The 20th Annual National Environmental Monitoring Conference

Monday, July 19th — Friday, July 23rd

Proceedings

Conference: Monday, July 19th – Wednesday, July 21st
Short Courses: Thursday, July 22nd – Friday, July 23rd

Wyndham Washington Hotel
1400 M Street, NW
Washington, DC

ILI

QUALITY TRAINING FOR THE LABORATORY COMMUNITY

NEMC is managed by the Independent Laboratory Institute (ILI), in association with the American Council of Independent Laboratories (ACIL) and Instant References Sources, Inc. under a cooperative agreement with the U.S. Environmental Protection Agency. ILI is the educational foundation affiliated with the American Council of Independent Laboratories.

NEMC 2004 Organizing Committee

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Larry Keith, Instant Reference Sources, Inc., Monroe, GA
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Gary Ward, Columbia Analytical Services, Kelso, WA
Llew Williams, Llew Williams Consulting, Naples, FL
Shen-yi Yang, US EPA, Office of Solid Waste, Washington, DC

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Welcome

Welcome to the 20th Annual National Environmental Monitoring Conference – NEMC 2004. The conference is managed by the Independent Laboratories Institute (ILI) in association with the American Council of Independent Laboratories (ACIL) and Instant Reference Sources, Inc. under a cooperative agreement with the U.S. Environmental Protection Agency (U.S. EPA). The symposium series was established as a means of fostering a partnership among the regulated community, its supporting laboratories and consultants and state and federal regulators. Key to implementing these goals are the technical sessions, composed of both oral and poster presentations, the table top exposition and a varied offering of short courses.

The conference has continued to grow and diversify in spite of difficult economic and geopolitical times. This year again we have over 100 technical presentations in four concurrent oral presentation sessions, a poster session and a plenary session. This ties last year's record for this venerable conference, long-known as the Waste Testing and Quality Assurance Symposium (WTQA). In this year's program, you will find papers that cover all aspects of environmental monitoring in all media (*i.e*., water, air, soil and wastes). Participants include experts from private industry, public agencies engaged in environmental monitoring (*e.g*., U.S. EPA, DOE, DoD and States) and academia.

In addition to the long-standing sessions on organic methods and inorganic methods, we have added several new topics this year. For example, environmental monitoring as it relates to homeland security, laboratory accreditation, ensuring the integrity of laboratory data, analysis of DOE mixed wastes, assessing the performance of new methods and innovative approaches to environmental monitoring. Leveraging on popular topics from last year we have sessions on advances in implementation of the Triad approach and measurement uncertainty and also advances in electronic data deliverables. Finally, a round-table discussion on changing federal requirements to manage environmental data will present the newest information on this subject.

Complementing the technical sessions are plenary session presentations from leaders in government and industry, a large table-top exposition and three short courses.

Join us in a relaxed atmosphere at the complimentary Opening Reception on Monday evening. This reception is sponsored in part by the generous contributions of Annual Reviews, Dionex Corporation, Environmental Research Programs, Environmental Resources Associates, Environmental Standards, Inc. and Severn Trent Laboratories. Enjoy the conference, learn about changing technology, make new contacts, visit with old friends and let us know how we can help you.

Overview

General Schedule

All sessions will take place at the Wyndham Washington Hotel, located at 1400 M Street, NW Washington, DC (Phone: 202-429-1700). Technical presentations and other sessions will run concurrently to allow participants the opportunity to attend those sessions most relevant to them.

- **Opening Plenary Session**

The opening plenary session will be held Monday, July 19th from 2:00–4:30 pm in the Monticello East and Monticello West rooms.

- **Oral Sessions**

Concurrent oral sessions will be held in four adjacent rooms on the Lobby Level from 8:15 am to 5:15 pm on July 20–21, 2004. Morning and afternoon sessions have three initial 30-minute presentations (which include time for questions), a 45 minute refreshment break and three final 30-minute presentations. Concurrent times for each presentation facilitate moving among various presentations if desired.

- **Poster Sessions**

All posters will be on display Tuesday, July 20th in the Vista B and C Ballrooms along with the Table Top Exhibition. Authors will be available to discuss their work from 9:45–10:30 am and from 3:00–3:45 pm each day. These times correspond to the breaks in the oral presentations. Poster boards 4' X 8' (with pins supplied) will be arranged for easy viewing and discussions with authors.

- **Short Courses**

Short courses will be offered Thursday and Friday, July 22 and 23, the days after the conference and each has an additional registration fee. Two full-day courses and one two-day course are offered.

- **Table Top Exhibition**

The Table Top Exhibition is in the Vista B and C Ballrooms along with the poster sessions. The exhibition is a feature of the Opening Reception on Monday evening from 5:00–6:30 pm and continues Tuesday and Wednesday, July 20-21 in conjunction with the poster presentations (on July 20) and the morning and afternoon refreshment breaks.

- **Opening Reception**

The opening reception will be held Monday, July 19th from 5:00–6:30 pm in the Vista B and C Ballrooms. Complimentary hors d'oeuvres and soft drinks will be served and a cash bar will also be available. The Table Top Exhibition is also a featured attraction of this reception. Please extend your thanks to representatives from Annual Reviews, Dionex Corporation, Environmental Research Programs, Environmental Resources Associates, Environmental Standards, Inc. and Severn Trent Laboratories who graciously contributed funds to help make this event possible at no cost to you.

Logistics

• Registration

Registration for the conference will be in the Woodlawn Room on the conference level (see map on page 6). Registration hours are 7:30 am–5:00 pm on Monday, July 19 through Wednesday, July 21 and 7:30 am–11:00 am on Thursday, July 22. Registrants may pick up name badges and registration materials during these hours. Facilities for on-site registration will be available at the registration desk.

• Continental Breakfast & Refreshment Breaks

A continental breakfast, in addition to morning and afternoon refreshment breaks, is provided for all conference registrants on Tuesday and Wednesday, July 20–21 from 7:30–8:30 am. The breakfast and all breaks are held in the Vista B and C Ballrooms in conjunction with the Table Top Exhibition and the poster sessions.

• Conference Abstracts and Proceedings

Conference Abstracts **(on a CD-ROM)** are in the materials provided to each registrant during registration. A few printed copies are also available in the registration area. They are also posted on the conference web site under "Conference Abstracts" at www.nemc.us.

Conference Proceedings **(on a CD-ROM)** will be mailed to each conference registrant after the meeting. This allows us to provide slides from all presenters who supply them as well as any late manuscripts that are received. *Conference Proceedings* contain full-length papers from authors who submitted them or abstracts from authors who did not submit full papers. These proceedings are produced in conjunction with the American Chemical Society Division of Environmental Chemistry.

• Message Board and Employment Opportunities Board

A communication board serving as a central location for messages and employment notices is located near the registration desk. Please check the board for messages at least twice a day as you walk by it.

• Transportation

The Wyndham Washington Hotel is at 1400 M Street, NW, Washington, DC, six miles from Reagan Washington National Airport, 35 miles from Baltimore-Washington International (BWI) Airport and 40 miles from Dulles International Airport. The Capital Beltway is four miles away.

Approximate one-way taxi fare from Reagan Washington National is $15 and approximately $40 from Baltimore-Washington International (BWI) or Dulles.

The Metrorail (subway) System has a stop at Reagan Washington National Airport and one located three blocks from the hotel (McPherson Square on the Blue and Orange lines). One-way cost is $1.70. The Metro runs from 5:30 am until midnight, Monday through Friday 8:00 am until midnight on Saturday and 10:00 am until midnight on Sunday. For specific bus and subway information, contact Metro Transportation at 202-637-7000.

Rail Transportation

Union Station provides Amtrak Service. Although group fares are not available, you may call 800-872-7245 for more details or to make reservations.

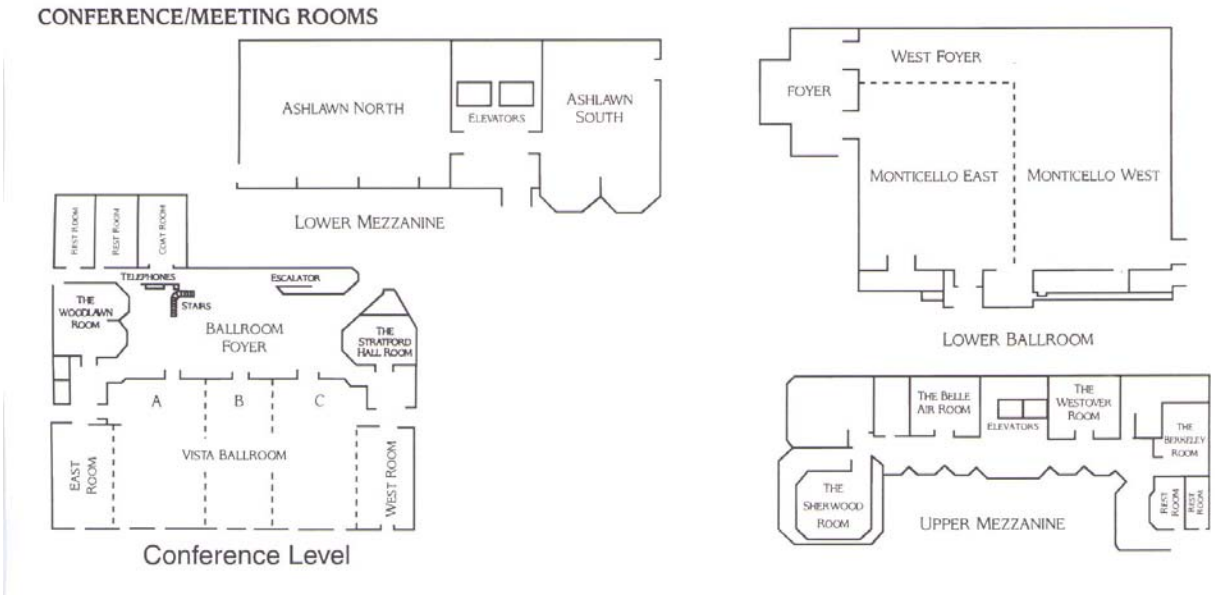
- **Parking**

Parking at the hotel costs $14 per day (early bird rates are offered at $6 per day before 9:00 am). Parking is located in a large garage below the hotel.

Hotel Information

Located in the heart of Washington at 1400 M St. NW, the Wyndham Washington Hotel is a beautiful hotel that captures the capital city's dynamic spirit. The atrium lobby offers spectacular skylight views and world-class service. You'll enjoy the comfort and convenience of the spacious guest rooms with thoughtful amenities such as pillowtop mattresses, cordless phones and high-speed Internet access.

When it's time to relax, there is plenty to do. The hotel location makes it easy to enjoy our nation's rich heritage by visiting some of the world-renowned buildings and historical monuments found throughout the city. You'll appreciate our country's rich history when you visit some of the area's many public exhibits and memorials, such as Capitol Hill, the White House, the National Mall and the Smithsonian Museums. Rooms in which the NEMC Technical Sessions, Seminars, Short Courses and Workshops, Exposition and Opening Reception are shown in the hotel map below.



NEMC 2004 Conference At A Glance – Morning

	Mon. 7/19	Tue. 7/20	Wed. 7/21	Thur. 7/22	Fri. 7/23
Morning **Oral Presentations 8:15–9:45 am** **Break 9:45-10:30 am** **Oral Presentations 10:30 am–noon** **Posters at break times – 9:45–10:30 am**	**ELAB meeting – Monticello East and West Rooms** **NRCC Environmental Analytical Chemist / Technician Certification Examination East Room**	**(1) Organic Methods Session #1 –** Maria Gomez-Taylor and Lynn Riddick **Monticello East Room** **(2) Inorganic Methods Session #1** – Shen–yi Yang and Skip Kingston **Monticello West Room** **(3) Ensuring the Integrity of Laboratory Data** Jack Farrell and Joan Cassedy **Vista Ballroom A** **(4) Characterization of Mixed Wastes at DOE Sites** – Daro Ferrara and Aruna Arakali **East Room** **Poster Session & Exhibition – Vista B &C Ball Rooms**	**(9) Sampling and Analysis for Homeland Security Session #1–** Douglas Lipka and David Mills **Monticello East Room** **(10) Laboratory Accreditation Session #1 –** Lara Autry and Jerry Parr **Monticello West Room** **(11) Advances in Electronic Data Deliverables Session #1** – Anand Mudambi and Joe Solsky **Vista Ballroom A** **(12) Advances in Implementing the Triad Approach and Documenting Measurement Uncertainty –** Deana Crumbling and Marlene Moore **East Room** **Exhibition - Vista B &C Ball Rooms**	**Short Course #1 – Implementing the Performance Approach - INELA – Part 1 -** Marlene Moore **Monticello West Room** **Short Course #2- ISO/IEC 17025 Overview– Part 1** – James H. Scott **Monticello East Room** **Short Course #3- Internal Audits and Corrective Actions Systems - Practical Tools for Management – Part 1 –** Jack Farrell **Vista Ballroom A**	**Short Course #1 – Implementing the Performance Approach - INELA Part 3 -** Marlene Moore **Monticello West Room**
Noon					

NEMC 2004 Conference At A Glance - Afternoon

	Mon. 7/19	Tue. 7/20	Wed. 7/21	Thur. 7/22	Fri 7/23
Afternoon **Oral Presentations 1:30–3:00 pm** **Break 3:00- 3:45 pm** **Oral Presentations 3:45–5:15 pm** **Posters at breaks times 3:00–3:45 pm**	**Opening Plenary** **2:00–4:30 pm** **Monticello East and West Rooms** **Michael H. Shapiro** U.S. EPA Office of Water and FEM Chair **Michael Gritzuk**, Director , Phoenix Water Services Department **Robert P. Johns** Director, Western Division, Office for Domestic Preparedness, U.S. Department of Homeland Security **Mary Kruger** Director, U.S. EPA Office of Homeland Security	**(5) Organic Methods Session #2 –** Maria Gomez-Taylor and Lynn Riddick **Monticello East Room** **(6) Inorganic Methods Session #2** – Shen–yi Yang and Skip Kingston **Monticello West Room** **(7) Assessing Performance of New Methods** – Elizabeth Mishalanie and Anita Mishra **Vista Ballroom A** **(8) Innovative Approaches to Environmental Monitoring** - Oksana Pozda and Llew Williams **East Room** **Poster Session & Exhibition - Vista B &C Ball Rooms**	**(13) Sampling and Analysis for Homeland Security Session #2 –** Douglas Lipka and David Mills **Monticello East Room** **(14) Laboratory Accreditation Session #2 –** Lara Autry and Jerry Parr **Monticello West Room** **(15) Advances in Electronic Data Deliverables Session #2 (1/2)** – Anand Mudambi and Joe Solsky **Vista Ballroom A** **(16) Roundtable: Changing Federal Requirements to Manage Environmental Data Quality** - Mike Carter **East Room** **Exhibition – Vista B &C Ball Rooms**	**Short Course #1 – Implementing the Performance Approach - INELA – Part 2 -** Marlene Moore **Vista Ballroom A** **Short Course #2- ISO/IEC 17025 Overview– Part 2** – James H. Scott **Monticello East Room** **Short Course #3- Internal Audits and Corrective Actions Systems - Practical Tools for Management – Part 2 –** Jack Farrell **Monticello West Room**	**Short Course #1 – Implementing the Performance Approach - INELA - Part 4 -** Marlene Moore **Vista Ballroom A**
Evening Activities	**Opening Reception** **Vista B &C Ball Rooms** **5:00–6:30 pm**				

Technical Sessions

Opening Plenary

Monday July 19, 2004 - Afternoon Plenary in the Monticello East and West Rooms

Michael Gritzuk
Director, Phoenix Water Services Department

Michael H. Shapiro
U.S. EPA Office of Water, Chair of the Forum on Environmental Measurements (FEM)

Robert P. Johns
Director, Western Division, Office for Domestic Preparedness, U.S. Department of Homeland Security

Mary Kruger
Director, U.S. EPA Office of Homeland Security

Poster Session (Titles linked to PowerPoint/Slides)

Tuesday, July 20 – Morning and Afternoon Posters in the Vista Ballrooms B &C

Paper No.	Authors and **Paper Title**
P-1	Robert Johnson - **Rapid Extraction of a Broad Spectrum of Chemical Compounds from Public Water Supplies Using EPA Method 3535A**
P-2	Brian A. Schumacher, John H. Zimmerman - **Composite Sampling for Soil VOC Analysis**
P-3	Jim Krol - **Determination of Perchlorate Anion in High Total Dissolved Solids Water Using LC/MS/MS**
P-4	John H. Zimmerman, Brian A. Schumacher - **To Purge or Not to Purge? VOC Concentration Changes During Line Volume Purging**
P-5	M. E. Benvenuti, A. E. Aubin, J. P. Romano, J. A. Krol - **High Speed Explosives Monitoring using UPLC ™**
P-6	Mark Krigbaum - **Evaluation of a New Purge-and-Trap On-line Interface for the Real-Time Analysis of VOCs in Aqueous Streams**
P-7	William L. Hall, Jr. - **Developing Stakeholder Input and Interaction on Environmental Policy and Practices: A Summary of the Proceedings of the Environmental Quality & Agriculture Conference**
P-8	Zoe Grosser, Laura Thompson - **Ultratrace Mercury Measurement in the Future**
P-9	Asoka I. Katumuluwa, Shahla Ameli, Prince A. Kassim - **Determination of Non-Metallic Inorganic Contaminants in Drinking and Wastewaters using a Simple and Rapid Discrete Multi-Chemistry Technique**
P-10	Stephen T. Zeiner, David R. Blye, Donald J. Lancaster, Jennifer N. Schott - **Evaluating Calibration Model Reliability**
P-11	Chatmon Thomas, Deborah Miller-Tuck, Delores E. Willis and Prince A. Kassim - **Analysis of Selected Gasoline Oxygenates in Drinking Water and Wastewater Using Modified EPA Method 8260B**
P-12	Laura Chambers and Michael L. Duffy - **Performance Results From a New Purge-and-Trap Sample Concentrator: Eclipsing Old-Style Technology**
P-13	Laura Chambers and Michael L. Duffy - **Analysis of Oxygenates Using a New Purge-and-Trap Sample Concentrator**
P-14	E. Barry Skolnick and Robert G. Hamilton - **"Legacy" Science Suggests Improved Surface-Testing Practices for Detection of Dispersed Bioagents (*e.g.*, *Bacillus anthracis* Spores) in Bioterrorism Response**

Tuesday, July 20 – Morning – Monticello East Room

1		**Organic Methods Session #1 –** Maria Gomez-Taylor and Lynn Riddick, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
1	8:15	Sejal Shah Iyer, David Lineman, H. M. Skip Kingston* - **Enhancements and Extensions of Microwave-Assisted Extraction for Environmental Applications**
2	8:45	Diane Gregg, Dave Kovacs, Meredith Clarage - **Comparison of Two Different Solid Phase Extraction/ Large Volume Injection Procedures for Method 8270**
3	9:15	Clifford T. Schmitt, L.G., L.H.G., Richard W. McManus - **Innovative Monitoring System to Manage the Risk of Release to the Subsurface Associated with Industrial and Commercial Uses of Volatile Organic Compounds**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
4	10:30	Robert S. Johnson - **New Technology for Automated Drying and Evaporation/Concentration of Environmental Samples for GC and GC/MS Analysis**
5	11:00	Jim Krol, Lawrence Zintek - **LC/MS Multi-Analyte Screening Method for Deleterious Organics in Drinking Water**
6	11:30	Dianne L. Poster, Michele M. Schantz, John R. Kucklick, Lane C. Sander, Patricia Schubert-Ullrich, Holly A. Bamford, Heather M. Stapleton and Stephen A. Wise - **Two New Particle-related Standard Reference Materials for Organic Contaminants**

Tuesday, July 20 – Morning – Monticello West Room

2		**Inorganic Methods Session #1** – Shen–yi Yang and Skip Kingston, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
7	8:15	Shen-yi Yang and Kim Kirkland - **National Inorganic Methods Program for RCRA**
8	8:45	Eric Fischer, Qiang Tu, Stuart Nagourney, Randy England, Brian Buckley - **Microwave-assisted Solvent Extraction for the Quantitative Simultaneous Extraction of Inorganic Mercury and Methylmercury from Soils**
9	9:15	G. M. Mizanur Rahman, H. M. 'Skip' Kingston, John C. Kern, Sara W. Hartwell, Raymond F. Anderson and Shen-Yi Yang - **Inter-laboratory Validation of EPA Method 3200 for Mercury Speciation Analysis using Prepared Soil Reference Materials**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
10	10:30	H. M. Skip Kingston*, Mizanur Rahman, John Kern, Matt Pamuku, Karin Rosen, Ye Han, Dingwei Huo, Theo Towns - **Elemental Speciation: An Environmental and Forensic Challenge and an Approach to the Analysis Uncertainty**
11	11:00	Zoe Grosser, Wilhad Reuter, Pamela Perrone and Ken Neubauer - **Simultaneous Determination of Several Inorganic Species in Water with a Dynamic Reaction Cell and ICP/MS**
12	11:30	Martin Nash, Phil Shaw, Bill Spence, Simon Nelms - **New Developments with HPLC-ICP-MS and GC-ICP-MS Instrumentation for Routine Speciation Analysis**

Tuesday, July 20 – Morning – Vista Ballroom A

3		**Ensuring the Integrity of Laboratory Data** – Jack Farrell and Joan Cassedy, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
13	8:15	Michael Daggett - **Laboratory Fraud**
14	8:45	John J. Pavlick - **Compliance and Oversight in the Aftermath of Enron and Arthur Anderson**
15	9:15	Arthur Burton - **Environmental Laboratory Data Integrity Initiative**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
16	10:30	Ken McInerney - **Learning, Unlearning and Relearning: The Emergence of Online Learning as an Essential Business Tool**
17	11:00	Gary K. Ward; Chuck Wibby, G. Keith Ward, Jr **- Performance Test Studies: Integral to Laboratory Data Integrity Programs**
17B	11:30	Steve Baker -

Tuesday, July 20 – Morning – East Room

4		**Characterization of Mixed Wastes at DOE Sites** – Daro Ferrara and Aruna Arakali, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
18	8:15	Steven E. Bohrer and Guy M. Marlette - **U.S. Department of Energy's Mixed-Analyte Performance Evaluation Program (MAPEP)**
19	8:45	Richard F. DeVault and James L. Clark - **Analysis of Low Molecular Weight Organic Acids by Ion Chromatography in DOE Tank Waste**
20	9:15	Paul V. Macek, Richard F. DeVault, Raymond T. Heinrich, Brandy L. Wilson - **Analysis of C_1 to C_3 Alcohols by Azeotropic Distillation and GC/MS in Simulated DOE Tank Waste**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
21	10:30	Rajat S. Ghosh, Sharon M. Drop and John R. Smith - **Performance of Anion Exchange Chromatography Method for the Routine Evaluation of Metal Cyanide Complexes in Solid Waste Leachates**
22	11:00	Daro Ferrara, Alex Cozzi, Christine Langton, Daniel McCabe and Delane Maxwell - **Demonstrating a Technical Basis for Immobilizing a Radioactive Salt Solution**
23	11:30	A. V. Arakali, D. Blumenkranz, L. A. Huffman, J. L. Meehan and J. Yokel - **Optimization of Regulatory Data Quality Objectives for Hanford Vitrification Process**

Tuesday, July 20 – Afternoon – Monticello East Room

5		**Organic Methods Session #2 –** Maria Gomez-Taylor and Lynn Riddick, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
24	1:30	David I. Thal and Kevin Kelly - **Decreasing GPC Cleanup Time for PCBs and PCDD/PCDFs Using Mobile Phase Modification**
25	2:00	Wayne J. Whipple and Troy Strock – **Low-Cost PCB Congener Analysis Using Solid Phase Extraction and Gas Chromatography-Tandom Ion Trap Mass Spectrometry Detection**
26	2:30	Lynn Riddick, Joan Cuddeback, Maria Gomez-Taylor, Bill Telliard - **Validation of EPA Method 1668A for PCB Congeners**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
27	3:45	Jianping Chen, Shili Liu and Peter Zack - **Analyzing Oxygenates in Environmental Samples by P&T/GC/MS**
28	4:15	H. Griffith, A. Tipler, L. Marotta - **Headspace Trapping Technology with GC/MS for Determining Volatile Organic Compounds (VOCs) in Environmental Samples**
29	4:45	Keith Strout, Michael Zimmerman, Clyde Hedin - **Comparison of 1,4-Dioxane as a Volatile and Semivolatile Analyte in Single and Multi-Laboratory Studies**

Tuesday, July 20 – Afternoon – Monticello West Room

6		**Inorganic Methods Session #2** – Shen–yi Yang and Skip Kingston, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
30	1:30	Bruce Richter, Sheldon Henderson, Doug Later and Rosanne Slingsby - **Accelerated Solvent Extraction (ASE) as a Sample Extraction Technique for Perchlorate in Solid Matrices**
31	2:00	Robert P. Di Rienzo, Kham Lin, Thomas T. McKay and Richard W. Wade - **Analysis of Perchlorate in Drinking Water, Groundwater, Saline Water, Soil and Biota by LC/MS**
32	2:30	Jay Gandhi and Joe Hedrick - **Perchlorate in Various Vegetables by IC/MS**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
33	3:45	Jon S. Kauffman - **LC/MS/MS Applications in the Environmental Laboratory**
34	4:15	Thomas W. Pearson - **Field Analysis of Chromium VI During and After Remediation of a Former Chrome-Plating Facility**
35	4:45	El-Nady, F. E. and E. A. Assery - **Monitoring of Trace Element Air Pollution at Urban Countries Along the Red Sea Coast**

Tuesday, July 20 – Afternoon – Vista Ballroom A

7		**Assessing Performance of New Methods** – Elizabeth Mishalanie and Anita Mishra, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
36	1:30	Barry Lesnik – **Methods' Development and Methods' Validation for the RCRA Program Including Both Program and Individual User Validation Applications**
37	2:00	Michele M. Schantz, Dianne L. Poster, John R. Kucklick and Stephen A. Wise - **Performance-Based Quality Assurance Programs for the Determination of Organic Species in Marine Tissue, Marine Sediment and Air Particulate Samples**
38	2:30	Amy Dindal and Stephen Billets – **U.S. EPA SITE Program Performance Verification Testing of Monitoring and Measurement Technologies for Dioxin and Dioxin-like Compounds in Soil and Sediment**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
39	3:45	Mike Purcell - **Benefits of Nitrogen Monitoring by High Temperature Combustion (HTC)**
40	4:15	Yi He, Yan Zheng and David C. Locke - **Cathodic Stripping Voltammetric Speciation of μg/L Level Arsenic in Water Samples**
41	4:45	Keith Strout, Michael Zimmerman, Clyde Hedin - **Evaluation of Interlaboratory Study Data using Vacuum Distillation Unit (VDU) and Gas Chromatography/ Mass Spectrometry (GC/MS) Analysis**

Tuesday, July 20 – Afternoon – East Room

8		**Innovative Approaches to Environmental Monitoring –** Oksana Pozda and Llew Williams, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
42	1:30	Ron Moore, James Parker and Linda Freeman - **Out-of-the-Box Approach to Automated Data Validation**
43	2:00	Mark Bruce, Ping Li, Raymond Risden, Riley Salmons, James Boyle, Terry Wright, Kaniz Siddiqui, Beverly Head, Ty Gouda - **Avoiding Sewer Fires with Vapor Space Organics Monitoring**
44	2:30	Mark L. Bruce - **Particle Size Reduction and Subsampling of Solid Materials**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
45	3:45	Simon Nelms, Bill Spence, Martin Nash - **Ultra-trace Quantification and Isotope Ratio Measurement of Uranium in Urine: A Monitoring Technique for Troops**
46	4:15	A. D. Sauter and L. Williams - **Less is More: Induction Based Fluidics and the Nanoliter-Microliter "Syringe"**
47	4:45	Carol Thielen - **Case Studies of Two Innovative Field Technologies using GC and GC/MS**

Wednesday, July 21 – Morning – Monticello East Room

9		**Sampling and Analysis for Homeland Security Session #1 –** Douglas Lipka and David Mills, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
48	8:15	L. Williams - **Inside and Outside the Box**
49	8:45	Peter Stein - **Using Sensor Networks to Detect Biological Threats**
50	9:15	Elias Greenbaum and Miguel Rodriguez - **AquaSentinel: A Continuous Monitoring Biosensor System for Primary-Source Drinking Water Protection**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
51	10:30	Charles Call and Ezra Merrill - **Bioaerosol Sensors for Homeland Security**
52	11:00	Oba L. Vincent - **Standardized Analytical Methods (SAM) for Homeland Security Sample Analysis**
53	11:30	Deborah Dixon Walker - **Sampling and Analysis Considerations at Chemical Warfare Materiel Sites**

Wednesday, July 21 – Morning – Monticello West Room

10		**Laboratory Accreditation Session #1 –** Lara Autry and Jerry Parr, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
54	8:15	Lara Autry and Jerry Parr - **Historical Perspective on the NELAC Model**
55	8:45	Rachael E. Trimpert - Laboratory Response Network-Chemical: Quality Assurance Program Overview
56	9:15	Dawn D. Thomas - **Accreditation of Field Sampling and Measurement Organizations (FSMO)**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
57	10:30	Jerry Diamond and Herb Brass - **Laboratory Accreditation and Ambient Water Quality Monitoring**
58	11:00	Michael Hartman – **Different Approach for the Accreditation of Air Emission Testing**

Wednesday, July 21 – Morning – Vista Ballroom A

11		**Advances in Electronic Data Deliverables Session #1** – Anand Mudambi and Joe Solsky, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
59	8:15	Bosco M. Ramirez - **Laboratory Perspective on the Challenges Associated with the Generation, Management and Submittal of Laboratory Deliverables**
60	8:45	Anand R. Mudambi and Joseph F. Solsky - **Status of SEDD: Implementation, Production and Review Software**
61	9:15	Joseph F. Solsky and Anand R. Mudambi - **Inner Workings of SEDD: Everything You Wanted to Know but Were Afraid to Ask**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
62	10:30	Buddy Wilson - **SEDD: Experiences in Programming and Implementation with Real-World Projects**
63	11:00	Scott M. Denzer and Pam A. Wehrmann - **Using SEDD Deliverables and Automated Data Assessment Software to Meet Project-Specific Electronic Data Management Goals**
64	11:30	Todd M. Pierce - **Using SEDD Files with the Web-Based Environmental Information Management (EIM) System from Locus Technologies**

Wednesday, July 21 – Morning – East Room

12		**Advances in Implementing the Triad Approach and Documenting Measurement Uncertainty –** Deana Crumbling and Marlene Moore, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
65	8:15	Deana M. Crumbling - **Triad Approach to Uncertainty Management and Environmental Data Quality**
66	8:45	Richard O. Gilbert, John E. Wilson and Brent A. Pulsipher - **Collaborative Sampling Design for Estimating and Testing Means**
67	9:15	Marlene Moore - **Measurement Uncertainty and Legal Defensibility**
	9:45	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
68	10:30	Robert O. Harrison - **Application of Method 4025 to Bring Dioxin Sites Into EPA's Triad Approach to Site Assessment and Remediation**
69	11:00	Stuart Nagourney and Brian Sogorka - **Laboratory Certification for Field Analytical Methods and Triad in New Jersey: Perfect Together**
70	11:30	Daniel M. Powell - **Triad's Systematic Project Planning Includes Legal and Business Concerns**

Wednesday, July 21 – Afternoon – Monticello East Room

13		**Sampling and Analysis for Homeland Security Session #2 –** Douglas Lipka and David Mills, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
71	1:30	Brian Frazer - **EPA's Response Protocol Toolbox**
72	2:00	Latisha S. Parker and Greg Grover - **National Sampling and Field Test Kit for Drinking Water**
73	2:30	Lawrence H. Keith, Herbert J. Brass, Steven C. Allgeier, Daniel J. Sullivan, Jerome M. Diamond and Chad Barbour - **Two New Analytical Methods Tools for Water Protection**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
74	3:45	Jackie Doan **- Quality Assurance and Emergency Response Data**
75	4:15	Dana Tulis - **Building Environmental Laboratory Capability in Support of Emergency Response**

Wednesday, July 21 – Afternoon – Monticello West Room

14		**Laboratory Accreditation Session #2 –** Lara Autry and Jerry Parr, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
76	1:30	Dave Speis - **Proficiency Testing and the NELAC Fields of Testing Model: Theory vs. Reality and the Need for Change**
77	2:00	Richard Amano - **Automated Audit Software for On-site Laboratory Audits and On-going Laboratory Assessment**
78	2:30	David Friedman - **Adoption of a Performance Paradigm for Laboratory Accreditation**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**
79	3:45	Brooke Connor - **Requirements for a Quality System**
80	4:15	Chuck Wibby - **Role and Utility of Proficiency Test Samples for Non-Traditional Methods and Analytes**
81	4:45	Barbara Finazzo, Bob Wyeth, Alfredo Sotomayor - **Possible Changes to the NELAC Requirements: A Panel Discussion**

Wednesday, July 21 – Afternoon – Vista Ballroom A

15		**Advances in Electronic Data Deliverables Session #2 (1/2)** – Anand Mudambi and Joe Solsky, *Co-Chairs*
Paper No.	*Time*	Authors and **Paper Title**
82	1:30	Paul Fjeldsted and Paul Banfer - **Advances in Electronic Data Deliverables (EDD): The EDD Designer, Generator and Checker Concept**
83	2:00	Mitch Beard, Michael F. Barinek and David E. Dougherty - **Real-time Data Discovery and Notification of Restoration Progress Through Automated Electronic Data Delivery**
84	2:30	Matthew L. Jones, R. Lee Norland and Norma Castaneda - **Environmental Data Transformer (EDT)**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**

Wednesday, July 21 – Afternoon – East Room

16		**Roundtable: Changing Federal Requirements to Manage Environmental Data Quality** - Mike Carter, *Chair*
Paper No.	*Time*	Authors and **Paper Title**
85	1:30	Mike Carter, Fred McLean, Robert Runyon and Maryellen Schultz - **Roundtable: Changing Federal Requirements to Manage Environmental Data Quality**
	3:00	**Break - Poster Session, Exposition and Refreshments – Vista B & C Ballrooms**

Short Courses – Thursday, July 22 and Friday, July 23

Short Courses Have Additional Registration Fees

Short Course #1 - Implementing the Performance Approach – INELA - (Two Days, Thursday and Friday) – Marlene Moore, Instructor. Vista Ballroom A

Short Course #2 - ISO/IEC 17025 Overview - (One Day, Thursday only) - James H. Scott, Instructor. Monticello East Room

Short Course #3 - Internal Auditing and Corrective Action - Practical Tools for Management (One Day, Thursday only) - Jack Farrell, Instructor. Monticello West Room

PAPERS (Titles linked to papers)

Posters

Organic Methods – I

Chairs: M. Gomez-Taylor and Lynn R. Riddick

Inorganic Methods – I

Chairs: S. Yang and S. Kingston

Ensuring the Integrity of Laboratory Data

Chairs: J. Farrell and J. Cassedy

Characterization of Mixed Wastes at DOE Sites

Chairs: D. Ferrara and A. Arakali

Organic Methods – II

Chairs: M. Gomez-Taylor and L. Riddick

Inorganic Methods – II

Chairs: S. Yang and S. Kingston

Assessing Performance of New Methods

Chairs: E. Mishalanie and A. Mishra

Innovative Approaches to Environmental Monitoring

Chairs: O. Pozda and L. Williams

Sampling and Analysis for Homeland Security – I

Chairs: D. Lipka and D. Mills

Laboratory Accreditation – I

Chairs: L. Autry and J. Parr

Advances in Electronic Data Deliverables – I

Chairs: A. Mudambi and J. Solsky

Advances in Electronic Data Deliverables – I (continued)

Advances in Implementing the Triad Approach and Documenting Measurement Uncertainty

Chairs: D. Crumbling and M. Moore

Sampling and Analysis for Homeland Security – II

Chairs: D. Lipka and D. Mills

Sampling and Analysis for Homeland Security – II (continued)

Laboratory Accreditation – II

Chairs: L. Autry and J. Parr

Advances in Electronic Data Deliverables – II

Chairs: A. Mudambi and J. Solsky

Roundtable: Changing Federal Requirements to Manage Environmental Data Quality

Chair: M. Carter

POSTERS

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RAPID EXTRACTION OF A BROAD SPECTRUM OF CHEMICAL COMPOUNDS FROM PUBLIC WATER SUPPLIES USING EPA METHOD 3535A

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The rapid determination of contaminants in public water supplies has become an important topic, especially so in light of recent world events. Government agencies and municipalities are seeking faster methods for extracting and analyzing contaminants. Compounds of interest span a wide spectrum of chemical classes and functionalities, each of which must be quickly and efficiently extracted from aqueous media prior to analysis. The benefits of automation, low solvent consumption and the elimination of emulsion formation make Solid Phase Extraction (SPE) a good candidate for fast extraction techniques because many samples can be extracted simultaneously, the evaporation/concentration times are reduced and emulsions do not impair the extraction process. In addition, the use of hydrophobic membranes to remove residual water from the extract eliminates the necessity of Na_2SO_4 in the drying step, further increasing performance and sample throughput.

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

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COMPOSITE SAMPLING FOR SOIL VOC ANALYSIS

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Data published by numerous researchers over the last decade demonstrate that there is a high degree of spatial variability in the measurement of volatile organic compounds (VOCs) in soil at contaminated waste sites. This phenomenon is confounded by the use of a small sample aliquot (5 g) in the standard low-level, purge-and-trap sample extraction method (*i.e.*, SW-846 Method 5035), which decreases the representativeness of the sample. In order to optimize sample representativeness, the number of samples collected at the site is generally increased; however, this greatly increases project costs. Compositing soil samples has been suggested as a cost-effective alternative means to obtain data which are representative of the overall conditions at a site. This study investigated this approach and its impact on representativeness.

To explore the feasibility of composite sampling for soil VOC analysis, core samples were collected and cut into sections at 20, 30, 40, 50, 60, 70 and 80 cm below the ground surface. After each cut, approximately 5 g of soil was removed from the newly exposed surface (top end of the cut) using a truncated syringe and placed in a preweighed 40-mL septum-sealed vial containing 5 mL of methanol. A second 5 g sample was removed from each core at the 20, 40, 60 and 80 cm intervals and combined in a preweighed 40-mL septum-sealed vial containing 20 mL of methanol. Samples were analyzed following SW-846 methods 5035/8260.

The results show both *cis*-1,2-dichloroethene (DCE) and trichloroethene (TCE) were ubiquitous at the site. Nearly 50% of the composite sample concentrations were greater than that of the individual sample means for DCE while 80% were greater for TCE. This indicates that the composite sample provided a good representative sample of the vertical heterogeneity within the soil column. Within a plot (5 core samples collected within 1 m of each other), the mean of the composite samples was typically greater than the mean of all the individual samples. However, the relative percent differences (RPDs) among the composite and individual sample means were generally less than 35% indicating that the composite samples provided data representative of the horizontal heterogeneity within the plot. In comparing the overall grand mean of all 70 individual samples to the mean of the composite samples for the entire site, a similar pattern was identified indicating that composite samples provided a valid means to effectively characterize the site with an associated cost savings.

Disclaimer: This is an abstract of a proposed presentation and does not necessarily reflect the United States Environmental Protection Agency (EPA) policy. The actual presentation has not been peer reviewed by EPA.

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DETERMINATION OF PERCHLORATE ANION IN HIGH TOTAL DISSOLVED SOLIDS WATER USING LC/MS/MS

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Using the EPA Information Collection Rule as a data base, drinking water facilities have been reporting higher than anticipated concentrations of perchlorate anion in environmental waters in 22 states. This is a cause for concern because of potential adverse health effects that can occur at low ppb concentrations (μg/L), including interference with iodine thyroid uptake, fetal nervous system development and a potential carcinogen. Due to its toxicity, perchlorate has an action limit of 4 ppb in Texas and California drinking water. EPA may propose a 1 ppb action limit. DoD and DoE are also interested in prechlorate, an ingredient in many munitions, from a soil contamination perspective.

The current EPA method 314.0 (Determination of Perchlorate Using Ion Chromatography…) uses anion exchange chromatography with suppressed conductivity detection. This method works well but becomes limiting as the total dissolved solids concentration increases, especially sulfate. Sample preparation to remove chloride and sulfate is necessary and the most difficult problem; requires the use of a O^{18} perchlorate internal standard to account for recovery.

This presentation will describe an LC/MS/MS method for perchlorate without the requirement for sample preparation. The key to solution is the chromatography of perchlorate relative to sulfate. As organic modifier concentration increases, perchlorate elutes faster than sulfate allowing the chromatographer to place perchlorate baseline separated between high chloride and high sulfate. With the direct injection of 100 μL of a solution containing 1000 ppm each of bicarbonate, chloride and sulfate, MS/MS detection can obtain a perchlorate detection limit (3:1 S/N) of 0.2 ppb. Larger injection volumes can be used to increase sensitivity.

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TO PURGE OR NOT TO PURGE? VOC CONCENTRATION CHANGES DURING LINE VOLUME PURGING

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Soil vapor surveys are commonly used as a screening technique to delineate volatile organic compound (VOC) contaminant plumes and provide information for soil sampling plans. Traditionally, three purge volumes of vapor are removed before a sample is collected. This study evaluated the VOC concentrations lost during purging for two different active sampling methods.

The two different active methods for soil vapor collection were: 1) micro-volume and 2) macro-volume. The micro-volume vapor sample had total line purge volume of 1.25 mL and the macro-volume vapor sample had a total line purge volume of 15 mL. Six line purge volumes were collected for each vapor sampling technique, with the fourth purge volume representing the traditional sample used for site screening data. Each sample was collected by gas tight syringe and transferred to a thermal desorption tube for sorption, transport and analysis. The vapor data was compared to collocated soil data to determine if any correlation existed between the VOC concentrations.

For both active vapor sampling techniques, the VOC concentrations in the first three purge volumes exceeded the VOC concentrations in the last three purge volumes. This implies that the general rule of removal of three purge volumes prior to taking a sample for analysis could lead to underestimating the level of VOC contamination present. At one of the sampling locations, the data show a general increase in concentration of VOCs as line volume purges were collected. The data did not show a correlation between the concentration of VOCs determined by either vapor sampling technique when compared to that of the collocated soil sample.

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HIGH SPEED EXPLOSIVES MONITORING USING UPLC™

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Rapid identification of explosive residues whether for pollution or terrorist concerns has become increasingly important in today's world. These residues contain nitroaromatic and nitramine compounds which pose significant health risks.

EPA Method 8330 describes the separation of fourteen analytes and degradation products of explosive compounds. Our poster will describe a new separation technology which will allow separation of these compounds in under ten minutes. This technology, known as Ultra Performance LC™ (UPLC) relies on columns with a particles size of 1.7 microns, leading to extremely high efficiency separations in very short run times. Applicability to real samples will be shown.

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EVALUATION OF A NEW PURGE-AND-TRAP ON-LINE INTERFACE FOR THE REAL TIME ANALYSIS OF VOCS IN AQUEOUS STREAMS

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The new On-line Purge-and-Trap Interface eliminates the need for “grab” sampling which can be error prone, labor intensive and time consuming. The interface provides a solution for Homeland Defense drinking water protection and spill detection by sampling water intakes on public water supplies such as rivers, lakes and reservoirs. In addition, water treatment facilities can monitor various stages of the water treatment process for

the generation of disinfection by-products (DBPs) such as trihalomethanes automatically.

The interface delivers water samples from up to six separate streams to the Velocity XPT™ Purge-and-Trap Concentrator for volatile organic compound (VOC) analysis. Standard solutions are automatically added to the 5 or 25 mL sample aliquot. The interface can also be configured in conjunction with a vial autosampler to run continuing calibration checks from vials intermixed with stream samples. The entire system is controlled using a special PC software allowing for unattended sampling and analysis at pre-arranged times. This new capability will allow water treatment facilities to configure alarm levels for continuous and unattended protection. Actual calibration, control sample and results data from a large water treatment utility will be reported along with setup and sequencing requirements.

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DEVELOPING STAKEHOLDER INPUT AND INTERACTION ON ENVIRONMENTAL POLICY AND PRACTICES: A SUMMARY OF THE PROCEEDINGS OF THE ENVIRONMENTAL QUALITY & AGRICULTURE CONFERENCE

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In November of 2003, a national meeting held in Iowa had as a goal to gather and formulate input on environmental policy matters affecting the agricultural community. The meeting (with a registration of 125 diverse participants) used educational workshops and facilitated work groups to focus discussions and formulate ideas addressing relevant environmental issues. This poster summarizes the activities, actions and proposals resulting from the input of the participants.

The mission statement of the conference follows. Mission: The conference will provide an educational program and opportunities for interaction to: Crop and Livestock Producers, Ag industry professionals, regulators, academia and others to address regulatory and environmental impacts of nutrient use and management practices in North America. The program will focus on BMP implementation with real life ideas for affecting practices and profits. The format will provide opportunities for stakeholders to

interact, through facilitated work groups to address nutrient management and public policy issues.

Specific educational topics included:

- Tools Used in Nutrient Management Plans
- Development of Comprehensive Nutrient Management Plans
- What is the Agricultural Communities' Role in Developing Workable & Effective TMDLs?
- Farming, Wildlife & Environment – Keeping the Balance
- Understanding & Implementing the P Index
- New Equipment & Tillage Technologies, Manure Recycling & Nutrient Management"
- Air Quality & Agriculture

Specific work group issues' and problems' addresses included:

- Funding for Assessment: Helping Citizens Understand & Solve Watershed Scale Problems
- Nutrient Management: Balancing Production Goals and Environmental Quality
- Why TMDLs Are Important - Legal Implications of Implementation & Enforcement
- Combining Agronomy & BMPs to Improve Nutrient Efficiency & Environmental Quality
- Innovative Alternate Land Uses - Better Management of Nutrients & Resource Conservation

In many cases, an important aspect of the presentations, conversations and proposed solutions involved the data used to make decisions. This data is often the direct result of piecemeal un-coordinated environmental monitoring programs. The applicability, accuracy and reliability of this data are of primary importance to stakeholders. Data gaps and the weight given to less reliable data were also concerns of the group. Suggestions to get buy-in from all parties in an affected area are important in the funding, sampling, analysis, reliability and appropriate use of environmental monitoring data.

In reality soil, nutrient and runoff sampling and analysis, nutrient monitoring and modeling are all environmental data used in the decision and policymaking aspects of agricultural inputs. Failure to integrate all of these segments of the agricultural system into a holistic approach will undoubtedly lead to an incomplete picture of the environmental impact (positive or negative) made by agricultural inputs and practices. The proposals of the conference are presented with special emphasis on those relating to data and environmental monitoring.

ULTRATRACE MERCURY MEASUREMENT IN THE FUTURE

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Introduction

Mercury is a significant element because of its toxicity and possible long-term cumulative effects at lower levels. It bioaccumulates in the food chain, which is of particular concern for those who eat fish regularly. The number of fish advisories issued has increased over recent years, reflecting greater contamination in fresh-water streams and lakes, although several marine advisories have been issued along the gulf coast. A recent EPA report states that approx 87% of the mercury emissions in the U.S. come from solid waste incineration and fossil fuel combustion.

Mercury does not respect country boundaries because of its volatility. It is truly a global pollutant. For example, it is possible that we may see mercury pollution in the everglades that arises from mining in South America. Interest in species is growing as the varying toxicity and bioavailability of the different forms are better understood.

This presentation summarizes the parameters in a mercury measurement system that can be optimized. An important fact is that the detector (atomic absorption consisting of light, cell and detector or atomic fluorescence consisting of light, cell and off-axis detector) is only one component of the system and the front end (consisting of sample digestion, tubing, gas/liquid separator, purging of optical path, etc.) contributes to the overall performance of the system. The theoretical difference between the two techniques is not clearly seen in working systems and depends on how carefully the system is optimized. We want to better understand the impact of each of these components.

Background

Selected U.S. and European regulations are summarized in Table 1. The regulated levels are shown in ng/L to make comparisons easy. Most of the regulated levels are in the part-per-billion concentration level, except for ambient water. Ultratrace level measurements are required for ambient water to truly understand the background levels in the environment. We generally recommend that customers choose an analytical technique with a detection limit 10x below the concentration where a decision is to be made. This ensures confidence at the decision point. Therefore, for most of the regulatory analyses that are performed, detection limits of 0.1-0.2 ppb will be sufficient.

Table 1. Selected Mercury Regulations

Medium	U.S. Maximum Contaminant Level (ng/L)	EU Regulatory Limit (ng/L)
Drinking Water	2000	1000
Wastewater (Chlor-Alkali-Mercury Cells) (new)	110,000 max for one day 48,000 avg. over 30 days	50,000 ng/L before it is mixed with other wastewater
Universal Treatment Stds	150,000 (wastewater) or 25,000-200,000 (nonwastewater)	
TCLP Extracts	200,000	
Soils	1-21 mg/kg cleanup goal (10,000-210,000 ng/L in solution, based on 1g sample)	0.5 - 10 mg/kg (1mg/kg for Agricultural soil) (5,000 –100,000 ng/L in solution, based on 1g sample)
Sludges		16-25 mg/kg (160,000-250,000 ng/L in solution, based on a 1g sample)
Ambient water	12 (freshwater cont. criteria) 1.8 (Quality Guidance for the Great Lakes)	Natural waters such as Lake Constance, Germany contain around 0.8 ng/L Hg

When a wastewater discharge is made into a sensitive environmental waterway, such as when the City of San Jose discharges into the South San Francisco Bay, lower mercury requirements may be written into the permit, close to the water quality criteria level (12 ppt). Lower detection limit measurement techniques, suitable for convenient routine operation are required. There are a number of techniques available to measure mercury and they are listed here with detection limits for comparison. It is interesting to note that the detection limit for mercury can be significantly improved with the use of newer dedicated mercury systems, rather than an older atomic absorption instrument. For example, a typical general-purpose AA system might achieve a detection limit of 100 ng/L. A dedicated mercury system using AA technology can improve the detection limit to **4 ng/L** because the system has been optimized for this analysis. Preconcentration using some form of amalgamation, whether it be on a gold-coated sand or Pt/gold gauze, can improve detection limits with a variety of detectors. The

detection limits will depend upon control of the blank and the amount of sample taken for the measurement.

Some of the U.S. EPA methods that include mercury are shown here. In the past several years a number of methods have been updated to include mercury as an analyte. Method 1631 is an ultratrace mercury method involving clean sample collection and handling. Method 1630 is a draft speciation method.

When multielement methods include mercury, it is important to note that the sample preparation method may need to be adjusted to retain the volatile mercury component. For example, drinking water is often measured with ICP-MS without a digestion step (less than 1 turbidity unit). TCLP samples have been demonstrated to give excellent results on ICP-OES without a digestion step. Microwave digestion is a closed form of digestion that will retain mercury and may be considered, depending on the workload and availability of equipment.

Method 1631 has been performed on the FIMS/amalgamation system and all the method requirements met. 15 mL will allow three replicates. Twenty milliliters of sample will give a slightly lower detection limit and still allow two replicates to be taken from a 50-mL autosampler tube.

What will laboratories be looking for in the future? Increasingly lower detection limits is one important item. Lower detection limits, now needed in a few NPDES situations, may become more broadly required. Routine application ideally requires easy sample handling, meaning protection from contamination of the sample, which can be a challenge. It is also helpful to have built-in quality control to identify contamination problems or other issues quickly, as soon as they arise, to minimize productivity impacts. Easy data handling and reporting is often the laboratory bottleneck and this measurement will require good documentation. We have addressed built-in quality control and data handling and will concentrate further on performance improvement opportunities.

Instrumental Component Evaluation

There are many factors in the chemistry of the analysis that will influence the quality of the determination. The first step is important and, if the collected sample is not properly preserved, the results will be influenced. The sample must be digested and the valence state properly established before the reduction step. The sample containers must be chosen to reduce the possibility of adsorption on the walls, diffusion through the walls, or precipitation from solution; PTFE is preferred.

The reduction step must reduce all the mercury, but not other elements present that might cause an interference. $SnCl_2$ is an excellent reductant and fewer interferences are observed than with sodium borohydride. The blank must be carefully controlled to get accurate measurements. There are many instrumental parameters that will influence the quality of the result and will depend on the individual manufacturer implementation, not just the technique employed.

The photometric noise of the detector is the ultimate limitation, but will often be overwhelmed by other factors. The absolute sensitivity of the technique will influence the detection limits, as will the amount of sample taken for analysis. Precision at higher concentrations will be as important as low concentrations for real world analyses where routine levels encountered are higher. Interferences are present in every technique and background absorbance, signal quenching (fluorescence) and matrix effects during amalgamation are influences. Amalgamation can help to remove quenching effects such as water vapor and a two-stage trap is recommended if fluorescence is used.

The FIMS consists of a low-pressure mercury light, optimized cell and solar-blind solid state detector. The valves and pumps on the front are used for sample measurement, introduction and transport. Preconcentration using amalgamation can be coupled with the system for method 1631. Sample volumes of 10-20 mL or more can be used. In this case, the valve is positioned after the gas/liquid separator to minimize any carryover. The amalgamation unit is a separate unit, as shown in Figure 1, positioned on top of the FIMS.

Figure 1. FIMS and amalgamation unit

The brightness of the light source will contribute to the signal in AA to a certain extent, although not as dramatically as to atomic fluorescence. We tested an electrodeless discharge lamp which is brighter than the low-pressure mercury lamp currently used and saw a slight improvement in signal intensity.

Mercury-containing fluorescence lamps and sunlight contain mercury wavelengths that could contribute to spurious signals if they get to the detector. Shielding the light path and detector from possible stray light did not seem to have an effect on performance.

There are two parts of the optical path that might benefit from purging oxygen from the path. The path between the lamp and the cell might absorb some of the light, reducing intensity. The path from the cell end to the detector may also absorb light intensity and contribute to reproducibility. These effects are expected to be much greater if the

alternate mercury line at 184.9 nm is used. A small enhancement was seen at the usual wavelength 253.7 nm.

The gas controls regulate the flow of argon through the cell and may add noise to the signal if not constant. When amalgamation is used the gas flow transfers the mercury from the cell to the amalgamation gauze and the constant flow rate is not as critical. A more controlled gas flow will be tested with the FIMS.

The gas/liquid separator is expected to be a big contributor to the performance. The current plastic or glass separator has been optimized for low sample volumes (0.1-1mL). When large sample volumes (tens of mLs) are used another design might be faster and more efficient. Several candidates will be tested to observe the effects of design components. Sample handling is also an important consideration and will be evaluated.

The amalgamation unit has a gold/platinum trap to preconcentrate mercury vapor before introducing it into the cell for measurement. The use of a second trap is mandatory for fluorescence in order to completely eliminate water vapor, which causes signal quenching effects. It may improve small signal shape for atomic absorption, however, and will be evaluated.

Even when all the front-end components are optimized are we ultimately going to be limited by the capability of the detector? (Whatever type it is AA or AF) In order to understand if the detector was at its limit now, or if the front-end was limiting the detection limit, the detector system was isolated from the front-end.

Mercury vapor was precisely measured and injected directly into the cell. The baseline noise and signal was observed. The detection limit was estimated and compared with the detection limit observed with the front end components included. We thought about using a gas-tight syringe to inject a measured amount of vapor and then realized we'd be introducing another set of variables into the analysis. The TurboMatrix Headspace system is designed to do what we are looking for, but is usually used with organic materials equilibrated above a solid or water sample, which are automatically injected into a GC. In our case, we are interested in the mercury vapor above a mercury liquid bead sealed in a headspace vial.

The transfer line from the headspace was pushed into the connector so that contact with any tubing was minimized before introduction into the cell. Headspace is a well-known technique in GC and allows a measured amount of vapor to be reproducibly transferred to a GC for separation and measurement. In the first step the sample is allowed to equilibrate either with heating or without (without, in this case, for mercury work) to allow a constant amount to be present in the headspace of the vial.

The needle passes through the septum (Teflon lined for the mercury work) and pressurizes the vial to a reproducible, set pressure.

The decaying pressure pushes the analyte out of the vial into the moving gas stream which takes the sample to the GC (usually) or the FIMS cell in our case. The system is shown in action in Figure 2. The vial with the mercury bead (shown in small photo) is actually being sampled in the system shown. The blank vial is seen next to the "screw" in the autosampler tray. The vial is brought up to the needle and the process takes place.

Figure 2. Headspace unit used to precisely introduce mercury vapor.

Zero withdrawal time was used on the headspace to minimize contamination and carryover because we were dealing with a pure liquid. Because we know the temperature, pressure and vapor pressure of mercury we can calculate that more mercury was observed than when introduced by the front end, meaning that we could improve the front end. The detector is not at its limit yet; further improvements in the front end may yield significant improvement in the detection limit. We are looking to reduce front-end noise and improve sample delivery to the detector. Coupled with possible amalgamation system improvements it is likely that much lower detection limits could be achieved.

Conclusion

Although the system is very good in most routine measurement applications and offers data handling, built-in QC and automation, further improvement can be made to the system for low-detection limit work. Future work will complete the evaluation of the parameters and implementation of changes to assess the overall improvement that can be achieved.

DETERMINATION OF NON-METALLIC INORGANIC CONTAMINANTS IN DRINKING AND WASTEWATERS USING A SIMPLE AND RAPID DISCRETE MULTI-CHEMISTRY TECHNIQUE

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Introduction

Continuous flow techniques, such as Segmented Flow Analysis (SFA), Flow Injection Analysis (FIA) and Ion Chromatography (IC), are commonly used for the determination of inorganic anions by high-productivity environmental laboratories. In this study, colorimetric methods have been developed using an automated discrete multi-chemistry technique[1,2] for the determination of six nutrients: ammonia, orthophosphate, total phosphorus, total Kjeldahl nitrogen, nitrite and combined nitrate and nitrite in drinking water and wastewater samples following U.S. EPA accepted methodologies (Table 1).

Table 1. Current Analyses

ANALYTE	EPA METHOD
Ammonia (NH_3)	350.1
Orthophosphate (OP)	365.1
Total Phosphorus (TP)	365.4
Total Kjeldahl Nitrogen (TKN)	351.2
Nitrate + Nitrite (NO_2 + NO_3 (NO_{23}))	353.2
Nitrite (NO_2)	353.2

Instrumentation and Method

All analyses were performed using an AQ2 Multi-Chemistry Discrete Analyzer from SEAL Analytical (Figure 1). The main components of this system include: a refrigerated reagent compartment (15 X 45 mL reagent reservoirs), a removable sample tray (57 x 2 mL sample vials), a temperature-controlled reaction ring (180 reaction wells), a sampling station with a 1000 μL syringe and a sample probe, an aspirator consisting of a robotic arm and a probe and a photometer (Figure 2). In this technique, standards, unknown samples, quality controls and reagents are initially pipetted into the reaction wells. After mixing and incubation for a pre-set time period at 37^{o}C, the reaction product is delivered to a temperature-controlled flow cell, where the flow is stopped and the absorbance is measured at an appropriate wavelength. Concentrations of analytes in

unknown samples are determined by comparing sample responses with a calibration curve.

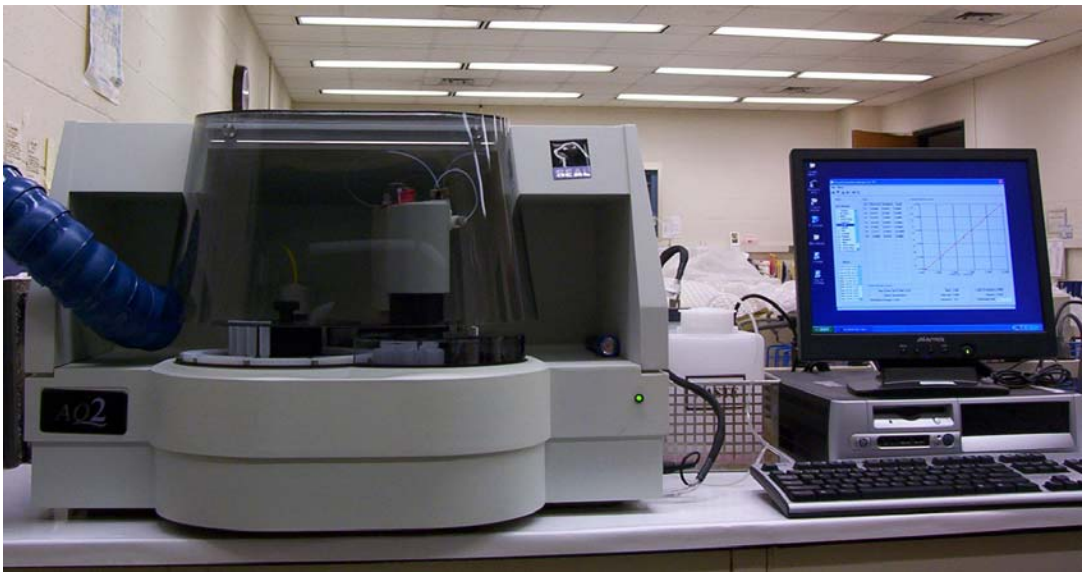


Figure 1. AQ2 Multi-Chemistry Discrete Analyzer (At Maryland Department of Health & Mental Hygiene)

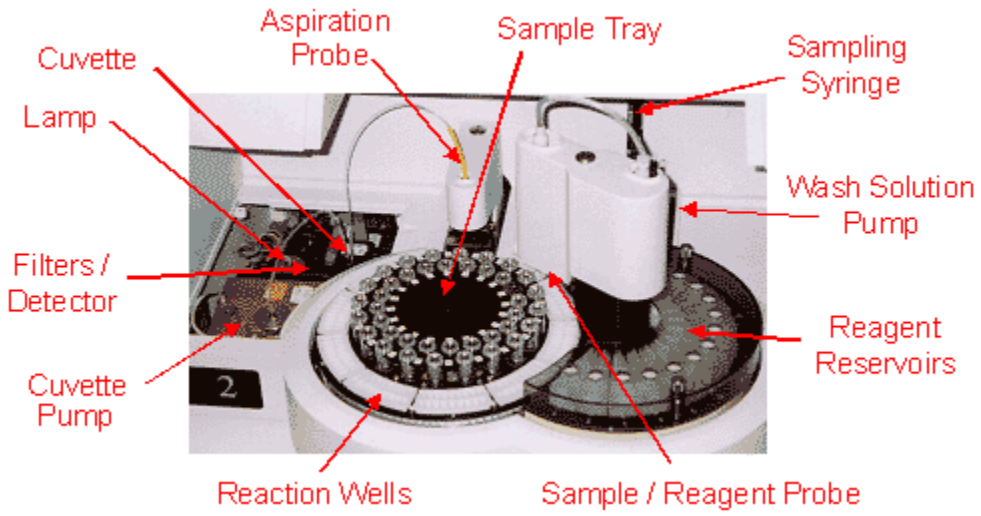


Figure 2. Main Components of AQ2 (Reprinted with permission of SEAL Analytical)

Results

For the six nutrients studied, the calibration ranges have been established and the method detection limits calculated (Table 2). The precision of the technique has been established by analyzing unknown samples in duplicate and the accuracy by analyzing sample spikes and external quality control samples over a period of several months

(Figures 3, 4 and 5, respectively). Comparison studies have been carried out with SFA (Technicon AA II) or FIA (Lachat) (Figure 6).

Table 2. Method Detection Limits+

TEST	CALIBRATION RANGE, PPM N OR P	CONCENTRATION, PPM N OR P								
		rep. 1	rep. 2	rep. 3	rep. 4	rep. 5	rep. 6	rep. 7	Standard Deviation	MDL
NH_3	0.2 - 10	0.203	0.208	0.200	0.196	0.206	0.201	0.202	0.004	0.013
OP	0.2 – 10	0.217	0.218	0.199	0.194	0.205	0.219	0.216	0.010	0.031
TP	0.2 – 10	0.192	0.208	0.196	0.204	0.183	0.174	0.185	0.012	0.038
TKN	0.2 – 10	0.194	0.222	0.173	0.175	0.182	0.165	0.175	0.019	0.060
NO_2	0.01 – 1.0	0.024	0.019	0.024	0.022	0.019	0.016	0.019	0.003	0.009
NO_{23}	0.2 - 10	0.202	0.190	0.203	0.185	0.197	0.205	0.182	0.009	0.028

+ Concentration of the standard used: 0.02 ppm N for NO_2; 0.20 ppm of N or P for all other analytes

MDL = Standard deviation x Student t-value*
* 3.143, for 7 replicates

Figure 3: Precision using Sample Duplicates

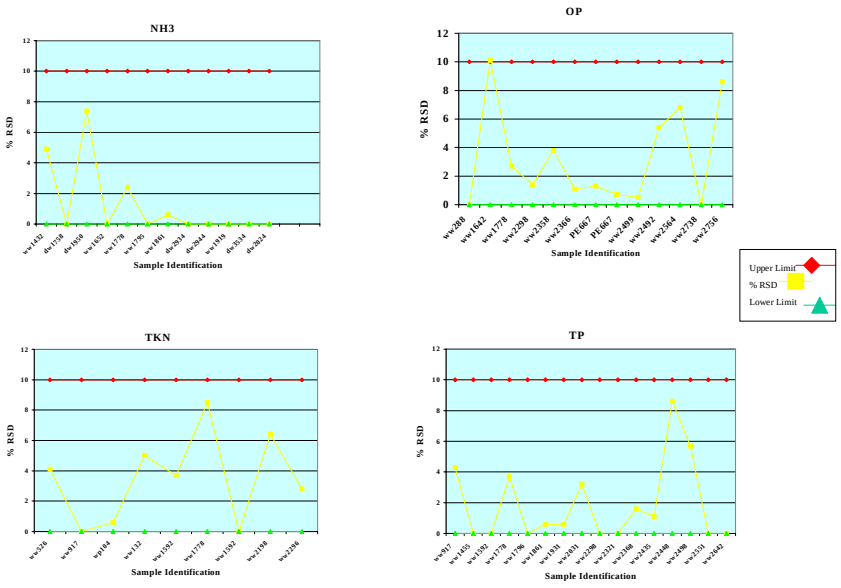


Figure 4: Accuracy using Spike Recovery

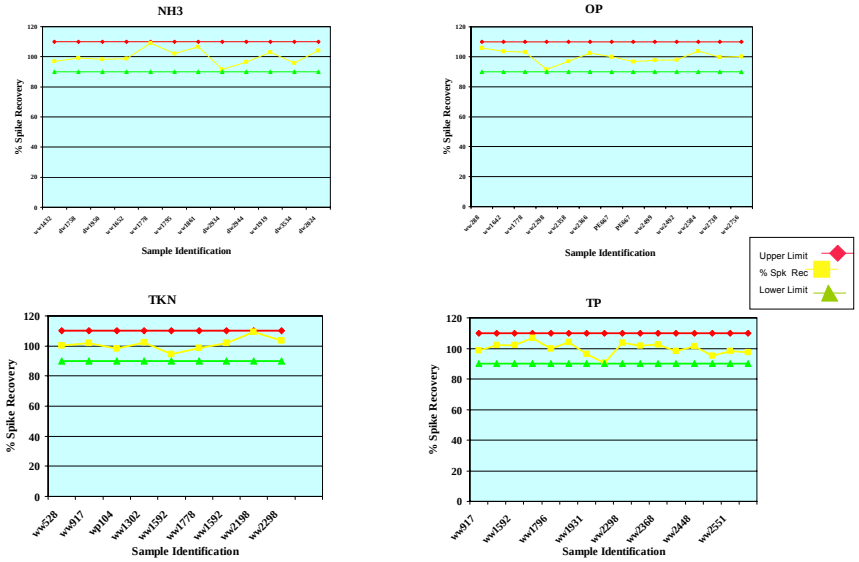


Figure 5: Accuracy using an External QC

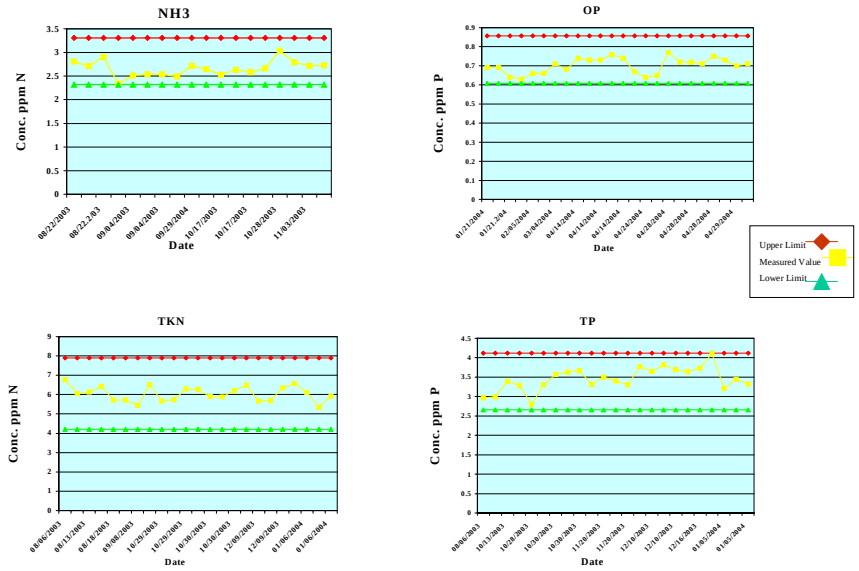
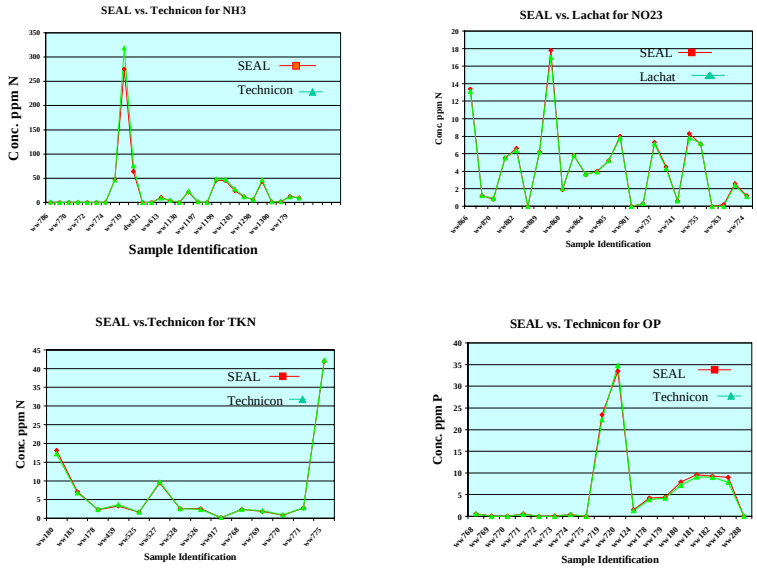


Figure 6: Data Comparisons



Discussion

Method validation studies indicate that this technique meets all method and quality control requirements for the six analytes studied. Following is a summary of the advantages of this technique:

- fast start up: computerized chemistry; automated check of reagent levels; no baseline stabilization
- increased productivity and short turn-around time: simultaneous and independent operation of aspiration system for reaction products and the ample/reagent processing system; pre- and post- auto-dilution of samples; temperature-controlled reaction resulting in faster analysis and greater stability; walk-away operation; overnight analytical runs
- flexibility: automated multiple chemistry selection for each sample with no hardware changeovers; quick change of concentration range
- savings: low reagent consumption (Table 3) resulting in reduced reagent cost and reduced waste generation; savings on waste removal; very little routine maintenance
- no carryover or cross-contamination
- maximized signal-noise ratio: absorbance taken after stopping the flow
- automated instrument shutdown

Table 3. Reduced Reagent ⇨ Usage Reduced Waste

TEST	RANGE, PPM N OR P	VOLUME OF SAMPLE/TEST, µL	VOLUME OF REAGENT(S)/SAMPLE, µL	TOTAL WASTE VOLUME/SAMPLE, µL
NH_3	0.20 - 10	150	323	473
OP	0.20 - 10	40	455	495
TP	0.20 - 10	100	395	495
TKN	0.20 – 10	110	450	560
NO_{23}	0.20 – 10	220	755	975
NO_2	0.01 – 1.0	52	423	475

Conclusions

The multi-chemistry feature of this technique has significantly enhanced the efficiency of our laboratory. The short analysis time, automated pre- and post-dilution capability and the capability to set up overnight runs have improved sample analysis turn-around time. Its very low reagent consumption along with a corresponding decrease in waste generation has reduced the cost for both reagents and waste disposal. This technique would be most beneficial when multiple assays are to be performed on a small number of samples. At the present time, we are in the process of completing validation studies for silica. Future analytes include hardness and sulfate.

Acknowledgements

We thank Jeffrey Fernandez and Rohanie Janack for valuable suggestions and assistance provided in the preparation of the poster presentation.

References

1. Operator Handbook, Discrete Multi-Chemistry Analyzer, Seal Analytical, Inc., April 2003.
2. User's Guide, AQ Series Software, Seal Analytical, Inc., April, 2003.
3. Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, March 1983.
4. Methods for the Determination of Inorganic Substances in Environmental Samples, U.S. Environmental Protection Agency, EPA/600/R-93/100, August 1993.

EVALUATING CALIBRATION MODEL RELIABILITY

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Abstract

Initial calibration is the process of delineating the relationship between the amount of an analyte introduced into an instrument and the instrument's response using standards of known concentrations. This relationship may be expressed as a simple ratio or may require the generation of a linear or non-linear calibration model (known as the "calibration curve"). Typically, an average response ratio (*i.e.*, the response factor) will be used for sample quantitation when the calibration variance criterion stated in the method is met. When the variance criterion to use the average response factor is not met, laboratories often default to a linear or non-linear calibration curve. An evaluation of gas chromatographic data generated using internal and external standard calibration techniques has revealed that linear and non-linear calibration curves are subject to poor quantitation at the extreme ends of the calibration range, even when method acceptance criteria have been met.

Several examples will be presented identifying instances when very high or very low recoveries were observed and the calibration standard data were re-fit to the calibration model. This issue directly impacts the reporting limit (RL) for the analyte since the RL is established by the low-level calibration standard. Poor quantitation of these low-level standards requires the RL to be raised to the next-lowest level standard with an acceptable recovery. Inability to meet RLs may have significant political and/or environmental implications in cases where the RL represents a regulatory or action level. Proposed usability criteria for the evaluation of linear and non-linear calibration curves will be presented.

Introduction

"Initial calibration" refers to the process involved in describing the relationship between an instrument's response to the amount of an analyte. The mathematical function describing the relationship is known as the calibration model. Calibration models may be expressed as a simple ratio, a linear curve or a nonlinear curve depending on the target analyte(s) and the behavior of the detector.

Calibration models are established based on the analyses of several standards of varying target analyte concentration. Analytes may be calibrated using external standard calibration or internal standard calibration. External standard calibration involves the comparison of an instrument response to the responses of target analytes in the calibration standards. The calibration factor, calculated as the ratio of instrument response to analyte amount, is determined for each analyte and used for sample quantitation. Internal standard calibration utilizes calibration standards of varying analyte concentrations containing a constant amount of one or more internal standard

compounds. The response of each target analyte is compared to the response of the appropriate internal standard compound to generate relative response factors (RRFs). Sample quantitation is based on the RRF from the initial calibration and the response of the target compound and internal standard in the sample.

For the gas chromatographic (GC) analyses examined in this paper, calibration models were simple ratios and linear curves. Linear and nonlinear calibration curves are generated by plotting the least-squares regression of the analyte amount (or amount ratio) against the instrument response (or response ratio). The correlation coefficient (r) or coefficient of determination (r^2) is calculated for linear or nonlinear calibration models to provide a measure of how well the equation represents the calibration data.

Analytical Method Requirements

The analytical data examined herein were generated according to "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition" (SW-846) 8000 Series methods. SW-846 requires the analyses of at least five initial calibration standards at varying analyte concentrations. Quadratic and third-order calibration models require the analyses of additional calibration standards due to statistical considerations. The average of the calibration factor from the initial calibration may be used for sample quantitation when the relative standard deviation (RSD) between the calibration factors is $\leq$ 20% for external standard methods and $\leq$ 15% for internal standard methods. When the variance criterion is not met, a linear or nonlinear calibration curve must be generated. Calibration curves must have r or r^2 values greater than 0.99 to be acceptable. SW-846 Method 8000C suggests the recalculation of the calibrations' standards for all linear and non-linear calibration curves. SW-846 Method 8000C suggests the use of 80-120% recovery for acceptance.

The PCB analytical data examined herein were generated according to a project-specific Standard Operating Procedure (SOP) for the Analysis of PCBs based on SW-846 Method 8082, which utilizes external standard calibration. The project-specific SOP for SW-846 Method 8082 requires that a linear calibration curve be prepared regardless of the RSD and sample quantitation performed using the linear calibration curve. To be acceptable, the RSD must be $\leq$ 20% and the linear curve must have an r or r^2 value greater than or equal to 0.99.

The volatile and semivolatile organic analysis data examined for this paper were generated using SW-846 Method 8260B and 8270C, respectively. These methods utilize an internal standard calibration technique. Unlike the PCB compound data, the calibration models for volatile or semivolatile analysis data examined were required to meet either the RSD or r^2 requirements, not both.

Compound Data Analysis

The raw data for the initial calibrations from several volatile organic, semivolatile organic and PCB compound analyses were collected and were processed using the Microsoft® Excel program. The laboratory-generated response factors and calibration curve equations were reproduced, the calibration standard data were re-fit to the calibration

model and the recovery of each standard was determined. The resulting data were then examined to identify instances of poor quantitation. Recovery limits of 70-130% were employed for the purposes of this paper; however, it should be noted that SW-846 Method 8000C recommends more stringent recovery limits of 80-120% when examining a calibration curve for acceptability.

Several examples have been identified that demonstrate that volatile, semivolatile and Aroclor calibration curves may not provide appropriate quantitation of low-level standards despite their ability to meet the requirements cited above. The phenomenon is not limited to a single laboratory or a single method. The following five examples represent volatile, semivolatile and PCB data originated at different laboratories and represent separate initial calibration sequences performed for several different instruments. In general, greater deviation from the actual standard amount was observed for volatile and semivolatile data than for PCB compound analysis data.

Example 1: Aroclor-1221

Aroclor-1221 was initially calibrated at five different standard concentrations, as required by the project-specific SOP for SW-846 Method 8082. The average response factor was calculated to be 130 mL/ng, with 9.3% RSD.

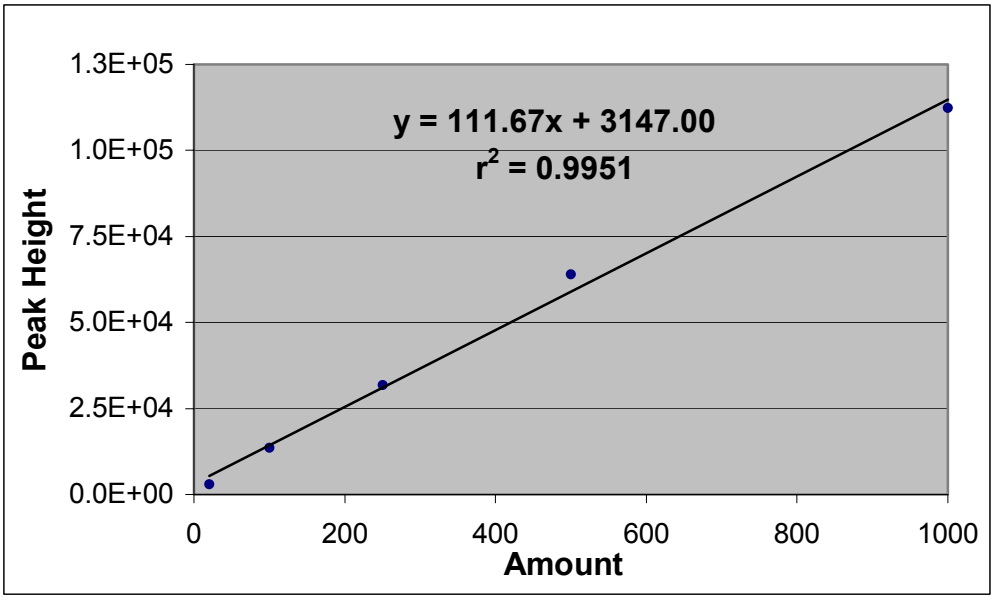

Figure 1. Linear Initial Calibration Curve for Aroclor-1221

Table 1. Aroclor-1221 Calibration Standard Re-Fit Data

Standard Amount	Calculated Amount (Linear)	% Recovery	Calculated Amount (CF)	% Recovery
20	**-2.221**	**-11.1%**	22.35	111.7%
100	93.765	93.8%	104.98	105.0%
250	256.859	102.7%	245.38	98.2%
500	544.486	108.9%	492.98	98.6%
1000	977.110	97.7%	865.40	86.5%

The initial calibration acceptance criteria have been met for Aroclor-1221; however, a negative recovery was observed for the 20-ppb initial calibration standard. Although the calculated concentrations for all standards were within recovery limits when the average CF was utilized for quantitation, the average CF was not used for sample quantitation due to the requirements of the project-specific SOP for SW-846 Method 8082.

Example 2: Aroclor-1254

Aroclor-1254 was calibrated using the five standards specified in the project-specific SOP for SW-846 Method 8082 and an additional 2000-ppb standard. The average response factor was calculated to be 105471 mL/ng, with 8.9% RSD.

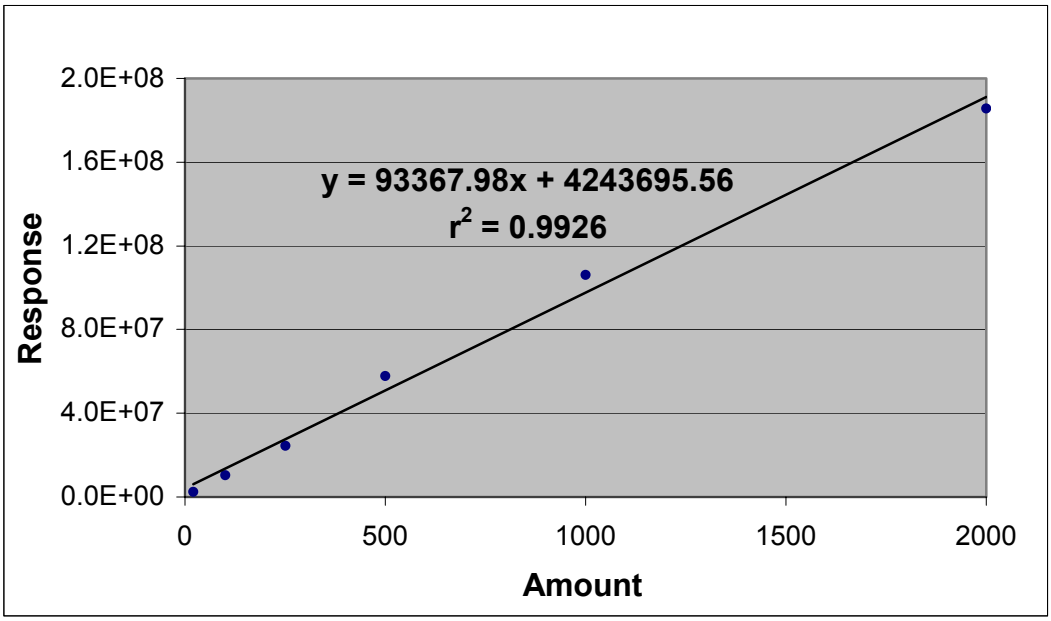

Figure 2. Linear Initial Calibration Curve for Aroclor-1254

Table 2. Aroclor-1254 Calibration Standard Re-Fit Data

Standard Amount	Calculated Amount (Linear)	% Recovery	Calculated Amount (CF)	% Recovery
20	**-20.534**	**-102.7%**	22.058	110.3%
100	**65.558**	**65.6%**	98.270	98.3%
250	217.322	86.9%	232.619	93.0%
500	575.162	115.0%	549.398	109.9%
1000	1090.142	109.0%	1005.283	100.5%
2000	1942.351	97.1%	1759.700	88.0%

As in example 1, the acceptability criteria for the initial calibration have been met. However, as is evident on Table 2, poor quantitation was demonstrated for both the 20-ppb and the 100-ppb Aroclor-1254 initial calibration standards. Although, the standard concentrations for all standards were within recovery limits when the average CF was utilized for quantitation, the average CF was not used for sample quantitation due to the requirements of the project-specific SOP for SW-846 Method 8082.

