}(GS)_5$ species. Asterisk indicates enzymatically mediated biotransformation.



Children's Institute Patients (Scott Faber, MD)



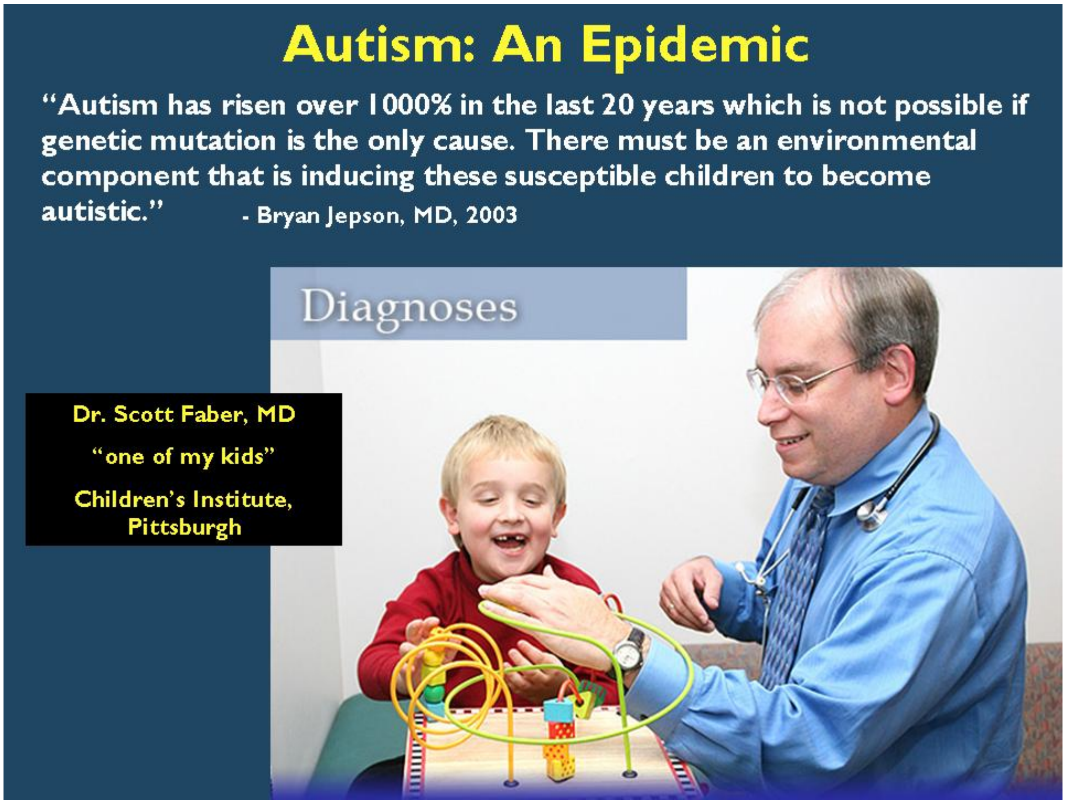
>400 Children's Institute Patients (Scott Faber, MD)



Zn and Cu concentrations and ratio in children with autism spectrum disorders

Subgroups of Cohort Data	Cu (ug /dL)	Zn (ug /dL)	Zn/Cu Ratio	No. of Patients
Entire data set	131.37 ± 3.30	77.38 ± 1.89	0.611 ± 0.021	231
All autism patients	129.68 ± 6.57	76.89 ± 3.18	0.619 ± 0.037	78
All PDD patients	135.57 ± 4.37	77.07 ± 2.59	0.585 ± 0.028	110
All Asperger's patients	123.77 ± 7.39	79.15 ± 5.59	0.658 ± 0.055	43
Male autism patients	132.10 ± 6.62	77.26 ± 3.70	0.607 ± 0.041	63
Female autism patients	119.49 ± 21.22	75.31 ± 6.36	0.667 ± 0.084	15
Male PDD patients	134.19 ± 5.09	77.66 ± 2.92	0.597 ± 0.034	82
Female PDD patients	139.59 ± 8.88	75.35 ± 5.85	0.555 ± 0.054	28
Male Asperger's patients	124.69 ± 8.51	79.85 ± 6.74	0.661 ± 0.066	35
Female Asperger's patients	119.75 ± 17.81	76.06 ± 8.26	0.648 ± 0.101	8
All male patients	131.61 ± 3.61	77.95 ± 2.21	0.613 ± 0.024	180
All female patients	130.57 ± 8.25	75.45 ± 3.71	0.602 ± 0.041	51