Example 3: *cis*-1,2-Dichloroethene

The initial calibration of *cis*-1,2-dichloroethene was performed according to SW-846 Method 8260B and used eight calibration standards with concentrations ranging from 0.4 ppb to 200 ppb. The RRF was calculated to be 0.227, with 15.5% RSD; consequently, a linear calibration model was generated.

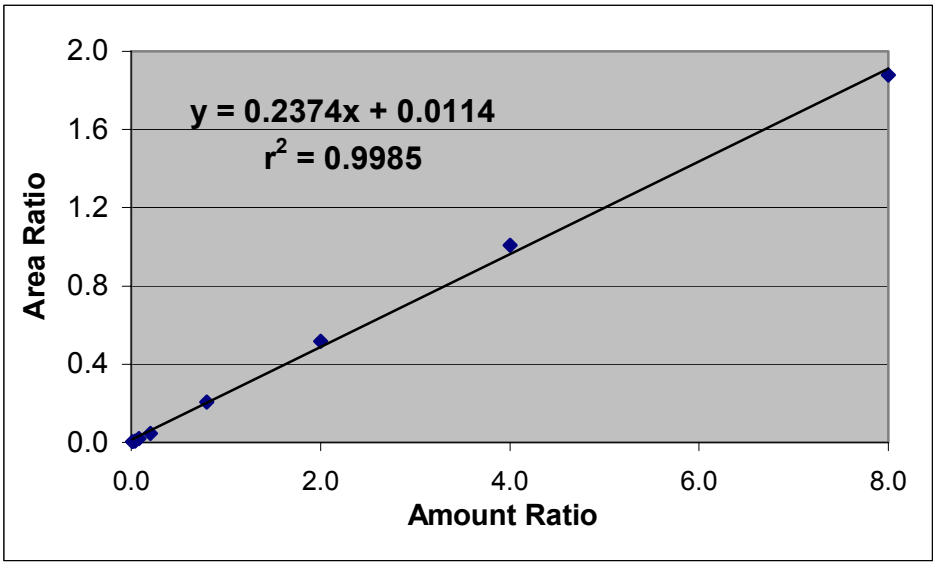

Figure 3. Initial Calibration Curve for *cis*-1,2-Dichloroethene

Table 3. *cis*-1,2-Dichloroethene Calibration Standard Re-fit Data

Amount	Calculated Amount (Linear)	%Recovery	Calculated Amount (RRF)	%Recovery
0.4	**-0.942**	**-235.6%**	**0.2702**	**67.5%**
1	**-0.345**	**-34.5%**	0.8955	89.6%
2	**0.719**	**36.0%**	2.010	100.5%
5	3.581	71.6%	5.005	100.1%
20	20.513	102.6%	22.73	113.7%
50	53.278	106.6%	57.03	114.1%
100	104.819	104.8%	111.0	111.0%
200	196.777	98.4%	207.2	103.6%

The linear calibration model for *cis*-1,2-dichloroethene is compliant with the requirements in the analytical method. Very poor recovery was observed for the three lowest calibration standards when the calibration data were re-fit to the calibration model. The use of the average RRF provided better quantitation at the lower end of the calibration curve, but a low recovery was still observed for the 0.4-ppb standard.

Example 4: *cis*-1,3-Dichloropropene

The compound *cis*-1,3-dichloropropene was analyzed in accordance with SW-846 Method 8260B. The average RRF for *cis*-1,3-dichloropropene was calculated to be 0.626, with 18.2% RSD, so a linear calibration model was created.

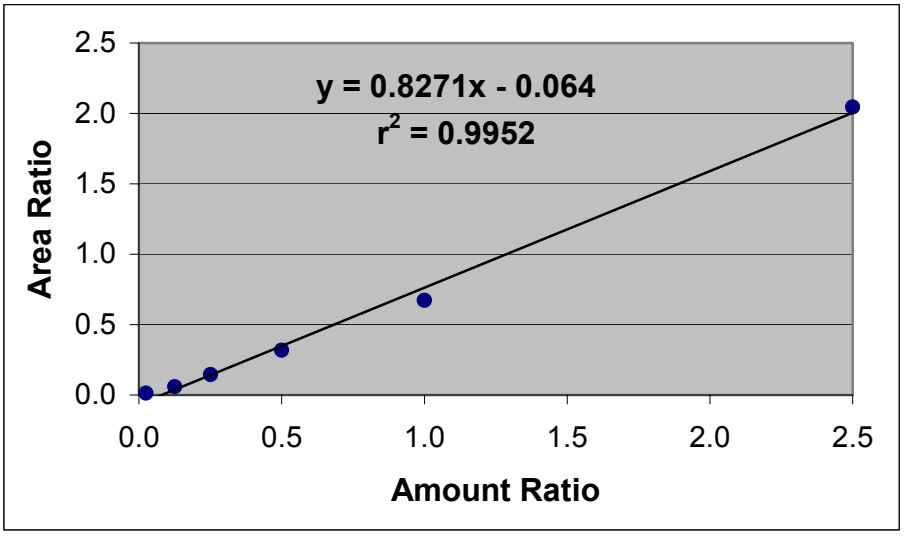

Figure 4. Linear Initial Calibration Curve for *cis*-1,3-Dichloropropene

Table 4. *cis*-1,3-Dichloropropene Calibration Standard Re-fit Data

Amount	Calculated Amount (Linear)	%Recovery	Calculated Amount (RRF)	%Recovery
1	**3.7785**	**378%**	0.9040	90%
5	6.0157	120%	3.8580	77%
10	10.1534	102%	9.3215	93%
20	18.3923	92%	20.2004	101%
40	35.7209	89%	43.0812	108%
100	101.9393	102%	**130.5169**	**131%**

Unlike the previous examples, a high bias was observed for the low-level *cis*-1,3-dichloropropene calibration standard. When the initial calibration data were quantitated using the average RRF, a high bias was observed for the upper-level calibration standard; however, the bias identified using the average RRF was considerably less than the bias identified for the calibration curve.

Example 5: Acenaphthene

Acenaphthene was analyzed in accordance with SW-846 Method 8270C. The average RRF for acenaphthene was calculated to be 1.143 with 9.6% RSD. The project samples associated with this calibration were quantitated based on the average RRF because the RSD criteria were met. For the purpose of comparison, a linear calibration model was generated for acenaphthene.

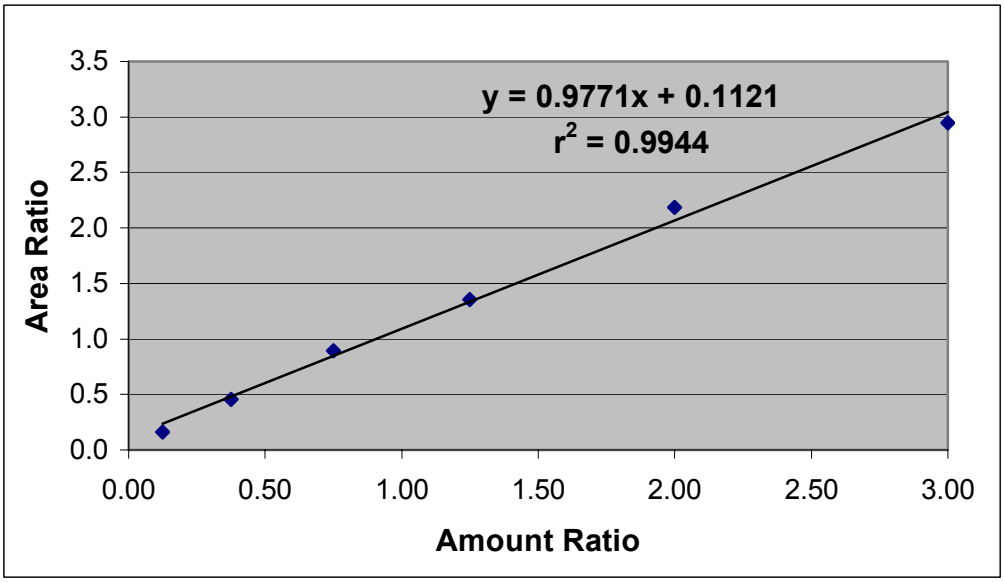

Figure 5. Linear Calibration Curve for Acenaphthene

Table 5. Acenaphthene Initial Calibration Standard Re-fit Data

Amount	Calculated Amount (Linear)	%Recovery	Calculated Amount (RRF)	%Recovery
5	**1.9903**	**40%**	5.6244	112%
15	14.1485	94%	16.0208	107%
30	31.9444	106%	31.2380	104%
50	50.9311	102%	47.4735	95%
80	84.8837	106%	76.5063	96%
120	116.1020	97%	103.2010	86%

The linear calibration model for acenaphthene is compliant with the requirements in the analytical method. A low recovery was observed for the 5-ppb initial calibration standard with the linear calibration model. Example 5 illustrates that calibration models with relatively stable instruments (low RSDs) can be subject to poor low-level recovery.

Conclusions

As the examples presented have demonstrated, unless an analyst specifically evaluates a calibration model for acceptability, poor quantitation at the extreme ends of the calibration range will likely go unnoticed. This is due, in part, to the fact that calibration verification standards and other quality control samples usually have concentrations near the midpoint of the calibration range, where a bias is least likely to be exhibited. When the variance (*e.g.*, %RSD) criterion is not met for an analyte, laboratories often default to a linear or nonlinear calibration model and based on the assumption that accurate quantitation will be provided. As the examples in this presentation have shown, quantitation based on the average response factor or calibration factor may better represent actual sample concentrations even when the RSD is outside of method limits.

The impact of this anomaly is most significant when the low-level standard concentration cannot be accurately reproduced based on the calibration data used for sample quantitation, the method quantitation limit (MQL) is effectively raised to the level of the next-higher calibration standard that meets the recovery acceptance limit. Negative biases such as those identified in this presentation may lead to false negative results for compounds in project samples. Additionally, MQLs often represent a regulatory or action level; the inability to detect target species at these levels can have significant political and/or environmental ramifications.

In order to detect bias in a calibration model, it is imperative that analysts review the calibration curves. By simply recalculating calibration standard amounts using the calibration model generated, potential weaknesses can be readily identified and an alternate calibration model can be selected or the instrument can be recalibrated.

ANALYSIS OF GASOLINE OXYGENATES IN DRINKING WATER AND WASTEWATER USING MODIFIED EPA METHOD 8260B

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Contamination of groundwater from leaking underground gasoline storage tanks has been a major health concern in various communities in the State of Maryland. With the exception of MTBE incorporated into Method 524.2, no single method applicable for the analysis of the gasoline oxygenates as a group has been written by the EPA with the capability to provide positive identification and low sensitivity. In an effort to monitor and evaluate possible gasoline contaminated water, the Maryland Environmental Public Health Laboratory has modified and validated EPA Method 8260B "*Volatile Compounds by Gas Chromatography/Mass Spectrometry*" for the routine testing of six target gasoline oxygenates.

Analyte	Acronym	CAS #	Formula	Category
• Acetone	----	67-64-1	C_3H_6O	By-product
• Diisopropyl ether	DIPE	108-20-3	$C_6H_{14}O$	Additive
• Ethyl *tertiary* butyl ether	ETBE	637-92-3	$C_6H_{14}O$	Additive
• Methyl *tertiary* butyl ether	MTBE	1634-04-4	$C_5H_{12}O$	Additive
• *Tertiary* amyl methyl ether	TAME	994-05-8	$C_6H_{14}O$	Additive
• *Tertiary* butyl alcohol	TBA	75-65-0	$C_4H_{10}O$	By-product

In this method, the gasoline oxygenates and/or their biodegradation products are extracted (purged) from the sample by bubbling an inert gas (helium) through a measured volume of the sample contained in an unopened glass vial with a Teflon septum. Purged target analytes are trapped on a sorbent in a tube (VOCARB 4000) containing multiple beds of hydrophobic adsorbents in order to capture a broad range of polar and non-polar and high and low molecular weight compounds. When purging is complete, the sorbent tube is heated and back-flushed with helium to desorb the trapped components onto a capillary column (Agilent DB-VRX fused silica capillary column 60 m x 0.25 mm x 1.4 μL film thickness) in a gas chromatograph with a split/splitless injection port operating in the splitless mode. The column is temperature programmed as follows to separate the target analytes that are subsequently identified and quantified by the mass spectrometer:

- Initial @ 45 ˚C (*hold for 10 min*)
- Ramp 1 @ 12 ˚/min to 190 ˚C (*hold for 2 min*)
- Ramp 2 @ 6 ˚/min to 225 ˚C (*hold for 1 min*)

The column is interfaced to a mass spectrometer operating in the selected ion monitoring mode. The mass spectrometer used is a Finnigan/ThermoQuest Trace 2000 MS capable of electron ionization at a nominal voltage of 70 eV.

Samples are collected in 40 mL VOA glass vials and filled to overflowing. No air bubbles should pass through the sample as the vial is filled, or be trapped in the sample when the vial is sealed. Adjust the pH of each sample to < 2 by adding one drop of HCl (1+1) to each vial as a preservative. Chill vials to 4 ˚C. Place each vial in the Tekmar Precept II Robotic Arm Autosampler to be purged by the P&T system which automatically spikes each vial with 50 ppb internal standard (1,4-Difluorbenzene) and 50 ppb surrogate (pentafluorobenzene). Analyze samples in batches to include an MS tune (4-bromofluorobenzene–25 ng), reagent blanks, 6-point multi-level calibration standards (10, 20, 40, 60, 80 and 100 ppb), an ERA QC, unknown samples and a low and high QC.

The mass spectrometer is set to select specific ions to enable identification and quantification of target compounds. The identification of the eluting compounds can be determined by comparing the measured mass spectra of the target compounds to reference spectra in a database. The reference library used with this system is the NIST/EPA/NIH Mass Spectral Library. Peaks are automatically integrated using the Xcalibur software (version 1.0) provided with the GC/MS system. Peak area and other pertinent information are exported into a Microsoft Excel spreadsheet for reporting and storage. All statistical analyses are performed using an Excel software. Manual calculations can be performed as stated below.

The concentration of each identified target analyte is calculated by first determining the response factor for that analyte which is depicted by the following equation.

$$\text{Response Factor (RF)} = \frac{(A_S)\,(C_{IS})}{(A_{IS})\,(C_S)}$$

Where:

A_S = area of the quantitation ion of the analyte
A_{IS} = area of the quantitation ion of the internal standard
C_{IS} = Concentration of the internal standard
C_S = Concentration of the calibration standard

Subsequently, the concentrations of the unknowns are calculated using the following equation:

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_S)\,(C_{IS})}{(A_{IS})\,(RF)}$$

Where:

A_S = area of quantitation ion of the analyte to be measured
A_{IS} = area of the quantitation ion of the internal standard

C_{IS} = concentration of the internal standard
RF = average response factor from previous calculation

A method detection limit study was performed for each of the six target analytes and resulted in a range from 2.69 to 3.28 ppb. A linear dynamic range (1-200 ppb) using a multi-level calibration (9 points) showed good linearity for the six analytes (r^2 = 0.994-0.999). Mean recoveries for the low and high QCs in drinking water was 91.9-99.5 and 97.3-106.3 respectively. Mean recoveries for the low and high QCs in wastewater was 91.0-104.3 and 99.5-109.3 respectively. All of the relative standard deviations for the six oxygenates was < 20%. The reported values from the performance evaluation study were within the acceptance limits. The reporting level for the each of the six target oxygenates in water using this method is 10 ppb.

This method utilizes existing instrument configuration and is suitable for the analyses of both drinking water and wastewater samples suspected of gasoline contamination.

PERFORMANCE RESULTS FROM A NEW PURGE-AND-TRAP SAMPLE CONCENTRATOR: ECLIPSING OLD-STYLE TECHNOLOGY

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Introduction

OI Analytical introduced the new Model 4660 Eclipse Purge-and-Trap Sample Concentrator (Figure 1) at Pittcon 2003. Following the conference, the Eclipse was installed at Lancaster Laboratories in Lancaster, PA. The instrument was used in a production capacity analyzing client samples daily by USEPA Method 8260. This application note presents results from the first three months of continuous operation, which are representative of the exceptional data that can be expected from this instrument.

Figure 1. OI Analytical Model 4660 Eclipse Purge-and-Trap Sample Concentrator

Experimental

The Eclipse Sample Concentrator was installed in the spring of 2003 in the VOC laboratory at Lancaster Laboratories in Lancaster, PA. In addition to the Eclipse, the system configuration included an OI Analytical Model 4552 Water/Soil Autosampler, an Agilent® 6890 Gas Chromatograph (GC) and an Agilent 5973 Mass Selective Detector (MSD or MS). The Eclipse replaced an existing Model 4560 Sample Concentrator and was immediately put into service running samples by USEPA Method 8260. Although the Foam Buster™ option was installed on the Eclipse, it was not activated because only nonfoaming samples were run during the period described here.

Table 1 lists all instrument operating conditions for the system configuration. Figure 2 shows a chromatogram from one of the calibration standards with inserts illustrating chromatography of some of the oxygenate compounds.

Table 1. Operating conditions for the Eclipse and other system instrumentation. All data presented in this application note were acquired using the OI Analytical Eclipse Sample Concentrator and the Model 4552 Water/Soil Autosampler in water mode.

Parameter	Setting
Purge-and-Trap	**Eclipse Sample Concentrator**
Trap	#10 (Tenax®, silica gel, carbon molecular sieve)
Purge	11 min with trap at 20°C (ambient)
Desorb	1 min with trap at 190°C
Bake	6 min with trap at 210°C
Water management fitting	100°C at purge 0°C at desorb 240°C at bake
Sparge mount temperature	40°C
Sample temperature	40°C
Foam Buster	Installed but not used (not needed for nonfoaming samples)
Dry purge	Not necessary
Desorb preheat	Not necessary
Autosampler	**OI Analytical Model 4552Water/Soil Autosampler**
Mode	Water
Sample size	5 mL (no dilutions)
Rinses	2 x 5 mL each
Stirring	No
Syringe flushes	3
Purge time	11 min
Desorb time	1 min
GC/MS	**Agilent 6890 Gas Chromatograph** **Agilent 5973 Mass Selective Detector**
Column	Agilent DB-624, 30 m x 0.25 mm I.D. x 1.4-µm film
Carrier gas	Helium, 0.8 mL/min constant flow
Inlet temperature	240°C
Split ratio	35:1
Oven program	45°C for 4.5 min 12°C/min to 100°C, hold 0 min 25°C/min to 240°C, hold 1.3 min
Solvent delay	1.5 min
MS acquisition mode	Scan, 35–300 amu
MS quad temperature	150°C
MS source temperature	230°C
Total Desorb-to-Desorb Cycle Time	**23–24 min**

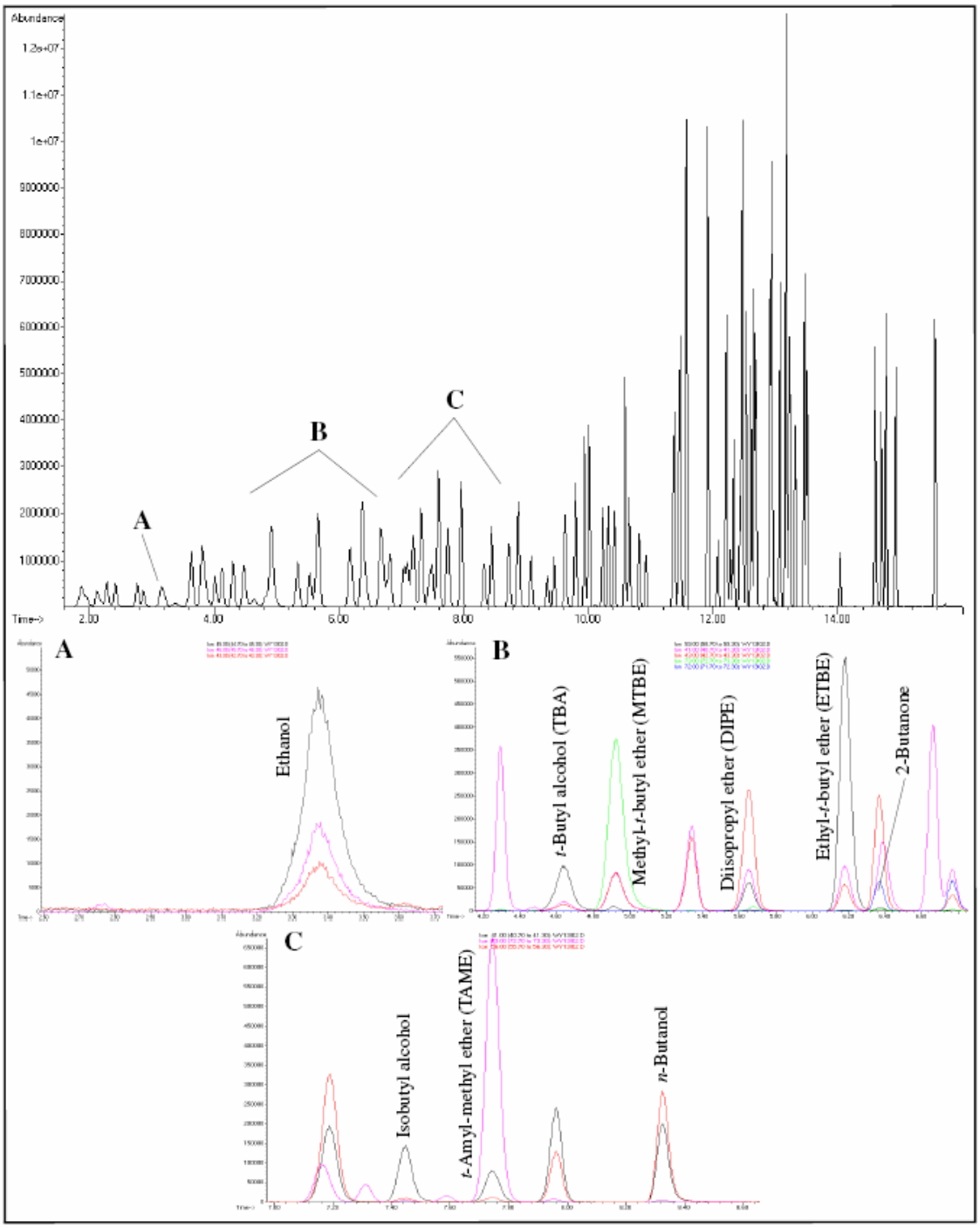

Figure 2. Chromatogram from a calibration standard run on the Eclipse. The inserts show the chromatography of some of the more difficult oxygenates. See Table 1 for operational details.

Results and Discussion

The tables and figures on the following pages show representative data that were acquired during the first three months of continuous operation. There was no instrument

downtime during the three-month period represented here and only routine instrument maintenance was necessary.

Table 2 lists the initial calibration results from the Eclipse, which were run immediately following installation. The calibration mixture was composed of 96 target analytes, including many of the alcohols, ketones and ethers commonly referred to as oxygenates. The calibration also included four internal standards and four surrogate standards; each of the four surrogate standard response factors (RFs) were calculated a second time using alternate quantitation ions. Ethanol and *t*-butyl alcohol (TBA) were quantified using TBA-d_{10} as the Internal Standard. All but one compound (2-propanol) had single-digit %RSDs across the calibration range and all met method calibration criteria for both USEPA Methods 8260 and 524.2 Rev. 4. All calibration check compounds (CCC) and system performance check compounds (SPCC) met the additional quality control (QC) criteria specified in Method 8260. The average %RSD over all compounds was 3%. The calibration data shown here remained valid beyond the initial three-month period and the instrument did not require recalibration during that time.

Table 2. Initial calibration data for Method 8260 analyte list acquired with the OI Analytical Eclipse P&T Sample Concentrator. All QC criteria were met for USEPA VOC methods and the calibration was used continuously for over three months.

Compound Name	Initial Calibration			
	Avg. RRF	%RSD	Calibration Method	Qualifier
Dichlorodifluoromethane	0.368	3	RRF	
Chloromethane	0.382	5	RRF	#
Vinyl chloride	0.343	4	RRF	*
Bromomethane	0.236	4	RRF	
Chloroethane	0.199	4	RRF	
Trichlorofluoromethane	0.398	4	RRF	
Ethanol	0.132	6	RRF	
Acrolein	0.076	2	RRF	
1,1-Dichloroethene	0.226	4	RRF	*
Freon® 13	0.234	2	RRF	
Acetone	0.034	6	RRF	
Methyl iodide	0.444	3	RRF	
2-Propanol	0.031	19	1st Degree	
Carbon disulfide	0.737	3	RRF	
Allyl chloride	0.456	3	RRF	
Methylene chloride	0.266	6	RRF	
t-Butyl alcohol	1.312	4	RRF	
Acrylonitrile	0.138	3	RRF	
trans-1,2-Dichloroethene	0.269	3	RRF	
Methyl-*t*-butyl ether	0.861	3	RRF	
n-Hexane	0.364	5	RRF	
1,2-Dichloroethene (total)	0.284	3	RRF	
1,1-Dichloroethane	0.461	4	RRF	#
Diisopropyl ether	0.924	2	RRF	
2-Chloro-1,3-butadiene	0.381	2	RRF	
Ethyl-*t*-butyl ether	0.897	2	RRF	
cis-1,2-Dichloroethene	0.299	3	RRF	
2-Butanone	0.045	3	RRF	
2,2-Dichloropropane	0.411	3	RRF	
Propionitrile	0.051	2	RRF	
Methacrylonitrile	0.138	2	RRF	
Bromochloromethane	0.167	2	RRF	
Tetrahydrofuran	0.043	3	RRF	
Chloroform	0.461	3	RRF	*
1,1,1-Trichloroethane	0.422	3	RRF	
Cyclohexane	0.447	3	RRF	
1,1-Dichloropropene	0.349	3	RRF	
Carbon tetrachloride	0.381	2	RRF	
Isobutyl alcohol	0.015	4	RRF	
Benzene	1.073	2	RRF	
1,2-Dichloroethane	0.384	3	RRF	
1,2-Dichloroethane (m/z 98)	0.035	4	RRF	

Table 2. (Continued)

Compound Name	Initial Calibration			
	Avg. RRF	%RSD	Calibration Method	Qualifier
t-Amyl methyl ether	0.853	1	RRF	
n-Butanol	0.013	7	RRF	
Trichloroethene	0.295	2	RRF	
1,2-Dichloropropane	0.278	2	RRF	*
Methyl methacrylate	0.253	2	RRF	
Dibromomethane	0.184	1	RRF	
1,4-Dioxane	0.004	5	RRF	
Bromodichloromethane	0.348	1	RRF	
2-Nitropropane	0.103	2	RRF	
2-Chloroethyl vinyl ether	0.213	2	RRF	
cis-1,3-Dichloropropene	0.472	1	RRF	
4-Methyl-2-pentanone	0.417	4	RRF	
Toluene	0.920	1	RRF	*
trans-1,3-Dichloropropene	0.565	1	RRF	
Ethyl methacrylate	0.522	4	RRF	
1,1,2-Trichloroethane	0.341	2	RRF	
Tetrachloroethene	0.438	3	RRF	
1,3-Dichloropropane	0.571	2	RRF	
2-Hexanone	0.382	5	RRF	
Dibromochloromethane	0.419	3	RRF	
1,2-Dibromoethane	0.381	2	RRF	
Chlorobenzene	1.089	2	RRF	#
1,1,1,2-Tetrachloroethane	0.400	2	RRF	
Ethylbenzene	1.780	3	RRF	*
m/p-Xylene	0.735	2	RRF	
Xylene (Total)	0.730	2	RRF	
o-Xylene	0.719	1	RRF	
Styrene	1.187	3	RRF	
Bromoform	0.309	5	RRF	#
Isopropylbenzene	1.853	4	RRF	
Cyclohexanone	0.018	6	RRF	
1,1,2,2-Tetrachloroethane	0.882	3	RRF	#
trans-1,4-Dichloro-2-butene	0.296	4	RRF	
Bromobenzene	0.861	2	RRF	
1,2,3-Trichloropropane	0.285	2	RRF	
n-Propylbenzene	3.659	7	RRF	
2-Chlorotoluene	0.830	3	RRF	
1,3,5-Trimethylbenzene	2.744	4	RRF	
4-Chlorotoluene	0.863	2	RRF	
tert-Butylbenzene	0.680	3	RRF	
Pentachloroethane	0.494	3	RRF	
1,2,4-Trimethylbenzene	2.816	4	RRF	
sec-Butylbenzene	3.489	7	RRF	

Table 2. (Continued)

Compound Name	Initial Calibration			
	Avg. RRF	%RSD	Calibration Method	Qualifier
p-Isopropyltoluene	3.118	6	RRF	
1,3-Dichlorobenzene	1.671	3	RRF	
1,4-Dichlorobenzene	1.719	2	RRF	
n-Butylbenzene	2.730	6	RRF	
1,2-Dichlorobenzene	1.620	2	RRF	
1,2-Dibromo-3-chloropropane	0.203	2	RRF	
1,2,4-Trichlorobenzene	1.269	3	RRF	
Hexachlorobutadiene	0.556	7	RRF	
Naphthalene	3.711	7	RRF	
1,2,3-Trichlorobenzene	1.239	3	RRF	
2-Methylnaphthalene	2.584	5	RRF	
Surrogate Standards				
Dibromofluoromethane	0.278	3	RRF	
1,2-Dichloroethane-d_4	0.070	3	RRF	
Toluene-d_8	1.355	3	RRF	
4-Bromofluorobenzene	0.548	3	RRF	
Dibromofluoromethane (m/z 111)	0.285	3	RRF	
1,2-Dichloroethane-d_4 (m/z 104)	0.045	3	RRF	
Toluene-d_4 (m/z 100)	0.898	2	RRF	
4-Bromofluorobenzene (m/z 174)	0.473	2	RRF	
Average %RSD		3		

Internal Standards (IS) were *t*-butyl alcohol-d_{10}, fluorobenzene, chlorobenzene-d_5 and 1,4-dichlorobenzene-d_4.
Qualifier notes: # = Minimum RRF for SPCC = 0.10 (0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane; * = Maximum %RSD for CCC = 30%

Table 3 lists the results of the method detection limit (MDL) study and the initial demonstration of proficiency that were performed prior to running any client samples. The MDL study was run using seven replicate 5-mL aliquots of spiked blank water. Most compounds on the list were spiked at 0.5 µg/L (ppb). However, some of the polar, water-soluble compounds were spiked at 1, 5, 10 or 50 ppb, as noted in the table. As expected, the alcohols and ketones had the highest MDLs. The initial demonstration of proficiency included four replicate aliquots. Table 3 includes a summary of these results. One compound, 1,4-dioxane, had a standard deviation of 12.7 µg/L, which computes to 2.8%RSD and was the highest %RSD on the list. Each compound had different recovery and standard deviation QC criteria and all analytes fell easily within the required specifications.

Table 3. Method Detection Limit study (MDL) and Initial Demonstration of Proficiency results using the Eclipse Sample Concentrator. All QC criteria were met for USEPA VOC methods.

Compound Name	MDL Study (n = 7)		Initial Demonstration (n = 4)			
	Spike Amount (µg/L)	MDL (µg/L)	Spike Amount (µg/L)	Measured (µg/L)	Std. Dev. (µg/L)	In Spec?
Dichlorodifluoromethane	0.5	0.06	20	21.3	0.3	Yes
Chloromethane	0.5	0.07	20	20.7	0.2	Yes
Vinyl chloride	0.5	0.05	20	20.1	0.3	Yes
Bromomethane	0.5	0.14	20	20.2	0.2	Yes
Chloroethane	0.5	0.07	20	21.2	0.2	Yes
Trichlorofluoromethane	0.5	0.06	20	19.3	0.3	Yes
Ethanol	50	14.5	500	544.7	8.4	Yes
Acrolein	5.0	1.08	150	138.1	1.5	Yes
1,1-Dichloroethene	0.5	0.08	20	21.4	0.2	Yes
Freon 13	0.5	0.08	20	21.4	0.3	Yes
Acetone	1.0	0.82	150	135.1	1.4	Yes
Methyl iodide	0.5	0.05	20	21.1	0.3	Yes
2-Propanol	10	5.15	150	167.6	2.4	Yes
Carbon disulfide	0.5	0.05	20	22.5	0.3	Yes
Allyl chloride	0.5	0.09	20	19.5	0.3	Yes
Methylene chloride	0.5	0.08	20	20.4	0.2	Yes
t-Butyl alcohol	10	1.01	200	194.4	0.9	Yes
Acrylonitrile	0.5	0.36	100	92.4	0.3	Yes
trans-1,2-Dichloroethene	0.5	0.10	20	20.2	0.3	Yes
Methyl-*t*-butyl ether	0.5	0.05	20	19.8	0.1	Yes
n-Hexane	0.5	0.08	20	22.1	0.3	Yes
1,2-Dichloroethene (total)	1.0	0.17	40	40.1	0.5	Yes
1,1-Dichloroethane	0.5	0.09	20	20.3	0.2	Yes
Diisopropyl ether	0.5	0.23	20	20.0	0.2	Yes
2-Chloro-1,3-butadiene	0.5	0.11	20	21.3	0.2	Yes
Ethyl-*t*-butyl ether	0.5	0.07	20	19.5	0.2	Yes
cis-1,2-Dichloroethene	0.5	0.09	20	19.9	0.2	Yes
2-Butanone	1.0	0.62	150	128.9	0.5	Yes
2,2-Dichloropropane	0.5	0.21	20	19.7	0.2	Yes
Propionitrile	10	3.18	150	152.1	1.0	Yes
Methacrylonitrile	5.0	1.52	150	154.8	0.3	Yes
Bromochloromethane	0.5	0.39	20	20.1	0.2	Yes
Tetrahydrofuran	1.0	0.89	100	105.8	1.1	Yes
Chloroform	0.5	0.09	20	19.8	0.2	Yes
1,1,1-Trichloroethane	0.5	0.05	20	19.6	0.2	Yes
Cyclohexane	0.5	0.22	20	21.8	0.3	Yes
1,1-Dichloropropene	0.5	0.11	20	19.8	0.2	Yes
Carbon tetrachloride	0.5	0.09	20	19.7	0.2	Yes
Isobutyl alcohol	25	16.8	500	491.5	2.1	Yes
Benzene	0.5	0.16	20	20.0	0.2	Yes
1,2-Dichloroethane	0.5	0.06	20	19.6	0.1	Yes
1,2-Dichloroethane (m/z 98)	na	na	na	na	na	na

Table 3. (Continued)

Compound Name	MDL Study (n = 7)		Initial Demonstration (n = 4)			
	Spike Amount (µg/L)	MDL (µg/L)	Spike Amount (µg/L)	Measured (µg/L)	Std. Dev. (µg/L)	In Spec?
t-Amyl methyl ether	0.5	0.05	20	19.4	0.1	Yes
n-Butanol	50	22.3	1000	946.9	13.4	Yes
Trichloroethene	0.5	0.07	20	19.6	0.2	Yes
1,2-Dichloropropane	0.5	0.10	20	20.0	0.2	Yes
Methyl methacrylate	0.5	0.14	20	18.0	0.1	Yes
Dibromomethane	0.5	0.13	20	19.8	0.1	Yes
1,4-Dioxane	25	5.17	500	456.0	12.7	Yes
Bromodichloromethane	0.5	0.09	20	19.3	0.1	Yes
2-Nitropropane	1.0	1.48	20	18.4	0.1	Yes
2-Chloroethyl vinyl ether	0.5	0.13	20	19.6	0.1	Yes
cis-1,3-Dichloropropene	0.5	0.09	20	19.7	0.3	Yes
4-Methyl-2-pentanone	1.0	0.54	100	93.0	0.3	Yes
Toluene	0.5	0.08	20	19.4	0.2	Yes
trans-1,3-Dichloropropene	0.5	0.13	20	19.0	0.2	Yes
Ethyl methacrylate	0.5	0.12	20	20.0	0.1	Yes
1,1,2-Trichloroethane	0.5	0.10	20	19.3	0.1	Yes
Tetrachloroethene	0.5	0.07	20	19.5	0.3	Yes
1,3-Dichloropropane	0.5	0.12	20	19.4	0.1	Yes
2-Hexanone	1.0	0.63	100	88.0	0.1	Yes
Dibromochloromethane	0.5	0.09	20	18.9	0.1	Yes
1,2-Dibromoethane	0.5	0.09	20	19.2	0	Yes
Chlorobenzene	0.5	0.04	20	19.5	0.1	Yes
1,1,1,2-Tetrachloroethane	0.5	0.06	20	19.3	0.2	Yes
Ethylbenzene	0.5	0.07	20	19.4	0.2	Yes
m/p-Xylene	1.0	0.08	40	38.8	0.5	Yes
Xylene (Total)	0.5	0.07	60	58.0	0.6	Yes
o-Xylene	0.5	0.06	20	19.3	0.2	Yes
Styrene	0.5	0.08	20	19.0	0.1	Yes
Bromoform	0.5	0.11	20	18.7	0.1	Yes
Isopropylbenzene	0.5	0.05	20	19.4	0.1	Yes
Cyclohexanone	25	7.04	500	477.3	5.7	Yes
1,1,2,2-Tetrachloroethane	0.5	0.03	20	19.2	0.1	Yes
trans-1,4-Dichloro-2-butene	5.0	0.90	100	96.8	0.7	Yes
Bromobenzene	0.5	0.05	20	19.1	0.2	Yes
1,2,3-Trichloropropane	0.5	0.12	20	19.3	0.2	Yes
n-Propylbenzene	0.5	0.06	20	19.9	0.2	Yes
2-Chlorotoluene	0.5	0.03	20	19.3	0.2	Yes
1,3,5-Trimethylbenzene	0.5	0.04	20	19.4	0.2	Yes
4-Chlorotoluene	0.5	0.06	20	19.4	0.2	Yes
tert-Butylbenzene	0.5	0.07	20	19.3	0.2	Yes
Pentachloroethane	0.5	0.09	20	18.2	0.2	Yes
1,2,4-Trimethylbenzene	0.5	0.04	20	19.3	0.2	Yes
sec-Butylbenzene	0.5	0.04	20	19.9	0.2	Yes

Table 3. (Continued)

Compound Name	MDL Study (n = 7)		Initial Demonstration (n = 4)			
	Spike Amount (µg/L)	MDL (µg/L)	Spike Amount (µg/L)	Measured (µg/L)	Std. Dev. (µg/L)	In Spec?
p-Isopropyltoluene	0.5	0.05	20	19.5	0.2	Yes
1,3-Dichlorobenzene	0.5	0.03	20	19.1	0.1	Yes
1,4-Dichlorobenzene	0.5	0.05	20	19.3	0.1	Yes
n-Butylbenzene	0.5	0.04	20	19.5	0.2	Yes
1,2-Dichlorobenzene	0.5	0.06	20	19.2	0.2	Yes
1,2-Dibromo-3-chloropropane	0.5	0.52	20	18.7	0.2	Yes
1,2,4-Trichlorobenzene	0.5	0.09	20	18.9	0.1	Yes
Hexachlorobutadiene	0.5	0.07	20	18.3	0.3	Yes
Naphthalene	0.5	0.09	20	19.2	0.1	Yes
1,2,3-Trichlorobenzene	0.5	0.09	20	19.0	0.1	Yes
2-Methylnaphthalene	0.5	0.17	20	16.9	0.1	Yes

Once the initial calibration, MDL and initial demonstration of proficiency were completed, the instrument was put into service analyzing client samples by USEPA Method 8260. With the 24-minute desorb-to-desorb cycle time for the system (see Table 1), approximately 30 standards and samples could be run in a 12-hour tune period. Each 12-hour analytical sequence consisted of the following samples:

1. BFB tune check
2. Continuing Calibration Verification (CCV) standard
3. Method Blank
4. Laboratory Control Sample (LCS)
5. LCS Duplicate (LCSD) (optional, run if there is no MS/MSD in the sequence)
6. Samples
7. MS/MSD

The first five samples in each sequence are run to evaluate the system integrity and to verify that the equipment is performing properly and can meet all method QC criteria. During the second month of the three-month period, 14 analytical sequences were run on the Eclipse and each sequence included one CCV standard and one or more LCS. The following charts illustrate the exceptional performance of the CCV and LCS/LCSD on the Eclipse over this continuous representative one-month period.

The CCV standard is evaluated in several different ways. First, the response factors (RFs) for a group of six calibration check compounds (CCC) must fall within ±20% of the RFs from the initial calibration. Figure 3 shows the percent drift of the individual CCC RFs when compared to the initial calibration. The data represent all 14 distinct sequences run during a single month and the RFs easily met the ±20% criteria. In addition to the CCC criteria, the five system performance check compounds (SPCC) in the CCV must meet specific minimum RF criteria. The minimum RF criteria were easily met for each SPCC over the one-month period, as illustrated in Figure 4.

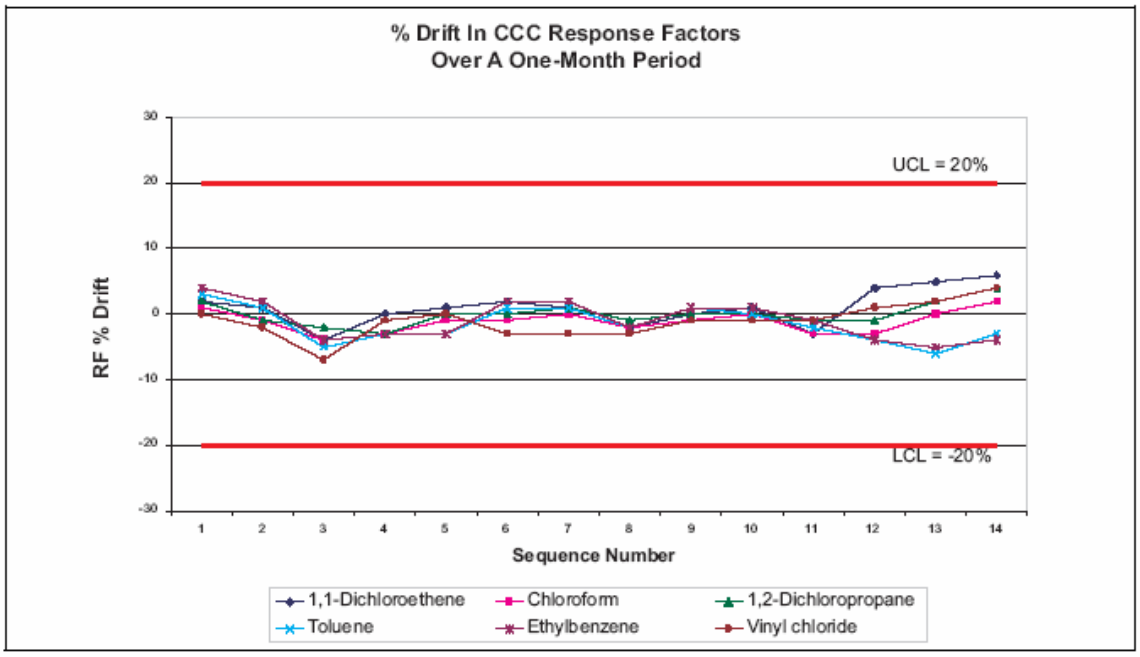

Figure 3. Percent drift in CCC response factors during the 14 sequences run in a representative one-month period. All RFs remained exceptionally stable and easily met the method QC acceptance criteria of ±20%.

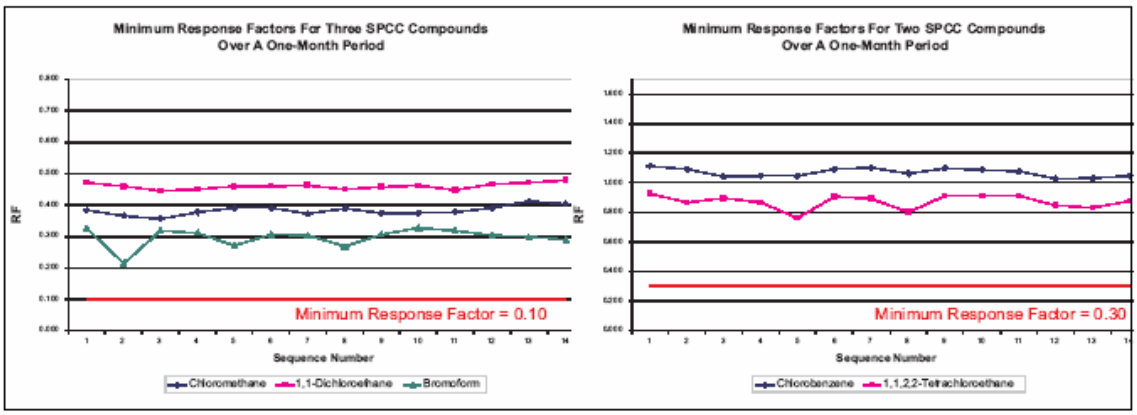

Figure 4. Minimum response factors for the five SPCC compounds in 14 sequences run during a representative one-month period. All QC acceptance criteria were met without difficulty and without requiring any re-analyses.

Finally, although Method 8260 only requires that RF criteria be met for the five SPCCs (Section 7.3.5.4) and the six CCCs (Section 7.3.6.3), many regulatory agencies call for additional QC criteria to be met on all target compounds in the standard mixture. As an example, Figure 5 illustrates the percent drift in RFs of the six gas compounds over the one-month period, compared to the initial calibration. Since Method 8260 does not specify QC criteria for these compounds (other than for vinyl chloride), examples of

typical upper and lower control limits are shown as ±30% and ±50%. USEPA Method 524.2 Rev. 4 specifies control limits of ±30%. The average percent drift for the six gases, selected oxygenates and BTEX over the one-month period are shown in Table 4. Average percent drift over all 96 compounds for the month was 1.2%.

Table 4. Average percent drift in RF over a one-month period for selected compounds including the six gases, oxygenates and BTEX. Percent drift is measured relative to the initial calibration RFs. The average percent drift for all 96 compounds over the one-month period was 1.2%.

Compound Name	Avg. % Drift in RF	Compound Name	Avg. % Drift in RF
Dichlorodifluoromethane	-4.4	Ethyl-*t*-butyl ether	-0.4
Chloromethane	0.2	2-Butanone	5.8
Vinyl chloride	-1.1	Isobutyl alcohol	10.0
Bromomethane	-2.6	Benzene	0.1
Chloroethane	-1.6	*t*-Amyl methyl ether	-0.6
Trichlorofluoromethane	-5.2	*n*-Butanol	13.9
Ethanol	0.4	4-Methyl-2-pentanone	-1.6
Acetone	12.4	Toluene	-1.5
2-Propanol	10.8	2-Hexanone	-0.9
t-Butyl alcohol	-4.2	Ethylbenzene	-1.0
Methyl-*t*-butyl ether	-1.4	*m/p*-Xylene	-1.0
Diisopropyl ether	1.4	*o*-Xylene	-1.5

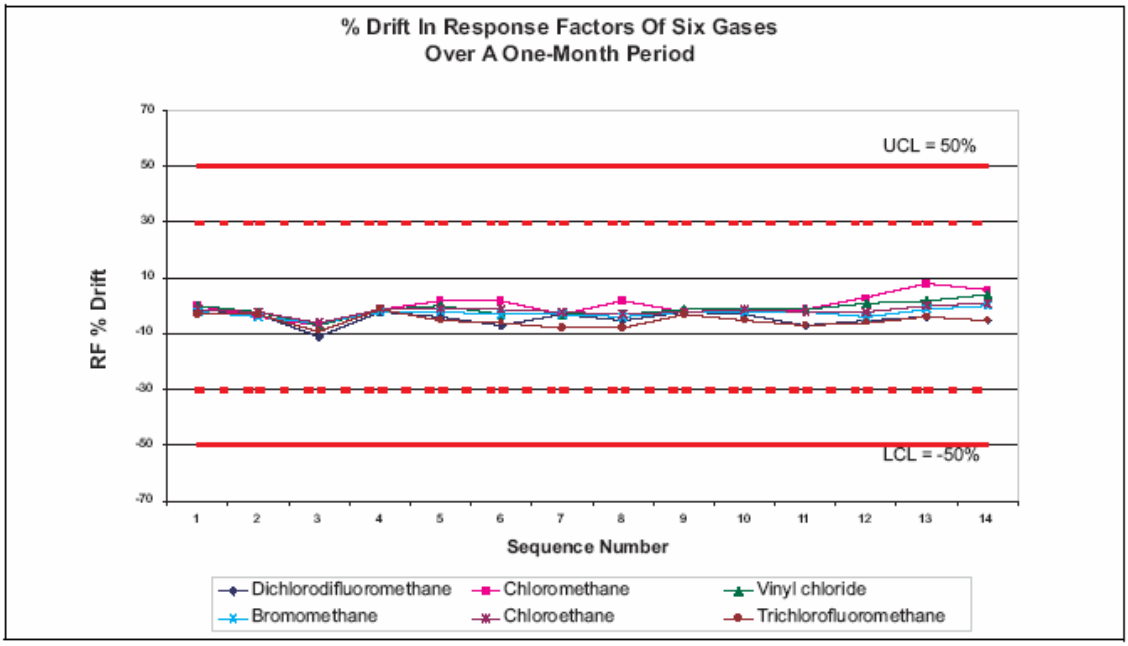

Figure 5. CCV chart illustrates percent drift in RFs of the six gases during 14 sequences run during the second month of a three-month period. Percent drift is measured relative to the initial calibration. The upper and lower control limits of ±30% and ±50% are typical QC criteria used by many laboratories and regulatory programs for Method 8260. USEPA Method 524.2 specifies limits of ±30%.

In addition to the CCV standard, each sequence includes at least one laboratory control sample (LCS) that is prepared as a blank spike using standards from an independent source. The percent recovery QC criteria for the LCS are different for each compound, making it difficult to show all of the data here. Figure 6 illustrates the percent recovery of 12 selected compounds in 14 sequences run during the second month of the three-month period. The compound list included six frequently requested oxygenates (ethanol, TBA, MTBE, DIPE, ETBE and TAME) plus BTEX and was chosen based on a project run on the instrument during the month. In general, the upper and lower recovery limits represent ±3 standard deviations from the mean value over a six-month data collection period and can vary significantly from compound to compound. The upper and lower control limits shown in Figure 6, 130% to 70%, are representative of the individual limits for 11 of the 12 compounds. One compound, ethanol, had control limits that were significantly broader than the others, at 43% to 159%, which were established for this laboratory based on six months of data from the Model 4560 Sample Concentrator. All 12 compounds included in the project easily met the percent recovery QC criteria on a daily basis and the traditionally difficult oxygenate compounds performed as well as the ordinary BTEX compounds.

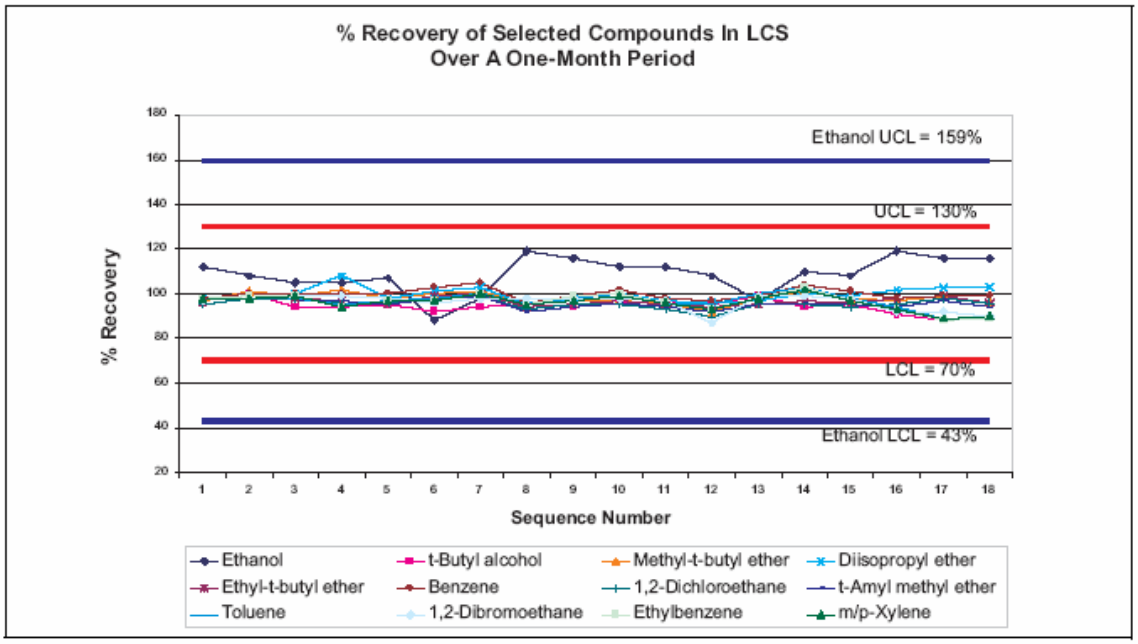

Figure 6. Percent recovery of 12 selected compounds in the LCS during a one-month period analyzed on the Eclipse Sample Concentrator. The list includes six oxygenate compounds as well as BTEX. All recoveries met the QC acceptance criteria without difficulty.

One additional way to monitor system performance is to track the internal standard response in each sample over a specific period of time, usually a 12-hour tune. Figure 7 shows three control charts used to monitor internal standard response in each sample over 14 different 12-hour tune periods or sequences. The total number of samples run in each sequence varied from 15 to 28. All internal standards met the method defined criteria of –50% to +100% effortlessly, as indicated on the charts.

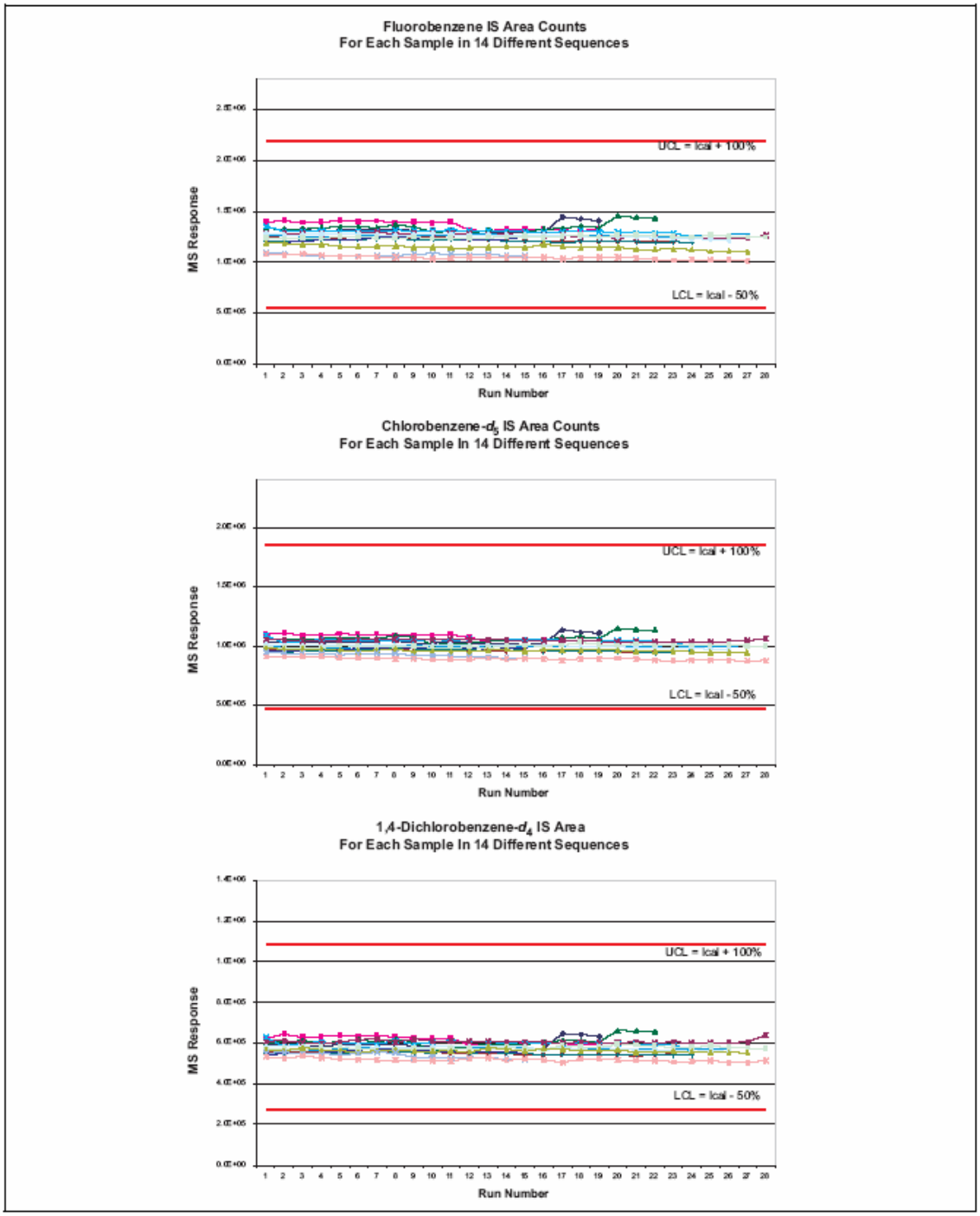

Figure 7. Charts illustrating internal standard area count stability for each sample in 14 sequences. All individual sequences were acquired during a representative one-month period using the same initial calibration. The number of samples in each sequence varied from 15 to 28 samples. All IS responses met the QC acceptance criteria outlined in USEPA Method 8260.

Conclusion

The data presented here are characteristic of the exceptional performance of the Eclipse Sample Concentrator at Lancaster Laboratories in Lancaster, PA. The instrument performed without problems over the initial three-month period and produced data that consistently passed all USEPA Method QC requirements.

Note: For Part I of this study and data from an additional laboratory, see Application Note 1934. For information on VOC cycle times and recommended P&T operating conditions see Application Notes 1932 and 1908i, respectively.

Acknowledgements

OI Analytical thanks Trent Sprenkle, Group Leader, GCMS Volatiles at Lancaster Laboratories in Lancaster, PA, for his support and enthusiasm during this project. Customers' feedback is an important and integral part of designing new instruments. We sincerely appreciate their participation.

ANALYSIS OF OXYGENATES USING A NEW PURGE-AND-TRAP SAMPLE CONCENTRATOR

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Introduction

Fuel oxygenates are oxygen-containing compounds such as ethers or alcohols, which are added to gasoline to boost octane rating and to make fuel burn more cleanly. The two most common oxygenate additives have been methyl-*tert*-butyl ether (MTBE) and *tert*-butanol (TBA). Fuel oxygenates are being found in increasing concentrations in groundwater and, in recent years, the U.S. Environmental Protection Agency's Leaking Underground Storage Tank (LUST) program has generated a great deal of oxygenate data. Unfortunately, the lack of a single validated performance-based method for determining fuel oxygenates in environmental matrices has raised concerns about the quality of the data already collected and how they should be interpreted, as well as questions about which method should be used going forward.

The USEPA recognizes SW-846 Method 8260 using gas chromatography and mass spectrometry (GC/MS) and Method 8015 using GC/flameionization detection (FID) as being the two most appropriate determinative methods for oxygenates, with Methods 5030 and 5035 (purge-and-trap (P&T) and closed system P&T) cited as the most appropriate sample preparation techniques for low-level detection. Both the MS and FID detectors are capable of detecting oxygenates at low concentrations, but only the MS is capable of positive compound identification based on the mass spectrum, making

Method 8260 the preferred method. Modifying the determinative GC/MS method to include analysis of fuel oxygenates is not necessary or desirable. Only the calibration and sample preparation steps need modifying and those should be altered as little as possible so that the oxygenates can be included in the already standardized analyses without significant changes.

Fuel oxygenate compounds are highly soluble in water, difficult to purge and can be reactive under certain conditions, making analysis by standard P&T methods challenging. One specific problem with interpreting existing data is that environmental samples have been historically preserved with acid to pH <2. If the acidic sample is then heated to ~80°C during purge, MTBE in the sample can undergo hydrolysis to TBA. This can result in an artificially low MTBE number and a high bias for TBA. To counteract this effect, the USEPA is considering a recommendation to preserve samples that will be analyzed for oxygenates to pH >11 with trisodium phosphate dodecahydrate (TSP). Purging the sample at a more moderate temperature of 40° to 45°C can also help minimize MTBE hydrolysis under acidic conditions.

This application note explores the P&T variables that can be modified to obtain optimum and reliable performance for fuel oxygenates without making fundamental or extreme changes to previously standardized P&T procedures.

Experimental

A series of experiments were designed to test the effects of three variables that could be easily modified without making any fundamental changes to the standard P&T method. The variables tested were sample size (5, 10 and 25 mL), sample temperature set point (ambient, 40°C, 60°C and 80°C) and trap type (Tenax®/silica gel/carbon molecular sieve and VOCARB®). All analyses were performed using the OI Analytical Model 4552 Water/Soil Autosampler and the Model 4660 Eclipse Sample Concentrator (Figure 1). Operating conditions for both instruments are listed in Table 1. The analyses were performed on an Agilent® 6890 GC and 5973 Inert MS using standard GC/MS operating conditions described previously (see OI Analytical Application Note 1937 for a full description of all operating parameters).

Figure 1. OI Analytical Model 4660 Eclipse Sample Concentrator

Table 1. Instrument operating conditions

Parameter	Setting
Autosampler	**Model 4552 Water/Soil Autosampler**
Sample type	Soil mode
Sample volume	3 mL (volume of clean water used to transfer standards to the vial)
Number of rinses	0 (sparge tube rinses not necessary with soil analysis mode)
Standard 1	Yes (internal standard addition)
Standard 2	No
Sample preheat stirring	Yes (magnetic stir bar added to each vial)
Stir	Yes
Syringe flushes	0
Preheat	Yes
Preheat temperature set point	Ambient, 40°, 60°, and 80°C
Actual maximum sample temperature	Ambient, 37°, 46°, and 62°C (see "Results and Discussion")
Preheat time	1 minute
Purge time	11 minutes
Desorb time	0.5 minute
Soil transfer line temperature	110°C
Sample concentrator	**Model 4660 Eclipse**
Trap	#10 (Tenax/silica gel/carbon molecular sieve) #11 (VOCARB)
Purge	11 minutes with trap at 20°C
Dry purge	Not necessary with the patented water management fitting
Desorb preheat	ON #10 trap to 180°C #11 trap to 230°C
Desorb	0.5 minute #10 trap at 190°C #11 trap at 240°C
Bake	5 minutes #10 trap at 210°C #11 trap at 250°C
Water management fitting	Factory default settings 110°C at purge, 0°C at desorb, 240°C at bake
Sparge mount temperature	40°C
Valve oven temperature	110°C
Transfer line temperature	110°C

A primary standard supplied by Restek® contained the five oxygenates commonly required for analysis by the State of California: *tert*-butanol (TBA), methyl-*tert*-butyl

ether (MTBE), isopropyl ether (DIPE), ethyl-*tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME). TBA was present in the mix at a concentration five times that of the four ethers. A large volume of secondary standard was prepared at 5 ppb (25 ppb TBA) and used for all of the sample size and sample temperature analyses. Duplicate aliquots of each sample size (5, 10 and 25 mL) were analyzed at each of the four temperature set points (ambient, 40°, 60° and 80°C), for a total of 24 analyses on each trap.

Once the optimum sample size and temperature set point were established, an estimated LOQ (limit of quantitation) determination was made for each trap. Standards were prepared at 5 ppb (25 ppb TBA), 1 ppb (5 ppb TBA) and 0.2 ppb (1 ppb TBA) and analyzed in triplicate using the established optimum size and temperature conditions. During the LOQ tests and the size and temperature analyses, the mass range was extended to include *m/z* 18 so the amount of water to the GC/MS system could also be monitored.

An eight-point calibration curve was run covering a range from 0.2 to 200 ppb (1–1,000 ppb TBA) and a statistical MDL study was performed by analyzing seven replicate aliquots of a 0.5 ppb standard (2.5 ppb TBA). Finally, tap water was spiked with 1-ppm unleaded gasoline and 100-ppb oxygenates and analyzed using the recommended conditions to demonstrate performance of the instrumentation on a real-world sample.

All experiments described here were designed to use the same GC and MS parameters previously optimized for detecting and quantifying all analytes in USEPA Method 8260. Other than the temporary change in mass range to include *m/z* 18, no changes were made to the GC or MS operating conditions.

Results and Discussion

Sample Size, Sample Temperature and Trap Selection

The results of the sample size and temperature analyses are shown in Figure 2 and Figure 3. Each bar in the charts represents the average response from duplicate analyses. The small number above the bar is the relative percent difference (RPD) between the two runs. All responses are reported relative to the response of a 5-mL aliquot analyzed at ambient temperature.

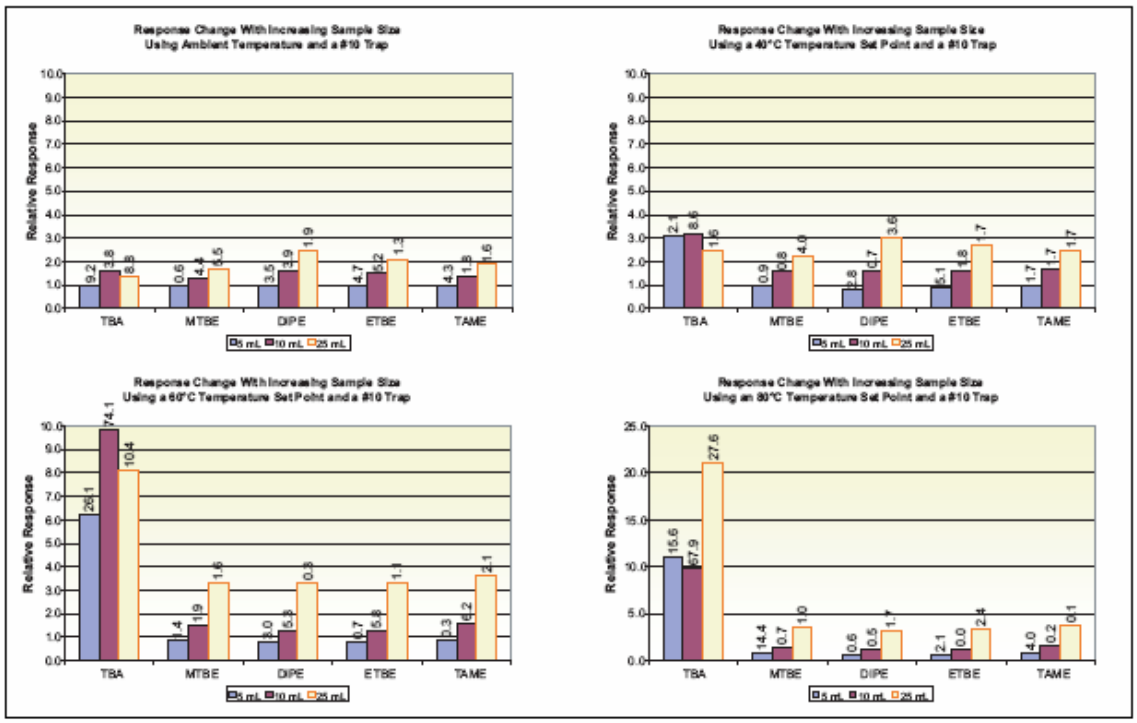

Figure 2. Charts illustrating relative response changes on a #10 trap using different sample sizes and temperature set points. All responses are reported relative to analysis of a 5-mL aliquot at ambient temperature. Each bar represents the average response from duplicate analyses and the small number above the bar is the relative percent difference (RPD) between the two runs. The chart for the 80°C sample temperature is shown in a different scale to accommodate the increased TBA response.

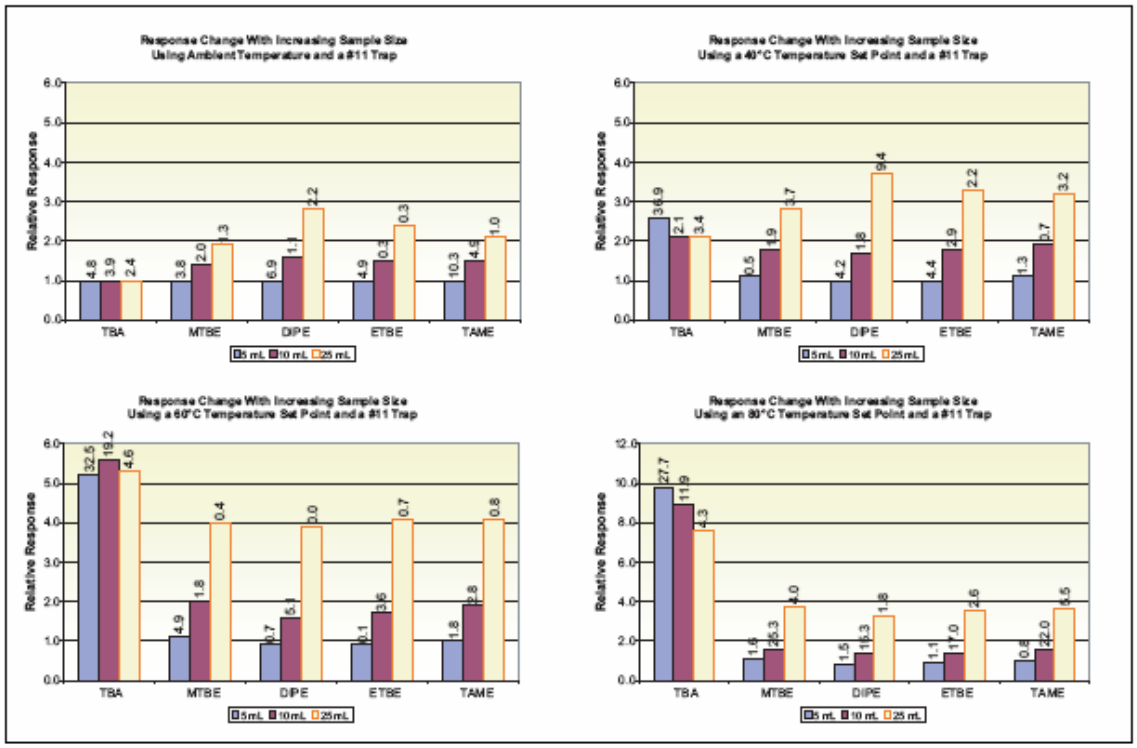

Figure 3. Charts illustrating relative response changes on a #11 trap using different sample sizes and temperature set points. All responses are reported relative to analysis of a 5-mL aliquot at ambient temperature. Each bar represents the average response from duplicate analyses and the small number above the bar is the relative percent difference (RPD) between the two runs. The chart for the 80°C sample temperature is shown in a different scale to accommodate the increased TBA response.

In general, the four ethers behaved uniformly and as predicted. Responses increased with increasing sample size at all temperatures and on both traps. Average relative response of the four ethers on the #10 trap at a 60°C temperature set point were 0.9 (5 mL), 1.5 (10 mL) and 3.4 (25 mL), and on the #11 trap they were 1.0, 1.8 and 4.0, respectively, indicating a slightly higher increase in response on the #11 trap. This difference in response between the two traps is illustrated in Figure 4 and Table 2. In contrast, increasing the sample temperature had only a minor effect on the ether response, as can be seen in Table 3. For the ethers, the chromatography and RPD between duplicate runs were excellent at all sample sizes and temperatures and no significant analytical difficulties were encountered.

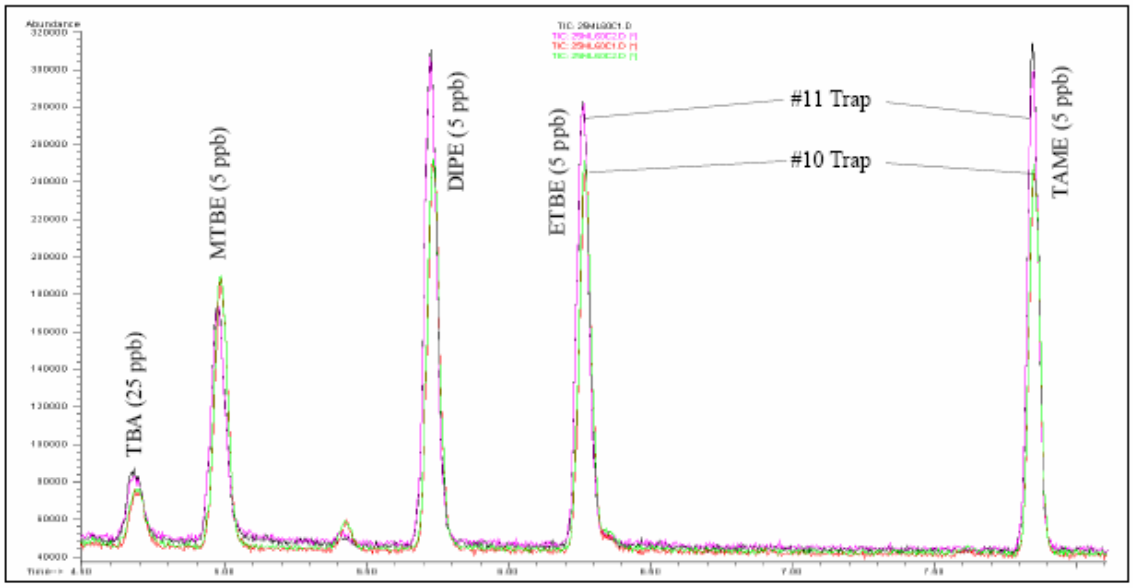

Figure 4. Overlaid chromatograms of two runs on the #10 trap and two runs on the #11 trap (25-mL sample size and 60°C set point). Chromatography on the two traps was nearly identical. However, most analytes showed a slight but distinct increase in sensitivity on the #11 trap.

Table 2. Effect of sample size on average relative response (RR) of the ethers on two different traps (60°C sample temperature set point). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Sample Size	Ether Average RR	
	#10 Trap	#11 Trap
5 mL	0.9	1.0
10 mL	1.5	1.8
25 mL	3.4	4.0

Table 3. Effect of sample temperature set point on average relative response (RR) of the ethers on two different traps (25-mL sample size). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Temperature Set Point	Ether Average RR	
	#10 Trap	#11 Trap
Ambient	2.1	2.3
40°C	2.6	3.2
60°C	3.4	4.0
80°C	3.5	3.5

TBA did not behave in the same manner as the four ethers. The TBA average relative response increased with sample temperature set point, but only a small and

unpredictable change in response was observed with increases in sample size. The quantitative results are summarized in Table 4 and Table 5. Although the quantitative data suggest that the best operating temperature set point would be 80°C, chromatographic performance of TBA worsened significantly at the highest temperature, producing unacceptable tailing as shown in Figure 5. Purging at 80°C is also undesirable because of potential MTBE hydrolysis.

Table 4. Effect of sample size on TBA average relative response (RR) on two different traps (60°C sample temperature set point). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Sample Size	TBA Average RR	
	#10 Trap	#11 Trap
5 mL	6.2	5.2
10 mL	4.2	5.6
25 mL	8.1	5.3

Table 5. Effect of sample temperature set point on average TBA relative response (RR) on two different traps (25-mL sample size). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Temperature Set Point	TBA Average RR	
	#10 Trap	#11 Trap
Ambient	1.4	1.0
40°C	2.5	2.1
60°C	8.1	5.3
80°C	21.1	7.6

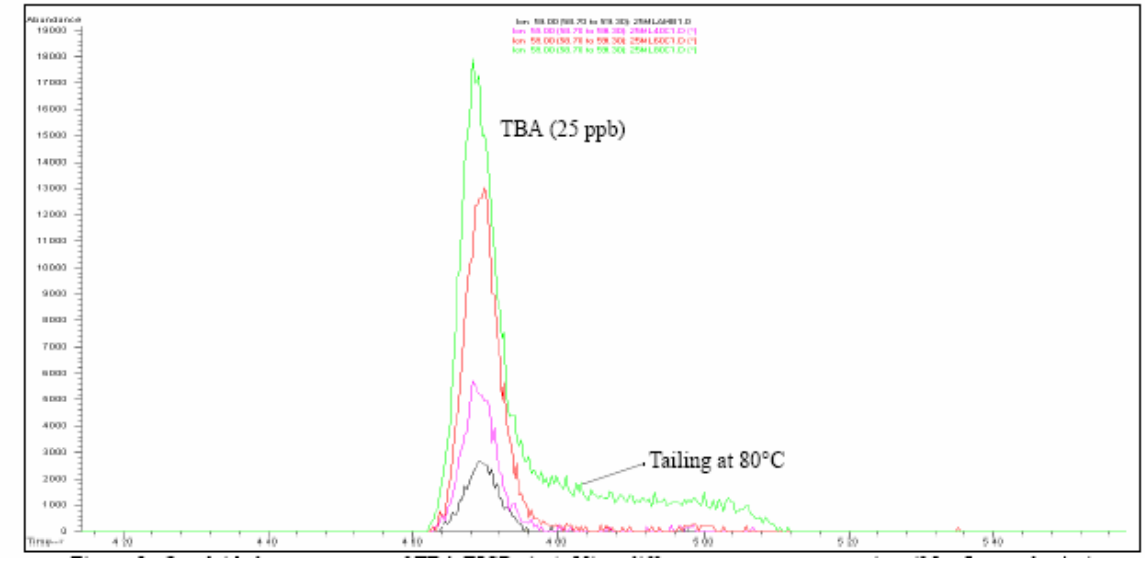

Figure 5. Overlaid chromatograms of TBA EICPs (*m/z* 59) at different temperature set points (25-mL sample size) illustrating unacceptable tailing at 80°C.

A Note About Temperature Set-Points

When the Model 4552 Autosampler operates in soil mode, the sample purges directly in the 40-mL VOA vial using a needle sparger, as described in USEPA Method 5035. Also as part of the method, a magnetic stir bar stirs the sample during purge and a heated collar around the vial brings the sample to the desired temperature, usually 40°–45°C. Using a thermocouple placed directly in the sample during preheat and purge, it was determined that the actual temperature of the sample did not reach the instrument set point when the set point was above ambient. The maximum temperatures achieved for set points of 40°, 60° and 80°C were 37°, 46° and 62°C, respectively. The Eclipse's patented Infra-Sparge™ sample heater is much more rapid and accurate than the collar-type heater; therefore, if choosing water mode and samples purge and heat in the Eclipse sparge vessel, the sample temperature set point should be reduced to between 40° and 45°C, accordingly.

LOQ

The limit of quantitation (LOQ) is sometimes referred to as the practical quantitation limit. It represents the lowest compound concentration that can be accurately quantified using a given analytical method and is often used as the lowest calibration standard when developing a calibration curve. For this test, triplicate aliquots of three different low-level standards were analyzed on each trap to estimate the lowest practical LOQ for the five analytes. The results are shown in Table 6 and Figure 6.

Table 6. Percent Relative Standard Deviation (%RSD, n=3) from triplicate analyses of three different concentrations on the two test traps (25-mL sample size, 45°C actual sample temperature)

Concentration (ppb)	%RSD (n=3)					
	0.2 ppb Ethers 1.0 ppb TBA		1.0 ppb Ethers 5.0 ppb TBA		5.0 ppb Ethers 25.0 ppb Ethers	
	#10 Trap	#11 Trap	#10 Trap	#11 Trap	#10 Trap	#11 Trap
TBA	10.9	6.0	24.3	21.0	47.9	15.3
MTBE	3.6	3.3	10.5	15.5	12.4	7.6
DIPE	2.2	2.7	2.8	4.6	5.0	3.8
ETBE	3.5	2.8	5.0	6.1	7.1	4.9
TAME	4.9	4.9	6.3	7.9	12.3	6.9

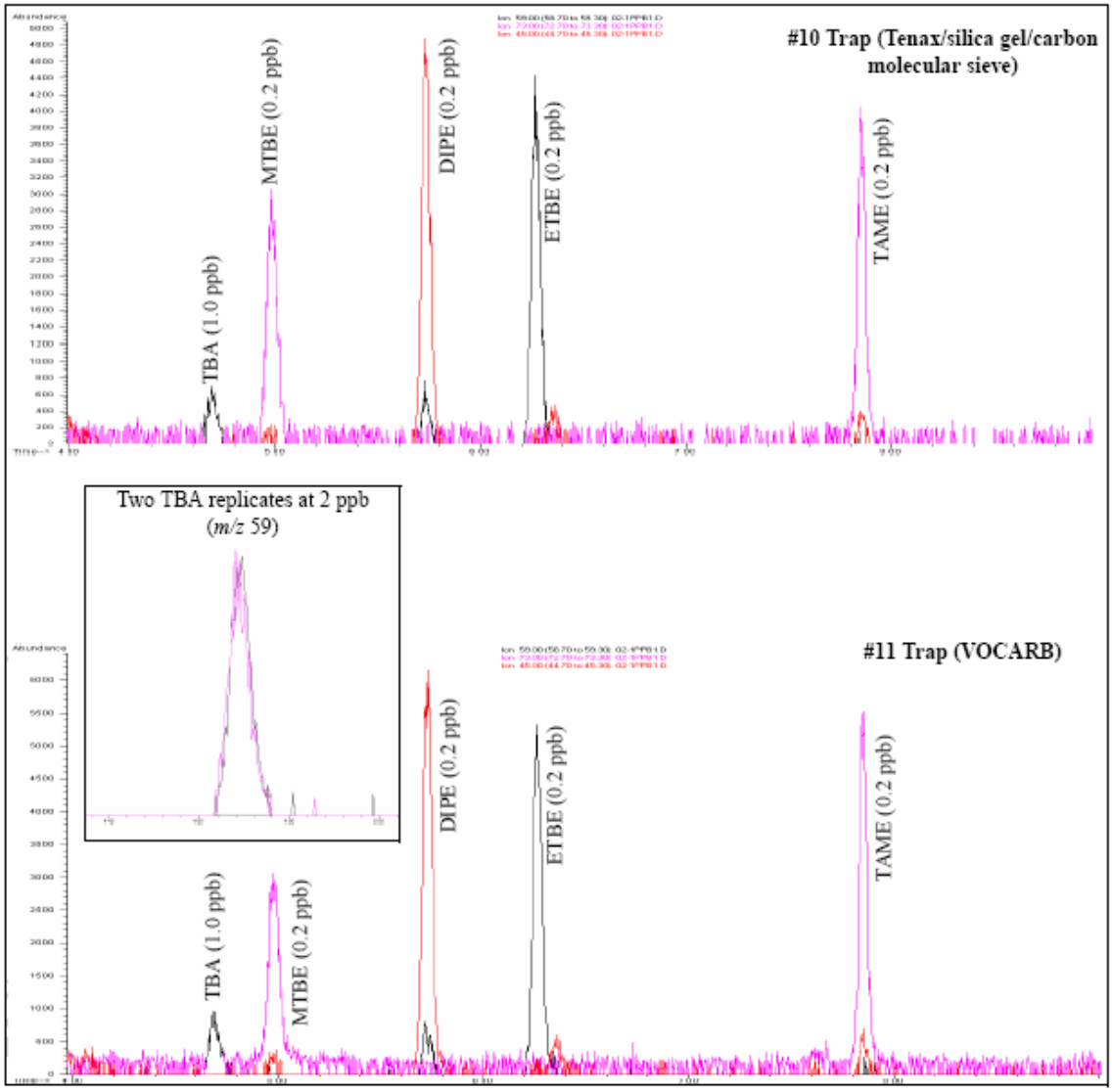

Figure 6. EICPs of TBA and the four ethers at the lowest LOQ test concentration of 0.2 ppb (1.0 ppb TBA) for the two traps tested. Chromatography for all compounds was excellent and sensitivity of the ethers allowed easy integration and quantitation at this low concentration. The insert shows overlaid EICPs of TBA at 2.0 ppb from duplicate calibration runs.

All four of the ethers, including MTBE, showed good response on both traps at 0.2 ppb using a 25-mL sample and an actual temperature of about 45°C and could be easily integrated and quantified at this low concentration. Chromatography and repeatability (measured as %RSD) were also excellent at this concentration for all four ether compounds. TBA had only a marginal response at 1.0 ppb. An LOQ of two-to-five times this level produced a more acceptable and quantifiable peak, as verified with the analyses at 2.0 ppb TBA in the second calibration standard. In general, repeatability was better for the ethers than for TBA and better on the #11 trap than on the #10 trap.

Calibration and Statistical MDL Results

An eight-point calibration curve was prepared with the ether concentrations at 0.2, 0.4, 1.0, 5.0, 10, 20, 100 and 200 ppb. TBA concentrations were five times the concentration of the ethers and ranged from 1 to 1,000 ppb. The calibration curve and MDL study were both acquired using a 25-mL sample size, an actual sample temperature of about 45°C and the #11 (VOCARB) trap. Each concentration level was analyzed in duplicate. A response factor (RF) was calculated for each analyte at each concentration level using fluorobenzene (80 ppb) as an internal standard. The calibration %RSD for all five compounds in the mix were below 15% and easily met the calibration criteria specified in USEPA Method 8260 and Method 524.2, Rev. 4. Using the less desirable linear calibration mode and coefficient of determination (R^2) was unnecessary for any of the compounds.

A statistical MDL determination was made by analyzing seven replicates of a standard at a concentration 0.5 ppb (2.5 ppb TBA). The MDL was calculated using the standard deviation of the seven measured concentrations and the Student's t-test. The statistically calculated MDL for TBA was 1.40 ppb and ranged from 0.03 to 0.05 ppb for the four ethers. The Initial Calibration and statistical MDL results are listed in Table 7.

Table 7. Results from the Initial Calibration and statistical MDL determination

Compound	Calibration			MDL		
	Range (ppb)	Avg. RRF	%RSD	Spike Amt.(ppb)	Std. Dev.(ppb)	Statistical MDL (ppb)
TBA	1.0–1,000	0.017	12.3	2.5	0.44	1.40
MTBE	0.2–200	0.497	7.8	0.5	0.02	0.05
DIPE	0.2–200	0.693	7.4	0.5	0.01	0.04
ETBE	0.2–200	0.606	9.4	0.5	0.02	0.05
TAME	0.2–200	0.516	9.2	0.5	0.01	0.03

Water Results

Because of the extreme water solubility of the oxygenate compounds, how well the P&T sample concentrator handles water removal becomes critical. For part of this experiment the MS mass range was extended to include *m/z* 18 to monitor the amount of water going to the GC from the P&T. As can be seen in Figure 7, the Eclipse's patented water management fitting (WMF) consistently removed all but a very minimal water amount from the sample stream as it transferred to the GC, regardless of sample size or temperature. The #11 VOCARB trap transferred slightly less water (approximately 5–10%) to the GC, probably because of its more hydrophobic character. In all cases, the water was baseline-resolved from TBA and MTBE and did not interfere chromatographically with any of the compounds. The patented WMF operated using factory-default settings and any modification to accommodate water-soluble compounds was unnecessary.

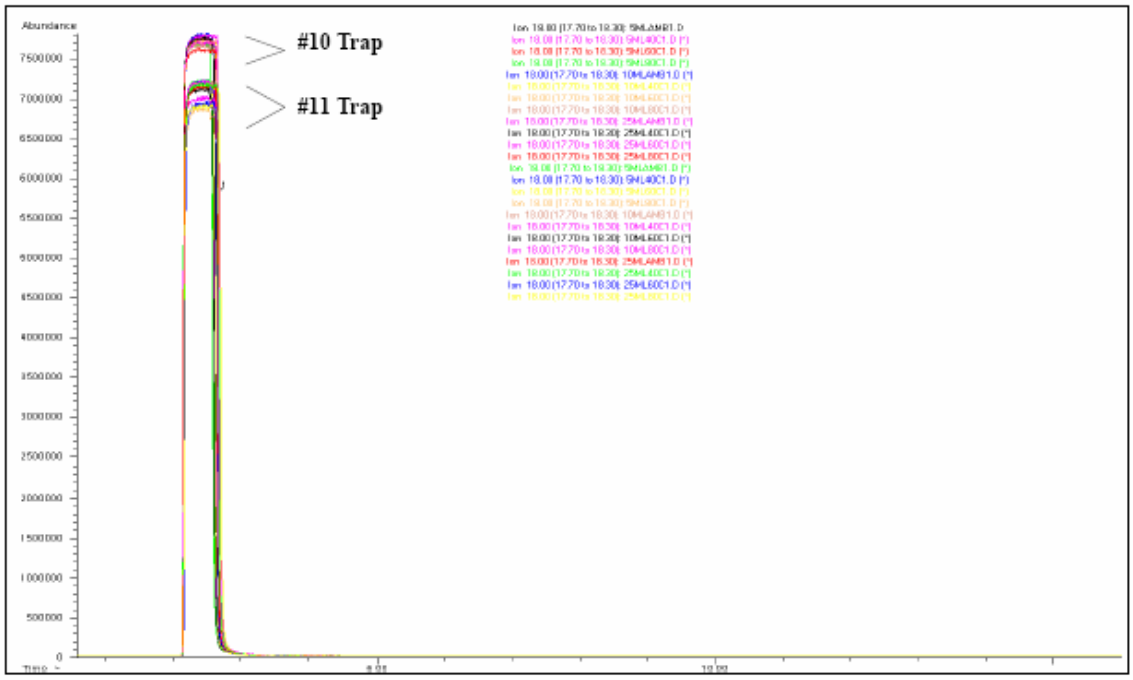

Figure 7. Overlaid EICPs (*m/z* 18) from 24 analyses illustrating the efficient and consistent water removal of the patented water management fitting, regardless of sample size, sample temperature or trap type. The WMF operated using factory default settings.

Real-World Sample

Groundwater and wastewater samples encountered in laboratories often contain volatile gasoline components that can complicate the analysis. To simulate this real-world situation, a sample was prepared by spiking tap water with 1-ppm gasoline and 100-ppb oxygenates and analyzed using the prescribed conditions (#11 trap, 25-mL sample size, 45°C actual sample temperature). Figure 8 shows the total ion chromatogram (TIC) from this analysis with the oxygenate EICPs overlaid. Chromatography was excellent and peak identification in this simulated "dirty" matrix was unambiguous using the MS.

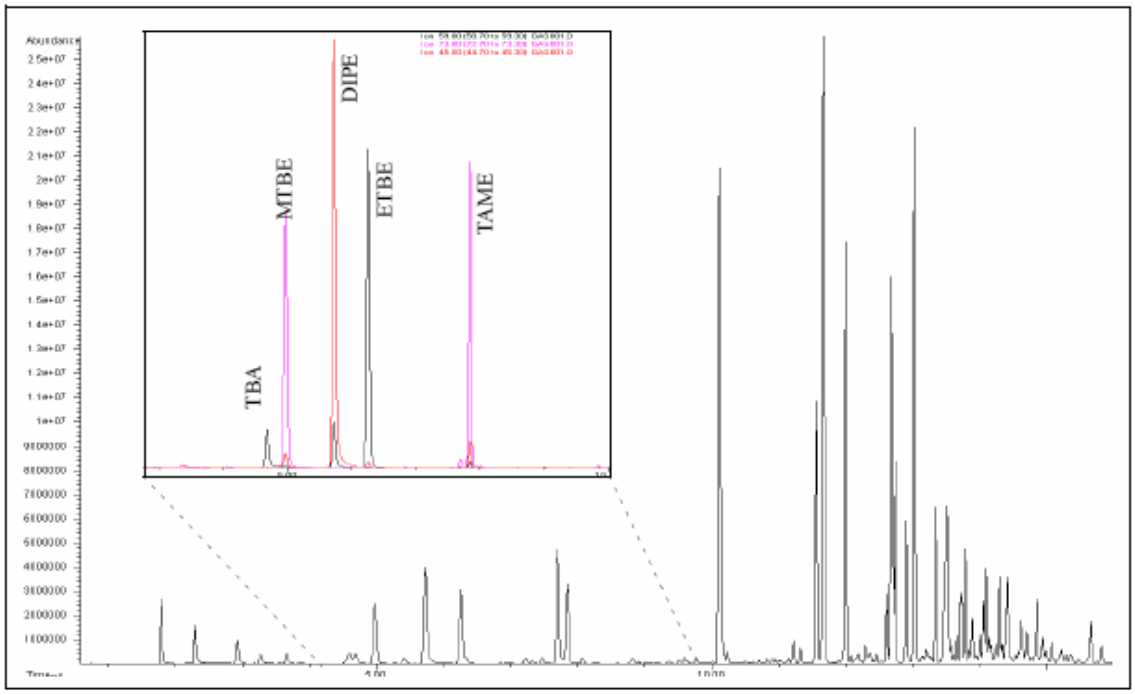

Figure 8. Chromatogram of water spiked with 1-ppm gasoline and 100-ppb oxygenates and analyzed using the Eclipse Sample Concentrator. The overlaid EIPCs show the MS ions used for quantitation of the oxygenate compounds.

Results From Other Laboratories

Immediately after introducing the Eclipse, it was run in a high-throughput production laboratory that routinely includes an extensive list of oxygenate compounds in its Method 8260 analyses. That laboratory used equipment identical to the instrumentation described here, but ran their Model 4552 Autosampler in water mode rather than soil mode. They also used a #10 trap and a 5-mL sample instead of a 25-mL sample. The samples transferred to the Eclipse fritted sparge vessel, where they heated during purge to 40°C with the patented Infra-Sparge sample heater. (Note that the Infra-Sparge sample heater raised the sample temperature to the actual set point of 40°C in less than one minute, where the collar heater in the Model 4552 Autosampler required a set point of 60°C to reach approximately the same temperature after six minutes.) Selected results from those analyses are shown in Figure 9 and Figure 10, and Table 8.

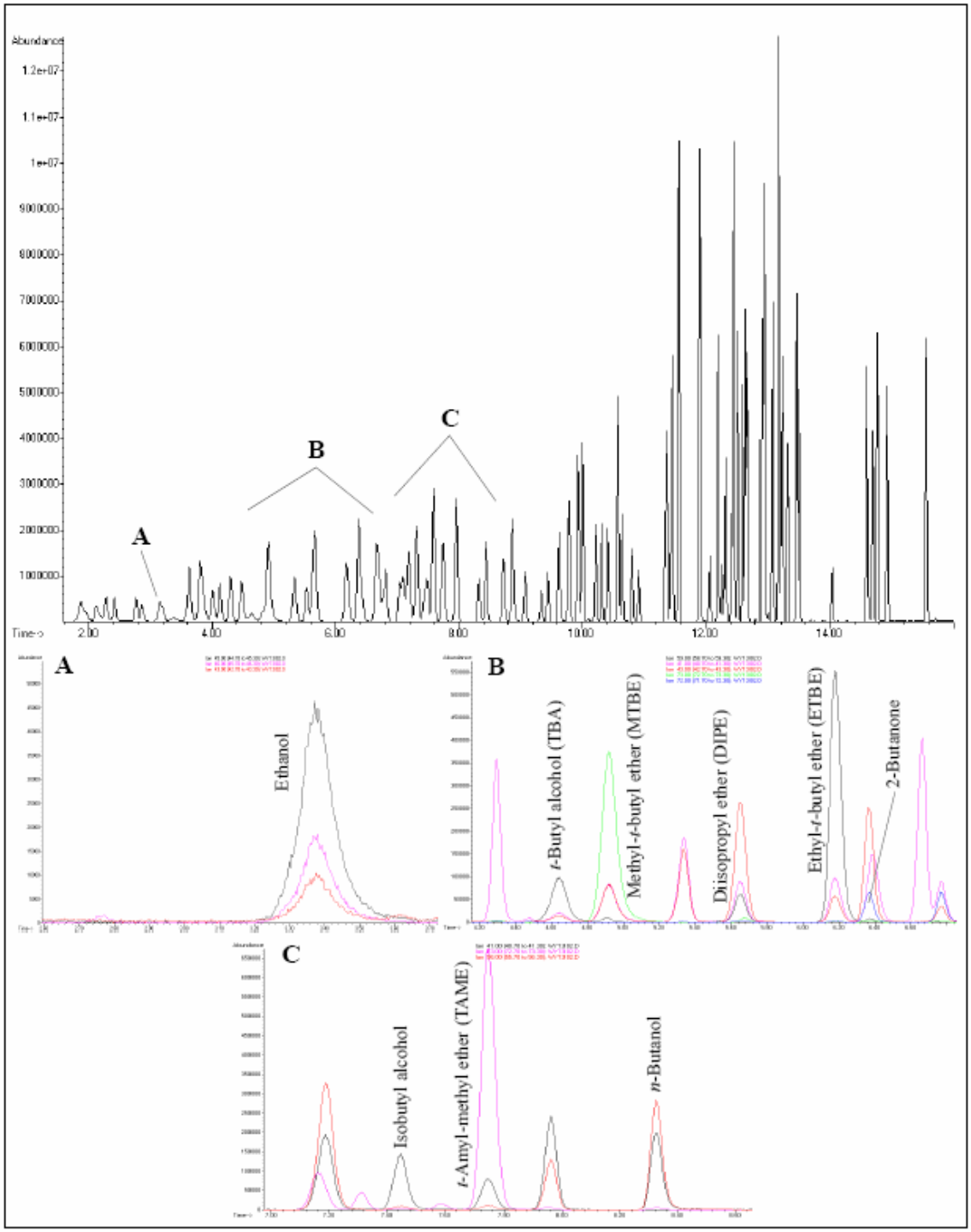

Figure 9. Chromatogram from a calibration standard run on the Eclipse at a commercial production laboratory using standard conditions optimized for Method 8260. The inserts show the chromatography of some of the more difficult oxygenates. See OI Analytical Application Note 1937 for complete analytical details.

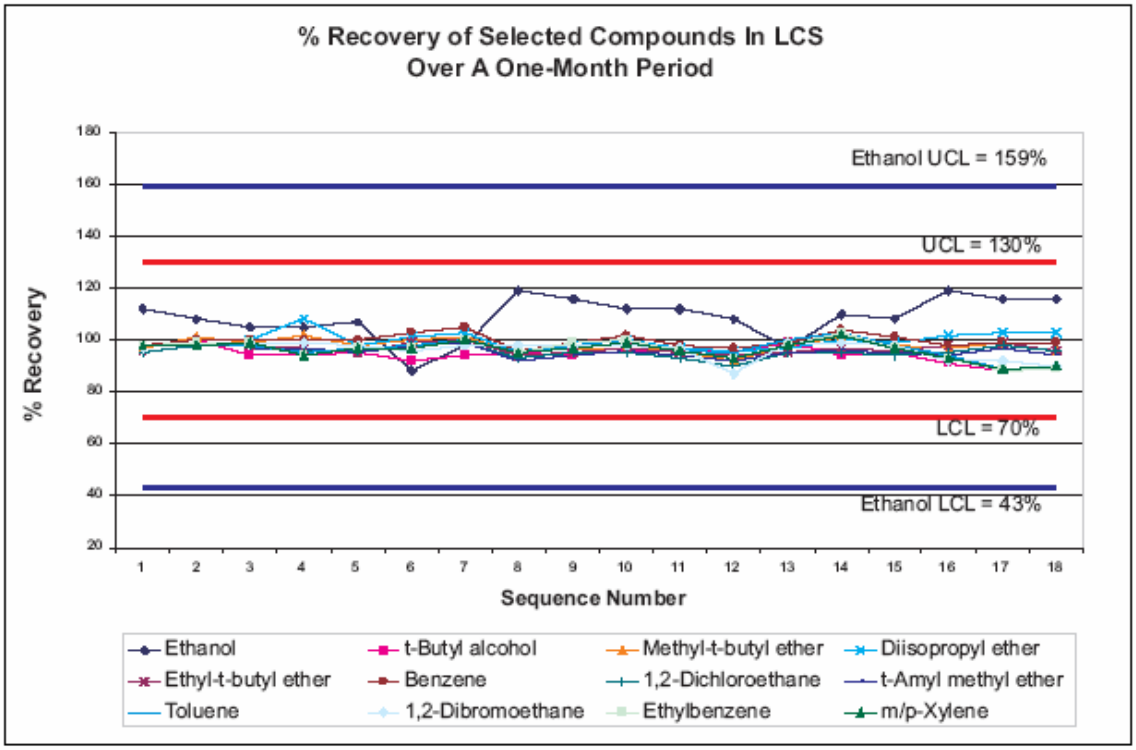

Figure 10. Percent recovery of 12 selected compounds in the laboratory control sample (LCS) analyzed on the Eclipse during a one-month period. The six oxygenate compounds performed as well as the BTEX. All recoveries met the QC acceptance criteria without difficulty.

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Table 8. Selected results for fuel oxygenates from a high-throughput production laboratory. The laboratory routinely includes an extensive list of oxygenate compounds in its Method 8260 analyses and does not modify their instrument operating conditions to accommodate additional compounds. See OI Analytical Application Note 1937 for full results.

Compound	Calibration			MDL		Initial Demonstration (n=4)			
	Range (ppb)	Avg. RRF	%RSD	Spike Amt. (ppb)	MDL (ppb)	Spike Amt. (ppb)	Measured (ppb)	Std. Dev (ppb)	Pass?
Ethanol	50–7,500	0.132	6	50	14.5	500	544.7	8.4	Yes
TBA	20–1,500	1.312	4	10	1.01	200	194.4	0.9	Yes
MTBE	1–300	0.861	3	0.5	0.05	20	19.8	0.1	Yes
DIPE	1–300	0.924	2	0.5	0.23	20	20.0	0.2	Yes
ETBE	1–300	0.897	2	0.5	0.07	20	19.5	0.2	Yes
2-Butanone	2–600	0.045	3	1.0	0.62	150	128.9	0.5	Yes
Isobutyl alcohol	50–3,750	0.015	4	25	16.8	500	491.5	2.1	Yes
TAME	1–300	0.853	1	0.5	0.05	20	19.4	0.1	Yes
n-Butanol	100–7,500	0.013	7	50	22.3	1000	946.9	13.4	Yes

The calibration produced single-digit %RSDs for all oxygenates on the extended list and the same initial calibration curve was used for over three months. All ongoing quality control (QC) check standards (CCV, LCS, IS responses, etc.) met the method and laboratory QC criteria during the same three-month period. Other than including the oxygenate standards in the calibration mixtures, modifying any of instrument operating conditions to accommodate the additional compounds was unnecessary.

Salting Techniques

Another commonly discussed technique for enhancing oxygenate performance is modifying the matrix by salt addition to increase the ion content of the solution. This technique has been shown to work; however, most highthroughput laboratories do not want to add the labor-intensive step of modifying the sample matrix prior to analysis. In addition, salting can add significantly to routine instrument maintenance, causing additional instrument downtime and lost revenue.

Conclusions and Recommendations

In general, response of the four ethers increased with increasing sample size and the more polar TBA responded better when the sample temperature was raised. The best performance for all compounds was achieved by using a large sample volume (25 mL) and heating the sample to 40° to 45°C during purge. Higher sample temperatures were not necessary and the more moderate temperature of 40°–45°C will minimize the possibility of MTBE hydrolysis. The patented WMF provided excellent water management using factory default settings. Both traps gave approximately equivalent results with slightly higher response seen on the #11 trap. Either trap should be expected to perform favorably under these temperature and sample size conditions.

Using the conditions described here, the four ethers were accurately quantified at 0.2 ppb and TBA at 1.0 to 2.0 ppb. Statistical MDLs were 0.03 to 0.05 ppb and 1.40 ppb, respectively, with single-digit %RSDs for calibration of most compounds.

Many laboratories routinely include the fuel oxygenates in the Method 8260 analyte list. They achieve excellent and consistent results using the Eclipse, meeting all QC criteria and low detection limits without making any significant changes to their P&T or GC/MS methods.

Acknowledgements

OI Analytical thanks Trent Sprenkle, Group Leader, GC/MS Volatiles at Lancaster Laboratories in Lancaster, PA, for providing data from his laboratory, which illustrates how fuel oxygenates can be added to Method 8260 without making significant changes to the methodology. OI Analytical thanks Restek Corporation for supplying the oxygenate analytical standard (PN 30465-510) and capillary GC column (Rtx-624, 30 meter x 0.25 mm I.D. x 1.4-μm film) used in this project.

References

1. USEPA Method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December 1996.

2. USEPA Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.0, August 1992.
3. USEPA Method 5030B, Purge-and-Trap for Aqueous Samples.
4. USEPA Method 5035, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.
5. OI Analytical Application Note 1937, *The Eclipse Purge-and-Trap Sample Concentrator Initial LaboratoryTest Results, Part II*.

"LEGACY" SCIENCE SUGGESTS IMPROVED SURFACE-TESTING PRACTICES FOR DETECTION OF DISPERSED BIOAGENTS (*e.g.*, *BACILLUS ANTHRACIS* SPORES) IN BIOTERRORISM RESPONSE*

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Abstract
The U.S. anthrax incident of bioterrorism elicited multi-agency crisis- and consequence-management responses in 2001-2. Most technical assessment of viable anthrax-spore contamination involved three types of culture-based microbiological testing of surfaces – swab-rinse, wipe-rinse and HEPA[1]-vacuum-rinse assays – applied to survey indoor environments for "rule-out" bioagent detection. A surface-sampling test comprises environmental specimen collection and microbiological laboratory plate-count assay analysis. Decontamination assessments relied in part on similar methods for direct verification sampling. The limited technical reporting of outcomes suggests that all three surface-testing techniques exhibited problematic performance in actual practice. Anthrax-incident and prior art literature was surveyed to see if applied microbiology offered any empirical basis for improved surface-testing practices. This initiative involved review of authoritative Internet postings and of scientific publications and personal communications with some government technologists involved with the 2001-2 anthrax incident responses at Federal facilities. All disclosed surface-testing procedures appear essentially *ad hoc* in specified technical details, lacking reference to any earlier published works, such as NASA's[1] spacecraft-testing activity for planetary protection. The literature suggests numerous improvements from the prior art of microbiological surface-testing. Sixteen elements of the disclosed testing procedures are specifically identified for investigation of such likely possibilities. Needed attention to relevant legacy

science and scientific peer review of environmental surface-testing practices should enable much-improved preparedness for any future need of them in bioterrorism response.

Introduction

"…It is possible to do a poor job of decontamination
and to make it look good
by doing a poor job of sampling and analysis."
– Dr. Ellen Raber, Lawrence Livermore National Laboratory, March 2002[2]

"...Other difficulties involved the interpretation of negative sampling results (viable spores of *B. anthracis* not detected in the sample). To date, no sample efficiency data are available to scientifically and statistically interpret results for *B. anthracis*. A result of 'zero viable spores' cannot be related to a concentration. As such, risk-based determinations are estimated and the only true assurances are that, in the areas sampled appropriately, high levels of spore contamination are not present when results are negative."

– Rich Rupert, EPA On-Scene Coordinator, Capitol Hill Anthrax Site, August 2002[10]

In a context of "zero tolerance" remediation criteria[3,4] for residual bioterrorism-associated indoor *Bacillus anthracis* ("anthrax") spore contamination, three** non-validated[5] microbiological testing methods for viable anthrax spore detection *on* ***surfaces*** were practiced with USPS[1], CDC[1] or EPA[1] supervision during the 2001-2 "anthrax incident" response[6] technical assessments at Capitol Hill and postal facilities, *i.e.*:

- *Swab-rinse assay*[5,7-10] (*see* **Figure 1**),
- *Wipe-rinse assay*[5,9,10] (*see* **Figure 2**) and
- *HEPA*[1]*-vacuuming-rinse assay*[5,9,10](*see* **Figures 3a/b**),

according to reports and Federal agency disclosures.

Each procedure involved on-site collection of environmental specimens in sterile fibrous media (*see* **Table 1**), followed by mechanical wet-extraction processing (the "rinse") at a public health laboratory[11] under BSL-3[1] containment to obtain inoculum for plate culture. Plate-count assays were then performed, following recognized clinical microbiological protocols[12] for the presumptive "rule in/rule out" identification of growing *B. anthracis* colonies.

Four sampling sorties were needed at the anthrax-contaminated Wallingford, CT, postal facility before any positive test-outcomes were obtained, [14] suggesting questionable reliability of more than one "rule-out" surface-testing practice. One widely-deployed incident procedure (*i.e.*, the USPS-prescribed[8] "dry" swab-rinse assay method) has been shown by empirical studies to be relatively insensitive.[9,15] In May, 2003, Congressional hearing testimony, the GAO[1] questioned ruling-out postal-facility

contamination based solely on this procedure's negative results[16] and we also criticized such a use of dry swabs, as lacking any evident scientific foundation. [17]

Inspection of the limited accessible anthrax-incident surface-testing data[9,13,14,16] suggests that high variabilities in test-outcomes characterized all three surface-assay methods.[19] Each incident method disclosed to-date contains some technical ambiguities which might account for variability in actual practice. However, unlike associated air-testing methods[5], these surface-testing procedures (some compiled hurriedly in 2001, reportedly by "conference-call consensus"[20,21]) lack any cited empirical antecedents, thus appear to be *ad hoc* in nature (extemporaneous). Study of the relevant literature in applied microbiology may therefore reveal a scientific basis for possible technical improvements to these important surface-testing practices.

Table 1. Some Environmental Surface-Sampling Methods

Specimen Type	Agency	Material	Wetting agent	Area Sampled	Collection Pattern	Ref.
Dry Swab	USPS	Dacron or Rayon (non-cotton) sterile swab	None	100 cm^2 ("about the size of half a sheet of paper")	Horizontal S strokes, *rotate*, then vertical S strokes (*illustrated*)	8
Wet Swab	CDC	Non-cotton (*e.g.*, Rayon) sterile swab	Sterile water, saline or PBS*	<100 cm^2 ("Avoid letting the swab dry completely")	"Enough vertical S strokes to cover area completely" (*not illustrated*)	5
Wet Swab (for "surface "bioburden" of spacecraft hardware)	NASA	Autoclaved then dried sterile cotton	Sterile water (10 ml)	No more than 26 cm^2 (2 in x 2 in)	Rotational swabbing motions in three 90-degree changes of direction, then immerse in water	23
Wet Wipe	CDC	3 in x 3 in or smaller synthetic (non-cotton) gauze pad (gauze, Handi-Wipe^R, sterile sponge)	Sterile water, saline or PBS* (moisten)	Approximately 1 ft^2 (0.0929 m^2) ("Avoid letting the gauze pad dry completely.")	Vertical S strokes, *fold*, then horizontal S strokes	5
Wet Wipe (for "surface "bioburden" of spacecraft hardware)	NASA	Autoclaved then dried 100% polyester-bonded clean room wipes, 26 cm x 26 cm (~10 in x 10 in)	Sterile distilled water (15 ml)	Unspecified; routinely up to 0.74 m^2 (8 ft^2), according to Kirschner and Puleo (1979)	Rotational rubbing motions in three 90-degree changes of direction w/folding	23, 24
HEPA VacuumDust Collection Filter ("Nozzle Sock")	CDC	HD polyethylene filter (1 μm nom. porosity) in high volume air (28 cfm) intake device	None	No area specified	One pass at 12"/sec; 1-2 tablespoons debris/dust needed/desired	5
Microvacuum (modified personal air sampler)	EPA	Gelatin filter (3 μm nom. porosity) in low volume air (4 cfm) intake device	None	100 cm^2 (defined by template)	Slow back-and-forth motion, first in one direction, then 90 degrees perpendicular	5, 13

* PBS = phosphate buffered saline

Adapted from: Congressional testimony of R. G. Hamilton, May 19, 2003[17]

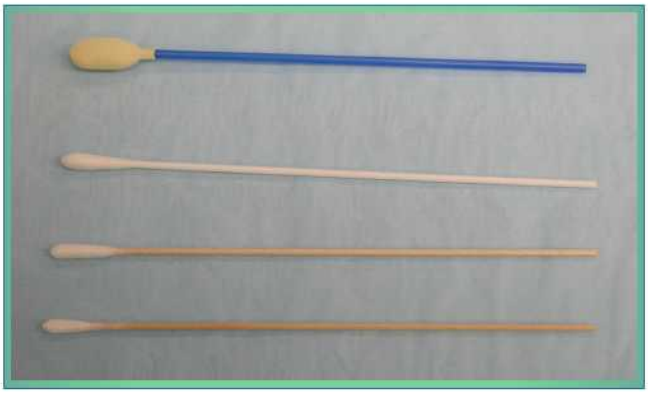

Figure 1. Four types of commercially-available sterile dry swabs:

- Macrofoam (VWR, Suwanee, GA, cat#10812-046)
- Cotton (Baxter Healthcare Corp., McGaw Park, IL)
- Rayon (Pur-Wraps, Hardwood Products Co., Guilford, MA)
- Polyester (Falcon, Beckton Dickson and Co., Sparks, MD)

Adapted from: L. Rose *et al*. (2003)[15].

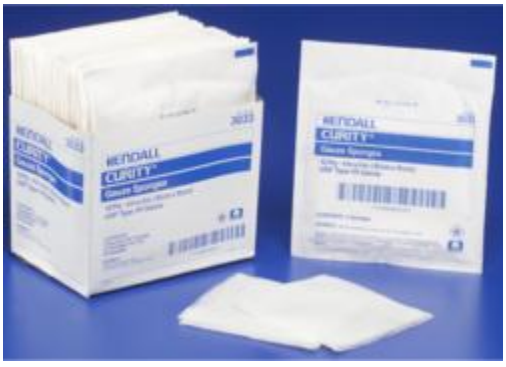

Figure 2. A commercial type of sterile cotton gauze wipe (12-ply pad). Similar cotton-gauze wipes were found to be relatively insensitive in wipe-rinse assays of anthrax spores[18]. Source: The Kendall Company, Mansfield Mass. URL: http://www.kendallhq.com/catalog/images/curitycottip.jpg.

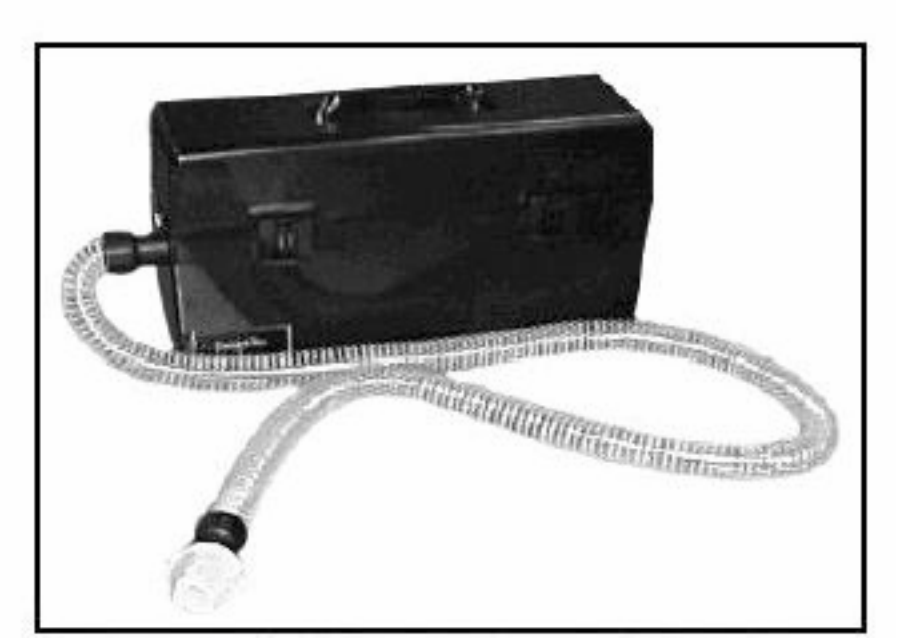

Figure 3a. Photograph of HEPA vacuum cleaner and sock sample Adapted from: Sanderson *et al*. (2003)[9].

Figure 3b. "Cleanup personnel use a HEPA vacuum in a Congressional office". EPA Photo, adapted from: GAO-03-686[51].

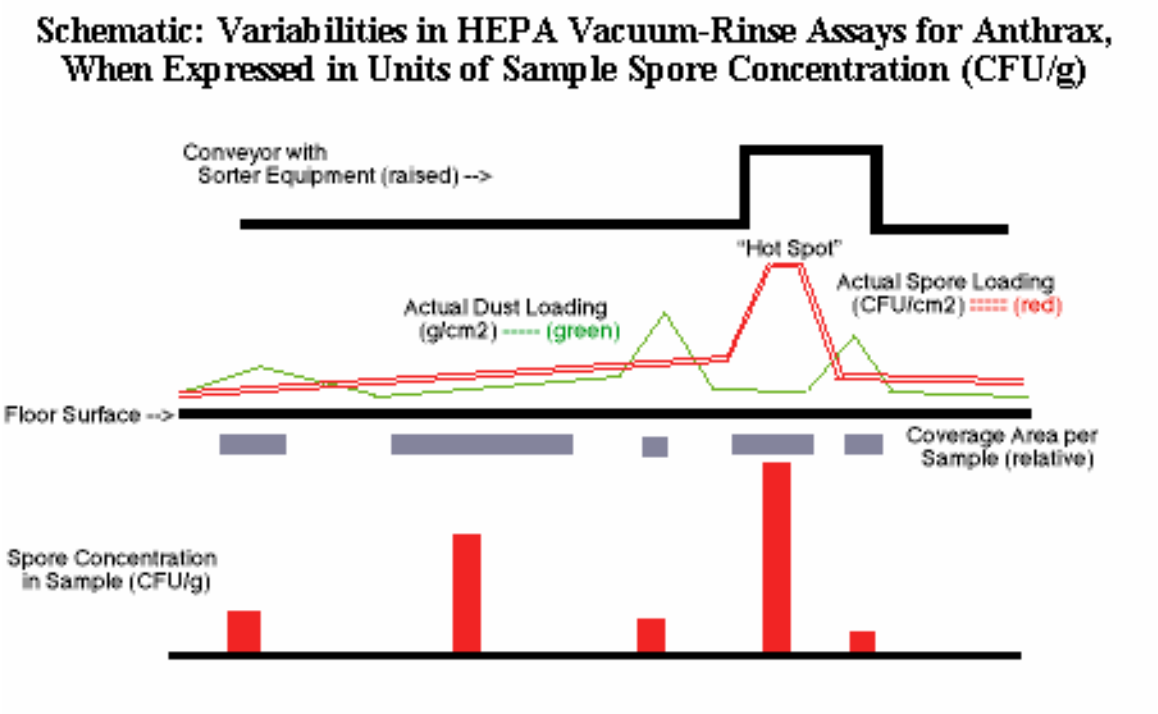

Figure 4. Schematic illustrating the possible ambiguity associated with the units (CFU^1/g versus CFU/cm^2) used to report sample spore concentration derived from HEPA[1] vacuum-rinse assay data. The top panel indicates a theoretical conveyor-belt room in a mail distribution center, in which the raised area indicates the sorter equipment location. If a letter with anthrax passes through the room, a "hot spot" of settled spores is created on the floor, as illustrated in the middle graph (*double-lined curve*). The spore-concentration values reported in the lower panel as CFU/g are computed as the ratios of total spores detected to the total weight of dust mass collected (*vertical bars).* The CFU/g levels can vary greatly because of large differences in sampling-surface coverage areas (*horizontal gray bars*) and do not reflect actual spore surface-loading (CFU/cm^2). This results from sample collection areas being adapted to varying levels of surface dusts (*single-lined curve*) – in order to maintain consistency in total dust mass collected – rather than being held constant so that the total quantity of spores in a sample would be proportionate to any actual differences in *Bacillus anthracis* spore surface-loading levels (population density) at the floor locations tested (*double-lined curve*). Graphic prepared by: Johns Hopkins DACI Reference Laboratory, Johns Hopkins University School of Medicine, Baltimore Md. 21224. Adapted from: Congressional testimony of R. G. Hamilton, May 19, 2003[17].

Methods

The limited accessible anthrax-incident reports and the "prior-art" open scientific literature (1917-2001) were surveyed to see if applied or environmental microbiology offered any empirical basis for improved microbiological surface-testing practices applicable to detection of dispersed anthrax spores in bioterrorism response. Understanding of the recent Federally-sanctioned practices was based on information obtained from authoritative Internet postings, the few related scientific publications to-

date and personal communications with government technologists involved or familiar with the 2001*et seq.* anthrax-incident responses at Federal facilities. Extensive holdings and research facilities of the USDA's National Agricultural Library in Beltsville, MD, and of The Johns Hopkins University were utilized to accomplish the open literature survey. No Federal funds were used to support this project.

RESULTS

Sixteen technical elements of surface-testing practices used during the 2001-2 anthrax incident response were either deficient or likely improvable, with reference to analogous empirical techniques described in the scientific literature. Our comparative and conjectural concerns can be grouped into six categories: *quality assurance, surface-sample collection, specimen rinse-extraction, bacterial spore enrichment, culture inoculatio;* and *test-outcomes data terminology*.

Quality Assurance Issues

Common to all the disclosed methods, these include:

(1) **No "positive control" provisions**[5,7-9] to support proficiency training and enable monitoring of actual testing practices, thereby reducing risks of "false negative" testing outcomes.[22] Cf. sample "blanks" were collected as "negative controls", to monitor for "false positive" cross-contamination.[5,7-9] Standardized positive controls for calibration and quality control are a universal feature of certifiable testing methods. Without them, the efficacy of a testing method cannot be determined. NASA's[1] standardized microbiological surface-testing methods for planetary quarantine (now "planetary protection") have utilized ambient fallout- or spore-seeded test strips as positive sampling controls, since the 1960s.[23,24] Laboratories need positive controls (*e.g.*, suitably-"seeded" sampling media[24]) as realistic environmental-specimen surrogates for protocol validation and training.

(2) **Ambiguities of described procedures**:[5,7-9] Important variables are unspecified of manual swab and wipe surface-contact (*e.g.*, media moistness[25], firmness of applied pressure[26,27], angle-of-attack[23], track patterns and "rolling" rotations during sweeping motions[19,23]) of surface-vacuuming nozzle-handling technique[5] (*see* **Figure 3b**) and of wet-extraction mechanics[24]. By analogy, *consider the many ways to use a toothbrush – some more effective than others.*[17]

Surface-Sample Collection Issues

(3) Specified **surface coverage areas** per swab sample (100 cm^2)[5,7-9] or per wipe (1 ft^2)[5] are unsubstantiated and may be excessive. Prior standardized swab-rinse methods have prescribed much smaller areas, *e.g.*, 26 cm^2 (APHA[1,30], NASA[1,23]) or 20 cm^2 (DIN[1,28]). One incident study[9] reported adverse overloading of surface soils and dusts on swabs and wipes, suggesting the need for clear guidance on adjustment of coverage areas to avoid overloading. NASA's long-practiced wipe-rinse assay[23] employs folded 10x10 in. clean-room cloth wipes, not 3x3 in. (or smaller) gauze wipes, as the incident procedures specify; 3x3 in. cotton gauze wipes have proved problematic[18] (*see* **Figure 2**).

(4) Use of **synthetic rather than cotton-fiber swabs**[5,7-9] (recommended for unsupported reasons[18]) may reduce spore-recovery efficiency[15]: literature

suggests that natural cotton swab-bud "disentanglement"[29,30] or "disintegration"[31-33] was the desired end-point of mechanical extraction (*e.g*., by "hand strike") for more efficient microbial recoveries. A completely-disintegrating collection medium (such as calcium alginate[34]), if otherwise suitable, may prove the best solution to refractory spore retention within collectors, for sensitive "rule-out" surface-assays in bioterrorism response.

(5) Use of **dry swabs** (*i.e*., no wetting agent used) for sampling dry environmental surfaces[8]: this practice lacks any known scientific foundation in the swab-rinse assay literature since 1917 which we surveyed[17,35] and its relative insensitivity has recently been demonstrated experimentally.[9,15]

(6) **No surfactant included** in wetting agents for swab or wipe sampling media[5,7,9] may reduce spore-removal efficiency from surfaces and extraction recovery efficiency[32]. Also, **no** report of titrated **sporacide-neutralizing agent** (*e.g*., antioxidant[30]) included in wetting agents **for "verification sampling"** specimens (*i.e*., samples collected to assess decontamination success following vapor fumigation or surface-treatments) risks progressive attrition of viable spores by any collected sporacidal residues, under the moistened conditions *in situ*; surfactant additives for germicidal residue neutralization in swab specimens (*e.g*., nonionic Tween® detergent and lecithin) have been used routinely since the 1940s,[30, 36,37] addressing both of these issues (and if employed, might coincidently mitigate some reported electrostatic attraction phenomena[13]).

(7) **"Dry" transport** of swab and wipe specimens to the assay laboratory[5,7-9] is unprecedented since 1917[35] and may reduce extraction efficiency while increasing safety risks of re-aerosolization exposures to laboratory workers. It may also aggravate risk of viable spore attrition in verification samples. Practice of dry transport suggests confusion of swab-rinse assay with the clinical *swab-smear assay*, which is clearly suitable only for clinical – not environmental – specimens.

(8) **"Nozzleless" HEPA-vacuuming** arrangement – the prescribed placement of filtering dust collectors in tubular hose-end adapters, with no restrictive intake-nozzle attachment placed upstream[5,9] (*see* **Figure 3a/b**) – is contraindicated in studies of the Sandia National Laboratory's 1960s-design "vacuum probe",[38-41] which demonstrated the importance of "critical orifice" design in achieving high-efficiency removal of bacterial spores seeded on non-porous surfaces and it also suggests problematic ergonomics.

<u>Environmental Specimen Rinse-Extraction Issues</u>

(9) **Detergent not included in the rinse solution** for wet-extractions[8] may substantially reduce extraction efficiency: detergents have routinely been rinse adjuvants since the 1940s[23,24,32,36,37, 42] (*see also* item (6) above).

(10) Mechanical wet-extraction by **brief vortexing**[5,-9] **or shaking**[9] **may be inadequate** to release spores efficiently into liquid extract. Early (1930s) "hand-strike" extraction techniques resulted in visible swab-bud disintegration,[29-33] not recently reported as achieved by vortexing. Similar concern may have prompted an unusual and isolated manual swab "**maceration**" extraction technique

reportedly practiced at one Naval laboratory on surface-specimens from the Capitol Hill Anthrax Site.[13]

(11)**Sonication not included** in the wet-extraction of specimen media:[5-9] improved swab- and wipe-specimen extraction methods developed in the 1970s for microbiological surveys of spacecraft hardware surfaces (for NASA's planetary protection program) incorporated a bath-sonication step,[23,24] adding *insonation* forces to vortexing or shaking shear, as has been shown to improve efficiency of release of microorganisms from these sample-collection media.[43]

(12)**Concentrating** large-volume **extracts by centrifugation** and resuspension:[9] this raises particulates-binding artifact concern (*e.g*., induced spore agglomeration) which may variably affect accuracy of subsequent plate-counts; large-volume microbial sample extract concentration by filtration rather than by centrifugation has been a recognized standard practice in the sterile medical devices manufacturing industry.[44]

Bacterial Spore-Enrichment Issues

(13)Prescribed **conditions of "heat shock"** for spore enrichment varied among the reported protocols.[7-9] Risk of substantial attrition of viable bacterial spores by heat-shock has been reported, varying by species,[45,46] with an alternative, non-heating treatment (ethanol plus dipicolinate) also reportedly shown to be able to achieve both spore selection and germination activation.[45-47] Heat-shock of stressed viable spores in verification samples may prove to be especially problematic.

Plate-Culture Inoculation Issues

(14)**Replicate plating was disallowed** in the USPS swab-rinse procedure[8] – which deviates from laboratory "best practices"[22] due to its risk of "sampling error".

(15)**Excessive "splitting" of extracts** into small-volume aliquots (*e.g*., 100-150 μL) for plate inoculation by surface-spreading: incident procedures[7,8] specified culture of only a tenth to a fifteenth of total specimen extract-volume, suggesting high risk of statistical sampling errors (false negatives or inaccuracies) in "rule out" tests for low-level contamination. The pour-plate assay alternative to spreading[30] used by NASA[23] (if practicable for assay of *B. anthracis*) would enable culturing of 40-80% or more of total extracted volumes. Also, no provision was indicated for some reserve of extracts to enable repeat assays of specimens, if initial plate cultures were either defective or "too numerous to count".

Test-Outcomes Data Terminology Issues

(16)**Qualitative** or "quantal" data (positive/negative) **rather than quantitative data** were generally reported for swab- and wipe-rinse testing outcomes;[9,10,13,14,18,48] quantitative results for HEPA-vacuuming tests were reported as collected sample concentrations (CFU^1/gm of total dust-mass). These reporting units[49] have little utility for estimating contamination surface-burdens (*e.g*., CFU per m^2; *see* Figure 4) and suggest lack of a coherent doctrine for decision-makers' interpretation and

use of surface-testing data in anthrax incident management.[14,16,17] No such doctrine has publicly surfaced to-date.[4]

CONCLUSIONS

Suggestions of relatively poor or uncertain performance of the recent surface-testing practices for anthrax detection are not surprising, in light of the numerous technical deviations of the disclosed procedures from their close analogs in the scientific literature. Improvements appear likely if the "prior art" is considered. Prudent initiatives should enable better civil preparedness for any future need of sensitive and reliable surface-testing in bioterrorism response: (a) attention focused on the details of testing technique, with respect for the relevant "legacy" science, (b) disciplined application of the recognized principles of quality assurance, (c) adequate Federal R&D support for such improvements (lacking to-date[50]) and for formal validation of testing methods, commensurate with their demonstrated importance to homeland security preparedness and (d) rigorous scientific peer review of the initial technical specifications, evaluations, validations, training and logistics of any environmental testing procedures authorized for use in a bioterrorism response.

References

1. *Abbreviations used:* ANSI: American National Standards Institute; APHA, American Public Health Association; APHL: Association of Public Health Laboratories; ASM: American Society for Microbiology; BSL: Biological Safety Level; CDC: Centers for Disease Control and Prevention; CFU: Colony Forming Units; DHS: Department of Homeland Security; DIN: Deutsches Institut für Normung e.V ("German Institute for Standardization"); EPA: U.S. Environmental Protection Agency; GAO: U.S. General Accounting Office; HEPA: High Efficiency Particulate Air; HEPA-vac: vacuum cleaners with HEPA filters installed for safety to remove fine-particulate aerosols from the exhaust airstream (different, non-HEPA "nozzle sock" filters were installed in intake hoses to collect environmental specimens); ISO: International Organization for Standardization; LRN: Laboratory Response Network for Bioterrorism; NASA: National Aeronautics and Space Administration; SBCCOM: U. S. Army Soldier and Biological Chemical Command; URL: Uniform Resource Locator; USPS: United States Postal Service.
2. Dr. Ellen Raber interview, Science & Technology Review, March, 2002. Lawrence Livermore National Laboratories, Livermore CA. Source URL: http://www.llnl.gov/str/March02/Raber.html.
3. EPA's Fact Sheet for the Hart Senate Office Building Cleanup, November 20, 2001. Available at URL (accessed January 23, 2002): http://www.epa.gov/epahome/headline2_112001.htm. *See also* U. S. Senate (2001) Approps. Subcmte. Hearing on the EPA and Federal Workplace Safety, November 28, 2001, Chairman: Sen. Barbara Mikulski (D-Md), Witnesses: EPA Administrator Christine Todd Whitman and Dr. John Marburger, Director, White House Office of Science & Technology Policy. Washington, DC. Streaming video archive available at URL (accessed August 8, 2003): http://cspanrm.fplive.net:554/ramgen/cspan/mdrive/ter112801_epa.rm. Ref. URL:

http://www.c-span.org/Search/basic.asp?BasicQueryText=workplace&safety &SortBy =date.

4. National Response Team (2003) Technical Assistance for Anthrax Response, Interim Final Draft, Phase I Update, November 2003. Available at URL (accessed May 22, 2004): http://www.nrt.org/production/nrt/home.nsf/Resources/publications1/$FILE/TADwithGAO_Revised11_4.pdf.
5. Comprehensive Procedures for Collecting Environmental Samples for Culturing *Bacillus anthracis*. CDC[1], April 25, 2002. URLs (superceded original 11/2001 release (*see* Note 7); accessed June 29, 2002): http://www.bt.cdc.gov/Agent/Anthrax/environmental-sampling-apr2002.asp; http://www.bt.cdc.gov/Agent/Anthrax/environmental-sampling-apr2002.doc; http://www.bt.cdc.gov/Agent/Anthrax/environmental-sampling-apr2002.pdf and http://www.cdc.gov/niosh/unp-envsamp.html.
6. For an epidemiological review of the 2001 multifocal-outbreak "anthrax incident" attributed to bioterrorism *via* letters mailed to U.S. Senators Daschle and Leahy and others, and of related public health responses, *see* Jernigan, D. B. *et al*. (2002) BIOTERRORISM-RELATED ANTHRAX: Investigation of Bioterrorism-Related Anthrax, United States, 2001: Epidemiologic Findings. *Emerg. Infect. Dis*. **8**(10):1019-1028. Available at URL (accessed October 6, 2002) http://www.cdc.gov/ncidod/EID/vol8no10/pdf/02-0353.pdf. For a broader perspective, *see* Atlas, R. M. (2001) "Bioterrorism Before and After September 11" *CRC Critical Reviews in Microbiology* **27**(4):355-379. Available on-line by subscription, at URL: www.crcjournals.com/.
7. Procedures for Collecting Surface Environmental Samples for Culturing *Bacillus anthracis*. CDC[1], Atlanta GA, November 13, 2001. URLs (accessed December 7, 2001): http://www.bt.cdc.gov/DocumentsApp/Anthrax/11132001/final42.asp and http://www.bt.cdc.gov/DocumentsApp/Anthrax/11132001/final42.pdf. Unaccountably, the included LRN[1] "Level A" laboratory procedures for processing swab specimens were omitted from the revision of this document (*see* Note 5).
8. Interim Guidelines for Sampling, Analysis, Decontamination and Disposal of Anthrax for U.S. Postal Service Facilities. USPS[1], Washington, DC, issued December 4, 2001. Available at URL (accessed May 2, 2002): http://www.apwu.org/departments/ir/s&h/anthrax/Protocol/120501_uspsissued_version.doc).
9. Sanderson, W. T., Hein, M. J., Taylor, L., Curwin, B. D., Kinnes, G. M., Seitz, T. A., Popovic, T., Holmes, H. T., Kellum, M. E., McAllister, S. K., Whaley, D. N., Tupin, E. A., Walker, T., Freed, J. A., Small, D. S., Klusaritz, B. and Bridges, J. H. (2002) Surface sampling methods for *Bacillus anthracis* spore contamination. *Emerg. Infect. Dis*. **8**(10):1145-1151. Available at URLs (accessed October 6, 2002): http://www.cdc.gov/ncidod/EID/vol8no10/02-0382.htm and http://www.cdc.gov/ncidod/EID/vol8no10/pdf/02-0382.pdf. *Also* Sanderson, W. T., Stoddard, R. R., Echt, A. S., Piacitelli, C. A., Kim, D., Horan, J., Davies, M. M., McCleery, R. E., Muller, P., Schnorr, T. M., Ward, E. M. and Hales, T. R. (2004) Bacillus anthracis contamination and inhalational anthrax in a mail processing and distribution center. *Jour. Appl. Microbiol*. **96**:1048–1056.

10. Rupert, R. Federal On-Scene Coordinator's Report for the Capitol Hill Site, Washington, DC. EPA[1] Region 3, Philadelphia, PA, 125 pp., August, 2002.
11. During the 2001 anthrax incident response, responsibility for the initial (presumptive) laboratory analysis for viable anthrax of environmental surface specimens was assigned exclusively to laboratories participating in the CDC[1]-administered LRN[1]: *i.e.*, local clinical labs (LRN Level A, for swab specimens only), and state and Federal labs (LRN Levels B/C, for swab, wipe and HEPA-vac[1] specimens). In 2002, these initial "rule out" testing responsibilities for environmental specimens were reportedly restricted to LRN Level B/C (since redesignated "confirmatory reference") labs exclusively; LRN Level A (now "sentinel") labs were restricted to analysis of clinical specimens only: *see* Note 5; *also* URL: http://www.bt.cdc.gov/lrn/factsheet.asp.
12. Basic diagnostic testing protocols for level A laboratories for the presumptive identification of *Bacillus anthracis*. CDC[1], ASM[1], APHL[1], Washington DC, October 24, 2001. Formerly available at URL (accessed January 26, 2002): http://www.asmusa.org/pcsrc/ban.asm.la.cp.102401f.pdf. Superceded by Laboratory Response Network (LRN) Level A Laboratory Procedures for Identification of *Bacillus anthracis*. CDC, Atlanta, GA, March 18, 2002. Available at URL (accessed June 25, 2002): http://www.bt.cdc.gov/Agent/Anthrax/LevelAProtocol/ban-la-cp-031802.pdf.
13. Weis, C. P., Intrepido, A. J., Miller, A. K., Cowin, P. G., Durno, M. A., Gebhardt, J. S. and Bull, R. (2002) Secondary Aerosolization of Viable *Bacillus anthracis* Spores in a Contaminated US Senate Office. *J Am Med Assoc* **288**(22):2853-2858. December 11, 2002. Available at URLs (accessed December 11, 2002): http://jama.ama-assn.org/issues/v288n22/rfull/joc21393.html and http://jama.ama-assn.org/issues/v288n22/rpdf/joc21393.pdf.
14. Report to the Ranking Minority Member, Committee on Governmental Affairs, U.S. Senate. U.S. Postal Service: Better Guidance Is Needed to Improve Communication Should Anthrax Contamination Occur in the Future. GAO-03-319, GAO[1], Washington, DC, April 2003. Available at URL (accessed April 22, 2003): http://www.gao.gov/new.items/d03316.pdf. *See also* Teshale, E. H., Painter, J., Burr, G. A., Mead, P., Wright, S. V., Cseh, L. F., *et al*. (2002) Environmental sampling for spores of Bacillus anthracis. *Emerg Infect Dis* **8**(10):1083-1087. Available at URLs (accessed November 8, 2002): http://www.cdc.gov/ncidod/EID/vol8no10/02-0398.htm and http://www.cdc.gov/ncidod/EID/vol8no10/pdf/02-0398.pdf.
15. Rose, L., Jensen, B., Peterson, A., Banerjee, S. N. and Arduino, M. J. (2004) Swab materials and Bacillus anthracis spore recovery from nonporous surfaces. *Emerg Infect Dis* **10**(6):1023-1029. Available at URLs (accessed May 25, 2004): http://www.cdc.gov/ncidod/EID/vol10no6/03-0716.htm and http://www.cdc.gov/ncidod/EID/vol10no6/pdfs/03-0716.pdf. *Also* Rose, L., Jensen, B., Westbrook, G., Peterson, A., Gallagher, K., Carr, J., Banerjee, S. N. and Arduino, M. J. (2003) Recovery Efficiency of Swabs for Sampling Hard Nonporous Surfaces for *Bacillus anthracis* Spores. CDC[1]/NICD/DHCQP, Atlanta, GA. Poster Q-369, ASM[1] Gen. Mtg. Washington, DC, May, 2003. Abstract available at URL: http://www.asmusa.org/memonly/abstracts/AbstractView.asp?AbstractID=80883.

16. Rhodes, K. and Ungar, B. (2003) U.S. Postal Service: Issues Associated with Anthrax Testing at the Wallingford Facility, Testimony Before the Subcommittee on National Security, Emerging Threats and International Relations, Committee on Government Reform. GAO-03-787T, May 19, 2003. GAO[1], Washington, DC. Available at URL (accessed April 22, 2003): http://reform.house.gov/UploadedFiles/051903%20KR%20ts.pdf. All written testimonies at this hearing (named "Stamping Out Anthrax in USPS Facilities: Technologies and Protocols for Bioagent Detection") are accessible at URL: http://reform.house.gov/NSETIR/Hearings/EventSingle.aspx?EventID=172. *See also ibid.*, URL: http://www.gao.gov/new.items/d03787t.pdf.
17. Hamilton, R. G. (2003) Written testimony before the Subcommittee on National Security, Emerging Threats and International Relations, Committee on Government Reform, U.S. House of Representatives. Available at URL (accessed June 11, 2003): http://reform.house.gov/UploadedFiles/051903%20RH%20ts.pdf. *See also* Hamilton, R. G. and Skolnick, E. B. (2003) *Ibid.*, oral testimonies: viewable as a C-Span streaming RealPlayer® media video archive, URL: http://cspanrm.fplive.net:554/ramgen/cspan/jdrive/smil/ter051903_anthraxhearing.smi, at elapsed times 00:22:28-00:29:45 and 01:35:50-01:45:00, respectively, of video Clip 1. Accessible *via* keyword search of c-span.org's long-term terrorism-related video archives, at URL: http://www.c-span.org/Search/basic.asp?BasicQueryText=anthrax&SortBy=date.
18. Evaluation of *Bacillus anthracis* Contamination inside the Brentwood Mail Processing and Distribution Center - District of Columbia, October, 2001. CDC[1], Atlanta, GA December 21, 2001. *Morb Mortal Wkly Rep* **50**(50):1129-1133. URL (accessed January 24, 2002): http://www.cdc.gov/mmwr/PDF/wk/mm5050.pdf.
19. See also variabilities revealed in one pre-9/11 comparative study at the Dugway Proving Ground UT of decontaminant systems, based on swab-rinse assay analysis: O'Connor, L. E. (2001) IRP-TR- A comparison of decontamination technologies for biological agent on selected commercial surface materials. April, 2001. SBCCOM[1] Biological Weapons Improved Response Program, Aberdeen Proving Ground, Maryland. Available at URL (accessed January 22, 2002): http://208.184.25.73/pdf/SBCCOM-Decon_tech_bio_agent1.pdf.
20. Thompson, M. W. The Killer Strain: Anthrax and a Government Exposed. 1st ed. April 1, 2003, HarperCollins, 256 pp, ISBN: 006052278X.
21. Maddox, M. (2002) APHL[1] Provides Leadership in Time of Terror, Brings "Order To Chaos" For USPS. *The APHL Minute* 2002(**2**):1, 26-29, March-April, 2002. Available at URL (accessed May 2, 2002): http://www.aphl.org/docs/newsletter/Mar.pdf.
22. Cf. Holmes, E. W.: Establishment and verification of reference values. Chapter 143, *Manual of Clinical Laboratory Immunology*, Sixth ed., 2002, American Society for Microbiology Press, American Society for Microbiology, Washington, DC.
23. NASA Standard Procedures for the Microbial Examination Of Space Hardware. NPG: 5340.1D (Final Draft). NASA[1], Washington, DC, January, 2000. URL (accessed February 14, 2002): http://centauri.larc.nasa.gov/discovery/FinalNPG_5340.1D.PDF. Preceded by versions successively designated as: NPQ-1 (June, 1966); NHB 5340.1 (1967), NHB 5340.1A (October, 1968) and NHB 5340.1B (March, 1980).

24. Kirschner, L. E. and Puleo, J. R. (1979) Wipe-rinse technique for quantitating microbial contamination on large surfaces. *Appl. Environ. Microbiol.* **38**(3):466-470.
25. Favero, M. S., McDade, J. J., Robertson, J. A., Hoffman, R. K. and Edwards, R. W. (1968) Microbiological Sampling of Surfaces. *J Appl Bacteriol* **31**:336-343. Also Angelotti, R., Foter, M. J., Busch, K. A. and Lewis, K. H. (1958): A Comparative Evaluation of Methods for Determining the Bacterial Contamination of Surfaces. *Food Res*. **23**:175-185.
26. Walter, W. G. and Hucker, G. J. (1941) Proposed method for the bacteriological examination of flat surfaces. *Amer. J. Publ. Hlth*. **31**(5) 487-490.
27. Walter, W. G. (1955) Symposium on methods for determining bacterial contamination on surfaces. *Bacteriol. Rev*. **19**(4):284-287.
28. Bestimmung des Oberflächenkeimgehaltes auf Einrichtungs- und Bedarfsgegenständen im Lebensmittelbereich - Teil 1: Quantitatives Tupferverfahren ("Determination of surface colony count on fitment and and utensils in foodareas - Part 1: Quantitative swab method"). DIN 10113-1 [1997-07]: DIN[1], Berlin, 9 pp. Catalogued at URL: http://www2.din.de/index.php?lang=en [Search on the term: "10113-"].
29. Speck, M. L. and Black, L. A. (1937) Effectiveness of cotton-swab methods in bacteriological examination of paper ice cream containers. *Food Res*. **2**(6):559-566.
30. Tiedeman, W. D., Fuchs, A. W., Gunderson, N. O., Hucker, G. J. and Mallmann, W. L. (1944) A proposed method for control of food utensil sanitation. Progress Report of the Subcommittee on Food Utensil Sanitation of the Committee on Research and Standards for 1943. *Am. J. Publ. Hlth*. **34**(3):255-258.
31. Buck, Jr., T. C. and Kaplan, E. (1944) A sterile cutting device for swab vial outfits utilizing wood applicators. *J. Milk Technol.* **7**:141-142.
32. Buchbinder, L., Buck, Jr., T. C., Phelps, P. M., Stone, R. V. and Tiedeman, W. D. (1947) Investigations of the swab rinse technic for examining eating and drinking utensils. *Am. J. Publ. Hlth*. **37**(4):373-378.
33. Powers, E. M. (1967) Microbiological burden on the surfaces of Explorer XXXIII spacecraft. *Appl. Microbiol*. **15**(5):1045-1048.
34. Barnes, J. M. (1952) The removal of bacteria from glass surfaces with calcium alginate, gauze and absorbent cotton wool swabs. *Proc. Soc. Appl. Bacteriol.* (Gr. BRit.) **15**:34
35. Manheimer, W. A. and Ybanez, T. (1917) Observations and experiments on dishwashing. *Amer. J. Publ. Hlth*. **7**(7):614-618. *See also* Note 25.
36. Stedman, R. L., Kravitz, E. and Bell, H. (1954) Studies on the efficiencies of disinfectants for use on inanimate objects. I. Relative activities on a stainless steel surface using a new performance test method. *Appl. Microbiol*. **2**(3):119-124.
37. Favero, M. S., Gabis, D. A. and Vesley, D. (1984) Environmental Monitoring Procedures. *In* Compendium of methods for the microbiological examination of foods, 2nd edit., Speck, M. L., ed., American Public Health Association, Washington, DC.
38. Whitfield, W. J., Beakley, J. W., Dugan, V. L., Hughes, L. W., Morris, M. E. and McDade, J. J. (1969) Vacuum probe: New approach to the microbiological sampling of surfaces. *Appl. Microbiol*. **17**(1):164-168.

39. Petersen N. J. and Bond, W. W. (1969) Microbiological evaluation of the vacuum probe surface sampler. *Appl. Microbiol*. **18**(6):1002-1006.
40. Whitfield, W. J. and Morris, M. E. (1970) The vacuum probe sampler. *Contamin. Control* **9**(2): 10-15, 25.
41. Farmer, F. H., Tulis J. J., Taylor, L. A. and Pace, Jr., V. A. (1971) Laboratory evaluation of the plastic vacuum probe surface sampler. *J. Amer. Assn. Contam. Control* **3**(2):15-18.
42. Marshall, R. T., *Ed.* (1992) *Standard Methods for the Examination of Diary Products*, 16th Edit., APHA[1], Washington, DC.
43. Puleo, J. R., Favero, M. S. and Petersen, N. J. (1967). Use of ultrasonic energy in assessing microbial contamination on surfaces. *Appl. Microbiol*. **15**(6):1345-1351.
44. Sterilization of medical devices - Microbiological methods - Part 1: Estimation of population of microorganisms on products. First ed., 1995-12-01. Ref. No. IS0 11737-I:1995(E). ISO[1]. Available for purchase from ANSI[1], Washington, DC. at URL: https://webstore.ansi.org/ansidocstore/product.asp?sku=ISO%2011737-1:1995.
45. Favero, M. S. (1968) Problems Associated with the Recovery of Bacterial Spores from Space Hardware, *Devel. Indust. Microbiol*. **9**(1):88-98.
46. Favero, M. S. (1971) Microbiologic assay of space hardware. *Environ. Biol. Med*. **1**(1):27-36.
47. Busta, F. F. and Ordal, Z. J. (1964) Use of calcium dipicolinate for enumeration of total viable endospore populations without heat activation. *Appl. Microbiol.* **12**(2):106-110.
48. Notice to Readers: Use of Onsite Technologies for Rapidly Assessing Environmental *Bacillus anthracis* Contamination on Surfaces in Buildings. December 7, 2001. CDC[1], Atlanta GA. *Morb. Mortal. Wkly. Rep.* **50**(48):1087. Available at URL (accessed January 24, 2002): http://www.cdc.gov/mmwr/PDF/wk/mm5048.pdf.
49. Reporting measured environmental analytes (*e.g*., household allergens) as amounts assayed per unit weight of collected dust mass (*e.g*., as μg/gm) has been the suitable analytical norm in recent clinical immunology practice, where a presumption that analytes of interest *are distributed uniformly in reservoir dusts* (which is unlikely for recent indoor dispersals of bioagents associated with acts of bioterrorism) appears to correlate well with clinical diagnoses. *E.g*., *see* Chew GL, Higgins KM, Gold DR, Muilenberg, M. L. and Burge, H. A. 1999. Monthly measurements of indoor allergens and the influence of housing type in a northeastern U.S. city. *Allergy* **54**:1058-1066. Available at URL (accessed January 9, 2004): http://www.blackwell-synergy.com/links/doi/10.1034/j.1398-9995.1999.00003.x/pdf.
50. Despite our diligent search, the only Federal extramural research support program yet identified post-9/11/01 which may have encompassed R&D support on improved environmental surface-testing methods within its stated mission area is the vaguely-worded EPA/ORD Special SBIR Phase I Solicitation No. PR-NC-03-10274, Safe Buildings and Water Security, issued March 27, 2003. Available at URL(accessed March 27, 2003): http://es.epa.gov/ncer/rfa/current/SBIR_special_phase1_s.pdf. Even here, no specific requirement for surface-testing methods improvement is stated and other program descriptions suggest that the scope of EPA's expressed

interest in such methods within this "Safe Buildings Program" may have been limited to remediation, *i.e.*, verification sampling (post-decontamination assessments) only. *See* Adams, N. The EPA Safe Buildings Program: Protection and Decontamination of Indoor Environments. November 14, 2002. EPA/ORD, Cincinnati OH. Available at URL (accessed February 3, 2003) http://www.ttclients.com/epatechbit_reg_sur/downloads/08_safebuildings.pdf. A recent DHS[1] solicitation offers some indication of supporting surface-testing methods-improvement R&D (see URL: http://www.hsarpabaa.com/Solicitations/FAQforBAA04-03-v15.pdf).

51. Report to the Chairman, Committee on Finance, U.S. Senate. Capitol Hill Anthrax Incident EPA's Cleanup Was Successful; Opportunities Exist to Enhance Contract Oversight. GAO-03-686, GAO[1], Washington DC, June 2003. Available at URL (accessed June 18, 2003): http://www.gao.gov/new.items/d03686.pdf.

*Revised from contents of Poster 205(M) (Topic Area: Environmental Sensors), as presented on March 9, 2004 at the ASM[1]-sponsored 2004 Biodefense Research Meeting in Baltimore, Maryland; Ref. URL: http://www.asmbiodefense.org/2004tueabs.asp#205M.

** A fourth "microvacuuming" method[5,1] (*see* **Table 1**) had little reported systematic use, and was not examined in the present study.

ORGANIC METHODS I

Extended abstract not received in time for printing.
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ENHANCEMENTS AND EXTENSIONS OF MICROWAVE-ASSISTED EXTRACTION FOR ENVIRONMENTAL APPLICATIONS

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The analysis of samples for organic analytes usually involves two major steps, sample preparation and instrumental quantitation. Advances in analytical chemistry have led to the development of instruments with extremely low detection limits and high sample throughput. In comparison, progress in sample preparation has lagged behind in sophistication and instrumentation. While analysis can be performed in a few minutes, sample preparation can take anywhere from hours to even days for completion.

Microwave-assisted-extraction (MAE) of organic analytes from different matrices is gradually gaining acceptance and preference in the present day analytical laboratory. The use of microwave-enhanced chemistry offers many advantages over traditional heating methods. Closed-vessel microwave extraction allows extraction solvents to be rapidly heated to 2-3 times higher than their atmospheric boiling points resulting in shorter extraction times (10-30 minutes). The amount of solvent consumed is considerably less (20-30 ml). Stirring is possible which makes the extraction conditions more homogenous, promotes interaction with the solvent and assists in releasing the analyte from the matrix. Integrated microwave extraction (IME) is perceived as an enhancement for microwave-assisted solvent extraction (MAE). Solvents are optimized for chemistry and microwave absorption is modified using secondary microwave absorbers enabling unlimited solvent applications. The salient features of IME are its equipment integration and secondary heating technology, which are aimed at overcoming deficiencies of MAE. Chemically specific solvent extractions can be carried out using this mechanism. This allows the analyst more selection over the compounds which are extracted from the matrix and also permits the traditional chemistry to be preserved. In addition, IME utilizes an equipment integration theme, which reduces some physical transfer steps for the analytes thereby decreasing the possibility of error.

A novel extension of MAE is microwave-assisted test tube extraction (MATTE). In MATTE, a small volume (1-3 mL) of a water sample is placed into a common test-tube and spiked with stable isotopes to be used for quantitation. To the test-tube, 0.5mL of the microwave transparent solvent *n*-nonane is added. Microwave energy is applied to the sample for 60-90 seconds. The high boiling (150ºC) nonane is a water immiscible solvent and is less dense than water. The short duration of microwave energy allows the water to rapidly heat up, driving any non-polar analytes into the nonane phase, which remains cool relative to the water. GC-MS analysis is then performed by a direct

injection of the nonane layer. MATTE followed by direct injection-GC-MS has been performed successfully on both water and soil samples and can even be extended to include volatile analytes that have traditionally been analyzed by purge-and-trap technologies.

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COMPARISON OF TWO DIFFERENT SOLID PHASE EXTRACTION/ LARGE VOLUME INJECTION PROCEDURES FOR METHOD 8270

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The first system is an automated closed system assembled from three principal units: a Spark Holland "Triathalon" autosampler and a "Prospekt II" dual solid phase extraction cartridge exchanger with a 2 mL syringe "HPD" solvent delivery pump, an ATAS GL Optic 3 for a 105 μL large volume injection (LVI) and an Agilent Technologies 6890 Gas Chromatograph with 5973 Mass Spectrometer. Sample application and solvent desorption were performed using Spark HySphere® C18 HD 7 μm and Varian Focus® Prospekt cartridges connected in series. It was found that the two different sorbent cartridges connected in series were required in order to obtain successful extraction of both polar and nonpolar compounds. Because the entire sample extract (105 μL) is transferred to the GC LVI port, the method is very sensitive and can use less sample (10 mL vs 1000 mL) and still provide detection at 10-100 times below the recommended Method 8270 limits. This system, coupled with a GC/MS, is the first of its kind in the United States.

The second system is comprised of the Horizon 4790 Solid Phase Extractors modified to accept 40 ml VOA vials, the ATAS GL Optic 3 Injection port and the Agilent Technologies 6890/5973 GC/MS. The Horizon 4790 Extractors accept samples from the original sample collection container, thereby eliminating a sample transfer step. The extractions which take approximately 30 minutes were performed using the JT Baker

H_2O-Philic DVB Bakerbond Speedisk® with 1 g of sorbent material. The sensitivity requirements of the method were met by injecting 25 µl of extract into the Optic 3 injection port with subsequent analysis by GC/MS using Method 8270.

Real samples from a creosoting site in Texas were used for the comparison study. Ten (10) samples containing low to high concentrations of PAHs, phenols and chlorophenol targets were extracted by both reduced volume procedures. The analytical results using the reduced volume methods were compared with routine methodology employed at the U.S. EPA Region 6 Laboratory. A cost/benefit analysis was also performed for all three methods. Method validation of the on-line system has included the analysis of four commercial performance test mixes (Environmental Resource Associates, blind study) including base/neutrals, acids, organochlorine pesticides and nitrogen pesticides. Method validation of the off-line system included an initial demonstration of capability, a method detection limit study and participation in performance test study.

INNOVATIVE MONITORING SYSTEM TO MANAGE THE RISK OF RELEASE TO THE SUBSURFACE ASSOCIATED WITH INDUSTRIAL AND COMMERCIAL USES OF VOLATILE ORGANIC COMPOUNDS

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Introduction

Industrial solvents such as methylene chloride, trichloroethene, tetrachloroethene (PCE) and other volatile organic compounds (VOCs) are used by a broad range of businesses, including auto body shops, printing firms, machine shops and dry cleaner facilities. The U.S. Environmental Protection Agency (EPA) estimates that solvent releases to the environment have led to VOCs being present in 20 percent of the nation's water supplies (Jennings *et al*. 1996). Many of these compounds are known or suspected carcinogens. VOCs used in industrial and commercial applications are released to the environment by spills or from leaking pipes, underground storage tanks or other mechanisms. When releases are discovered, environmental regulations mandate detailed investigation and design and implementation of a remedial action. The cost to business owners, property owners and insurance companies for mitigation of a release can be substantial.

Federal regulations have been passed mandating that petroleum storage facilities be designed to minimize the potential for spills and leaks and that these facilities be equipped with leak detection systems. The purpose of leak detection systems is to

identify releases to the environment soon after a release has taken place, before extensive impact to the environment occurs.

Such regulations have been effective in reducing VOC releases associated with the storage and use of petroleum. However, little has been done to effectively monitor for releases of VOCs in the majority of other commercial applications.

Releases of VOCs to the subsurface from these commercial VOC users often remain undetected until environmental investigations related to a property sale or an inspection conducted on an adjoining property detects the presence of VOCs in groundwater. At this point, the release may be years or decades old. Liability for a release and its associated cleanup costs falls back on the property owner and on the business, if the business still exists.

The dry cleaning industry is a classic example of this problem. Dry cleaner facilities use VOCs in commercial laundry machines to clean customers' clothing. PCE, a chlorinated VOC, is the most widely used solvent in the industry. The PCE is filtered after cleaning each load of clothing and is reused until the spent PCE is removed for recycling and the machine is recharged with new PCE. One recent study estimated that of the 36,000 active dry cleaning facilities in the United States, 75 percent are contaminated as a result of a PCE release (Linn *et al*. 2003). The principal source area has been the soil beneath the dry cleaning facility floor slab (Linn, 2004). The cost to remediate soil and groundwater associated with a release of PCE to the subsurface at a dry cleaner facility can range from $100,000 to over $1,000,000.

Farallon has developed a VOC monitoring system to monitor for releases to the subsurface at facilities where VOCs are used or stored. The Farallon VOC Monitoring System takes advantage of the head space created by porous soil beneath the effectively impermeable surface covering provided by concrete building foundation slabs or asphalt pavement. When released to the subsurface, VOCs diffuse into the soil vapor. The surface seal provided by a concrete building slab or asphalt surface prevents soil vapor from escaping to the atmosphere. The Farallon system employs a monitoring probe to facilitate soil vapor sample collection beneath building foundation slabs and other impervious surfaces. Routine collection of soil vapor samples and testing for the presence of VOCs using inexpensive detector tubes can identify a VOC release to the subsurface in a timely manner.

Volatile Organic Compound Behavior in the Subsurface

VOC contaminants are transported in the vapor phase by two means: advection and diffusion. VOC movement by advection is the physical transport of the contaminants by movement of the soil vapor. In soil, this can be the result of pressure gradients created by changes in atmospheric pressure and by thermal gradients that create density-driven flow. These advective mechanisms can create significant movement in soil vapor, particularly in the near surface.

In addition to advective mechanisms, VOC vapors are transported radially from a source by gaseous diffusion. Gaseous diffusion is the slow process of molecular intermingling and transport caused by random molecular motion and is described by Fick's first law (Hartman, 1997, 1998):

$$\textbf{Flux} = D_e \times dC_{sg} / dX$$

Where:

Flux = The rate of movement of a compound per unit area
$\mathbf{D_e}$ = Effective diffusion coefficient in the vadose zone
$\mathbf{dC_{sg}}$ = Contaminant concentration gradient in the soil vapor
dX = Distance

As applied to the movement of contaminants in the vadose zone, the mean distance VOC vapors can travel has been estimated using the following equation (Hartman 1997):

$$\textbf{Distance} = (2 \times D_e \times t)^{1/2}$$

Where:

$\mathbf{D_e}$ = Effective diffusion coefficient in the vadose zone
t = time

A conservative approximation of D_e for gaseous diffusion in soil is 0.01 cm^2/s (Hartman 1997). Thus, the mean distance that contaminant vapors can travel in the vadose zone in one year has been estimated as follows to be approximately 25 feet:

$$\textbf{Distance} = (2 \times 0.01 cm^2/sec \times 60\ sec/min \times 60\ min/hr \times 24\ hr/day \times 365\ day/yr)^{1/2}$$
$$= \sim 800\ cm$$
$$= \sim 25\ feet$$

Variables that affect the distance contaminated vapors will move are soil porosity and moisture content. The effective diffusion coefficient, D_e, increases with increased soil porosity. Conversely, D_e decreases with increased soil moisture (San Diego County, 2004).

VOC vapors in most porous soils can be expected to migrate distances of at least 25 feet within a 1-year period, with no consideration given to movement resulting from advective mechanisms. Advective mechanisms, in many cases probably the more significant of the two means of contaminated vapor movement, would serve to increase this distance. Thus, it can be expected that VOC vapors will migrate substantial distances in the subsurface, following a release to porous soil.

Farallon Volatile Organic Compound Monitoring System

Routine soil vapor sample collection and testing using a monitoring probe can monitor for the presence of VOCs in soil gas beneath a building foundation slab in areas where spills are likely to occur. Detection of VOCs in the soil gas would indicate the likely occurrence of a VOC release.

To facilitate the monitoring of soil vapor VOC concentrations, Farallon has designed a monitoring probe for installation in concrete slabs. The monitoring probe consists of a monitoring probe body, a monitoring probe cap, a monitoring port installation tool, a cap installation tool, a floor expansion fitting and a sampling adaptor.

Farallon VOC Monitoring System probe, including cap installation tool (top left), probe installation tool (bottom left), expansion fitting, monitoring probe with end filter and sampling adaptor.

The monitoring probe is installed in a 1 1/4-inch hole drilled into a concrete floor slab. The expansion fitting is inserted into the hole and expanded in-place with a bolt and spacer. The monitoring probe, with extension tube and end filter, is inserted through the building slab and into the soil below. The length of the monitoring probe can be adjusted to position the end filter in the soil just beneath the concrete slab. The probe is screwed securely in place with the probe installation tool. The probe installation tool sets into the probe with an unique male-female connector to prevent removal by others. Before the probe is screwed in place, the area around the probe is abraded and an epoxy adhesive is applied to ensure an air- and liquid-tight seal. The probe is closed with a double O-ring-sealed cap. The cap is screwed in place with the cap installation tool. The cap installation tool also sets into the probe with an unique male-female connection to prevent removal by others.

Farallon VOC Monitoring probe with cap partially installed. Also shown is cap installation tool.

To collect soil vapor samples from beneath the building foundation slab, the cap is removed and a sampling adaptor is installed. The adaptor facilitates connection to an air pump to purge soil vapor and collect soil vapor samples. Soil vapor VOC concentrations can be measured directly by using a variety of VOC detection instruments or by using colorimetric detector tubes designed to measure VOC concentrations.

Farallon technician measures VOCs in soil vapor using a detector tube.

The monitoring probe was developed to meet the following design criteria:

- Flexibility – The monitoring probe can be assembled in varying lengths to accommodate differing floor slab thicknesses and subsurface conditions. Floor

slab thicknesses vary, generally from 3 to 10 inches. The length of the probe can be varied to extend the filter into the soil beneath the slab.

- Robust – The monitoring port is designed for many years of use in commercial and industrial environments. The probe can be manufactured in brass or stainless steel to withstand potential abuse in these environments.
- Easy Installation – The system is easy and inexpensive to install. In less than one hour, the system can be installed and the first sample collected.
- Tamper-Proof – The monitoring probe cap can be installed or removed only by using an unique tool. Similarly, the monitoring probe itself can be installed or removed only by using an unique tool.
- Easily Sampled – The ease and low cost of conducting soil vapor sampling events make Farallon VOC Monitoring System use affordable. Routine soil vapor sampling can be accomplished in less than 10 minutes.
- Unobtrusive – The low-profile monitoring port design is unobtrusive and almost invisible in daily operations, which is desirable in commercial settings. The monitoring port also can be recessed into a concrete slab for an almost-flush surface installation.

Cost Advantages

The options available for VOC release detection are limited:

- Monitoring wells are used to detect contaminants that reach groundwater.
- Automated systems can detect leaks using electrical resistivity and thermal conductivity (Minnesota Pollution Control Agency 2001).
- Soil gas surveys can be used where soil access is possible at a facility.
- Soil gas also can be monitored using monitoring wells.

The expense associated with each of these approaches is considerable, ranging from several thousand dollars per soil gas survey to $10,000 or more for installation of an automated system.

Using the Farallon monitoring system to monitor soil vapor beneath a building where VOCs are used or stored can be relatively inexpensive. Samples can be collected within minutes and tested for the presence of VOCs using detector tubes that cost less than $10 each. A program of routine soil vapor monitoring can be implemented for as little as $500 per year.

Using the presence of VOCs in soil gas as an indicator of a VOC release to the subsurface enables detection of a release within months of occurrence. Although some contaminant migration in the subsurface will result, detection while impacts are relatively minor is facilitated, frequently before VOCs can migrate to groundwater and off the property, which would greatly increase the scope of subsequent remediation activities.

The costs associated with a subsurface release of VOCs escalate with the passage of time. A small quantity of a VOC release that reaches the subsurface can be relatively

inexpensive to remediate, if detected early. By applying inexpensive technologies such as soil vapor extraction, a shallow release in a porous soil generally can be cleaned up for between $10,000 and $175,000, inclusive of legal, consulting and construction costs. Once groundwater becomes involved, remediation costs can increase significantly. Even with only limited groundwater contamination on the property, a small-quantity VOC release can still cost as much as $650,000 to remediate. After groundwater contamination has moved off the property, remediation costs can easily escalate to over $1,000,000.

The cost of a routine soil vapor monitoring program, as low as $500 per year, is small relative to the enormous remediation liability associated with a release that goes undetected for years.

Current Applications and Results

The Farallon VOC Monitoring System is currently being used to monitor for PCE releases from dry cleaning facilities and for the presence of VOCs in soil gas beneath homes located above shallow groundwater contaminated with VOCs. At one dry cleaning facility in the Seattle area, the Farallon system is being used to monitor soil vapor beneath a building where a release occurred and was remediated using soil vapor extraction technology. Background levels of PCE ranging from 13 to 38 micrograms per liter have been measured in the soil gas. These levels are attributed to residual PCE in the soil that remains following remediation. This site is being monitored every 6 months for any significant increase in soil gas PCE concentrations that may indicate that a new release has occurred.

In homes in southwest Washington, the Farallon VOC Monitoring System is being used to determine if VOCs are migrating from a contaminated groundwater plume into the vadose zone and are affecting home indoor air quality. Farallon monitoring probes have been installed in homes to measure VOC concentrations in soil gas beneath home foundations.

References

Hartman, Blayne. 1997. “The Upward Migration of Vapors.” *L.U.S.T. Line Bulletin 27.* New England Interstate Water Pollution Control Commission. November.

———. 1998. “The Downward Migration of Vapors.” *L.U.S.T.Line Bulletin 28*. New England Interstate Water Pollution Control Commission. February.

Jennings, Gregory D., R.E. Sneed and M.B. St. Clair. 1996. “Volatile Organic Compounds (VOCs) in Drinking Water.” North Carolina Cooperative Extension Service. Publication Number AG 473-5. March.