Uncertainties are in 95% Confidence Intervals



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." - Bryan Jepson, MD, 2003

Diagnoses

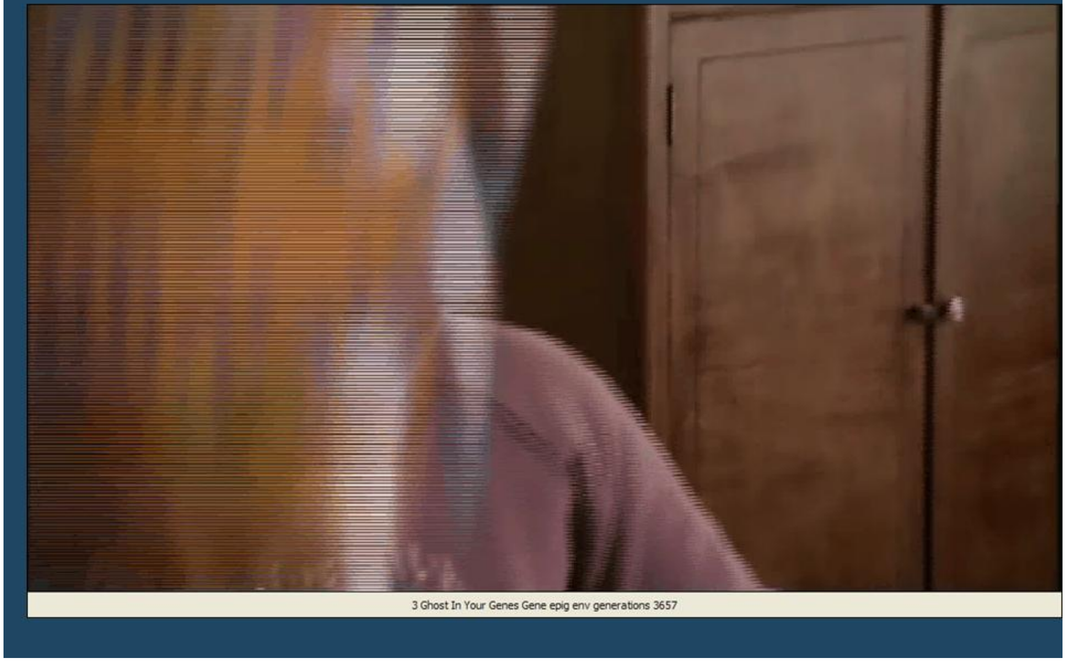
Dr. Scott Faber, MD

"one of my kids"

Children's Institute, Pittsburgh

What are the state(s)-of-the-art measurements in Speciation?

- Specific chemical forms of elements and molecules and complex molecular system not elements (used mainly for mass balance)
- Endocrine Disruptors – triggering inappropriate responses
- Epigenetic Species Interactions change who we are at the genetic level
- Chemical and Biochemical Markers indicating disease or effects of species on our Epigenome
- Measuring and linking envirionmental health is where we are headed in speciation.



3 Ghost In Your Genes Gene epig env generations 3657

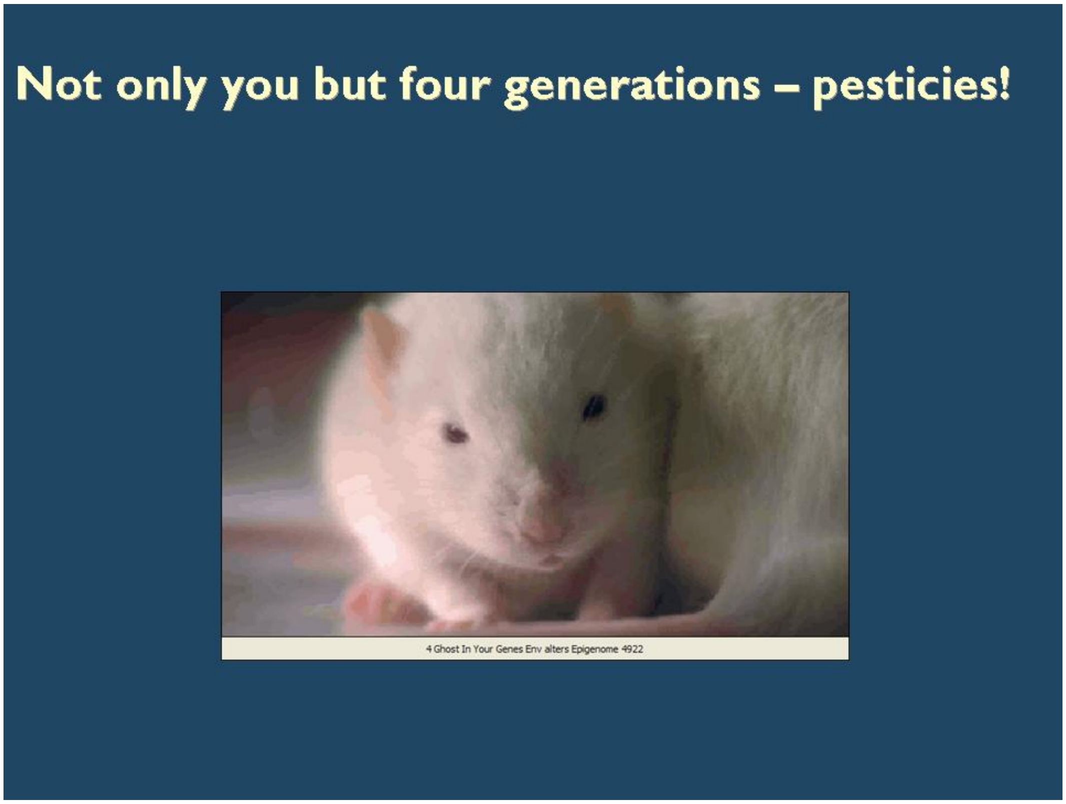
What this new knowledge is leading us to – some observations:

We require scientific, educational and legislative collaboration as the problem is too complex for any one discipline.

New quantitative methods and standards for measurement are needed. Only then, can we draw the appropriate links between human health and the environment.

Collaboration and coordination between and among different branches of government (federal and states) is essential.

Entire communites of environmental and medical science must come together on human health environmental issues.



Not only you but four generations – pesticies!

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Thank you.

Questions?

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