Linn, William, *et al*. 2003. “Conducting Contamination Assessment Work at Drycleaning Sites.” No date. http://www.drycleancoalition.org/. (June 16, 2004.)

Linn, William, and Kristin Mixell. 2004. “Reported Leaks, Spills and Discharges at Florida Drycleaning Sites.” http://www.drycleancoalition.org/download/leaks/. (June 16, 2004.)

Minnesota Pollution Control Agency. 2001. “Leak-detection Systems for On-ground Hazardous Waste Tanks.” Waste/Hazardous Waste #2.19 Fact Sheet. June.

San Diego County. 2004. *Site Assessment Manual*, Appendix F: "Examples – Vapor-Phase Migration and Risk Evaluation." February 18.

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NEW TECHNOLOGY FOR AUTOMATED DRYING AND EVAPORATION/CONCENTRATION OF ENVIRONMENTAL SAMPLES FOR GC AND GC/MS ANALYSIS

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Extractions of aqueous samples typically require three steps to be performed: extraction, drying and concentration. Extraction is achieved by partitioning the analytes to a liquid (LLE) or solid (SPE) phase. Drying can be accomplished by sodium sulfate or PTFE membranes. Samples are concentrated by solvent evaporation.

Many LLE methods have been converted to SPE to take advantage of low solvent usage, better precision and automated extraction equipment. Automated SPE equipment produces approximately 20 mL of extract compared to 180 mL by LLE. The extract contains a mixture of analytes, solvents and residual water. Therefore, the sample must be dried and concentrated before analysis. Sodium sulfate is often used to dry the extract; however, hydrophobic membranes are now becoming popular because they are inherently inert and faster. They are comprised of a PTFE membrane which prevents water from passing through. Organic solvents and dissolved analytes, however, can easily pass through the membrane. Since the membrane has an infinite capacity to block water it eliminates the drying times (as much as 10 min) required for the SPE disk when using sodium sulfate.

This paper will present recently developed techniques and automated equipment for drying and concentrating environmental extracts. Recovery levels for many acid, base and neutral compounds will be presented in order to identify sample losses resulting from the concentration, drying and SPE steps. Finally, the overall extraction process will be characterized for a typical suite of EPA Method 8270 compounds.

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LC/MS MULTI-ANALYTE SCREENING METHOD FOR DELETERIOUS ORGANICS IN DRINKING WATER

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The determination of deleterious organics in drinking water is one of the particular areas of the Homeland Security Presidential Directive (HSPD-9) that will impact the EPA. It mandates that the EPA Office of Water expand monitoring and surveillance systems for recognizing a terrorist attack or a significant change in water quality. This is a daunting task because of the breadth of organics, coupled with the numerous water sources required to be monitored.

The ability to perform a multi-analyte "screen" for numerous organics simultaneously would help maximize efforts to note the presence and significance of poisonous agents. This requires a broad analytical approach strategy utilizing the specificity of liquid chromatography/mass spectrometry (LC/MS and LC/MS/MS). Many of these organics are not amendable to gas chromatography/mass spectrometry) GC/MS. Universal detection with high sensitivity is the key.

For non-MS detection methods, analyte resolution is critical for identification and quantification. However, the capability of MS to detect a single m/z (molecular weight/charge) gives analyte detection specificity that does not require chromatographic resolution. Thus, an "universal" reversed phase gradient providing a degree of analyte separation coupled with the specificity of mass spectrometry allows for the "screening" for multi-analytes simultaneously.

This presentation will discuss the development of a single, multi-analyte screening strategy for several deleterious pesticides and herbicides in drinking water using HPLC/electrospray mass spectrometry. This work is being conducted in collaboration with USEPA Central Region Laboratory Region 5. Several analytical issues will be raised to stimulate audience discussion and to solicit input to evolve this LC/MS strategy into a validated screening method template.

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TWO NEW PARTICLE-RELATED STANDARD REFERENCE MATERIALS FOR ORGANIC CONTAMINANTS

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A major component of particulate matter mass in ambient air is due to the association of organic chemicals with the material. Many of these may be source tracers or toxic that may ultimately cause adverse human and ecological health effects. As a result, the measurement of organic chemicals in atmospheric particles or particle-related samples, such as diesel exhaust, is often on-going in major cities throughout the world *via* ambient particle monitoring networks or chemical source profiling. Particle-related standard reference materials (SRMs) that are well characterized for organic chemicals assist with organic chemical measurement quality assurance and are useful for validating complete analytical procedures for these compounds including quantification. Several particle-related SRMs are available from NIST for the determination of organic chemicals, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, and pesticides, and these consist of actual particulate material. The newest particle-related material, SRM 1650b, diesel particulate matter, has been characterized for a range of PAHs, including alkyl and nitrogen-substituted PAHs. SRM 1650b is intended to replace its predecessor SRMs: SRM 1650 (originally issued in 1985 with an update provided in 1991) and SRM 1650a (issued in 2000). Both predecessors are no longer available, *i.e.*, their supplies are depleted. However, the diesel particulate material that was used to prepare SRMs 1650 and 1650a is the same as that used for the development of SRM 1650b. The material represents particles emitted from diesel fueled engines (four-cycle) operated over a variety of conditions. It has been bottled (in units of 100 mg) and analyzed using multiple methods of analysis to provide a range of certified and reference values for PAHs. SRM 1650b complements two other diesel particulate-related SRMs that are currently available: SRM 2975, diesel particulate matter (industrial forklift) and SRM 1975, diesel particulate extract which is a dichloromethane extract of the same material used to prepare SRM 2975. The second newest particle-related SRM is SRM 2585, household dust, is composed of actual household dust and will be characterized for PAH, PCBs, pesticides and even polybrominated diphenyl ethers (PBDEs). The characterization of the PAH content, including the nitrosubstituted PAHs, of SRM 1650b will be presented. PAH concentrations will be compared to those determined in the previously available dieselparticulate matter SRMs (1650 and 1650a). Also, several higher molecular mass

PAHs (300 and 302) were determined in SRM 1650b using a selective liquid crystal gas chromatographic column. These measurements will be reviewed and compared to those present in other SRMs including a coal-tar extract. In addition, the determination of the concentrations of organic contaminants, including PBDEs, in SRM 2585, household dust, will be presented.

INORGANIC METHODS I

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NATIONAL INORGANIC METHODS PROGRAM FOR RCRA

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This presentation gives an overview of the RCRA Inorganic Methods Program. This presentation will discuss the important current as well as future RCRA Inorganic Methods Program activities, including the publication of the final Methods Innovation Rule (MIR) and Update IIIB, IVA and IVB methods; the status of the RCRA Waste Sampling, Draft Technical Guidance and the new SW 846 methods for mercury speciation, for metal cyanide complexes and for clarification of the scope and applicability of existing preparation methods for metals analysis.

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MICROWAVE-ASSISTED SOLVENT EXTRACTION FOR THE QUANTITATIVE SIMULTANEOUS EXTRACTION OF INORGANIC MERCURY AND METHYLMERCURY FROM SOILS

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The need for mercury speciation analysis techniques has necessitated development of a rapid and efficient solvent extraction method capable of removing both inorganic and organic mercury species from a soil matrix. A microwave-assisted extraction method

was developed using a mixture of organic and inorganic solvents with resultant high extraction efficiency. The samples were then analyzed by ion chromatography coupled to inductively coupled plasma mass spectrometry. Optimization studies showed that extraction conditions must be controlled carefully in order to prevent incomplete extraction or interconversion of species during extraction. Under optimized conditions, recoveries for inorganic mercury (Hg^{2+}) and monomethylmercury (CH_3Hg^+) were measured to be 97 ± 10 % and 96 ± 3 %, respectively. The detection limits, defined as three times the standard deviation of nine repeated scans of a spiked soil extract, were 3 and 15 ng/mL for Hg^{2+} and CH_3Hg^+, respectively. The developed method was successfully applied to mercury speciation analysis in two soil samples and a NIST soil standard reference material with a certified total mercury concentration.

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INTER-LABORATORY VALIDATION OF EPA METHOD 3200 FOR MERCURY SPECIATION ANALYSIS USING PREPARED SOIL REFERENCE MATERIALS

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Mercury speciation analysis from environmental samples has been a field of growing interest. Such interest is mainly due to the toxicological impact, ecological problems and biogeochemical cycling of mercury involving distribution, accumulation, transformation and transport pathways in the natural environment. The techniques used for the determination of mercury species in soils and sediments generally involve a series of analytical steps (*e.g.* extraction, separation, detection) that may all be prone to systematic errors. An inter-laboratory validation study of the EPA Method 3200 was conducted by the United States Environmental Protection Agency (U.S. EPA) on two

specifically prepared soil reference matrices. The study has been performed successfully by a limited number (six) of participating laboratories. Evaluation of the reported data compared to the literature methods demonstrates that draft method 3200 is more highly efficient for extraction of methylmercury than inorganic mercury. EPA Method 6800 was used to validate this method and found that, in comparison to the other literature methods, it had the highest extraction efficiency for both inorganic and methylmercury fractions and did not induce transformations of the mercury species. The design of the draft method 3200, including mass balance options, permits mercury recovery in multiple ways. Several options for species categories include semi-mobile and non-mobile mercury, the less mobile and less toxic inorganic species and other species categories.

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ELEMENTAL SPECIATION: AN ENVIRONMENTAL AND FORENSIC CHALLENGE AND AN APPROACH TO THE ANALYSIS UNCERTAINTY

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Elemental speciation is one of the most challenging analytical measurements. To make matters worse, there is a devastating lack of both standards and diagnostic tools inhibiting the progress of the field. Some elemental species undergo conversion or degradation of the species of interest during sampling, storage, sample preparation and the measurement steps. Two elements that are well known examples of difficult species that exhibit this behavior are the many species of mercury and chromium. Until recently there have been no diagnostic tools to trace the fate of species since conventional speciation methods can only measure the species' concentrations in the final solutions at the time of measurement. Knowing the transformation of the species is critical in the development and validation of methods and for the certification of standard reference materials.

Speciated isotope dilution mass spectrometry (SIDMS, RACA method 6800), which addresses the correction for such degradation or conversions[1,2], has been developed

and successfully addresses these difficult measurement needs. It has been demonstrated to accurately determine the species' concentrations at both the time of spiking and measurement. SIDMS has the potential to be used as a diagnostic tool to validate other methods and to certify speciated standards. By spiking the sample at each step with enriched stable isotopes of the same species, SIDMS can be used as a diagnostic tool to identify the steps at which the species are altered[3]. The unique sample preparation requirements of species in samples will be addressed.

The method of SIDMS, Method 6800, has been evaluated and validated or is under validation for different species[4,5]. The SIDMS method will be presented with practical examples and demonstrations of real and difficult measurements. SIDMS is also a diagnostic tool, as well as being a legally-defensible measurement method. This method enables the development of other test methods that are needed to evaluate environmental and other dynamic species but are not capable of self-validation.

Speciated measurements are not about mass spectrometers, and never have been, as these are tools to measure mass. Speciation is all about sample preparation to enable speciated measurement in dynamic chemistries. Speciated measurements of many kinds are now evolving as a key to understanding and controlling not only environmental but also industrial, biological, medical and many other applied areas. Speciated equilibrium where a delicate balance controls the conditions are now addressable by the SIDMS method and a new depth of chemical understanding is achievable.

One limitation that has been retarding the use of SIDMS is the lack of standards that are isotopically enriched for use in this method. Up until recently they have not been available and now are just starting to be made to support this method[6]. Enabling support will be described to permit access by laboratories to the SIDMS procedure for many types of speciated measurements. In addition, mathematical support is being prepared at Duquesne University in conjunction with EPA RCA to enable the solving of one, two and three species transformational problems. This support is being developed by a diverse team of researchers to enable laboratories to gain access to this technology.

1. "Chapter 10: Application of Isotope Dilution in Elemental Speciation: Speciated Isotope Dilution Mass Spectrometry". Dengwei Huo and H. M. "Skip" Kingston. In *Elemental Speciation-New Approaches for Trace Element Analysis*, Sutton, K. L. and Caruso, J. A. Eds.; Elsevier Science, Amsterdam, Netherlands, 2000.
2. Kingston, H. M. "Skip". Patent 5,414,259. "Method of Speciated Isotope Dilution Mass Spectrometry", U.S. Patent Office, Granted May 9, 1995.

SIMULTANEOUS DETERMINATION OF SEVERAL INORGANIC SPECIES IN WATER WITH A DYNAMIC REACTION CELL AND ICP/MS

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Introduction

Speciation of metals is increasingly important for environmental and biomonitoring. The form of the metal can alter the toxicity, bioavailability and potential to migrate in the environment. These considerations for speciated analysis will be discussed. The development of methodology for two applications and the potential for rugged analyses will be explored.

Arsenic, chromium and selenium speciation in drinking water and wastewater was examined. Separation by HPLC and detection with ICP-MS was optimized. The potential for measuring three elements in the same run was evaluated. The developed method was tested on a number of water samples and results will be presented.

This offers an alternative, sensitive measurement compared to current methods and may also offer advantages in interference reduction. Detection limits and recoveries in samples demonstrate method capability. The resulting fast, sensitive method will be described and the utility in routine laboratories explored.

Experimental

Tables 1 and 2 show the HPLC and ICP-MS conditions developed for the method. The water samples examined were obtained from home taps, purchased bottled water and a municipal wastewater plant. The samples were stored chilled, without acid added. Dilutions were made with mobile phase to minimize pH disturbances.

Table 1. HPLC Conditions used for separation of species.

HPLC System	PerkinElmer® Model 200 Quaternary Pump, Column Oven and Autosampler
Column	Pecosphere C8 – 3 mm packing, 3-cm long
Mobile Phase	0.1 mM TBAOH + 0.15 mM NH_4CH_2COOH + 0.15 mM + EDTA (K salt) + 5% MeOH
pH	7.5
pH Adjustment	Dilute HNO_3, NH_4OH
Injection Volume	50 μL
Sample Preparation	Dilute with mobile phase (2-10x); heat at 50-55^{o}C for 10 min.
Samples	Various waters (non-acidified)

Table 2. DRC ICP-MS instrumental conditions.

Instrument	PerkinElmer ELAN DRC™ II
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Analytes	AsO^+ (m/z 91) Se^+ (m/z 78) Cr^+ (m/z 52)
Reaction Gas	O_2 = 0.7 mL/min
RPq	0.6
Dwell Time	330 ms (per analyte)
Analysis Time	150 sec

The ELAN DRC II was chosen for the analysis because of the ability to achieve low detection limits and remove interferences that degrade detection limits. The Dynamic Reaction Cell (DRC) is used to react the sample with a gas, prior to entering the analytical quadrupole, to remove the interference or to move the desired analyte to a different mass. The reactions are well-controlled and competing reactions removed. Arsenic was measured at mass 91, as the oxide, to eliminate the interferences from $CaCl^+$ and $ArCl^+$ at mass 75.

Method development included the evaluation of salt content on the chromatographic separation. This is important since the salt content of waters varies significantly. The chromatographic separation becomes critical when additional analytes are combined into a fast run. Although the detector is very specific, species separation must be achieved. Salt does influence the chromatography, but separation can be achieved in most waters.

Calibration was performed for each species over the range 0.25-10 ppb. Figure 1 shows the calibration curves obtained for Cr.

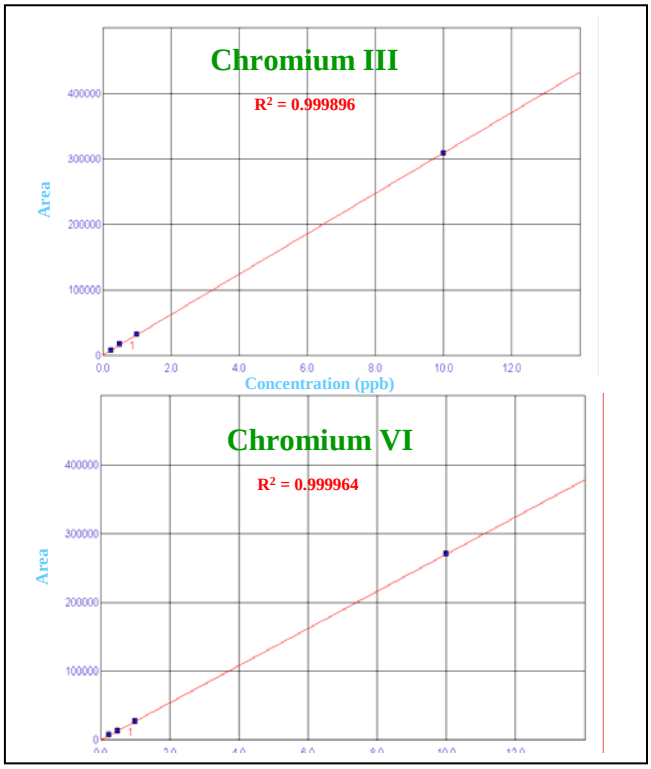

Figure 1. Calibration curves for Cr^{+3} and Cr^{+6}

Results and Discussion

A variety of water samples were examined to evaluate the developed method. Each type of water sample, in fact each individual water sample, is different and may provide unique challenges. Water from public supplies, residential wells, bottled water and municipal wastewater were examined. Figures 2-5 show representative chromatograms of various samples.

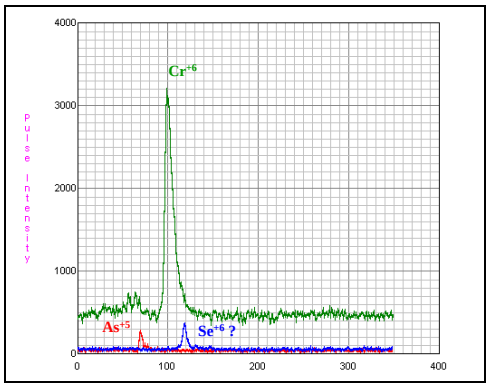

Figure 2. Glendale public water, 4x dilution

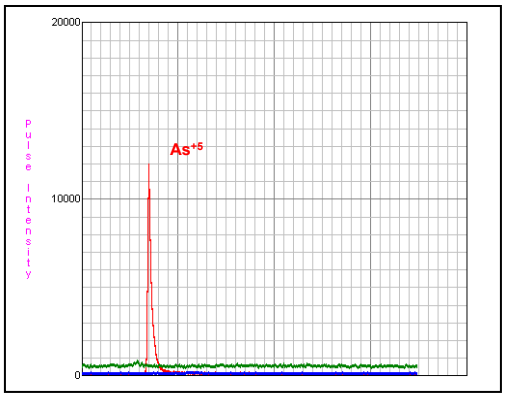

Figure 3. Oxford well water, 10x dilution

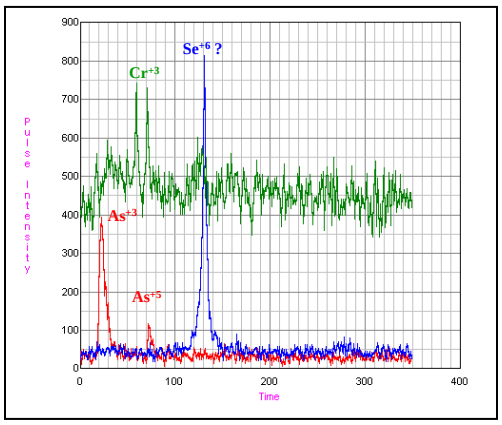

Figure 4. Bottled water A

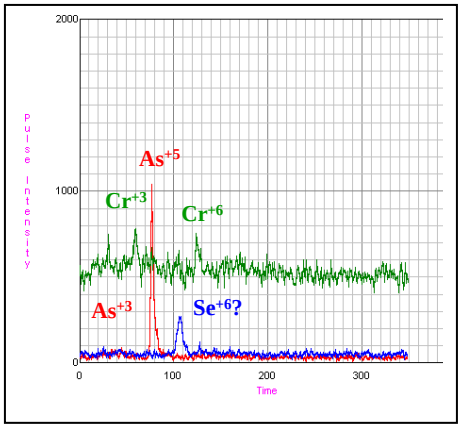

Figure 5. Municipal wastewater, 2x dilution

In several cases unidentified selenium species were detected. It is unclear if the species are selenium VI species that have shifted due to pH or matrix conditions or if they are a different species. Further investigation may more clearly identify the species.

Table 3 shows quantitative results for a variety of water samples.

Table 3. Results for speciated analysis of a variety of waters (ppb)

Sample	As^{+3}	As^{+5}	Cr^{+3}	Cr^{+6}	Se^{+4}	Se^{+6}	SeCN
Glendale Public	---	0.15	---	4.3	---	2.4	---
Oxford Well	---	30	---	---	---	1.6	---
Guangzhou Public	0.16	---	0.003	---	0.18	1.1	---
Municipal Wastewater	---	0.40	---	---	---	1.2	---
Bottled - A	0.36	0.03	---	---	---	2.7	---

Conclusion

Speciated analysis continues to develop. Understanding of the effects of pH and matrix components on the chromatography continues to advance. The ability to examine multiple elemental species in a short chromatographic analysis more closely matches the chromatography to the rapid multielemental analysis capability of the ICP-MS. Low detection limits, free from interferences, are critical in detecting the small amounts of each species present in natural samples.

Although speciation analysis in general is not routine, water analysis is rapidly moving in this direction. The sample preservation and preparation steps are less well understood and are minimal for this type of sample. Separation and detection of the species has advanced to a multielement form for several elements. Investigations into additional elements, singly, or in combination with the elements discussed, continue.

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NEW DEVELOPMENTS WITH HPLC-ICP-MS AND GC-ICP-MS INSTRUMENTATION FOR ROUTINE SPECIATION ANALYSIS

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The technique of chemical speciation has been a popular research area for almost twenty years, with the use of hyphenated techniques becoming *de-rigueur*. As the sample preparation and quantitation techniques have become more robust, it has become more viable to formulate legislation based on acceptable concentration levels of speciated metals. The possibility of legislation is prompting a growing interest in speciation analysis from laboratories that are engaged in the routine, commercial application of ICP-MS.

This presentation will highlight new developments with HPLC-ICP-MS and GC-ICP-MS instrumentation for routine speciation analyses and describe methodologies to enable rapid separations of some topical elemental species in selected environmental and biological samples. Topics covered will include the actual hardware and software required as well as aspects important to a routine laboratory such as ease of use, flexibility to do other work and productivity. The latter is influenced not only by the

sample throughput but also the expected change-over and setup times for the majority of laboratories who will not have a dedicated speciation ICP-MS.

ENSURING THE INTEGRITY OF LABORATORY DATA

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LABORATORY FRAUD

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This presentation deals with the occurrence and types of laboratory fraud that are being found by the Office of Investigations at environmental laboratories across the country. Current trends will be discussed as well as our strategic plan to deal with the problem.

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COMPLIANCE AND OVERSIGHT IN THE AFTERMATH OF ENRON AND ARTHUR ANDERSON

John J. Pavlick
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John J. Pavlick, a partner in the Washington office of the law firm Venable LLC, will examine and discuss the role of compliance, oversight and accountability following the financial scandals involving Enron, Arthur Andersen, Tyco and others. He will examine the reaction of Congress in passing Sarbanes-Oxley and other legislation addressing corporate responsibility and accountability. While much of this legislation is aimed at large, publicly traded companies, some of the laws passed by Congress in response to these scandals have much broader application. In addition, these laws and related regulations and policy changes have generated an increased focus on the responsibility of officers and directors of corporations of all sizes for the actions of their companies. This is coupled with the need to have effective controls in place to ensure that companies do not break the law or mislead or defraud investors or the public. Mr.

Pavlick will discuss what this means for companies of all sizes and how officers and directors can avoid problems.

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ENVIRONMENTAL LABORATORY DATA INTEGRITY INITIATIVE

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The Environmental Laboratory Data Integrity Initiative (ELDII) is a program of the American Council of Independent Laboratories (ACIL) dedicated to enhancing both ethical practices and data integrity in our industry through the application of a systems approach. This is a rigorous process of guaranteeing your laboratory's data quality and integrity while promoting greater acceptance and recognition for your firm in both the public and private sector. The program, founded on 15 basic principles, is designed to bring laboratories to a point where production of data of known and documented quality is assured and where such data become a fundamental product of our industry. Laboratory application to Signatory status begins with a careful review of the ELDII Policy Statement, available on the ACIL Web site at www.acil.org under Publications. The Guidance Document and application are also available there. Application also involves a stringent review and possible site visits by the independent consultant reviewers.

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LEARNING, UNLEARNING AND RELEARNING: THE EMERGENCE OF ONLINE LEARNING AS AN ESSENTIAL BUSINESS TOOL

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"The illiterate of the 21st century will not be those who cannot read and write, but those who cannot learn, unlearn and relearn." Alvin Toffler, futurist

Compared to even five years ago, it would be hard to find a set of corporate goals and objectives that does not make reference in some way to the lofty goal of "continuous learning" for its employees. Companies large and small—from the five-person laboratory to the multi-national conglomerate—have fallen hard for "human capital improvement" strategies that strive to make employees more effective, entrepreneurial, ethical, innovative and competitive over time.

What's not to like about this trend? In a perfect world, it makes perfect sense to empower employees and organizations with a continuous stream of knowledge strategies—or learning paths—that enhance performance.

Unfortunately, while the benefits are undisputable, the learning paths most traveled (or at least, often traveled) by companies involve strategies that either:

- Have a hard time making it from the drawing board to front line or
- Suffer from perennial fatal flaws, such as poor content and organization, excess expense or inconvenience.

To address some of these concerns, many companies have turned to online learning as a means of incorporating additional layers of control, accountability and efficiency into their "learning organizations." And, while online learning is no panacea for inherent corporate performance issues, many corporate leaders believe that a practical, well-constructed online learning approach offers companies a real opportunity to effect change without encountering some of the more traditional pitfalls.

This paper provides conferees with an overview of the "emergence of online learning as an essential business tool", with sections that focus on:

- Who is doing what and how in corporate America?
- Online Education: More convenient, More effective and Less expensive

- Accessibility: Education Driving Technology instead of Technology Driving Education
- PowerPoint Presentations and Talking Heads Versus Interactive Instructional Design: What's the difference?
  - o Content Organization and Presentation
  - o Passive Learning Versus Active Learning: Using Learning Challenges to Support Comprehension
  - o What's Going On? Individual and Corporate Diagnostics
  - o The "Take Away": Providing Learners with a Portable Toolset to Meet "Real World" Challenges.

Example: The new ACIL/ILI online ethics program designed to satisfy EPA ethics training requirements.

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PERFORMANCE TEST STUDIES: INTEGRAL TO LABORATORY DATA INTEGRITY PROGRAMS

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Performance test (PT) studies have long been a critical component of environmental laboratory certification and approval programs. Laboratory quality assurance programs often use the PT results for corrective actions in operations to ensure continuing certification to perform analyses or qualification for analytical contracts. PT studies, however, are now becoming an integral part of the modern laboratories data integrity programs. This paper discusses the implementation of PTs into a laboratory data integrity program. The PT studies are used to document analyst and laboratory capability as outlined in the Environmental Laboratory Data Integrity Initiative (ELDII) developed by the American Council of Independent Laboratories (ACIL). Single blind PTs are the typical test samples where the analyst and laboratory know it is a test but do not know the components or concentration. Single blind PTs are useful for certifications and for demonstrating adherence to laboratory procedures and method requirements. Although single blind PT samples are known tests, these samples are

analyzed with the routine calibrations and instrumentation used for routine samples. Double blind PTs are test samples that the laboratory does not know are test samples and generally provide more information on the routine analyses in the laboratory. Double blind PTs can also be used to monitor and document everyday operations. Questions of data integrity that can arise from possible improper practices can often be addressed effectively from both single- and double-blind PT data, particularly regarding calibration and instrument operational issues or long-term systematic improper practices. Even the knowledge of potential double-blind and single-blind PT samples being included in the laboratory routine analytical runs helps deter questionable behavior or momentary loss of ethics in an organization.

Data will be compared from single-blind PT results with double-blind PT results to evaluate the effectiveness of the double-blind studies. The use of the PT samples in addressing data integrity problems, protecting laboratories from questionable practices and validating laboratory performance will be demonstrated.

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LABORATORY INAPPROPRIATE PRACTICES: PAST AND PRESENT

Steve Baker

No abstract available.

ENSURING THE CHARACTERIZATION OF MIXED WASTES AT DOE SITES

U.S. DEPARTMENT OF ENERGY'S MIXED-ANALYTE PERFORMANCE EVALUATION PROGRAM (MAPEP)

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The Mixed Analyte Performance Evaluation Program (MAPEP) is administered by the U.S. Department of Energy's Radiological and Environmental Sciences Laboratory (RESL). The MAPEP is the only PE program that targets radiological and non-radiological constituents (*i.e*., mixed analytes) from the same sample for quantification and analytical performance evaluation. MAPEP standards are representative of real-world DOE samples where radiological contaminants are commonly found in the environment with stable inorganic or organic contaminants. The term "mixed" refers to the presence of different analyte types and does not mean that MAPEP is a mixed-waste sample or program or that MAPEP samples become mixed waste when analyzed. Instead, the purpose of the program is for MAPEP participants to efficiently demonstrate their proficiency in radiological, stable inorganic and organic analyses from the same single blind performance evaluation sample.

The MAPEP was created by the Analytical Services Division of DOE Environmental Management in 1994 to evaluate performance of laboratories analyzing samples containing mixtures of analyte types for DOE. Participation in the program is primarily for laboratories performing work in support of the DOE mission. MAPEP standards are prepared and reference values are derived from spiking a background natural matrix with National Institute of Standards and Technology (NIST) traceable standards whenever feasible. As part of an ongoing quality assurance program, RESL participates in a Radiological Traceability Program with NIST. Through continuing successful participation in this program, RESL is traceable to NIST for both sample preparation and analysis. Analyte concentrations in MAPEP standards are typically well above detection limits, with the exception of the false positive tests which will be discussed later. MAPEP is performance-based, meaning that laboratories may use any method of their choosing to analyze the samples. Acceptance criteria for analytical data are listed in Table 1.

Table 1. MAPEP acceptance criteria.

FLAG	MEANING	CRITERIA FOR RADIOLOGICAL AND INORGANIC ANALYTES	CRITERIA FOR ORGANIC ANALYTES
"A"	Acceptable	Bias <= 20%	Absolute value of Z-score <= 2.0
"W"	Acceptable with Warning	20% < Bias <= 30%	Absolute value of Z-score 2.0 < Z-score <= 3.0
"N"	Not Acceptable	Bias > 30%	Absolute value of Z-score > 3.0

MAPEP samples were previously distributed twice per year, with the soil matrix being distributed in July and the water matrix in January. In response to the recent termination of the Quality Assessment Program (QAP), a memorandum from Frank Russo (EH-3) dated June 8, 2004, directed RESL to "provide additional performance testing to former QAP participants through the MAPEP…." which perform analytical work that supports the DOE mission. As a result, RESL has expanded the MAPEP program to provide additional matrices and increased distribution frequency. The following matrices will be distributed twice per year, in July and January: mixed-analyte soil (containing radiological, inorganic and semi-volatile organic constituents), mixed-analyte water (containing radiological and inorganic constituents), water containing semi-volatile constituents, gross *alpha*/*beta* water, gross *alpha*/*beta* air filter, air filters containing radiological constituents only and vegetation containing radiological constituents only. Distribution of these matrices will begin July 2004 except for the vegetation, which will begin in January 2005.

An unique feature of MAPEP is false positive testing. A false positive result occurs if the analyte is detected in a sample, when in fact the analyte is not in the sample or is present below the detection threshold of the measurement. MAPEP requires that laboratories report results, including total propagated uncertainties (TPU), for a variety of radionuclides, some of which may not have been added to the standard. If the range of the result $\pm$ 3 times the TPU does not include zero, the result is flagged as a false positive and the laboratory receives an "N" on their report. False positives reported by a laboratory may result in increased cleanup costs due to increased sampling and analysis requirements. Repeated false positives also lead to decreased public confidence in the cleanup process if these results are reported and then later retracted. If non-radioactive analytes are present at hazardous concentration levels, as defined by the Resource Conservation and Recovery Act (RCRA), and radioactive material is also present, a mixed analyte material may become a mixed waste. Mixed waste has very stringent and expensive disposal requirements and DOE must ensure there are no

compliance violations. Conversely, the taxpayer should not pay for a mixed waste disposal if there is no reason to do so.

Results of MAPEP false positive tests show a considerable number of false positives reported by the laboratories. Nearly half of the laboratories reported false positives for ^{238}Pu and ^{90}Sr in water. The overall false positive rate for the radiological constituents is 34%. Clearly, this is a problem for DOE and it is particularly worrisome because of the single-blind nature of the MAPEP standards. The laboratories know that they are analyzing and reporting on a known PE sample, therefore one would expect that this represents their maximum capability. These results should lead data reviewers to question how many false positives may be reported on routine samples.

Table 2. Percentage of laboratories reporting false positives.

Nuclide	Water	Soil
^{238}Pu	49%	35%
$^{239/240}Pu$	35%	19%
^{241}Am	15%	32%
^{90}Sr	48%	37%

Another problem identified by the MAPEP program is the under-reporting of antimony (Sb) in soil. Antimony results for the MAPEP-03-S10 study are shown in Figure 1. The EPA Method 3050B “Acid Digestion of Sediments, Sludges and Soils” provides an alternative leaching scheme for the analysis of antimony, which most laboratories are not using. Using the alternate leaching scheme, RESL determined the antimony value to be 19.84 mg/Kg, with the reference value being 19.89 mg/Kg. However, using the standard leaching scheme resulted in values of about 20% of the reference value. This case illustrates a potential for false negative results if the laboratory does not use the proper digestion procedure on DOE samples.

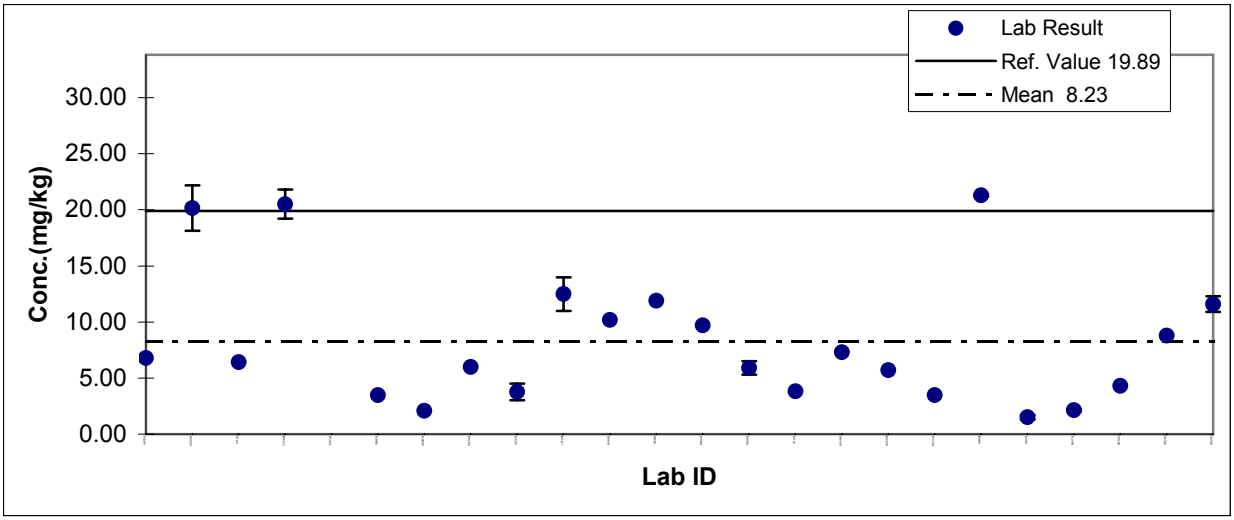

Figure 1. Antimony results for MAPEP-03-S10

The MAPEP program has great flexibility to respond to the needs of DOE facilities and to prepare standards that are relevant to the DOE mission. Plutonium (Pu) at DOE facilities may be in a refractory form, making it difficult to dissolve for analysis. The MAPEP-02-S9 soil was prepared to contain refractory ^{239}Pu and non-refractory ^{238}Pu. The results of the two nuclides were compared to evaluate the effectiveness of the laboratories' procedures for the analysis of refractory Pu. A comparison of ^{238}Pu and ^{239}Pu results for each laboratory is presented in Figure 2. Overall, the laboratories performed well, with only one laboratory receiving an "N" flag and two receiving "W" flags. There is a noticeable trend that the ^{239}Pu results tend to be biased lower than the ^{238}Pu results. Had both nuclides been in the same chemical form, there should be no difference between isotopes. The more negative bias of the ^{239}Pu results indicates that the laboratories are getting less of the refractory isotope out during the digestion procedure than the non-refractory ^{238}Pu.

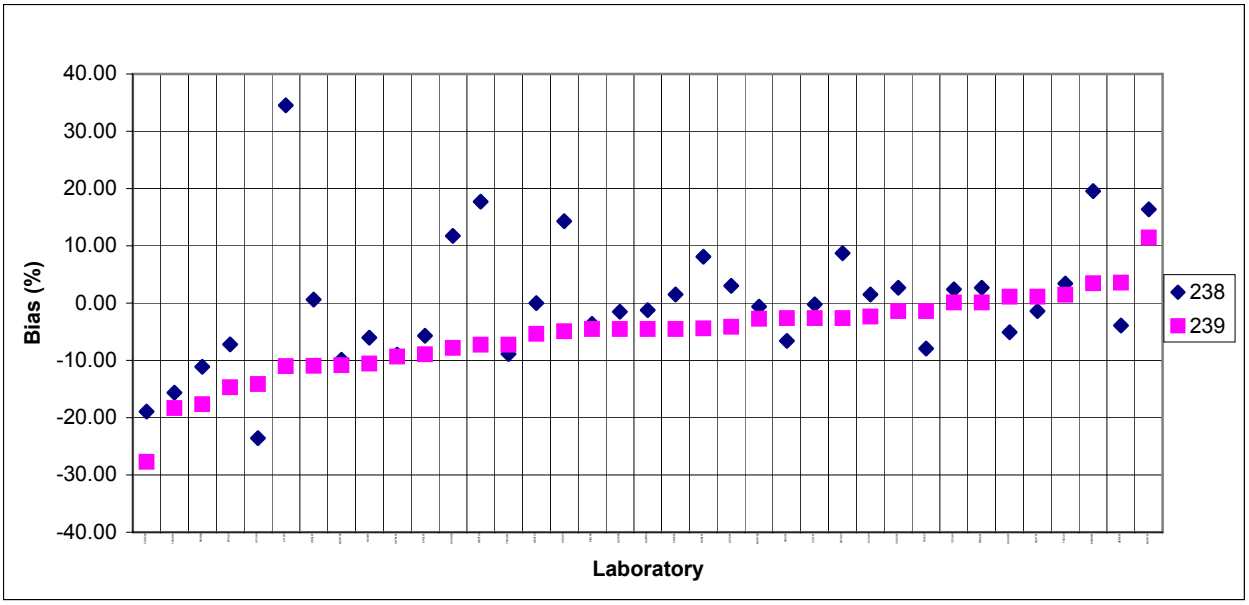

Figure 2. ^{238}Pu and ^{239}Pu bias by laboratory.

In addition to the results, MAPEP requests that laboratories submit information related to the analyses of the standards, such as the type of sample preparation, sample size, instrumentation used, etc. This gives MAPEP more data to help evaluate the possible reasons for failure or success of laboratories in the program. MAPEP provides technical support to help laboratories understand and solve quality problems that are identified by their participation in the program. MAPEP is in the process of updating its web-based reporting system (http://mapep.inel.gov/). Participants will be able to request samples, report results, receive reports and create historical reports of their performance from this web site. Other parties interested in the performance of particular laboratories may also get this information by contacting Guy Marlette at marletgm@id.doe.gov.

Accurate, defensible analytical data are essential to DOE. Decision makers must have correct information and confidence in those data to make important decisions regarding the ongoing cleanup and continued monitoring of DOE sites. MAPEP provides quality assurance to this process through performance testing of the laboratories that provide analytical data to the programs. DOE sites can use MAPEP as an oversight tool to monitor continuing performance of contract laboratories or to verify a laboratory's capability before awarding contracts. It is also valuable to the laboratories as an external validation of their procedures and capabilities or as a tool to identify opportunities for improvement.

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ANALYSIS OF LOW MOLECULAR WEIGHT ORGANIC ACIDS BY ION CHROMATOGRAPHY IN DOE TANK WASTE

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As part of an overall plan to better characterize radioactive waste, the objective of this work was to develop an ion chromatography method to analyze for low molecular weight organic acids. Initially, a simulated DOE tank waste was used for the purpose of the method development and demonstration. The organic acids in this study were citrate, glycolate, formate, acetate, succinate, acrylate and oxalate. An ion exclusion column was used to separate and quantify all species other than oxalate. There was an overwhelming interference for oxalate on the ion exclusion column, due to the very high ionic strength of the simulant. Therefore, an alternate column, AS14, was employed for the analysis of oxalate. To a much lesser extent, the concentration of nitrite present in the simulant was an interference for formate, but a correction could be applied. The methods developed using the simulant were carried over for the analysis of the organic acids in the radioactive solid waste. A radioactive solid waste sample was analyzed in triplicate including a matrix spike (MS) and matrix spike duplicate (MSD). The samples were leached in water (1g/50mL), and after twenty-four (24) hours filtered to remove remaining suspended solids. Each leachate sample was filtered through an ion exchange filter designed to remove ^{90}Sr and greatly reduce its activity prior to analysis. Only oxalate, formate, succinate and acetate were found to be present in the sample, with acetate just at its detection limit of 0.25 ppm. RPDs for oxalate and formate were 5% and for succinate at 15%. Percent recoveries for the MS and MSD of all the organic acid species were within ± 15%. Acrylate was not spiked into the MS and MSD samples.

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ANALYSIS OF C_1 TO C_3 ALCOHOLS BY AZEOTROPIC DISTILLATION AND GC/MS IN SIMULATED DOE TANK WASTE

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The analysis of low molecular weight alcohols in environmental matrices has been, for many years, a challenging task. Many environmental chemists have used heated headspace, direct injection of aqueous matrices, or water extraction of solids, followed with analysis by a GC/FID method. The flame ionization detector's universality has worked against the environmental chemist because many environmental samples are of complex, unknown matrices, making positive identification of analytes difficult. The lack of an acceptable concentration technique has kept detection limits high. BWXT Services, Inc. has successfully implemented a rapid, cost effective GC/MS method for methanol, ethanol, 1-propanol and 2-propanol. The technique chosen was the microdistillation method from SW-846 Method 5031, "Volatile, Nonpurgeable, Water-soluble Compounds by Azeotropic Distillation", coupled to a slightly modified version of Method 8260B. This technique provided full scan GC/MS results for all four C_1 to C_3 alcohols from water and from a simulated Department of Energy tank waste. The macrodistillation technique was not evaluated since the intent was to use the method for highly radioactive samples. Absolute recovery of the analytes from the distillation process was significantly better than the 10% to 40% recovery predicted by Method 5031 and often exceeded 70% from a water matrix. Statistically determined method detection limits from deionized water were less than 250 μg/L. Several deuterium labeled compounds were evaluated as surrogates and internal standards. Care was taken to avoid using compounds in which active hydrogens were deuterium-labeled, as isotopic exchange would be expected in an aqueous matrix. Deuterium-labeled methanol, ethanol, 1-propanol, 2-propanol and acetone are commercially available. Interference from diatomic nitrogen and oxygen were not as significant a problem as had been anticipated. Calibration curves were linear over a factor of 25 with %RSDs ranging from 3.5% for isopropanol to 7.6% for injection techniques and by developing a SIM method. Development of an isotope dilution technique is also a methanol. Goals for the future may be to reduce detection limits through improved possibility.

PERFORMANCE OF ANION EXCHANGE CHROMATOGRAPHY METHOD FOR THE ROUTINE EVALUATION OF METAL CYANIDE COMPLEXES IN SOLID WASTE LEACHATES

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Introduction

Cyanide is a contaminant that can sometimes be present in solid wastes, leachates and waters associated with disposal sites due to current and historical practices from a variety of industrial operations. The most common dissolved forms of cyanide include the various metal cyanide complexes, where the cyanide moiety is bonded to a transition metal cation. Based on the affinity of the metal cation towards the cyanide ion, these complexes can be classified into weak and strong metal cyanide complexes. Weak cyanide complexes include the cyanide complexes of Cu, Ni, Zn, Cd, Ag and Hg; while strong metal cyanide complexes include the cyanide complexes of Co, Pt, Pd, Fe and Au. Since the toxicity of these metal cyanide complexes is regulated by their ability to release free cyanide under relevant exposure conditions, measurement of individual metal cyanide complexes is required to assess the environmental risks at a site as well as address cyanide mass balance in site samples. For this reason, understanding the chemical speciation of cyanide in the environment is critical for assessing environmental impact and developing appropriate methods for disposal, treatment and remediation.

Current regulatory methods do not differentiate between individual metal cyanide complexes. In March of 2004, validation study data on an ion chromatography method, capable of determining single transition metal cyanide complexes at mg/L and μg/L concentration levels in waters and solid waste extracts, was submitted to the EPA Office of Solid Waste. In this paper, we briefly describe the performance data of that method when applied to different solid phase leachate matrices at high (mg/L) and low (μg/L) concentration level of detection. The ion chromatography method described in this paper employs anion exchange separation and UV spectroscopy (ASTM, 2004) for differentiating and quantifying metal cyanide complexes of Fe, Co, Ag, Au, Cu and Ni ($[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Ag(CN)_2]^{-}$, $[Au(CN)_2]^{-}$, $[Cu(CN)_3]^{2-}$, $[Ni(CN)_4]^{2-}$) in a variety of solid waste extracts generated *via* EPA Method 9013 (USEPA, 1996).

Methods

Study Matrices

This interlaboratory validation (ILV) study has involved three ion chromatography users who evaluated the method for reproducibility, linearity, accuracy, precision and spiked recovery from four sample matrices – clean Ottawa sand leachate (OSL), manufactured gas plant soil leachate-a (MGPLa), manufactured gas plant soil leachate-b (MGPLb) and aluminum reduction plant soil leachate (ARPL). These leachates were generated from four soil types namely, clean Ottawa sand (OS), MGP soil a (MGPa), MGP soil b (MGPb) and ARP soil (ARP), using EPA Method 9013 extraction followed by filtration

(0.45 μm) and pH adjustment of the extract (11<pH<12). Table 3 provides the background cyanide concentration in the field matrices.

Sample Analysis Plan

The sample analysis plan consisted of two separate tasks: (i) EPA Method 9013 Total Cyanide Spike Recovery Study (performed only by the custodial lab) and (ii) Youden Pair Precision and Bias Study.

Total Cyanide Spike Recovery Study

Of the four matrices selected for the ILV study, 100 g each of the three solid matrices, namely, MGPa, ARP and OS were spiked with 50 mg of total cyanide as reagent grade ferric ferrocyanide or Prussian Blue. Following spiking, each matrix was re-homogenized and 25 g of sample from the re-homogenized matrix was subject to Method 9013 extraction for cyanide. Following extraction, the extract was filtered (0.45 micron) and subjected to total cyanide distillation using EPA Method 9012 and the average recovery was calculated for each matrix.

Youden Pair Precision and Bias Study

For determination of method precision and bias, a round-robin collaborative study was completed. For the round-robin study, each laboratory spiked each of the leachate matrix with six different concentration levels of individual metal cyanide complexes using three sets of Youden pairs as per ASTM D2777 specification (ASTM, 2002) and analyzed these matrices for recovery of individual metal cyanide complexes. The Youden pair spiking concentrations were prepared by the custodial lab. The concentrations were not revealed to the individual laboratories. As a perspective, each Youden pair consists of two concentration levels at close proximity (≤ 20 RPD). Tables 1 and 2 presents the high and the low level solution concentrations following spiking by each Youden pair. Matrix spike/matrix spike duplicate (MS/MSD), blank solutions as well as samples for limit of detection (LOD) study were analyzed as part of the round-robin collaborative study.

Table 1. High Level Test Matrix Concentration Levels Following Spiking

Youden pair	$[Ag(CN)_2]^-$, mg/L	$[Au(CN)_2]^-$, mg/L	$[Co(CN)_6]^{3-}$, mg/L	$[Cu(CN)_3]^{2-}$, mg/L	$[Fe(CN)_6]^{4-}$, mg/L	$[Ni(CN)_4]^{2-}$, mg/L
1	21	10	15	0.20	1.0	20
	23	12	18	0.24	1.2	24
2	46	20	46	0.9	9.0	85
	51	22	50	1.0	10.0	95
3	85	40	83	1.6	17.5	175
	90	42	90	1.7	18.5	185

Table 2. Low Level Test Matrix Concentration Levels Following Spiking

Youden pair	$[Ag(CN)_2]^-$, µg/L	$[Au(CN)_2]^-$, µg/L	$[Co(CN)_6]^{3-}$, µg/L	$[Cu(CN)_3]^{2-}$, µg/L	$[Fe(CN)_6]^{4-}$, µg/L	$[Ni(CN)_4]^{2-}$, µg/L
1	20	15	12	1.1	1.6	55
	24	18	14	1.3	1.8	60
2	50	57	95	2.3	9.5	75
	54	60	105	2.5	11	80
3	110	85	180	4.4	17	90
	115	90	190	4.6	18	95

Results and Discussion

Total Cyanide Spike Recovery Study

Table 3 provides the results from the total cyanide spike recovery study using SW-846 Method 9013. As shown in Table 3, the total cyanide recovery for the three matrices ranged from 78 to 95% with the highest recovery observed for the MGP soil–a matrix.

Table 3. Matrix Characteristics and Prussian Blue Spiking Study Results

Matrix Types	Background Cyanide Concentration (mg/kg)	Prussian Blue Spiking Concentration (mg/kg)	% Recovery (n=2)
Manufactured Gas Plant Soil-a	0.44	500	95 (±3)
Manufactured Gas Plant Soil-b	7.64	-	-
Aluminum Reduction Plant Soil	0.17	500	78 (±0.3)
Clean Ottawa Sand	ND	500	86 (±0.9)

Precision and Bias Study

The data obtained from the validation study was evaluated statistically using a Youden-pair study design according to procedures listed in Table 4.

Table 4. Overview of Statistical Analyses

Statistical Analysis	Reference Document
Precision and Bias	ASTM D 2777-98 Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water (ASTM, 2002)
Limit of Detection	Pooled mean and standard deviation
MS/MSD	Range of precision and accuracy
Regression Analysis	Regression of measured versus true values

High Level Precision and Bias Analysis

Table 5 summarizes the precision and bias analysis results for all analytes in all matrices. As shown in this table, low bias (within ± 25% of the theoretical value) and high precision (± 25% SD or better) were observed for all analytes in each of the matrices tested.

Table 5. Precision and Bias Analysis for Individual Metal Cyanide Complexes

Matrix	$[Ag(CN)_2]^-$			$[Au(CN)_2]^-$		
	S_0 (%)	S_t (%)	Bias (%)	S_0 (%)	S_t (%)	Bias (%)
Ottawa Sand leachate	1.0	1.3	5.1	2.6	4.1	2.2
MGP Soil-a Leachate	1.1	2.3	0.7	2.0	2.2	1.6
MGP Soil-b Leachate	1.0	1.0	2.7	1.9	12.1	-3.1
ARP Soil leachate	0.4	1.0	0.8	3.7	3.8	2.9
Matrix	$[Co(CN)_6]^{3-}$			$[Cu(CN)_3]^{2-}$		
	S_0 (%)	S_t (%)	Bias (%)	S_0 (%)	S_t (%)	Bias (%)
Ottawa Sand leachate	0.5	2.7	2.7	2.2	5.0	9.1
MGP Soil-a Leachate	0.5	3.4	0.5	1.2	8.8	8.2
MGP Soil-b Leachate	0.6	3.5	1.2	6.3	14.5	15.2
ARP Soil leachate	0.4	3.5	-0.2	1.4	9.7	-0.13
Matrix	$[Fe(CN)_6]^{4-}$			$[NiCN)_4]^{2-}$		
	S_0 (%)	S_t (%)	Bias (%)	S_0 (%)	S_t (%)	Bias (%)
Ottawa Sand leachate	1.3	2.9	4.7	0.6	4.4	4.9
MGP Soil-a Leachate	0.8	2.9	3.1	0.5	1.7	3.1
MGP Soil-b Leachate	1.1	2.6	1.8	1.0	0.9	4.1
ARP Soil leachate	0.9	4.0	0.0	1.0	2.1	2.5

Note: S_0 and S_t represent the relative single operator and the overall standard deviation, respectively

High Level LODs

Based on four replicate analyses performed near the lowest calibration range for each of the cyanide species, LODs may be established. The LOD aims at establishing a low enough concentration for each metal cyanide complex that is reliably detected using standard ion chromatography equipment. These LODs are presented in Table 6.

Table 6. Summary of LODs in Leachates for High Level Ion Chromatography Method

LOD, mg/L	$[Ag(CN)_2]^-$	$[Au(CN)_2]^-$	$[Co(CN)_6]^{3-}$	$[Cu(CN)_3]^{2-}$	$[Fe(CN)_6]^{4-}$	$[Ni(CN)_4]^{2-}$
	0.95	1.01	1.06	0.18	0.52	1.0

Low Level Precision and Bias Analysis

A precision and bias calculation according to ASTM D 2777 could not be performed for the low level method because only one laboratory participated in the study. However, single laboratory bias and precision were calculated and compared against analogous measurements obtained by pooling all the data from the high level study. This comparison was performed for the Ottawa sand leachate matrix, which is the only matrix analyzed for the low level study. The first measure is the average bias of the measured values. The second measure is the relative standard deviation of the ratio of the measured versus the true values. This relative standard deviation is representative of the scatter of the measured values around the true values and is, thus, related to the precision of the method. Table 7 presents the result from that comparison between the low and high level precision and bias analysis.

Table 7. Comparison of Low Level and High Level Precision and Bias Results from EPA OSW Leachate Study

	$[Fe(CN)_6]^{4-}$		$[Cu(CN)_3]^{2-}$		$[Ag(CN)_2]^-$		$[Au(CN)_2]$-		$[Co(CN)_6]^{3-}$		$[Ni(CN)_4]^{2-}$	
	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX
	OSL Matrix											
3-Labs High Level Avg Bias Range*	2.3%	6.6%	5.0%	14.1%	3.5%	5.7%	0.8%	6.2%	0.2%	4.3%	3.5%	7.6%
3-Labs High Level Avg StDev Range	1.4%	5.0%	3.0%	6.9%	1.3%	1.9%	1.0%	5.2%	0.6%	2.3%	1.4%	3.3%
Dionex Low Level Avg Bias*	5.1%		74.2%		3.8%		4.5%		1.6%		5.1%	
Dionex Low Level StDev	3.6%		4.6%		15.7%		2.4%		4.7%		2.4%	
Is Dionex Avg Low Level Bias < Max High Level Bias?	YES		NO		YES		YES		YES		YES	
Is Dionex Low Level StDev < Max High Level StDev?	YES		YES		NO		YES		NO		YES	

*Absolute Value

As shown in Table 7, except for copper cyanide, the absolute average bias in the low level and high level methods are comparable for all other complexes. For copper cyanide, a much higher bias (in absolute value) was obtained for the low level method than for the high level method. Regarding the precision of the measurements, as measured by the relative standard deviation of the data, the results of the low level and high level studies are comparable, except for silver cyanide and cobalt cyanide. The low level silver cyanide measurements show a relative standard deviation of 15.7%, which

is about three times higher than the highest relative standard deviation for this species obtained in the high level study. This is mostly due to the low recovery (about 75%) obtained at the lowest measured concentrations (20 and 24 μg/L). For cobalt cyanide, the low level relative standard deviation is about twice the highest relative standard deviation measured in the high level study (4.7% vs 2.7%). Although not significant, this is also mostly due to the lower recovery (about 95%) obtained at the lowest measured concentrations (12 and 14 μg/L).

Low Level LODs

Based on four replicate analyses performed near the lowest calibration range for each of the cyanide species, LODs may be established. Table 8 presents the low level LODs.

Table 8. Summary of LODs in Leachates for Low Level Ion Chromatography Method

LOD, μg/L	$[Ag(CN)_2]^-$	$[Au(CN)_2]^-$	$[Co(CN)_6]^{3-}$	$[Cu(CN)_3]^{2-}$	$[Fe(CN)_6]^{4-}$	$[Ni(CN)_4]^{2-}$
	12	9.2	8.7	0.4	1.0	47

Conclusions

Overall, the high level ion chromatography method for quantifying metal cyanide complexes performed well in all the solid waste leachate matrices tested. This is reflected by the low bias and the lack of any significant variation in the precision and bias data for all the matrices. The LOD data analysis yielded a consistent and repeatable concentration for metal cyanide complexes near their respective lowest calibration range. The low level single laboratory study also performed well for five metal cyanide complexes (Au, Fe, Co, Ni and Ag) in the Ottawa sand leachate matrix. Copper cyanide complex showed high bias, probably due to some degree of dissociation that affected quantitation at the lowest level of detection. Based on these analytical results, it thus seems reasonable to conclude that the method as it currently stands is suitable for application to solid waste leachates and water matrices.

References

ASTM (2002) *Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water - ASTM D 2777-98*, ASTM International, West Conshohocken, PA.

ASTM (2004) *Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water using Anion Exchange Chromatography with UV Detection - D 6994-04*, ASTM International, West Conshohocken, PA.

USEPA (1996) *Cyanide Extraction Procedure for Solids and Oils - SW-846 Method 9013*, USEPA OSWER, Washington DC.

DEMONSTRATING A TECHNICAL BASIS FOR IMMOBILIZING A RADIOACTIVE SALT SOLUTION

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As part of the strategy for immobilization of radioactive waste at the Savannah River Site (SRS), some radioactive salt solutions will be immobilized in a grout referred to as saltstone. The resulting waste form will be disposed of at a disposal facility at SRS. One of the first materials being considered for processing at the SRS Saltstone facility is a salt solution currently being stored in tank 41H at the SRS tank farm. Samples of the tank 41H salt solution were characterized to demonstrate the technical basis for immobilizing and disposing of this radioactive salt solution as a saltstone waste form.

Characterization of tank 41H salt solution showed that by filtering the solution, all waste acceptance criteria (WAC) could be met except the current limits on sodium, ^{14}C and ^{135}Cs. Compliance with these three limits is currently being evaluated. Characterization also showed the tank 41H saltstone would qualify as a Resource Conservation and Recovery Act (RCRA) nonhazardous radioactive waste form and would require a Class 3 Industrial Solid Waste Landfill (ISWLF) for disposal because of high nitrate and *alpha*-emitting radionuclide concentrations in Toxicity Characteristic Leaching Procedure (TCLP) leachate.

Introduction

Approximately 100,000,000 liters of radioactive waste is currently being stored in underground tanks at SRS. As part of the SRS waste tank closure strategy, some radioactive salt solutions will be immobilized in saltstone and disposed of in a disposal facility on site. The tank 41H salt solution is one material being considered for immobilization at the SRS Saltstone facility. Before initiating a treatment process for the tank 41H salt solution, the technical basis is being examined for the disposition options.

Demonstrating the technical basis for processing the tank 41H salt solution as saltstone required demonstrating

- The waste stream solution can be processed at the SRS Saltstone facility.
- The resulting saltstone waste form would qualify as a nonhazardous radioactive waste form.
- The resulting saltstone waste form will be compatible with the disposal facility.

To demonstrate the compatibility with processing at the SRS Saltstone facility, the tank 41H salt solution had to be shown to meet the Saltstone facility WAC. These criteria included limits on physical properties and chemical and radionuclide content. To demonstrate the tank 41H saltstone would meet the definition of a nonhazardous waste form, TCLP leachates had to be shown to contain less than established limits for RCRA hazardous contaminants. To demonstrate feed material would be compatible with the

proposed disposal facility, a determination was made as to whether a Class 1, 2 or 3 ISWLF would be required.

The purpose of this report is to summarize results from the tank 41H salt solution characterization and to evaluate the results with respect to the technical basis necessary for immobilization at the SRS Saltstone facility. If approved for processing at the Saltstone facility, the first step in the process would be to transfer the tank 41H salt solution into tank 50H. The Saltstone facility feed would be a combination of the tank 41H salt solution and the tank 50H salt solution. The emphasis of the current report is on the tank 41H. A similar technical basis demonstration has also been performed for the tank 50H salt solution.

The Approach

Table 1 is a list of methods used to characterize the tank 41H salt solution. Activities association with this work can be grouped into three tasks.

- The Savannah River National Laboratory (SRNL) characterized a sample of the Tank 41H salt solution.
- SRNL prepared saltstone from a tank 41H salt solution sample.
- BWXS Technologies, Inc. (BWXT) performed the TCLP analyses on tank 41H saltstone samples.

Table 1. Analytical Methods Used to Characterize Tank 41H Salt Solution and Salt Stone Samples

	Method		
	WAC Analyses[a]	**TCLP Leachate Analyses**	
		Description	**SW-846 Method**
TCLP	Not Performed	Leaching Procedure	1311
Miscellaneous Metals	Emission Spectroscopy (b)	Emission Spectroscopy[d]	6010B
Sb, Pb	Emission Spectroscopy (b)	Emission Spectroscopy[d]	6010B
As, Se	Absorption Spectroscopy	Emission Spectroscopy[d]	6010B
Cs, K	Absorption Spectroscopy	Emission Spectroscopy	6010B
Hg	Absorption Spectroscopy	Absorption Spectroscopy[d]	7470A
Anions	Ion Chromatography	Ion Chromatography[e]	9056
Ammonium	Ion Chromatography	Not Analyzed	Not Analyzed
CO_3^{2-}, Base, Free OH^-	Titration	Not Analyzed	Not Analyzed
Semivolatile Organics	Mass Spectrometry	Not Analyzed	Not Analyzed
Phenol	Liquid Chromatography[c]	Mass Spectrometry	8270C
EDTA	Ion Pair Chromatography	Not Analyzed	Not Analyzed
Phenylborates	Liquid Chromatography[c]	Not Analyzed	Not Analyzed
Volatile Organics	Mass Spectrometry	Mass Spectrometry	8260B
Actinides	Mass Spectrometry[b]	*Alpha* Counting	Non-SW-846
^{99}Tc	Mass Spectrometry[b]	*Beta* Counting	Non-SW-846
^{135}Cs	Mass Spectrometry[b]	Not Analyzed	Not Analyzed
Alpha	*Alpha* Counting[b]	*Alpha* Counting	9310
Beta	*Beta* Counting[b]	*Beta* Counting	9310
^{238}Pu and $^{239/240}$Pu	*Alpha* Counting[b]	*Alpha* Counting	Non-SW-846
^{241}Pu	*Beta* Counting	*Beta* Counting	Non-SW-846
^{129}I and ^{14}C	*Beta* Counting[c]	Not Analyzed	Not Analyzed
Pure *Beta* Emitters	*Beta* Counting[b,c]	*Beta* Counting	Non-SW-846
^{137}Cs	*Gamma* Energy Analysis[b]	*Gamma* Energy Analysis	Non-SW-846
***Gamma* Emitters**	*Gamma* Energy Analysis[b,c]	*Gamma* Energy Analysis	Non-SW-846
Insoluble Solids	Gravimetry[c]	Not Analyzed	Not Analyzed

(a) Unless note with a (c), samples were filtered prior to analysis.
(b) Prior to this analysis, samples were treated with a nitric acid and hydrofluoric acid dissolution.
(c) Samples were not filtered prior to this analysis.
(d) Analysis was performed on TCLP leachates from samples cured 32 days and samples cured 5 days.
(e) In addition to TCLP leachates, total concentrations of these analytes were determined in the saltstone.

On July 10, 2003, four hundred milliliters of salt supernate was sampled from tank 41H. Most analyses were performed after the sample had been filtered. Analyses noted with "(b)" in Table 1 were performed on sample aliquots that had been digested with nitric acid and hydrofluoric acid at 115 ^{o}C. As shown in Table 1, phenol, phenylborate, carbon-14 and iodine-129 were determined on the as-received sample, without filtration or acid digestion. Miscellaneous *gamma*-emitting radionuclides and miscellaneous pure-*beta*-emitting radionuclides were determined on an unfiltered aliquot of the sample that had been digested.

For the TCLP analyses, 404 grams of a Tank 41H salt supernate sample was mixed with 400 grams of a premix (10 % cement, 45 % slag and 45 % fly ash) and allowed to cure. After 32 days, samples of the cured saltstone were crushed and shipped to BWXS where the crushed saltstone samples were subjected to a TCLP. The resulting leachate was digested and analyzed using the methods indicated in Table 1. A set of TCLP tests were also performed for the 8 RCRA metals used to determine if a waste form is characteristically hazardous. Results have not been included for the samples that were cured 5 days.

Results

Results given in this section are averages of duplicate or triplicate analytical values. For constituents of potential concern (COPCs) that were analyzed but not detected, minimum detection limits (MDLs) or estimated quantitation limits (EQLs) have been preceded by "<". This is equivalent to the standard "J" flag used in Contract Laboratory Program data packages and other regulatory documentation. For TCLP results that did not meet specified data quality objectives (DQOs), analyses were on the Saltstone sample itself to determine the COPC concentrations in the Saltstone.

Waste Acceptance Criteria Analyses-Can We Process the Tank 41 Salt Solution at the Saltstone Facility?

Results from analysis of the WAC salt solution sample have been given in Table 2. These results were averages from two or three replicate analyses. Unless otherwise noted, these results were from filtered aliquots of the sample. Also included in Table 2 are the WAC limits for each of the analytes. Results noted with "(a)" exceeded the WAC limit. Results noted with "(b)" met the WAC limit after filtration, but exceeded the limit in samples that were not filtered.

Table 2. Results from Analysis of the Tank 41H WAC Salt Solution Sample.

COPC	Concentration (pCi/mL)	
-	WAC Limit	Tank 41H
^{3}H	1.13×10^{5}	$< 9.3 \times 10^{2}$
^{14}C	46.8	1.4×10^{3} [a]
^{26}Al	2.88×10^{3}	< 57
^{59}Ni	1.13×10^{3}	$< 2.1 \times 10^{2}$
^{63}Ni	1.13×10^{3}	$< 5.3 \times 10^{2}$
^{60}Co	4.50×10^{4}	< 78
^{79}Se	1.13×10^{3}	$< 3.6 \times 10^{2}$
^{90}Sr	8.44×10^{6}	4×10^{4}
^{90}Y	8.44×10^{6}	4×10^{4}
^{94}Nb	1.53×10^{4}	< 83
^{99}Tc	6.75×10^{4}	4.7×10^{4}
^{106}Ru	3.38×10^{4}	$< 7.3 \times 10^{2}$
^{125}Sb	2.25×10^{4}	2.4×10^{2}
^{125m}Te	1.13×10^{3}	$< 2.4 \times 10^{2}$
^{126}Sn	1.13×10^{3}	4.89×10^{2}
^{126}Sb	1.13×10^{3}	68
^{126m}Sb	1.13×10^{3}	4.85×10^{2}
^{129}I	24.3	13.5
^{134}Cs	9.63×10^{3}	< 85
^{135}Cs	16.3	4.0×10^{2} (a)
^{137}Cs	2.64×10^{7}	9.97×10^{7}
^{144}Ce	4.40×10^{3}	$< 4.6 \times 10^{2}$
^{144}Pr	4.40×10^{3}	$< 4.6 \times 10^{2}$
^{147}Pm	5.63×10^{5}	$< 6.3 \times 10^{2}$
^{151}Sm	2.25×10^{3}	$< 9.0 \times 10^{2}$
^{154}Eu	9.00×10^{4}	1.3×10^{2}
^{155}Eu	1.13×10^{3}	$< 1.8 \times 10^{2}$
^{226}Ra	8.73×10^{3}	$< 1.5 \times 10^{3}$
^{229}Th	1.62×10^{5}	$< 2.0 \times 10^{2}$
^{230}Th	6.03×10^{5}	$< 5.4 \times 10^{2}$
^{232}Th	0.271	$\leq 4.3 \times 10^{-3}$
^{232}U	5.88×10^{-2}	$< 3.1 \times 10^{2}$
^{233}U	16.3	5.3×10^{2}
^{234}U	5.40	2.27×10^{3}
^{235}U	0.183	2.65
^{236}U	0.821	30.9
^{238}U	4.47	2.32
^{237}Np	7.94	2.18×10^{2}
^{238}Pu	1.88×10^{5}	2.96×10^{4} [b]
^{239}Pu	3.07×10^{3}	1.17×10^{3}
^{240}Pu	1.42×10^{3}	2.75×10^{2}
^{241}Pu	9.27×10^{4}	1.75×10^{4}
^{242}Pu	2.78	< 98
^{244}Pu	7.11×10^{4}	< 0.46
^{241}Am	2.08×10^{4}	8.1×10^{2}
^{242m}Am	1.90×10^{2}	$< 1.7 \times 10^{2}$
^{242}Cm	2.06×10^{3}	< 2.7
^{244}Cm	2.06×10^{4}	1.1×10^{2}
^{245}Cm	1.53	< 37
Total β,γ	2.35×10^{8}	1.15×10^{8}
Total α	2.50×10^{5}	4.99×10^{5}

COPC	Concentration (mg/L)	
-	WAC Limit	Tank 41H
$Al(OH)_4^-$	2.85×10^{5}	4.28×10^{4}
NH_4^+	3.80×10^{3}	$< 1.00 \times 10^{2}$
CO_3^{2-}	9.24×10^{4}	2.02×10^{4}
Cl^-	3.05×10^{3}	29.5
HCO_2^-	4.00×10^{3}	4.46×10^{2}
F^-	2.63×10^{3}	< 20.0
OH^-	1.71×10^{5}	1.44×10^{4}
NO_3^-	4.70×10^{5}	3.05×10^{5}
NO_2^-	2.05×10^{5}	1.10×10^{4}
$C_2O_4^{2-}$	6.56×10^{3}	2.12×10^{2}
PO_4^{3-}	8.89×10^{3}	3.29×10^{3}
SO_4^{2-}	6.13×10^{4}	2.28×10^{4}
As	3.24×10^{2}	< 0.656
Ba	60.0	2.42
Cd	60.0	< 1.44
Cr	1.39×10^{3}	1.70×10^{2}
Pb	1.02×10^{2}	40.5
Hg	2.25×10^{2}	23.5
Se	4.50×10^{2}	< 0.721
Ag	60.0	< 2.23
Sb	None	41.3
B	60.0	11
Be	None	< 0.506
Ca	1.47×10^{3}	29.8
Ce	6.00×10^{2}	< 19.6
Cs	2.56×10^{2}	< 1.31
Co	60.0	Not Analyzed
Cu	5.34×10^{2}	< 1.44
Gd	None	< 1.71
Fe	4.00×10^{3}	1.24×10^{2}
La	None	< 2.35
Li	60.0	< 7.21
Mg	60.0	0.854
Mn	60.0	23.2
Mo	60.0	< 34.2
Nd	78.8	Not Analyzed
Ni	60.0	< 11.0
K	1.46×10^{4}	3.08×10^{2}
Ru	87.8	Not Analyzed
Si	6.90×10^{3}	77.0
Na	1.61×10^{5}	1.81×10^{5}
Sr	60.0	5.87
Sn	None	< 28.4
Ti	60.0	< 1.01
V	None	2.08
Zn	6.47×10^{2}	≤1.31
Zr	60.0	< 1.83
Total Organics	1.50×10^{3}	< MDL
COPC	**Concentration (%)**	
-	WAC Limit	Tank 41H
Insoluble Solids	5.0	0.3

(a) This result did not meet the current saltstone WAC for this analyte.
(b) This result met the current saltstone WAC for this analyte only after the sample was filtered.

TCLP Results-Is the Waste Form RCRA Hazardous and What Is the Appropriate Disposal Facility?

Results from TCLP leachate analysis of the tank 41H saltstone have been given in Table 3. These results were averages from three replicate analyses and were from saltstone samples that had cured 32 days. For results that did not meet the data quality objectives (DQOs), total COPC concentrations were determined in the saltstone samples. These results were divided by 20 L/Kg to determine the concentration in a TCLP leachate if the COPC were to be completed leached during a TCLP test.

Table 3. Results from Analysis of the Tank 41H Saltstone TCLP Tests.

COPC	Concentration (mg/L)			
-	RCRA	MCL[a]	PRG[b]	Tank 41H
As[c]	5	1×10^{-2}	-	1.8×10^{-2}
Ba[c]	100	2	-	0.128
Cd[c]	1	5×10^{-3}	-	2.4×10^{-3}
Cr[c]	5	0.1	-	2.72×10^{-2}
Pb[c]	5	1.5×10^{-2}	-	$< 2.8 \times 10^{-2}$
Hg[c]	0.2	2×10^{-3}	-	5×10^{-4}
Se[c]	1	5×10^{-2}	-	0.156
Ag[c]	5	0.1	-	$< 5 \times 10^{-3}$
Al	-	-	-	0.40
Sb	-	6×10^{-3}	-	<0.028
B	-	-	3.3	0.46
Be	-	4×10^{-3}	-	1.1×10^{-3}
Co	-	-	2.2	$< 2.6 \times 10^{-3}$
Cu	-	1.3	-	$< 5.9 \times 10^{-3}$
Fe	-	0.3	-	0.071
Li	-	-	0.73	0.75
Mn	-	0.05	-	6.5×10^{-3}
Mo	-	-	0.18	0.47
Ni	-	-	0.73	$< 6.9 \times 10^{-3}$
K	-	-	-	60
Si	-	-	-	37
Na	-	-	-	3.9×10^{3}
Sr	-	-	22	0.96
Zn	-	5	-	0.052

COPC	Concentration (mg/L)		
-	MCL	PRG	Tank 41H
Br^-	-	-	< 1 [d]
Cl^-	2.5×10^{2}	-	< 1 [d]
F^-	4	-	1.1 [d]
NO_3^-	-	-	5.5×10^{3} [d]
NO_2^-	-	-	< 1 [d]
$NO_3^- + NO_2^-$ as N	10	-	1.2×10^{3} [d]
PO_4^{3-}	2.5×10^{2}	-	< 1 [d]
SO_4^{2-}	-	-	4.9×10^{2} [d]
Benzene	5.0×10^{-3}	-	2.9×10^{-3}
n-Butanol	-	3.6	< 0.10
Toluene	1.0	-	1.2×10^{-3}
Phenol	-	22	< 1.0

COPC	Concentration (pCi/L)	
-	MCL	Tank 41H
^{90}Sr	-	8.1×10^{5}
^{99}Tc	-	8.4×10^{4}
^{137}Cs	-	7.2×10^{8}
^{238}Pu	-	7.3×10^{3}
$^{239}Pu/^{240}Pu$	-	3.1×10^{2}
^{241}Pu	-	3.4×10^{3}
^{244}Cm	-	6.6×10^{3}
^{226}Ra	5	$< 4.2 \times 10^{4}$
^{228}Ra	5	$< 3.5 \times 10^{4}$
Total α	15	1.8×10^{4}

(a) MCL-Maximum Contamination Limit
(b) PRG-Preliminary Remediation Goal
(c) This COPC was also measured in TCLP leachates from saltstone cured 5 days. Results were similar.
(d) Results are from analysis of the total COPC concentration in the saltstone sample divided by 20 L/kg.

Discussion and Conclusions-What Does It All Mean?

The result given in Table 2 and Table 3 along with support documentation will be the technical basis for immobilizing the current tank 41H salt solution in the SRS Saltstone facility. These results show

- All WAC were met except the limits on sodium, carbon-14 and cesium-135.

- A tank 41H saltstone would meet the criteria of a nonhazardous radioactive waste form.
- Disposal of a tank 41H saltstone would require a Class 3 ISWLF.

Of the 94 WAC that would need to be met for processing of the tank 41H salt solution at the SRS Saltstone facility, only three were not met. To meet some of the WAC, undissolved solids needed to be removed from the sample. This suggests the contents of the tank 41H tank would need to be allowed to settled prior to being transferred to the SRS Saltstone facility feed tank (tank 51). Alternatively, the salt solution could be filtered prior to the transfer.

Sodium, carbon-14 and cesium-135 concentrations in the tank 41H WAC sample were above the WAC limits for these COPC. In addition, cobalt, neodymium and ruthenium were not determined. Prior to immobilization of the tank 41H solution at the SRS Saltstone facility, these six WAC would need to be evaluated to determine what further actions would be necessary to safely process the tank 41H salt solution.

Results from analysis of the tank 41H saltstone TCLP leachate showed this waste form would meet the definition of a RCRA nonhazardous waste form. All results in Table 3 were from saltstone samples that had cured for 32 days. A TCLP was also performed on samples after 5 days of curing. Results from samples cured 5 days were similar to results from samples cured 32 days. Results from analysis of samples cured 5 days have not been presented here.

A Class 3 ISWLF is required when the TCLP leachate concentration of any COPC is greater than thirty times the MCL. Results from tank 41H saltstone TCLP leachate analysis showed this waste form would require a Class 3 ISWLF because of high nitrate and *alpha*-emitting radionuclide concentrations in the leachate. Anion analyses did not meet all the DQOs. Therefore, the total anions concentrations were measured in the tank 41H saltstone.

If the descision is made to immobilize the tank 41H salt solution in saltstone, the saltstone facility feed would be a mixture of the salt solutions currently in tanks 41H and 50H. This report has focused on results from characterization of tank 41H. A similar task has been performed on the salt solution in tank 50H. The tank 50H evaluations have shown that this salt solution met all WAC, the resulting tank 50H saltstone would be a RCRA nonhazardous waste form and the resulting saltstone would require a Class 3 ISWLF.

The Savannah River Site and South Carolina Department of Health and Environmental Control are optimizing the approach to be taken toward evaluating the technical basis for other Saltstone facility feed salt solutions. Currently, the Saltstone disposal facility is being evaluated to ensure that it is equivalent to a Class 3 ISWLF. Once this facility has been granted Class 3 ISWLF equivalency status, all saltstone waste forms will be disposed of at this facility. Since this is the most stringent classification of a RCRA

nonhazardous waste form, TCLP tests may not be needed for any COPCs beyond those necessary to establish the waste form as RCRA nonhazardous.

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OPTIMIZATION OF REGULATORY DATA QUALITY OBJECTIVES FOR HANFORD VITRIFICATION PROCESS

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The optimization of Regulatory Data Quality Objectives (RDQO) was recently completed to provide updates and data needs identified by U. S. Department of Energy (USDOE) and Washington State Department of Ecology during the development of RDQO for the Hanford Tank Waste Treatment and Immobilization Plant (WTP) process. The WTP will vitrify mixed waste stored in underground storage tanks. The RDQO task focused on the characterization of tank waste prior to transfer to WTP.

The optimization process included demonstration of analytical capabilities and achievable detection limits using EPA SW-846 methodologies for sludge and supernatant matrices. The analytical capabilities included selection of appropriate SW-846 methods, quality control criteria and sample preparation techniques for demonstrating achievable detection limits. Inputs for the detection limits and identification of contaminants of concern (COCs) were obtained from WTP permitting, land disposal restriction (LDR), risk assessment (RA) and delisting petition activities.

ORGANIC METHODS II

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LOW-COST PCB CONGENER ANALYSIS USING SOLID PHASE EXTRACTION AND GAS CHROMATOGRAPHY-TANDOM ION TRAP MASS SPECTROMETRY DETECTION

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A method has been developed for the determination of PCB congeners in water using Solid Phase Extraction with GC Ion Trap Tandem Mass Spectrometry (GC/MS/MS). PCBs are often analyzed by EPA methods 8082 and 625 for arochlor analysis. These methods provide inaccurate quantitation and no speciation of PCB congeners that can be used for risk-based assessment or the environmental fate of the PCBs. The preferred PCB congener method uses GC- high resolution mass spectrometry (HRMS). The expense of the instrumentation and isotopically-labeled standards make the cost of congener analysis excessive. This method uses a cost-effective instrument that can approach the sensitivity of a HRMS and match the selectivity in identifying the proper PCB congener. The method uses a minimal amount of isotopically-labeled internal standard to minimize that cost but still provide the necessary quantitative integrity for environmentally sensitive congeners. River and Lake Michigan water were spiked with a mix of approximately 150 congeners at 2 ppt and 10 ppt concentrations. The extracts were analyzed and results are given.

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VALIDATION OF EPA METHOD 1668A FOR PCB CONGENERS

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In March of 1997, EPA released Method 1668 for determination of the 13 dioxin-like congeners listed by the World Health Organization (WHO) in 1994. Method 1668 employs isotope dilution coupled with high resolution gas chromatography/high resolution mass spectrometry techniques to allow for determination of individual PCB congeners at low concentrations. Between 1997 and 1999, EPA expanded Method 1668 for determination of all 209 congeners and validated the expanded method in an extensive single laboratory study. EPA performed a peer review of the expanded method and revised the method based on comments received in the peer review. The revised, peer-reviewed method was renumbered as Method 1668A. In 1999, EPA published a report of the single-laboratory validation study and the peer review.

Since 1999, EPA has been collecting comments on Method 1668A, including corrections and suggestions for improvement. These comments, corrections and suggestions were incorporated into an August 2003 revision in preparation for an interlaboratory method validation study that began in November, 2003. The study involves 14 laboratories, including commercial labs located in the U.S. and Canada, as well as EPA Regional laboratories. This presentation describes the study design, study status and preliminary results of the interlaboratory study.

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ANALYZING OXYGENATES IN ENVIRONMENTAL SAMPLES BY P&T/GC/MS

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The Clean Air Act requires the use of reformulated gasoline. To meet this requirement, MTBE, TAME, TBA and other oxygenates have been added to gasoline. The new trend is to use ethanol to replace MTBE as the main oxygenate because it is the only viable substitute available in sufficient quantities for the gasoline market. Analysis of those oxygenates in environmental samples, therefore, has been a crucial task for every environmental analytical laboratory. A simple and efficient method has been developed and used in routing analysis by little revising the widely available P&T/GC/MS method to handle many of the typical oxygenates (see the table below for the compound list) as well as the other VOCs in one instrumental run. Performance data for separation and interference from the original VOC analytes, detection limits, linearity and reproducibility has been collected. The net GC/MS run time is less than 15 minutes. This method has been used in routing analysis for verities of samples including air, soil gas, soil and water in field in our mobile laboratory. It has been especially useful for the indoor/outdoor air/gas sample field screening analysis under emergency response situation.

Oxygenates	CAS #
Methyl-t-butyl ether (MTBE)	1634-04-4
tert-Butanol (TBA, 2-Methyl 2-Porpanol)	75-65-0
tert-Amyl methyl ether (TAME)	994-05-8
Ethanol	64-17-5
Ethyl ether (Diethyl ether)	60-29-7
Ethyl-tert-butyl ether (ETBE)	637-92-3
Diisopropyl ether (DIPE, Isopropyl ether)	108-20-3
2-Pentanone	107-87-9

HEADSPACE TRAPPING TECHNOLOGY WITH GC/MS FOR DETERMINING VOLATILE ORGANIC COMPOUNDS (VOCs) IN ENVIRONMENTAL SAMPLES

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Introduction

Headspace GC is a widely accepted technique for the determination of volatile organic compounds (VOCs) in material-testing, environmental and pharmaceutical applications. The performance and convenience of this classical technique has been unmatched by any other technology. However, there are some limitations. For example, during many volatile analyses, minimal injection volume is sampled from the headspace and thus makes the technique unsuitable for very trace analyses.

A large number of EPA methods have required a purge and trap instrument to perform many trace volatile analyses on environmental samples. This has been a standard requirement for many years. Most labs find these purge and trap instruments expensive, difficult to use and high in maintenance. They require purchasing a purge and trap system with a separate, expensive autosampler. In addition, they can only purge one sample at a time and require a separate water bath for line purging. However, because of the trace levels required in EPA methods it has been difficult to find an alternative to this system, until now.

The new headspace trap technology gives operators the benefits of traditional headspace and now adds a trap option to meet the needs of lower detections limits. This trap technology is capable of sampling up to 100% of the headspace by a pulsed pressure headspace extraction process with analytes refocusing on an adsorbent trap. The details of this technology and its application in environmental laboratories will be presented.

Experimental

The headspace trap system used in this experiment for monitoring VOCs consists of a GC (Clarus 500, PerkinElmer), a MS (Clarus 500 MS, PerkinElmer) and a Headspace Trap (TurboMatrix Headspace Trap, PerkinElmer). Glass, 22mL vials were filled with 10 mL of high purity water and sealed. These vials were then placed into the headspace trap system for analysis.

The samples were heated in a 15 position, aluminum alloy oven located in the headspace trap system. After reaching equilibration a needle pressurizes the vial (see Figure 1) and the trap is loaded with the pressurized headspace from the vial (see Figure 2). The trap is then rapidly heated to desorb the trapped analytes and carrier gas sweeps them *via* an optional splitter as a narrow band onto the GC column. There are

substantial gains in sensitivity as a result of the increased sample volume injected (up to 100x in some instances).

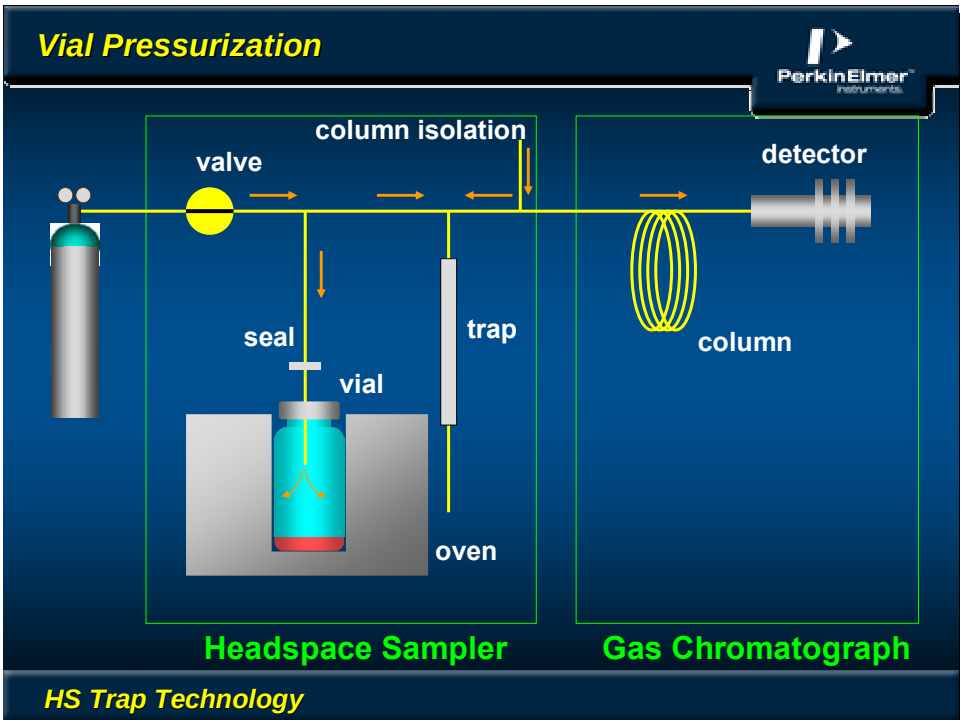

Figure 1.

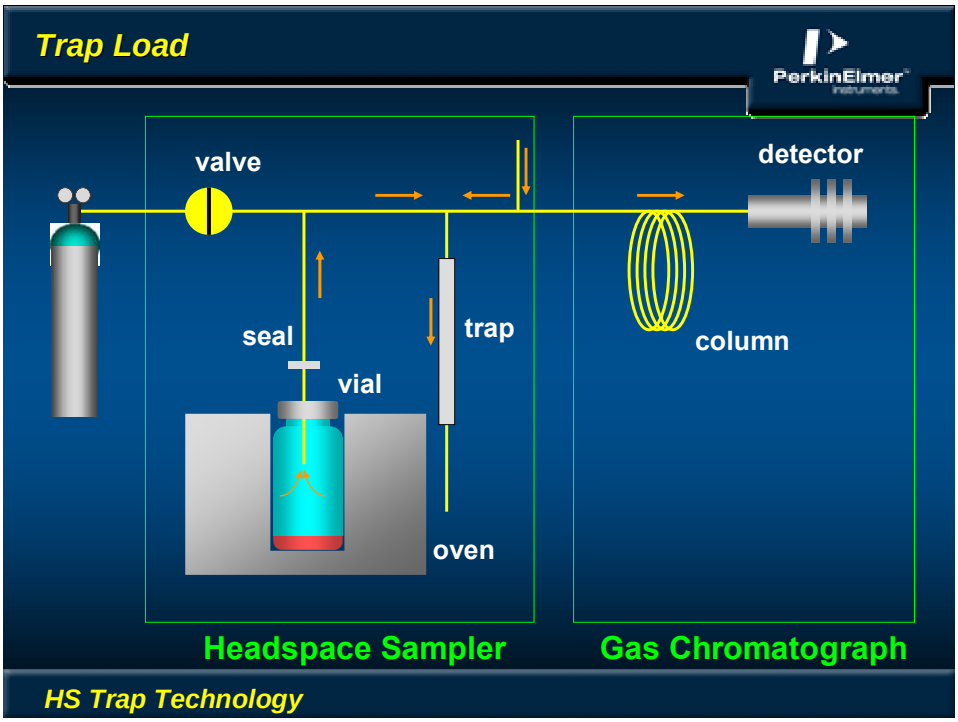

Figure 2.

Results and Discussion

Because the headspace trap system uses a heated headspace vapor and does not require purging a sample, it has the ability to sample all types of environmental matrices (gas, liquid or solid) making the system flexible for a variety of needs.

Water management is critical to environmental analysis. The headspace trap uses an unique dry purge technology to remove water from the trap during sampling, see Figure 3.

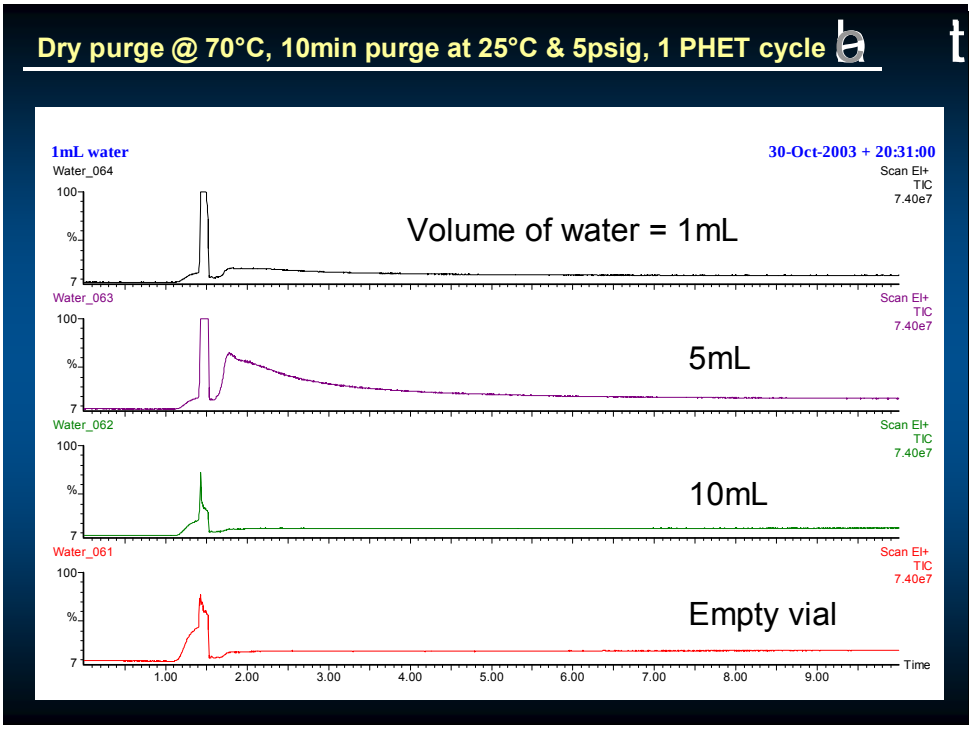

Figure 3.

Due to the nature of the technology, the full range of chromatographic options such as split flow, pneumatic flow control and column selection are still available to the chemist and so no change in existing laboratory procedures is required.

Using standard EPA 8260b (Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry) methodology the system produces results for the whole range of compounds required by a majority of environmental labs, as well as meeting all detection limits, see Figure 4.

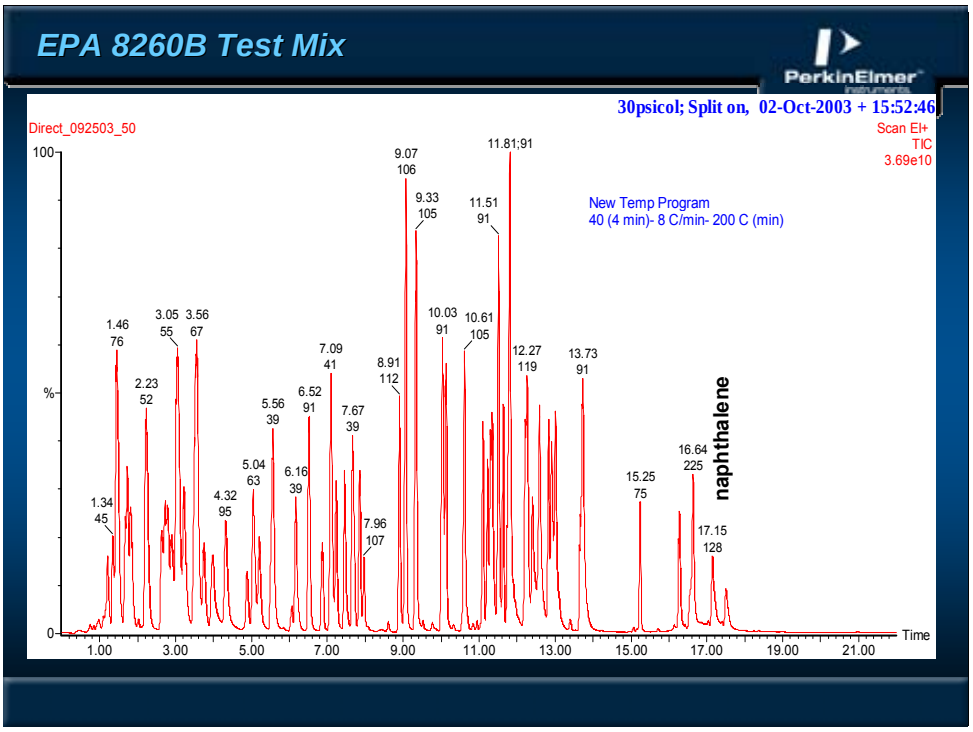

Figure 4.

Conclusion

The new headspace trap technology gives operators the benefits of traditional headspace and now adds a trap option to meet the needs of lower detections limits. Utilizing techniques such as dry purging and overlapping thermostating, environmental samples are quickly and easily processed. Low detection limits, clean chromatography and good linearity have all been observed using the headspace trap for difficult environmental methods such as EPA method 8260b.

COMPARISON OF 1,4-DIOXANE AS A VOLATILE AND SEMIVOLATILE ANALYTE IN SINGLE AND MULTI-LABORATORY STUDIES

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Introduction

Several analytical events have recently been conducted by the EPA Quality Assurance Technical Support (QATS) Laboratory to assess the analytical characteristics of 1,4-dioxane as both a purgeable (volatile) and extractable (semivolatile) compound. Initially, a single laboratory (QATS) study was performed to determine and evaluate optimum conditions for the analysis of 1,4-dioxane as both a purgeable and extractable compound. Purgeable analysis parameters which were evaluated to optimize analyte recovery included purge temperature, purge flow and purge volume, as well as full-scan and selected ion monitoring (SIM) GC/MS detection. Extractable analysis parameter variations were limited to full-scan and SIM GC/MS detection, with minor variations in the GC temperature program to accommodate the early elution of 1,4-dioxane. The next phase of this comparative evaluation includes the QATS Laboratory and external referee laboratory analysis of three performance evaluation samples (PESs) produced at the QATS facility for use in the USEPA Contract Laboratory Program (CLP) and to support other Superfund analytical activities. The final phase of this evaluation is a presentation of the results from a multi-laboratory study. The study used identical 1,4-dioxane samples which were analyzed as both a volatile and extractable analyte using optimized analytical parameters. The study results include a discussion of the use of 1,4-dioxane-d_8 as both an internal standard and as a deuterated monitoring compound (DMC).

Background

1,4-Dioxane ($C_4H_8O_2$) is a synthetic chemical which is primarily used as a stabilizer for chlorinated solvents which prevents the breakdown of the chlorinated solvents during the manufacturing process. It is also used as a solvent in lacquers, paints, varnishes, plastics, dyes, oils and several other products. 1,4-Dioxane is a cyclic ether which is extremely soluble in water, does not bind well to soil particles and does not easily biodegrade in the environment. It has been classified by the USEPA and other government agencies as a probable human carcinogen. Millions of pounds of this compound have been released into the U.S. environment and because of its high water solubility, it readily migrates into groundwater.

Detection of 1,4-dioxane at low parts per billion levels is dictated by the intensified interest in this compound and as regulatory agencies attempt to establish advisory or action limits. Commercial laboratories typically analyze for 1,4-dioxane in water using one of three methods: USEPA Method 524.2 for drinking water and USEPA Method 8260 (purgeable) or Method 8270 (extractable) for groundwater and hazardous waste. Because of the high water solubility and poor purging efficiency of 1,4-dioxane, Method 8260 without modifications results in high detection limits for this compound, typically greater than 100 μg/L (ppb).

1,4-Dioxane is a proposed volatile target analyte in the USEPA CLP Draft Statement of Work (SOW) SOM01.X (05/2004). Associated contract required quantitation limits (CRQLs) for this analyte are 2.0 μg/L (25 mL trace analysis using modified purge parameters and SIM GC/MS), 25 μg/L (25 mL trace analysis using full-scan GC/MS) and 125 μg/L (5 mL low/medium concentration analysis using full-scan GC/MS). Historically, commercial laboratories have used a modified Method 8260 to achieve lower detection limits for 1,4-dioxane. Use of a heated purge, increased purge flow, addition of sodium sulfate (salting-out) and SIM GC/MS detection typically results in lower detection limits around 2 μg/L (2 ppb). Typically, the modified method results in inconsistent detection limits and non-reproducible results and the addition of sodium sulfate can cause systematic problems in purge and trap and autosampler units. Recently, many commercial laboratories have indicated that lower detection limits and reproducible results are achieved using a modified Method 8270 approach. The method includes liquid-liquid extraction, isotope dilution quantitation using 1,4-dioxane-d_8 and SIM MS detection to increase sensitivity. The objective of this comparative study is to evaluate both the purgeable and extractable method for the analysis of 1,4-dioxane and determine the mode of analysis for the CLP which will provide the lowest detection limits and highest precision and accuracy for this compound.

Single Laboratory Study

Method

Purgeable - Several calibration sets of 1,4-dioxane using the volatile organic purge and trap technique outlined in the CLP Draft SOM01.X SOW were analyzed using varying conditions and purge volumes. All of the analyses were performed using 1,4-dioxane-d_8 as an internal standard assuming that the recovery and response of the deuterated analog should mimic the native analyte, thus providing greater accuracy and precision in the quantitation of 1,4-dioxane. The parameters which were varied included the purge temperature, volume and flow rate. All of the calibration standards were analyzed on the same GC/MS system under the same analytical conditions except for those detailed in Table 1 (Results and Discussion Section). All of the other analytical conditions are in accordance with those recommended in the CLP Draft SOM01.X SOW.

Extractable - A set of seven (7) water samples spiked with 1,4-dioxane and 1,4-dioxane-d_8 was extracted using the liquid-liquid extraction technique in the CLP Draft SOM01.X SOW. The samples were spiked with 1,4-dioxane using a range of 5, 10, 20, 40, 60, 80 and 100 μg/L (ppb) and all of the samples were spiked with 1,4-dioxane-d_8 as a DMC at 40 μg/L (ppb). After extraction, the samples were analyzed by GC/MS using both full-

scan and SIM MS detection along with a corresponding set of calibration standards. The full-scan calibration range included 5, 10, 20, 40 and 80 µg/mL standards and the SIM range included 0.5, 1, 2, 5, 10, 20, 40 and 80 µg/mL standards. To accommodate the early eluting 1,4-dioxane (b.p. 101 ºC) and eliminate detector saturation and interference from the solvent front, the starting temperature of the GC program was lowered from 40 ºC to 35 ºC. 1,4-Dichlorobenzene-d_4 was spiked into the sample extracts as the internal standard.

Results and Discussion

Purgeable - Table 1 presents the analytical conditions and statistical calculations for the purgeable calibration standards. Statistics for analytical set number 4 were not determined (ND) because no analytical recovery for 1,4 dioxane was achieved below 2 µg/L (ppb). This analytical set included standards at 0.5, 1, 2, 5, 10 and 20 µg/L (ppb) using a 25 mL non-heated sample purge, a purge flow of 40 cc/min and full-scan MS detection.

Table 1

Analytical Set	Sample Volume (mL)	Sample Temperature (° C)	Purge Flow (cc/min)	MS Detection	Calibration Range (ug/L)	Average RRF	RSD
1	5	Ambient	40	Full-Scan[1]	10 - 200	1.036	14.1
2	5	50	50	Full-Scan	10 - 200	1.070	9.3
3	5	50	50	SIM[2]	0.5 - 200	1.085	9.3
4	25	Ambient	40	Full-Scan	0.5 - 20	ND	ND
5	25	50	50	SIM	0.5 -20	1.243	17.9

1 Full-Scan range is m/z 35-300.
2 SIM includes m/z 58 & 88 (1,4-dioxane) and m/z 64 & 96 (1,4-dioxane-d_8).

As indicated in Table 1, with the exception of analytical set number 4, all of the calibration sets demonstrated good linearity throughout the specified range with RSD values less than 20 percent. Generally, heating the sample and increasing the purge flow increases the recovery of 1,4-dioxane by a factor of two. The purging efficiency of a 25 mL sparge vessel is less than a 5 mL sparge vessel because of the vessel design and increased volume. Although the 5 mL, nonheated, full-scan analytical set for 1,4-dioxane is linear in the range of 10 to 200 µg/L, the absolute response for this compound is very low and interference from other target compounds is possible. A review of the data, chromatograms and statistics indicate that the analysis of 1,4-dioxane using a 5 mL heated purge, accelerated sample purge flow and SIM MS detection results in the most linear calibration range from 0.5 µg/L to 200 µg/L, concurrent with the highest signal-to-noise (s/n) ratio. The 25 mL purge volume with similar analytical conditions provides similar results with a narrower calibration range (0.5 to 20 µg/L). Several additional purge and trap analyses were conducted for 1,4-dioxane altering various parameters in order to optimize the recovery of this compound. The sample temperature was increased up to 70 ºC and the sample purge flow was

increased up to 60 cc/min. Through these additional analyses, it was determined that the optimal sample temperature is approximately 50 ºC, and the optimal sample purge flow is approximately 50 cc/min for the analysis of 1,4-dioxane as a purgeable analyte on this system. Increasing the temperature and/or the sample purge flow beyond the optimal results in erratic recoveries and poor chromatography of 1,4-dioxane, presumably due to the increased amount of moisture introduced into the purge and trap concentrator and analytical system. It should be noted that all reported results for the analysis of 1,4-dioxane as a purgeable compound were collected using a moisture control module device on the purge and trap concentrator in the active mode and all of the transfer lines were heated to 150 ºC.

Extractable - Table 2 presents the calculated statistics for the two (2) calibration sets analyzed for 1,4-dioxane as an extractable compound.

Table 2

Analytical Set	Detection Method	Calibration Range (ug/mL)	Compound	Average RRF	RSD
1	Full-Scan (m/z 35-500)	5 - 80	1,4-Dioxane	0.337	13.8
			1,4-Dioxane-d8	0.418	5.4
2	SIM[1]	0.5 - 80	1,4-Dioxane	0.429	10.3
			1,4-Dioxane-d8	0.528	3.1
3	Full-Scan	5 - 80	1,4-Dioxane	0.861	10.0
4	SIM	0.5 - 80	1,4-Dioxane	0.812	11.9

1 SIM includes m/z 58 & 88 (1,4-dioxane), m/z 64 & 96 (1,4-dioxane-d_8) and m/z 115 & 152 (1,4-Dichlorobenzene-d_4).

Analytical sets 1 and 2 were processed using 1,4-dichlorobenzene-d4 as the internal standard, 1,4-dioxane-d8 as a DMC and 1,4-dioxane as the target compound. Analytical sets 3 and 4 were processed using 1,4-dioxane-d_8 as the internal standard (isotope dilution) and 1,4-dioxane as the target compound. As indicated in Table 2, good linearity is demonstrated for all four calibration sets (5 to 80 μg/L full-scan and 0.5 to 80 μg/L SIM, using both internal standards for each) with RSD values all less than 20 percent. Recovery data and calculated statistics for the extracted sample set for both full-scan and SIM MS detection, using both 1,4-dichlorobenzene-d_4 and 1,4-dioxane-d_8 (isotope dilution) as internal standards, are summarized in Table 3.

Table 3

Full Scan	#1 % Rec.	#2 % Rec.	#3 % Rec.	#4 % Rec.	#5 % Rec.	#6 % Rec.	#7 % Rec.	Ave. % Rec.	RSD
1,4-Dioxane-d8[1]	66	61	64	56	55	57	61	60	6.9
1,4-Dioxane[1]	76	73	70	65	65	64	61	68	8.0
1,4-Dioxane[2]	121	123	125	123	125	120	122	123	1.5
SIM	**#1 % Rec.**	**#2 % Rec.**	**#3 % Rec.**	**#4 % Rec.**	**#5 % Rec.**	**#6 % Rec.**	**#7 % Rec.**	**Ave. % Rec.**	**RSD**
1,4-Dioxane-d8[1]	63	60	59	53	54	55	57	57	6.3
1,4-Dioxane[1]	69	68	67	59	62	60	64	64	6.2
1,4-Dioxane[2]	110	113	113	113	115	110	112	112	1.6

1 Results using 1,4-dichlorobenzene-d_4 as the internal standard.
2 Results using 1,4-Dioxane-d_8 as the internal standard.

The results in Table 3 demonstrate that the percent recovery of 1,4-dioxane as an extractable compound is consistent across the range of 5 to 100 μg/L (ppb) with good precision as indicated by the low RSD values for both the full-scan and the SIM analytical method. Although slightly elevated at over 100 percent, greater accuracy and precision is demonstrated by the average recoveries of 1,4-dioxane using 1,4-dioxane-d_8 as the internal standard. The SIM calibration range demonstrates that 1,4-dioxane is certainly detectable at levels as low as 0.5 μg/L. Although this study extracted a sample set with concentrations ranging from 5 to 100 μg/L (ppb), the linearity of the SIM method, the recovery of the extracted samples and the MS response from the lowest concentration sample indicate that the method detection limit may be below 0.5 μg/L (ppb) which is lower than desired CRQL using the SIM trace volatiles method in the CLP Draft SOM01.X SOW.

PES Analysis

Method

Purgeable - An ampulated 1,4-dioxane PES designed for analysis using aqueous purgeable methodology was designed and produced at the QATS Laboratory. Replicate analyses of this PES have been conducted by QATS, an external referee laboratory and an USEPA Regional laboratory using the isotope dilution quantitation method with 1,4-dioxane-d_8 as the internal standard.

Extractable - Two ampulated 1,4-dioxane PESs designed for analysis using aqueous extractable methodology were designed and produced at the QATS Laboratory. Replicate analyses of this PES have been conducted by QATS and an external referee laboratory using 1,4-dichlorobenzene-d_4 as the internal standard. QATS results are also presented using 1,4-dioxane-d_8 (isotope dilution) as the internal standard.

Results and Discussion

Purgeable - Table 4 presents the individual laboratory results and the composite results for the single purgeable PES. All of the laboratories used the isotope dilution method with 1,4-dioxane-d_8 as the internal standard.

Table 4

PES #1	Nominal Conc. (ug/L)	Average Conc. (ug/L)	Average % Recovery	RSD	n
Lab 1	10	9.2	92	4.3	8
Lab 2	10	9.4	94	7.2	5
Lab 3	10	11	110	9.8	10
Composite	10	9.8	98	10.0	23

The individual laboratory and composite averages and RSD values presented in Table 4 indicate that all three laboratories achieved a high level of accuracy and precision in the analysis of this single blind PES using the isotope dilution method of quantitation.

Extractable - Table 5 presents the individual laboratory results and the composite results for the two extractable PESs. QATS (Lab 1) results are provided using both 1,4-dichlorobenzene-d_4 and 1,4-dioxane-d_8 (isotope dilution) as the internal standard for quantitation. Lab 2 results are presented using 1,4-dichlorobenzene-d_4 only as the internal standard.

Table 5

PES #1	Nominal Conc. (ug/L)	Average Conc. (ug/L)	Average % Recovery	RSD	n
Lab 1[1]	5	3.2	64	8.3	10
Lab 2[1]	5	4.0	80	9.5	5
Composite[1]	5	3.5	70	13.4	15
Lab 1[2]	5	4.5	90	3.3	10
PES #2	**Nominal Conc. (ug/L)**	**Average Conc. (ug/L)**	**Average % Recovery**	**RSD**	**n**
Lab 1[1]	10	6.5	65	11.1	10
Lab 2[1]	10	8.3	83	7.2	5
Composite[1]	10	7.1	71	15.2	15
Lab 1[2]	10	9.4	94	4.3	10

1 Results using 1,4-dichlorobenzene-d_4 as the internal standard.
2 Results using 1,4-dioxane-d_8 as the internal standard.

Composite results presented in Table 5 indicate that extractable 1,4-dioxane recovery is approximately 70 percent when quantitated vs. 1,4-dichlorobenzene-d_4. Laboratory 1 results indicate an average recovery of approximately 65 percent using 1,4-dichlorobenzene-d_4 as the internal standard and approximately 92 percent, with a higher degree of precision as indicated by the RSD values, when quantitated vs. 1,4-

dioxane-d_8 (isotope dilution). Laboratory 2 results using isotope dilution quantitation are not available.

Multi-Laboratory Study

A multi-laboratory study was conducted to compare the analytical behavior of 1,4-dioxane as a purgeable and an extractable analyte. Three laboratories participated in the study including the QATS Laboratory and two commercial CLP laboratories. QATS provided ampulated 1,4-dioxane and 1,4-dioxane-d_8 standard solutions to all of the participants to ensure that all samples and calibration standards originated from the same source.

Method

Purgeable - The laboratories were instructed to follow the procedures in the CLP Draft SOM01.X SOW for the analysis of 1,4-dioxane using the Trace SIM method. The calibration range includes 2, 4, 20, 40 and 80 μg/L (ppb) standards for both 1,4-dioxane and 1,4-dioxane-d_8. Laboratories were instructed to quantitate both compounds vs. the SOW internal standard, 1,4-difluorobenzene. The method requires beginning-sequence and ending-sequence method blanks and continuing calibration verification (CCV) standards, with quantitation performed using the average relative response factor (RRF) from the initial calibration. Laboratories were instructed to analyze quadruplicate spiked samples at three (3) different concentrations: 2, 5 and 20 μg/L (ppb) using a 25 mL purge volume. Laboratories were allowed to use a heated purge and accelerated purge flow to enhance recovery of the analytes.

Extractable - The laboratories were instructed to follow the procedures in the CLP Draft SOM01.X SOW for the analysis of select semivolatiles using the SIM method guidelines. The calibration range includes 2, 4, 20, 40 and 80 μg/mL (ppb) standards for both 1,4-dioxane and 1,4-dioxane-d_8. Laboratories were instructed to quantitate both compounds vs. the SOW internal standard, 1,4-dichlorobenzene-d_4. The method requires beginning-sequence and ending-sequence method blanks and continuing calibration verification (CCV) standards, with quantitation performed using the average relative response factor (RRF) from the initial calibration. Laboratories were instructed to extract and analyze quadruplicate spiked samples at three (3) different concentrations; 2, 5 and 20 μg/L (ppb) using a 1 liter sample volume concentrated to a 1 mL sample extract. Laboratories were allowed to modify the GC temperature program to compensate for the early-eluting 1,4-dioxane and deuterated analog.

Results and Discussion

Purgeable - Table 6 above presents the initial calibration data for all three laboratories. It includes data and statistics for 1,4-dioxane and 1,4-dioxane-d_8 using the SOW internal standard as well as data and statistics for 1,4-dioxane using 1,4-dioxane-d_8 as the internal standard (isotope dilution). As expected due to poor purging efficiency, the RRFs for 1,4-dioxane and 1,4-dioxane-d_8 vs. the SOW internal standard are extremely low. RRFs are much higher using isotope dilution since the purgeability of 1,4-dioxane and the deuterated analog should be the same. The RSD values using the isotope

dilution method of quantitation for two of the laboratories are lower indicating higher precision and the RSD values are nearly identical for the other laboratory.

Table 6

Lab	Target Compound	RRF 2 ppb	RRF 4 ppb	RRF 20 ppb	RRF 40 ppb	RRF 80 ppb	Ave RRF	SD	RSD
1	1,4-Dioxane-d8	0.0090	0.0059	0.0060	0.0073	0.0047	0.0066	0.002	24.9
	1,4-Dioxane	0.0042	0.0041	0.0042	0.0045	0.0029	0.0040	0.0006	15.6
	1,4-Dioxane[1]	0.465	0.689	0.707	0.609	0.615	0.617	0.0095	15.5
2	1,4-Dioxane-d8	0.013	0.013	0.009	0.013	0.013	0.012	0.002	14.7
	1,4-Dioxane	0.021	0.014	0.012	0.012	0.016	0.015	0.004	24.9
	1,4-Dioxane[1]	1.626	1.074	1.302	0.888	1.230	1.224	0.275	22.5
3	1,4-Dioxane-d8	0.016	0.017	0.013	0.012	0.018	0.015	0.003	17.0
	1,4-Dioxane	0.018	0.017	0.015	0.013	0.021	0.017	0.003	18.1
	1,4-Dioxane[1]	1.138	0.974	1.137	1.106	1.172	1.105	0.077	7.0

1 Data using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 7 presents the data and statistics for Laboratory 1 for the analysis of the 2, 5 and 20 μg/L (ppb) spiked samples.

Table 7

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	21	25	28	20	24	3.7	120	15.7
1,4-Dioxane	2	3.3	3.3	3.6	2.9	3.3	0.3	165	8.8
1,4-Dioxane[1]	2	3.1	2.5	2.5	2.8	2.7	0.3	135	10.5
1,4-Dioxane-d8	20	22	22	26	19	22	2.9	110	12.9
1,4-Dioxane	5	6.2	6.0	6.7	6.6	6.4	0.3	128	5.2
1,4-Dioxane[1]	5	5.7	5.5	5.1	7.0	5.8	0.8	116	14.1
1,4-Dioxane-d8	20	20	21	19	19	20	1.0	100	4.8
1,4-Dioxane	20	22	20	23	20	21	1.5	105	7.1
1,4-Dioxane[1]	20	21	19	24	23	22	2.2	110	10.2

[1] Results using 1,4-Dioxane-d8 (isotope dilution) as the internal standard.

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 8 presents the data and statistics for Laboratory 2 for the analysis of the 2, 5 and 20 μg/L (ppb) spiked samples.

Table 8

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	9.6	11	11	11	11	0.7	55	6.6
1,4-Dioxane	2	1.7	1.6	1.5	1.6	1.6	0.08	80	5.1
1,4-Dioxane[1]	2	3.6	3.0	2.7	3.1	3.1	0.4	155	12.1
1,4-Dioxane-d8	20	11	10	9.6	11	10	0.7	50	6.8
1,4-Dioxane	5	3.1	3.0	2.6	3.3	3.0	0.3	60	9.8
1,4-Dioxane[1]	5	5.7	5.9	5.4	5.8	5.7	0.2	114	3.8
1,4-Dioxane-d8	20	11	10	12	11	11	0.8	55	7.4
1,4-Dioxane	20	12	11	11	12	12	0.6	60	5.0
1,4-Dioxane[1]	20	21	21	20	22	21	0.8	105	3.9

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 9 presents the data and statistics for Laboratory 3 for the analysis of the 2, 5 and 20 μg/L (ppb) spiked samples.

Table 9

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	18	20	19	19	19	0.8	95	4.3
1,4-Dioxane	2	1.9	2.4	2.2	1.9	2.1	0.2	105	11.7
1,4-Dioxane[1]	2	2.1	2.4	2.3	2.0	2.2	0.2	110	8.3
1,4-Dioxane-d8	20	8.1	12	18	12	13	4.1	65	32.6
1,4-Dioxane	5	4.3	3.1	4.9	3.0	3.8	0.9	76	24.3
1,4-Dioxane[1]	5	10.5[2]	4.9	5.4	5.1	5.1	0.3	102	4.9
1,4-Dioxane-d8	20	16	17	19	17	17	1.3	85	7.3
1,4-Dioxane	20	15	17	19	16	17	1.7	85	10.2
1,4-Dioxane[1]	20	19	20	20	20	20	0.5	100	2.5

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.
2 Outlier result not included in statistical calculations.

Table 10 presents the composite averages for all laboratories for each spike level. Note that 1,4-dioxane-d_8 was spiked into all samples at a concentration of 20 μg/L (ppb).

Table 10

Compound	2 ug/L (ppb) Spike			5 ug/L (ppb) Spike			20 ug/L (ppb) Spike		
	Ave.	% Rec.	RSD	Ave.	% Rec.	RSD	Ave.	% Rec.	RSD
1,4-Dioxane-d8	18	89	33.3	15	75	39.8	16	80	24.7
1,4-Dioxane	2.3	116	32.7	4.4	88	36.2	17	83	26.3
1,4-Dioxane[1]	2.7	134	17.5	5.6	112	10.1	21	104	7.3

1 Results using 1,4-Dioxane (isotope dilution) as the internal standard.

The results from Laboratory 1 indicate that the 1,4-dioxane-d_8 recovery is consistent in all three sample sets at approximately 110 percent with an RSD value of approximately 14 percent, indicating good precision. The average recovery of 1,4-dioxane in all three sample sets is greater than the spiked values at approximately 133 percent. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 120 percent. The highest percent recoveries are from the 2 µg/L (ppb) spike samples which is possibly due to carry-over contamination from previous samples. Carry-over contamination has historically been a problem with the 1,4-dioxane purgeable method and method blank contamination has been observed in this study.

The results from Laboratory 2 indicate that the 1,4-dioxane-d_8 recovery is also consistent in all three sample sets, however it is much lower than Laboratory 1 at approximately 55 percent with an RSD value of approximately 7 percent, indicating good precision. The average recovery of 1,4-dioxane in all three sample sets also coincides with the 1,4-dioxane-d_8 recovery at approximately 67 percent. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 125 percent which is skewed high by the relatively high recovery in the 2 µg/L (ppb) sample set at 155 percent. Again, the highest percent recoveries are from the 2 µg/L (ppb) spike samples which is possibly due to carry-over contamination as previously mentioned.

The results from Laboratory 3 indicate that the 1,4-dioxane-d_8 recovery is consistent in two of the sample sets with lower recovery and less precision in the 5 µg/L (ppb) set. The average recovery in the low and high level sample set is 90 percent, whereas it is 65 percent in the 5 µg/L (ppb) sample set. The average recovery of 1,4-dioxane in all three sample sets is lower than the spiked values at approximately 89 percent. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 104 percent with a higher level of precision indicated by the low RSD values. As with Laboratories 1 and 2, the highest percent recoveries are from the 2 µg/L (ppb) spike samples which is possibly due to carry-over contamination.

The composite averages presented in Table 10 also indicate that the highest recovery for 1,4-dioxane was demonstrated in the 2 µg/L (ppb) sample set at 116 percent, whereas the average recoveries in the 5 and 20 µg/L (ppb) sets are approximately 85 percent. Using the isotope dilution method of quantitation results in a higher recovery for

the 2 µg/L (ppb) set at 134 percent. The accuracy of recovery at the 5 µg/L (ppb) level is approximately the same regardless of the quantitation method and is more accuarate at the 20 µg/L (ppb) level at 83 percent and 104 percent recovery for the conventional and isotope dilution method, respectively. At all three levels, the significantly lower RSD values for the isotope dilution method indicate a higher level of quantitation precision.

Extractable - Table 11 presents the initial calibration data for all three laboratories. It includes data and statistics for 1,4-dioxane and 1,4-dioxane-d_8 using the SOW internal standard as well as data and statistics for 1,4-dioxane using 1,4-dioxane-d_8 as the internal standard (isotope dilution). The RSD values using the isotope dilution method of quantitation for all of the laboratories are significantly lower indicating a higher degree of precision.

Table 11

Lab	Target Compound	RRF 2 ppb	RRF 4 ppb	RRF 20 ppb	RRF 40 ppb	RRF 80 ppb	Ave RRF	SD	RSD
1	1,4-Dioxane-d8	0.459	0.519	0.558	0.529	0.491	0.511	0.04	7.4
	1,4-Dioxane	0.621	0.693	0.739	0.687	0.645	0.677	0.05	6.8
	1,4-Dioxane[1]	1.353	1.336	1.325	1.298	1.312	1.325	0.02	1.6
2	1,4-Dioxane-d8	0.321	0.299	0.336	0.295	0.315	0.313	0.02	5.3
	1,4-Dioxane	0.349	0.321	0.355	0.313	0.337	0.335	0.02	5.3
	1,4-Dioxane[1]	1.088	1.074	1.056	1.062	1.072	1.070	0.01	1.1
3	1,4-Dioxane-d8	0.525	0.533	0.595	0.583	0.599	0.567	0.04	6.2
	1,4-Dioxane	0.539	0.539	0.607	0.594	0.607	0.577	0.04	6.1
	1,4-Dioxane[1]	1.025	1.013	1.021	1.017	1.017	1.019	0.005	0.4

1 Data using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 12 presents the data and statistics for Laboratory 1 for the analysis of the 2, 5 and 20 µg/L (ppb) spiked samples.

Table 12

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	11	11	11	10	11	0.5	54	4.7
1,4-Dioxane	2	1.0	1.1	1.1	0.98	1.0	0.06	52	6.1
1,4-Dioxane[1]	2	1.8	2.0	2.0	1.9	1.9	0.1	96	5.0
1,4-Dioxane-d8	20	10	11	11	11	11	0.5	54	4.7
1,4-Dioxane	5	2.5	2.8	2.7	2.7	2.7	0.1	54	4.7
1,4-Dioxane[1]	5	5.0	5.0	4.9	4.9	5.0	0.06	99	1.2
1,4-Dioxane-d8	20	9.3	9.7	8.7	9.6	9.3	0.5	47	4.8
1,4-Dioxane	20	9.2	9.7	8.7	9.6	9.3	0.5	47	4.9
1,4-Dioxane[1]	20	20	20	20	20	20	0.0	100	0.0

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 13 presents the data and statistics for Laboratory 2 for the analysis of the 2, 5 and 20 μg/L (ppb) spiked samples.

Table 13

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	14	12	12	11	12	1.3	61	10.3
1,4-Dioxane	2	1.9	1.6	1.5	1.1	1.5	0.3	76	21.7
1,4-Dioxane[1]	2	2.7	2.7	2.5	2.2	2.5	0.2	126	9.4
1,4-Dioxane-d8	20	12	9.3	11	12	11	1.3	55	11.5
1,4-Dioxane	5	3.4	2.5	3.0	3.5	3.1	0.5	62	14.7
1,4-Dioxane[1]	5	5.4	5.3	5.4	5.6	5.4	0.1	109	2.3
1,4-Dioxane-d8	20	10	12	10	10	11	1.0	53	9.5
1,4-Dioxane	20	11	12	10	10	11	1.0	54	8.9
1,4-Dioxane[1]	20	20	19	20	20	20	0.5	99	2.5

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.

Table 14 presents the data and statistics for Laboratory 3 for the analysis of the 2, 5 and 20 μg/L (ppb) spiked samples.

Table 14

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	13	12	11	11	12	1.0	59	8.1
1,4-Dioxane	2	1.3	1.2	1.1	1.1	1.2	0.1	59	8.1
1,4-Dioxane[1]	2	1.9	1.9	1.9	2.0	1.9	0.1	96	2.6
1,4-Dioxane-d8	20	12	11	12	13	12	0.8	60	6.8
1,4-Dioxane	5	3.1	2.9	3.0	3.1	3.0	0.1	61	3.2
1,4-Dioxane[1]	5	5.0	5.0	5.0	5.0	5.0	0.0	100	0.0

Target Analyte	Spike (ug/L)	S1 (ug/L)	S2 (ug/L)	S3 (ug/L)	S4 (ug/L)	Ave (ug/L)	SD	Ave % Rec.	RSD
1,4-Dioxane-d8	20	13	13	11	14	13	1.3	64	9.9
1,4-Dioxane	20	14	14	11	14	13	1.5	66	11.3
1,4-Dioxane[1]	20	21	21	21	20	21	0.5	104	2.4

1 Results using 1,4-Dioxane-d_8 (isotope dilution) as the internal standard.
2 Outlier result not included in statistical calculations.

Table 15 presents the composite averages for all laboratories for each spike level. Note that 1,4-dioxane-d_8 was spiked into all samples at a concentration of 20 μg/L (ppb).

Table 15

Compound	2 ug/L (ppb) Spike			5 ug/L (ppb) Spike			20 ug/L (ppb) Spike		
	Ave.	% Rec.	RSD	Ave.	% Rec.	RSD	Ave.	% Rec.	RSD
1,4-Dioxane-d8	12	60	9.4	11	55	8.9	11	55	15.9
1,4-Dioxane	1.2	60	22.4	2.9	59	10.8	11	56	17.6
1,4-Dioxane[1]	2.1	106	15.3	5.1	103	4.6	20	101	2.9

1 Results using 1,4-Dioxane (isotope dilution) as the internal standard.

The results from Laboratory 1 indicate that the 1,4-dioxane-d_8 recovery is consistent in all three sample sets at approximately 52 percent with an RSD value of approximately 5 percent, indicating good precision. The average recovery of 1,4-dioxane in all three sample sets approximates the 1,4-dioxane-d_8 recovery at approximately 51 percent with an RSD value of approximately 5 percent, also indicating good precision. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 98 percent with an average RSD value of approximately 2 percent.

The results from Laboratory 2 indicate that the 1,4-dioxane-d_8 recovery is also consistent in all three sample sets and slightly higher than Laboratory 1 at approximately 56 with an RSD value of approximately 10 percent, indicating good

precision. The average recovery of 1,4-dioxane in all three sample sets is higher than the 1,4-dioxane-d_8 recovery at approximately 64 percent with a higher average RSD value at 15 percent. The 1,4-dioxane recovery from this lab appears to decrease as the spike value increases with an approximate 10 percent difference between each sample set as the spike value increases. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 111 percent which is skewed high by the relatively high recovery in the 2 µg/L (ppb) sample set at 126 percent. Again, precision tends to increase using the isotope dilution quantitation method with an average RSD value of approximately 5 percent.

The results from Laboratory 3 indicate that the 1,4-dioxane-d_8 recovery is consistent in all three sample sets with an average recovery of 61 percent and an RSD value of 8 percent. The average recovery of 1,4-dioxane in all three sample sets approximates the 1,4-dioxane-d_8 recovery at 62 percent, also with an average RSD value of approximately 8 percent. Using the isotope dilution method of quantitation provides a more accurate average recovery of 1,4-dioxane at approximately 100 percent with a higher level of precision indicated by the average RSD value of 2 percent.

The composite averages presented in Table 15 indicate that the recovery of both 1,4-dioxane and 1,4-dioxane-d_8 are very similar in all three sample sets at approximately 60 percent with an average RSD value of 14 percent. Using the isotope dilution method of quantitation results in very similar average recoveries for all three sample sets with more accurate recoveries which approximate the spiked values at approximately 103 percent, associated with greater precision with an average RSD value of 8 percent.

Conclusions

Results and statistics presented here from the single laboratory study indicate that both the purgeable and extractable CLP methods can be modified for the analysis of 1,4-dioxane. Detection limits as low as 0.5 µg/L (ppb) are achievable for both methods using SIM MS detection. The purgeable method can be performed using either a 5 or 25 mL sample volume with heated sparging and an accelerated purge flow without the addition of sodium sulfate. However, poor chromatography can result when the purge temperature and/or purge flow are too high. Optimum conditions should be determined for each purgeable system. Single laboratory extractable results demonstrate calibration linearity in the 0.5 to 80 µg/mL range using SIM MS detection. Data and statistics demonstrate consistent recovery of 1,4-dioxane in a 5 to 80 µg/L sample set, with a higher degree of accuracy and precision using isotope dilution quantitation and SIM MS detection.

Data and statistics from three laboratories performing replicate analysis of a purgeable single blind PES using a modified Method 8260 presented here indicate a high degree of recovery and precision, with 98 percent average recovery and 10 percent average RSD, respectively. The individual laboratory average recoveries fall within the range of 90 to 110 percent, all with RSD values less than 10 percent. Two laboratories also performed replicate analysis of two (2) extractable single blind PESs using a modified Method 8270 with consistent results. Composite results indicate an average analyte

recovery of 70 percent which is well within the expected recovery range of the method using CLP conventional quantitation methods. A 30 percent increase in recovery from 64 percent to 94 percent was demonstrated using the Laboratory 1 results using the isotope dilution method of quantitation compared to the conventional method of quantitation. The isotope dilution quantitation method also demonstrated higher precision for the replicate analyses with a drop in RSD values from 10 to 4 percent.

The multi-laboratory results presented here are probably the most important because they allow both a comparison of the methods (purgeable vs. extractable) and a comparison of the quantitation method (conventional vs. isotope dilution) from three different laboratories. The purgeable calibration standards demonstrated extremely low relative response factors (RRFs) for 1,4-dioxane and 1,4-dioxane-d_8 when quantitated against the SOW internal standard. This was expected due to the high water solubility of these compounds resulting in poor purging efficiency. Isotope dilution quantitation results in higher RRFs which is expected since the native and deuterated analytes should exhibit similar purging efficiency. Using conventional quantitation methods, the average recovery of 1,4-dioxane-d_8 in all sample sets was 81 percent, whereas the average recovery of 1,4-dioxane was 96 percent. Theoretically, one would expect the recoveries of these two compounds to be very similar, yet the deuterated analog average recovery is 15 percent lower than the native compound average recovery. Similarly, the average recovery of 1,4-dioxane in all sample sets is 116 percent when using the isotope dilution method of quantitation. The lower recovery of 1,4-dioxane-d_8 relative to 1,4-dioxane may result in an average recovery of 1,4-dioxane which is biased high when using the isotope dilution method of quantitation. As previously mentioned, a higher degree of precision is associated with the isotope dilution method of quantitation compared to the conventional method, based on associated average RSD values for all sample sets of 12 and 32 percent, respectively.

The extractable initial calibration standards for all of the laboratories demonstrated a linear range from 2 to 80 μg/mL with a high degree of precision using the convention method of quantitation and significantly lower RSD values when using the isotope dilution method of quantitation. The composite (all laboratories) average recoveries for 1,4-dioxane and 1,4-dioxane-d_8 in each sample set fall within the 55 to 60 percent range using the conventional quantitation method, and the recoveries for both compounds within a sample set are nearly identical. The recoveries exhibited in this study are well within the expected range for an extractable compound with the physical properties of 1,4-dioxane. Using isotope dilution quantitation, the composite average recovery of 1,4-dioxane in all sample sets is approximately 103 percent which is nearly 40 percent higher than with the conventional method and closely approximates the spiked values. Again, higher precision is associated with the isotope dilution method of quantitation with an RSD value of 8 percent compared to an average RSD value of 17 percent associated with the CLP conventional quantitation method.

The data and statistics from the single laboratory study, PES analysis and multi-laboratory study suggest that both a modified Method 8260 (purgeable) and modified Method 8270 (extractable) are viable alternatives in the CLP for the analysis of 1,4-

dioxane. However, the results of this comparative study suggests that the extractable method using the isotope dilution method of quantitation does provide for a more accurate and precise method of detection for 1,4-dioxane. The results from the multi-laboratory study also provide evidence that no matter which method is used, purgeable or extractable, the isotope dilution method of quantitation provides a higher level of accuracy and precision compared to the CLP conventional method of quantitation.

Aside from the data and statistics, there are other factors which might be considered in choosing the appropriate method of analysis for this compound. Carry-over contamination has been reported by commercial laboratories and was observed in this comparative study using the purgeable method. Carry-over contamination has not been reported to be a problem associated with the extractable method. Carry-over contamination can result in additional method or instrument blank requirements which ultimately results in additional costs and time. Another factor to consider is interference from other compounds in samples and standards. As a purgeable compound, 1,4-dioxane is a mid-eluting analyte with an extremely poor purging efficiency and very low RRF using CLP conventional quantitation methods. Using full-scan analysis with the proposed CLP Trace and Low/Medium level analysis, 1,4-dioxane will be analyzed along with 68 other target analytes, DMCs and internal standards, as well as potential non-target compounds, some of which could cause interference with the analysis of 1,4-dioxane. With the extractable method, 1,4-dioxane elutes immediately after the solvent front which lowers the chances of potential interference. Additionally, there are no modifications to the sample extraction procedures for 1,4-dioxane, other than spiking the sample with the deuterated analog. The sample extract which may have been required for CLP semivolatiles can simply be re-analyzed using SIM MS detection or can simply be analyzed using the full-scan method with the other semivolatile analytes, depending on the required quantitation limits.

Acknowledgements
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INORGANIC METHODS II

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ACCELERATED SOLVENT EXTRACTION (ASE) AS A SAMPLE EXTRACTION TECHNIQUE FOR PERCHLORATE IN SOLID

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The widespread presence of perchlorate in soils, water and vegetation has received increased attention by scientists, regulatory agencies and the general public. Isolating perchlorate, especially at the low levels necessary for risk-based monitoring, can be challenging. Several approaches for sample extractions are being explored as part of the overall analytical scheme. Accelerated solvent extraction (ASE) is an extraction technique that uses organic- or aqueous-based solvent for fast and efficient extractions. The use of elevated temperatures and pressures allow extractions to be done very quickly and with very little solvent. ASE fulfills the requirements of Method 3545A for the extraction of organic contaminants from solid waste samples.

However, aqueous solvent systems are widely used in ASE and this allows the extraction of very polar compounds. For example, ASE with chelating agents has been used for the extraction of metals from soils. ASE has also been used for ionic materials like chloride, sulfate, phosphate, bromate and perchlorate. This presentation will center on the use of ASE as an extraction method prior to perchlorate determination using ion chromatography (IC) with suppressed conductivity or mass spectrometry for detection. We have investigated the recovery of perchlorate from soils and vegetable samples. Vegetation extracts generally require a clean-up step prior to analysis. We explored various in-line clean-up procedures to remove interferences for the IC analysis. We will discuss ASE precision and accuracy results for the determination of perchlorate from these sample types and how the various operating parameters affect analyte recovery. We have found that extracts can be produced that require no further clean up prior to analysis by IC or ICMS.

ANALYSIS OF PERCHLORATE IN DRINKING WATER, GROUNDWATER, SALINE WATER, SOIL AND BIOTA BY LC/MS

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Introduction

A new method for the detection and confirmation of perchlorate has been developed. This new method utilizes liquid chromatography to separate perchlorate from interferences and mass spectrometry to confirm and quantify.

Perchlorate has been produced in 39 states and has been found in drinking water in 18 states. Prior to 1997, perchlorate could not be detected at less than 400 ppb. A new method developed by the California Department of Health Services[1] in 1997 could detect 4 ppb of perchlorate in drinking water. Perchlorate was listed by the USEPA on the "Contaminant Candidate List" for consideration for possible regulation in 1998.

In 1999 the USEPA[2] published method 314.0 designed for drinking water at or below 4 ppb and required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). This method was developed for drinking water and is sufficient to detect perchlorate at 1 to 4 ppb. Method 314.0 is based on ion chromatography with conductivity detection. Method interferences can be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus leading to discrete artifacts or elevated baseline in ion chromatograms. These interferences leading to elevated baseline noise can lead to false positive and increased detection limits for perchlorate. Sample matrices with high concentrations of common anions such as chloride, sulfate and carbonate can make the analysis problematic by destabilizing the baseline. Furthermore, highly ionic samples or dissolved solids can cause column degradation.

Perchlorate has been detected in drinking water in major metropolitan areas and groundwater associated with the production of solid rocket propellant. Even more recent is the discovery of perchlorate in lettuce samples that were irrigated with Colorado River water. These and other recent events have increased the need for the low detection of perchlorate in matrices such as ground water, saline water, soil and plant material. This level of concern about perchlorate detection in matrices other than drinking water has motivated instrument manufacturer, academia and commercial laboratories to develop methods for analyzing perchlorate in difficult matrices.

DataChem Laboratories, Inc. in conjunction with K'(Prime) Technologies, Inc. has developed a new liquid chromatography mass spectrometry method for the detection

and confirmation of perchlorate in drinking water, groundwater, saline water, soil and biota samples.

Method

Instrumentation

An Agilent 1100 LC/MSD system was utilized for this method. This method uses simple determinative techniques available to normal LC/MS technologies and does not require any instrumentation additions or systematic pretreatment of samples. The analysis is accomplished in under thirteen minutes and can process up to 20 samples in an eight hour sequence with all appropriate quality control and perchlorate identification by mass spectrometry. This new method uses a newly developed commercially available peptides impregnated reverse phase liquid chromatography column (KP-RPPX series columns) developed by K'(Prime) Technologies, Inc.

Eluent was prepared with ASTM Type II water and acetonitrile (ACN) mixed in two one-liter bottles. One bottle will contain 95% ACN and 5% water (v/v) and the other will contain 95% water and 5% ACN. A small aliquot of acetic acid will be added to each bottle. The solutions from the two bottles will be mixed at the instrument pump at 47% water and 53% ACN.

Calibration

A minimum of six calibration standards were used for internal standard calibration. An internal standard of oxygen-18 labeled perchlorate was used. The standard curve for perchlorate is established by plotting the area for each standard/internal standard ratio against the concentration. The calibration was verified immediately after calibration by the analysis of an initial calibration verification (ICV) Standard. The ICV was prepared from a separate source of perchlorate. Continuing calibration verification (CCV) standards were used for each analysis batch prior to conducting any analysis, every tenth sample, and at the end of the analysis sequence. Calibration is verified if the relative percent difference is less than 15%.

Sample Preparation

Water samples are prepared by adding an aliquot of sample to a 15-mL disposable centrifuge tube. An appropriate aliquot of internal standard and glacial acetic acid is added to each sample. Each sample is filtered through a 0.45 μm filter into an autosampler vial for analysis.

Soil samples are prepared by adding an aliquot of sample and 10 mL of ASTM Type II water to a 15 mL centrifuge tube. An appropriate aliquot of internal standards and glacial acetic acid is added to each sample. The mixture is vortexed, sonicated for at least 10 minutes and vortexed again. If necessary, the sample is centrifuged. The extract is then filtered through a 0.45 μm filter into an autosampler vial for analysis.

Biota (plant) samples are prepared by using a sufficient portion (at least 10 grams) of sample and ground through a hand-operated stainless steel grinder. ASTM Type II water is added to an aliquot of biota sample in a 50 mL centrifuge tube. An appropriate

aliquot of internal standard and glacial acetic acid are added to each sample. The mixture is vortexed and left overnight, which allows for complete saturation of the sample. Prior to analysis, the sample is vortexed again, then centrifuged at 5000 rpm for 30 minutes. A portion of the supernatant is then drawn through an activated C18 column, which removes a large portion of organic contaminants. The final extract is then filtered through a 0.45 μm filter into an autosampler vial for analysis.

The five matrices evaluated by this LC/MS method are presented in Table 1.

Table 1. Matrix Description and Preparation

Matrix	Sample Preparation
Drinking Water (DW)	Laboratory Distilled Water Conductivity = 1 μS
Soil	Soil extracted with water
Biota	Grass samples were homogenized, extracted with water and C-18 column cleanup
Synthetic Ground Water (SGW)	Laboratory Distilled Water with 1000 mg/L of chloride, sulfate and carbonate. Conductivity = 7700 μS
Great Salt Lake (GSL) Water	Water taken from the Great Salt Lake and diluted 10 fold Conductivity = 21000 μS

Experimental Design

Sensitivity

Method detection limits (MDL) studies following the USEPA[3] procedure were analyzed to determine sensitivity of this LC/MS method. Practical quantitation limits (PQL) in aqueous, soil and biota samples were based on the DoD Quality System Manual[4] guidance.

Selectivity

Mass spectrometry is used to monitor perchlorate at mass 83, which is achieved by the partial fragmentation of perchlorate to remove an oxygen atom. Using mass 83 eliminates known interference caused by sulfate at mass 99. Confirmation of perchlorate is obtained not only by retention time and mass but also by using the naturally occurring isotopic ratio of ^{35}Cl to ^{37}Cl, which is 3.065 [5], to monitor the ratio of mass 83 and 85 from perchlorate. The isotopic ratio of ^{35}Cl to ^{37}Cl is used to improve the selectivity of the method and to provide confidence that the detected signal is due to perchlorate and not an interfering compound[6]. Isotopically labeled perchlorate, ^{18}O LP, is used as an internal standard and added to each standard and sample. This internal standard is used for relative retention time confirmation, monitoring instrument performance and internal standard calibration.

Precision and Bias

Precision and bias validation studies were performed using the guidance presented in the NELAC 2003 Standard[7] Chapter 5, appendix C3. Briefly, five matrices including drinking water, soil, biota, simulated groundwater and saline water were spiked with perchlorate and analyzed. Three different concentrations in each matrix were analyzed on three consecutive days. Additionally, all samples submitted for analysis having difficult matrices and/or positive detections by method 314.0 were confirmed by this new method. A proficiency testing sample was also analyzed to assess bias of this method.

Robustness

A known amount of internal standard was added to each sample and standard and monitored at mass 89. The use of internal standard calibration adds stability to the calibration and eliminates the need for monitoring transition of perchlorate from mass 99 to 83.

Results and Discussion

Calibration

Calibration acceptance criterion for the initial calibration curve is a correlation coefficient of 0.995 or higher. Acceptance limits for ICV and CCV were set at ± 15% difference from the true value.

Sensitivity

The MDLs for five matrices were calculated using the procedures specified by the USEPA[3]. Seven aliquots of a fortified spike or indigenous level were analyzed. The MDL is calculated by multiplying the standard deviation of results by 3.143 (*t* statistic). The DW, SGW and soil samples were spiked with perchlorate while indigenous levels of perchlorate in biota and GSL were used to calculate MDLs. The MDLs were additionally verified by analysis of a MDL verification sample for each matrix. This procedure is described in the DoD Quality System Manual[4].

The PQL was set no less than the lowest calibration standard. Values below the PQL are reported with appropriate qualifiers. Additionally, the PQL was set at 3 to 5 times the MDL value. MDL and PQL data are presented in Table 2 and MDL Verification Results in Table 3.

Table 2. MDL and PQL Determinations

Matrix	n	Units	Spiked Conc	Mean Conc	Standard Deviation	%RSD	Ratio	MDL	PQL
DW	7	µg/L	0.200	0.200	0.0108	5.40%	5.89	0.0339	0.20
Soil	7	µg/Kg	2.00	2.26	0.258	11.4%	2.47	0.811	2.0
Biota*	7	µg/Kg	4.49	4.49	0.609	13.6%	2.34	1.92	6.0
SGW	7	µg/L	0.200	0.209	0.0257	12.3%	2.48	0.0807	0.20
GSL*	7	µg/L	0.219	0.219	0.0196	8.96%	3.55	0.0617	0.20

* Indigenous levels in these matrices were used to calculate MDLs

Table 3. MDL Verification Results

Matrix	MDL Verification Concentration	MDL Verification Result
Drinking Water	0.10 µg/L	0.11 µg/L
Soil	1.0 µg/Kg	1.0 µg/Kg
Biota	2.3 µg/Kg	1.6 µg/Kg
SGW	0.10 µg/L	0.11 µg/L
GSL	0.11 µg/L	0.12 µg/L

Selectivity

Mass spectrometry is used to monitor Perchlorate at masses 83 and 85. Internal standard is monitored at mass 89. Figure 2 through 6 show chromatograms of Perchlorate at mass 83, 85 and 89 in each matrix.

The ratio of 83/85 masses were monitored during this study for all matrices analyzed by this method. The data generated were used to calculate statistical process control limits. Differences in measurement error discussed in Experimental Statistics[8] may have an impact on the low and medium concentration samples shown in Table 4. The results of this scatter plot and table shows a lower 83/85 mean ratio at low concentrations of perchlorate. Based on error of measurement associated with low levels and the importance of confirming perchlorate, the 83/85 isotopic ratio statistical process control limits are set using ± 2 standard deviations at 2.2 to 3.3 which is calculated as follows.

$$MeanRatio_{83/85} \pm \left(2 \times Stdev_{83/85}\right)$$

Table 4. Perchlorate 83/85 Isotopic Ratio and Control Limits

Mean 83/85 Ratio by Concentration				
Low Conc	Average:	2.59	Std Dev:	0.28
	LCL[1]:	1.74	UCL[1]:	3.44
Med Conc	Average:	2.73	Std Dev:	0.32
	LCL[1]:	1.78	UCL[1]:	3.68
High Conc	Average:	2.89	Std Dev:	0.20
	LCL[1]:	2.27	UCL[1]:	3.50

Total 83/85 Ratio				
Average	Std Dev	n	LCL[2]	UCL[2]
2.75	0.29	121	2.16	3.34

1. ± 3 SD
2. ± 2 SD

Validation Study

Validation studies based on NELAC Chapter 5[7] were generated for five matrices by analyzing samples over three consecutive days at varying concentration levels. The study designed analyzed nine replicates for each matrix on a daily basis. The three concentrations are at or near the limit of quantitation, at the upper-range of the calibration (upper 20%) and at a mid-range concentration.

Precision

To compare the variability of performance (precision) the *F*-Test was performed on each matrix. Matrices were evaluated based on concentration levels, combined daily results and used to compare the precision of this method on the five matrices. All results were acceptable.

Bias

Analysis of the data to determine if the method has bias with respect to aqueous matrices was accomplished by multiple techniques. Proficiency testing, statistical comparison of means and a comparison of results from method 314.0 showed acceptable results.

Robustness

A single calibration curve was used for this entire study. The stability of the instrument calibration was acceptable. Use of an internal standard has reduced calibration runs and eliminates worrisome variation in the mass spectrometer due to matrix interferences. The internal standard area counts were monitored and must be within ± 30% of the daily calibration verification response. Perchlorate internal standard retention

time and the retention time of naturally occurring perchlorate is the equivalent and fluctuations due to temperature and pressure are negated.

Conclusions

LC/MS Method Quality Control Requirements

- The minimum quality control practices employed by LC/MS to analyze perchlorate should include:
- MDL procedures to determine the sensitivity based on accepted reference.
- PQL determinations to establish the reporting level for accurate quantitation.
- Validation studies for specific matrices.
- Instrument calibration using at least five levels of standards and having acceptability parameters defined.
- Internal standard using isotopic oxygen-18 labeled perchlorate added to each standard and sample and monitored to ensure instrument performance.
- Internal standard calibration used for quantitation.
- The isotopic ratio of 83/85 for perchlorate identification is assessed and statistical process control limits are employed to ensure identification.
- Retention time of internal standard and perchlorate are monitored and a retention time window of no more than 0.3%.
- Calculated Control Limits for LCS. See Table 12.
- Batch QC should include at a minimum method blanks and laboratory control samples and, if the project requires, both matrix spikes and matrix spike duplicates should be analyzed.

Statistical Analysis of Precision and Bias

Statistical analysis of precision and bias are employed to validate this method. These techniques ensure that data of known and documented quality can be generated using this method. In fact, the statistical approach validates the premise that as detection limits and reporting limits are pushed lower, the precision at these low concentration levels are usually statistically different then higher concentrations levels. If the documented precision of the low concentration meets the desired data quality objectives and decision-making criteria, it matters little if the low concentration data for precision is statistically different from the high concentration data. Each specific level must be assessed for acceptability for the level of documented quality needed for a particular project.

There are two reasons that methods should not be assessed with statistics only as prescribed by NELAC[5]. First is that the instrument error of measurement might affect the low concentration data more than the high concentration data. Second, that the largest variability in performance at any level is acceptable to meet specific project data quality objectives even though specific concentrations levels produce precision that may be statistically different.

In addition to statistics, other techniques should always be employed to validate a method. These techniques include replicates, the analysis of samples with a different method, reproducibility, the analysis of duplicate and spikes samples and proficiency testing samples.

Method Applications

This method has been validated to analyze samples in drinking water, soil, biota, groundwater and saline water. The method can analyze samples with both low and high levels of common ions, organic interferences and even highly saline samples. This method is quantitative and provides qualitative information to positively identify perchlorate. Any analysis of perchlorate with positive results without historical support should be analyzed to confirm the identity of perchlorate using a mass spectrometry technique.

References

1. "Determination of Perchlorate by Ion Chromatography", State of California, Department of Health Services, Sanitation and Radiation Laboratory, Rev. Nos. 0, (June 3, 1997).
2. "Determination of Perchlorate in Drinking Water using Ion Chromatography" USEPA Method 314.0, Rev 1, November 1999.
3. *United States Code of Federal Register* (CFR), Vol. **40**, Part 36, Appendix B.
4. "Department of Defense Quality Systems Manual for Environmental Laboratories", Final Version 2, June 2002.
5. Gessinger G. Hawley, "The Condensed Chemical Dictionary" 10th Edition, 1981.
6. Koester, C.J., Beller, H.R. and Halden, R.U., *Environmental Science and Technology*, 2000, **34**, 1862-1864
7. 2003 NELAC Standard, Chapter 5, Appendix C.3, EPA 600/R-04/003, Approved June 5, 2003.
8. "Experimental Statistics" Handbook 91, United States Department of Commerce, National Bureau of Standards, August 1, 1963.
9. J.C. Miller and J.N. Miller ,"Statistics for Analytical Chemistry", 1984.

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PERCHLORATE IN VARIOUS VEGETABLES BY IC/MS

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Since the West Coast has perchlorate contamination due to plumes in the ground and Colorado River waters, there is major concern for vegetables accumulating perchlorate. Therefore, a method for quantifying trace level perchlorate in vegetables like lettuce, spinach, lemons, strawberries, broccoli and alfalfa is required. IC-MS was successfully used for the analysis of perchlorate in vegetable extracts to low parts per billion detection limits. Superior suppressor technology from Metrohm IC enabled coupling an industry standard Agilent mass spectrometer for robust analysis without any matrix diversion or splitting. System configuration and sample results will demonstrate method performance.

LC/MS/MS APPLICATIONS IN THE ENVIRONMENTAL LABORATORY

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HPLC offers high precision and sensitivity and is the analytical tool most commonly used for assays and impurity determinations in the pharmaceutical industry. Also, the Environmental Protection Agency (EPA) has developed and promulgated various HPLC methods for the determination of non-volatile, thermally-labile and highly polar chemicals of environmental concern such as polynuclear aromatic hydrocarbons (PAHs), aldehydes, carbamates, explosives, paraquat, diquat and glyphosate. More and more requests from our clients are to develop methods for determining site-specific compounds. In many cases these compounds are not amenable to GC but more suited to HPLC or IC analysis. Advances in the last 10–15 years have greatly facilitated the pairing of HPLCs to mass spectrometric detectors and, thus, they have become much less cost prohibitive and more user-friendly. One of Lancaster Labs fastest growing analyses is LC(IC)/MS/MS. The excellent sensitivity and selectivity inherent to this

technique allows for a reduction in prep time and thus higher throughput and automation. In some applications, the target analytes were masked by interferences on the UV detector, but specific ions (masses) could easily be deconvoluted by monitoring "daughter ions" on the MS2 mass spectrometer (see Figure 1)

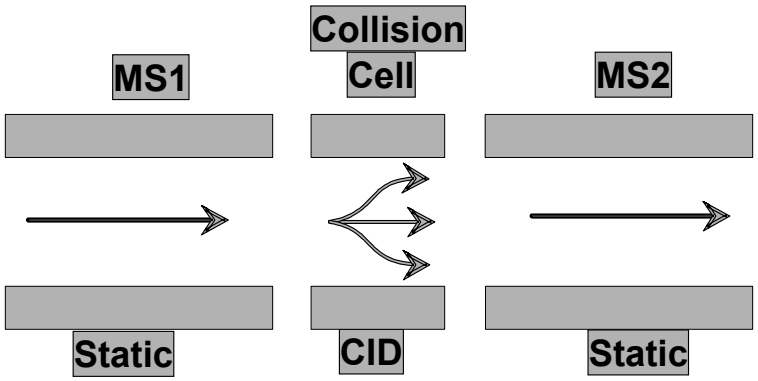

Figure 1.

In another example, we were able to apply LC/MS/MS to a method that required a lengthy extraction and cleanup followed by a cumbersome GC analysis. The resulting LC/MS/MS approach doubled throughput, while cutting the cost by four-fold over the traditional GC approach. Examples of three applications will be discussed: a) site-specific organic acids, b) nitrosamines and c) perchlorate.

Site-Specific Compounds

Industrial wastes were dumped into abandoned strip mines during the 1950s and 1960s. These wastes leached into groundwater and contaminated wells of over 900 homes and businesses covering a 20-square mile area. A state agency needed a procedure for determining site-specific chemicals. The method needed to be capable of achieving a detection limit of < 5 ppb for compounds that are typically difficult to analyze in water samples. The method evolved from HPLC/UV to HPLC/MS to HPLC/MS/MS. Earlier approaches detected large concentrations of one of the contaminants in some samples. Monitoring of daughter ions by MS/MS indicates that it was false positive due to interference from "hard water." The LC/MS/MS approach has been very productive: laboratory has analyzed over 300 samples, including many tap water samples from homes and businesses on a five-day turnaround time. Therefore, by providing high-quality data, the agency was able to 1) track the extent of contamination and take corrective action and 2) determine source of contamination and thus pursue settlement with appropriate PRP.

Nitrosamines in Tobacco

Tobacco-specific nitrosamines or TSNAs are some of the most abundant carcinogens found in tobacco.

N-nitrosonornicotine	(NNN)
(4-methylnitrosamino)-1-(3-pyridyl)-1-butanone	(NNK)
N-nitrosoanatabine	(NAT)
N-nitrosoanabasine	(NAB)

Figure 2.

These compounds are formed from nicotine and other secondary alkaloids during the processing of tobacco. Their concentration can be dependent on the amount of nitrate present in the tobacco. Our client needed a high volume screening method to monitor how the many parameters involved affect the concentrations of TSNAs.

Sensitivity of the LC/MS/MS approach allowed us to reach < 10 ppb limit of detection for all four TSNA compounds in a complex tobacco matrix without concentration of extract. The older GC approach required significant extract cleanup (running the sample through a column and then eluting the column 3x) to reduce interference.

This was accomplished by utilizing the multiple reaction monitoring (MRM) mode and monitoring of daughter ions by MS/MS. This efficient method has allowed us to run over 7000 samples on a five-day turn-around time. Older approaches took 2-3X as long to process samples. We can prepare 95 samples per shift for LC/MS/MS vs. 30 samples per shift for GC. Also, we can analyze 80-100 samples per day by LC/MS/MS vs. 40 samples per day by GC. This has allowed our client to make real time decisions in the field and save millions of dollars, study more parameters due to the more efficient analysis and ultimately reduce TSNAs in tobacco.

Perchlorate

Perchlorate is a common oxidant in rocket fuel and used in fertilizers. It has been found at elevated levels in the Colorado River and other areas of the southwestern United States. Once thought to be safe, this compound is now believed to cause some adverse affects on health. The typical manner to detect perchlorate is EPA Method 314, Ion Chromatography (IC) with conductivity detection. This method, however, is prone to false positives and ion suppression and may not offer sufficient sensitivity. We have set up an IC/MS/MS method that is run in multiple reaction monitoring (MRM) mode. The transitions monitored include $^{35}ClO_4$ (m/z 99 => 83) and $^{37}ClO_4$ (m/z 101 => 85). The natural isotopic abundances can be used as additional identification confirmation. The $^{35}Cl/^{37}Cl$ ratio is approximately 3.08. This approach yields sensitivity on the order of a magnitude better than EPA 314.

EPA 314 LOQ = 4 ppb IC/MS/MS LOQ = 0.4 ppb

The instrument is calibrated from 0.4 to 10 ppb and an internal standard (^{18}O labeled perchlorate) is spiked into all samples and QC to provide superior quantitation, asses method performance and minimize matrix effects. Furthermore, the analysis time is shorter allowing greater productivity.

EPA 314: 18 minute runtime IC/MS/MS: 6 minute runtime

Some samples run by EPA 314 were also run by the IC/MS/MS approach and the data is shown below.

Comparison Data

Sample	EPA 314	IC/MS/MS
X	ND	0.20 ppb
Y	ND	0.22 ppb

In general, LC(IC)/MS/MS is a valuable tool in the environmental analytical laboratory. This technique can provide superior sensitivity, selectivity, data quality and productivity.

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FIELD ANALYSIS OF CHROMIUM VI DURING AND AFTER REMEDIATION OF A FORMER CHROME PLATING FACILITY

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During the Summer of 2003, TechLaw Inc., as the Environmental Services Assistance Team (ESAT) contractor at the EPA Region 10 Laboratory, was tasked to provide field analytical assistance during the remediation of the Frontier Hard Chrome superfund site. The purpose of the analytical support was to show whether the remediation efforts were effective. The task involved taking push probe soil and water samples from various areas within the site after the treatment chemical and cement slurry had been injected by another contractor. There were about 40 sampling points on the site, based on one per 500 cubic yards of treated soil.

The soil and water samples were analyzed at the site for hexavalent chromium (Cr VI), pH and oxidation-reduction potential (ORP). Complicating the CR VI analysis was reaction of the chromium reagents with the residual treatment chemical in the samples. This necessitated dilution and filtration in most cases. Normal QC procedures such as matrix spikes were not feasible as the presence of the remediation chemical reduced any Cr VI added to the samples. The pH and ORP determinations were used to further demonstrate whether Cr VI could be present in the samples.

Following the conclusion of the remediation project, analysis of monitoring wells downstream from the site has continued on a quarterly schedule. This work will continue for several years. Further information on the site is available at http://yosemite.epa.gov/r10/cleanup.nsf/sites/fhc.

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MONITORING OF TRACE ELEMENT AIR POLLUTION AT URBAN COUNTRIES ALONG THE RED SEA COAST

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Metal contamination of ecosystems has gained increasing attention in recent decades. These metals, coming both from natural and anthropogenic sources, are pollutants distributed worldwide. Accumulation and persistence in the environment constitute a threat for biological life. On this point, dissolved and particulate trace element concentrations of Cd, Pb, Cu, Zn, Fe, Mn and Ni were determined in rain water samples collected from several cities at kingdom of Saudi Arabia of varied environmental conditions and compared with those collected from Alexandria City.

The studies performed up to data have highlighted the difficulties encountered in acquiring reliable and representative data on trace metals transferred by rain from the atmosphere to ground surfaces.

Results were statistically analyzed for correlations between parameters. Straight-line regression analysis showed several significant correlations at the 95% level, some even at the 99% level.

ASSESSING PERFORMANCE OF NEW METHODS

METHODS DEVELOPMENT AND METHODS VALIDATION FOR THE RCRA PROGRAM INCLUDING BOTH PROGRAM AND INDIVIDUAL USER VALIDATION APPLICATIONS

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Test Methods for Evaluating Solid Waste, or SW-846, is the compendium of analytical and test methods approved by EPA's Office of Solid Waste (OSW) for use in determining regulatory compliance under the Resource Conservation and Recovery Act (RCRA). SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements.

There seems to be an impression among methods' developers and the regulated community that there is some esoteric or mystical process that must be followed in order to get an analytical method "approved" by regulatory agencies like the USEPA. In this document, OSW would like to dispel these misconceptions, identify some basic principles and present a logical approach to methods development that is currently followed by OSW in developing methods for SW-846. This approach is based on sound scientific principles and methods developed according to this process should be acceptable for use in other Agency programs as well as OSW.

Two levels of methods development are covered in this guidance document, initial "proof of concept" and a formal validation. This guidance is applicable to both new methods submitted for potential inclusion in SW-846 or for adapting existing SW-846 methods for additional applications. When measurements for RCRA applications are required for which no validated methods exist, *e.g.*, from unusual matrices or below the quantitation limits of conventional SW-846 or other appropriate methods, qualified analysts can serve as "in-house" methods' developers to modify existing methods to meet these regulatory needs following the guidelines delineated in Elements 1 through 9.

The RCRA method development approach utilizes three basic principles for either demonstrating "proof of concept" or for use in a formal validation. These basic scientific principles are:

1) Identify the scope and application of the proposed method, (What is this method supposed to accomplish?)
2) Develop a procedure that will generate data that are consistent with the intended scope and application of the method and
3) Establish appropriate quality control procedures which will ensure that when the proposed procedure is followed, the method will generate the appropriate data from Step 2 that will meet the criteria established in Step 1.

In some cases, such as a demonstration of applicability for an intended application, using a variation of an existing SW-846 method using new equipment or a modified procedure, it is sufficient only to demonstrate validation to the "proof of concept" stage. For new technologies to be considered for inclusion in SW-846, it is necessary for the developer to perform the formal validation procedure including multi-laboratory validation.

PERFORMANCE-BASED QUALITY ASSURANCE PROGRAMS FOR THE DETERMINATION OF ORGANIC SPECIES IN MARINE TISSUE, MARINE SEDIMENT, AND AIR PARTICULATE SAMPLES

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Since the beginning of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program in 1987, the National Institute of Standards and Technology (NIST) has coordinated annual intercomparison exercises for the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners and chlorinated pesticides in marine tissue (mussel and fish) and sediment samples. These intercomparison exercises have become an excellent tool for assessing the comparability of analytical measurements among the marine environmental measurement community. In the 2003 exercise, 25 laboratories, representing federal and state government, private and university laboratories, reported results on 26 PAHs, 25 PCB congeners and 25 chlorinated pesticides in a fresh frozen mussel tissue homogenate and in a frozen marine sediment material.

Using the intercomparison program described above as a template, another program is ongoing within a working group of investigators who are characterizing and quantifying the organic compounds in particulate matter (PM) as part of the U.S. EPA's $PM_{2.5}$ research program and related studies. The working group was established five years ago to advance the quality and comparability of data on the organic composition of PM. This group has completed two interlaboratory comparison studies and is beginning the third one. The target analytes include polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs, alkanes (including hopanes and cholestanes), sterols, carbonyl compounds (ketones and aldehydes), acids (alkanoic and resin), phenols and sugars.

Because these are performance-based studies, laboratories are encouraged to use the methods that they are routinely using in their laboratories to analyze similar samples. Laboratories are requested to return data from three analyses (subsamples) of each sample provided along with a summary of the methods used. The data received from

the participating laboratories, following outlier testing, are then used to assign a consensus value to each analyte in the unknown samples. Laboratories receive a report showing their results relative to other participating laboratories. A number known only by the laboratory and NIST identifies each laboratory. Z-scores and p-scores are determined for assessment of accuracy and precision. The z-score assesses the difference between the result of the laboratory and the exercise assigned value and can be used to compare performance on different analytes and on different materials.

U.S. EPA SITE PROGRAM PERFORMANCE VERIFICATION TESTING OF MONITORING AND MEASUREMENT TECHNOLOGIES FOR DIOXIN AND DIOXIN-LIKE COMPOUNDS IN SOIL AND SEDIMENT*

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Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the U.S. Environmental Protection Agency (EPA). The Superfund Innovative Technology Evaluation (SITE) Program was established by the EPA Office of Solid Waste and Emergency Response and the Office of Research and Development under the Superfund Amendments and Reauthorization Act of 1986. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies, (2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and cleanup activities and (3) encourage the use of innovative technologies at Superfund sites as well as other waste sites or commercial facilities. The intent of a SITE demonstration is to obtain representative, high-quality performance and cost data on innovative technologies so that potential users can assess a given technology's suitability for a specific application. More information about the SITE Program can be found on the Program's Web site (www.epa.gov/ORD/SITE).

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, commonly referred to collectively as "dioxins," are of significant concern in site clean-up projects and human health assessments because they are highly toxic. Conventional analytical methods for determining dioxin concentrations are time-consuming and costly. For example, EPA standard methods require solvent extraction of the sample, processing the extract through multiple cleanup columns and analyzing the cleaned fraction by gas chromatography (GC)/high-resolution mass spectrometry (HRMS). The use of a simple, rapid, cost-effective analytical method would allow field personnel to quickly assess the

extent of dioxin contamination at a site and could be used to direct or monitor cleanup activities. More rapidly acquired data could be used to provide immediate feedback on potential health risks associated with the site and permit the development of a more focused and cost-effective sampling strategy. More affordable and quicker analytical techniques will not replace HRMS, but will complement an enhanced sampling design. However, before adopting an innovative alternative to traditional laboratory-based methods, an assessment of how commercially available technologies compare to conventional laboratory-based analytical methods using certified, spiked and environmental samples is warranted.

Five measurement technologies for dioxin and dioxin-like compounds participated in a field demonstration in Saginaw, Michigan, from April 26 to May 5, 2004. The demonstration was conducted in collaboration with the Michigan Department of Environmental Quality and the U.S. Fish and Wildlife Service. The technologies were operated by the developers in mobile laboratories or construction trailers equipped with fume hoods at the site. The developers and technologies that participated are:

- AhRC PCR™ Kit, Hybrizyme Corporation
- Coplanar PCB Immunoassay Kit, Abraxis LLC
- DF-1 Dioxin/Furan Immunoassay Kit, CAPE Technologies L.L.C.
- CALUX® by Xenobiotic Detection Systems, Inc.
- Dioxin ELISA Kit, Wako Pure Chemical Industries, Ltd.

The purpose of the demonstration was to evaluate measurement technologies for dioxin and dioxin-like compounds in soil and sediment in order to provide (1) potential users with a better understanding of each technology's performance and cost under well-defined field conditions and (2) developers with documented results that will assist them in promoting acceptance and use of their technologies. To meet these demonstration objectives, samples were collected from a variety of dioxin-contaminated soil and sediment sampling locations around the country (see Figure 1). The samples were homogenized and characterized prior to use in the demonstration so that a variety of environmentally-derived dioxin-contaminated samples with concentrations over a large dynamic range (< 5 to > 10,000 picogram/gram [pg/g]) were analyzed. The sample design also included performance evaluation (PE) samples, which contained certified concentrations of dioxins, furans and/or polychlorinated biphenyls (PCBs). Collectively, the demonstration samples covered a range of concentrations and chemical characteristics necessary to properly evaluate the technologies and ensured that the data sets produced were statistically sound.

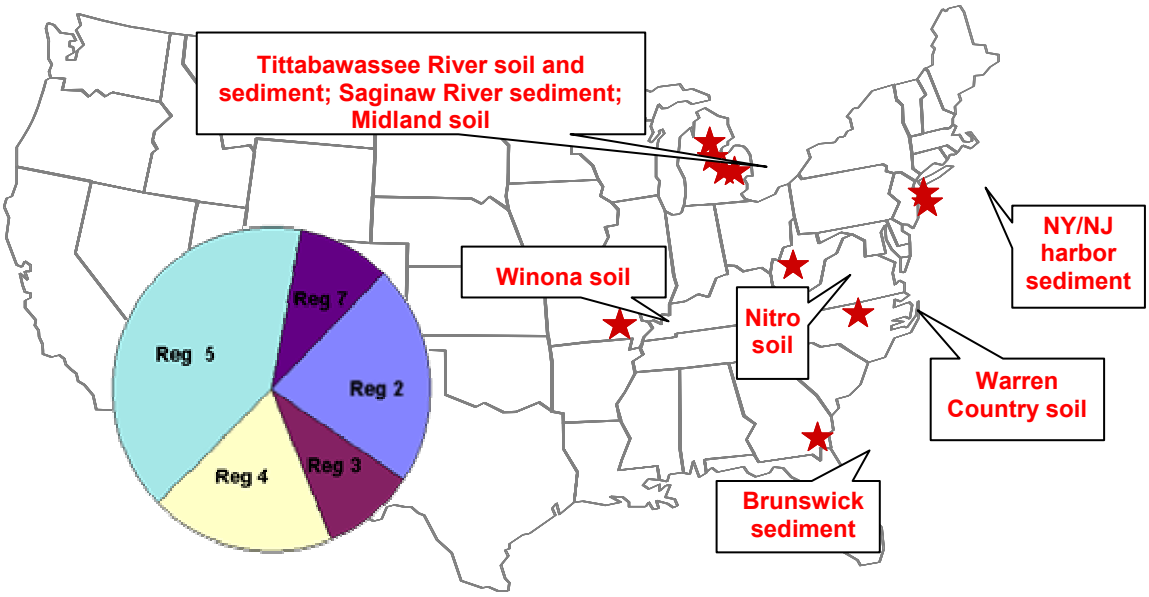

Figure 1. Summary of environmental sample locations

In SITE demonstrations, the performance and cost of each technology are compared to those of conventional, off-site laboratory analytical methods, so the selection of a reference laboratory is a critical decision. For this demonstration, the selection was a performance-based process which included completion of a questionnaire, blind analysis of audit samples and participation in on-site quality and technical systems audits. Criteria for final selection were based on the observations of the auditors, the performance on the audit samples and cost. From this process, it was determined that AXYS Analytical Services (Sidney, British Columbia, Canada) would best meet the needs of this demonstration, so AXYS was selected as the reference laboratory for this demonstration. Reference analyses by HRMS are currently on-going. Seventeen dioxin/furan (D/F) congeners will be determined by the reference laboratory using EPA Method 1613B. The reference laboratory will also measure 12 dioxin-like PCBs using EPA Method 1668A. The congener concentration data will be used to determine toxicity equivalents (TEQ) concentration because all of the developer technologies reported data in TEQ and none report data for individual congeners. As shown in Table 1, some technologies reported total TEQ from dioxin/furan contributions only (total $TEQ_{D/F}$) and total TEQ from dioxin-like PCBs only (total TEQ_{PCB}).

Table 1. Summary of Developer Technology Reporting Units and Comparison to High Resolution Mass Spectrometry (HRMS) Reference Values.

Developer	Reporting Units	Developer-Stated LOD	Comparison to HRMS
Abraxis LLC	Total TEQ_{PCB}	6.25	Total TEQ_{PCB} PCB 126 TEQ
CAPE Technologies	Total $TEQ_{D/F}$	1	Total $TEQ_{D/F}$
Hybrizyme Corporation	AhR units	10	Total $TEQ_{D/F}$ Total TEQ
Wako Pure Chemical Industries, Ltd.	2,3,7,8-TCDD EQ pg/g	20	Total $TEQ_{D/F}$ 2,3,7,8-TCDD TEQ
Xenobiotic Detection Systems	Total $TEQ_{D/F}$ Total TEQ_{PCB}	0.3	Total $TEQ_{D/F}$ Total TEQ_{PCB}

The demonstration has both primary and secondary objectives. The primary objectives are critical to the technology evaluation and require use of quantitative results to draw conclusions regarding technology performance. The secondary objectives pertain to information that is useful but does not necessarily require use of quantitative results to draw conclusions regarding technology performance.

The primary objectives for the demonstration of the participating technologies are as follows:

P1. Determine the accuracy.
P2. Determine the precision.
P3. Determine the comparability of the technology to the reference laboratory methods.
P4. Determine the method detection limit (MDL).
P5. Determine the frequency of false positive and false negative results.
P6. Evaluate the impact of matrix effects.
P7. Estimate costs associated with the technology.

The secondary objectives for the demonstration of the participating technologies are as follows:

S1. Document the skills and training required to properly operate the technology.
S2. Document health and safety aspects associated with operating the technology.
S3. Document the portability of the technology.
S4. Evaluate sample throughput.

Report preparation is currently on-going. The technology and reference method results will be compared to evaluate the performance and associated cost of each technology. The performance and cost characteristics of one technology will not be compared to those of another technology. A separate innovative technology verification report (ITVR) will be prepared for each technology. The ITVRs for the five technologies will be submitted to EPA in December 2004 for publication on the SITE Program's Web site.

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BENEFITS OF NITROGEN MONITORING BY HIGH TEMPERATURE COMBUSTION (HTC)

Brian Wallace
Teledyne Tekmar

Nitrogen monitoring can be a critical function for the process control of wastewater treatment and other industrial applications, as well as for seawater analysis. New advances in high temperature combustion (HTC) technology with chemiluminescence detection (CLD) provide a quick and easy way to monitor nitrogen loading by total nitrogen (TN) analysis. Since this analysis can be performed simultaneously with traditional total organic carbon (TOC) analysis, the analytical benefits can be achieved with minimal labor and capital expenditure, boosting productivity and lowering costs over existing nitrogen analysis techniques. The goal of this paper is to demonstrate the capability of HTC total nitrogen for a variety of key applications.

Introduction

Currently, Total Kjeldahl Nitrogen (TKN) is the standard method in many countries for organic nitrogen analysis. The objective of the TKN test is to convert nitrogen, from biological origins or organic forms, into ammonia through a digestion procedure. The ammonia is then determined through a titration procedure. Hence, TKN is the sum of organic nitrogen and ammonia.

TKN = Organic Nitrogen + NH_3

While effective, TKN has several drawbacks. Only organically-bound nitrogen, in the tri-negative state, is determined by most TKN methods. Therefore, nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime and semi-carbazone compounds are often not fully digested or detected. Problems during digestion can be caused by a high amount of salt or acid in the sample, causing the

digestion temperature to rise above the desired temperature resulting in a loss of nitrogen. Conversely, if the quantity of acid is too low the digestion temperature will be under the desired level, resulting in incomplete digestion.[1] Another concern with the TKN method is the extensive use of sulfuric acid as part of the sample digestion process. In most cases, the steps required to safely run this test, and the environmental precautions that have to be addressed, are actually more stringent than the care required in handling the samples. This is especially true when samples containing pesticides are being analyzed. In summary, Kjeldahl nitrogen is a time-consuming, environmentally unfriendly and labor-intensive test for laboratory personnel to perform.

The HTC Method of Detecting Nitrogen

The HTC technique can measure bound nitrogen, defined as TN_b, which consists of the organically and inorganically bound nitrogen, excluding the elemental nitrogen. The HTC technique eliminates the concerns raised from TKN analysis making TN analysis an ideal replacement or supplement to Kjeldahl nitrogen analysis in most wastewater applications.

Wastewater treatment facilities monitor their nitrogen for a variety of reasons. First and foremost, most governmental agencies regulate organic nitrogen in wastewater discharge. In addition to regulatory requirements, high amounts of ammonia (NH_3), nitrate (NO_3) or nitrite (NO_2) can cause severe problems in the wastewater treatment process costing tens of thousands of dollars and take days to recover. For these reasons, constant nitrogen monitoring should be performed to improve plant efficiency and minimize breakdowns in the nitrogen cycle.

This HTC technology is being utilized throughout Germany and many other European countries where determination of bound nitrogen is required in freshwater, seawater, drinking water, surface water, wastewater and treated sewage effluent samples. These requirements are defined in European Norms such as EN-12260 and DIN-EN-ISO 11905-2.[2,3] In these methods, the sample is combusted at up to 1,000°C with the nitrogen in the sample converting to nitric oxide. The nitric oxide is then reacted with ozone to produce an excited state of nitrogen dioxide (NO_2^*) which, when it decays to its ground state, emits light (reaction 1). The light produced is then measured with a chemiluminescence detector (CLD) and correlated to a specific amount of nitrogen in the sample.

Reaction 1: $NO + O_3 \longrightarrow NO_2^*$

$NO_2^* \longrightarrow NO_2 + h\upsilon$

Faster analysis time is a major benefit for the HTC technique over the TKN method. The time of HTC analysis is usually 5 minutes per replicate versus two to three hours with the Kjeldahl process. This is a significant time difference that allows facilities using the TN_b test method to make necessary adjustments to their treatment processes much faster than before, minimizing both treatment cost and risks to the environment from higher than allowed levels of organic nitrogen loading.

Getting TOC and TN in One Analysis

In addition to the analytical advantages, advances in HTC technology in recent years make implementing TN_b analysis easier than before. In the past, total nitrogen analyzers were available as stand-alone instrumentation. Today, modules that process the TN_b analysis can be added to HTC equipment at the time of purchase or to existing HTC instrumentation. These modules, which are substantially less expensive than a stand-alone instrument, can analyze total nitrogen simultaneously with TOC (figure 2). The TN Module (Figure 1) for the Apollo or ApolloHS has the capability to make TOC/TN triplicate measurements in only a few minutes longer than the standard TOC analysis, with minimal demand on the analyst. As a result, many labs are using these TOC/TN instruments to complement or replace both chemical oxygen demand (COD) and TKN testing in their facilities.

Figure 1. The TN Module with the Apollo 9000HS TOC Analyzer.

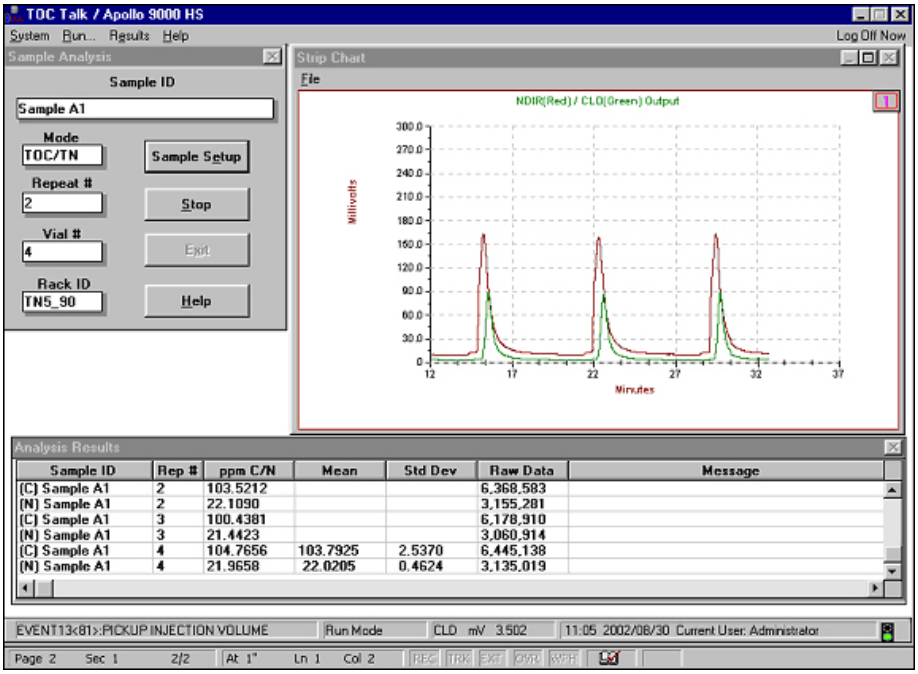

Figure 2. Example of TOC/TN Analysis on the Apollo 9000 TN Module.

Nitrogen Recovery and TKN Comparison Study

Table 1 yields the results of quality control proficiency standards specifically designed for TKN analysis by Environmental Resource Associates®.[4] Table 2 lists a comparison of a variety of nitrogen compounds, with different functional groups, analyzed by HTC-CLD and TKN.

Table 1. ERA™ Quality Control Proficiency Standards
TKN Comparison: Proficiency Standards

Sample (n=4)	QC Limits (ppm N)	Result (ppmN)	Std Dev (+/-) ppmN	RSD
WasteWatR™ Complex Nutrients	9.08 – 15.7	12.1774	0.1924	1.58 %
WasteWatR™ Simple Nutrients	11.37 –16.65	12.8863	0.1817	1.41 %

Table 2. Apollo 9000 TN Module vs. TKN results (from outside laboratory) for various nitrogen functional groups. All results from the TN module included 4 replicates and were less than 3% RSD (except for Hydrazine Sulfate, which was 6% RSD).

TKN Comparison: Nitrogen Compounds

Functional Group	Nitrogen Species	Nitrogen Concentration (ppmN)	Recovery by Apollo 9000 TN Module	Recovery by TKN
Amine	Methylamine HCl	20	98.0 %	19.2 %
Amines	Trimethylamine	23.7	97.1 %	22.8 %
Aminio Acids	Glutamic Acid	20	100 %	19.4 %
Aminio Acids	Glycine	10	98.2 %	96.1 %
Aminio Acids	Tryptophan	25	99.2 %	102 %
Azides	Sodium Azide [d]	10	22.3 %	Below DL [e]
Cyanoamides	Dicyanodiamide	100	99.1 %	99.0 %
Heterocyclic (N)	Isonicotinic Acid	25	103 %	97.6 %
Hetrocyclic (N)	Nicotinic Acid	10	102 %	94.8 %
Hetrocyclic (N)	Pyridine	20	100 %	102 %
Hydrazines	Hydrazine Sulfate [f]	10	8.90 %	16.1 %
Nitrophenols	*p*-Nitrophenol	20	105 %	26.2 %
Thioureas	Thiourea	20	98.4 %	97.5 %
Ureas	Urea	20	98.2 %	104 %
Ammonium Salt	Ammonium Sulfate	100	103 %	110 %
Mixture	KNO_3 / Ammonium Sulfate	50	99.5 %	130 %

[d]Sodium azide recovery was low for both analyses because elemental nitrogen was formed and not detected.

[e]Below detection limit of laboratory's TKN method.

[f]Hydrazine sulfate recovery was low for both analyses because elemental nitrogen was formed and not detected.

Discussion

HTC - CLD vs. TKN

Nitrogen analysis was performed on a variety of nitrogen-containing compounds for comparison between HTC – CLD (TN Module) and TKN. To define an assessment of each method, the TKN results were analyzed by an independent laboratory. All results from the TN module were 3% RSD or less for 4 replicates. Recoveries were comparable for the compounds except for amines, glutamic acid and nitrophenols, which gave poor (low) recovery for the TKN analysis. The 1:1 KNO_3/ammonium sulfate mixture yielded an excessively high recovery on the TKN test. Hydrazine and sodium azide both gave low recovery on TKN and HTC-CLD because they produce elemental nitrogen, which is not detected by TKN or chemiluminescence.

TKN proficiency standards were analyzed with the TN module. The “Complex Nutrients” sample contained a TKN standard. The “Simple Nutrients” sample contained ammonia and nitrate as forms of nitrogen. Results for both samples fell within the quality control limits and gave less than 2% RSD for four replicates.

Conclusion

During the process of screening for pollutants, observation of TN_b trends in point sources and surface waters is of utmost importance in the prevention of nutrient pollution. The implementation of TN_b and TOC simultaneously can provide essential information that may aid in an efficient pollution prevention process, with near on-line frequency. High temperature combustion offers significant improvements in nitrogen monitoring for wastewater, surface water, seawater and a variety of industrial applications. Current advances in HTC technology make implementation both a more cost effective and environmentally-sensitive alternative to standard Kjeldahl analysis. Because total nitrogen analysis can be performed simultaneously with TOC analysis, the use of this dual element detection technology can increase both productivity and monitoring effectiveness, improving the overall monitoring strategy.

References

1. *Standard Methods for the Examination of Water and Wastewater,* 20th Edition, A. D. Eaton, L. S. Clesceri and A. E. Greenberg. APHA/AWWA/WEF, Washington, DC, 2002.
2. *Water quality – Determination of Nitrogen, International Organization for Standardization*, Geneve, Switzerland, 1997, ISO method 11905-2.
3. *Water analysis – Determination of Nitrogen - Determination of bound nitrogen, after combustion and oxidation to nitrogen dioxide, using chemiluminescence detection,* European Committee for Standardization, Brussels, 1996, EN method 12260.
4. Environmental Resource Associates®, 5540 Marshall Street, Arvada, Colorado 80002. 303-431-8454, info@eraqc.com. WasteWatR™ Simple Nutrients (Catalog No. 505) and WasteWatR™ Complex Nutrients (Catalog No. 525).
5. *Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC),* European Committee for Standardization, Brussels, 1997, EN method 1484.

CATHODIC STRIPPING VOLTAMMETRIC SPECIATION OF μG/L LEVEL ARSENIC IN WATER SAMPLES

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A recent survey of some 30,000 groundwater wells, mostly in the western U.S.[1], indicates that about 10% contain As at levels > 10 μg/L[2]. Similar levels are also found in parts of New England, affecting about 100,000 residents in the region[3] and also in other eastern and central states, especially New Jersey, Michigan and Wisconsin[4]. With increasing knowledge and concern over the health effects of arsenic exposure from drinking water, the U.S. Environmental Protection Agency (EPA) will implement in January 2006 a new As maximum contaminant level (MCL) of 10 μg/L and also a MCL Goal of 0 μg/L[5].

Inorganic As(III) and As(V) are the major arsenic species in natural water samples. Organic arsenic compounds including methylarsonic acid (MMA) and dimethylarsinic acid (DMA) are also found in seawater[6] and some fresh water samples[7] as a result of biological activity[7,8] and anthropogenic contamination[9,10]. Because different arsenic species have different toxicities, rapid, reliable and accurate differentiation between toxic inorganic arsenic species and the usually less toxic organic arsenic species in water samples is necessary to assist implementation of the new drinking water MCL for As.

On-site arsenic speciation in water samples is preferred because inorganic As(III) is quickly air-oxidized to As(V) during transportation and preservation and attempts to prevent this change have met with limited success[11,12].

Two arsenic speciation methods based on differential pulse cathodic stripping voltammetry (DPCSV), applicable both in the laboratory and in the field, have been developed. They are simple, fast, portable, inexpensive, require only a small sample size and have a detection limit at the sub-μg/L level. The methods employ a hanging mercury drop electrode (HMDE), on which As(III) is deposited in the presence of Cu(II) and Se(IV) in HCl medium. As(III) is determined by direct measurement. The other arsenic species are differentiated by indirect measurement through converting As(V) and/or organic arsenic to As(III) and comparison of the differences in concentration. Efforts therefore focused on development and optimization of the conversion reagents and experimental conditions.

Method I

In the presence of Cu(II), Se(IV) and HCl, optimum DPCSV parameters for As(III) were determined using an Eco Chemie μAutolab voltammetric apparatus (Brinkmann Instruments, Westbury, NY) equipped with a Metrohm 663VA electrode stand, with a deposition potential of –0.44V and a deposition time of 60sec. The electrodes include a HMDE working electrode, a Pt auxiliary electrode and a Ag/AgCl/3M KCl double-junction reference electrode. The stripping potential was scanned from –0.4 V to –0.9 V vs. Ag/AgCl reference electrode with a 10 mV step potential, 50 mV modulation amplitude, 33.3 msec pulse width, 16.7 msec measurement time and 25mV/s scan rate.

An intermetallic compound, $Cu_xSe_yAs_z$, is assumed to form during the deposition procedure and the stoichiometric ratio of this compound affects the DPCSV response. The As(III) voltammetric peak increases with increasing Cu(II) concentration, but above a certain concentration further increase causes peak splitting, decreasing peak area and, finally, disappearance of the peak. At the optimized Cu(II) concentration, a major improvement in As peak shape was further achieved by addition of a trace level of Se(IV) to eliminate a shoulder on the peak. For a 10ml sample solution, the optimized Cu(II) and Se(IV) concentrations are 4.6 mg/L and 3.7 μg/L, respectively.

Determination of total As is performed by reducing As(V) to As(III) using sodium *meta*-bisulfite/sodium thiosulfate reagent stabilized with ascorbic acid. As(V) is quantified by difference. With a violent N_2 purge to eliminate interfering gaseous sulfur compounds generated during the reduction, As(V) can be quantitatively reduced to As(III) in 7 min in the presence of at least 2 mg/ml sodium *meta*-bisulfite and 0.2 mg/ml sodium thiosulfate.

Organic MMA and DMA give no DPCSV response using this method. Ions commonly found in groundwater containing arsenic (phosphate, iron (II) and manganese (II)) were found to have negligible interference.

The detection limit (S/N >3) is 0.5 μg/L and the linear range is from 4.5 g/L to 180 μg/L. At levels of 45 μg/L, 10 μg/L and 5 μg/L, the relative standard deviations (n=6) are 2.4%, 2.5%, 4.2% for As(III) and 8.0%, 6.8%, 9.0% for As(V), respectively. Analysis of the NIST 1640 natural water standard yielded a total arsenic concentration of 26.5 ± 3.4 μg/L (n=3) compared to the certified value of 26.7 μg/L. This method has been applied on-site to the analysis of groundwater at a Superfund site in Vineland, New Jersey. Results obtained compared well with those obtained by high resolution ICP-MS, GFAAS and IC-AFS.

Method II

Method II improves analysis throughput by using L-cysteine, a stable and fast-reacting reagent for reduction of As(V). It also has the capability to differentiate organic and inorganic arsenic. Water samples are reduced by L-cysteine in a batch mode, which is difficult to perform using the sodium *meta*-bisulfite/sodium thiosulfate reagent because the required purging of the gaseous sulfur compounds consumes instrument time; off-line purging is not convenient to perform in fieldwork. Total inorganic arsenic was

measured after L-cysteine reduction and As(V) was quantified as the difference of total inorganic arsenic and As(III). Organic arsenicals are photooxidized to inorganic As(V) in the presence of $Na_2S_2O_8$ and total arsenic (inorganic plus organic) is subsequently determined. The amount of organic arsenic is the difference between total inorganic arsenic and total arsenic.

L-cysteine reduction kinetics are affected by reductant concentration, temperature and solution acidity. Quantitative reduction of As(V) was observed in 6 min. for L-cysteine concentrations 0.02 M or higher at the optimized temperature of 70 °C in the presence of 0.03M HCl. Compared with Method I, a higher Se(IV) concentration, 7.4 μg/L, is required to eliminate the shoulder on the voltammetric arsenic peak. In the field, if no thermostat is available, an 80 min reduction time is required at ambient temperature. Samples containing 190 μg/L As(V) (the upper limit of the linear range) treated with L-cysteine were found to be stable for at least one week at room temperature.

UV photooxidation of organic arsenic was facilitated by $Na_2S_2O_8$. 100% oxidation was achieved in 6 min in the presence of 3 mM $Na_2S_2O_8$ using a 500W UV irradiator. However, this procedure is subject to interference by lower oxidation state ions such as Mn(II) and Fe(II) which are more easily oxidized than the organic arsenic compounds. Increasing the $Na_2S_2O_8$ concentration to 30 mM eliminated the Mn(II) and Fe(II) interference up to concentrations as high as 100 μM. Phosphate at concentrations up to 200 μM showed no interference.

The detection limits (S/N >3) for As(III), As(V), MMA and DMA are all 0.3 μg/L and the linear range for all is from 2.5 μg/L to 190 μg/L. The overall precision (RSD) was better than 8% for all species.

Method II was validated by analyzing the NIST 1640 water sample and spiked tap waters and groundwater. The results for NIST sample were no detectable As(III) and 26.9 ±2.0 μg/L As(V), compared to the certified value of 26.7 μg/L. Spiked arsenic(As(III), As(V), MMA and DMA) recoveries ranged from 80% to 115%.

Summary

The DPCSV technique provides a convenient approach for routine on-site arsenic speciation, applicable in water treatment facilities, pollution monitoring sites, and wild environments. Different reduction procedures and UV photooxidation make the method more versatile and user-friendly. The HMDE electrode effectively eliminates the memory effects of solid state electrodes such as Au or Pt by generating a fresh mercury drop for each analysis. CSV provides extremely low detection limits because of analyte enrichment in the drop during the deposition step. The Brinkmann voltammetric apparatus controlled by a notebook computer, is compact and portable. The instruments are inexpensive (US$10K to $20K, depending on specific model) and operational and maintenance costs are low.

References

1. http://co.water.usgs.gov/trace/arsenic/.

2. Welch, A. H., Westjohn, D. B., Helsel, D. R. and B., W. R., *Groundwater* **38** (2000) .
3. Ayotte, J. D., Montgomery, D. L., Flanagan, S. M. and Robinson, K. W., *Environ. Sci. Technol.* **37** (2003), 2075-2083.
4. Ryker, S. J., *Geotimes* (2001), 34-36.
5. http://www.epa.gov/safewater/ars/implement.html.
6. Andreae, M. O., *Limnol. Oceanogr*. **24** (1979), 440-452.
7. EPA, http://www.epa.gov/region02/superfund/npl/0200209.pdf.
8. Cullen, W. R. and Reimer, K. J., *Chem. Rev*. **89** (1989), 713-764.
9. Smith, E., Naidu, R. and Alston, A. M., *Adv. Agron*. **64** (1998), 149-195.
10. Taylor, D. A., *Environ. Health Persp*. **112** (2004), A50.
11. McCleskey, R. B., Nordstrom, D. K. and Maest, A. S., *Applied Geochem*. **19** (2004), 995-1009.
12. Bednar, A. J., Garbarino, J. R., Ranville, J. F. and Wildeman, T. R., *Environ. Sci. Technol*. **36** (2002), 2213-2218.

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EVALUATION OF INTERLABORATORY STUDY DATA USING VACUUM DISTILLATION UNIT (VDU) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) ANALYSIS

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United States Environmental Protection Agency (USEPA) SW-846 Method 8261 uses a vacuum distillation unit (VDU) to extract volatile organic compounds (VOCs), select semivolatile organic compounds (SVOCs) and polar non-purgeable compounds from a variety of environmental sample matrices. The compounds are subsequently separated, identified and quantitated using gas chromatography/mass spectrometry (GC/MS) instrumentation. Each sample is spiked with a known amount of a group of surrogate compounds which are used to assess the recovery and quantitation of the target compounds assigned to specific surrogates based on chemical and physical properties. Method 8261 was developed by the USEPA National Exposure Research Laboratory

(NERL) - Environmental Sciences Division (ESD) in Las Vegas, Nevada. NERL-ESD has developed an automated VDU which is now produced by a commercial vendor.

An interlaboratory study has been conducted using SW-846 Method 8261 to assess the performance of the commercially-available VDU. This paper presents the results and statistics from the four laboratories participating in the interlaboratory study. The results include calibration standard analyses, method detection limit (MDL) studies, matrix spike analyses and blind performance evaluation sample (PES) analyses using several different matrices including water, soil, salt water and glycerol.

INNOVATIVE APPROACHES TO ENVIRONMENTAL MONITORING

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OUT-OF-THE-BOX APPROACH TO AUTOMATED DATA VALIDATION

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Over the past few years, the environmental testing industry has realized close to a five-fold increase in data validation adding significant financial overhead to monitoring projects. The cost per sample can become compound as data validation is assumed at the laboratory, consulting and regulatory levels. Spurred on by fixed cost site management and renewed emphasis on returning environmental equity to productive use, data usability ultimately helps ensure value per remediation dollar. Estimates for overhead data validation costs may range from 5% to 20% of the fixed analytical cost. A software development project was undertaken to investigate the feasibility of a user described rules-based data processing engine that could electronically enhance or replace the human validation effort at a fraction of the cost. A modularized microprocessor-based Visual Basic.NET tool was designed for Microsoft TM Windows operating systems allowing access into new or existing databases, straight text, Excel, Access and XML. Data quality objectives can be user defined on a project specific basis. Data is accessed by the software through user a user defined EDVD (electronic data validation deliverable) or *via* direct link into the laboratory LIMS. This paper will describe critical aspects of the software engine and deployment along with in-house *beta* testing results from a variety of DOD and private sector remediation sites.

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AVOIDING SEWER FIRES WITH VAPOR SPACE ORGANICS MONITORING

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Vapor space organics (VSO) analysis was developed by the Cincinnati Metropolitan Sewer District (MSD) in response to a sewer fire in nearby Louisville, Kentucky, and potential hazards in the Cincinnati system in the early 1980s. Extensive property damage occurred. Testing for flammables in the sewer discharges was started as one tool to prevent a recurrence.

Since the VSO method was originally developed in 1984, GC technology and Quality Assurance practices have advanced. Severn Trent Laboratories has worked closely with the Cincinnati MSD to update the method in order to facilitate the use of state-of-the-art GC technology and more comprehensive QA.

An extensive search was performed to identify specific compounds to mark the beginning and end of the VSO integration window. Defining the VSO integration window with individual compounds facilitates the use of alternate GC columns (including capillary columns) and temperature programs in order to shorten the run time. A water miscible stock standard solution was developed to facilitate the use of laboratory control samples and matrix spiked samples with known concentrations of hexane.

Samples containing VSO analytes were analyzed by both the original and updated versions of the method. The average difference was 9%. This was within the normal variability of the method, thus the results are equivalent. The relative standard deviations were 11% for the original and 5% for the updated method. The improved precision was expected with the use of a headspace autosampler.

The results are reported as parts per million by volume of hexane in the headspace of the prepared sample. The quantitation limit is 30 ppmv with a method detection limit of 2.6 ppmv. The VSO method update process has produced a method able to incorporate new GC technology of today and facilitates the use of future technology advances to improve method productivity and cost. Also, incorporating current QA practices has improved accuracy and reproducibility.

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PARTICLE SIZE REDUCTION AND SUBSAMPLING OF SOLID MATERIALS

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Many environmental soil samples are heterogeneous, leading to large %D or %RSD when replicate analyses were performed. Drying and grinding samples have been used in other analytical chemistry fields to improve the reproducibility of the subsampling process. This has also been applied to environmental analyses for some non-volatile analytes. Recent work at STL has applied particle size reduction and representative subsampling to metals and PCB analyses.

These techniques have been applied to large scale environmental samples (~15 kg) and to large numbers of smaller samples (1 kg). Processes include air drying, sieving, cone and quarter, chopping, grinding and pour and scoop.

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ULTRA-TRACE QUANTIFICATION AND ISOTOPE RATIO MEASUREMENT OF URANIUM IN URINE: A MONITORING TECHNIQUE FOR TROOPS

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The depleted uranium (DU) (a dense and hard material) has been used as the base material (together with titanium) in the penetrator part of armour piercing shells. Depleted uranium is not particularly radioactive and for the general public, health effects from uranium radiation exposure are in most cases minimal. However, like other heavy

metals, such as cadmium, uranium is known to be toxic to the kidneys, where it is transported before excretion in the urine (which is why urine, rather than blood, is analyzed to determine uranium exposure). Consequently, mainly as a result of the use of DU in armour piercing shells in the Gulf War and Balkan conflicts, interest in (and concern about) the possible environmental and health consequences of this material has been growing in recent years. The major health risk associated with the use of DU in the penetrator part of these shells is exposure to DU dust, generated when the shells strike their targets. Inhalation of the dust leads to acute exposure of the lungs and other organs. It has been found that crews of military vehicles hit by DU penetrators during the Gulf War subsequently showed DU levels in their physiological fluids above the range of values observed for natural uranium in unexposed individuals. Very high orally administered doses of uranium have been found to cause kidney damage in humans and other studies have suggested that uranium exposure can also cause liver damage.

In 2000, as part of the National Primary Drinking Water Regulations; Radionuclides, the U.S. EPA set a new maximum contaminant level (MCL) for uranium in drinking water of 30 ng/ml, in response to concern over its potential toxic effects.

This paper describes the development and performance of a method for ultra-trace quantitation and isotope ratio measurement of uranium in urine (using a highly sensitive quadrupole ICP-MS) which satisfies the challenging analytical requirements for this demanding and important analysis.

LESS IS MORE: INDUCTION-BASED FLUIDICS AND THE NANOLITER-MICROLITER "SYRINGE"

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ABSTRACT
A technology introduced in 1997 and patented in 2000, called Induction-Based Fluidics (IBF), is a simple, electro-kinetic technology that allows one to transport liquids across a very large dynamic range from μL/sec to pL/sec, without moving parts, joule heating or adverse electrochemistry. With a single source of energy, IBF can move liquids through N channels with high accuracy and precision for many purposes. This simple capability has broad applications, *e.g.*, in the development of new drugs, in parallel sample preparation, parallel instrument introduction for FIA/LC/MS/MS and to other liquid handling tasks. Similarly, this technology has wide application in environmental laboratory work, including CB work of all types. Clearly, reducing the amount of reagents from the microliter (or higher) to the nanoliter regime can directly and dramatically reduce the cost of purchasing reagents. Working at nanoliter levels can

also reduce the likelihood and amount of risk posed to workers in the laboratory. Also, the utilization of nanoliter quantities of liquids dramatically reduces the production of hazardous wastes (and their associated disposal costs). In a typical lab performing LC, it costs more to throw away the expensive LC-grade solvents than to purchase them! The simple ability to manipulate low quantities of liquids with high accuracy and precision affords those doing environmental and other testing many new possibilities. For example, IBF can allow one to execute a one-million fold, one-step dilution without creating intermediate hazardous solutions. By simply using less toxic materials, operations in the nanoliter regime can make work with organo-phosphorus pesticides or CB agents (or hot materials in a radiochemistry lab) significantly safer simply by reducing potential exposure. By freezing nanoliter quantities of chemical reagents into "nanoliter-sicles", exact amounts of analytes can be "prepackaged" and aspirated with a dielectric probe, minimizing waste and limiting contamination. Alternatively, IBF dispensing can perform parallel LC with sample placement for MALDI TOF MS-based diagnostic testing of cancer where, for example, the identification of protein markers has been shown to be 100 percent effective in finding Stage 1 ovarian cancer at a stage when treatment success is 95 percent effective. For IBF to be widely used, specific tools must be developed. In this presentation, we discuss data generated from one very simple IBF tool, the "Nanoliter-Microliter Syringe." We present data and other analytical figures of merit of dispensing nanoliter quantities of liquids onto surfaces and into receivers such as beakers, vials or micro-titer plates using pixel counting and other techniques for calibration. To the extent possible, we will address both practical and technical issues of this tool and IBF in general – indeed less is really more!

For more information, visit our web site at www.nanoliter.com.

Introduction

Recent advances in analytical chemistry allow the detection and measurement of chemical analytes and biological contaminants at levels far below those possible even a few years ago. The development of field-portable techniques put a priority on small size, light weight and minimal reagent requirements. Advances in proteomics, DNA analysis, antigen-antibody and other "micro" techniques allow or require the use of small samples and minute quantities of reagents. Working in this micro environment dramatically reduces reagent costs (for both purchase and disposal), minimizes exposure of workers to toxic or otherwise hazardous materials and minimizes the hazards related to disposal of laboratory (whether environmental or clinical) wastes. This environment also puts a priority on non-contaminating techniques, as even minute amounts of contamination at these levels of operation are intolerable.

Historically, forces of adhesion and cohesion generally limited the size of drops of aqueous solutions that could be released from a syringe or other dispenser, without contacting a receptacle, to about 1-2 microliters. With the award of the Noble Prize to Fenn[1] for his development of Electrospray® ionization mass spectroscopy, the analytical world became aware that fine droplets of liquids could be dispersed electro-kinetically when an electrical charge was directly coupled to that liquid.

In 1997, another electro-kinetic technique for movement of liquids, Induction-based Fluidics (IBF), was demonstrated and was nominated as best new technology at PITTCON. This patented[2,3] technique does not require direct coupling between charge and liquid and rather than creating a spray of micro-fine droplets, it allows the user to dispense droplets of nanoliter and picoliter size accurately and reproducibly, singly or in parallel, from most any dispenser configuration, into receptacles of all kinds (*e.g.*, beakers, micro-titer plates, instrument inlets). Because the dispenser and the receptacle to which the sample or reagent being dispensed need not be in contact, the potential for contamination is greatly reduced. And because the liquids being moved are not directly coupled to an electrical charge, the likelihood of adverse electrochemistry in, or joule heating of the liquids is virtually eliminated. The new technology was described in a cover article of *American Laboratory*, October, 2001. Recently, the IBF concept has been applied to the development of a hand-held dispenser, called, appropriately, the nanoliter-microliter "syringe".

The Nanoliter-Microliter "Syringe"

Figure 1 shows a simplistic representation of how "energizing" a droplet of liquid allows it to overcome the adhesive and cohesive forces tending to keep it "attached" to the tip of a dispenser and allow gravity (and/or an electric field) to pull or push it free. Figure 2 further elaborates on this theme by comparing a conventional syringe with Electrospray® and with an IBF dispenser.

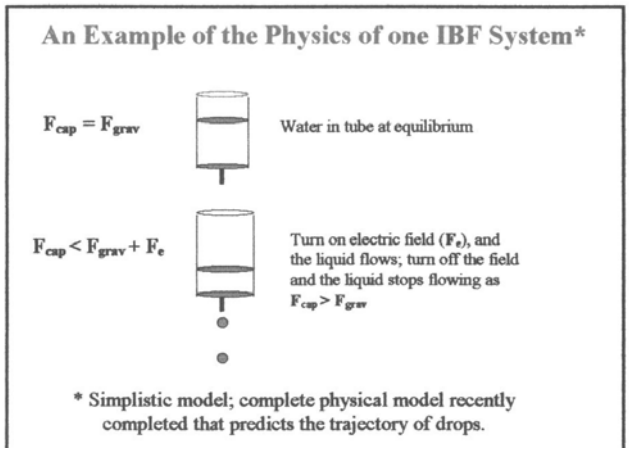

Figure 1. A simplified model of the physics of an IBF system

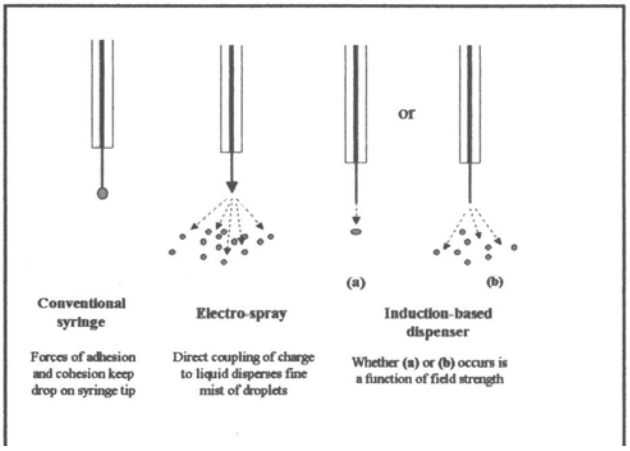

Figure 2. Comparison of ordinary syringe with Electro-spray® and an induction-based dispenser

Why should one consider IBF as a mechanism for moving or dispensing liquids? It moves liquids with no moving parts, without joule heating and without adverse electrochemical reactions. The simple electro-kinetic technology only needs a single, simple circuit to control one or many dispensers simultaneously (see Figure 3). This allows one to perform parallel liquid chromatography with sample placement, *e.g.*, for MALDI TOF cancer diagnostic testing. And as the dispenser is essentially geometry independent, the same container that is used for sampling can later be used to dispense that sample without intermediate steps that could introduce contamination. "Flying" individual droplets from an IBF "syringe" results in non-contact delivery that minimizes contamination, allows the operator to deliver to multiple targets sequentially or simultaneously, eliminates contact injury to a sensitive target (*e.g.*, tissue culture) and allows other than vertical dispensation to targets of various kinds.

The IBF technology has been well demonstrated for proof of concept and has been shown capable of consistently dispensing small (*e.g.*, 20-50 nanoliter) droplets with high (4%-7%) precision (see Nanoliter.com for data gathered under a variety of operational modes and for the photographs used in the presentation of these materials).

There are various ways to calibrate the IBF dispensing systems, depending on the mode or objectives of your operation. These include scanning and calibrating with Vision Builder™, with time/volume relationships (for flowing systems), with stable isotopic or other internal standards, with empirical or estimation models, using a "Calibration Stick" (patent pending) or with scales (problematic at low nanoliter drop sizes).

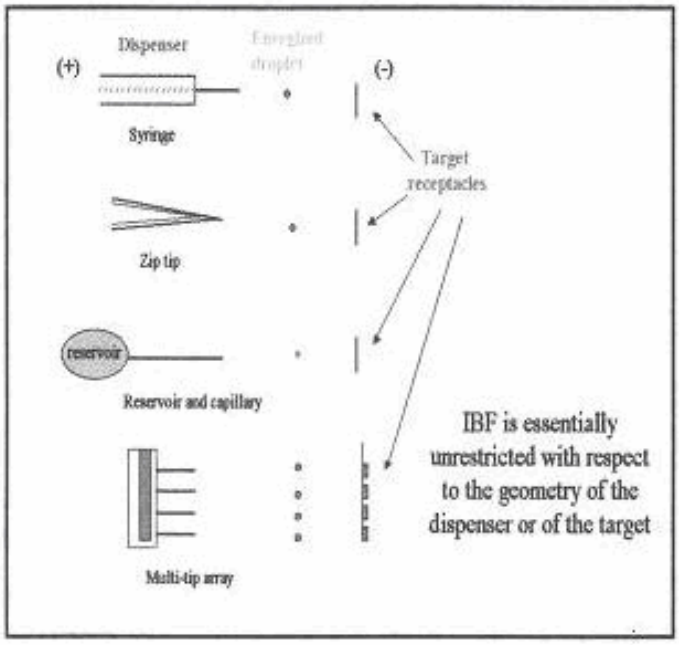

Figure 3. Some examples of IBF systems, showing geometry-independence of dispenser and target

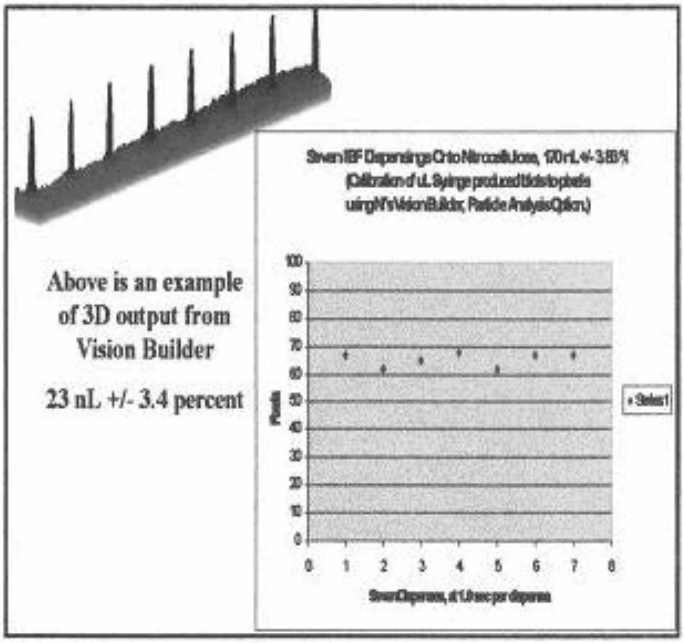

Figure 4. Precision of 7 simultaneous dispenses and an example of the Vision Builder™ output used to calibrate

Summary

The patented IBF technology has many non-environmental as well as environmental applications, *e.g.*, supporting highly accurate cancer diagnostic testing using MALDI TOF. The concept and prototype instruments have been demonstrated; the "syringe"

(patented and patent-pending) offers extremely wide dynamic range (from picoliters to microliters). Nanoliter has teamed with the U.S. Army on a 7-figure initiative based on the technology. Nanoliter is planning to offer courses on induction-based fluidics (lecture submitted for PITTCON 2005; course also to be offered at Duquesne University (TBA). The patented IBF technology (as well as patent-pending technology) is available for licensing. Nanoliter is seeking commercialization and development partners to support development of pre-production prototypes. Visit Nanoliter.com for more information, or contact A. D. (Drew) Sauter at Asauter@aol.com.

References

1. Fenn J. B., *et. al*, *Science* 1989, **246**:64.
2. A. D. Sauter, W. Fitch, J. Chakel, A. Affel, R. Willoughby and E. Sheenan, Approaches For Estimating ESI/MS/MS Relative Response, presented at Pittcon 97, New Orleans, LA, March 1997. Also visit http://www.uspto.gov, search "Sauter."
3. A. D. Sauter, Jr. and A. D. Sauter III, "Nanoliter's Onto Media, Use Of Electric Induction" *American Laboratory*, October 2001.
4. A. D. Sauter, Jr. and A. D. Sauter III, "Electric" Zip Tips For MALDI And Other Applications, *Journal for the Association of Laboratory Automation*, May-June 2002.

CASE STUDIES OF TWO INNOVATIVE FIELD TECHNOLOGIES USING GC AND GC/MS

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This paper describes real world applications of two portable instruments:

- A person-portable GC/MS used for on-site investigations and
- A portable GC with an in-situ purge & trap used for early warning detection of organic contaminants in drinking water supplies.

The first case study was an on-site investigation conducted by the U.S. Army Corps of Engineers (USACE) at the Monterey Peninsula Airport (MPA) in Monterey, CA. Field Portable Analytical (Cameron Park, CA) provided the on-site testing using an INFICON HAPSITE portable GC/MS with a headspace accessory. The work performed at this site is a good example of the USEPA Triad approach to site investigation in action.

At MPA, there was known contamination from petroleum product and groundwater monitoring wells were already in place. There was also one data point from one monitoring well which showed a small amount of TCE present. A residential subdivision was close by. The purpose of this phase, Phase I, was to determine if the petroleum

plume (by BTEX analysis) was migrating off site. After analyzing numerous samples of groundwater, the HAPSITE showed no BTEX in any of the samples but instead repeatedly found TCE. The on-site availability of the GC/MS made it possible to modify the scope of work on site. Now, using the HAPSITE, the crew could do a preliminary assessment of the unexpected TCE plume within the limits of their access to the site. What began as a search for BTEX turned into the mapping of a TCE plume.

In Phase II, the crew returned with permitted access to a wider area in order to determine where to place monitoring wells for the TCE plume. This work was the basis for EPA report EPA 542-R-01-011: Innovations in Site Characterization, Technology Evaluation: Real-time VOC Analysis Using a Field Portable GC/MS. The total cost of Phase II was $75,000 and 17 field days. The estimated savings using real-time data results were $27,000 and four field days.

In Phase III, the team returned to find the source of the TCE. Research showed that there was a sump which at one time held waste TCE, but sampling at the expected sump location showed no TCE. Using the portable GC/MS the team was able to move away from the expected location and continue to sample and analyze until the actual location of the sump was found. As a result, the monitoring well was installed in the correct location on the first attempt so that it would produce accurate, usable data.

Many people still do not believe that a portable GC/MS can produce accurate, quantitative data, but the HAPSITE has proven itself over and over again in extensive testing. In 1998, the U.S. EPA Environmental Technology Verification (ETV) program found it to be equivalent to laboratory GC/MS results for Method 8260. The HAPSITE performed so well in this ETV study that it was used as the reference method for a subsequent ETV study of water sampling devices. Most recently, the California EPA put the HAPSITE through a three-year testing program and certified the HAPSITE to be equivalent in performance to laboratory GC/MS for analysis of air, water, soil and soil vapor samples. Through a Memorandum of Understanding (MOU), this certification extends to the states of New Jersey, New York, Pennsylvania, Illinois and Massachusetts.

The second case study involved an INFICON portable GC with an *in situ* purge and trap accessory, configured for unattended, remote operation. While portable GCs themselves are not unique, the SituProbe, an *in situ* purge and trap device, is a new development.

This particular system was installed as a result of homeland security concerns with respect to contamination of the drinking water supply. While the initial concern was intentional contamination of a water source by terrorist organizations using chemical weapons, the GC monitoring system could also easily be used to track any unintentional contamination through accidents, chemical spills, etc. The idea was to monitor the water coming into a purification plant and to note any significant changes in the chemical composition. To monitor the change in volatile organic compounds (VOCs), the INFICON GC and SituProbe were chosen. If identification of an unknown VOC was

required, the *in situ* purge and trap could be interfaced to the HAPSITE for on-site GC/MS confirmation.

One of these systems was installed in the intake water line in an upstate New York water treatment facility. The system sampled and analyzed the incoming water every 30 minutes. On January 22, 2004, a spike of 9 ppb benzene and 38 ppb MTBE was detected. Plant operators were alerted to the incoming contamination and the intake pumps were shut down. The authorities were also alerted and the polluter was located.

The Ohio River Valley Water Sanitation Commission (ORSANCO) water district consists of a group of eight states and was established to monitor and abate water pollution in the Ohio River and its tributaries. There are 33 municipal water intakes serving over 5,000,000 people and 144 industrial intakes. ORSANCO has also implemented the use of INFICON SituProbe and GC to provide an early warning system for VOC contamination in the Ohio River Valley system.

In addition to the above application at the Monterey Peninsula Airport, the HAPSITE portable GCMS has also been used by Sentinel Mobile Laboratories (Plainville, CT) in conjunction with a Geoprobe Systems membrane interface probe (MIP) for sampling.

This project was conducted around a South Carolina landfill. Samplers in a nearby stream had detected chlorinated solvents and petroleum hydrocarbons. The hydrocarbons could be explained as coming from gasoline engine powered vehicles in and around the stream, but the chlorinated solvents were suspected to be coming from the landfill. The task was to find the exact location of the solvent leak.

Ten locations around the landfill were sampled and analyzed over a three-day period using the Geoprobe MIP to sample and a golf-cart-mounted HAPSITE with headspace accessory to analyze soil gas, soil and water samples at low ppb levels. Soil gas was analyzed by the HAPSITE at numerous depths as the MIP bored into the ground and samples of soil and water were taken and analyzed when the soil gas showed the presence of solvents.

The HAPSITE was uniquely suited for this application because it was able to distinguish the chlorinated solvents (PCE and vinyl chloride) from the hydrocarbon background, it was able to detect and identify these solvents at low (1-20 ppb) levels and it was able to be easily transported and operated in a remote location. Without the HAPSITE portable GC/MS, all samples would have had to be transported off site for analysis, thus adding several days or weeks to this project.

The HAPSITE portable GC/MS is being used extensively by all branches of the U.S. military, by foreign militaries, by the US National Guard and numerous domestic emergency responders to detect and positively identify chemical warfare agents and other toxic chemicals in response to homeland security directives. It is the only portable instrument available that can positively identify these chemicals at the low levels required to determine whether an area is toxic or non-toxic for humans.

SAMPLING AND ANALYSIS FOR HOMELAND SECURITY I

INSIDE AND OUTSIDE THE BOX

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Abstract
Development of long-discussed, stand-alone, early alert monitoring systems for air and water takes on new urgency with current terrorist threat levels. Ideal systems (1) would provide quick and unambiguous alerts to human health risks; (2) would be simple and inexpensive to produce so that large numbers of such units could be networked to a central action authority; (3) would be targeted to detect priority chemical or biological agents, yet be sufficiently flexible in design to accommodate additional targets as intelligence dictates; (4) would be tamper-proof or would provide a system alert if tampered with and (5) would provide extended monitoring service between required maintenance checks. If our desire is to provide a cost-effective approximation of this ideal, where do we look for the system elements? For rapid alert and automatic system shutdown, we can look to examples in the process analytical chemistry arena where flow-through detection systems must identify subtle changes in product specification, which if not caught, result in intolerable economic losses. Simplicity and economy go hand in hand, but often at the expense of unambiguous identification. For quick screens of a broad range of potentially lethal chemical agents, simple and reliable detectors of sudden changes in the levels of nitrogen, phosphorus, sulfur or halides currently exist. Diode array detectors could provide some of the flexibility to address additional target agents. The sealed "black box" flight recorder offers some clues to the design of a rugged, tamper-proof sensor/detector package. And great strides have been made in recent years to stabilize the electronics and the detector systems of analytical instrumentation to minimize downtime and frequency of required maintenance. Most, if not all of the parts needed for an operational early warning system exist in current technology. Assembling them into a cost-effective, responsive monitoring system will require some folks to think outside the box in determining what goes inside!

The U.S. Environmental Protection Agency (EPA) is the lead federal agency charged with protecting the nation's water infrastructure from terrorist attack. The EPA's strategic plan for homeland security identifies several infrastructure protection goals, of which two are particularly pertinent to the theme of this paper:

-- EPA will work with states, tribes, drinking water and wastewater utilities to enhance the security of water and wastewater facilities;

-- EPA will help to ensure that critical environmental threat monitoring information and technologies are made available to the private sector, federal counterparts and state and local governments to assist in threat detection.

Development of early alert monitoring systems to detect contamination of our air and waters has been a long-standing goal since long before the events of 9/11 projected a new level of urgency to those efforts. Particularly in the analytical chemistry area, great strides have been made in the technologies to detect and measure conventional as well

as priority pollutants at low concentrations in support of spill assessments and safe drinking water and hazardous waste detection and monitoring programs. Current terrorist threats require us to think far more broadly with respect to the nature and risk of intentional contamination of our water supplies. This paper discusses some of the options for, and barriers to water monitoring safety nets and provides some recommendations for moving forward in this area.

Table 1 lists key properties of an "ideal" real-time water monitoring system that could be appropriate for the early detection of contaminants intentionally introduced into a water supply.

Table 1. Properties of an Ideal, Real-time Water Monitoring System

- Secure from tampering
- Low false positive, no false negative rate
- Mass producible as an integrated system
- Self-calibrating, with 30-day unattended reliability
- Wireless connectable to "action central"
- Applicable to large or small systems
- Simple and affordable
- Flexible with regard to location, application
- Readily upgradeable to address new threats
- Combines and integrates older and newer technologies
- Combines qualitative "go/no go" with independent confirmation
- Capable of responding regardless of where the system is jeopardized

While the ideal system neither exists nor is likely to for many years to come, what are some of our current options for applying existing and imminent technology to create an effective water safety net in the near term? A number of the most likely water monitoring strategies are identified in Table 2.

Table 2. Potential Monitoring Strategies

- "Go/No Go" for sudden changes in water quality characteristics
- "Go/No Go" for high-likelihood contaminants
- "Go/No Go" for broad suite (comprehensive) of contaminants
- Quantitative for high-likelihood contaminants
- Quantitative for broad suite (comprehensive) of contaminants
- Hybrid approach

Tables 3a-f address the nature, advantages and disadvantages of the potential monitoring strategies identified in Table 2.

Table 3a. "Go/No Go" for Sudden Water Quality Change

Generic sensors for pH, conductivity, turbidity, TOC, TOX, P, S and N species in source water at intake; data compared with historical record

Advantages: Low cost, quick alert, continuous detection

Disadvantages: Requires seasonal history, complex algorithm; non-specific alert requires rapid lab confirmation; high false positives possible form natural WQ variations; may miss selected analytes; poor for biological contaminants

Table 3b. "Go/No Go" for High-likelihood Contaminants

Adds compound- or class-specific qualitative detectors according to list of contaminants selected for monitoring

Advantages: Relatively low cost, focused on target contaminants, less ambiguous results; better decisions for downstream protection

Disadvantages: May miss non-target contaminants; continuous detection of target biologicals untested; compatibility and reliability of desired techniques untested in integrated system.

Table 3c. "Go/No Go" for Comprehensive Suite of Contaminants

Might include automated versions of toxicity tests, laser microbial detectors, flow-through UV detectors

Advantages: Tight safety net if all systems operational; low false negative, moderately low false positives; some proven technology already exists

Disadvantages: Relatively high cost; size and complexity greatly increase; unattended reliability and compatibility of technology untested in an integrated system

Table 3d. Quantitative for High-likelihood Contaminants

Selected-ion, compound- or class-specific detectors, various spectroscopic/ spectrometric techniques, micro-arrays, flow-through laser "bug" detectors

Advantages: Excellent data (if a "hit"); unambiguous results; better decisions for downstream protection

Disadvantages: High cost; slower initial response; large and complex; may miss non-target contaminants; the various technologies haven't been tested in an integrated

Table 3e. Quantitative for Comprehensive Suite of Contaminants

Mobile-lab-type capabilities, *e.g.*, ICP-MS, GC-MS, PCR/DNA technology for bacteria/viruses, or equivalents

Advantages: Excellent data possible for action decision; tight safety net; low false positives and false negatives

Disadvantages: Impractical for continuous operation; very high initial and continuing costs, compatibility and reliability as an unattended, integrated package are untested

Table 3f. Hybrid Approach

Combines elements of "Go/No Go" systems with rapid, independent, confirmatory analyses for "hits"

Advantages: Relatively low cost for security achieved; simple, reliable and continuous monitoring combined with back-up safety net capable of producing decision-quality data; enables a variety of newer technologies in the confirmatory phase

Disadvantages: Doesn't totally overcome disadvantages of whatever "go/no go" front end ("inside the box") is selected; requires dedicated (or at least, priority-driven) laboratory confirmatory capabilities ("outside the box")

At this point we face a set of critical questions. Do we need it? Do we want it? If we need and want it, what do we expect it to do? Given our expectations, does the technology exist to meet the task? And, if it does . . . can we afford it?!? Regardless of how we answer these questions, we must be fully aware of the barriers that will confront us we attempt to move forward. Table 4 lists some of those barriers and Table 5 offers some recommendations to overcome them.

Table 4. Set of Barriers

- Lack of incentives to commercial sector
- Proprietary interests in new technologies
- Current low interest in environmental technology development
- Cost of large-scale implementation
- Federal committees arguing merits for years
- No guarantees to potential providers
- Low confidence (among some experts) in the near-term likelihood of a water safety net

Table 5. How to Break the Barriers

- All parties adopt a "war-time" mentality
- Provide incentives and protect proprietary interests
- Provide clear guidelines as to "what" is needed
- Let technology sector provide the "how"
- Emphasize and underwrite integration, not technology-by-technology development
- Rapidly declassify pertinent technology

I recommend that if we are serious about developing a meaningful water monitoring safety net, a "Water Security Super Team" should be identified and convened to match needs and expectations with existing and imminent technology and with the logistical practicalities and restraints to which the water treatment and distribution infrastructure is subject. Such a "Super Team" would include leaders in the technologies for detection of both biological and chemical contaminants in water (or applicable to water), system technologists and system engineers with experience in interfacing and integrating multiple technologies and the data derived therefrom, (and in securing those systems) and appropriate representatives from water treatment facilities. Until such an integrated effort is mounted, we will never know what could have been. Or how close we actually were to it!

USING SENSOR NETWORKS TO DETECT BIOLOGICAL THREATS

Peter Stein and Paul Sereiko
Sensicast Systems, Inc.

At a recent Homeland Security Summit in Washington, 95% of the attendees indicated that they believe there will be another terrorist attack on U.S. soil within the next 4-5 years. Increasing security and response measures to potential chemical or biological attacks can no longer be relegated to major events such as political party national conventions and world-class sporting events. A cost-effective, easy-to-implement system of monitoring, alarming and responding to threats is required to ensure that any building or structure that may be a terrorist target is protected as comprehensively as possible.

Bio Detection Needs

There are two main deployment scenarios for biological agent detection. The first is for continuously monitoring a facility for biological threats. Ideally, real-time monitoring will provide early detection of a hazard, immediately initiating the proper response to the

alarm. The second scenario is for emergency responses to biological incidents that take place in buildings or areas where biological agent sensors are not widely deployed or not deployed at all. Providing biological agent detection in this scenario can help provide information about decontamination levels or the spread of a threat.

Accurately and specifically measuring biological particulate levels is a difficult task. Effectively distinguishing between harmful substances and innocuous biological matter (such as dust mites) requires very complex equipment and analysis. Most existing biological agent detection systems are very expensive and, therefore, can be deployed only to detect a specific area. The shortfall of these systems is the inability to provide advanced warning of the threat or to monitor the spread of the biological agents throughout the facility or building. It has been stated by government officials that if a solution is too expensive to be purchased and deployed, then it clearly provides no benefit, regardless of the technology. The question must then be raised, how can one both inexpensively and adequately protect buildings and their occupants from a biological threat?

The "Smoke Alarm" Paradigm

The detection of biological threats must begin to be examined through a new lens. There is a method of sensor deployment that will provide early warning detection of a biological event, pinpoint the location of the event and the spread of the agent and avoid the spending of vast amounts of money to deploy an effective biosensing solution. This ideal solution is to deploy an entire network of inexpensive biological particle sensors throughout a building or facility that will continuously monitor the environment in real-time. The system will operate in an analogous manner to a network of smoke alarms (see **Figure 1**). A threat in one specific area of a building will be sensed and an alert will be generated and sent through the network to the proper fire or security system, which will in turn notify the appropriate responding resources. Benefits of such a distributed network of sensors include immediate notification and advanced warning of biological threats and the approximate location of the threat. Additionally, with a network in place, remote monitoring of the state of the facility can be accomplished easily over the Internet.

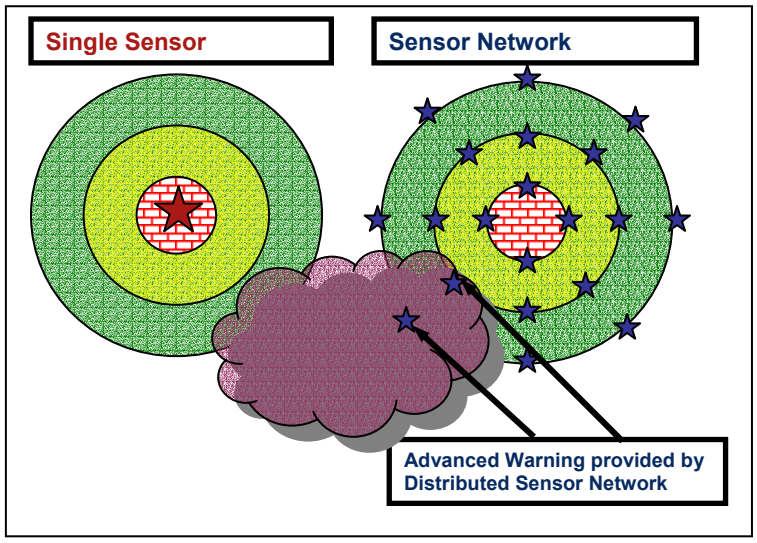

Figure 1. "Smoke Alarm" Analogy

Wireless Mesh Sensor Networking

An ideal biological agent sensor system would be one that is simple and inexpensive to install and maintain, is capable of supporting a large number of sensor points around a facility and can support remote alarm monitoring and network administration. New microelectromechanical (MEMS)-based sensors and new low-cost radio technology have been combined to provide the "smoke alarm" solution to biosensing. From the networking perspective, all of the stated features above can be realized through the new radio frequency (RF) technology called wireless mesh sensor networking. Wireless mesh sensor networks, or mesh networks, are ideal for use as the communication backbone for biological sensor networks, especially within existing buildings. Each individual sensor requires no data or control wiring and, thus, is perfectly suited for retrofit situations in buildings and other facilities. There are many existing structures, such as government buildings, where pulling wiring through large concrete or marble walls, or even from floor to floor is either costly or impossible. Wireless capabilities are required, but existing wireless solutions have issues with the complexity of the installation, unidirectional transmission nature, lack of multi-hopping messages and overall cost to purchase, install and maintain.

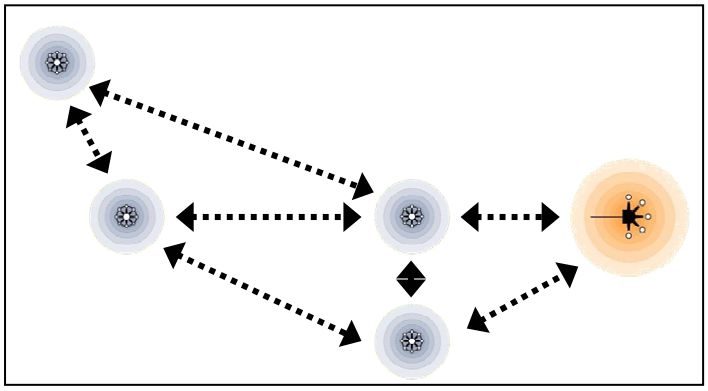

Figure 2. Mesh Networking Example

A mesh network, on the other hand, is a self-configuring network – meaning that the installation of the network consists of turning on the sensor and placing it in its appropriate location. All individual sensors "seek out" other sensors in order to join the network and form a wireless communication path between itself and the alarm annunciation system.

Wireless mesh sensor networks are extremely reliable and robust. They utilize bi-directional communication among all of the deployed biological agent sensors and between the mesh network and any appropriate response or control systems. This communication allows every message that is sent to be acknowledged by the recipient or it will continue to be sent. Since every sensor in the network can communicate with every other sensor, a mesh network forms (see **Figure 2**).

The resulting self-formed network also maintains a self-healing property such that if a wireless communication link is interrupted for some reason, the network will instantly re-configure and send the information through another route. In critical emergency situations, one cannot assume that the entire building infrastructure will be intact and operational. The resulting self-configured, self-healing network creates a robust web of communication links and ensures the reliable transmission of data, calibration information and alerts.

Deploying the Network

As previously mentioned there are two manners in which a biological detection system can be deployed. The first is a permanent or semi-permanent facility installation that continuously monitors the environment for increased levels of biological particulates. Upon a pre-specified rate of change in the moving average of the readings or upon the breaching of a pre-specified level, an alarm can be generated. Typically, this network would be deployed by placing nodes in every room or area within a facility. They would form a mesh network and pass readings and network status information through the network to an application that would monitor the readings and generate alerts, as necessary. In addition to allowing the remote monitoring of the application, the system

can be integrated with the existing fire and security system to alert the appropriate first responders.

The second scenario is one that truly demonstrates the effectiveness and power of a wireless mesh sensor network. In an emergency response situation, if a potential biological threat has been detected (even if it is only a false alarm), mobile sensors can be brought to the scene and immediately deployed throughout the facility by the emergency responders. The sensors will form a mesh network, read the levels of biological matter and then communicate their readings back to a gateway. The gateway will serve up the information and any threshold alerts to emergency response personnel stationed outside of the facility. These responders may have handheld devices or other wireless computers and can remotely monitor the levels of the threat and detect the spread of the contaminant. The system can also be used to indicate when the threat has dissipated.

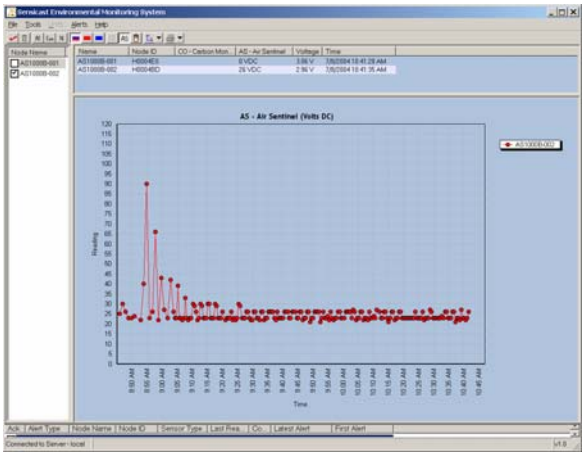

Figure 3. Biological Agent Monitoring

Current Status

Sensicast Systems has developed a wireless mesh sensor network that has been integrated with a new biological detection sensor, called AirSentinel, from Meso Systems. The combined product has been installed in a government facility and is currently monitoring levels of biological matter in the environment and reporting the information to a remote application. The system can support a large number of sensors and can be integrated with existing fire and security systems. Furthermore, different types of sensors can easily be added to the system and used for other Homeland Security applications, such as chemical and radiation sensors. These sensors can be integrated with the Sensicast Sensor Networking Platform to provide a robust, cost-effective means for ensuring the health and safety of a building or facility and its occupants.

Conclusion

Detecting biological threats in a sensible and comprehensive manner requires the deployment of a network of sensors. For existing buildings, wiring sensors in a “home-

run" fashion is expensive and, for some buildings of stone, marble or concrete structure, impossible. A reliable and flexible communications mechanism is needed to ensure that biological matter detection alerts are transmitted in real-time and are acted upon appropriately. Wireless mesh sensor networking is an ideal technology that allows for simple and inexpensive installation of sensors, easy network management and seamless integration between the mesh network and existing response systems.

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AQUASENTINEL: A CONTINUOUS MONITORING BIOSENSOR SYSTEM FOR PRIMARY-SOURCE DRINKING WATER PROTECTION

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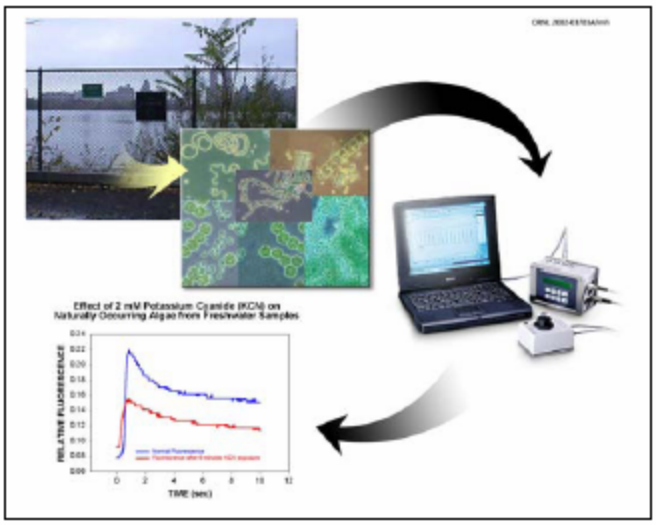
There is an urgent need for continuous real-time monitoring of water quality. AquaSentinel is a revolutionary biosensor system for primary-source drinking water protection. It uses naturally-occurring microscopic algae as fluorometric biosensors. State-of-the-art optoelectronic instrumentation measures fluorescence induction curves which are used as indicators of the physiological state of the algae. The accompanying figure illustrates the conceptual idea of AquaSentinel. We demonstrated the application of this technology for the detection of chemical warfare agents in primary-source drinking water. Model toxic agents selected for this purpose were the blood agent potassium cyanide, the acetylcholine esterase inhibitor methyl parathion and the herbicides Diuron and Paraquat. Experiments were performed with samples drawn from the Clinch River, the main source of drinking water for the City of Oak Ridge, TN. The key conclusion of our work is that proof-of-principal of this technology has been demonstrated: chemical toxins that are known to harm humans also harm the free-living algae that are present in all surfaces waters such as rivers, lakes, reservoirs, ponds, etc. United Defense, LP has acquired an exclusive commercial license from Oak Ridge National Laboratory for this technology in the United States.



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BIOAEROSOL SENSORS FOR HOMELAND SECURITY

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The detection of biowarfare agents disseminated by terrorists and in warfare has become a high priority throughout the world. The potential locations for biological terrorism threats are diverse, including military installations, embassies and anywhere within major metropolitan areas. Affordable, effective and compact systems to collect and diagnose airborne biological materials remain a critical homeland security need.

This presentation will describe:

- a rationale for evaluating bioaerosol sensor technology for homeland security applications
- a detailed analogy to smoke alarms for chem/bio sensor deployment in dense sensor networks
- a bioaerosol sensor being developed based on fluorescence spectroscopy that incorporates only low-cost components

By analogy to commercial fire sensor networks, early warning sensors for chemical or biological threats should have fast response times, modest false alarm rates and low cost-of-ownership. These characteristics allow widespread distribution of sensor networks capable of detection of bio-terror events near the source.

The fire and security industry today uses a two-tiered operational response to alarms in large commercial buildings and other types of critical infrastructure. The initial response usually involves an investigation by trained personnel prior to activation of disruptive measures such as sprinkler systems and evacuation. Dense sensor networks provide precise information regarding the source of the threat, allowing a focused response.

The AirSentinel™ bioaerosol sensor being developed by MesoSystems is based on ultraviolet (UV) light emitting diodes (LEDs) as the excitation source and photodiodes for fluorescence measurements. Excitation and emission wavelengths are chosen to allow some level of discrimination between actual threats and the fluorescence associated with the environmental background. An innovative aerosol concentration technology will be described which enables semi-continuous sampling and detection with low-cost components and without any consumables with a one-minute response time.

STANDARDIZED ANALYTICAL METHODS (SAM) FOR HOMELAND SECURITY SAMPLE ANALYSIS

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The U.S. EPA Laboratory Capacity and Capability Workgroup in conjunction with the National Homeland Security Research Center has developed a document entitled “Standardized Analytical Methods for Use During Homeland Security Events”. This document, currently in review, provides guidance for analytical laboratories during a homeland security event. The purpose of the document is to ensure that laboratories analyze materials consistently so that results will be as comparable as reasonably possible. The document was assembled by a team of professionals representing seven different government departments or agencies. The chemical and biological agents included were compiled from lists of materials of concern from multiple sources and expanded based on the range of materials capable of being analyzed by the method. Method summaries and links are included in the document as well as summary tables for hundreds of materials. The scheduled release of the initial version of the document is September of 2004. This presentation will discuss the procedure for selecting the methods, the use of the document and allow the audience to view some of the data compiled.

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SAMPLING AND ANALYSIS CONSIDERATIONS AT CHEMICAL WARFARE MATERIAL SITES

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Sampling and analysis at Chemical Warfare Material sites requires certain safety considerations, as well as the use of non-standard analytical methodology. The most common types of CWM sites addressed by USACE are Recovered Chemical Warfare Material (RCWM) sites and agent-contaminated media sites. USACE guidance document EP 75-1-3 (RCWM Response) is only required for RCWM sites. Currently, there is no parallel guidance for agent-contaminated media sites. Safety precautions prescribed within EP 75-1-3 for environmental sampling are also appropriate for agent-contaminated media sites.

This presentation will address each of the following:

- Terminology and types of CWM sites typically encountered
- Contaminants of concern, to include chemical agents and agent breakdown products (ABPs)
- Analytical methods for chemical agents and ABPs
- Department of the Army guidance (DA PAM 385-61) regarding environmental sampling requirements
- USACE guidance (EP 75-1-3) regarding environmental sampling requirements
- Typical laboratory requirements
- Available chemical-specific criteria for environmental media

LABORATORY ACCREDITATION I

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HISTORICAL PERSPECTIVE ON THE NELAC MODEL

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In July 1991, the Committee on National Accreditation of Environmental Laboratories (CNAEL) was chartered with determining the need and advisability of a national environmental laboratory accreditation program, alternatives to such a program and the role of EPA in any program. CNAEL was a Federal Advisory Committee composed of members from the laboratory and regulated industry communities, academia, other federal agencies, the states, public environmental interest groups and private accrediting bodies.

CNAEL identified and prioritized numerous issues which were of concern to each of the affected parties and reached agreement on an overall problem statement: to achieve data of needed quality in a cost effective manner. Fifteen alternative solutions were proposed and evaluated in relation to the problem statement. Multiple options for operation of program were identified and ranked. In addition, the scope of a program was defined in terms of environmental regulations, which laboratories should be included and which activities/tests should be included. At the conclusion of its deliberations CNAEL recommended that a national program for accreditation of environmental laboratories, which includes the key elements of on-site audits, performance evaluation testing and data audits, be implemented by enlisting states and/or third parties to perform the accrediting function with oversight of the accrediting bodies by a federal agency.

The CNAEL effort led to the formation of the National Environmental Laboratory Accreditation Conference (NELAC) in February 1995. In the intervening years, a national program was established using the key elements identified in the CNAEL report.

As this effort has developed, new and emerging issues (field measurements, sampling, homeland security, EPA's role, etc.) have challenged the fundamental design of the NELAC effort. This presentation will provide a historical perspective on how the NELAC effort developed, give an update on the current status of the effort and present a few key questions that need to be considered.

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LABORATORY RESPONSE NETWORK-CHEMICAL: QUALITY ASSURANCE PROGRAM OVERVIEW

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The LRN-C QA Program consists of three primary activities: LRN-C Materials Program, method-specific Laboratory Validation and the LRN-C Proficiency Testing Programs. The LRN-C Materials Program produces validation, proficiency testing and emergency response analysis materials for the following Chemical Terrorism Metabolite (CTM) analysis methods. With these materials, the CDC and other members of the LRN-C supporting CDC as surge capacity are prepared to analyze 10,000 clinical samples per method in the event of the release of a chemical terrorism agent.

The LRN-C QA Program establishes the evaluation criteria, reporting timelines and documentation procedures for the method-specific Laboratory Validation of CTM methods. Network laboratories are required to complete a Laboratory Validation for each CTM method transferred. The QA Program also establishes and implements the program guidelines, evaluation criteria, documentation procedures and PT event schedules for the Proficiency Testing programs for the CTM methods transferred to the laboratory network. The successful completion of both the Laboratory Validation and participation in a LRN-C Proficiency Testing program is required prior to a laboratory achieving a Qualified status which is required to act as surge capacity for CDC in the event of a CT agent incident.

ACCREDITATION OF FIELD SAMPLING AND MEASUREMENT ORGANIZATIONS (FSMO)

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The original charter of the National Environmental Laboratory Accreditation Conference (NELAC), when established in the early 1990s, was to “foster the generation of environmental laboratory data of known and documented quality through the development of national performance standards for environmental laboratories”.

However, it has been generally recognized within the environmental community, over the years, that the quality of environmental laboratory data can only be assured if minimum performance standards exist for field sampling and measurement activities – the "front-end" of the environmental data generation process. To assure the production of environmental data that are scientifically valid and can be used with a high degree of confidence by the end-user, control of environmental laboratory analytical processes **and** field sampling and measurement processes are of equal and significant importance. Accordingly, in July 1998, the Constitution of NELAC was amended to reflect the growing interest of many stakeholders to expand its scope to include both field sampling and measurement activities. Subsequent to this Constitutional amendment, the Field Activities Committee was officially established in 1999 as a NELAC standing committee responsible for the development of performance standards applicable to those organizations performing field sampling and measurement activities.

In July 2002, Chapter 7, *Field Activities Standard*, was added to the NELAC Standard to address minimum quality and technical requirements for field sampling and measurement activities. The initial draft of this chapter excerpted selected verbiage from Chapter 5, *Quality Systems*, of the NELAC Standard and did not specifically address other accreditation components (*e.g.*, proficiency testing (PT), on-site assessment and accreditation process) or requirements specific to various types of sampling matrices. As committee membership expanded from 1999-2002 to include representation from all stakeholder groups and as the public became more engaged in the standards development process for field sampling and measurement organizations (FSMO), it was clear that the initial draft of Chapter 7 needed substantive revisions and continued development.

In 2003, the INELA Field Activities Committee (FAC) began revision of the 2002 iteration of NELAC Chapter 7 with an initial focus on developing a comprehensive set of general quality system requirements for the FSMO. The committee established several objectives for this initial phase of Chapter 7 Standard development, which it believed to be essential for ensuring successful FSMO implementation of a nationally-recognized quality system designed to improve the quality of environmental data. These objectives were to develop a standard that conforms to ISO requirements, permits a certain degree of latitude for the development of FSMO-specific policies and procedures and can be effectively supported by sound guidance.

To maintain an internationally-recognized accreditation program and to eliminate the possibility of dual quality systems within an organization performing laboratory analyses **and** field sampling and measurement activities, the committee agreed that "ISO was the way to go". Similar to the Chapter 5 requirements for laboratories, quality system requirements for an FSMO had to conform to the requirements of the ISO/IEC 17025 Standard (where applicable), an internationally recognized standard adopted by NELAC as the basis for accreditation. However, the FAC believed that it would be unrealistic to simply impose all NELAC Chapter 5, *Quality Systems*, requirements on an FSMO because, although ISO-compliant, Chapter 5 had been developed for environmental laboratory use only. Due to the functional differences between the environmental

laboratory and the FSMO, it became obvious early on in the standards development process that only portions of Chapter 5 would be directly applicable to an FSMO.

Although sampling has, historically, been recognized as a major contributor to the overall measurement error, many organizations performing field sampling and measurement activities today are not currently subject to rigorous and prescriptive quality system requirements, accreditation or routine oversight. Additionally, FAC members recognized that it has taken the environmental laboratory industry 20+ years to "ramp up" to an ISO 17025/NELAC Chapter 5-type quality system and that it is, simply, not reasonable to expect the FSMO to accomplish the same in one-tenth the time. On the other hand, a 20+ years "ramp-up" for an FSMO was also unacceptable, as something having some impact now was needed. Accordingly, committee consensus was to take a practical and realistic first step towards improved environmental data quality by establishing quality system requirements for a FSMO that is less prescriptive than the NELAC Chapter 5 requirements. This "less is better" approach to standards development provides a high degree of flexibility for the FSMO in developing policies and procedures that address Chapter 7 requirements yet can be custom-built to also meet the unique needs of the FSMO. The FAC believes that, although different from the existing NELAC Chapter 5 Standard, this practical and realistic "first step" Chapter 7 quality system standard will have a higher probability of successful implementation by the currently unregulated FSMO community, ultimately, resulting in improved environmental data quality – the goal of NELAC.

To support the "less is better" approach to standards development and to facilitate successful implementation (and compliance) with NELAC Standards, development of proper guidance was determined by the committee as being a key element for realizing an improved outcome – sound and defensible data quality for better decisions. It is the long-term objective of the INELA FAC to "show the way" by providing necessary guidance with an eye towards making the guidance a standard requirement once it becomes a routine practice for the FSMO. The committee believes that this approach will accelerate the FSMO quality "learning curve" and improve "buy-in" to the NELAC process. Initially, guidance topics will include development of a quality system manual (template); review of requests, tenders and contracts; purchasing of services and supplies; control of nonconforming work; internal audits, management reviews and field quality control (QC).

Since 2003, the INELA Field Activities Committee has dedicated its efforts to completing the general quality system requirements portion of Chapter 7. This portion of the Standard is nearing completion and will be presented to the general public as an INELA Interim Standard in August of 2004, with an INELA consensus body vote to immediately follow this public meeting. If successfully passed by the INELA consensus body, then a Final Standard will be presented to the NELAC Standards Review Committee (SRC) in December of 2004 for approval.

Although the INELA Field Activities Committee has made significant strides to develop a FSMO performance standard, there is much work left to accomplish. The committee

continues to reach out to industry experts within the environmental community to participate in this fast-tracked development of Chapter 7. The committee is currently in the process of organizing work groups to develop matrix-specific appendices and is in the beginning stages of determining the actual "look and feel" of the accreditation model for the FSMO.

If Chapter 7, *Field Activities Standard*, ultimately, establishes FSMO performance standards for improved environmental data quality within the environmental community, then it cannot be limited in scope and must support existing and future state/federal environmental regulations governing field sampling and measurement activities. To this end, it is believed that the NELAC Chapter 7 Standard eventually will be applicable to organizations performing field activities in the air, biological, water, soil, waste and other sampling and testing arenas. However, a "one-size fits all" approach to standards development may not be appropriate for these diverse sampling and testing arenas. To address the nuances of various sample matrices encountered during routine environmental field activities, smaller committee work groups will be tasked with the development of matrix-specific appendices to Chapter 7, similar to the Chapter 5 appendices. These appendices will delineate additional quality and technical requirements, supplementing the general quality system requirements, for a FSMO engaged in different types of sampling and field measurement (*e.g.*, air, biological, water, soil, waste, etc). The development of matrix-specific appendices for air emissions and water are top committee priorities for the immediate future (next 6 months).

The final phase of standards development planned for Chapter 7 is to adapt the existing NELAC proficiency testing (PT), on-site assessment and accreditation process requirements for direct application to a FSMO. However, this final phase will be accomplished only if the committee can successfully address challenges similar to those encountered while developing the general quality system requirements. Once again, the committee has recognized that the existing NELAC Standards (Chapters 2, 3 and 4) for environmental laboratories, addressing PT, on-site assessment and the accreditation process, respectively, are not directly applicable to an FSMO for a variety of reasons.

Most (if not all) of the work performed by a FSMO is not conducted at one fixed location. Field sampling and measurement personnel, with varying degree of training and experience, typically operate in different geographic locations with minimal supervision. Thus, the qualification and competency of those performing the work is critically important for producing environmental data that are scientifically valid and can be used with a high degree of confidence by the end-user. In some sampling and measurement arenas (*e.g.*, air emissions and stack sampling/testing), there is aggressive state regulatory agency oversight for field activities. Consequently, additional requirements for "on-site assessment" (as required by NELAC Chapter 3) may be perceived as redundant, creating a potential for non-value-added steps within the environmental data generation process. Finally, in many sampling and field measurement areas, proficiency testing is not practical and/or available to be effectively utilized as an indicator of competency. As a result, the FAC has reached consensus, for the reasons given, that

the existing NELAC standards for PT, on-site assessment and accreditation process do not address the nuances of the FSMO and may not be logistically or economically possible to implement as currently outlined in NELAC Chapters 2, 3 and 4.

To address these fundamental differences between an environmental laboratory and a FSMO, it is anticipated that a "straw man" accreditation model (to include provisions for PT, on-site assessment and accreditation process) will be presented at the INELA Summer Meeting in August 2004 for discussion. As part of the accreditation model development process, the INELA FAC has reviewed and considered a variety of reference documents, including but not limited to: the Y2K version of the NELAC accreditation model produced specifically for air emissions and stack sampling/testing; ASTM E994, *Standard Guide for Calibration and Testing Laboratory Accreditation Systems General Requirements for Operation and Recognition*, matrix-specific accreditation models developed by non-regulatory industry experts and state accreditation models in use today by New Jersey and Louisiana. Thus far, the committee has reached consensus on the accreditation model objectives below and continues to work through a series of questions designed to focus committee discussions and, ultimately, committee consensus on the various components and aspects of an effective accreditation model.

Objectives of the FSMO Accreditation Model Are To:

- Demonstrate FSMO qualification and competency through observed performance and quality system and data/records review.
- Be flexible to accommodate requirements for various matrices (*e.g.*, air, water, soil, etc.).
- Be practical, functional and implement-able.
- Be auditable.

Throughout this INELA standards development process, the Field Activities Committee has been aggressively seeking input from all potential "users" and "producers" of this standard to build consensus and to achieve maximum "buy-in" for the INELA Final Standard to be presented to the NELAC SRC and other accrediting bodies for adoption. Today, the committee goal remains consistent with the 1998 NELAC Constitution - to foster the generation of environmental laboratory data of known and documented quality through the development of national performance standards. It is the intent of the committee, through its continued focus on the development of quality system requirements, matrix-specific appendices and an appropriate accreditation model, to produce a national performance standard for FSMOs that parallels (without being identical) the NELAC national performance standard for environmental laboratories. The INELA FAC is confident that this new FSMO national performance standard will comprehensively outline practical and realistically achievable requirements for the "front-end" of the environmental data generation process that have a high probability of

adoption by NELAC and others within the environmental community, ultimately, resulting in improved environmental data quality.

LABORATORY ACCREDITATION AND AMBIENT WATER QUALITY MONITORING

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Introduction

The National Water Quality Monitoring Council (Council) and its predecessor, the Interagency Task Force on Monitoring, recognized that poor or unknown data quality impedes our ability to use environmental information effectively (ITFM, 1995a; ITFM, 1995b; NWQMC, 2001). For example, unreliable data can raise uncertainties concerning wastewater facility or drinking water compliance with environmental regulations or standards. Data of known quality enhances our ability to make sound decisions, take appropriate remedial action and protect human health and the environment. An objective assessment of laboratory competence, including personnel training and experience, and performance evaluation testing, is an essential element for ensuring high quality data (Eaton and Diamond, 1999; NWQMC, 2001).

The Methods and Data Comparability Board (Board), a workgroup under the Council and the Advisory Committee on Water Information (ACWI), a committee chartered under the Federal Advisory Committee Act, was formed to help provide a framework and a forum for comparing, evaluating and promoting comparable methods of data collection in all appropriate water quality monitoring programs. The Board, like the Council, is a multi-agency committee representing all levels of government and the private sector including academia and the research community, private sector groups that develop and distribute consensus methods and guidelines, the regulated community and other organizations that collect or use water-quality information. The Board has several work groups that benchmark and coordinate current efforts, develop databases and guidelines, prepare position papers, make recommendations and develop and conduct pilot studies to achieve the following objectives:

- improve the scientific validity of water quality data,
- establish comparable approaches to collecting water quality monitoring information,
- provide a forum for advancing state of the art technology in water quality methods and practices and
- promote initiatives that lead to data comparability among federal, state and private sector organizations.

Ambient Monitoring and Federal Laboratory Accreditation Position Paper

The Laboratory and Field Accreditation Workgroup under the Board develops and promotes the Board's position on accreditation of laboratories and developing guidelines for a field sampling certification program. The work group has been coordinating various Board efforts with NELAC and, more recently, INELA. As part of its activities over the past four years, the Accreditation Workgroup spearheaded the development of a Board and Council position paper evaluating the need for federal laboratories, and those that contract to federal agencies, to be accredited by a national accrediting authority (NWQMC, 2002). The Board recognized that federal agencies such as USGS, EPA, Army Corps of Engineers, Fish and Wildlife Service and many others conduct a significant amount of environmental monitoring and analyses each year, much of which serves as the ambient water monitoring network in the U.S. Ambient monitoring data are used for a variety of purposes, such as documenting status and trends, measuring effectiveness of BMPs and other management/regulatory controls and identifying and prioritizing waterbodies in need of restoration, pollution controls or other improvements (*e.g.*, TMDLs). In this paper, the Board made three recommendations: (1) federal agency laboratories and outside laboratories that they use for monitoring purposes should become accredited under a recognized program, (2) NELAP is the accrediting authority of choice and (3) NELAP needs to continue its efforts to obtain more state participation and reciprocity, address standards for ambient monitoring, field sample collection and field measurements and promote the development of performance-based methods in the accreditation process. NELAP was selected as the recommended program by the Board for several reasons.

- Provides for reciprocity with other NELAC-approved accrediting authorities. Also includes recognition with some state accreditation programs.
- Provides uniform national standards to replace multiple accreditation programs and standards.
- Accredits a relatively wide range of analytical methods.
- NELAC is developing a performance-based approach to accreditation – the Board's position is that a performance-based approach is ultimately needed to improve method and data quality in water monitoring programs.
- Allows federal as well as state accrediting authorities.
- Quality system is based on ISO Guide 25 and its successor ISO 17025.
- Requires participation in a performance testing program. Results of performance testing analysis in one state are acceptable in other NELAC-approved states.

While the Board recognized that some other accrediting authorities also have many of the same advantages, no other program had all of the above strengths. The position paper was presented to ACWI who ultimately approved the recommendations noted above in 2002. Since that time, several federal laboratories have been accredited by NELAC including the USGS National Water Quality Laboratory and some EPA Region laboratories.

As noted above, the Board recognized that NELAC currently has some limitations that need to be addressed in order for it to be more useful and beneficial to public interests

and the monitoring community at large. One of the most important of these is greater inclusion of ambient monitoring methods and analytes, including field methods and *in situ* field measurements. NELAC standards were initially designed to accredit laboratories that primarily conduct testing as part of compliance with environmental laws and regulations. Methods and analytes that are not currently approved for compliance monitoring may not be accredited by NELAC at this point.

Furthermore, many states still operate only a drinking water laboratory certification program. A laboratory performing ambient monitoring may need to be accredited for drinking water in order for their data to be accepted by the state, even though the methods being used for ambient monitoring may be completely different than those for which they were accredited. This form of accreditation can lead to a false sense of confidence concerning the quality of data generated by laboratories.

The Board recognized that federal and state agencies are particularly impacted by current inconsistencies or limitations in accreditation programs because they often analyze water quality samples to meet various objectives (*e.g*., regulatory compliance, ambient water quality or new management needs). Depending on these objectives, the need for, and the type of, accreditation sought may vary. For example, compliance objectives can dictate higher reporting levels for a given analyte than those often required to meet ambient monitoring objectives. Thus, the type of monitoring performed by a given federal agency will have a large bearing on its data quality objectives and, consequently, the quality control standards and accreditation implemented to ensure that appropriate data quality criteria are met. Accreditation, therefore, needs to extend beyond regulatory compliance water methods to other equally important matrics, such as sediments and surface waters.

NELAC and Ambient Monitoring Accreditation

Recently, NELAC has made some progress on accrediting ambient monitoring methods. The recognition of non-potable versus potable water accreditation standards within NELAC has made it possible to achieve laboratory accreditation for some ambient monitoring methods. For example, the USGS National Water Quality Laboratory recently was accredited for 110 analytes involving ambient methods. While this is a major step forward, there remains a large number of methods and analytes awaiting accreditation, not only within USGS but also with the many other organizations that conduct routine ambient monitoring. Some of these include methods for emerging contaminants of concern such as pesticide metabolities or new pathogens.

Ambient monitoring often differs from compliance monitoring methods in that *in situ* or field measurements are often preferred in ambient monitoring due to the large number of sites being monitored. Analyses that are rapid, reliable and rugged enough to conduct in the field are advantageous to many ambient monitoring programs because this reduces field time and associated travel and personnel costs. NELAC has made significant progress developing accreditation standards for field methods; however, there is much yet to be done in this regard. Ambient monitoring, in particular, relies on trained field personnel and a variety of field techniques involving perhaps sampling,

sample processing and measurement. There is increasing interest in, and use of, for example, *in situ* probes, field kits and other field measurement systems that may not be currently included under NELAC accreditation of non-potable water methods. It is important for NELAC to address accreditation of such methods very soon because field technologies are likely to be commonplace in ambient monitoring in the very near future.

Given the advantages of using NELAC as a national accreditation program, the Board is actively coordinating accreditation-related activities with NELAC and INELA. Therefore, a prime objective of the Board is to correspond with workgroups in NELAC and INELA and to support NELAC's accreditation plan to (1) establish an uniform national accreditation process including the use of a performance-based system, (2) develop uniform and consistent accreditation-related policies and requirements, (3) avoid duplication of effort and (4) work to affect change in NELAC to better address ambient and field methods.

Future Methods Board Accreditation Activities

The Board is planning to develop a position paper concerning accreditation of state laboratories. States, like many federal agencies, also conduct extensive water monitoring, particularly ambient monitoring. But unlike federal agencies, states typically serve as accrediting authorities and, thus, may have unique issues in terms of accrediting its own laboratory as well as potential constraints due to state laws and resources. Other Board activities include the development of a white paper and a Fact Sheet on the *Value of Accreditation* (available on the Board website: http://wi-water.usgs.gov/methods/about/publications/accred_fs.pdf). The Board also plans to survey federal laboratories to determine the extent to which the ACWI-approved recommendations regarding accreditation are being followed and to identify current obstacles and potential solutions for achieving more widespread and comprehensive accreditation of laboratories conducting water monitoring. These efforts are intended to make NELAC more suitable to the needs of federal and state laboratories and other organizations.

Literature Cited

Eaton, A. and Diamond, J. 1999. Reservoir dogs and performance-based systems. *J. Environ. Testing and Analysis*, **8**: 18-19.

ITFM. 1995a. The Strategy of Improving Water Quality Monitoring in the U.S. Report #OFR95-742, U.S. Geological Survey, Reston, VA.

ITFM. 1995b. Performance-based approach to water quality monitoring. *In*: Strategy for Improving Water Quality Monitoring in the U.S., Appendix N, Report #OFR95-742, U.S. Geological Survey, Reston, VA.

NWQMC. 2001. Towards a Definition of Performance-Based Laboratory Methods. National Water Quality Monitoring Council, Technical Report 01-02, USGS, Reston, VA.

NWQMC. 2002. *Accreditation of Federal Laboratories for Water Quality Monitoring*. Position paper prepared by Methods and Data Comparability Board, http://wi.water.usgs.gov/methods/about/publications/accred_fs.pdf

Extended abstract not received in time for printing.
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DIFFERENT APPROACH FOR THE ACCREDITATION OF AIR EMISSION TESTING

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The Constitution, Bylaws and Standards for the National Environmental Laboratory Accreditation Conference were written in 2001 and took effect in July of 2003. "The purpose of the organization is to foster the generation of environmental laboratory data of known and documented quality in a cost-effective manner through the development of national performance standards for environmental laboratory accreditation." Field testing differs from laboratories in several areas:

1. The work is conducted at the client's location, which can be in any state.
2. Stack testers are routinely observed by the different State observers for each test.
3. The relevant paperwork is carried on-site.
4. The next job/test may be conducted in a different State.
5. Test plans and test reports are routinely reviewed by State observers.
6. Each test/report is a stand alone review.

The quality standards have been developed by a consensus organization and will be approved this summer/fall. They are based on ISO 17052 and are performance-based. Individual qualification has been added to measure the knowledge and training effectiveness.

Because of these differences, we propose a different approach to the on-site inspection. We propose that the existing on-site inspector (*i.e.,* State observer) be given a checklist to observe the additional requirements which are over and above their normal review of methods, equipment, methodology and reporting. These would include the quality requirements of the standard, *i.e.,* blanks, quality manual, error reporting, management practices and documentation of training/qualification. Since the work is being conducted in the field and the testing company should have all the relevant paperwork on-site, the complete on-site tests can be completed on-site with the existing State observers. These State observers should meet the minimum basic assessor requirements as outlined in Appendix A of Section 3 of the NELAC Constitution By-Laws and Standards. Most State observers exceed the technical requirements of these training and have the ethical standards and assessment knowledge.

No major areas of NELAC have been left out; however, most have been modified to be more cost-effective and to provide a better measure of quality.

ADVANCES IN ELECTRONIC DATA DELIVERABLES I

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LABORATORY PERSPECTIVE ON THE CHALLENGES ASSOCIATED WITH THE GENERATION, MANAGEMENT AND SUBMITTAL OF LABORATORY DELIVERABLES

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The ever-increasing demand for faster access to greater amounts of data has placed a great of deal of pressure on laboratories to manage, generate and submit a growing number of deliverable formats – electronic and hard copy. This presentation provides a laboratory perspective on the process involved in successfully responding to these challenges.

The focus will be on the production of Electronic Data Deliverables (EDDs) and the inherent obstacles posed by the lack of industry standards in this area. The presenter will provide a historical perspective on the growing demand and increaseD complexity of Electronic Data Deliverable (EDD) products.

Also covered:

- The cost of producing EDDs
- Key information needed to successfully develop an EDD
- An estimate of the number of formats in place
- Examples of format challenges
- A statement calling for basic standardization of EDD formats

STATUS OF SEDD: IMPLEMENTATION, PRODUCTION AND REVIEW SOFTWARE

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The Problem

Laboratories routinely have to support a large number of electronic data deliverables (in some cases over 300), in order to meet diverse client requirements. Most electronic data deliverables (EDDs) are customer specific and, thus, cannot be used by other clients. This leads to a lack of data exchange capability especially for Federal Agencies.

Most EDDs also use proprietary formats leading to issues with long-term data storage. At present there is no self-defining EDD that can meet diverse client needs.

The Solution - SEDD

SEDD stands for Staged Electronic Data Deliverable. The staged approach allows for meeting diverse reporting requirements. The common structure and data element dictionary also eases data exchange between various parties. The analytical data is reported in an Extensible Markup Language (XML) format. XML is fast becoming the industry standard for data exchange as it is designed for output from and input into a variety of databases. This language is a Final Standard recommended by the World Wide Web Consortium (W3C).

The SEDD specification consists of the following documents:

- An Overview Guide which gives the specifications and structure of SEDD.
- A Data Element Dictionary that gives the SEDD data elements and their corresponding definitions.

The latest versions of these documents are available at the following website:
www.epa.gov/superfund/programs/clp/sedd.htm

Both the Overview Guide and Data Element Dictionary are agency and program neutral - *i.e.*, they do not contain biases or requirements for any particular agency or program.

SEDD Stages

From the SEDD specification three (3) specific EDD formats (stages) have been created. These individual formats are unique in that each stage directly builds on the previous stage allowing the user to specify the level of detail as needed for a given program or project.

Stage 1 only uses a small part of the overall SEDD structure and contains a minimum number of data elements to transmit results-only data.

Stage 2 contains all of the Stage 1 structure and data elements but adds additional structural and data elements to report method quality control (Stage 2a) and instrument quality control (Stage 2b) information.

Stage 3 contains all of the Stage 2 structure and data elements but adds additional structural and data elements to allow for the independent recalculation of the reported results (*e.g.*, as required by CLP).

A fourth format (stage 4) is now under development that would build on stage 3 and allow for the reporting of all raw instrument data files.

SEDD Goals

The goals of SEDD are to create an uniform format for the transmission of environmental analytical data which will

a. be self defining and
b. meet diverse requirements by capturing the exact laboratory procedures used to analyze samples.

SEDD Pilots – Status

In order to ensure that SEDD can be implemented, pilots have been conducted since 2002 with over 15 laboratories ranging from commercial to government and from small business to large networks. Laboratories already delivering compliant SEDD Stage 2a and 2b files, which can be inputted and evaluated by Automated Data Review software.

SEDD Inter-Agency Efforts and Implementation Plans

Offices from the U.S. EPA, U.S. Army Corps of Engineers (USACE), U.S. Air Force, U.S. Department of Energy, and U.S. Navy and others are cooperating to implement SEDD. As of June 2004, delivery of SEDD is required for the USACE FUDS program. The USACE Seattle District has SEDD as a requirement in a July 2004 Request for Procurement (RFP) and the U.S. EPA Contract Laboratory Program will require SEDD in the new solicitation scheduled to be in place by early 2005.

SEDD Pilots – Progress and Upcoming Efforts

Based on feedback received in 2003, numerous changes were made to the SEDD in order to ensure a smooth implementation. These included making general Document Type Definitions (DTDs) for each SEDD stage (instead of separate DTDs for each analytical method and stage), updating the SEDD Specification to meet Federal XML standards and posting example files for commonly used environmental analytical methods.

Upcoming efforts include posting of more example files for other methods, setting valid values for certain key data elements to ensure data exchangeability, developing SEDD for radiochemical and microbiological methods and continuing outreach to agencies and the private sector.

Contact Information for SEDD
Please contact Anand R. Mudambi (U.S. EPA) for more information regarding the SEDD Implementation.

INNER WORKINGS OF SEDD: EVERYTHING YOU WANTED TO KNOW BUT WERE AFRAID TO ASK

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Introduction
In today's information age, more and more laboratories are being required to report data to most of their clients in an electronic format along with the required hard-copy report. Many different formats currently exist for these electronic data deliverables (EDDs). Each of these formats is specifically designed to deliver data to a single client or small groups of clients using that client's specific data structure and acceptable values for each of the data elements being reported. The complexity of these formats can vary significantly between clients. The use of a single electronic format that would be usable and acceptable to all clients has been an elusive dream.

The SEDD (Staged Electronic Data Deliverable) Specification was developed specifically to deal with these issues and offers an alternative approach to the current EDD dilemma. This paper will discuss what SEDD is and what sets it apart from the other EDD formats currently in use today.

What is SEDD?
The SEDD Specification provides a common structure and data element dictionary to electronically report a wide variety of data (chemical, radio chemical, biological, etc.) to multiple clients. The SEDD specification allows for reporting of data in multiple formats that are fully compatible with each other ranging from simple sample concentrations all the way to a CLP-type data package and beyond.

The SEDD Specification allows clients to link the final results being reported to the underlying laboratory activities and processes to provide full traceability of the data. All samples are reported in 'batches' that allow each sample to be associated with its corresponding Quality Control (QC) sample(s). This would allow the linking of a given sample to its associated Method Blank or Laboratory Control Sample. This would also allow the linking of that same sample to its associated Continuing Calibration Verification standard or to its associated Initial Calibration. In addition, each reported

result is linked to the specific analysis that generated that result. Data from multiple analyses, such as from dilutions, reinjections and reanalyses, can now be reported with specific analytes being reported from the analysis that produced the final reported result. Any spikes that may have been added to a given sample can be fully traced to the specific vendor and lot number. Any internal standards used can be linked to the specific analyte(s) that were quantitated against them.

The SEDD Specification also provides a means for reporting complex analytical relationships. The reporting of initial calibration curves has always presented a challenge for any given EDD. Using SEDD, for any given analyte, the actual initial calibration strategy can be reported. This could include the reporting of data for a simple calibration/response factor model, a linear regression model, a quadratic model or beyond. In addition, different calibration strategies can be reported for analytes within the same method. For the reporting of initial calibration curves for the multi-peak analytes, such as the PCBs, either individual calibration curves can be established for each of the unique peaks used or a summed single calibration curve can be established. Either calibration curve strategy can be accommodated by SEDD.

All of the above scenarios can be reported using SEDD because the SEDD specification views reporting of data in the same manner as the laboratory produces it - *i.e*., it is based on the way data is generated in the laboratory for the analysis of a sample. In addition, whole words, not codes, are typically used.

SEDD uses XML technology and EDDs created using SEDD are transmitted as XML documents. XML stands for eXtensible Markup Language and provides a common approach for transmitting information over the Web. This language is a Final Standard recommended by the World Wide Web Consortium (W3C).

A SEDD EDD consists of a series of data elements that are nested within the various structural elements (nodes). All data elements within the SEDD specification use a tagged, self-defining format. Each data element uses real words rather than codes such that they are readily understandable by others. For example one of the data elements used in SEDD is AliquotAmount, which stands for “The amount (weight or volume) of sample subjected to an analysis” as defined by the SEDD Data Element Dictionary. This data element would contain the amount of sample used (*e.g*., 1.00 as reported in the example below) for this method. An example XML file for reporting the preparation information for the separatory funnel extraction of a liquid sample that will be analyzed using a typical semivolatile GC/MS method would look as follows:

```
<PreparationPlusCleanup>
    <ClientMethodID>3510C</ClientMethodID>
    <PreparedDate>03/06/2003 08:00</PreparedDate>
    <AliquotAmount>1.00</AliquotAmount>
    <AliquotAmountUnits>L</AliquotAmountUnits>
    <FinalAmount>1.0</FinalAmount>
```

<FinalAmountUnits>mL</FinalAmountUnits>

<PreparationBatch>WG12114-03/06/2003-1</PreparationBatch>

</PreparationPlusCleanup>

All aspects of this preparation procedure have been captured and reported electronically.

SEDD Stages

From the SEDD specification three (3) specific EDD formats (stages) have been created to date. These individual formats are unique in that each stage directly builds on the previous stage allowing the client to specify the level of detail as needed for a given program or project. This is one of the aspects of SEDD that makes it truly unique.

Stage 1 only uses a small part of the overall SEDD structure and contains a minimum number of data elements to transmit results-only data.

Stage 2 contains all of the Stage 1 structure and data elements but adds additional structural and data elements to report method quality control (Stage 2a) and instrument quality control (Stage 2b) information.

Stage 3 contains all of the Stage 2 structure and data elements but adds additional structural and data elements to allow for the independent recalculation of the reported results (*e.g.*, as required by CLP). This is another aspect of SEDD that makes it truly unique. The final reported result for any reported analyte can be independently reconstructed outside of the original software that was originally used to produce the result from an integrated peak area count or a background corrected peak intensity measurement. This feature will give laboratories the ability to independently verify all reported data to ensure that all algorithms used are correct. This feature will also give third party data validators the ability to independently verify the reported data using the project specific requirements.

A fourth format (stage 4) is now under development that would build on stage 3 and allow for the reporting of all raw instrument data files. Instrument vendors typically store the raw data as generated for any given analysis in a proprietary format. The long-term storage and archiving of this raw data has caused problems for both laboratories and clients. Laboratories have had to resort to saving the original software and, in some cases, the original hardware in order to be able to retrieve this data. Some laboratories have resisted software upgrades solely to maintain compatibility with these older stored files even though the newer versions of this software would offer higher efficiencies. A Stage 4 SEDD file would contain these raw data files, where these raw data files would also be stored in the nonproprietary XML format. These raw data files would be the original complete raw data files, not a 'PDF' picture of a single chromatogram.

SEDD Documentation

The SEDD specification consists of the following documents:

- An Overview Guide which gives the specifications and structure of SEDD.
- A Data Element Dictionary that gives the SEDD data elements and their corresponding definitions.

The latest versions of these documents are available at the following website:
www.epa.gov/superfund/programs/clp/sedd.htm

Both the Overview Guide and Data Element Dictionary are agency and program neutral - *i.e*., they do not contain biases or requirements for any particular agency or program. On the same website, Document Type Definition, Instruction and example files are also posted.

Three (3) specific SEDD stages have been developed to date. A set of rules has been established for each of these stages that includes what specific structure and the specific data elements can be included within each stage. These rules are contained in a Document Type Definition (DTD). A single generic DTD has been developed for the SEDD Stage 2a. This DTD was developed such that it could be used to report data for all common inorganic and organic analytical methods. Organic-specific DTDs have also been developed for the SEDD Stage 2b and Stage 3. These DTDs were developed such that they can be used to report data for all common organic analytical methods. Users of SEDD must use these DTDs since they have been designed to accommodate the requirements for multiple clients across private sector and government programs.

Since the DTDs that have been developed were designed to accommodate the needs of multiple methods and multiple clients, Instruction Files have been created to specifically define how each method and each client/program would be implemented. These instructions would convey the QC samples that would be required, the data elements that would be used for each type of sample reported and the valid values that would be required for these specific data elements.

The example SEDD XML files contain real data and give data generators and data users an idea of how the data should be assembled and reported using the Stage 2a, Stage 2b and Stage 3 DTDs. Since XML technology is being used, files generated using the SEDD specification can be readily viewed/edited using third party software products like XML Notepad.

What's Next With SEDD?
Offices from the U.S. EPA, U.S. Army Corps of Engineers, U.S. Department of Energy, U.S. Navy, U.S. Air Force and others are cooperating to review and use this specification for delivery of environmental chemical data and radio chemical data. Face-to-face meetings, conference calls and video conferences are being held on as-needed basis to ensure that the SEDD Specification can meet program specific needs (while remaining generic enough for data exchange between the agencies). Numerous laboratories have submitted test files for review during earlier pilot projects. Throughout this process, SEDD has evolved and will continue to evolve. The current version of SEDD (Draft 5.0) is being required as the EDD for many projects and programs. The

final version of SEDD is expected to be released in Fall 2004. The issue of 'Valid Values' will be addressed with this release.

Contact Information for SEDD
Please contact Joseph Solsky (U.S. Army Corps of Engineers) for more information regarding the SEDD Specification, SEDD Interagency Efforts or development of tools for evaluating and processing EDDs based on the SEDD Specification.

SEDD: EXPERIENCES IN PROGRAMMING AND IMPLEMENTATION WITH REAL-WORLD PROJECTS

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Introduction
The last several years have seen a steady trend towards the movement of environmental sampling and laboratory data into centralized data management repositories where they are combined with project-related data to provide engineers, regulators and other interested parties with a more complete picture than they've ever been able to obtain before.

One of the major issues in this developing trend is the way in which data are transferred from the various parties involved in the overall effort. The *Staged Electronic Data Deliverable* provides one of the best ways for transporting and storing environmental laboratory data we've seen yet. As such, the format represents a significant evolutionary step in the continuing laboratory data management process.

About Promium
Promium is a LIMS Vendor specializing in LIM Systems for environmental testing laboratories. Every single one of the facilities currently using our LIMS is an environmental laboratory.

Our clients range in size from small, 5-person laboratories up to larger ones with over a hundred people and include EPA Regional Laboratories and U.S. Army Corps laboratories.

All of the technical people in the company (programmers, installers, trainers, help-desk) have experience working in Environmental Testing Laboratories.

The Evolving Role of LIMS in Application Interaction

The LIM system is just one of many pieces of software associated with environmental analysis. In order for it to benefit its users, it must interact smoothly with a number of other applications by way of electronic data transfer. As a LIMS vendor in this industry, we've become familiar with a broad array of electronic data transfer formats.

Our system currently supports 12 electronic Chain-of-Custody Import Formats - including the EPA's *Forms II-Lite* program and the EDMS *eChain* format often used within Corps of Engineers laboratories.

We support import of analytical data from over 68 different analytical instrument data systems including industry standards such as ChemStation, Target, TurboChrom, WinLab and ThermoSpec.

We provide financial exports in support of 15 different accounting formats.

Our system natively provides over 35 Standard EDD Formats including industry standards such as ERPIMS, GISKey, Equis, Adapt/ADR, COELT, EDF and, of course, ***SEDD***.

…and we frequently find ourselves providing our client laboratories with custom EDD formats to support a somewhat never-ending series of requests from *their* clients in order to support their own various commercial or home-grown data management systems.

SEDD: It's not just another pretty EDD

The SEDD format represents a significant improvement in the overall evolution of data management in this industry because of some very key points.

It is the first EDD format I've seen that is truly able to represent the sample and quality control associations within the environmental testing laboratory. It supports preparation batching, analysis batching, instrument calibration, sample cleanup and pre-preparation handling concepts through well-defined 'linkages' between critical data elements in its various nodes. This seems to have been a particularly difficult set of associations to accommodate within previous generations of standard electronic deliverable designs.

The use of XML as the data medium allows designers and generators of the format to add additional elements or even re-define existing elements much more easily than would be the case with traditional ASCII flat-file formats or relational table designs.

The data element tags within the design are relatively straightforward. They are not unnecessarily cryptic and their existence within the format structure makes it relatively easy for experienced EDD generators to understand their intended purposes. In addition to this, the developers of the format provide excellent documentation, instructions, example files and even file export development tools to help laboratories produce SEDD files.

Real-world SEDD projects

Several laboratories using Promium's LIM system have participated in trials of the SEDD as part of real projects running through their laboratories. Promium assisted these laboratories by providing updated versions of the SEDD draft within its standard EDD library (a Dynamic Link Library or 'DLL' distributed with the LIMS) and then making modifications to the routines that generate the SEDD within that library based upon feedback from users of the generated files.

The laboratories participating in the trials worked primarily on EPA and Corps of Engineers projects but also tested the format on commercial projects. In most cases, the SEDD file was just one of the deliverables for the project. Most of them also involved generation of hard-copy data packages and report summaries along with EDD files in legacy data formats.

The majority of the files produced were SEDD stage 2a Draft Revisions 5.0 and 5.1.

The majority of the files were sent to Laboratory Data Consultants (LDC) for parsing into their Adapt/ADR file format with subsequent evaluation using their proprietary data validation processes.

Because the ADR application was originally designed for relational database data, data type restrictions and field size limitations for it were written into Promium's SEDD routines so that the data elements within the generated SEDD file would more easily translate to the ADR file format.

The ADR format utilizes 'valid values' for a number of its critical fields. The SEDD format did not yet have a defined set of valid values at the time of the trials. To accommodate this, some data elements, such as matrix identifiers and analysis method identifiers, were interpreted and matched to hard-coded valid values by the SEDD generating routines within the LIMS. Translation of analyte identifiers was handled *via* initial method setup in the LIMS or through translation against ADR Project Libraries during the SEDD file parsing process.

Issues Identified

The real-world trials of the SEDD format brought several issues to light. Most resulted in tweaks to the generation code on our part (LIMS vendor), minor modifications to the SEDD file parser on the part of LDC, enhancements to the instructions and data element definitions and some minor adjustments to the SEDD format itself on the part of the EPA and USACOE. There were some issues from the SEDD trials that were especially note-worthy.

Generic DTDs substantially sped up the process of developing and updating SEDD-generation capability within our LIMS.

A comprehensive set of valid values will be needed for the SEDD.

Laboratories generating SEDD files would like to have an independent application that could verify the structure and linkages in the file before it is sent to a third party.

The SEDD file uses newer technologies and has more complicated information with fewer limitations than many of the validation applications and data repositories where its information is destined to be used. This means that legacy systems may need updating, modification or some sort of 'buffer-application' in order to accommodate SEDD files.

Generic DTDs

One of the most significant issues identified during trials of the SEDD was the value of generic DTD files. The SEDD format lends itself to project or analysis-specific customization through use of differing Document Type Definition (DTD) files wherein data elements might be added, removed or redefined.

From the perspective of the LIMS vendor, method-specific or program-specific DTDs require a great deal more programming to check, validate and accommodate different DTDs. Programming against a single, comprehensive or generic superset DTD is much easier. It also provides a better scope for testing the format against real-world projects.

Another benefit of generic DTDs is that there are usually several different users of the resulting SEDD file. Different users are typically more interested in different parts of the file: Project engineers, for example, are not as concerned about surrogates, calibration data and QC samples as data validation chemists are. Also, data elements originally deemed insignificant within the file by some users may eventually be quite important to subsequent reviewers of the data within a larger project scope or within a comprehensive historical context.

Initial versions of the SEDD specification employed different DTDs for different analyses. This is a reasonable approach when a project uses only a few, well-defined protocols such as those associated with the EPA's Contract Laboratory Program (CLP) but it causes unnecessary difficulties in the much more broad scope of environmental methods used in environmental projects. It would be extremely tedious to keep track of and work with different DTDs for all the possible analyses encountered in real-world environmental projects. Since these analyses have a great deal of data elements in common with each other, it is easier to accommodate them by expanding the definition of a single DTD. If data elements are populated but not necessarily needed by the data users for certain methods, there is no harm. Conversely, if it is later determined that a data element would have been useful to data users, it usually requires a great deal of effort to recover the information and incorporate it into the file.

The SEDD format, with its underlying XML foundation, has the potential to be extraordinarily flexible. As designed, it already has a great deal of flexibility by virtue of its multiple stages. Flexibility, however, is the arch-enemy of standardization. It is the hope of many in the environmental testing industry that *some* format will rise to the top of the currently expansive heap of company-specific, project-specific, database-specific and program-specific EDD formats to become the prevailing standard for the industry.

The implementation of comprehensive, generic DTDs helps make the SEDD format a viable candidate for this role and removes some of the impetus for users to customize it.

Need for Valid Values

Valid values provide the basis for users to communicate analytical information between computer systems, different languages and legal agencies by mapping one entity's identifier for a critical piece of information to the other entity's identifier. The most basic items requiring translation are analytical method references, analyte or parameters names, sample matrices and result units.

There are a few internationally recognized standards for parameter identifiers or chemical compound names (CAS numbers, IUPAC names, STORET numbers) but anyone working on a real-world environmental project quickly discovers that their project seems to have some, if not many, parameters that cannot be uniquely related to an internationally recognized identifier. Additionally, there do not seem to be any internationally recognized identifiers for things like analytical method references, sample matrices and analytical units.

Beyond the most common valid values, transfer of analytical testing information requires universally excusive comparisons for 'key' items such as sample and QC types, instruments and detectors, company names, government agencies, sample identifications and even reviewer comments. It is easy to neglect these items or assume that they are self-evident but confusion about them could lead to serious misapplication of environmental testing information.

Valid values are usually implemented for purposes of transferring data from one data system to another, completely independent, system. These values include identifiers that affect the actual structure, organization and linkages within the overall data set – not just how something is identified between two different users of the information. As such, they are a first critical step when trying to integrate with legacy data systems.

SEDD Checking Tool

As users of our LIM system started producing SEDD files for their real-world project trials, one of the most frequently mentioned support requests we received from them was for some sort of application that could be used to verify that the file produced by our system was compliant with the SEDD specification and did not contain any stupid mistakes. We decided to start working on such a tool as either a separate, stand-alone application or as a web service for our clients. At this time, the tool is still under design with hopes for release later this year or soon after the SEDD specification is finalized.

One of the critical issues we identified in designing the tool was that it should not be identified as a data validation tool. Data validation is a complex process involving a great deal of information from non-laboratory sources as well as a high level of expert judgment.

The primary purpose of the tool is that it should save laboratories and receivers of SEDD files significant time and effort by preventing unnecessary multiple reviews and revisions of the file for simple issues that can readily be identified through an automated process. Its primary design features are that it will:

- Validate File Stage and Structure
    - Evaluate header information
- Check for Missing Elements and Nodes
    - Compare against published specification
- Identify Unmatched/Invalid Values
    - QCTypes, Analytes, etc.
- Verify Critical Linkages
    - Prep, Analysis, Method and Handling Batches
- Flag Obvious Errors
    - *i.e.*, date/time mismatches, MDL>MRL

Integration with Legacy Systems

As our users starting sending their SEDD files for review and data validation, we quickly discovered that, whereas the SEDD format with its XML foundation allows for a wonderful amount of flexibility in data types and field sizes, legacy systems will still need certain key pieces of information to follow defined data type rules and field length requirements. We were able to work through these issues by making some changes to our own routines. The handlers of the legacy system also, quite graciously, made changes to their system to accommodate things as well. Negotiating and resolving these data type and field length issues represented the major portion of the overall time that it took to get a compliant SEDD file generated from the laboratory and through the validation process.

In our case, the data type and field size issues were being handled by two companies working amicably towards a common goal. This may not always be the scenario for future situations where the SEDD file needs to be converted for incorporation into pre-existing data systems.

My observation is that this major hurdle can be handled either through

1. careful management of data type and field length compliant valid values at the beginning of the process or
2. through use of translation utilities that will take the SEDD files and translate its valid values to compliant values for the legacy system.

My preference is for the latter option because it allows generators of the SEDD file to concentrate on producing and checking one form of the file for compliance against the standard SEDD format. Legacy system managers can then use their own understanding of their system along with the well-documented design of the SEDD format to create the best possible conversion of SEDD data into their system. Obviously, this puts the onus of the conversion on the handlers of the legacy system. These people may have

difficulty with the conversion for reasons such as a lack of understanding regarding valid value matches, lack of familiarity with the legacy system or simply limited funding. Without a clear benefit to them and their system, it is unlikely that users of legacy data systems will be willing to shoulder this burden.

Summary

Our experience with the SEDD format, through the participation of some of our clients in real-world projects with SEDD submissions, is that the format has proven itself quite viable for purposes of transferring analytical data from our LIM system to independent reviewers and users of the data within other, completely independent, data-handling systems. The format of the SEDD proved extremely well-suited to the broad range of environmental analyses involved in the projects. The issues we identified as problems during the trial projects are already being addressed by several parties, including ourselves, who want to see the SEDD format evolve into an industry standard – an objective that this format is very likely to attain in the next several years.

USING SEDD DELIVERABLES AND AUTOMATED DATA ASSESSMENT SOFTWARE TO MEET PROJECT SPECIFIC ELECTRONIC DATA MANAGEMENT GOALS

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Introduction

One of the challenges facing professionals in the environmental arena today is the collection and assessment of large amounts of environmental analytical data. The assessment of the quality of that data is essential as multi-million dollar decisions for environmental site cleanups and/or long-term monitoring efforts are made based on the analytical results. Also critical to environmental programs is the sharing and access of data across multiple data users. The ability to share data allows for better use of the limited resources available to clean up and monitor contaminated environmental sites. Standardization of an electronic data deliverable (EDD) allows for collection of data from multiple data generators into a single database for use by numerous data users and stakeholders on a project. The Staged Electronic Data Deliverable (SEDD) format provides a common format for the reporting of data from a variety of analytical methods and allows a given program or project the ability to specify the level of detail required in the deliverable. This paper discusses the successful application of data review, data quality assessment and data management tools to analytical data presented in the

SEDD format. The standardized SEDD format and data assessment tools provide an ability to perform project planning and data review and assessment throughout the duration of the environmental project.

The benefits of a standardized deliverable

Although many benefits can be achieved through the standardization of the electronic data format, three main benefits stand out. First, a standardized deliverable allows a laboratory to streamline the process of generating EDD and generating software applications to verify integrity of the EDD. Second, it provides project chemists with the ability to deploy software tools that assist with the assessment of the analytical data against project data quality objectives. Third, a standard electronic format allows multiple analytical laboratories and contractors involved in a project over its various phases to easily transmit and/or share the environmental data that has been collected in a single compatible database.

A standard deliverable provides the means for establishing a comprehensive database for the project, or multiple projects, regardless of which contractor collected the data, which lab analyzed the data and which phase of the environmental assessment and cleanup process that the project is in. Data collected from portable field labs and from multiple fixed site labs can be combined into a single database that can be queried. The analytical data can be managed and evaluated for cleanup objectives or for trends over time, such as is required of long term ground water monitoring programs and monitoring of natural attenuation remediation processes.

The SEDD format allows laboratories to streamline the process of generating EDD and developing and deploying existing software tools that verify the EDD immediately for completeness and compliance. In addition, the SEDD format allows project chemists to interface existing environmental data quality management systems and analytical laboratories and environmental contractors to transmit and/or share environmental data in a single comprehensive and compatible database.

The SEDD format is based on extensible markup language (XML) and accommodates varying levels of detail (SEDD stages): a SEDD Stage 3 file contains more detail than Stage 2 file and Stage 2 file contains more detail than Stage 1 file. The XML format and design of SEDD files allow parsing tools to be developed that capture the data required for existing software applications without having to redesign the software application.

Interfacing SEDD with existing data assessment and data management software

Software applications designed to enhance the environmental data quality management system and previously developed by Laboratory Data Consultants, Inc. (LDC) under contract with the Army Corps of Engineers (USACE), Sacramento District can now interface with SEDD files. The applications consist of the Contract Compliance Screening (CCS), Automated Data Review (ADR) and Environmental Database Management System (EDMS). In addition, LDC has also developed an internet-based version of the Environmental Data Management System (EDMSi). The applications provide the laboratory with the ability to verify compliance with project and electronic

deliverable specifications, the project chemists with tools to automate the data review process and data users with discrete data qualification flags. The qualified data is exported into a master database for overall project use.

Without having to redesign the CCS, ADR and EDMS applications, LDC, under contract with the USACE, developed the SEDD Parser Tool to capture data from the various stages of SEDD files (*i.e*., Stage 1, Stage 2, Stage 3, etc.) for upload into the existing software.

The SEDD Parser Tool allows the USACE, Sacramento District to utilize their existing software applications while advancing a standard deliverable format the SEDD file provides for laboratories.

Performing automated review and data quality assessment

Once project planning is complete and Data Quality Objectives (DQOs) and Measurement Quality Objectives (MQOs) have been determined for the project, the DQO and MQO requirements are documented in the Quality Assurance Project Plan (QAPP) and entered as a project library in the ADR application. ADR project libraries are easily updated and revised over the life of the project as project goals change. Most of the development of the initial project library is based on standard EPA analytical method libraries that are available in the software module. The standard library can then be edited to match the specific quality needs of the project throughout all phases of the project using simple dropdown menu selections and mouse-click operations.

The ADR project library and the CCS application are provided to the laboratory in order for the laboratory to determine compliance with SEDD specifications and project specifications. The SEDD format includes QA/QC batch links and routine accuracy and precision parameters such as surrogate, matrix spike, and laboratory control sample recoveries. In addition, initial and continuing calibration and GC/MS tuning data can be provided in a Stage 2b and Stage 3 format. After the CCS application has processed a parsed SEDD file, non-conformances in the SEDD file are detailed in an outlier report. The laboratory uses the report to address all non-conformances before forwarding the SEDD file to the client for performing an automated data review. This saves project time and money by providing the laboratory with tools to verify the SEDD file immediately for completeness and compliance.

The ADR module is used as a data review tool by a project chemist to review analytical data against criteria specified in the project library. During the automated review process, data qualifiers are automatically assigned. The project chemist completes the review process by reviewing the assigned qualifiers and layering on professional judgment. Forms and reports within ADR aid in the review of data qualifiers. After the data has been approved, the project chemist transfers the data into EDMS or EDMSi. Automated data review processes save projects time and money by allowing all of the data to be reviewed and not just a “representative” portion of the data set. This is truly cost effective on large projects where review of mountains of hard copy data can be a daunting, if not impossible, task. The Sacramento District has realized an almost 50%

reduction in data review costs by implementing automated data review on a large-scale ground water monitoring project. Automated data review also allows for nearly real-time review of analytical data quality issues so that data gaps can be assessed and addressed quickly.

In addition to serving as a repository of both field and analytical data, EDMS and EDMSi provide features for performing post-review data quality assessment. Some of the features contained in EDMS and EDMSi include the ability to compare data from a primary laboratory and a QA split laboratory, the ability to compare project results against project action limits, Preliminary Remediation Goals (PRGs), Maximum Contaminate Levels (MCLs) and historical levels of contamination. EDMS and EDMSi provide an automated means of evaluating project completeness goals (including project completeness, analytical completeness, technical completeness and field sampling completeness) for each analytical method over any period of time. Above all, EDMS and EDMSi provide users tools that simplify data retrieval and data export processes.

Summary

The SEDD format provides a standardized format for analytical project data and allows for data from various contractors and sources to be combined into a single database. The SEDD Parser Tool provides a vehicle to transfer data from SEDD files to existing support software previously developed for environmental data quality management systems. The CCS, ADR, EDMS and EDMSi software programs were developed as tools to support technical staff in the data review and evaluation of analytical chemistry data using an expedited and cost-effective automated process. The SEDD format allows for streamlining at the laboratories to produce data deliverables that can be verified immediately using CCS software for completeness and compliance against project specific data quality criteria and non-conformances can be immediately corrected. ADR is an automated data review tool to assist a project chemist during the data review process. And at the end of the process, EDMS and EDMSi provide repositories for field and analytical data as well as tools for data users to efficiently evaluate large data sets for key indicators and ultimately determine the usability of the data for making project decisions.

USING SEDD FILES WITH THE WEB-BASED ENVIRONMENTAL INFORMATION MANAGEMENT (EIM) SYSTEM

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Overview

The Environmental Information Management (EIM) system is a web-based application developed by Locus Technologies that lets users manage, query and report their analytical and geotechnical data. EIM is used to manage analytical, field, survey, geologic and other environmental data for almost 4,000 sites.

Figure 1. The EIM System from Locus

To take advantage of web-based data management systems such as EIM, analytical laboratories need a way to deliver data that can be understood by any web based system. One data delivery format that meets this requirement is the Staged Electronic Data Deliverable (SEDD) format. By generating data in SEDD format, an analytical laboratory ensures that its data can be used by any web service or XML-based web application. The analytical data 'life cycle' can thus be made quicker and more efficient from sample collection through lab analysis to final report preparation.

The SEDD Format and XML

The Staged Electronic Data Deliverable (SEDD) is an inter-agency effort spearheaded by the U.S. Environmental Protection Agency (EPA) and the U.S. Army Corps of Engineers (USACE) to create a generic format for electronic delivery of analytical data for environmental programs.

SEDD is being implemented in stages to allow analytical laboratories time to adapt their procedure to the new format.

- Stage 1 includes basic analytical data elements (such as the sample ID, analyte, result and qualifier) to convey results to the end user.
- Stage 2a adds method Quality Control (QC) data to Stage 1.
- Stage 2b adds instrument QC data to Stage 2a.
- Stage 3 adds additional measurement data to Stage 2b to allow for independent recalculation of reported results.
- Stage 4 adds the raw instrument data files to Stage 3.

The format is based on the eXtensible Markup Language (XML), which is rapidly becoming the standard for data transfer on the web. According to Microsoft, "XML is revolutionizing how applications talk to other applications – or more broadly, how computers talk to other computers – by providing an universal data format that lets data be easily adapted or transformed". XML is not a programming language but rather is a format for structuring data. An XML file contains data nodes, elements and tags that describe the data in the file. In this way the file is self-descriptive and can be understood by any XML-compliant web application. An XML can also have a related Document Type Definitions (DTDs) file to impose a data format and allow for data verification.

SEDD and Web Services

Because SEDD uses XML, it is a perfect fit for use with a new Internet technology called Web Services. A web service can best be described as a "site intended for use by computer programs instead of by human beings" (Microsoft, 2002). Each web service is a small task-oriented application accessible through the Internet. Since web services use XML for transferring information, they can act as the bridge between different applications, computers, intranets and database systems. Again from Microsoft, web services "let applications share data, and - more powerfully - invoke capabilities from other applications, regardless of platform".

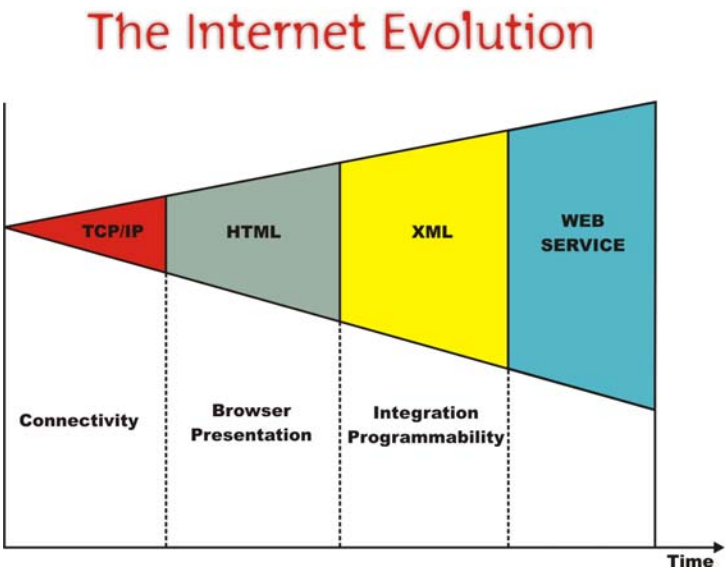


Figure 2. The Advent of Web Services

Common examples of web services include the various news and stock tickers, weather forecasts and sports score applications that can be installed on a desktop PC. The applications query a dedicated web service for the latest news, sports or weather in XML format and push the data on the desktop. Locus has developed a similar application that lets a user load a SEDD file into EIM.

The Locus SEDD 2a File Helper

Locus has developed the Locus SEDD 2a File Helper application to let the user:

- check a SEDD file with a DTD.
- load a SEDD file into EIM.

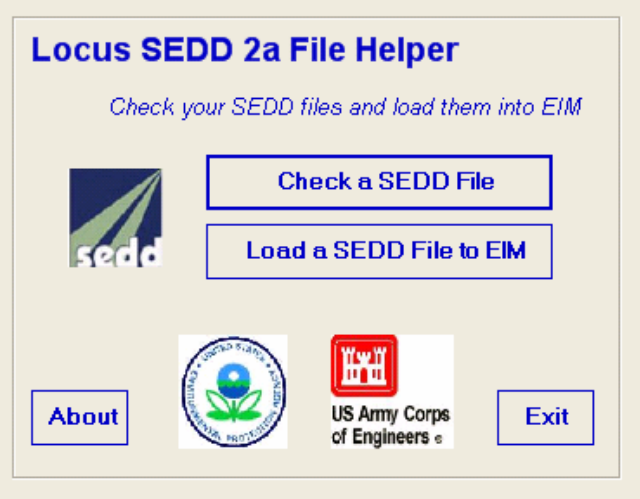


Figure 3. The Locus SEDD 2a File Helper

The application, which runs on a client PC, was developed using the Microsoft Visual Basic.NET programming language. Currently the application only supports Stage 2a SEDD v 5.0 files. The application calls a Visual Basic.NET Web service to perform the data transfer to EIM.

Checking a SEDD File
The "Check a SEDD File" button opens a form where a SEDD file can be selected.

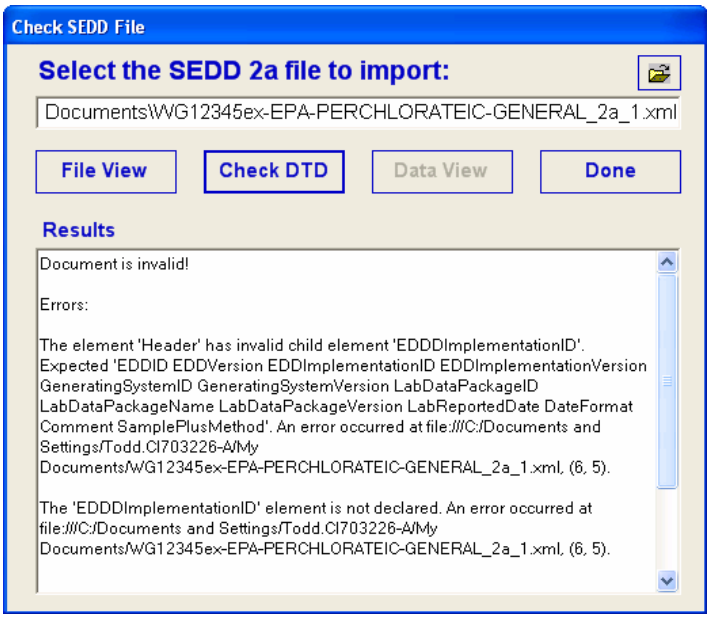


Figure 4. A SEDD File with DTD Errors

The user can preview the SEDD file before performing the file check with the "File View" button. The "Check DTD" button checks the file against the DTD referenced in the SEDD file. These DTDs are stored and updated on the Locus Web server. DTDs can be custom-built for different clients and programs.

The file checking is done on the local PC using Microsoft .NET XML validation objects. If a file passes the DTD check, the "Data View" button lets the user preview the file. If the file fails the check, the user is shown diagnostic information.

Loading a SEDD File to EIM
The "Load a SEDD File to EIM" button opens a form where a user logs in to EIM.
The user must first select the target database and site in EIM. The "Load to EIM" button then transfers the file to a Locus web service. The web service loads the data into EIM and converts the SEDD data to EIM format using SQL stored procedures.

SEDD to EIM Table Translation
The SEDD stage 2a file has five nodes that are mapped to EIM tables.

- SEDD Header Node → EIM Dataset table.

- SEDD SamplePlusMethod Node → EIM Field Sample and Lab Sample tables.
- SEDD Reported Result Node → EIM Field Sample Result and Lab Sample Result tables.
- SEDD Analysis Node → EIM Field Sample Result and Lab Sample Result tables.
- SEDD PreparationPlusCleanup Node → EIM Field Sample Result and Lab Sample Result tables.

The SEDD Handling, AnalysisGroup and Analytes nodes are not yet used by Locus clients.

SEDD to EIM Field Translation

Converting the SEDD data elements to EIM fields is mostly a straightforward translation, with some issues.

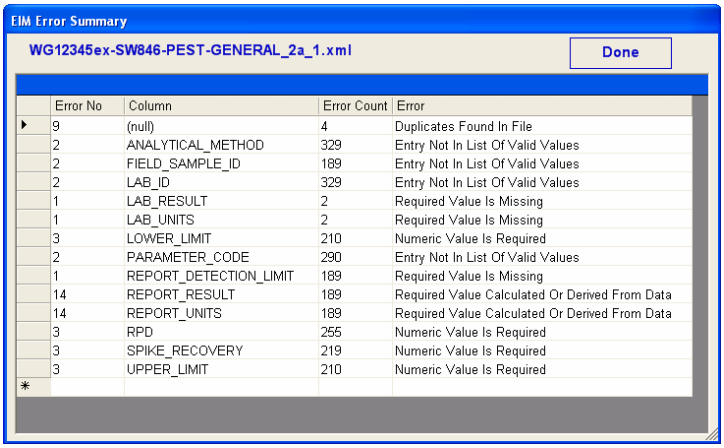
- Some EIM fields are shorter than SEDD elements and must be checked for truncation; the DTD file can store these length requirements.
- The SEDD date/time elements must be split into separate date and time fields.
- The SEDD elements ResultBasis and MatrixID must be examined to set the EIM leached and filtered flag fields.
- Care must be taken to correctly handle the QC sample links in SEDD.

SEDD to EIM Value and Null Translation

In most cases the actual data in a SEDD element can be copied straight to the matching EIM field, but some valid value translations must be made. For example, a SEDD AnalyteType value of 'Surrogate' becomes an EIM value of 'SUR'. Also, some SEDD elements which allow NULL values must be handled separately. For example, a null AnalyteType in SEDD becomes a EIM value of 'TRG'.

EIM Error Checking

After the SEDD file has been translated to a set of EIM tables and field values, EIM runs checks on the data and reports errors caused by missing values, wrong data types and invalid sample relationships. The "View Error Summary" button shows a list of errors by type and column. The "View Errors" button shows all SEDD records with errors, linked to an error list for each record.



Error No	Column	Error Count	Error
9	(null)	4	Duplicates Found In File
2	ANALYTICAL_METHOD	329	Entry Not In List Of Valid Values
2	FIELD_SAMPLE_ID	189	Entry Not In List Of Valid Values
2	LAB_ID	329	Entry Not In List Of Valid Values
1	LAB_RESULT	2	Required Value Is Missing
1	LAB_UNITS	2	Required Value Is Missing
3	LOWER_LIMIT	210	Numeric Value Is Required
2	PARAMETER_CODE	290	Entry Not In List Of Valid Values
1	REPORT_DETECTION_LIMIT	189	Required Value Is Missing
14	REPORT_RESULT	189	Required Value Calculated Or Derived From Data
14	REPORT_UNITS	189	Required Value Calculated Or Derived From Data
3	RPD	255	Numeric Value Is Required
3	SPIKE_RECOVERY	219	Numeric Value Is Required
3	UPPER_LIMIT	210	Numeric Value Is Required

Figure 5. An Error Summary for EIM Errors

If a file has EIM errors, the user can login to the main EIM interface to review and fix errors and save the SEDD data to the final database tables. If a file has no EIM errors, the user must still login to EIM to sign off on the data and save it to the final tables.

Using SEDD Data in EIM

A laboratory could generate a SEDD file and upload it to the EIM system for data format verification by an engineer or geologist, and data validation by a chemist or data validator. Once the data is fixed and saved to EIM, the data can be queried into tables, spreadsheets or reports, posted to a map in a geographic information system (GIS) or exported back to SEDD or other formats for transmittal to regulatory agencies or other consultants or PRPs. The data can also be accessed from a user's PC using the Locus EIM Query web service. This web service lets users download EIM data directly into ESRI's ArcView9, Microsoft's Excel or AutoCAD's Autodesk.

Conclusions

- The SEDD format is based on XML and, hence, is well-suited for data transfer to databases using Web services.
- Some work is required to convert SEDD data to a specific format, but the work is made easier by the use of SQL stored procedures.
- Using DTDs with SEDD files enables SEDD file generators to ensure the files are consistent and correct before sending the files to the data loaders and users.
- A Web service for loading SEDD files can facilitate quick transfer of SEDD data into a data management application for use in queries, tables and maps as well as exports to other formats.
- SEDD helps make the analytical data "life cycle" quicker and more efficient from sample collection through lab analysis to final report preparation.

Web Services - Some Definitions

- SOAP (Simple Object Access Protocol) is the XML-based set of rules for the call-and-response communication between Web service-enabled applications. SOAP

is the glue that holds Web services together by ensuring reliable delivery of messages.

- WSDL (Web Services Description Language) describes the design of a Web Service so a client can discover how to invoke and use it.
- UDDI (Universal Description, Discovery, and Integration) is the standard for registering all available Web services in use. UDDI is like a phone book for locating a particular Web service.
- XML (eXtensible Markup Language) is rapidly becoming the de facto standard for transferring data between databases and applications on the World Wide Web.

For More Information

- World Wide Web Consortium: http://www.w3.org
- EPA: http://www.epa.gov/cdx
- SEDD: http://www.epa.gov/superfund/programs/clp/sedd.htm
- XML: http://www.xml.org
- Microsoft: http://www.microsoft.com/net/basics/webservices.asp
- UDDI: http://www.uddi.org, http://services.xmethods.net/
- Locus and EIM: http://www.locustec.com

References

The SEDD web site above was the primary source of information on the SEDD format. The Microsoft quotes were obtained from the above Microsoft link on web services. The World Wide Web Consortium web site above was the source of information on the XML format.

ADVANCES IN IMPLEMENTING THE TRIAD APPROACH AND DOCUMENTING MEASUREMENT UNCERTAINTY

TRIAD APPROACH TO MANAGING THE UNCERTAINTY IN ENVIRONMENTAL DATA

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Introduction

The first-generation data quality model that equated environmental data quality with analytical quality was a useful starting point for the site restoration community. However, for many contaminated site projects this model for establishing reliable data fails in practice because it does not consider numerous relevant variables. The inability of the "analytical quality = data quality" model to ensure data representative of the intended decision is an important reason why cleanup projects tend to take years of repeated site characterization efforts to get to closure or successful remediation. Cost-effective, efficient and defensible cleanup projects depend on an environmental data quality model that explicitly includes all major contributors to data uncertainty.

The U.S. EPA has articulated the Triad approach as a practical framework that synthesizes new technologies and advancing science with evolving regulatory and engineering practices governing site cleanup. The Triad approach rests on the foundation of managing decision uncertainty. Managing data uncertainty, especially sampling uncertainties, is critical when decisions will be based on data. The second-generation framework offered by the Triad approach not only increases decision confidence, but also decreases project lifecycle costs by evolving the site conceptual model in real-time (using dynamic work strategies) whenever feasible. Projects implemented using Triad principles typically show lifecycle cost savings in the neighborhood of 30-50% as compared to first-generation strategies for site work. A key reason for Triad cost-savings is that characterization is performed very efficiently and accurately, avoiding decision errors that waste resources.

The purpose of site investigation and characterization is to develop an understanding of the nature and extent of contamination that is accurate enough to support correct decisions—whatever those decisions may be. The most important decision early in a project may simply be: Is there contamination present in quantities that could pose a risk to receptors such that more in-depth investigation is required? If the answer is yes, a more accurate conceptualization of contaminant mass, distribution and mobility will need to be developed to support subsequent decisions about exposure risk and risk mitigation. If the early decision is faulty because isolated data points give misleading information, two types of decision errors are possible 1) resources spent needlessly characterizing insubstantial contamination; or 2) unacceptable exposure risk from significant contamination that was missed by the sampling program.

Contamination that is uniformly distributed throughout a matrix is to detect if it is present, or to conclude it is not present if isolated samples do not detect it. However, the physical mechanisms by which pollutant release and migration occur ensure that contaminants are rarely spread evenly throughout a site's boundaries. As illustrated later in this paper, contaminant heterogeneity easily leads to both kinds of decision errors unless the decision maker develops and tests predictions about where contamination would be if present. Heterogeneity can also produce misleading pictures of contamination if data uncertainties are not controlled. The model that predicts and describes contaminant nature and extent is termed the "conceptual site model" or CSM. It is the mental picture on which decision maker ultimately bases all project decisions. Consensus among stakeholders and other involved parties is possible only when all are confident that the final CSM accurately represents site contamination.

The Conceptual Site Model

The CSM is the "story" about

- how contamination was released and what mechanisms cause migration or transformation,
- what distinct spatial patterns or contaminant distributions are created by mechanisms of release, fate and transport,
- what receptors might be exposed to contamination and to how much and
- what might be done to cost-effectively and efficiently mitigate potential exposures.

The preliminary or initial CSM is built (*i.e.*, predicted) from

- information gleaned from the site history,
- knowledge of how contaminants are typically released,
- knowledge of how they behave once released to the environment and
- existing site data, not just for contaminant concentrations, but also for parameters that influence contaminant behavior (*e.g.*, pH, organic carbon content, particle size, porosity, stratigraphy, topology, etc.).

The preliminary CSM functions as the working hypothesis about site contamination that will be continually tested and refined as more information (including data) are integrated into the contamination model. The more closely the CSM depicts reality with respect to the intended decisions, the more cost-effective and successful those decisions can be. The more the model deviates from actual site conditions, the more likely that risk decisions and remedial designs will be incorrect. The CSM guides design of sampling and analysis plans to fill data gaps obstructing confident decision-making. The CSM is the tool used to

- predict the degree of contaminant heterogeneity and the nature of spatial patterning,
- verify whether those predictions were accurate,
- assess whether heterogeneity can compromise the performance of statistical sampling plans,

- understand "data representativeness,"
- communicate a common understanding and vision of the project among all stakeholders and
- integrate knowledge of heterogeneity and spatial patterning into decisions about exposure pathways, remedy selection, treatment system design and strategies for long-term monitoring.

An important function of the CSM is to identify and delineate different contaminant populations. Contaminant release and migration mechanisms typically create spatially distinct populations where impacted media are interspersed among non-impacted media. This inter-mingling of populations can occur on macro (between-sample scales) and micro (within-sample) scales. Both can have severe repercussions on the ability of contaminant concentration results to reliably represent contaminant nature and extent. Contaminants may migrate through narrow flow channels (termed preferential pathways) whose small spatial volumes are hard to detect, but may be a primary exposure route.

Knowledge of the physical mechanisms of contaminant release and migration can be used to predict contaminant locations and the degree of spatial patterning. These predictions form the basis for drawing up the preliminary CSM (or perhaps two or three competing preliminary CSMs), which are then tested as data collection confirms, rejects or modifies the current CSM. Populations are most productively defined by combining knowledge of spatial patterning with potential site decisions. For example, Figure 1 depicts a wind deposition scenario creating surface soil contamination in a pattern of coarse concentration contours that span five orders of magnitude.

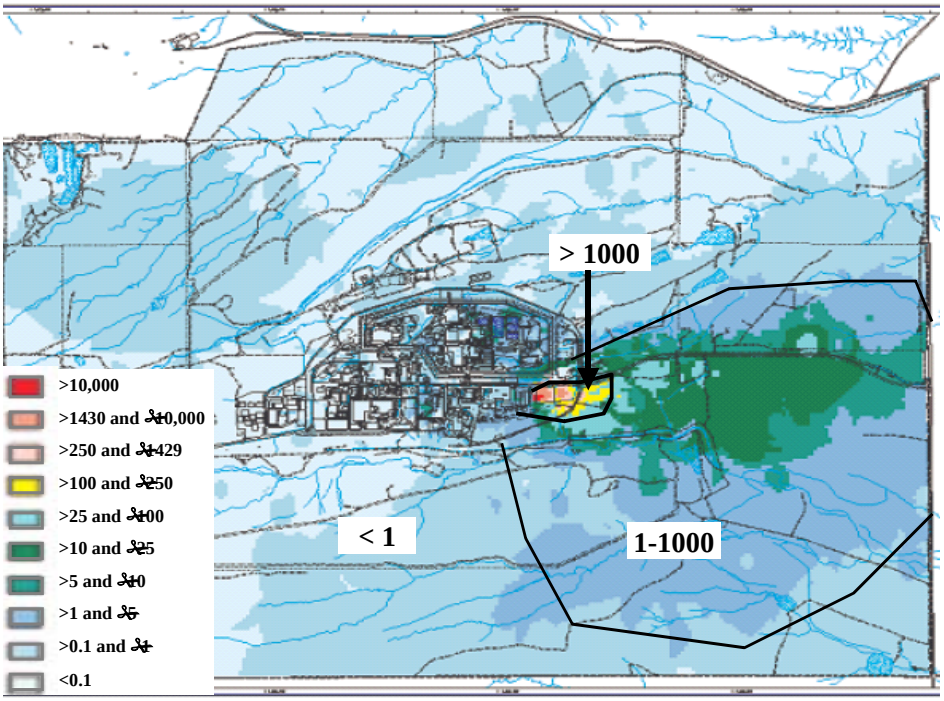

Figure 1. Surface contamination pattern caused by atmospheric deposition as influenced by regional wind patterns.

Obviously, a high sampling density (and a large budget) is required to achieve delineation at the fine scale depicted in Figure 1. A fine scale may not always be needed to effectively manage a site. Target populations can be defined using the project decision framework to determine the scale required for delineation. By way of illustration, a hypothetical scenario depicted in Figure 1 might require delineation of just three populations to support decisions about contaminated soil removal to support land reuse: natural background (up to 1, for which no action is required), between 1 and 1000 (for which landfill disposal is the likely remedial option) and greater than 1000 (destructive treatment is required). Efficient characterization is possible only if the decision framework is understood *before* the sampling and analysis plan is designed: a one-size-fits-all sampling plan will not work.

"Sampling uncertainty" occurs because environmental matrices are heterogeneous in both physical composition and in pollutant distribution. The term embraces a number of factors that introduce variability into analytical results. Analytical data can be misleading when sampling variables are not controlled. Decision errors occur when accurate analytical results generated from tiny samples are assumed by data users to represent the concentrations of much larger volumes of matrix, but that extrapolation is invalid because confounding variables have not been acknowledged or controlled. Figure 2 illustrates how unjustified extrapolation of analytical results to larger volumes of matrix can produce inaccurate CSMs that lead to faulty decisions. The CSM portrayed by the black outline predicts the extent of contaminated surficial soils requiring removal based on data collected using a traditional Remedial Investigation (RI) approach of statistical

sampling with fixed laboratory analysis. Before cleanup could be implemented, the team became concerned about excessive uncertainty in the bounded areas. Taking data uncertainty into account, the volume of soil needing removal and disposal (at $300 per cubic yard) could range as low as 3,000 or as high as 46,000 cu. yd. Confident remedial planning based on the RI data was impossible, but newer technologies were available to provide high density, real-time data that could manage the decision uncertainty. The team decided to implement an adaptive sampling and analysis program that was integrated in real-time with soil removal activities. By the end of the cleanup, the actual (very high confidence) CSM for surficial soil contamination was demonstrated to be the shaded areas. The total volume removed (both surficial and deeper layers) was 45,000 cu. yd. Post-cleanup sampling confirmed that on-site cleanup goals were attained. Pre-disposal testing of waste soil confirmed the "dirty" status of removed soil. Under a Triad approach, $200,000 was spent to re-characterize the site to manage both decision uncertainties. If the CSM predicted by traditional sampling and analysis had been followed, over $1.5 million would have been wasted just to needlessly remove and dispose of clean soil. Since post-remediation sampling would have discovered that 8,000 cu. yd. of "dirty" soil were missed, one more repeat cycle of characterization and removal would have been required (assuming an accurate CSM was achieved the second time). By breaking the characterize poorly—remediate poorly—recharacterize cycle, a $200,000 investment yielded an estimated savings of $10 million in cost-avoidance (DOE, 2001).

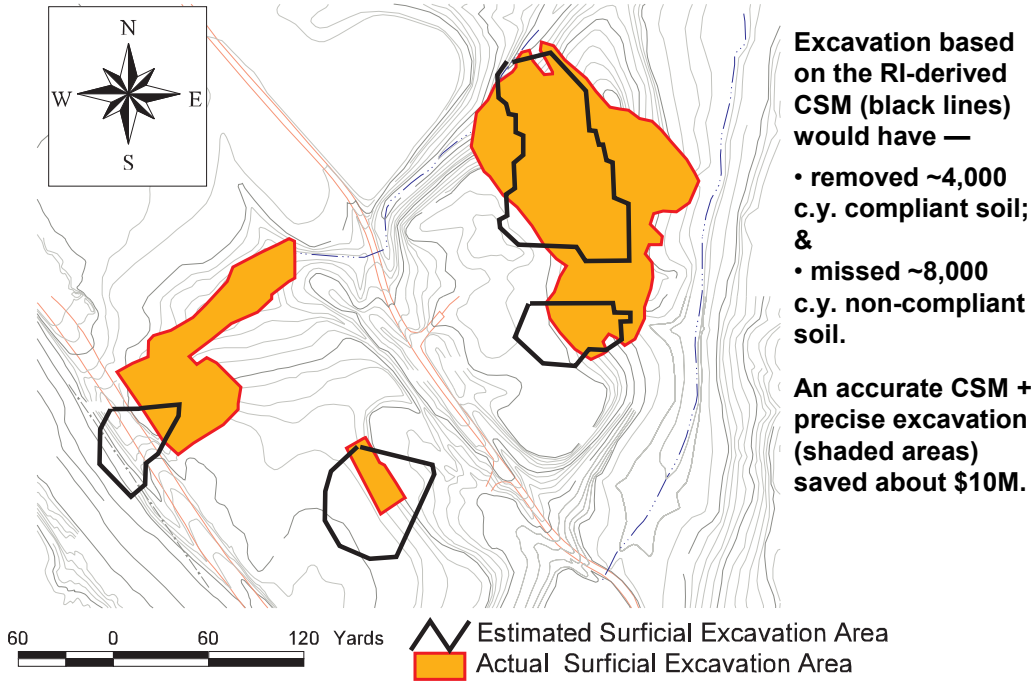

Figure adapted from Argonne, 2002

Figure 2. An inaccurate CSM can lead to costly decision errors.

Studies with modern tools show that heterogeneity impacts groundwater sampling as well. There is now ample evidence that vertical stratification of common pollutants occurs in many lithological settings. The concentration of contaminants can change drastically over short depth intervals. For example, chlorinated volatile organic compounds' (VOCs) concentrations were observed to change 2,500 µg/L over a vertical distance of 3.4 feet in one well and from 7,300 to 17,500 µg/L over a vertical distance of 5 feet in another well (Vroblesky and Peters, 2000).

When well screens span different populations, purging and sampling the well can cause uncontrolled mixing between distinct populations, creating intermediate data results that produce erroneous CSMs. This is illustrated by Figure 3, which shows the results of a U.S. Geological Survey (USGS) study comparing sampling techniques for wells with long screens (Huffman, 2002). Chlorinated VOCs were analyzed by the same analytical method on water samples collected in two different ways: traditional low-flow purging with a submersible pump (left-hand panel) versus passive diffusion bag samplers (PDBs, right-hand panel). PDBs consist of a semi-permeable polyethylene "baggie" filled with distilled water that is lowered into a groundwater well. The PDB remains undisturbed in the well for two to three weeks, which allows certain contaminants to pass through the bag into the distilled water. After equilibration, the sampler is removed from the well and emptied into traditional vials for submittal to analysis. Figure 3 compares the two different sampling techniques for the same well field for trichloroethane (TCA) results. It is clearly evident that vertical stratification exists in wells 6-S-21 and MW-7. In well 6-S-21, mixing at the population boundary by the traditional sampling technique created an intermediate result. The PDBs preserved information about distinct contaminant populations, producing a different, yet more accurate CSM to guide decisions about contaminant extent and remediation.

TCA results from purged/mixed well water sample

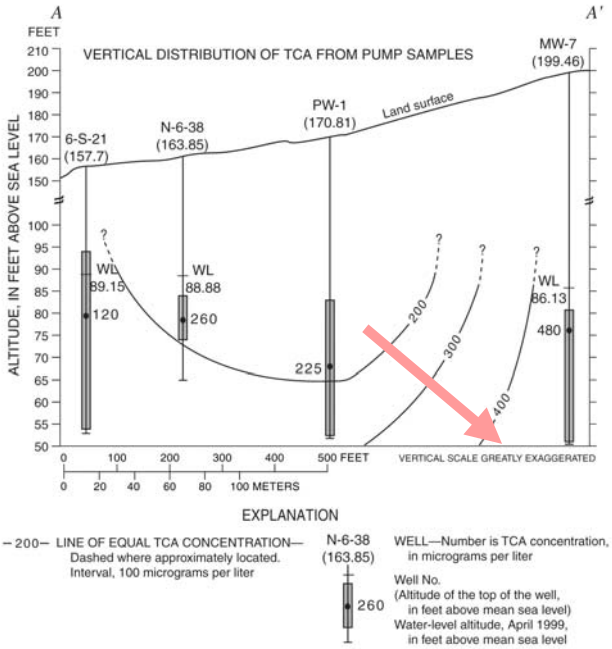

Figure 6. Vertical distribution of TCA concentrations in ground-water samples collected with the diffusion samplers and submersible pump.

TCA results from depth-discrete well water sample

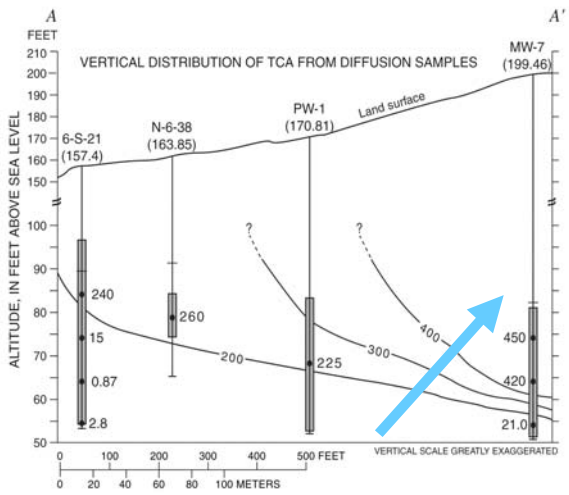

Figure 6.—*Continued.*

Figure adapted from Huffman, 2002.

Figure 3. Sampling the same well field in different ways produces different CSMs.

The Challenge of Data Representativeness

Generating "representative" data is not a simple matter when heterogeneous environmental matrices are involved. Figure 4 introduces the range of variables that have been found to impact the ability of data to provide reliable information for decision-making purposes. Variables that contribute to the data uncertainty can be coarsely grouped into three categories. The length of this paper limits discussion to only one variable, but a very important one regularly neglected by the environmental community. Yet each variable forms a link in the data quality chain and each link must be intact if data are to be representative of the intended decision. The first step for ensuring representative data is to understand exactly how the data will be used in the decision-making process. The intended decision will define what population should be targeted by data collection and analysis. Sampling and analytical procedures must be tailored to the target population to avoid a common cause of data uncertainty — uncontrolled mingling of different populations. Since contaminated sites typically encompass two or more contaminant populations, no facet of data collection and analysis can be left to chance. Each variable must be selected to maintain the chain of "data representativeness." Breaking that chain can produce data that misleads decision-makers into erroneous conclusions and actions.

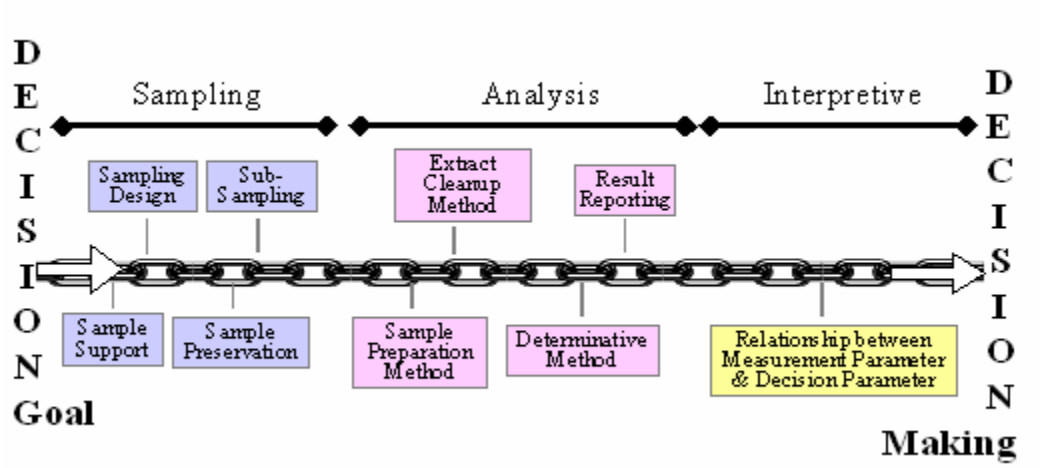

Figure 4. Variables that contribute to data representativeness.

Sample Support: A Critical Variable for Representative Data

The term "sample support" is unfamiliar to the environmental field, yet the term was introduced to the cleanup community in several EPA documents in the early 1990s. The term even appeared in a widely circulated U.S. EPA Superfund guidance (EPA, 1993, p. 41), but the concept never caught on. The term comes from statistics language to collectively describe the physical attributes of a specimen that helps determine what the analytical result will be. These attributes apply both to samples taken from the parent matrix in the field and to subsamples taken from jars in a laboratory. For environmental samples, they commonly include 1) the mass/volume of the sample or subsample, 2) the spatial orientation/dimensions of the sample collection device which helps determine the spatial dimensions of the sample (for example, visualize a long thin corer versus a flat-bottomed scoop and 3) particle size. Differences in sample support can cause analytical results to be different, independent of any variability in the analytical method itself. The reason is that these attributes help define different contaminant populations. Sample support is listed in Figure 4 as the first variable in the second-generation data quality because it is a critical variable that must be controlled in order to target the correct contaminant population for sampling and analysis.

In the groundwater sampling example discussed above, the difference between purged sampling and diffusion bag samples is their different sample supports in relation to the vertical stratification of adjacent populations. Inadvertently mixing two different populations through careless sample supports (when only one population is expected) creates misleading data. On the other hand, differing sample supports can produce non-comparable data sets, even if the samples are analyzed side-by-side by the exact same analytical method.

A number of newer analytical devices often used in situ, such as x-ray fluorescence (XRF), direct-push (DP) deployed laser-induced fluorescence (LIF) or DP-deployed membrane-interface probe (MIP) with specific detectors, have very small sample

supports. Figure 5 illustrates trichloroethene (TCE) data generated by a MIP equipped with an electron capture detector (ECD) useful for chlorinated organics. Small sample supports can locate spatially discrete contaminant sources and migration conduits often missed by conventional monitoring wells. Monitoring wells have traditionally been placed "blind." Without a tool like the direct push MIP that develops the CSM (by detecting distinctly different populations) before well placement, data results and interpretation are highly uncertain. A well placed in the location represented in Figure 5 could be screened in any one of many possible configurations of depth and screen length, as illustrated by wells A, B and C. The TCE concentration expected from well configuration A could be very different from data produced by other configurations placed in the same bore hole. These different analyte concentrations are not the product of analytical uncertainty, but of sampling uncertainty. Data can be misleading if the sample support variable is not controlled.

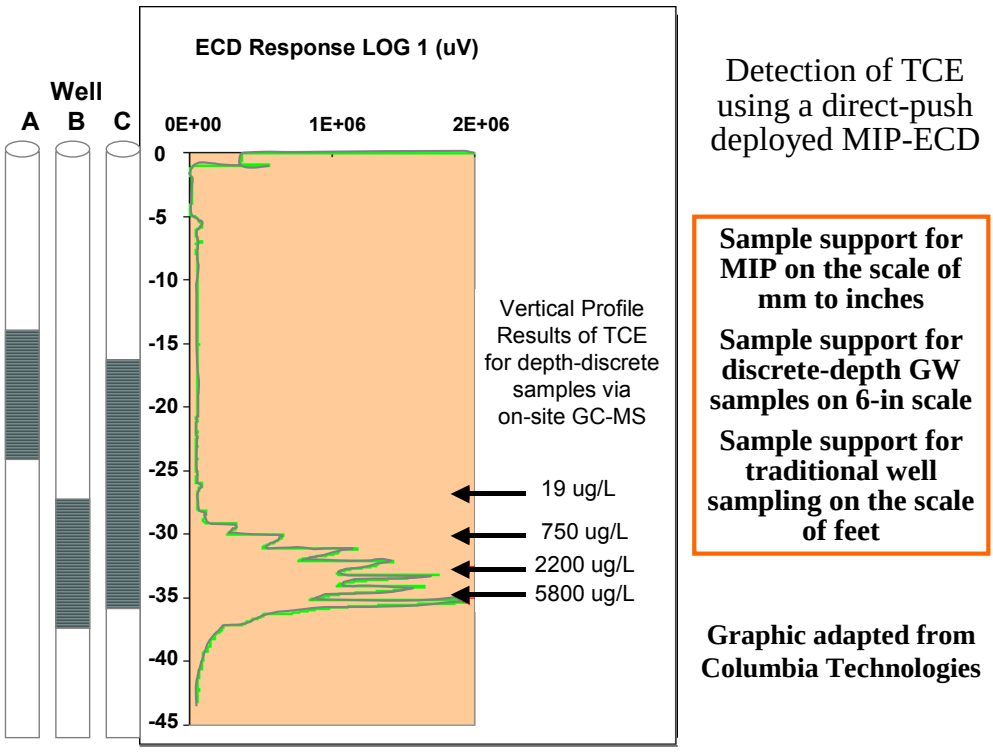

Figure 5. Different Sample Support Changes Analytical Results for GW.

Particle size is another aspect of sample support that must be controlled when micro-scale heterogeneity is present (i.e., different populations are present in the same specimen). Table 1 summarizes a study that examined the relationship between the size of native soil particles and lead concentration at a firing range site (ITRC, 2003). The smaller the particle size, the higher the lead concentration. The bulk average concentration is about half the concentration of the smallest particles. Whether the bulk average is the correct sample support depends on the decision. Suppose the decision is to assess exposure risk from dust blowing off-site into local homes, sticking to children's

fingers, which go into their mouths—the smallest particle size is representative of this exposure decision. Using the bulk average value as a default could underestimate true exposures by a factor of two.

Table 1. Lead Concentration as a Function of Particle Size (after ITRC, 2003).

Soil Grain Size (Standard Sieve Mesh Size)	**Soil Fraction-ization (%)**	**Pb Conc. in fraction by AA (mg/kg)**	**Lead Distributio n**
Greater than 3/8" (0.375")	18.85	10	0.20
Between 3/8 and 4-mesh"	4.53	50	0.24
Between 4- and 10-mesh	3.65	108	0.43
Between 10- and 50-mesh	11.25	165	2.00
Between 50- and 200-mesh	27.80	836	25.06
Less than 200-mesh	33.92	1,970	72.07
Totals	100%	927 (wt-averaged bulk)	100%

Particle size also impacts laboratory subsampling procedures. What particle sizes are preferentially captured by subsampling? A spoon-shaped scoop will retain a different mix of particle sizes than a narrow, flat spatula. Has the laboratory been advised what particle size they should target to maintain data representativeness for the specific decision(s) intended by the data users or project manager?

The phenomenon of highly concentrated particles encountered in Table 1 helps explain why smaller sample and **subsample volumes** produce more highly variable analytical results. A study in 1978 by the Department of Energy demonstrated this with soil from an area contaminated with americium-241 (^{241}Am, a radionuclide). A large volume of soil was sampled and containerized. It was carefully homogenized by drying, ball-milling and sieving through a 10-mesh screen. Twenty subsamples each of various masses were taken and analyzed separately. The results are summarized in Table 2. Obviously, the larger the subsample, the less variable the results and the much more reliably any single subsample result estimated the true mean (1.92 ppm) for the original sample. A decision error could occur if a data user got the result of 8 ppm from a 1-gram subsample and then assumed that the result represented the true concentration for the entire jar of sample (an error of about 400%). The error would be further compounded if that 8 ppm result was extrapolated to represent the concentration of ^{241}Am for a large portion of the site. Even with homogenization (which is never perfect), the smaller the subsample, the less likely that its result represents the average concentration for the original jar of soil. This is a problem for analytical chemistry — as instrumentation becomes more and more sophisticated, the mass of sample used by the laboratory to actually generate the analytical result is trending lower and lower. One gram is a standard sample size for soil digested for metals' analysis. Results are viewed as "gold-plated" simply because of the accuracy of the determinative method (refer to Figure 4).

But that is simply the last link in a chain of events made of weak links that are largely uncontrolled by standard practices for project planning and laboratory analysis.

Table 2. Subsampling Variability (adapted from Doctor and Gilbert, 1978)

Subsample Volume (g)	Range of Results for 20 Individual Subsamples (ppm)
1	1.01 to 8.00
10	1.36 to 3.43
50	1.55 to 2.46
100	1.70 to 2.30

References

Doctor, P. G. and R. O. Gilbert. 1978. "Two Studies in Variability for Soil Concentrations: With Aliquot Size and with Distance." in "Selected Environmental Plutonium Research Reports of the Nevada Applied Ecology Group" (NAEG), Las Vegas, NV. pp. 405-423 and 439-442.

Huffman, R.L. 2002. Comparison of Passive Diffusion Bag Samplers and Submersible Pump Sampling Methods for Monitoring Volatile Organic Compounds in Ground Water at Area 6, Naval Air Station Whidbey Island, Washington. U.S. Geological Survey Water-Resources Investigations Report 02-4203. Available on-line at http://water.usgs.gov/pubs/wri/wri024203/.

Interstate Technology and Regulatory Counsel (ITRC). 2003. Characterization and Remediation of Soils at Closed Small Arms Firing Ranges. Available: http://www.itrcweb.org/SMART-1.pdf.

U.S. Department of Energy (DOE). 2001. Innovative Technology Summary Report: Adaptive Sampling and Analysis Programs (ASAPs). DOE/EM-0592. August. Available: http://cluin.org/download/char/ASAPs_ITSR_DOE-EM-0592.pdf.

U.S. Environmental Protection Agency (EPA). 1993. Data Quality Objectives Process for Superfund: Interim Final Guidance. EPA540-R-93-071. Sept.

Vroblesky, D. A. and Peters, B. C. 2000. Diffusion sampler testing at Naval Air Station North Island, San Diego County, California, November 1999 to January 2000: U.S. Geological Survey Water-Resources Investigations Report 00-4812.

COLLABORATIVE SAMPLING DESIGN FOR ESTIMATING AND TESTING MEANS

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Abstract

This paper presents an innovative environmental sampling design called Collaborative Sampling (CS) that can be more cost-effective than simple random sampling for estimating or testing hypotheses about the mean of a target population. The CS design uses two measurement methods: a field-based, relatively-inexpensive measurement method and an off-site laboratory-based more expensive method. The idea behind CS is to obtain a better estimate of the mean with less cost by using a relatively small number of expensive laboratory measurements with a larger number of the less expensive field-based measurements. The CS design for estimating and testing means complements the U.S. EPA Triad approach, which uses a combination of many field-based and fewer lab-based measurements to increase confidence that correct decisions about contaminant presence, location, fate, exposure and risk reduction are made. The CS design for estimating and testing means has been added to the suite of designs in the Visual Sample Plan (VSP) software, which can be downloaded free at http://dqo.pnl.gov/vsp. This paper discusses the CS methodology, assumptions and implementation in VSP.

Introduction

The importance of selecting a sampling design for obtaining sufficiently representative environmental data for estimating parameters or making decisions cannot be disputed. The application, benefits and limitations of several basic and innovative sampling designs are discussed in EPA (2002). The Collaborative Sampling (CS) design, although not discussed in EPA (2002), can be more cost effective in some situations than simple random sampling for estimating the mean and testing hypotheses about the mean. We note that discussions of the CS design for estimating means (as in Section 2.0 below) can be found in Gilbert (1987) and Cochran (1977) under the title of "Double Sampling."

The CS design uses two measurement methods: the standard analysis (sometimes called the "lab-based" method or the "expensive" method) and a less expensive and possibly less accurate measurement method (sometimes called the "field-based" method or the "less expensive" method). The idea behind CS is to replace the need for obtaining so many expensive measurements with collecting a larger number of the less expensive measurements. The less expensive method is used at *n'* locations and the expensive method is used at a randomly selected *n* of those *n'* locations, where *n'* is typically much larger than *n*.

The CS design has recently been added to the Visual Sample Plan (VSP) software tool (*beta* version 2.5) for three sampling objectives: estimate a mean, compute a confidence limit on the mean or test whether the mean exceeds an upper threshold value. VSP is a map-based, user-friendly visual tool that helps the user determine the number and location of samples needed to ensure sufficiently confident decisions. VSP also conducts statistical data analyses for some design modules.

The CS design for estimating and testing means complements the U.S. EPA Triad approach (ITRC 2003, EPA 2004), which uses a combination of many field-based and fewer lab-based measurements to increase confidence that correct decisions about contaminant presence, location, fate, exposure and risk reduction are made. The Triad approach focuses on developing an accurate conceptual site model (CSM) of heterogeneous environmental situations through the use of a high density of field-based, relatively inexpensive measurements, but with confirmation of the conclusions (derived from the full data set) or of individual results using lab-based measurements. The field-based measurement methods used in the application of the Triad method may be suitable for use in the CS design for estimating and testing of means at the site.

Estimating the Mean

Suppose the sampling objective is to estimate the mean of a contaminant in surface soil over a defined geographical region. One design that might be considered is simple random sampling (or perhaps systematic grid sampling) to select sampling locations and then use the standard ("expensive") laboratory analysis method on the collected samples. Should the CS design be used instead? As discussed in Gilbert (1987, Chapter 9) and Cochran (1977, Chapter 12, Section 12.6) the following conditions must hold for CS to be more cost-effective for estimating the mean than using the entire measurement budget to obtain expensive measurements on samples collected using a simple random sampling design.

- There is an underlying linear relationship between the two types of measurements, *i.e*., the regression of the expensive measurements (plotted on the Y axis) and the inexpensive measurements (plotted on the X axis).
- there is a sufficiently high correlation, ρ, between the two types of measurements made at the same locations.
- The ratio $R = C_{ex} / C_{inex}$ is sufficiently large, where C_{ex} is the cost of a single expensive measurement and C_{inex} is the cost of a single inexpensive measurement.

An additional assumption is that the magnitude of the scatter (variance) of expensive measurements about the linear regression line is constant for all values of the inexpensive measurements along the line.

When the objective is to estimate the mean, CS will be more cost efficient than simple random sampling if the following inequality holds (Gilbert 1987, Equation 9.5):

$$\rho^2 > \frac{4R}{(1+R)^2} \tag{1}$$

In practice, the true value of ρ will be uncertain and should be estimated using a "pilot" study in which the proposed inexpensive and expensive measurement methods are used in realistic field and laboratory conditions for, say 20 or more locations. Also, these pilot study data should be plotted in a regression scatter plot to assess the linearity and constant variance assumptions.

If CS is cost-effective and the constant variance assumption is fulfilled, then equations in Gilbert (1987, page 109) can be used to compute the number of samples, *n'* and *n*, needed. Gilbert provides equations for two cases:

- Minimize the variance of the estimated mean for a given fixed measurement budget
- Minimize the total measurement cost subject to the constraint that the variance of the estimated mean is no greater than the variance of the mean that would be obtained based on *n* expensive measurements obtained using a simple random sample design.

After the measurements have been obtained, the VSP user can enter them into VSP. Then VSP will estimate the mean for the target population by computing $\bar{x}_{cs}$ (cs stands for collaborative sampling) using Equation 9.1 in Gilbert (1987, p. 107), *i.e.*, by computing

$$\bar{x}_{cs} = \bar{x}_{Ex} + b\left(\bar{x}_{n'} - \bar{x}_{Inex}\right) \tag{2}$$

where $\bar{x}_{n'}$ is the mean of the *n'* inexpensive measurements and $\bar{x}_{Ex}$ and $\bar{x}_{Inex}$ are the means of the *n* expensive and *n* inexpensive measurements, respectively, obtained for *n* field locations (recall that the *n* locations are a subset of the *n'* locations) and b is the slope of the estimated regression line of expensive on inexpensive measurements.

VSP also computes the standard error (standard deviation of $\bar{x}_{cs}$) using Equation 9.2 in Gilbert (1987, p. 107), *i.e.*, using

$$SE = \sqrt{s^2\left(\bar{x}_{cs}\right)} = \sqrt{s^2_{Ex.Inex}\left[\frac{1}{n} + \frac{\left(\bar{x}_{n'} - \bar{x}_{Inex}\right)^2}{(n-1)s^2_{Inex}}\right] + \frac{s^2_{Ex} - s^2_{Ex/Inex}}{n'}} \quad (3)$$

where $s^2_{Ex.Inex}$ is the estimated residual variance about the estimated linear regression line (assumed constant along the line) and s^2_{Ex} and s^2_{Inex} are the estimated variances of the *n* expensive and *n* inexpensive measurements, respectively.

The above methodology (testing for cost efficiency, computing *n'* and *n*, and computing $\bar{x}_{cs}$ and SE) can be easily accomplished using the VSP software code. After booting VSP, simply click on **Sampling Goals > Estimate the Mean > Data Not Required to be Normally Distributed > Collaborative Sampling > Simple Random Sampling** or **Systematic Grid Sampling** to access the dialog box for inputting the required Data Quality Objectives (DQOs).

Confidence Limits on the Mean

Suppose the sampling objective is to estimate the mean and also compute a one-sided upper or lower confidence limit or a two-sided confidence interval on the mean. A method for computing the required *n'* and *n* samples for this sampling objective has been incorporated into VSP. The VSP user gains access to this method by clicking **Sampling Goals > Construct Confidence Interval on the Mean > Can Assume Data will be Normally Distributed > Collaborative Sampling > Simple Random Sampling** or **Systematic Grid Sampling**.

This CS module is similar to the CS VSP module discussed in Section 2.0 above. First, the VSP user inputs the following DQOs into the VSP dialog box:

- the desired width of the confidence interval
- the desired confidence level in percent
- an estimate of the total standard deviation among expensive measurements, $\sigma_{total,ex}$
- the correlation between the inexpensive and expensive measurements, ρ
- the measurement costs C_{ex} and C_{inex}.

Then VSP determines if CS is cost-effective using ρ and $R = C_{ex} / C_{inex}$ in Equation 1.0 above.

If CS is cost-effective, then VSP computes *n'* and *n* such that the total measurement cost, C, is minimized subject to the constraint that the width of the confidence interval (CI) will be no greater than a CI width that would be obtained using n_v samples obtained using simple random sampling and measured using only the expensive measurement method. This value of n_v is computed using an iterative procedure (Gilbert 1987, page 30). Then *n'* and *n* are computed using n_v and Equations 9.8, 9.9 and 9.10 in Gilbert (1987, page 109).

After the *n'* and *n* measurements have been obtained, the VSP user can enter them into VSP. Then VSP computes:

- the mean ($\bar{x}_{cs}$) and the SE using Equations (2) and (3) above
- the confidence interval on the mean assuming the data are normally distributed or that *n'* and *n* are large enough such that the estimated mean is normally distributed
- the estimated correlation coefficient, $\hat{\rho}$, between the two types of measurements
- the estimated standard deviation of the expensive measurements.

The confidence intervals (CIs) on the mean are computed as follows:

Lower one-sided CI: $$\bar{x}_{cs} - Z_{1-\alpha} s(\bar{x}_{cs}) \quad (4)$$

Upper one-sided CI: $$\bar{x}_{cs} + Z_{1-\alpha} s(\bar{x}_{cs}) \quad (5)$$

Two-sided CI: $$\bar{x}_{cs} \pm Z_{1-\alpha/2} s(\bar{x}_{cs}) \quad (6)$$

where

$Z_{1-\alpha}$ = $(1-\alpha)^{th}$ percentile of the standard normal distribution and

$Z_{1-\alpha/2}$ = $(1-\alpha/2)^{th}$ percentile of the standard normal distribution.

The correlation and standard deviation are computed to allow the VSP user to see if they differ substantially from the value of those parameters that were entered into the VSP DQO dialog box to obtain *n'* and *n*. If there are differences, the new values from the data can be entered into VSP to obtain revised values of *n'* and *n*. VSP also produces a regression plot of the inexpensive and expensive measurements so the user can graphically evaluate the linear regression and constant residual variance assumptions. In addition, VSP provides a warning that the computed confidence interval may be too short if *n'* and *n* are very small.

If CS is not cost-effective, then VSP uses simple random sampling rather than CS. VSP computes the required number of samples, *n* (for which only lab-based measurements will be obtained) using the iterative procedure in Gilbert (1987, page 30). Once the *n* expensive measurements are entered into VSP, then VSP computes the confidence interval (CI) assuming the data are normally distributed, *i.e.*, by using the t distribution with *n*-1 degrees of freedom, as follows:

Lower one-sided CI: $$\bar{x} - t_{1-\alpha,n-1} s(\bar{x}) \quad (7)$$

Upper one-sided CI: $$\bar{x} + t_{1-\alpha,n-1} s(\bar{x}) \quad (8)$$

Two-sided CI: $$\bar{x} \pm t_{1-\alpha/2,n-1} s(\bar{x}) \quad (9)$$

where

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{10}$$

$$s(\bar{x}) = \sqrt{\frac{1}{n(n-1)}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2} \tag{11}$$

$t_{1-\alpha,n-1}$ = (1-α)th percentile of the t distribution with *n*-1 degrees of freedom and

$t_{1-\alpha/2,n-1}$ = (1-α/2)th percentile of the t distribution with *n*-1 degrees of freedom.

Test if the Mean Exceeds a Fixed Threshold Value

Suppose the sampling objective is to estimate the mean and conduct a one-sample test of the null hypothesis that the mean exceeds a fixed threshold value. The methodology for computing *n'* and *n* needed for the test has recently been incorporated into VSP. The VSP user can access the dialog box for this methodology by clicking **Sampling Goals > Compare Average to Fixed Threshold > Can Assume Data will be Normally Distributed > Collaborative Sampling > Simple Random Sampling** or **Systematic Grid Sampling.**

First, the VSP user inputs the following DQOs into the VSP dialog box:

- the null hypothesis of interest, either
  - H_o: true mean ≥ threshold value or
  - H_o: true mean ≤ threshold value
- the tolerable probability that the test will falsely reject the null hypothesis, α
- the tolerable probability that the test will falsely accept the null hypothesis, β
- the width of the gray region in the Decision Performance Goal Diagram, Δ
- an estimate of the total standard deviation among expensive measurements, $\sigma_{total,ex}$
- the correlation between inexpensive and expensive measurements, ρ
- the measurement costs C_{ex} and C_{inex}

Then VSP uses Equation (1) above to determine if CS is cost-effective relative to simple random sampling for estimating the mean.

If CS is cost effective, then VSP computes *n'* and *n* using the following equations, which were derived by the authors using the method of proof in Appendix A of EPA (2000b):

$$n' = \left[\frac{\left(z_{1-\alpha} + z_{1-\beta}\right)^2 \sigma^2_{total,ex}}{\Delta^2} + \frac{1}{2}z^2_{1-\alpha}\right]\rho\left(\sqrt{R\left(1-\rho^2\right)} + \rho\right) \tag{12}$$

$$n = \left[\frac{\left(z_{1-\alpha} + z_{1-\beta}\right)^2 \sigma^2_{total,ex}}{\Delta^2} + \frac{1}{2} z^2_{1-\alpha} \right] \left[1 - \rho^2 + \rho \sqrt{\frac{\left(1-\rho^2\right)}{R}} \right] \quad (13)$$

Then the *n'* inexpensive and *n* expensive measurements are obtained and entered into VSP so that VSP can compute:

- the estimated mean, $\bar{x}_{cs}$, and SE using Equations (2) and (3) above,
- the estimated correlation coefficient between the two types of measurements,
- the estimated standard deviation of the expensive measurement and
- a Z test of the selected null hypothesis, H_o.

If the VSP user selected H_o: true mean $\geq$ threshold value, then the Z test is conducted by computing

$$Z = \frac{\bar{x}_{cs} - ThresholdValue}{s_{\bar{x}_{cs}}} \quad (14)$$

H_o is rejected if $Z \leq -z_{1-\alpha}$, where $z_{1-\alpha}$ is the (1-α)th percentile of the standard normal distribution.

If the VSP user selected H_o: true mean $\leq$ threshold value, then the Z test is conducted by computing Z using Equation (14) and H_o is rejected if $Z \geq z_{1-\alpha}$.

VSP also constructs a regression plot of the data so the VSP user can see if the linear relationship and constant residual variance assumptions are valid. VSP also warns the user that the test result may not be reliable if both *n'* and *n* are small. Furthermore, VSP automatically reduces the value of ρ entered in the dialog box by 0.10 units (say from 0.80 specified in the dialog box down to 0.70) and re-computes *n'* and *n*. This permits the VSP user to see how *n'* and *n* change if the original value of ρ was too large by 0.10.

Finally, VSP conducts a sensitivity analysis to determine how the magnitudes of *n'* and *n* are affected by changing the DQO input parameters. This analysis is included in the automatically-generated VSP design report, which can be inserted in a Quality Assurance Project Plan or other project documents and publications.

If CS is not cost-effective, then VSP does not use the CS design, but instead computes the number of expensive measurements, *n*, needed to test the selected null hypothesis. The value of *n* is computed using the following equation (from Appendix A of EPA 2000b):

$$n = \frac{\left(Z_{1-\alpha} + Z_{1-\beta}\right)^2 \sigma^2_{total,ex}}{\Delta^2} + \frac{1}{2} Z^2_{1-\alpha} \qquad (15)$$

The *n* locations are determined using simple random sampling. After the *n* expensive lab-based measurements are obtained, VSP computes the mean and its standard deviation using Equations (10) and (11) above. Then VSP performs the test of the selected null hypothesis using Equation (14) except that $\bar{x}_{cs}$ is replaced by $\bar{x}$ and $s_{\bar{x}_{cs}}$ is replaced by $s_{\bar{x}}$.

An example of the use of VSP when CS is cost effective is shown in Figure 1, which shows the VSP dialog box and DQO inputs, the resulting number of samples (*n'* and *n*) computed by VSP, and the location of samples on the map of the site.

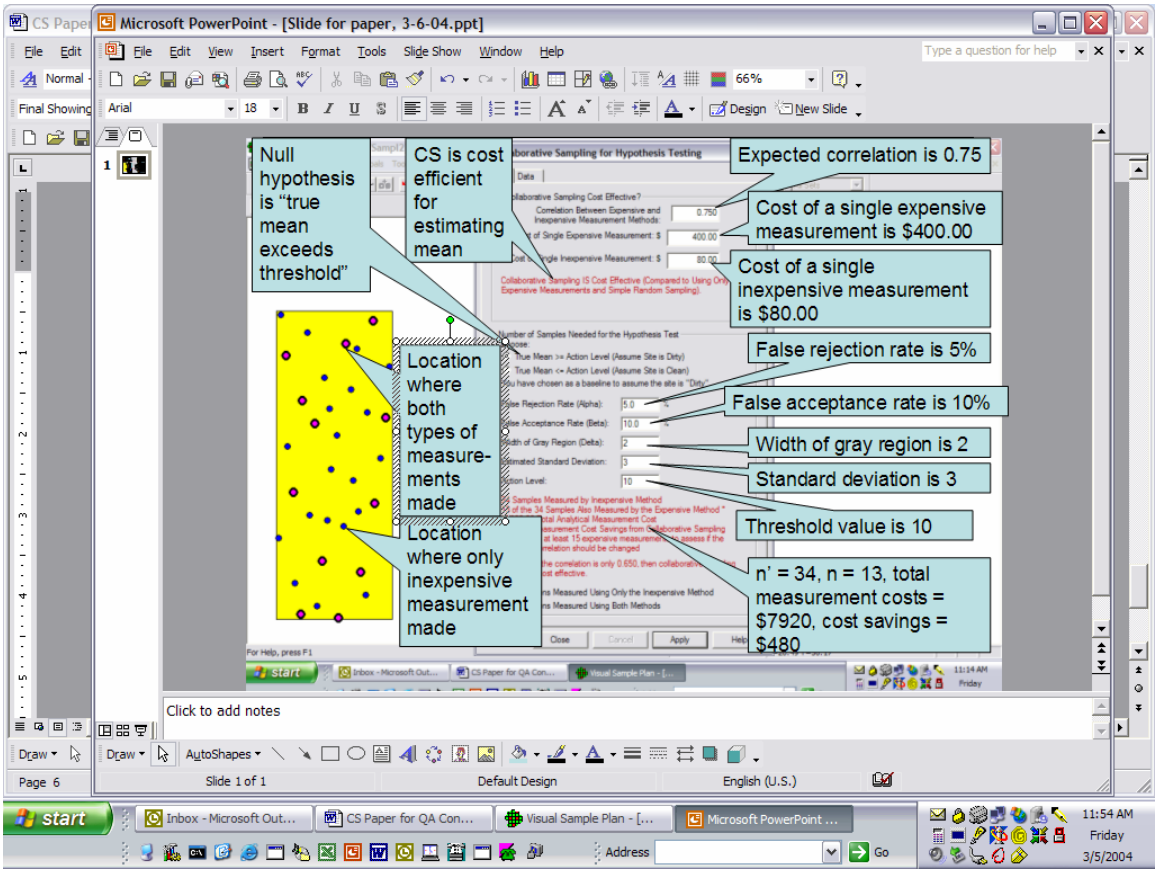

Figure 1. Example VSP Dialog Box and Map for Hypothesis Testing

References

Cochran, W.G. 1977. *Sampling Technique,* 3rd edition, Wiley & Sons, New York.

EPA 2000a. *Guidance for Data Quality Assessment, Practical Methods for Data Analysis, EPA QA/G-9*, EPA/600/R-96/084, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC. Available for download from http://www.epa.gov/quality/qa_docs.html.

EPA 2000b. *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, EPA/600/R-96/055, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, D.C. Available for download from http://www.epa.gov/quality/qa_docs.html.

EPA 2002. *Guidance on Choosing a Sampling Design for Environmental Data Collection , EPA QA/G-5S,* EPA/240/R-02/005, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, D.C. Available for download from http://www.epa.gov/quality/qa_docs.html.

EPA 2004. *Improving Sampling, Analysis, and Data Management for Site Investigation and Cleanup*, EPA-542-F-04-001a. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C. Available for download from http://cluin.org/char1_edu.cfm.

Gilbert, R.O. 1987. *Statistical Methods for Environmental Pollution Monitoring*, Wiley & Sons, New York.

ITRC 2003. *Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management*, Interstate Technology & Regulatory Council, December 2003. Available for download from http://www.itrcweb.org/SCM-1.pdf.

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MEASUREMENT UNCERTAINTY AND LEGAL DEFENSIBILITY

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The estimation of measurement uncertainty is defined in the ISO requirements and was adopted by NELAC in 2002. This term is defined by the international community to allow representation of all the factors that contribute to the variability of the measurement including sampling, the sample and the test method. The measurement uncertainty is expressed in terms of an interval about the result reported (*e.g.*, a plus/minus value). The mathematical model for representing this is defined in international documents, but is not widely accepted within the environmental community. The calibration community, industrial community and others such as food are adopting and implementing this international definition.

The estimation of uncertainty when applied to environmental measurement (*e.g.*, Visual Sample Plan (VSP)) provides the decision maker with the necessary information relative to range of values where the estimated true value lies. The estimation of uncertainty in the laboratory can only be related to the contributors from the laboratory method such as the bias, precision and other factors that determine the correctness and reliability of the method as performed by the laboratory on the specific sample container received. The measurement uncertainty to represent the estimate for the site or project can only be developed when the client, sampling organization and laboratory work together to optimize sampling and test method performance for the specific project or sample matrix being tested.

The measurement uncertainty of the reported value is possible when a series of samples is measured and the average result is calculated along the expanded uncertainty. The reporting of the range of values provides for legal defensibility of the data by demonstrating the confidence the decision maker has in how close the value lies to the action limit.

APPLICATION OF METHOD 4025 TO BRING DIOXIN SITES INTO EPA'S TRIAD APPROACH TO SITE ASSESSMENT AND REMEDIATION

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The three components of EPA's Triad approach to site assessment and remediation are systematic planning, dynamic work strategies and real-time measurement technologies (which include analytical methods). EPA Method 8290 (dioxin/furan analysis by high resolution gas chromatography-high resolution mass spectrometry) is a crucial tool for dioxin measurement, but it is not capable of the turnaround time and sample throughput rates demanded by Triad.

Kit based analytical methods, such as embodied by the U.S. EPA's 4000 series of SW-846 methods, comprise an established technology area with demonstrated capability to supply the quantity of real-time data required for Triad implementation. With the addition in 2001 of Method 4025 (Dioxin Screening in Soil by Immunoassay) to the SW-846 Compendium of Solid Waste Methods, it is now possible to implement EPA's Triad for dioxin sites.

While on-site dioxin analysis (in a mobile lab) using Method 4025 provides the third leg of the Triad, it also carries with it a number of issues that must be addressed during

implementation. Some of these are familiar to 4000 series method users, including analyst training, quality assurance requirements, integration of screening methods into a project and education of consumers of field generated data. However, some issues are unique to kit-based dioxin analysis, including sample preparation and safety requirements, flexibility of cleanup protocols, effect of varying congener profiles on TEQ correlation and test calibration for quantitative results.

Selected customer examples will be used to illustrate the importance of these issues. Both successes and failures will be presented to demonstrate right and wrong approaches to implementation. Barriers to implementation will also be discussed, including education of regulators about the advantages and limitations of Method 4025, development of a trained analyst base and education of project managers about implementation issues.

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LABORATORY CERTIFICATION FOR FIELD ANALYTICAL METHODS AND TRIAD IN NEW JERSEY: PERFECT TOGETHER

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New Jersey has more than 10,000 contaminated sites, many of them brownsfields' areas where timely remediation is critical to commercial viability. The Triad approach promoted by the United States Environmental Protection Agency and the Interstate Technology Regulatory Council, has been adopted by the New Jersey Department of Environmental Protection (NJDEP) as a way to expedite the cleanup of such contaminated sites.

A key component to the implementation of Triad within the NJDEP is convincing its staff and management that reliance upon field analytical measurements to make site evaluations helps reduce decision uncertainty as well as saving time and money. The fallacy that data generated in permanently-sited laboratories using SW-846 methodology is definitive and leads to certain decisions, while data generated in the field is only of screening quality and therefore leads to uncertain decisions, is commonly

accepted in the NJDEP. This erroneous thinking must be corrected if the implementation of Triad is to succeed.

Two NJDEP units, one responsible for laboratory certification and the other for management of site cleanups, have collaborated to improve the confidence in and acceptability of field analytical data by management and staff within the NJDEP. The mechanism to achieve this objective is to extend laboratory certification to several categories of field analytical methods, requiring that any data for these categories be performed by a certified business entity. This paper will discuss the technical and institutional barriers to implementing this program and the results to date.

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TRIAD'S SYSTEMATIC PROJECT PLANNING INCLUDES LEGAL AND BUSINESS CONCERNS

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The primary purpose of the Triad approach is to achieve scientifically defensible, yet highly cost-effective, project decisions. But scientific and engineering activities supporting site cleanup are embedded within a complex infrastructure of regulatory and business concerns. As part of Triad's grounding in the management of decision uncertainty, Triad systematic planning also includes addressing the non-scientific aspects of project management that contribute to decision uncertainty.

For example, real-time decision-making utilizing field-generated data is a key mechanism used by Triad projects to increase decision confidence while decreasing project costs. The perception that these data are less legally-defensible than off-site laboratory analysis can be a significant obstacle to using these tools. In actuality, however, neither federal nor state rules of evidence distinguish between field-generated data and data generated by fixed laboratory methods. No matter how data are generated, courts need to be convinced that the methods followed are scientifically valid, the persons implementing them are competent and followed appropriate procedures and that documentation demonstrates the validity of the results and the conclusions drawn from those results. Triad projects are structured to provide that kind of assurance.

Environmental insurance and redevelopment economics are business-related issues that favorably interact with Triad projects. Insurance companies have a natural interest in the Triad approach because insurance premiums are designed and priced through a quantitative evaluation of uncertainty. The dollar value assigned to the benefits of uncertainty management by insurance products helps project planners quantify the benefits of investing in the Triad approach. As the emphasis in site cleanup increasingly shifts towards redevelopment, Triad can help answer questions of whether anything has been missed or if contamination is adequately characterized to support timely cleanup and redevelopment. Lenders, developers and community leaders want development projects to run smoothly and on schedule. They do not want to face unplanned delays to address unforeseen contamination issues that would slow a project down or significantly increase project budgets. The Triad approach has proven effective in minimizing the likelihood of such occurrence, thereby increasing the confidence of business decisions.

SAMPLING AND ANALYSIS FOR HOMELAND SECURITY II

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EPA'S RESPONSE PROTOCOL TOOLBOX

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Objective: To provide a framework for evaluating contamination threats to drinking water systems and responding appropriately to the threat. The intended outcome of the application of this tool is the reasonable investigation of water contamination threats without overreaction to threats that are not credible.

Users: Drinking water utilities, drinking water primacy agencies, technical assistance providers, laboratories, emergency responders, environmental response teams, public health agencies, law enforcement agencies and federal agencies such as EPA and CDC.

Application: To meet this overarching objective and the specific needs of the various users, the Response Protocol Toolbox (RPTB) was developed as six interrelated modules, each dealing with a specific aspect of the management of and response to contamination threats. Instructions on the use of the RPTB state that the material from the various modules should be applied to meet the needs and responsibilities of the particular user.

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NATIONAL SAMPLING AND FIELD TEST KIT FOR DRINKING WATER

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Module 3 of EPA's *Response Protocol Toolbox* provides guidance for responders in planning site characterization and sampling activities in response to drinking water contamination events. As part of its water security responsibilities, EPA plans to provide sample collection and field test kits to assist drinking water utilities and other members of the response community in preparing for and responding to water contamination threats and incidents. The sampling kits and field test kits should correlate with and complement the *Response Protocol Toolbox*. EPA has convened a Sampling/Test Kit Workgroup to carry out this effort. The Workgroup is responsible for:

- Identifying criteria for and composition of the sampling and field test kits and
- Determining appropriate placement and distribution of each type of kit.

EPA plans to fast track this effort to have the sampling and test kits assembled and available to responders during Fall 2004.

TWO NEW ANALYTICAL METHODS TOOLS FOR WATER PROTECTION

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The events of 9/11/2001 resulted in an evaluation of security risks in the many infrastructures that our nation's health and well-being depend upon, including public water supplies. Historical evidence suggests that the threat of intentional contamination is possible and probable. Since the first step in responding to such a terrorism event – real or potential – is to identify the contaminant, one of the new tools being developed is a database of methods to analyze for chemical, biological and radiological (CBR) agents that could pose a threat to our public water supplies. The World Health Organization advises that, although it is neither possible nor necessary to plan for an attack by all possible CBR agents, the targeting of preparations and training on a limited but well chosen group of them will provide the necessary capability to deal with a far wider range of possibilities. Knowledge of how to analyze for such a representative group will enable analytical protocols to be used, perhaps with modifications, against many other agents.

The success of the *National Environmental Methods Index* (*NEMI* - a freely accessible database searchable on the Internet at www.nemi.gov) in providing a useful framework for assessing analytical methods is being captured in a companion effort; the *NEMI – CBR* database. Mirrored on the former database, *NEMI-CBR* presents data on methods that may be applied to identifying chemical, biological and radiological contaminants emanating from a terrorist attack on water supplies. However, *NEMI-CBR* contains three additional fields of information that are important for anti-terrorism uses: (1) rapidity of analysis, (2) analyte/organism specificity and (3) class specificity. Typically methods that are useful for identifying groups of analytes or organisms have poor specificity for individual analytes and *visa versa*. A core expert group is providing guidance for the effort.

A variety of method types are included in the database. Confirmatory methods are those used for monitoring water for analytes and/or organisms of interest and typically have good performance characteristics (*e.g.*, high precision, low bias, good sensitivity and good analyte selectivity). Conversely, methods used to respond to an incident must be rapid and, if possible, used on-site in the field. Field analytical methods typically exhibit lower precision, higher bias, less sensitivity and less analyte selectivity than

confirmatory methods. Sometimes less analyte selectivity may be desirable when performing initial analyses where "classes" of analytes or organisms may be desired.

An additional feature of *NEMI-CBR* is a companion expert system, the *CBR Methods Advisor*, which helps a user to find the best methods for various scenarios. The expert system can be used for an emergency response to an incident or it may be used to find methods to confirm a suspected analyte or organism identity. It helps the user to assess which methods may be most applicable to the needs and also provides advice on methods that may not be appropriate for the situation at hand. In addition, since there may be dangers involved in collecting samples of potentially hazardous materials for analysis under a threat scenario, the expert system incorporates the logic and advice of EPA's Response Protocol Toolbox. The expert system may be entered at any of several points that involve classifying threat warnings, initial threat evaluation, immediate response operations, site characterization, initial site evaluation and entry, where and how to collect samples, packaging and shipping samples to a laboratory, selecting methods for initial analysis and selecting methods for confirmatory analysis.

The CBR Methods Advisor may be used for planning and training or in response to an event and different menu selections are provided, as appropriate, for each use. Forms provided in the Response Protocol Toolbox may be accessed to read or to fill out from links within the appropriate sections of the expert system. The expert system is reached from a link on the home page of the NEMI-CBR database. However, the expert system can also be placed on a CD-ROM and used with a laptop computer when it is complete. This would provide access to advice and the methods in the event of an emergency involving loss of electricity or phone lines or if it was needed to be used in the field.

While both the methods' database and expert system are currently restricted to methods and information concerning water analysis, the frameworks of both software products are such that they could easily be expanded to include other non-water matrices.

QUALITY ASSURANCE AND EMERGENCY RESPONSE DATA

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For the past four years there has been added focus on the data management process for emergency and rapid response projects. EQ has a unique situation in that we have five current Emergency and Rapid Response Service Contracts, as the prime and four additional regions as subs. We have been working in Region 5 since 1993. As a result of this extensive experience we have developed a specific quality assurance program for handling this unique data.

EPA defines Quality Assurance as 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. The technical requirements of the ERRS Contract includes emergency response, sampling, monitoring, site stabilization, controlling spilled materials, waste treatment, restoration, removal actions, transportation and disposal. In support of these technical requirements the need for on-site and off-site analytical activities for chemical and physical analysis on a 4-72 hour turnaround basis is required. The data generated from these activities is used to make decisions in the field regarding removal, waste disposal and air monitoring, as well as other activities encountered during site stabilization or containment and other response activities.

The following scenario represents what can easily occur and certainly has occurred for a prime contractor for ERRS. You receive a call on Friday afternoon or Saturday morning. The Response Manager indicates that they need to take samples this afternoon (or they have just taken them) and they need a lab. The analysis is TCLP Volatiles and they need results on Monday afternoon. What do you do, besides expressing your dissatisfaction to the Response Manager on the timing — you need to move quickly. How do you find a lab that will work weekends and provide data that will give you some level of confidence on the quality, as well as provide sufficient information that will allow a review of the data to provide data usability recommendations to the EPA On Scene Coordinator.

An emergency response site presents a complex and difficult situation for documenting and ensuring data quality. There is often little time to develop detailed project specific plans or procedures to address data acquisition and evaluation of the usability of the data. This includes the procedures from sampling to data assessment. Although there are most likely contract wide plans in place, it is impossible to include every scenario in a contract quality plan. Another aspect of an emergency response site is the involvement of multiple contractors. While one contractor may procure the laboratory, another contractor will perform the sampling. This requires open communication with the EPA OSC, the START member and the prime contractor's chemist or lab coordinator. Understanding the timing in the project of the sampling activity, the objective of each sampling task and the capabilities and procedures of your laboratory are key elements in assessing the data on a rapid basis.

An effective data quality assurance program for emergency response work begins with ensuring that you have a Quality Management Plan that is not only clear and precise, but also implemented. A supplement to the plan is appropriate standard operating procedures. EQ has developed SOPs for not only the emergency response data review process, which is slightly different that the EPA procedures for data review and validation, but also laboratory evaluation and selection.

Critical to the process is to ensure that you have a sufficient number of laboratories that have been pre-qualified, which may include on site systems audits. Familiarity with a laboratory's procedures, quality evaluations, reviews and corrective actions will

introduce a level of confidence to your process. It is most likely that the laboratory's quality control limits will be used during the data review phase. The next step is obtaining all relevant information regarding the sampling task. The obvious elements include matrix, parameters and applicable action levels. However, the end use of the data will drive how conservatively the evaluation of the data and the associated quality control data is completed. For example if the data will be used for assessment sampling for lead removal activities at a high school, the precision and accuracy of the data set may drive which areas with results below the action level that may be considered for excavation.

The review of the data can be performed manually; however, with the development of standard electronic deliverables from labs, the data review process can be performed electronically. This review process is done upon receipt of the data results, not the data package. As most decisions regarding data for an emergency response site are made within one day from receipt of results. It is imperative that the laboratory understands this aspect of data review and provide sufficient quality control results for decisions to be made on the data usability. The generation of QC summary forms, along with the data summary forms is a capability that most laboratories have.

A critical step prior to the shipment of samples is for the laboratory to know what deliverables are required at each phase. For example on a quick turnaround time for reporting of results, 48 hours for TCLP volatiles, not only the data summary page listing results, method, sample id, data of analysis, but the TCLP extraction blank, method blank, laboratory control sample, matrix spike, matrix spike duplicate results are required to be reported. By having the subcontract laboratory provide associated quality control results for each set of sample analysis you can quickly review the data and identify any potential influences on the data usability. This step is similar to the data verification step identified in the EPA guidance document G-8, Guidance for Environmental Data Verification and Validation.

The data review process is not initiated upon receipt of the preliminary data report from the lab. The data review process is initiated immediately after sampling has been completed or, at a minimum, upon receipt of samples at the laboratory. Review of the chain of custody and sample login information from the lab is performed the day samples are received at the lab. Communications with the laboratory during the analysis process is a very important aspect. Encountering interferences and exceedence of quality control limits will impact the usability of the final data, delivery of results and potentially impact site operations. Open communications with the laboratory during these steps will provide more complete information that is used during the data review process. This is important, since data quality is based on review of the data summary forms, along with the QC summary forms and not the final data package. The data summary process need not be elaborate, but must still be documented. The use of forms and checklist during this review process is necessary. The following is an example of the type of form that EQ uses during this process. It is very important at this step to communicate with the site personnel, most likely the EPA On-Scene Coordinator

regarding any data quality issues and what impact this will have on providing the data, as well as the usability.

Preliminary QC Data Check for COC# 00111
PN/Site Name: 030228.0001 Sample IDs/Matrix: SS001 to SS010
Laboratory: ABC Laboratories, Inc.
Reviewer/Date: Jane Smith / 01-01-00

Initial Report	VOAs/5035,8260	SVOAs/8270	Metals/6010, 7470
Narrative	√	√	√
QA/QC Signoff	√	√	√
Sample Summary	√	√	√
QC Summary	√	√	√
Method Blank	√	√	√
TCLP Blank	NA	NA	NA
Duplicate	NA	NA	√
Matrix Spike/Matrix Spike Duplicate	√	√	MS only
Lab Control Sample	√	√	√
Interference Check Standard	NA	NA	√
Surrogate Recoveries	√	√	NA
Final Report			
Data Package Inv/TOC & Checklist	√	√	√
Initial Calibration	√	√	√
Continuing Calibration	√	√	√
GC/MS Tuning Criteria	√	√	NA
Internal Standards	√	√	NA
Tent. Identified Compounds	NA	NA	NA
Raw Data of Sample Runs	√	√	√
Raw Data of QC Runs	√	√	√
Example Calculations	√	√	√

NA – not applicable

Summary of QC Outliers/Missing Data from Preliminary Review Checklist
C.O.C.#(s)_____

Reviewer/Date: _____

Analytical Method	*Outlier*	*Corrective Action*	*Impact on Data*
5035/8260	Surrogate recoveries below acceptable limits	Re-analysis confirmed low recoveries	J, data flagged as estimated, potential low bias
8270	LCS recovery of several compounds above acceptable limits	None	Compounds below detection levels in samples, data acceptable

The implementation of this type of process and documentation leads to documented quality of data and informed decisions based on data results for emergency response sites.

References

Guidance for Environmental Data Verification and Data Validation, Office of Environmental Information, U.S. Environmental Protection Agency (EPA/240/R-02/004).
Data Verification and Validation, EQ SOP # QA-2, July, 2004.
Laboratory Evaluation, EQ SOP # QA-5, September, 2003.

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BUILDING ENVIRONMENTAL LABORATORY CAPABILITY IN SUPPORT OF EMERGENCY RESPONSE

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In the event of an actual or suspected terrorist incident, comprehensive laboratory resources will need to be called upon to allow the nation to deal with any situation. An

extensive laboratory network, managed by CDC, exists for dealing with clinical medical samples, but another group of sampling and analytical requirements related to environmental samples also exists. The President's National Homeland Security Strategy calls upon EPA to be the primary agency responsible for environmental sampling and analyses in response to a terrorist incident. This Strategy also directs EPA "to provide diagnostic surge capacity for environmental samples during crises." The Department of Homeland Security, the Centers for Disease Control, the law enforcement community and our partners in state and local government expect EPA to put in place some form of an intergovernmental network capable of environmental sample analyses for chemical, biological and radiological contaminants of concern for all environmental media.

New homeland security policy directives are being issued which create new demands for a supporting laboratory capability which is not in place.

At the present time, EPA possesses finite capabilities and capacities to analyze environmental samples for chemical, biological and nuclear materials associated with Weapons of Mass Destruction (WMD). *The Agency's primary analytical capability is oriented toward routine analysis of industrial chemicals, pesticides and conventional pollutants.* EPA's state environmental laboratory counterparts are similarly constrained. While the problem of dealing with clinical samples resulting from an attack has been identified early and is being addressed by the Centers for Disease Control, environmental samples associated with a potential terrorist event have not. An approach to address this problem will be presented based on three precepts:

- to the extent possible make use of the nation's current laboratory resources
- address the problem in the most cost-effective manner
- develop a solution as quickly as possible

LABORATORY ACCREDITATION II

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PROFICIENCY TESTING AND THE NELAC FIELDS OF TESTING MODEL: THEORY VS. REALITY AND THE NEED FOR CHANGE

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Laboratory accreditation under the National Environmental Laboratory Accreditation Conference (NELAC) is linked to a program concept termed Field of Testing (FOT). Field of Testing is defined as an analyte or analyte group within a technology or method which is specific to a sample matrix. Laboratory proficiency testing (PT) is linked to the Analyte/Matrix/Method combination.

In theory, laboratory clients and regulators would be able to access sufficient accreditation information to determine which tests the laboratory was competent and qualified to perform. In practice, the NELAC model is not functioning smoothly and has resulted in unnecessary complications, which negatively impact secondary accreditation and interstate reciprocity. Individual Accrediting Authorities (AAs) have established State Specific Fields of Testing, which has created accreditation difficulties and program divergence between states. In some cases State Specific FOTs are linked to State-mandated PTs directly affecting the accreditation program reciprocity NELAC was designed to promote.

The FOT model difficulties will be discussed and several examples illustrating the accreditation complications the current approach has caused will be presented. Possible solutions including Fields of Testing consolidation and de-emphasis of the link between compound specific PT requirements and accreditation will be proposed.

AUTOMATED AUDIT SOFTWARE FOR STREAMLINING ON-SITE LABORATORY ASSESSMENTS AND MANAGING ON-GOING LABORATORY PERFORMANCE

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Abstract

As part of improving the process for performing on-site laboratory audits and maintaining and managing QA/QC documentation in a readily available electronic format, Laboratory Data Consultants, Inc. (LDC) under contract to the South Florida Water Management District (SFWMD) developed a Microsoft ACCESS-based software program to streamline the audit preparation, on-site audit process, final reporting and long-term documentation. The program has two primary components: (1) a master database which contains laboratory information including names of key staff, certification status, performance evaluation (PE) data, past audits and corrective action, SOPs and a list of methods in which the lab is certified and (2) a "briefcase" database which is downloaded from the master database prior to performing the on-site audit. This "briefcase" database is taken to the on-site audit and contains the laboratory specific audit checklists based on SFWMD, Florida DEP and NELAC standards.

This presentation will show how the use of this audit software program has made the audit process more consistent, technically sound, cost effective and real-time for the auditor. The main features of this program include

- Guides the auditor step-by-step through a NELAC type audit.
- Allows for easy electronic access to all past audits and associated corrective action
- Ability to prepare specific questions on the audit checklist based upon past audits.
- Access to past SFWMD PE sample results.
- Provides e-mail notification of critical dates in the audit process.
- Tracks time each auditor has spent on the audit.
- Embedded reference documents such as Chapters 3 and 5 of the NELAC standards and the SFWMD QA Manual are available for electronic review during the audit process.
- Reference tables that link findings to specific sections of NELAC documents.
- Direct input of findings into a laptop computer.
- Automated final report generation based upon findings listed during the on-site audit and information retrieved from the master database.
- Tracks findings and corrective action responses from the laboratory.

In summary, the SFWMD Automated Audit software has demonstrated to be an extremely powerful tool in aiding the auditor to be better prepared and perform on-site audits in a cost effective, technically sound and consistent manner. Additionally, LDC and the SFWMD are in the process of expanding the software to accommodate field audits.

Introduction

Preparation for an audit has long been a time-consuming process involving the review of multiple documents such as laboratory-specific SOPs, laboratory Quality Assurance Manuals (QMs), internal quality assurance audit results, historical certification audit results, EPA and state-specific analytical methodologies, proficiency and round-robin testing results, training records, raw data and more. Once the audit process begins, the auditor generates another stack of documents. There are standardized checklists and issue-specific questions/issues to investigate, lists of findings and related corrective actions/recommendations, response from the lab to the auditor's findings, the auditor's response indicating acceptability of the lab's corrective action plan, etc.

The automated audit software developed by Laboratory Data Consultants, Inc. (LDC) under contract to the South Florida Water Management District (SFWMD) addresses the difficulties associated with the preparation for and execution of an on-site audit as well as the sometimes overwhelming task of organization, storage and retrieval of the massive amount of documentation associated with the audit process.

Conducting the Audit

The auditor does all the preparation work in the central database. The auditor is guided step-by-step through the preparation. The first step involves importing relevant documents (QMs, SOPs, previous audits, etc.) into the central database. These documents are either supplied in electronic format by the lab or scanned and converted to pdf files for electronic storage and retrieval.

Once the database is populated with these documents, the auditor begins the process of building an electronic "briefcase" which will be downloaded to a laptop computer and taken to the on-site audit. The auditor tags the documents and references to be imported and can hyperlink these documents to questions in the checklist. The auditor can then open any of the references during the course of the audit by simply clicking on the embedded hyperlink.

The auditor next selects the analytical and prep methods to be audited from a list of the more common test methods in use by SFWMD. Methods not on the list can be easily added by the auditor through a wizard-style interface.

The standard checklist consists of questions based on SFWMD, FDEP and NELAC requirements and regulations. The standard checklist can be easily appended by the auditor in several categories including previous audit results, performance testing results, internal audit results and miscellaneous. Questions can be added either during the preparation in the central database or in the briefcase during the course of the audit.

The program also contains a schedule and timeline tracker which is accessible from both the central and briefcase modules to keep track of critical dates in the audit process. The scheduler will send a reminder email to the auditor one month in advance of scheduled audits. A timelog is also embedded in the product so that the auditor can keep track of the hours spent on preparation and execution of the audit.

After the auditor has selected the lab, methods, reference documents and any additional questions, the entire audit package is then saved as a "briefcase" database. The auditor next imports this file into the briefcase module of the software which is normally on a laptop computer. The auditor will take this to the on-site audit where he can work either directly from the electronic forms or from a printed hardcopy. Additional pertinent documents such as run logs, training records, raw data, etc. may also be added to the briefcase as pdf files during the course of the audit.

A tabular summary of findings and an audit assessment report are generated based on responses to questions in the audit checklist and the opening meeting worksheet. The summary of findings is then immediately available for distribution to the lab staff at the closing meeting. This tabular summary can be exported in MS Excel format as well.

The auditor may add freeform conclusions and make minor modifications to the assessment report; however, use of the template both streamlines the preparation and standardizes the format of the assessment report.

The report is sent to the lab in both hardcopy and electronic formats. The laboratory's response is then imported and a letter of acceptance or further action required is generated from a template. This process is repeated as necessary until resolution of all issues is complete. Once completed, the briefcase database is then uploaded back to the central database for archiving, virtually eliminating the need for paper filing and storage.

Conclusion

In summary, the SFWMD Automated Audit software is an extremely powerful tool in aiding the auditor to be better prepared and perform on-site audits in a cost effective, technically sound and consistent manner. The software can be used to perform both internal and external audits. LDC is currently in the process of developing a module for conducting field and quality systems audits as well.

Attachments

A series of screenshots from a mock audit follows this section showing details of some of the key screens and features of the software.

Figure 1 shows the main screen of the Central Database Version. From here, the auditor can choose to begin a new audit, edit or delete an existing audit, upload a completed audit briefcase to the central database or perform various file maintenance functions such as importing documents, adding labs or personnel, modifying the checklist, etc.

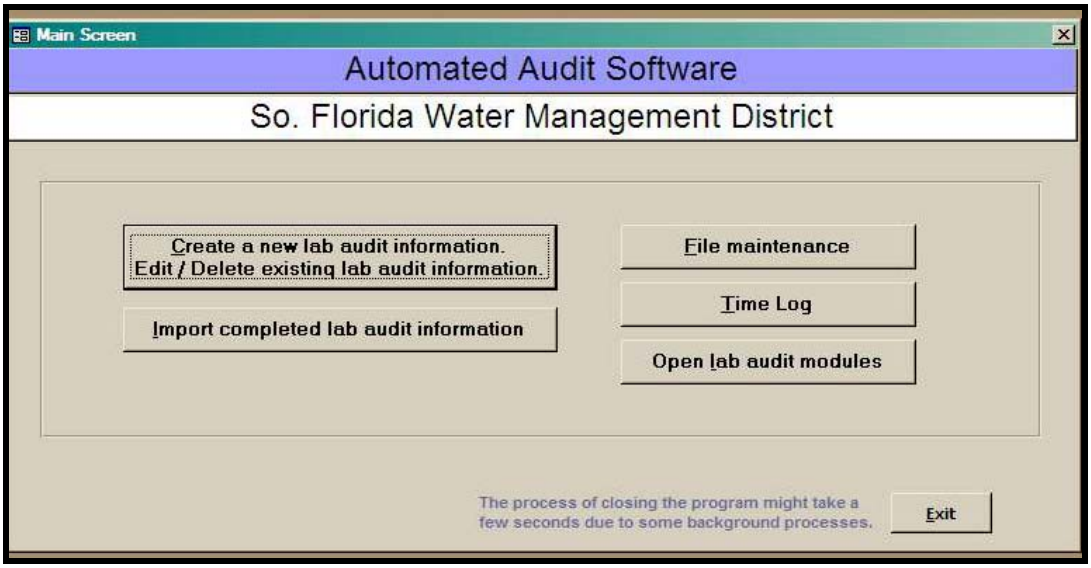

Figure 1. Central Database

Figure 2 shows the main screen of the Briefcase version. This is where the on-site audit is conducted and reports are prepared.

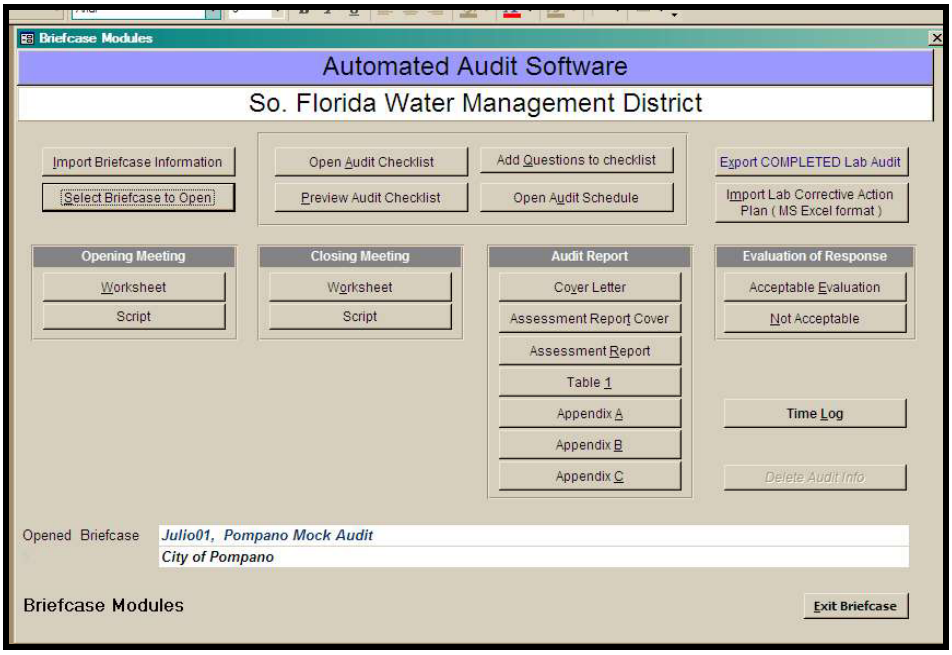

Figure 2. Briefcase

Figure 3 shows a portion of the audit checklist. Separate sections of the list are opened by clicking on the appropriate button. This screenshot shows the analytical method worksheet. This checklist is filled out for each method being audited.

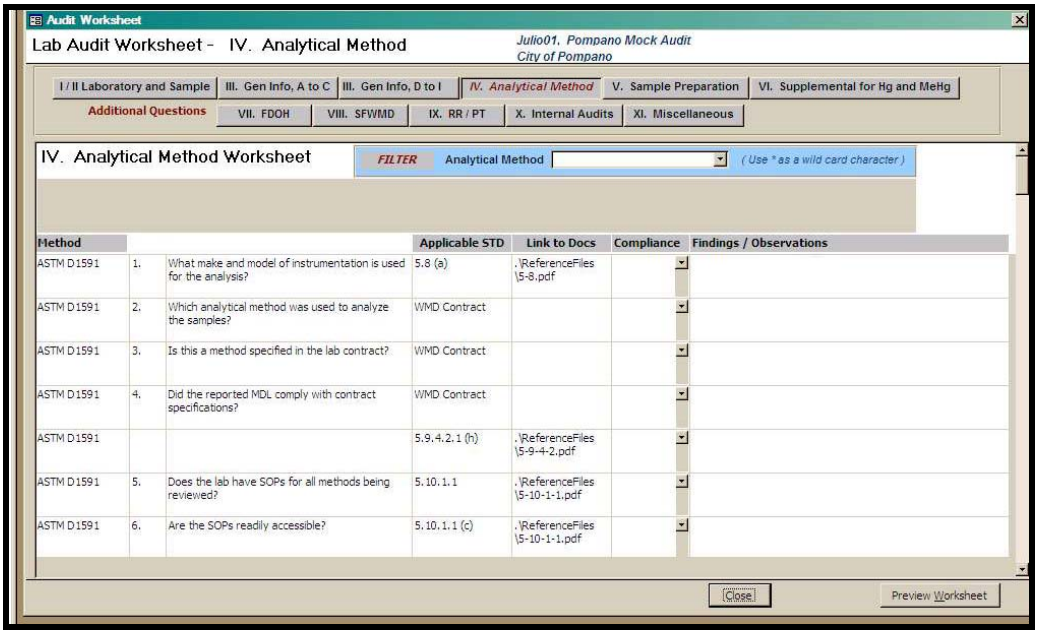

Figure 3. Audit Checklist

Figure 4 shows the opening meeting worksheet. Information entered here is directly imported into the final assessment report template.

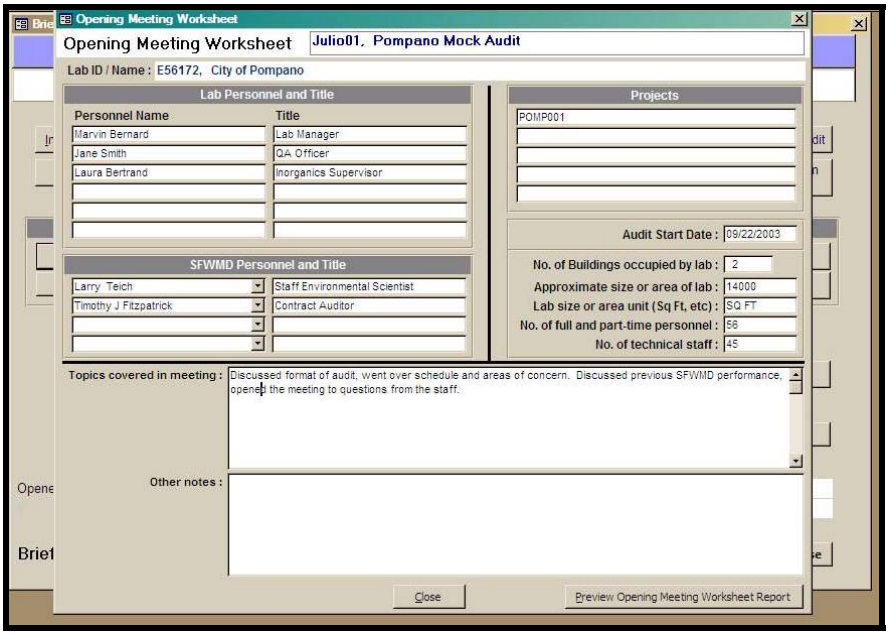

Figure 4. Opening Meeting Worksheet

Figure 5 shows the Assessment Report template. The report is prepared automatically based on entries made in the checklists. The auditor may add freeform conclusions and make minor modifications to the text of the template.

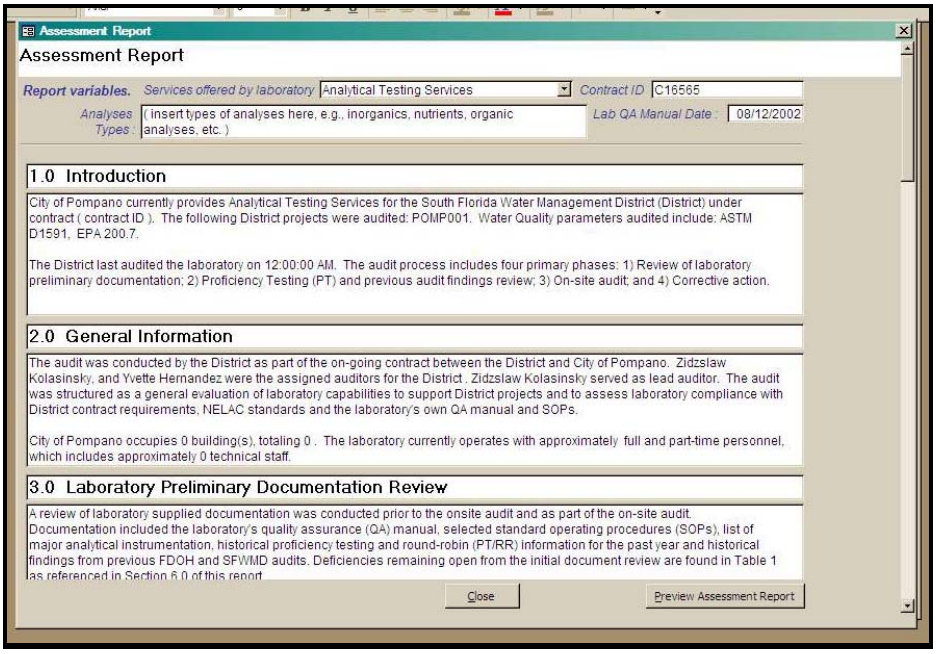

Figure 5. Assessment Report

Figure 6 shows the format of the tabular summary of findings and recommendations. Clicking on ***Show Record Detail*** will take the auditor directly to the checklist entry which produced the finding.

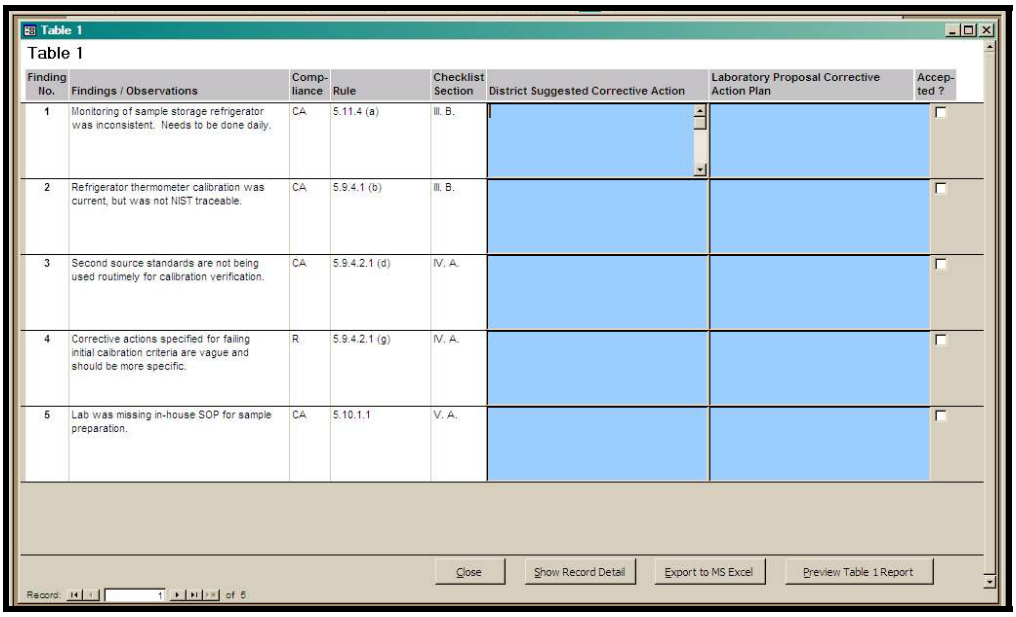

Figure 6. Summary Table

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ADOPTION OF A PERFORMANCE PARADIGM FOR LABORATORY ACCREDITATION

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The performance paradigm is an approach to specifying testing requirements that focuses on the performance standards that the analytical system has to achieve and document in order to achieve scientifically valid data appropriate for the particular environmental decision. This presentation will review the efforts of the Environmental Protection Agency (EPA) and the National Environmental Laboratory Accreditation Conference (NELAC) to transition from a methods-based system of regulation and accreditation to one that is performance-based. It will review the history of the effort, the current status of the change, work that has and is being done by other organizations to assist EPA, NELAC and the environmental community in the transition and efforts of the newly created EPA Forum on Environmental Measurements (FEM) to accelerate the regulatory adoption process within EPA. The author will briefly review some of the impacts to the current NELAC laboratory accreditation process that might result from the adoption of the performance paradigm with emphasis on both fields of accreditation and the procedures used to audit or assess environmental laboratories.

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REQUIREMENTS FOR A QUALITY SYSTEM

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Even though the term "Quality System" is increasingly familiar to the environmental laboratory community, it still is perceived as an unpleasant documentation exercise for many. With each revision of the NELAC quality systems standards, requirements have increased or changed, but few if any were omitted. It seems that everyone agrees it is time to try to rethink these requirements and pare down what is actually required versus what would be nice to have documented. The point after all, is to have better (known, documented) data as the outcome of the implementation of the quality system. Writing more about a process doesn't make the data better. And, a good laboratory is more than good data.

Quality systems require communication, documentation and audits to assure that the commitment to quality data flows throughout the organization. For progressively larger laboratories, it seems reasonable that communications are more complex; require more detail and more documentation. For a one- or two-person organization, a small subset of a larger organization, or a researcher, the communication needs are minimized because the functions of the people overlap or are entirely performed by the same person. It is logical that less documentation should be required under these situations.

Until NELAC can catch up with the need to minimize documentation requirements, the implementation of a quality system will remain a gigantic task for the smaller organizations and few will attempt it unless required. The newest evolution in the 2002 NELAC standards attempts to lessen the emphasis on documentation through a simple definition change found in the glossary:

Procedure: Specified way to carry out an activity or a process. Procedures can be documented or not.

This simple addition of two words may open the way for auditors to interpret documentation needs "appropriate to the type, range and volume of environmental testing activities it undertakes" (5.4.2.a, January 12, 2004).

Another change that needs to take place is to make clear how much documentation is required. The rumor in the environmental community is that the standards are so

documentation-oriented that they will require you to identify the type and sizes of pencils, staples and tape that you use. The misunderstanding of what things are important to fully document comes from the use of at least 15 different terms to imply documentation. Most of these terms are undefined at this point. We need to limit the terms used and categorize the amount of documentation based on function. Data production activities require the most documentation. Management functions require documentation, but not step-by-step instructions on how to do them. Support functions such as ordering, temperature records and tracking training records would require nothing more than an entry in a logbook or spreadsheet. Three terms are suggested to match these functions: 1) fully documented (such as an analytical method or descriptive SOP), 2) documented (such as a paragraph in a quality manual or a sentence or two in an SOP) and 3) recorded (such as a temperature logbook, invoices or email). With this small change in wording, we can make changes to the negative perception of the quality system process and help smaller organizations to achieve accreditation.

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ROLE AND UTILITY OF PROFICIENCY TEST SAMPLES FOR NON-TRADITIONAL METHODS AND ANALYTES

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In 1992, when CNAEL issued its report calling for the development of a national laboratory accreditation program, proficiency testing (PT) was identified as one of the three key elements of the program. Since its inception, NELAC has endorsed a PT program requiring two challenges per year. Currently, the NELAC program has over xxx analytes in potable water, wastewater and solid and hazardous materials. However, this comprehensive program does not begin to address all of the analytes, media, methods and concentration ranges of interest in environmental testing. Should it?

This presentation will explore the role and utility of PT samples in general and, more specifically, for those methods, analytes and matrices where PT is not currently performed.

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POSSIBLE CHANGES TO THE NELAC REQUIREMENTS: A PANEL DISCUSSION

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After 10 years, any major program needs an evaluation of what it has accomplished and what needs to be done. The NELAC program has been remarkably successful as measured by the number of laboratories who are accredited and the high level of participation in this program by laboratories, state and federal agencies and many others. However, much remains to be done both to improve the operation of the basic program as well as expand the effort into new areas.

This panel, representing the laboratory community, state agencies and federal agencies, consists of individuals who have been engaged in the NELAC effort since its inception. The panel will share their thoughts on what has transpired during this special session, highlighting those activities which should become the major focus of the NELAC stakeholder community over the next few years.

ADVANCES IN ELECTRONIC DATA DELIVERABLES II

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ADVANCES IN ELECTRONIC DATA DELIVERABLES (EDD): THE EDD DESIGNER, GENERATOR AND CHECKER CONCEPT

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The EDD Designer, Generator and Checker Concept provides an unique approach to seamlessly passing analytical data from business to business. This concept is extremely productive, flexible and manageable while maintaining quality and integrity.

Today's laboratory is becoming more difficult to manage due to the increasing diversity of client deliverables. These diverse deliverables affect a lab's quality, integrity, growth and productivity…all of which affect revenue. *EISC* believes that laboratories' inability to easily produce the number of varying deliverables is having a negative affect on the industry, as lab management has been required to shift its focus from the lab's core analytical competence to production of a client's electronic data deliverable.

Is developing a super, all-encompassing EDD format the answer to this issue? In some instances the answer is "yes". However, in the majority of instances the answer is "no". Most labs have a host of continually changing EDDs, an aspect of lab production not likely to change. A lab is then forced to shift its focus from its core analytical competence (the lab equivalent of "jumping through hoops"), in order to focus on the actual production of the deliverable. This shift in focus is beleaguered with the potential for error, inconsistency and chaos in the analytical process.

An alternative process/approach that keeps the analytical result closer to the source of generation could alleviate this dilemma. It is important for technological tools to allow a laboratory to remain focused on its core analytical competence, maintain data quality and integrity and produce client EDDs in a seamless transfer of data, regardless of the EDD format. Let's teach a process and build tools for these laboratories to get back to their core competence of analytical results.

Building the perfect EDD Generation Process

The goals: Impeccable Quality
Maintain Integrity
Make it manageable

Make it flexible
Make it extremely productive
Make it easy to distribute. Spread the workload throughout the lab.

The mechanisms: The EDD Designer
The EDD Generator
The EDD Checker

REAL-TIME DATA DISCOVERY AND NOTIFICATION OF SEDD SUBMISSIONS THROUGH EQuIS AUTOMATED ELECTRONIC DATA DELIVERY

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Abstract
Electronic management of environmental data continues to become increasingly standard. A highly scaleable, cost-effective enterprise Staged Electronic Data Deliverable (SEDD) management system has been developed to provide government project managers and industry consultants the ability to rapidly and effectively evaluate the progress of environmental restorations of contaminated geographic locations. The system provides automated SEDD acceptance, validation assistance and database import by standardizing data delivery formats. The system includes an interface for real-time data discovery and monitoring.

An integrated data management system provides much more than just the ability to archive data electronically. Current site characterization software technologies provide highly-trained professionals essential desktop tools for solving environmental management problems. The enterprise system integrates and builds upon these vital technologies by providing automated front-end data loading of chemical and geological data into a Relational Database Management System (RDBMS). Electronic deliverables containing site, location, sample and result data are seamlessly imported without manual user intervention, permitting real-time access to shared data for making mission critical environmental decisions. Benefits include being able to manage data more quickly and accurately which, in turn, contributes to better decision-making and response.

EQuIS and the Automated Data Discovery and Notification Process

- What is data discovery and notification?

  - Data Discovery
    - The system discovers problems at your site
    - Examples may include: new analytes detected, results above action level, pumping wells under performing
  - Notification
    - The system immediately notifies you about these problems
    - Includes a variety of channels for notification delivery

      Environmental Information Agents

      'Push' Reports
- Benefits
  - Know about problems faster
  - Gain this knowledge routinely
  - Find solutions faster
- Net results
  - Shift from reactive to proactive
    - The system informs you of potential problems
  - Better risk management and communication

Individual sites or across multiple sites

- Pushes the responsibility of submitting correct/complete data to the data provider
  - The data provider submits a SEDD directly to the automated system
  - Forces compliance with the SEDD format
  - Simple projects (USTs) can live with simple formats, but Superfund and Base Closure programs need more data
  - Common concern
    - "It's too difficult to meet the specification"

Provide software to the Data Provider for preparing and submitting SEDDs

- Disconnected checking for the Data Providers for preparing and submitting SEDDs
  - Desktop Electronic Data Processor (EDP)
  - Provide disconnected syntax and reference value checking
    - Local XML Schema for formats
    - Local XML Database for reference values
  - Includes a mechanism for receiving local XML updates from the Enterprise system
- Desktop EDP is **same code** as Enterprise EDP
- Ensures same checks on both sides of data transaction:

  - Desktop EDP offers privacy, advanced checks, color-coded error designations, can be called programatically from LIMS or other data collection software.
  - Enterprise EDP offers web or email interface, high throughput, automated responses with complete error log with SEDD rejections, automated data loading into EQuIS
- Ensures complete, correct transaction
- Server-side 'Intelligent Agents'
  - Triggered
    - New data, new 'hits'
      - For example: If we have a new Arsenic 'hit', then generate:
        - New Arsenic contours
        - New Arsenic trend charts
  - Scheduled
    - Weekly, monthly regular events
  - On-demand
    - Ad Hoc
- Automated Generation of reports, graphs, graphics, models, statistics, visualizations, exports, etc.

Conclusion

How far our new environmental technology will take us is still difficult to imagine. Environmental characterization and modeling is a science that, while still complex, is improving as the tools used by the scientists improve and applications become more tightly integrated. Data collection and use provide many areas where quality can quickly go awry. SEDD and EQuIS provide systems that contribute to higher levels of data quality.

We must continue to press forward, however, because the opportunities put forward by effective data quality control, data management and application integration are substantial and accrue benefits to all involved. A recent study by the California Policy Research Center determined that it cost the state of California $10 billion annually to combat nine environmentally-related diseases for which economic data was available. If tracking the occurrence of these diseases led to no more than a 1% disease reduction, the state would save $100 million annually (Lashof, *et al*.).

Using the appropriate SEDD structures and software to manage, analyze and visualize the data, the scientist is able not only to apply more advanced analyses, but also to investigate various scenarios. Regulatory agencies, consultants and industrial companies worldwide are reaping the benefits of an environmental data management system with integrated visualization and analysis applications. These benefits include not only much more efficient management and visualization of multimedia data but also more accurate and cost-effective decision-making and response.

The key to better decision-making is to maintain high-quality data for use in a variety of ways. The data warehouse with powerful data quality checking tools provides a foundation for better decision-making. The ability to interface to a wide variety of analytic tools appropriate to a user's task provides the capstone.

References

CDPHE. (2003) http://www.cdphe.state.co.us/hm/samsmain.asp.

FIELDS (**FI**eld **E**nvironmenta**L** **D**ecision **S**upport), http://www.epa.gov/region5fields/.

Gray, A. L. (2003) Telephone Conversation, May 2003.

Lashof, J. C., McKone, T., Grass, R., Horton, M., Lyou, J., Needham, L., Pease, W., Rice, D., Ritz, B., Satariano, W., Schulte, P. and Solomon, G. "Strategies for Establishing an Environmental Health Surveillance System in California: A Report of the SB 702 Expert Working Group," California Policy Research Center, University of California, forthcoming.

NJDEP, Bureau of Safe Drinking Water. (2003) Private Well Testing Act Program Electronic Data Deliverable Manual, p. 5.

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ENVIRONMENTAL DATA TRANSFORMER (EDT)

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Background

Environmental data from various media have been collected at the Rocky Flats Environmental Technology Site (RFETS) to support environmental cleanup and site closure. The historical data is stored in a legacy database that will be the legal repository for data. The legacy database is a data store for site and sample descriptions, data package submittals from analytical laboratories and validated analytical results obtained from electronic data deliverables and hard copy data deliverables. Because the primary goal for the legacy database is as a repository for all environmental data collected at the site, the database and related processes were designed to be inclusive of all data as received in the electronic data deliverables and

hard copy data packages. These data, collected over a period of 16 years, were not readily usable for analysis and decision-making due to inconsistencies in the data caused by changes to laboratory agreements for data submittals and data collection for various purposes.

The Remedial Action Decision Management System (RADMS) requires consistent data possessing a singular level of data quality to enable fully-automated decisions. The Environmental Restoration (ER) group at RFETS uses RADMS to perform accelerated actions, contaminant-of-concern screenings and risk assessments in a fully-automated fashion. RADMS' applications such as Contaminant-of-Concern, Risk and Accelerated Action perform comparisons and calculations on analytical data that must possess correctly assigned attributes such as media, media occurrence, sample type, analyte information, units, data qualifiers and others.

Functions

EDT provides a robust set of functions for transforming, scrubbing, integrating and loading data into the RADMS environmental database. EDT delivers the following functions.

- Consumption of XML documents, with a specific schema, containing environmental data from any source
- Business rule checking for various environmental data business objects
- Automated application of business rules to fix environmental data containing violations of fundamental business rules
- Automated documentation of business rule violations
- Automated documentation of business rules applied
- Automated transformation and loading of data into the RADMS environmental data model

Environmental Data Consumed

EDT will consume and process environmental data derived from sample planning to field collection and resulting validated analytical data. The fundamental environmental data objects and supporting data objects are listed below.

Primary data objects

Sampling plan	Sampling execution event	Sampling execution plan	Site
Sample	Sampling method	Analytical order	Bottle
Sample container	Chain-of-custody	Lab sample	Lab batch
EDD	Analytical result	Validation	Site result

Supporting data objects

Sample type	Sample use type	Analyte	Analyte group
Analytical method	Company	Ordering agreement	Person
Analytical suite	Laboratory	Analytical order catalog item	Matrix
Matrix context	Unit	Result type	Other

Process

The EDT process (Figure 1) is bounded by environmental data in some data source and the RADMS database – the ultimate destination. The EDT solution begins the process by consuming new or altered data previously consumed from some data source such as a legacy database or an EDD in a text, spreadsheet, XML or proprietary database format. These data are placed into a standard XML document by an agent specifically designed to extract data from the data source. The XML document is provided to the EDT agent for consumption. The EDT agent consumes the environmental data and applies business rules to fix problematic data while recording these fixes for subsequent documentation. Business rule violations that still persist in the data are found, recorded and documented as such. Valid data are loaded into the RADMS database for use in decision making. The recorded pass/fail information, business rule violations and data fixes applied are documented in the data source.

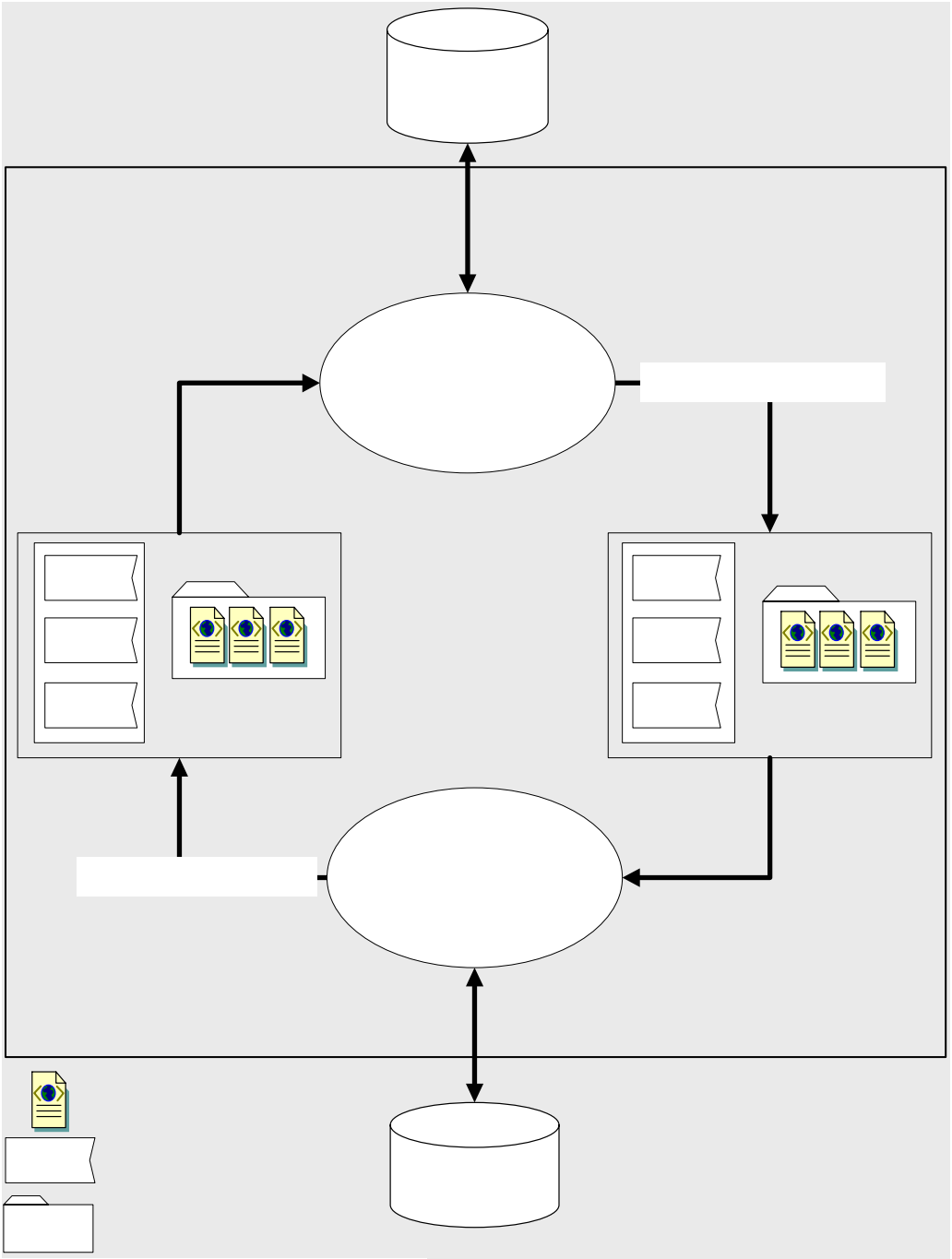

Figure 2. EDT process diagram

Environmental Business Rules

EDT applies business rules to fix common environmental data problems. The application will also find data that do not adhere to a set of environmental data business rules.

Business Rules EDT Applies

EDT applies a set of business rules to correct common problems with environmental data. It also applies business rules to fix problems that are specific to environmental data at RFETS. EDT provides a framework for applying any rule that can be articulated for environmental data. Examples of some of the existing rules implemented by EDT are listed below.

- Corrects reversed coordinate data
- Normalizes analytical result units
- Scrubs misspellings and data entry errors
- Translates inconsistent data into consistent data
- Identifies non-detects
- Standardizes analyte information for decision-making
- Standardizes data qualifiers for decision-making

Business Rules EDT Checks

EDT checks all environmental data processed against a core set of environmental business rules. Examples of some of these rules are listed below.

- Data types and lengths
- Logical rules
- Is the site within the study area?
- Is the sample matrix consistent with the sample type?
- Are sample depths consistent?
- Sample type is required. Is it provided?
- Is the matrix value invalid?
- Are result units consistent with matrix and analyte information?

Benefits

The most significant benefit to the ER group at RFETS is that EDT has provided consistent decision quality data for use in accelerated actions and risk assessment. The business rules that EDT enforces and applies were documented so that all individuals using the data understand the singular level of quality that the data possess. This increases confidence in the data and therefore the decisions. The software was validated to guarantee that all rules were implemented as documented. Because the data possess a singular level of quality, the decision management system using these data could be fully automated. The quality data promotes significant time savings for developing decision support tools and also use of these tools.

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ROUNDTABLE: CHANGING FEDERAL REQUIREMENTS TO MANAGE ENVIRONMENTAL DATA QUALITY

Mike Carter

Mike Carter works for EPA's Federal Facilities Restoration and Reuse Office (FFRRO). FFRRO chairs the Intergovernmental Data Quality Task Force (IDQTF) and Mike has been involved in the development of both the *Uniform Federal Policy for Implementing Quality Systems* (UFP-QS) and the *Uniform Federal Policy for Quality Assurance Project Plans* (UFP-QAPP). He will discuss the products from the EPA Headquarters perspective. **Fred McLean** works for Naval Sea Systems Command (NAVSEA) in Charleston, SC. He has participated in the Environmental Data Quality Workgroup development of the *Quality Systems Manual for Environmental Laboratories* (QSM) as well as QAPP workgroup of the IDQTF. He will be presenting the DoD perspective on data quality. **Robert Runyon** is the chief of the Hazardous Waste Support Branch in EPA's Region 2. He has chaired the QAPP workgroup of the IDQTF and will discuss the benefits of the UFP-QAPP and associated tools. **Maryellen Schultz** of Region 3 has been an active member of the QAPP workgroup and will present the EPA Regions' perspective.

AUTHOR INDEX

NOTES

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